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Epitaxy and Surface Forces

by

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A thesis submitted for the degree of
Doctor of Philosophy of The City University,
London.

October 1975

Supervisor:- Mr. B. O. Field

ACKNOWLEDGEMENT

I would like to take this opportunity to thank the lecturing and technical staff of the Chemistry and Physics Departments of the City University for their assistance in this study. Also to [REDACTED] for without his knowledge of photography, high vacuum and electronics this study would not have been accomplished.

I especially wish to extend my sincere appreciation to Mr. B.O. Field for his continued enthusiasm, patience and personal guidance throughout my studentship.

I acknowledge also the support of the Science Research Council during the course of this study.

ABSTRACT

The epitaxial growth of a range of amino acids deposited from the vapour phase onto alkaline halide substrates has been studied. An unexpected interaction of some of these deposits with atmospheric water was discovered and the physical parameters influencing this phenomena were defined.

A simple electrostatic point charge model for explaining epitaxial behaviour has been extended to accommodate more complex substrate surfaces. The extended model has been used to examine the epitaxial amino acid deposits together with the results from a comparative study of the behaviour of glycine and anthraquinone overgrowths on sodium chloride, mica and quartz substrates.

The concept of long range forces, arising as a result of electrical inhomogeneity within the bulk substrate, being capable of influencing epitaxial growth has been extensively investigated. The existence of structure in the previously considered amorphous interfacial barriers was inferred from Low Energy Electron Diffraction and Auger Electron Spectroscopy. Resulting from these observations a new theory of long range transmission of forces effecting epitaxial growth has been formulated.

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INTRODUCTION

1.1 Epitaxy

The term epitaxy (arrangement on) was introduced by Royer (1928) to denote the phenomenon of the oriented growth of one crystal upon another.

This phenomenon has been recognised for well over a century. Some of the first reported observations date back to 1825 (1,2) although Frankenheim (3) in 1835 reported the first serious study on crystal oriented overgrowths in his solution studies on the orientation of alkali halides on the cleavage face of mica as well as sodium nitrate on that of Calcite. Surprisingly enough Frankenheim was able to develop some fairly modern ideas about the efficiency and radius of molecular forces.

Most of the epitaxial observations in this early period were, however, connected with mineralogical investigations and were characterised by macroscopic observations. It was generally agreed that a rational plane existed along which the two participants were intergrown, each participant having a parallel edge to this plane.

The first extensive summaries of epitaxy were published at the turn of the century by Mugge (4) and Wallerant (5). The former describing about seventy reported examples of epitaxy and developing some valuable ideas concerning overgrowth laws. Viola (6) and Baumhauer (7) attempted unsuccessfully to locate an exact crystallonomic relationship for epitaxy. Their attempts failed mainly because of the lack of crystallographic and structural information.

It was not until the discovery of X-rays and the subsequent structure determinations that epitaxy really advanced. It appeared that a sound structural theory would be forthcoming on the comparison of crystal structures of the intergrowth pair.

Royer (8, 9) proposed his theory relating to epitaxy in 1928, which constituted the matching of two dimensional lattice networks of the intergrowth pair. His theory led him to believe that only heteropolar substances would form epitaxial deposits (10), because he found that certain matching lattice networks existed between various materials where intergrowth did not occur.

Although Royer's postulates were unsound, due to epitaxial deposits growing on homopolar substances with no lattice misfit restriction, his theory remained acceptable in principle until a more elaborate and consistent approach was forthcoming. Seifert et al (11, - 14) for example studied the epitaxy of salts of the isomorphic series of alkali perchlorates-fluorates on barite as substrate. The interpretation of these results were based on a dimensional analogy between the intergrowth pairs as propounded by Royer.

With the discovery of electron diffraction techniques very thin layers of deposit could be studied. It was now possible to examine deposits other than those grown from solution, and to study earlier stages of growth. Very thin chemically grown layers (15, 16, 17) electrodeposited metal films (18, 19) and metal layers condensed from the vapour phase (20) were all found to be oriented in at least some cases. One of the most striking features of these results is that Royer's rule concerning a good numerical fit between the substrate and the overgrowth is not always obeyed. This applied particularly to the case of metals condensed on to heated rocksalt substrates (20) for which misfits as big as 38% were observed. Attempts were made to explain the occurrence of these large misfits by consideration of the formation of initial layers which are oriented with a low misfit, and upon which other orientations formed at a later stage. A mechanism of this kind, in which the occurrence of twinning played a vital role was considered in detail by Menzer (21, 22, 23) for the case of silver and nickel on rocksalt.

A further concept which was introduced by Finch and Quarral (24, 25) as a result of electron diffraction studies, is that of 'basal plane pseudomorphism'. This involves the formation of an initial oriented film which has an abnormal crystal structure. The bulk structure of the deposit material is constrained so that the lattice plane parallel to the surface is identical in size to that of the substrate.

Frank and Van der Merwe (26, 27, 28) developed this concept, and expanded a theory of epitaxy which involves as a necessary condition of orientation, the formation of an initial pseudomorphic layer. This theory predicts limiting misfits of the same order of magnitude as those observed by Royer. However, later experiments, concerning the stability of such layers (29) have failed to explain the necessity of a small misfit (30,31). In addition examination of extremely thin layers (mean thickness of less than 10 Å) of copper on silver (32) provided evidence of the structure of the initial nuclei of an oriented deposit and no support for basal plane pseudomorphism was found.

During the earlier considerations of epitaxial growth, the process of heterogenous nucleation was completely ignored. However, more recent theories of epitaxy have considered the role of nucleation processes towards the production of an oriented overgrowth (33 - 38). It is considered that heterogenous nucleation during oriented crystal growth is a fundamental property of epitaxy and knowledge of the process involved is essential to an understanding of the phenomenon.

The following section (1.2) discusses briefly the role of heterogenous nucleation together with the more relevant epitaxial theories to date.

1.2 Heterogenous Nucleation of Epitaxial Overgrowths

1.21 Classical Approach

The initial stages of crystal growth begins with the formation of isolated three-dimensional nuclei (39, 40, 41) although it is recognised that two-dimensional monolayer growth is possible the examples are fairly limited (42, 43). Other intermediate modes of growth will be considered later. Classical Nucleation theory is based on the concept of the existence of a critical sized nucleus which must be produced before a condensate phase is formed (44). This is because of the small size of the nucleus which has a vapour pressure higher than that of the bulk condensed phase. The increased vapour pressure is overcome by applying an effective supersaturation so that the applied pressure is greater than or equal to, the vapour pressure of the nucleus. The nuclei once formed are presumed to be in equilibrium with the parent molecules and the nucleation rate can be expressed as

$$I = Z \cdot N_1^* \cdot W \quad (45, 46)$$

where N_1^* is the equilibrium concentration of critical size nuclei W is the growth frequency of the critical size nuclei or the rate of monomer addition to a nucleus, and Z the so called Zeldovich factor (46) based on the non-equilibrium character of the process.

Figure 1 shows the classical processes involved in the nucleation and growth of a condensed phase from the vapour (36).

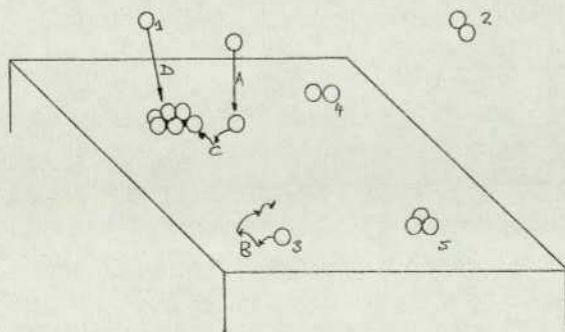


Figure 1

Nucleation and Growth of a Condensed Phase

Key to Figure 1

- | | |
|---------------------------------|--|
| 1) Adsorption direct to Nucleus | A) Adsorption to surface |
| 2) Dimer in vapour | B) Surface diffusion |
| 3) Monomer adsorbed | C) Growth of embryo by surface diffusion |
| 4) Dimer adsorbed | D) Growth by direct impingement |
| 5) Trimer adsorbed | |
| 6) Embryo | |

The shape and structure of the nuclei, and the free energy of formation, will depend on the surface free energy of the substate. For crystals of isotropic surface energy the shape will be that of a spherical cap and for anisotropic surfaces the shape will be a more complex figure depending on the anisotropy present.

All the classical theories relating to nucleation, require the assumption that the small nuclei behave as in their bulk phase. Having accepted this assumption the shape of the nucleus can be determined by the contact angle θ given by the equation

$$\sigma_s = \sigma_i + \sigma_o \cos\theta \quad (\text{See also figure 2})$$

where σ_s , σ_i , σ_o are the surface free energies of substate, interface, and overgrowth respectively. The equation is most easily visualised as an equilibrium between forces acting at the point of contact of the nucleus to the substate.

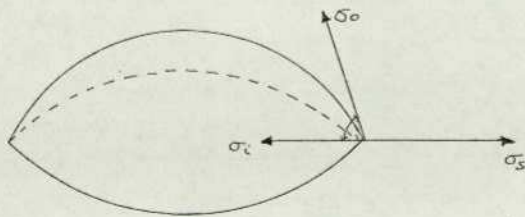


Figure 2

Cap-shaped Model of a Nucleus

For very small nuclei the equilibrium shape will also depend on the line tension resulting from peripheral contact of the nucleus and the surface. It must also be questioned again whether bulk values of surface free energies have any significant meaning when applied to such small nuclei (47 - 51).

For the case when θ is greater than zero three dimensional growth is expected, while if θ is equal to or less than zero complete 'wetting' of the surface should occur and two dimensional growth develops. This is not the only criteria for monolayer growth, if the substrate temperature is low or the deposition rate very high one would expect this mode of growth to prevail. Under these conditions polycrystalline or amorphous films will result (42, 52).

1.212 Some Documented studies of Heterogenous Nucleation and different modes of Crystal growth

It is not the object of this section to define all the parameters used in current nucleation theory, but merely to give a brief outline of the various approaches used. More detailed accounts can be found in excellent reviews in the literature, for example, Pound and Robertson (53), Lewis (54) and Stoyanov (55).

In an attempt to study the nucleation processes, it has been necessary to use very well defined systems, and using materials that would behave in a predicted fashion. As a result of this, most studies of nucleation employ metals as the deposit, and metals or alkali halides as the substrates.

The occurrence of separated crystallites in a layer evaporated onto a flat substrate surface must result from the mobility of the deposit atoms. The manner in which this mobility leads to nucleation, is not well understood, and there exists two possible mechanisms. In a 'gradual nucleation' mechanism the deposit atoms are mobile over the surface until

they lose sufficient thermal energy and become trapped on the surface, either at a random lattice site or at some energetically preferred place such as a hole edge or step. Once trapped the deposit atom acts as a preferential point for the trapping for other deposit atoms, so the nucleus, which may or may not be oriented grows by a diffusion and adatom process.

The alternative mechanisms, would be by a 'spontaneous nucleation' process, where crystallisation occurs via an intermediate stage, which could be one of an amorphous or liquid state. When the amount of deposit material is increased to a certain critical value, a crystallisation process occurs, and the nuclei are spontaneously formed.

The difference between these two mechanisms is only relevant where the critical size of the nucleus is large. The critical size for different arrangements of small clusters of deposit atoms (f.c.c. metals on rocksalt) has been considered by Walton (51, 56) and it is argued that the most probable nuclei are those which are stable with the fewest atoms. The critical nucleus, defined as the smallest cluster which has a probability of greater than one-half of growing, contains one atom less than the smallest cluster. It has been estimated that the critical nucleus for a (111) stable orientation is just a pair of adsorbed atoms, for (100) orientation it has three atoms, and for the rarely observed (110) orientation it has four atoms.

Nucleation Rate Expressions

A considerable number of nucleation rate expressions have been derived using an idealized cap-shaped model approach (36, 49, 51, 57, 58) as well as geometric variations of this model.

Hirth and Moazed (36) have derived expressions for Z , N_1^* and W in the nucleation rate equation and obtained the nucleation rate I as:

$$I = C_1 P \exp\{(\Delta G_{DES} - \Delta G_D - \Delta G_i)/kT\}$$

where C_1 is a constant of $\approx 10^{17} \text{ N}^{-6} \text{ sec}^{-1}$

p is the effective vapour pressure

ΔG_{DES} is the activation free energy for desorption

ΔG_D is the activation energy for surface diffusion

ΔG_i is the free energy formation of the i th size cluster

Atomistic Approach

Walton et al (59) have employed a method which effectively treats the clusters as though macromolecules in terms of potential energies and partition functions. This is the so called 'atomistic theory' of heterogeneous nucleation. It is similar to the classical approach in as much as the nucleation rate is equal to the rate at which critical nuclei grow by monomer capture to supercritical sizes. The difference being the atomistic model can be used to describe the properties of very small clusters.

Most workers now employ this approach to the nucleation event. Zinsmeister (60, 61, 62, 63) introduced and exploited the master equation approach. This has since been developed and in several ways, simplified by other workers (64, 65).

A general set of equations describing the rate of change of the concentration of cluster containing j atoms are used

$$\frac{dn_i}{dt} = R - \frac{n_i}{T_a} - 2U_1 - \sum_{j=2}^{\infty} U_j \quad - \quad (1a)$$

$$\frac{dn_j}{dt} = U_{j-1} - U_j \quad (j \geq 2) \quad - \quad (1b)$$

where U_j is the net rate at which j clusters grow to form $(j + 1)$ clusters. Eqn 1a, describes the adatom concentration, and differs from eqn 1b by the inclusion of the incident flux R , and the desorbing flux n_i/T_a where T_a is the mean adatom residence time on the substrate.

Each U_j is the difference of the two terms, describing cluster growth and decay by adatom disassociation. Equation 1b then sub-divides into two groups

$$\frac{dn_i}{dt} = 0, \quad 1 < j \leq i \quad - \quad 1b_1$$

$$\frac{dn_j}{dt} = U_{j-1} - U_j, \quad j > (i + 1) \quad - \quad 1b_2$$

Summing equation 1b₂ from $j = (i + 1)$ to infinity leads to

$$\frac{dn_x}{dt} = n_i \quad - \quad 1c$$

where n_x is the density of stable clusters.

Equation 1c gives the nucleation rate. Now if the assumption that all clusters with $j > i$ are absolutely stable is made the decay terms can be ignored

$$U_i = \sigma_i D n_1 n_i$$

where D is the adatom diffusion co-efficient and σ_i is the constant "Capture Number" (64, 65).

These equations are said to be an adequate description of the very early stages of the nucleation event (66) which cannot be explored in detail by experiment. They are, however, of limited use when describing the stage where electron microscopic observations can be made with good accuracy. (See section 1.2.3)

Various modifications have been introduced to incorporate surface inhomogenities (67), coalescence effects (68) and surface concentration differences (69) into nucleation theory. But despite the impressive advances made, the basic process involved in the initial stages of the film formation is far from being clearly understood.

It is not intended to extend further a theoretical consideration of the nucleation event, because it is not necessary for the development of the present theme.

1.22 The effect of Impurities and Imperfections on Nucleation

There have been several studies of nucleation that have demonstrated the importance of surface inhomogeneity in the growth of nuclei. Perhaps the first specific example was reported by Andrade and Martindale (70) in their experiments with gold and silver sputtered on to quartz or glass surfaces. It was observed that preferential nucleation occurred at surface microcracks. This has since been reviewed by Hirth and Pound (44) and Pashley (40). Basset (71) with his work of vapour deposited gold on different surfaces has shown that preferential nucleation on the monotomic steps produces a spectacular decoration pattern. Growth spirals steps and slip planes have been observed on crystals of rocksalt, by this technique. These observations were confirmed by Chakraverty and Pound (72) with vapour deposited gold on the (100) face of rocksalt and lithium fluoride.

Impurity adsorption has shown to both increase and decrease nucleation rates, Backman and Shin (73) found that nucleation varied with the presence of residual gas in the vacuum chamber. Sears (74) showed that Fe^{3+} ions increases the nucleation rate during the crystallisation of LiF from solution. Robins and Rhodin (75) have shown that nucleation of gold on magnesium oxide is consistent with randomly distributed defect sites (e.g. solute atoms) and this has been corroborated by other workers in this field (73). A number of other measurements that qualitatively demonstrate preferential nucleation on imperfections, and the role of impurities are reviewed by Hirth et al (36, 44).

Nuclei often form along surface steps, presumably because of a decreased formation energy. This has been observed experimentally by Basset (71), Bethge (76) and Bartlett et al (77) with evaporated metal films on alkali halides. Chakraverty and Pound (72) treated the subject theoretically and deduced that a strong preference for nucleation at surface steps would arise when the contact angle between overgrowth and substrate is less than 90° .

Young (78) observed that the oxidation of copper occurs preferentially at the emergence points of dislocations on the surface, however, such positions cannot be important in the majority of nucleation sites. This is because dislocation line densities of crystals are of the order of 10^5 cm^{-2} , while the nucleation density of metals on well annealed surfaces is of the order of 10^{12} cm^{-2} (79).

Walton and Hauser (80) have shown that low angle boundaries appear to be the most effective nucleation sites in their studies of epitaxy with di-halogen-benzenes on alkali halides. Evaporation and redeposition showed the same sites to be active in successive experiments until the surface became too contaminated. Etching experiments also revealed that many defects were not at all effective in nucleation.

1.3 Some Documented Results on Epitaxial experiments

Comprehensive reviews containing results obtained by optical and electron microscopy, X-ray and electron diffraction have been presented by Neuhaus (81) in 1951, Van der Merwe (82) in 1949, Seifert (83) in 1953, Pashley (39, 40) in 1956, 1965 and Darling (84) in 1973. These reviews, between them cover most of the observed results. In the following section, only the more relevant and interesting cases are considered, to illustrate how different theories and models of epitaxial growth have been formulated.

1.3.1. Monolayer and Pseudomorphic Growth

As predicted by the Youngs capillarity expression there are two main modes of growth, in the first case in which the condition $\sigma_s \geq \sigma_i + \sigma_o$ is satisfied the growth as a monolayer is expected.

Perhaps the best known example of monolayer growth, is the growth of lead on the (111) surface of silver. This was first discovered by Newman (42), and studied in detail by Grunbaum (43). Other specimens which exhibit monolayer-like growth are evaporated deposits of gold on silver (85) and deposits of platinum on gold (86).

In these specimens the surface energy condition for monolayer growth is not satisfied. The surface energies of silver, gold and platinum are about 1140, 1400 and 1800 ergs/cm² respectively. Thus, even if the energies of the interfaces are assumed to be zero, the contact angles are greater than zero. This means that continuous deposits of gold on silver, and of platinum on gold are unstable and that their energies would decrease if the deposits became three-dimensional islands. This is found to be observed in practice, when a film of platinum on gold is heated while under observation inside an electron microscope, the platinum film breaks up to form three-dimensional islands (86).

As stated earlier Frank and Van der Merwe, suggested that an epitaxially aligned single-crystal film would strain to reduce the difference between its normal lattice parameters and that of its substrate. Misfit in excess of that accommodated elastic strain would be taken up by a grid of interfacial or misfit dislocations. Van der Merwe has since extended this theory (82), and a number of experiments have shown the validity of this approach for some very well defined systems. This will be considered in more detail later (section 1.65), and only mentioned here for continuity.

It is significant to mention here that in the early stages of metal-metal deposition, strained distorted layers or pseudomorphic layer structures have been reported. Recently (87) copper deposited onto tungsten in an ultra high vacuum at 78°K involving field-emission spectroscopy suggested that the first four to six atomic layers of the deposit were constrained to fit the substrate lattice. The evidence for pseudomorphic growth lies in the close similarity between the field emission patterns of the tungsten and copper deposits.

There are other well documented examples of pseudomorphic growth, such as, cobalt on nickel (the 100 planes parallel) (88) and cobalt on copper (88, 89).

1.32 Three-Dimensional Growth

The vast majority of epitaxial deposits grow via the formation of three-dimensional nuclei. These nuclei or islands grow in size with the addition of more material, and in some cases eventually coalesce. This coalescence process has been studied by Basset (90), Pashley and Stowell (91), Pashley et al (92), Poppa (93, 94) and Jacobs et al (95). These authors grew evaporated deposits inside the electron microscope, and directly observed the nuclei coalesce. The most striking feature of their observations was the liquid-like behaviour of the coalescing nuclei. This behaviour is particularly noticeable when the nuclei are very small. If a pair of small (about $200\text{\AA}$ dia) rounded gold or silver nuclei coalesce at 350°C then the pair of nuclei change into one larger rounded nucleus in less than 0.1sec. Large nuclei take much longer to approach the equilibrium configuration. If a small and a large nucleus join one another then the small nucleus seems to flow into the large. The liquid like behaviour of coalescing nuclei is not because the nuclei are actually liquid (92); it results from the diffusion of atoms over the surface of the nuclei. The stage at which nuclei coalesce to form a continuous film depends on the shape of nuclei and the number of nuclei generated per unit area.

The accommodation of misfit between a hemispherical nucleus and its substrate has been treated by Cabrera (96). The magnitude of the strain is about 1% for a nucleus $100\text{\AA}$ in diameter and is inversely proportional to the radius of the hemisphere. Jesser et al (97) measured the strain and its variation with radius of annealed electrodeposits of platinum on gold. The strains were calculated from the direction and spacing of moire fringe patterns visible in the electron micrographs.

Misfit in excess of that accommodation by elastic strain is taken up by a network of interfacial or misfit dislocations (98 - 101).

Examples of misfit dislocations in a nucleus of an unidentified material on a chromium bromide substrate were observed by Delavignette et al (102). Grunbaum and Mitchell (103) found misfit dislocations between islands of nickel bromide grown epitaxially on chromium bromide.

The difference between misfit dislocations found in specimens which grow as pseudomorphic continuous films, and the dislocations found in specimens which grow as three dimensional islands, result from the different modes of misfit dislocations formed. In deposits which grow as pseudomorphic continuous films the misfit dislocations glide from the upper or lower specimen surface into the interface. To do this they must have burger vectors inclined to the interface. In deposits which grow as on three dimensional nuclei this restriction no longer exists.

Misfit dislocation and movement of dislocations are very important to the theory of epitaxy suggested by Van der Merwe, and will be discussed further in that context.

1.4 Epitaxy of Organic Materials

Although there are many hundreds of well authenticated examples of ionic and metallic overgrowths reported by different investigators, very little attention has been directed towards the study of organic materials. The disadvantages of using organic materials are their complex structures and the sometimes difficult handling problems. However, the advantages of low melting points, good crystalline form and convenient solution properties can often outweigh the structural problems, especially now that complex organic structures are readily elucidated by diffraction techniques.

Neuhaus (104 - 115) and Willems (116 - 124) in a series of investigations have published systematic reports of epitaxy with organic materials. Unfortunately their choice of compounds appears to be random and there has been very little correlation between the structures of overgrowth and its substrate.

Initial studies concerning organic materials suggested that a structural similarity was necessary between the substrate and its deposit overgrowth (125). This was soon found to be totally invalid by the work of both Neuhaus and Willems with the orientation of hexamethylene on the (010) face of gypsum, 1,4- naphthaquinone, anthraquinone and 1,4,6- trichloro-anthraquinone on the (100) face of alkali-halides (126). Willems also achieved orientation of non-polar molecules on non-polar surfaces (120, 124) contradicting the views held by Neuhaus (110, 115) that polar groups were necessary for epitaxy to occur.

The general conclusions obtained from the results of organic depositions was that the parallel face of the depositing crystal was of a low miller index and in general there was at least a one-dimensional structural analogy between the two materials (117, 123). This dimensional analogy was interpreted as a similarity in periodicity of an atom or group in the deposit lattice with that in the substrate lattice together with a parallel alignment of these periodically occurring atoms or groups. This does not mean that the best 'matching' lattice networks were epitaxially the most favourable, because of the complex structural problems it was not possible to explain some of the anomalies in the organic deposition experiments.

An excellent review of organic overgrowths has been compiled by Darling (84), however, unfortunately many of the organic overgrowths used in earlier epitaxial experiments do not always include lattice orientations. The exact contact plane is difficult to determine, because many deposits are not stable in the electron beam, therefore can only be determined by growing large well defined crystals for observation in the optical microscope.

Seifert et al (127 - 137) have studied the orientation of amino-acids and their derivatives on quartz surfaces. Crystal deposition has been from the vapour and from solution and large molecules such as vitamin B₁₂ were found to exhibit epitaxial properties. In these investigations it is interesting to note that the optical antipodes of quartz crystals have different epitaxial properties even though they are chemically identical. Seiferts' interest in this phenomenon stems from the silicosis behaviour exhibited by quartz surfaces. Different quartz crystal faces have different molecular orientational properties and by studying the orientation of amino-acids and their polymeric combinations, Seifert hopes to obtain information on the cause of silicosis and related diseases.

Carr et al (138) have succeeded in growing oriented deposits of oligopeptides on the (001) cleavage plane of alkali halides. Inferences have been drawn in some cases to the relationship between the molecular structure of the deposit and the substrate surface. Comparisons between epitaxial crystallisation of the oligopeptides and the oriented overgrowth of chain macromolecules on the same surface has also been made. In a similar manner to Seiferts' experiments Carr found that certain important amino-acid sequences in collagen exhibit a specific and positive mode of association on a mineral surface.

Walton et al (139) have studied the epitaxial growth of polymers on ionic substrates. As a result of heterogenous nucleation and epitaxial growth they found structural modifications and altered mechanical properties. In particular potassium hydrogen phthalate causes epitaxy of polypropylene and the salt induces nucleation of the unusual β -phase. This is a good example of modified structure due to epitaxy.

Darling (84) studied the deposition of anthraquinone on urea and thiourea substrates, and a series of substituted ureas on an urea substrate. He found some correlation between the polarity of dominant species of substrate and deposit with the orientation observed.

1.5 Conditions for Epitaxial Growth

In order to obtain well defined epitaxy, it is frequently necessary to control the deposition conditions in a specific manner. The most important variables are; (a) Substrate preparation, (b) substrate temperature, (c) rate of deposition and (d) the deposit thickness. It would appear that the latter variable is only significant for metal deposition where the crystallite size is extremely small. For solution growth and vapour phase ionic or organic growth, the deposit thickness does not appear to be a controlling step.

It has been suggested that a small misfit, less than about 15% was a prerequisite for the occurrence of epitaxy (8). There are now numerous examples, with very large misfits, which support the opposite view that small deviations from lattice fit are not an essential prerequisite for epitaxial growth. Perhaps the most striking examples of oriented overgrowth between a pair of materials with large misfits was observed by Shultz (30, 31). Vacuum deposition of alkali halides on each other always resulted in parallel orientation, the misfits cover a range from -39% (LiF on KBr) to +90% (CsI on LiF).

There often appears to be a match of symmetry at the deposit substrate interface which is more dominant than a small misfit along a particular lattice row, and it is now recognised that the best lattice fit does not necessarily correspond to the observed epitaxial orientations.

1.5.1 Substrate Preparation

The preparation of a substrate surface is extremely important in obtaining good epitaxial results. The geometric and electrical influence has been shown by Basset et al (41, 144) with gold decoration of ionic surfaces, the deposition occurring at steps and dislocations on the surface. The most important property of a surface however, is its cleanliness. If the surface has been contaminated in any way during its preparation then this can effect the results of epitaxial experiments.

When crystals are cleaved in air their surface properties differ to those which are cleaved in vacuum (77). A cleaved rocksalt crystal exhibits a very different step structure if cleaved in air than from the cleaved vacuum surface, the water vapour present in the air causing a rearrangement of the surface geometry of NaCl cleavage surface (140). Some of the first evidence for the effect of contamination layers on the surface with regards to epitaxy were obtained by Ino et al (141, 142). They demonstrated that the so-called epitaxial temperature was much lower for the vacuum cleaved samples.

Harsdorf (143, 144) observed the detailed effect of gas contaminants on the perfection of epitaxy. The gases were assumed to have formed a contaminated layer on the surface of the substrate. He found that the degree of perfection of epitaxy is a periodic function of temperature and explains these rather curious results by a stepwise desorption process of the adsorbed gases on the substrate immediately after air cleavage.

Evidence on the need for contamination of the substrate surface in the production of good epitaxial deposits has been obtained by Matthews and Grunbaum (145, 146). With vacuum cleaved rocksalt crystals, deposits of gold gave several orientations but if the surface was exposed to moist air prior to deposition predominantly parallel orientations were produced. It was concluded from these results that the moisture modified the (100) surface of rocksalt in such a way that it enhanced the epitaxial growth of f.c.c. metals upon it.

Solvents can play a part in effecting orientation on a crystal surface. This effect can be visualised as a gross contamination problem with the substrates coated with adsorbed solvent molecules. Sloat and Menzies (147) have studied the effect of using different solvents on the epitaxial ability of a substrate. The solvents used included furfural, ethanol, methanol, acetone and water. They concluded, that the higher the polarity of the solvent the greater is its influence. In some cases the solvent may enhance epitaxy while in others have a completely inhibiting effect. The correlation between polarity and influence has not been observed in many systems. Darling (84) in his study of P.V.C. on rocksalt found no connection between the polarity of the solvents and their effect on epitaxy.

The influence of surface preparation on epitaxy is a very real effect although not entirely understood.

1.5.2 Effect of Temperature

The importance of an epitaxial temperature was revealed by Bunn (148), Bruck (20), Uyeda (149), Elleman and Wilman (150), Rhodin (151) and Neuhaus (152). As experimentally evidenced the deposition on a substrate has an epitaxial quality ranging from 1 to 100% according to the temperature of the substrate T_E , below which no epitaxy can be obtained for a given substrate, deposit and incident flux, however, lower fluxes allow lower epitaxial temperatures T_E .

In general the effect of temperature can be summarized as aiding epitaxy in the following ways, (a) a cleansing effect on the substrate surface, removing a certain amount of unwanted contamination by a desorption mechanism, (b) providing some of the activation energy which is required to enable the deposit atoms to take up positions of energy minima with respect to the substrate, and (c) by increasing surface diffusion which enables adsorbed atoms or molecules of the deposit to migrate to the

growing nuclei. Because several independent factors are involved it is not possible to define a precise value for epitaxial temperature, and it can only be experimentally determined.

1.6 Theories of Epitaxy

Most workers in the epitaxy field nearly state the experimentally observed orientation results, any attempt to completely explain the results by a unified theory have been unsuccessful. The first principle relating to the theory of oriented overgrowths (8, 9) was based on a survey of a large number of experiments between 1920 and 1935 on epitaxy of ionic compounds on other ionic surfaces. It was assumed that epitaxy required geometrically similar planar atomic lattices having nearly equal inter-atomic distances, or possibly integral multiples of these. Royer, in his attempt to explain the observed cases of epitaxy put forward three rules:

- (1) That there exists lattice planes with networks, elementary or multiple which are identical in form and of nearly the same dimension in the two structures. It is implied that these two networks grow parallel to one another.
- (2) That, where ionic crystals are involved, the ions of the overgrowth should take up positions which corresponding ions of the substrate of the same polarity would have occupied had the substrate continued to grow.
- (3) That the substrate and overgrowth crystals should have the same type of bonding.

As can be seen from the evidence in the foregoing sections Royer's postulate for epitaxy is misleading, Bruck (20) tried to explain his own epitaxial results of metals on alkali halides by saying that the depositing atoms in the lattice took up positions such that a minimal sum of the distances of these atoms to the nearest anions or cations in the substrate existed.

Although this principle covered a few specific cases in general it was a very poor attempt. Thompson and Cochraine (154) criticised this suggestion and pointed out that the orientation of the first cell formed would be unfavourable to the second. Also Bruck had not considered both the cation and anions of the substrate.

Thompson et al (154, 155) pointed out that no surface is atomically smooth, but consists of a series of terraces and ledges according to the work of Stranski (156 - 158). Thompson concluded that epitaxy was governed by the irregularity in the surface structure, this however, seems unlikely because of the high degree of order exhibited by most epitaxial results. It is improbable that the surface inhomogeneity could account for such a phenomenon. Wilman (159) in fact considered that steps were not necessary to epitaxy, though they may control the course of crystallisation.

It is true that many experimental observations indicated some geometric correlation between the substrate and deposit, but it cannot be so strictly defined as postulated by Royer. Since these rules, all theoretical studies have been based on the need for structural similarity between planar nets in oriented overgrowths.

1.6.1 Dankov's Theory

Over a certain degree of misfit between the lattice constants of the intergrowth pair Dankov (160) considered that the interfacial energy would be a minimum if the deposit phase took up the repeat distances of the substrate lattice during crystallisation. Energy of elastic deformation would be small if the misfit was also correspondingly small, and this would favour two-dimensional nucleation. If the misfit was large (>15%) it would imply that the deformation energy in the nucleus would also be large and an unoriented nucleus would be more favourable.

It was assumed that such a nucleus would be roughly equivalent to a three-dimensional one, and the critical difference was deduced by comparing the deformation energy of the two-dimensional nucleus with energy of formation for a three-dimensional one. Dankov concluded that;

$$\Delta a = \frac{2a\alpha}{C_1 + C_2}$$

where, Δa is the limiting difference in lattice constants, a being the lattice constant of the overgrowth, C_1 and C_2 the elastic moduli for a two-dimensional nucleus in tension and shear and α the surface tension of a three dimensional nucleus.

Because of the uncertain quantities , C_1 , and C_2 , the above formula is almost unusable. Dankov found, however, by using some rough approximations that oriented overgrowths would occur for sodium chloride on sodium metal with a misfit of about 9%. This misfit limit was also found in the approximation of a few other intergrowth pairs.

The theory of Dankov has not been supported by experimental evidence and has since been ignored as an acceptable explanation of epitaxial phenomena.

1.6.2 The Theory of Menzer

This theory was proposed to explain results which correspond to a large misfit in lattice parameters. The proposition by Menzer (121 - 123) suggested that good lattice matching occurred during the earlier stages of growth which on subsequent deposition of further material resulted in reorientation through a series of twins to give a deposit orientation corresponding to a large lattice misfit. This theory was initially put forward to explain the epitaxy of nickel and of silver on rocksalt, and was based on Bruck's data (20) which showed that such deposits are predominantly twinned on their (111) planes when the film thickness is of several hundred angstroms.

As more data became available this theory showed little promise and was soon disregarded.

1.6.3 The Theory of Engel

Engel (161, 162) attempted to explain the observed orientation of metals on rocksalt and the experimentally observed epitaxial temperature. She disagreed with the concept that there were Van der Waals forces between the metal and the salt (162) and considered that such forces could only operate in the initial stages of deposition. Later these metal atoms became ionised resulting in a two-dimensional interaction between the metal and the salt. The final result was the formation of an intermediary metal salt layer between the rocksalt surface and the pure metal, the orientations of all three have to be considered. Engel treated the monolayer of metal salt via an improved form of the rule that the orientation must be such as to provide the maximum bond to the substrate base from the largest depositing aggregate. The probability of an orientation is then determined by summing the attractive and repulsive forces between the ions of the deposited metal and the surrounding ions, the summation being performed for all positions in which there is a reasonably small discrepancy between the base and metal salt. Further, the oriented layer of metal salt must then exert the necessary orienting action on further depositing metal.

The epitaxial temperature was explained as a capacity of the base to take up electrons and ionise the incident atoms, which occurs only above a certain temperature. The ionisation potentials for the usual ionised states of some metals appear to be related to the critical temperature in this way, but reasonably perfect oriented overgrowth did not occur when other metals (lead, antimony and tin) chosen in accordance with ionisation potentials, were deposited on to rocksalt at the requisite temperature and

ionisation potential (39, 41) and hence further discussion is probably required on this approach.

1.6.4 Dixit's Theory

The theory of Dixit was originally proposed for the orientation of metal films on amorphous substrates (163) which was later extended into a theory of epitaxy (164). He assumed that for an evaporated film on an amorphous substrate that the latter merely acts as a support. Because of Van der Waals interaction forces the basic assumption is not strictly true. Dixit further assumed that the adsorbed atoms in the first layer behaved as a two-dimensional gas subject to the ideal gas laws.

It was pointed out that the packing density of different planes governs the temperature at which a plane sets itself parallel to the substrate surface. When a crystalline substrate is used the orientation of the base is important and Dixit attempted to account for the orienting effect of the substrate as well as the natural depositing orientation of the overgrowth at that temperature.

The disadvantages of this theory lies in the fact that it is only applicable to monolayers, it does not apply to the formation of isolated three-dimensional nuclei.

1.6.5 The Theory of Frank and Van der Merwe

Initially (27, 65, 98) this theory proposed that in the early stages of deposit growth an oriented monolayer was formed which was elastically deformed to exactly fit the substrate. Then, through a series of dislocations the oriented, homogeneously deformed, deposit was modified back to the structure of the bulk phase.

The authors used a one-dimensional dislocation model, which was extended to two dimensions, and represented the initial monolayer as a set of identical spheres held by identical links exerting a force μ .

The base was represented by a periodic force, the potential energy being the first term in a Fourier series and having an amplitude $W/2$. When the monolayer itself contained no dislocations and was completely pseudomorphic with the substrate surface, Frank and Van der Merwe predicted a critical misfit of 9%. This was later increased to 14%, if one misfit dislocation was present in the interface over a period of 100 repeat units.

Van der Merwe (34, 102, 166, 167) has since modified this theory owing to the lack of evidence for pseudomorphism. His revised theory now relates epitaxy to a series of misfit dislocations from the initial deposit. The model used for investigating the problem theoretically takes into account the degree of misfit, the growing crystal thickness, and the boundary in and between the deposit and substrate crystals. This theory has quantitatively explained many metal-metal results where the deposit-substrate orientations are completely parallel. Unfortunately the theory becomes mathematically too cumbersome when attempting to deal with orientations which deviate from direct parallelism.

Matthews (168, 169) has recently observed the generation of misfit dislocations in three-dimensional islands of copper deposited on to a nickel substrate. In the electron microscope misaligned moire fringes were observed in the islands, and these were thought to result from discrete changes in misfit strain, which would accompany the generation of individual misfit dislocations. Stoop and Van der Merwe (170) Stoop (171, 172) and Van der Merwe and Snyman (173) have postulated a model to account for these observations. The basis of the model is that a three dimensional island could grow by the addition of consecutive layers in an atom-by-atom process, and the first layer could be thought to strain as in the monolayer growth process suggested earlier.

This model is mathematically much simpler, but can still only be applied to a restricted number of metal deposits. There is also direct experimental evidence (84) that infers that three-dimensional islands do not grow by a layer-by-layer process. Therefore, although the epitaxial orientation of some deposits can be explained, the process of growth chosen for the model is a matter of mathematical convenience, and does not describe the experimentally observed growth process.

1.6.6 Fluid Cluster Concept

Halpern (69), Lewis (68) and Venables (65) have introduced the concept of treating the crystals embryo as a fluid cluster, and the epitaxial orientation is determined at the stage when the embryo loses its fluid-like mobility.

The growth process of metal nuclei on alkali halide substrates kept at a suitably high temperature can be summarized as follows:

- (1) A single adatom forms a stable nucleus in the sense of its having a higher probability for growth than for decay.
- (2) Initially, clusters grow mainly through atom-by-atom addition.
- (3) These initial atomic clusters tend to be close packed, with the 111 faces parallel to the (100) substrate surface.
- (4) All clusters tend to grow three-dimensionally, with the metal-metal bonds becoming increasingly more saturated as the embryo size increases. These embryos are relatively fluid but rapidly become rigid as their size increases.
- (5) Initially formed clusters, while sufficiently small, have high mobility on the substrate surface comparable with that of single adatoms.

- (6) Migrating islands can interact with one another, as well as with single migrating adatoms or impinging atoms from the vapour, through inelastic collisions, thereby undergoing internal rearrangement. The collision energy, supplemented by the thermal energy vested in the substrate temperature supplies the necessary activation energy. Such interaction has been confirmed by Metois et al (174).
- (7) The energy gained activates the clusters and the suitable atomic rearrangement process occurs, leaving an oriented embryo.

The size of the critical nucleus is defined by the Coincidence number N^* , N^* is defined from the following relationship.

For a particular orientation the lattice misfit is calculated in the normal way

$$\text{i.e. } W = \frac{b - a}{a}$$

and $N^*-1 \sim 1/W$ where N^* is rounded off to the nearest neighbour.

Therefore where large N^* are necessary the fluid cluster is already too large, and hence too rigid for atomic rearrangement to occur, hence good epitaxy for a particular system would not be observed.

Experimental observations of the growth behaviour of a number of f.c.c. metals on alkali halides substrates show very good agreement with the theory (175).

Kotze et al (175) conclude the complete formulation of the fluid cluster concept involves a number of unknown parameters such as cluster mobility, collision cross sections of clusters of a given size, the energy difference between different based clusters of the same size etc. Most of these quantities would be certainly difficult to estimate, and their incorporation in the rate equation governing epitaxial nucleation vastly complicate the theory.

Nevertheless it should in principle at least, be possible to arrive at a mathematical description of the epitaxial process. A 'discrimination ratio' towards the formation of epitaxial nuclei, derived as described should depend on the prevailing experimental conditions of substrate temperature and evaporation rate.

1.6.7 Long-Range Forces

There is an increasing amount of evidence being accumulated by Distler and his co-workers suggesting that epitaxy and oriented overgrowths are brought about by long-range forces of the magnitude of hundreds of angstroms.

Distler et al (176 - 225) have published a considerable number of papers, concerning these long-range forces. They have investigated their anisotropy, range of action, and the possible causes from which they arise. Point defects dislocations, aggregates of point defects and similar inhomogeneties are assumed to be responsible for the forces bringing about nucleation and epitaxy.

Amorphous boundary layers have been coated on to crystal surfaces and by using an epitaxial decoration technique Distler et al have been able to measure the extent of the orienting capabilities of different surfaces.

Because of the possible importance of this quite revolutionary approach to epitaxy, Distler's work is reviewed in detail in Chapter Six. This chapter also includes objections to this work by other experimenters who failed to repeat Distler's results.

1.7 Conclusions

Until quite recently the theories for explaining epitaxial phenomena have been concerned with surface forces of a very short range ($0 - 10\text{\AA}$), and in nearly every case some form of geometrical relationship was suggested between the intergrowth pair. The early theories of Engel

Menzer and others, have become outdated because of their dependance on pseudomorphism, while experimental evidence suggested otherwise.

The revised theory of Van der Merwe has some validity for parallel orientation of metals, but relies on the growth of the deposit by molecular layers rather than three dimensional nuclei.

The fluid cluster, theory explains many of the epitaxial results obtained with metals on alkali halides, but does to a large extent depend only on lattice parameters, and cannot be extended when organic deposits are used.

The approach of Distlers would appear to be a more useful concept. Long-range forces and their ability to orient nuclei up to several hundred angstroms away, can explain the vast majority of epitaxial observations. This theory still remains the most modern approach, which has not up to this stage been fully explored to discover its true merits. This has been attempted in this study.

2.0 Experimental Methods

The experimental procedures involved can be broadly categorised as; sample preparation, observation of results and, general handling of the materials. Using this framework as a guide, this chapter deals with the techniques involved in the study of epitaxial growth of organic materials.

The preparation of a sample requires the deposition of the overgrowth onto a single crystalline substrate of known orientation. Observations of the prepared samples includes Optical and Electron microscopy. The general handling technique of the materials is to ensure a minimum of unwanted contamination, as this will, as discussed earlier, inevitably modify the result obtained.

2.1 Sample Preparation

(i) Substrate preparation

The substrates used in this study were sodium chloride, muscovite mica, and quartz. Sodium chloride and mica were freshly cleaved immediately before deposition. Micro-tweezers were used for all necessary handling, and contact with the cleaved surface completely avoided.

Because crystalline quartz does not contain a natural cleavage plane, this surface was prepared by grinding, polishing and chemical etching.

This process involved grinding the natural quartz face (hexagonal $10\bar{1}0$ face) initially on a glass slide successively with three grades of carborundum abrasive, using water as the lubricant. The grades used were 180, 320 and 600. This was continued until the surface was visibly smooth and contained no deep pits or scratches. The next stage was to remove the disrupted layer caused by the grinding process, this was done by the process of 'lapping'.

Lapping differs from grinding because a continuous flow of abrasive dispersed in a water lubricant is used. This ensures no scratching, and no build up of removed material. A cloth covered eighteen inch lapping wheel was used electrically driven at a speed of approximately 250 revolutions/min. The same grades of abrasive were used until a smooth surface was obtained.

Once a suitable surface was prepared the surface was cut into sections of 5mm x 10mm approximately 3mm thick; by a ten inch Diamond impregnated copper wheel, driven by a 'Rock Rascal Model J motor'. The cutting process was lubricated by a light oil/water emulsion.

The side opposite the prepared surface was now ground parallel, to do this, the prepared surface was held on to a microscope glass slide by means of Canada balsm, the opposite to this face was then ground flat by a rotating grinder. The specimen could then be removed by dissolving the Canada balsm in Xylene. The prepared surface was then polished on successive 6, 2 and 1 micron diamond wheels. The polishing process was lubricated with oil.

After the final polishing the quartz face was chemically etched with a 48v/v% aqueous hydrofluoric acid solution. The etching times used are described later in the text (section 3.24). After the required times, the surface was washed thoroughly with distilled water, and vacuum dried at room temperature.

(ii) Deposit preparation

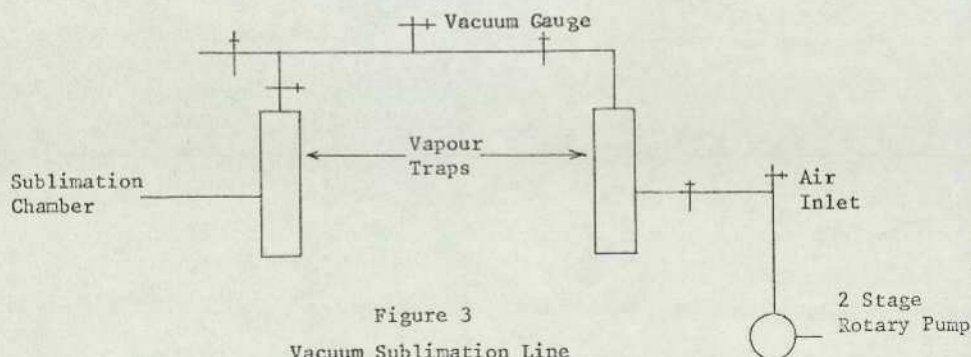
In order to be able to characterise the epitaxial interactions all depositing materials must be of known crystal structure and the surface orientation clearly characterised. It is very important to use high purity depositing materials because unwanted surface contamination is more likely to occur from the sublimate vapour, rather than being an inherent part of the surface initially.

2.2 Deposition

Deposition has been in all cases by vacuum sublimation, this was done because epitaxy is more likely to occur from vapour deposition than from solution deposition (147). The depositing materials were all organic in nature because of the relative ease in which they can be sublimed. Many depositing materials were initially purified by recrystallisation, and in some cases by vacuum sublimation as well. The sublimates used were a series of amino-acids and anthraquinone. All these materials would sublime within the convenient temperature and pressure ranges, 50 to 250°C and atmospheric to 10^{-3} Torr respectively.

2.21 Vacuum Sublimation Apparatus

The requirements of any apparatus used for deposition by vapour phase methods are; the temperature of the sublimate and substrate must be accurately controlled and known, the distance of the substrate from the deposit be variable and the pressure controllable. The temperature of substrates were varied by circulating heated water, and the temperature of the sublimate was varied by circulating heated oil. The operation of the sublimation apparatus can be seen from figures 3, 4 and 5. As many variables are involved, the growth of epitaxial deposits from the vapour is very much an empirical situation, and further discussion of the apparatus is now left to appropriate sections later in the text.



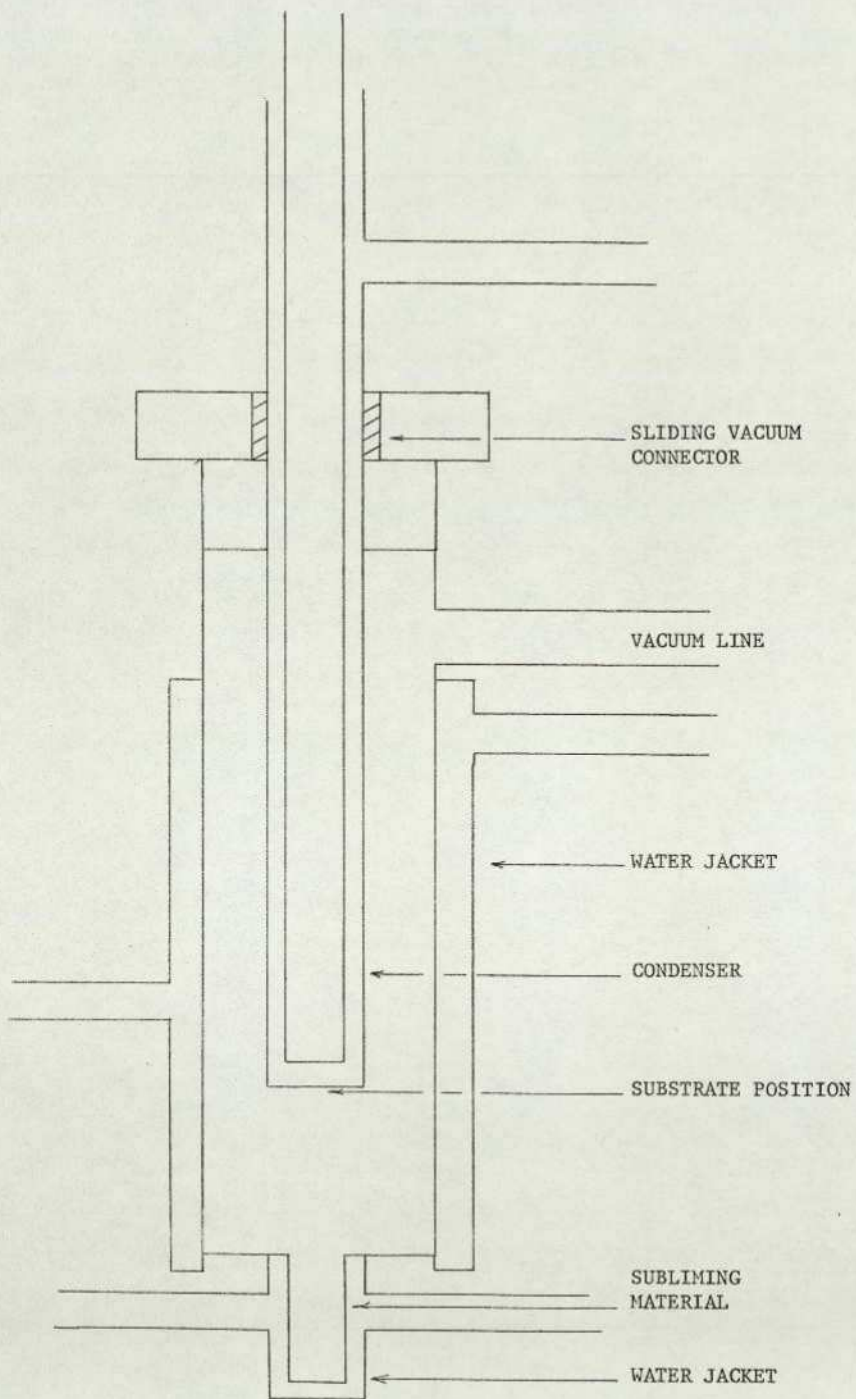


Figure 4
Sublimation-Deposition Apparatus

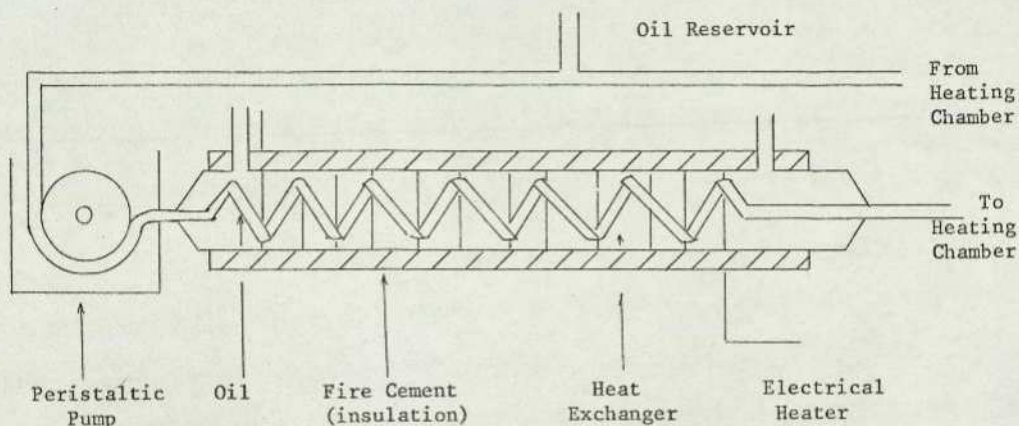


Figure 5

Oil Heat Exchanger

2.3 Observational Methods

2.31 Optical Microscopy

Since all the deposit materials used in this study have been organic in nature, they are all optically active. Only crystals of cubic symmetry are optically isotropic, and hence the deposits are well suited for observation with polarised light.

Deposits were observed on a Vickers Photoplan polarising microscope.

2.32 Electron Microscopy

The resolution of the electron microscope is far greater than that of the optical microscope, and by the use of electron microscopy, deposits could be observed at the initial stages of growth. Also the increased depth of vision enabled the crystal morphology of the deposit to be determined.

A carbon platinum replica technique was employed for the observation of the samples, because samples must be of the order of a few thousand angstroms thick, and the sample must be stable in the electron beam. Neither of these conditions are met by the samples themselves.

Preparation of a Carbon-Platinum Replica

The method used for the preparation of a carbon platinum replica is to deposit several hundred angstroms of carbon on to the sample, and then to improve definition and contrast, shadow the sample at a known angle with platinum. The geometry of this process is shown in figures 6 and 7. The prepared replica is then removed from the sample and mounted on copper 200 mesh grids, suitable for mounting in the electron microscope.

The stages of replication involved initially the fixing of several samples on to a glass slide, and this was placed into the vacuum deposition chamber. A drop of low pressure diffusion pump oil on a white slide acts as an excellent indicator for the carbon thickness. A very approximate estimation of the thickness of the deposited carbon film can be made from the colour of the film on the drop of oil. When the pressure in the chamber is reduced to 10^{-6} Torr carbon can be evaporated, this was done by means of resistance heating. Two 5mm carbon rods are sharpened and placed with their points touching, when a high current is passed through the rods, the increased resistance at the tips cause the temperature to rise to the evaporation temperature of carbon. Using this technique, a large quantity of carbon is evaporated very rapidly, and the required carbon film is deposited after only a few seconds of evaporation. The appearance of a dark brown film on the oil drop approximately corresponds to a carbon film of the order of two hundred angstroms thick.

Once the carbon has been deposited the sample is shadowed with platinum at the required angle. Platinum is evaporated by winding a small loop of platinum wire on the tips of two sharpened carbon rods. Initially the current is passed slowly through the rods to allow the platinum wire to melt and form a drop which is held firmly between the tips of the rods by surface tension. The current is then rapidly increased, until the temperature necessary for platinum evaporation is reached.

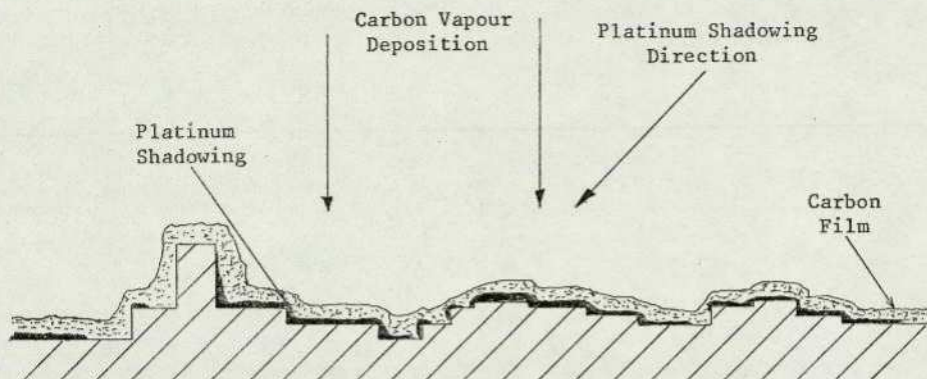


Figure 6
Platinum-Carbon Replication of a Surface

As the platinum shadowing angle and the distance from the sample to the platinum source are known, the height of any crystallites or steps on the surface can be determined.

The replica was detached from the sample by dissolving the sample in water, and floating the detached replica onto electron microscope grids. However, this method could only be used when the substrates were alkali halides which are water soluble.

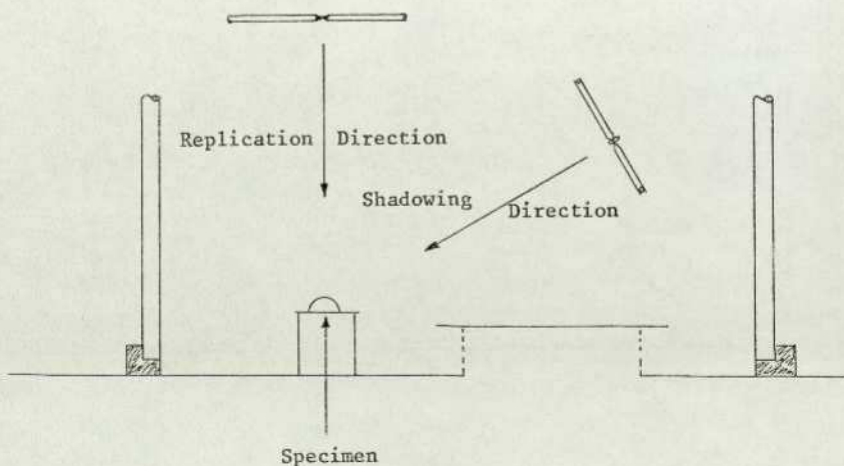


Figure 7
Apparatus for Replication

Other techniques of atomic adsorption, low energy electron diffraction etc. were also used during the course of this study, and they are discussed in detail in the appropriate sections.

3.0 Results and Discussion

The results of this study have been divided into the two following sections:-

The growth of a series of amino acids on a sodium chloride substrate.

The growth and behaviour of glycine and anthraquinone deposits on sodium chloride, mica and quartz substrates.

3.1 The growth of a series of amino acid single crystals on a freshly cleaved surface of Sodium Chloride

A series of amino acids were chosen for depositing materials because, their crystal structures are well defined, they have similar crystal structures and they sublime and grow easily as single crystals. Gross et al (226) have previously studied the vacuum deposition of amino acids and have shown that the majority of them are stable to vacuum sublimation.

The amino acids used in this study were:-

α -Glycine, β -Alanine, γ -amino-butyric acid, DL-Alanine, L-Alanine, L-valine, L-Aspartic acid, L-Arginine, L-Proline, L-Cystine, L-Cystiene and L-Phenylalanine.

3.12 α -Glycine on Sodium Chloride

Glycine was deposited under a variety of conditions and good orientation was observed in all cases. Typical experiment conditions used were a substrate temperature of 42°C, a sublimate temperature of 114°C and deposition times of 2 - 6 minutes.

The orientation of the crystallites was determined by observation of the deposit under polarised light.



PLATE 1

Oriented Glycine Deposit
6,000X

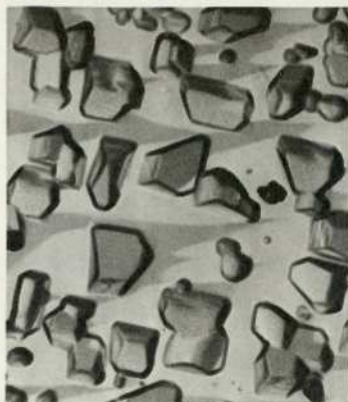


PLATE 2

Crystal Habit of Glycine
18,000X



PLATE 3

as (2)
10,000X



PLATE 4

Glycine (010) face
5,000X

On rotation of the sample, all the light was extinguished at the same angle, indicating a single crystal oriented overgrowth. Although various substrate and sublimate conditions were used it was not possible to grow large enough individual crystals of glycine to be observed directly with the optical microscope. Because of this, very thin deposits of glycine were grown and replicated for observation with the electron microscope.

Plates 1 - 4 show clearly the epitaxial deposit, and the high degree of crystal faceting of the individual crystallites. From the electron micrographs, the interfacial angles of the deposit were measured and the orientation of this system corresponds to:

$$(010) \text{ Glycine } [100] // [100] \text{ Sodium chloride } (001)$$

3.13 β -Alanine on Sodium Chloride

It is normal in the study of epitaxy, to go through quite separate modes of growth on a substrate for a particular deposit. Many metals grow epitaxially on a substrate only when the substrate is heated to the critical substrate temperature for a particular set of deposit conditions. With organic deposits the conditions for epitaxy are not normally highly critical, and only two modes of growth are usually observed, which are single crystal oriented growths and polycrystalline growth. The growth of β -Alanine, however, occurred in three separate modes, which clearly illustrated the importance of depositing conditions.

The most easily variable parameters in the growth of any deposit are, the subliming rate, and the temperature of the substrate. With β -Alanine when a high subliming rate is used, (typically sublimate boiler at $120 - 140^{\circ}\text{C}$) and a cool substrate (typically $30 - 50^{\circ}\text{C}$) the conditions exist for a rapid growth of the deposit. Under these conditions, β -Alanine grew as a glassy solid, as though it had grown by the rapid solidification of a liquid. (This type of growth is shown on Plate 5)

If a lower rate of sublimation is used (typically 100°C) with a cool substrate the conditions exist for a much slower growth. Under these conditions deposition times of 10 - 20 minutes were required to obtain sufficient deposit for observation with the optical microscope, and β -Alanine grew in a most unusual way.

Plate 6 shows the growth after 20 minutes deposition. The surface of the prepared sample is broken into a large number of domains, and each domain is bordered by areas of polycrystalline or fibrous growth. Close examination of this sample (see plates 6, 7 and 8) suggests that there exists a large proportion of the surface containing very little deposit. This observation indicates, a high mobility of the deposit, and areas of very low nucleation density on the substrate. This would not be expected from the observed behaviour of glycine on the same substrate, where growth was characterised by a high nucleation density.

In an attempt to determine if this unusual growth was induced by surface irregularities in the substrate, progressively thinner deposits were prepared. This led to the quite unexpected observation, that inside each domain there infact existed a very thin film of single crystal deposit. This is shown on plate 9. The existences of a number of light and dark areas, when observed under polarised light, which change on rotation of the sample, indicate that those areas of the same light intensity contain the same crystalline plane with the substrate.

When the substrate temperature was increased to $60 - 70^{\circ}\text{C}$ more deposit grew within the domains, and some of this deposit was of sufficient definition, to enable the orientation to be determined under high magnification.



PLATE 5

Glassy-like deposit
of Alanine
100X

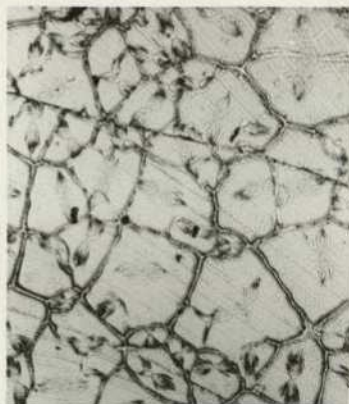


PLATE 6

Domain regions of Alanine
40X



PLATE 7

Same as (6) under polarised
light

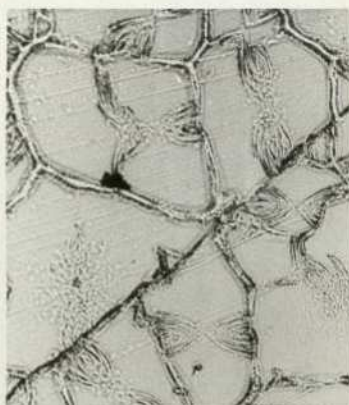


PLATE 8

Area of deposit under
100X

A number of crystal orientations are observed. These orientations exactly correlate with the observations made under polarised light, that is those areas which are of the same intensity at a particular rotation of the sample contain the same orientation of the crystallites. (These orientations can be seen on plates 10.1 - 10.4)

The many observed orientations of a
thin deposit of Alanine on Sodium Chloride



PLATE 9

40X



PLATE 10.1

Orientations of
Alanine inside the Domains
400X



PLATE 10.2

Different Orientations
in different Domains
100X

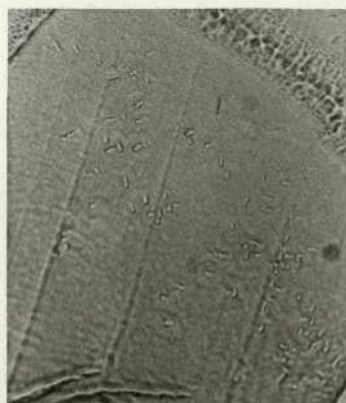


PLATE 10.3

same as 10.1
400X

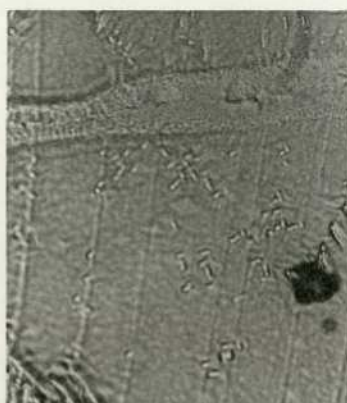


PLATE 10.4

same as 10.1
400X

ORIENTATIONS OF ALANINE

At still higher substrate temperatures ($70 - 90^{\circ}\text{C}$) growth of the deposit occurred preferentially within the domains, and the fibrous growth which made up the boundaries completely eliminated. In order to obtain sufficient deposit on the substrates a much higher subliming rate was required. By increasing the subliming rate the overall fraction of the deposit lost by resublimation from the hot substrate was reduced.

Under these conditions the samples prepared were predominantly oriented, and of single crystals, but again no single unique orientation was dominant.

The high degree of crystal faceting, and the different orientations can be clearly seen on plates 11 and 12, and further examples of the deposit are shown on plates 13 - 16.



PLATE 11

Well defined Crystals of Alanine
under polarised light
400X



PLATE 12

Orientation of Alanine
400X

Summary of the Growth of β -Alanine

The study of β -Alanine on sodium chloride serves as a unique example of the balance between the crystal growth parameters and the epitaxial growth parameters.

Under the conditions suitable for a high growth rate of the deposit a glassy type of solid was produced that was due to the rate of deposit growth being too rapid for the forces on the substrate surface to exert any orienting influence. The surface under these conditions acted merely as a non-orienting nucleating centre. As a means of confirming this suggestion β -Alanine was grown rapidly on the surface of a glass slide. Although identical results would not be expected due to the quite different nucleation properties of the two surfaces; sufficient similarity in the two deposits was observed to confirm the epitaxial inactivity of the sodium chloride substrate under these conditions.

When the growth rate was reduced, by the reduction in the subliming rate, the deposit grew initially as a partially crystalline film. Separate areas of this film were nucleated, and this led to the formation of different crystallisation fronts. There is no reason to assume that there exists a greater probability of nucleation in one unique area, so it is likely that all the nucleation events took place within a limited space of time. This is confirmed by the similar areas occupied by the domains. As the crystallisation continued the meeting of two crystallisation fronts led to the formation of the boundaries. These boundaries would appear as polycrystalline because of the mixture of orientations that are likely. In some cases the crystallisation fronts do not end abruptly at the domain border, but by some mechanism merge, this led to different orientations being observed apparently within the same domain, as seen from plate 10.3.

Under the slow growth rate, these domain boundaries act as preferential nucleation sites, because of their irregular surface, for the further incoming deposit and consequently the sample is dominated by the thick polycrystalline boundaries.

When the substrate temperature is further increased, the difference between nucleation and growth at a polycrystalline boundary or within a domain is reduced, and therefore more growth occurs in the domain regions, although growth at the boundaries remained predominant.

At the very high substrate temperature condition there is a further reduction in the difference and most growth takes place in the domain areas. Also under these conditions the formation of an epitaxial deposit is energetically more favourable, and instead of the random nucleation which occurred under the cooler substrate conditions, more epitaxial nucleation takes place which in turn reduces the number of possible orientations.

The different orientations within separate domains on the surface has been previously observed with Alanine. Ickert (229) reported the changes in crystallisation of Alanine crystals on the surface of mica single crystals. Ashida (230) postulated that the different water content of separate areas of the surface caused by the various thermal treatments was responsible for this phenomena.

The possible importance of the water interaction was observed when attempts were made to produce very thin films. To determine under what conditions an amorphous film could be produced, very thin deposits were required for examination in the electron microscope. Unfortunately this was not possible, as very thin films interacted strongly with atmospheric moisture, and made subsequent observations impossible.

Due to crystals of β -Alanine being orthorhombic they contain no measurable angle to allow the orientation of the crystal planes with respect to the substrate orientation to be made. In addition the contact plane of the deposit could not be found. To overcome this difficulty thick oriented deposits were covered with carbon and mechanically stripped from the substrate for examination with the electron microscope for diffraction studies. But like many organic materials the deposit was not sufficiently stable to the electron beam. However, some predictions concerning the orientations and contact planes of the deposit are possible from the results of epitaxial model calculations, and these are discussed in detail in Chapter Five.

(cont.)

3.14 γ -Amino-butyric acid (GABA) on sodium chloride

The water interaction observed with the very thin deposits of β -Alanine, also occurred with deposits of GABA. Under all normal conditions where an epitaxial deposit would be expected, the deposit interacted strongly with atmospheric moisture. Various combinations of sublimate and substrate temperatures were used, but in all cases observation of the crystalline deposit was impossible. Very thick deposits were prepared, but this only resulted in the production of a coalesced film, and the deposit was not sufficiently stable under the electron beam for the orientation or contact plane to be determined by the normal selected area diffraction technique.

The solid on the surface of the substrate could be observed under the microscope dissolving and recrystallising. A sample prepared on a substrate at 45°C with a sublimate temperature of 110° shown on plates 17 and 18 illustrate the gradual formation of a liquid film over the surface of the deposit. The appearance of this deposit under polarised light shown on plate 19, illustrate the existence of quite distinct areas on the surface of similar light intensity at a particular rotation of the sample. This would indicate that some of the deposit must incorporate the same contact plane, although the various orientations are quite different than those observed in the domains of β -Alanine.

The initial dissolving stage of the deposit was a very rapid process, and always, the time taken to mount the sample for observation under the microscope was longer than the time required for water interaction. As a result only the recrystallisation process could be observed and photographically recorded. The liquid film, seen on plates 17 and 18 is thought to be a second dissolving phase, although no second recrystallisation was observed from this particular specimen.

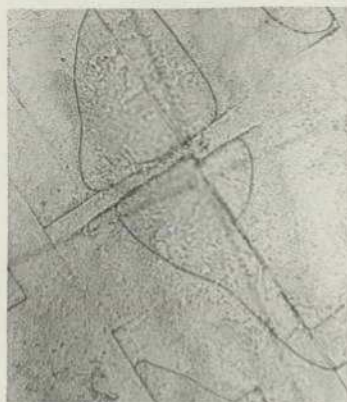


PLATE 18

Same as 17
100X



PLATE 17

Liquid Film on GABA Deposit
40X

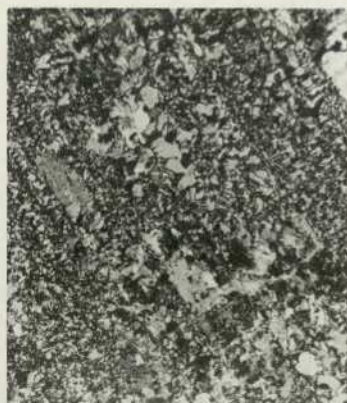


PLATE 19

Deposit under Polarised light
100X



PLATE 20

Same as 19 under normal light

The early indications of an extent of ordered growth predicted from plate 19 was confirmed by the growth of later deposits. The deposits shown on plates 21 and 22 illustrate rather more clearly the existence of ordered growth. The appearance of single individual crystals on plate 21 together with the ordered growth would suggest the possibility of the production of an epitaxial deposit.

Some control over the recrystallisation process was possible by incorporating a simple heating stage on the microscope, but an epitaxial deposit could still not be prepared.

It was thought that eventually with an improvement in the temperature control, and control of the immediate environment around the recrystallising deposit an epitaxial film could be grown. But it seemed unlikely that an epitaxial deposit could be grown from the deposition from the solution and not from the deposition from the vapour. Due to this water interaction it was not possible to determine if the initial deposit was oriented.

To overcome this difficulty a small cell was constructed around the substrate, with a shutter mechanism incorporated which could keep the prepared sample dry. See figures 9 and 10.

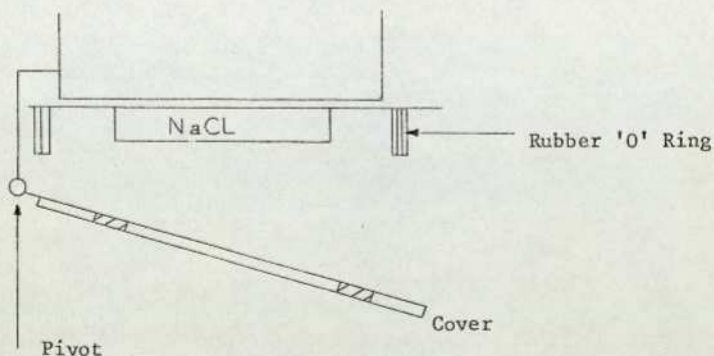


Figure 9
Dry Cell



PLATE 21

Partially Oriented Deposit of GABA
under Polarised light
100X



PLATE 22

Same as 21
100X

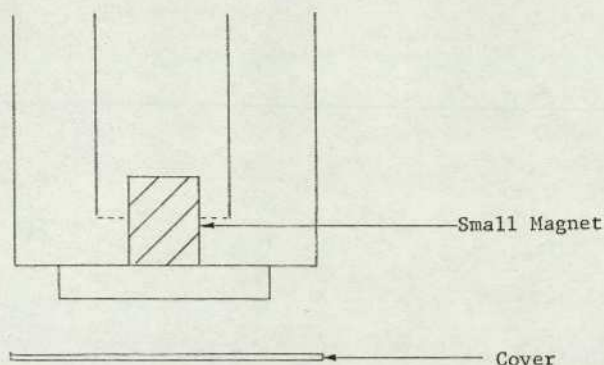


Figure 10

The small magnet held inside the condenser, was of sufficient strength to attract the metal ring and seal the sample. A stronger magnet held outside the chamber held the cover away from the specimen while the material was subliming, after deposition the larger magnet was removed and the cover attracted to the condensor sealing the sample. As a further precaution the vacuum inside the sublimation chamber was released with air which had previously passed through a drying column.

This technique had a limited success but as the cell was in no way air tight, the deposit still adsorbed sufficient water onto its surface to make microscopic observation very difficult. This technique was finally abandoned due to the experimental difficulties, and the inconclusive results obtained.

Experiments were carried out with various concentrations of solutions of GABA in water on the heating stage of the microscope, and the stages of crystallisation were carefully followed, but this gave no further insight into the mechanisms involved in the interaction of atmospheric moisture with a deposit on a sodium chloride substrate.

This did, however, demonstrate the possible importance of the substrate, and it was thought that a freshly deposited film would contain a surface of high surface energy.

This would result in the surface being very active because its surface energy could be reduced by an adsorption process, which could be achieved by a surface interaction with water, and this would be made more probable by the increased thermal energy of the heated substrate.

Samples were prepared on substrates held at room temperature, but no orientation was observed although the interaction with water appeared much less. This is a purely qualitative observation due to the fact that no recrystallisation was observed, but only a gradual clouding of the deposit.

The technique was adopted of heating the substrate while the deposition takes place, and then cooling the substrate to below room temperature prior to removal of the specimen from the sublimation chamber.

The temperature of the coolant was found to be very critical, because if the sample was excessively cooled it was dissolved by the water naturally condensing on the cold surface.

Various combinations of substrate and coolant temperatures were used, and it was discovered that a temperature in excess of 45°C was required to obtain epitaxial orientation. Plates 23 - 26 show the improving proportion of epitaxial deposit achieved by increasing the substrate temperature. To reduce the atmospheric water interaction sufficiently for observation of the deposits, the substrate and sample had to be cooled to $14 - 18^{\circ}\text{C}$ prior to exposure to air.

By using the coolant technique, and also varying the deposition rate, deposits were prepared that showed good orientation and good single crystal definition. This can be seen on plates 27 - 29.

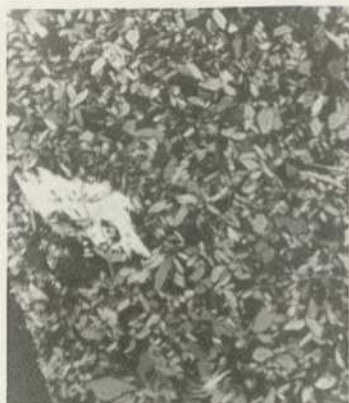


PLATE 23

100X



PLATE 24

100X



PLATE 25

100X



PLATE 26

100X

VARIOUS ORIENTATIONS OBSERVED WITH DEPOSITS OF GABA

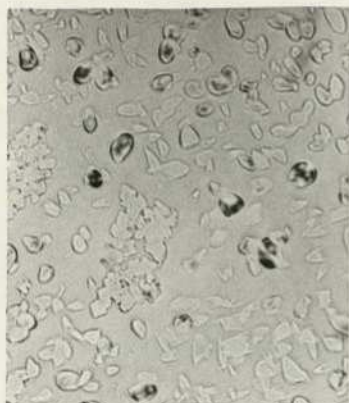


PLATE 27

Oriented Deposit of GABA
100X

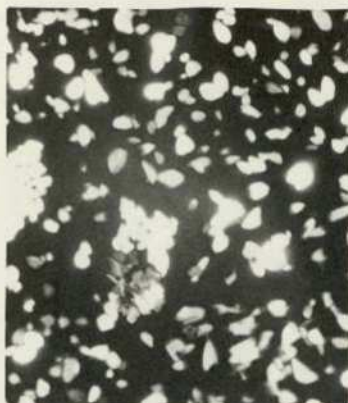


PLATE 28

Same as 27 in Polarised light
100X



PLATE 29

Oriented Deposit of GABA
100X



PLATE 30

Deposit of GABA grown on
Substrate at 70°
40X

A very interesting growth was observed when GABA was deposited slowly onto a substrate at a temperature above 70°C . A large film-like deposit was observed, which although single crystal was not oriented. This is shown on plate 30. The reason for this type of growth is not known, and due to the long deposition times required for these slow sublimation rates a thorough investigation was not undertaken. However, it may be due to the random nucleation observed with β -Alanine although under quite the reverse conditions.

The exact crystallographic planes involved in the orientation of GABA on sodium chloride are discussed in detail in Chapter Five together with the predictions of the epitaxial model.

The effect of the coolant on water interaction is thought to operate by, in some way 'freezing' the deposit on the substrate by lowering the thermal energy of the sample. As a result of this the surface energy is reduced, and also the activity of the surface towards atmospheric moisture is reduced. The magnitude of this activity can be compared with the fact that more water would be expected to be adsorbed on a cool inert surface than on a heated one. Therefore the presence of the active surface must compensate for this difference before it can interact with water. Also the effect of the temperature would be expected from a consideration of surface activity, which is strongly temperature dependant.

Further evidence for this behaviour has recently been indirectly demonstrated by theoretical calculations of a conformational analysis of the GABA molecule (231). These calculations predicted the existence of discrete hydration sites with groups of GABA molecules. Although it is not possible to extend this to the solid state, the correct orientation of the crystals on the substrate may expose a surface where a hydration process is more favourable.

3.15 DL-Alanine and L-Alanine on Sodium Chloride

Both DL-Alanine (232, 233) and L-Alanine (234, 235) are orthorhombic and the lattice parameters are nearly identical (see table 1), however, the crystal packing is different.

Table 1

	<u>DL-Alanine</u>	<u>L-Alanine</u>
Lattice Parameters	a = 6.0	a = 6.0
	b = 12.1	b = 12.0
	c = 5.75	c = 5.8

The racemate, contains alternating chains of each isomer, and both the racemate and the pure isomer were used as deposits in an attempt to discover if any difference in their behaviour on a sodium chloride surface existed.

Under normal deposition conditions both materials interacted with water, although not as strongly as GABA because no recrystallisation was observed. DL-Alanine has a lower solubility than GABA in water, and it was expected that a higher coolant temperature would be sufficient to eliminate the water interaction. (This is largely an intuitive prediction as no simple correlation would exist between the bulk solubility of a material and the activity of a freshly formed surface.)

In practice it was found that a coolant temperature of just below room temperature (18 - 20°C) was sufficient to eliminate the water interaction, and good epitaxial growth was obtained. The oriented deposit is shown on plates 31 - 34.

During the course of this study no evidence was found to suggest that DL-Alanine and L-Alanine behaved differently on the substrate, and further discussion of the orientational relationship can be found in Chapter Five.

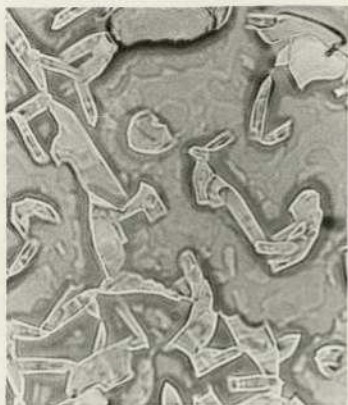


PLATE 31

400X



PLATE 32

400X



PLATE 33

100X

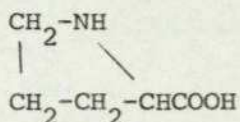


PLATE 34

100X

ORIENTED DEPOSITS OF DL ALANINE
GROWN USING THE COOLANT TECHNIQUE

3.16 L-Proline on Sodium Chloride



As with the other amino acid deposits previously discussed, L-Proline deposits on the surface of sodium chloride were found to interact strongly with atmospheric moisture. This was not expected for this compound because Kayushina et al (236) in their structure determination of L-Proline mention the stability of the single crystal towards water.

The interaction between the deposit and water was far more easily followed and studied with L-Proline than any of the previous compounds. This was largely due to the fact that very large and well defined single crystals were obtained with L-Proline, and the dissolving and recrystallisation stages were very much slower. The growth of such large and well separated crystals could only occur if the deposit possessed a high mobility on the sodium chloride surface, and although various growth rates were used no film growth was obtained. This was done because in practice the water interaction appears greatest with thin films. Because the individual crystals could be observed so readily on the surface, the subsequent water interaction could be observed and followed around each crystal.

This effect can be clearly seen from plates 35 and 36 where many of the crystals are surrounded with water. On these two plates the completely dissolved material can be seen by the drops containing no solid deposit. To determine whether any solid material remained in these drops, the drops were carefully examined under polarised light, while a fine needle was held in contact with the drops to induce nucleation. The result of this examination was the confirmation that no solid deposit existed, or could be induced to crystallise by external forces. Plates 37 and 38 show two important additional features that is, two drops coalescing to form a large drop.

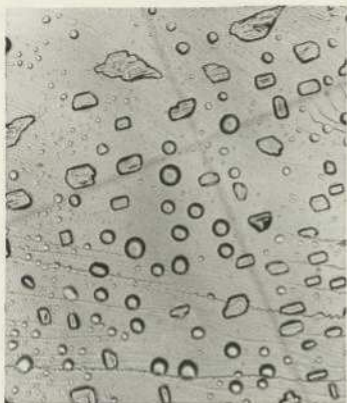


PLATE 35

100X

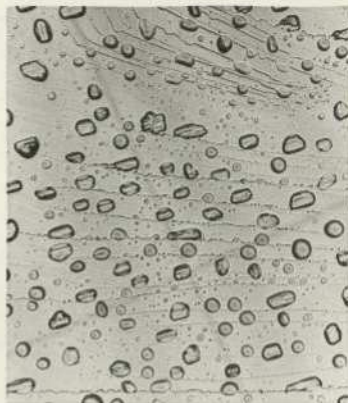


PLATE 36

100X

ORIENTED DEPOSITS OF L-PROLINE
INTERACTING WITH ATMOSPHERIC WATER

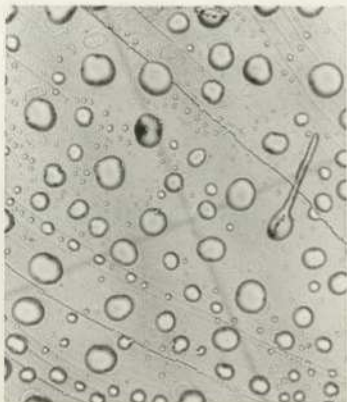


PLATE 37

100X



PLATE 38

100X

ALL SOLID DEPOSIT DISSOLVED IN
THE ABSORBED WATER

The result of this is the formation of a larger but still well oriented single crystal, and the second is the gradual disappearance of some solid inside a drop.

The coolant technique was also employed with these deposits, but with no success, and no temperature dependance was found. The only effect observed was the gradual heating of a sample, resulted in the evaporation of the water, but on cooling the deposit simply redissolved. The dissolving and recrystallisation stages occurred many times before a type of equilibrium was reached, usually this was a crystalline phase, probably due to the heat of the microscope illumination.

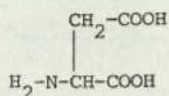
The reason for this quite unique behaviour is not clearly understood, however, as a result of experiments on solutions of L-Proline where this effect was not observed, the sodium chloride surface clearly was an important factor in this process.

Other alkali halides, (sodium bromide and potassium iodide) were used, and although the effect was not as pronounced as on sodium chloride it did nevertheless still occur.

A possible explanation for this phenomena is that the close proximity of the sodium chloride surface, which would almost certainly contain some water on it, allowed the water to interact slowly on the crystals of L-Proline surface. This water then evaporates slowly from the crystals and the process repeats itself until such time as the L-Proline surface has no longer an affinity for water, or when sufficient water is adsorbed on to lower its surface energy without resulting in complete dissolution.

The actual crystallographic orientations of L-Proline is discussed in Chapter Five.

3.17 L-Aspartic Acid on Sodium Chloride



L-Aspartic acid was found to be unique in its behaviour on a sodium chloride substrate. From its low water solubility (0.82 at 25°C and 4.79 at 75°C) a water interaction would not be expected or if it did occur should be easily eliminated using the coolant technique.

The water interaction was infact quite different with L-Aspartic acid, as it was complete and to an extent irreversible. A feature of this compound was the inability to produce a thick film on the substrate, this was primarily due to the high temperatures required for sublimation, temperatures of 200 - 230°C were frequently used. Under some conditions there were signs of decomposition, as L-Aspartic acid melts with decomposition at 251°C and Gross (226) reported in his study the very low degree of recovery of this compound. A number of variations in the substrate temperature, residual pressure of the system, and long deposition times were used but on no occasion could a thick deposit be grown.

After the deposition of the material only a few features could be observed on the substrate, and even under polarised light and high magnification no additional details could be observed. However, after a period of about 20 minutes, a very rapid change took place which could only be observed under polarised light. Unfortunately this process was far too rapid for photographic recording of separate stages and only the final state could be recorded.

Plates 39 and 41 show the final state of the deposit accompanied by Plates 40 and 42 which illustrate the details under polarised light.

The concentric ring appearance of this deposit with its grain-like texture is quite different from anything previously observed in this study.

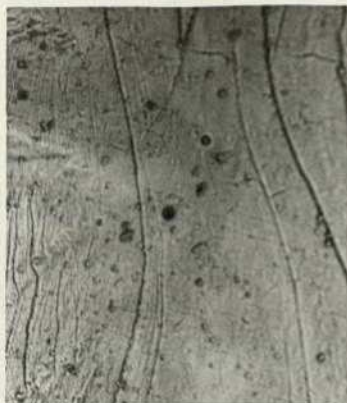


PLATE 39

Appearance of Aspartic Acid
Deposit under normal light
40X



PLATE 40

Same as 39 under
Polarised light
40X

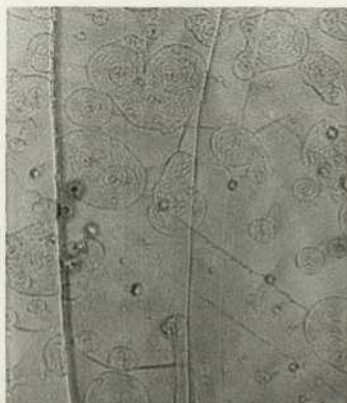


PLATE 41

Aspartic Acid Deposit
Showing the grain-like
texture
100X

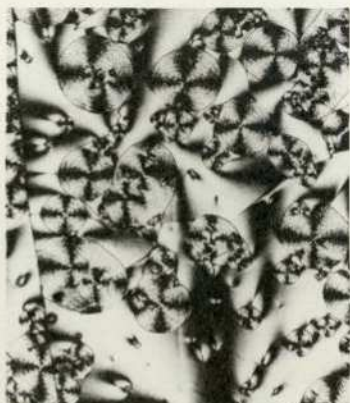


PLATE 42

Same as 41 under
Polarised light
100X

The appearance of these deposits under polarised light show another two quite remarkable features. The first of these and the most significant is the so called 'Malteze Cross' effect. As the sample is rotated, the dark areas constituting the cross pattern do not move, this is surprising because this effect is characteristic of either rapid crystallisation, or the existence of a new mesomeric phase. The other most distinctive feature is the very large areas of optical activity that surround the concentric rings. These can be more clearly seen on plates 43 - 47.

The rapid crystallisation of the type suggested is termed, spherulitic growth, which is a form of the one-dimensional dendritic growth, where crystallisation begins at the centre, and tiny almost one-dimensional crystal fronts simultaneously proceed in a radial fashion. Because of this unusual crystallisation, the unique optical effects of the malteze cross may be observed.

This type of growth is usually reserved for high molecular weight polymers, or compounds that crystallise rapidly from the melt or highly supersaturated solutions.

A number of samples were prepared, some using the dry cell, and coolant technique previously described (section 3.14), but in every case the same effect was observed. It seems surprising that inspite of this compounds low water solubility, it appears deliquescent on the surface of sodium chloride.

A possible explanation for this phenomena, is that due to only a very thin layer of this compound being deposited, in a film like covering it will posses a high surface area which will be extremely active (see section 3.14 for explanation). This surface adsorbs and interacts strongly with atmospheric moisture, which in some way changes its state. After a long induction time, for reasons not clearly understood, the material recrystallises very rapidly by a spherulitic mechanism.



PLATE 43

400X

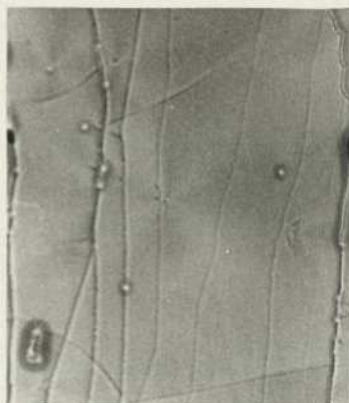


PLATE 44

400X

APPEARANCE OF ASPARTIC ACID DEPOSIT
UNDER HIGH MAGNIFICATION

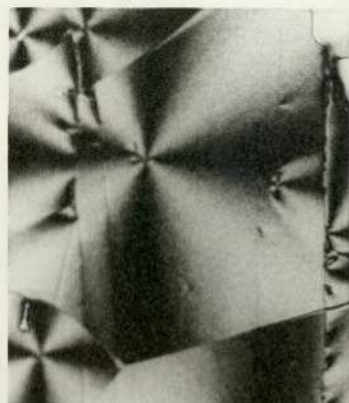


PLATE 45

400X

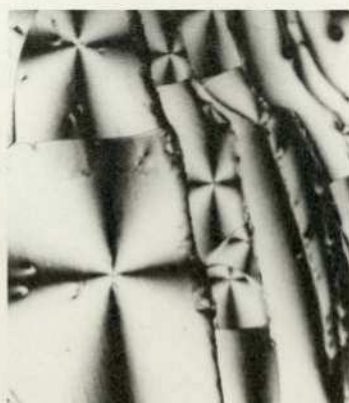


PLATE 46

400X

DEPOSITS SHOWING THE MALTEZE CROSS
EFFECT UNDER POLARISED LIGHT

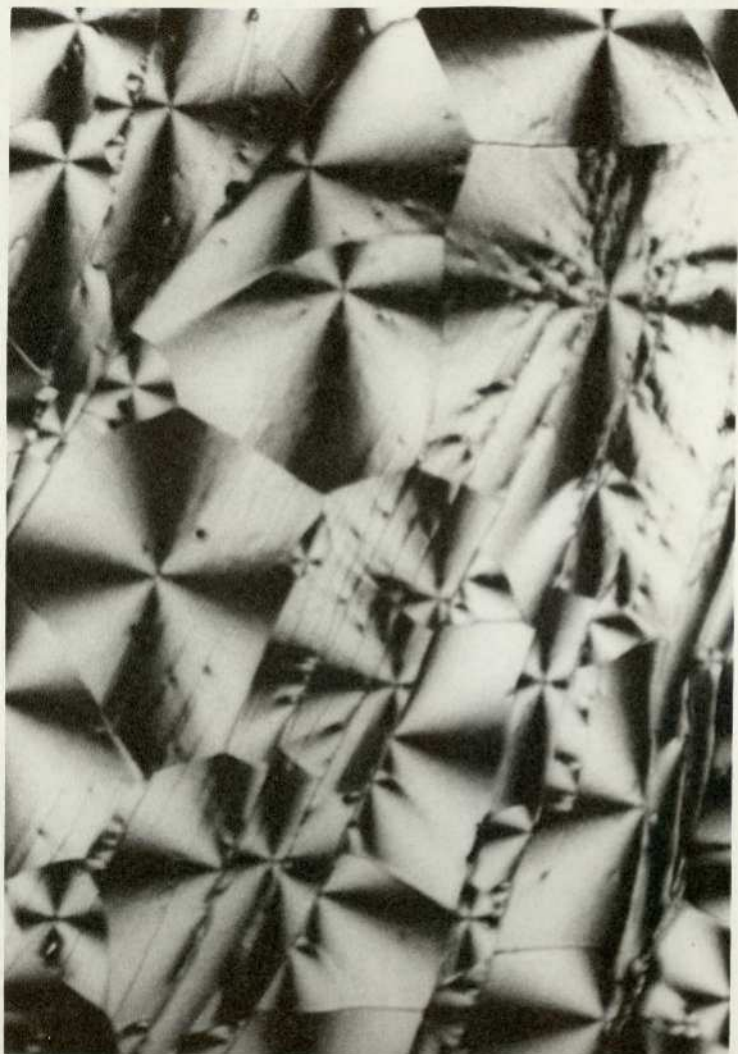


PLATE 47

400X

Aspartic Acid Deposit
under Polarised light

The grain-like concentric ring texture observed on plates 41 and 42 is not easily explained by this mechanism, as it is difficult to understand how a rapid one-dimensional growth radiating from the centre of a circle also produce concentric rings about this same centre.

In order to check if any chemical change had taken place during the sublimation process, the infra-red spectrum and the C.H.N. content of the sublimed material was recorded, but were exactly the same as the unsublimed material.

An interesting alternative explanation for this phenomena could be the existence of an intermediary state or new mesomeric phase, termed the 'liquid crystal state'. This is a very ill defined term and is used to cover all states from solids which under certain circumstances behave more like liquids, to liquids or solutions that contain a type of microstructure. In recent years it has been used to describe more the latter case than the former.

The classic example of a liquid-crystalline state is the properties exhibited by some cholesteryl esters and related compounds. (for further information see references 237 - 240) For these compounds, a state usually exists just before the melting point, where the properties abruptly change normally accompanied by some visual effect of going darker or lighter, or appearing translucent or transparent. The most common properties of the new mesomeric phase is the liquid may be effected by electric fields, and possess quite a different optical activity. Robinson (241) recognised this state with some concentrated polypeptide solutions, but it has never been observed with any amino acids.

A standard way of confirming the existence of a mesomeric phase (241) is that it will be produced between well defined transition temperatures, and only exist within this region.

An experiment was designed to determine whether an aspartic acid/water mixture would produce such a phase. The exact role of the sodium chloride substrate in the formation of this phase is not clearly understood, but must be necessary as these effects are not observed with normal aspartic acid/water mixtures. The new phase would be recognised by its appearance under polarised light while remaining transparent to normal light.

A small quantity of finely ground aspartic acid was placed on the face of a freshly cleaved crystal of sodium chloride, and sufficient water added slowly to dissolve the material, considerable care is required in this operation to ensure the substrate is not excessively changed. This was placed on a constructed heating stage and observed with the optical microscope. (see figure 11)

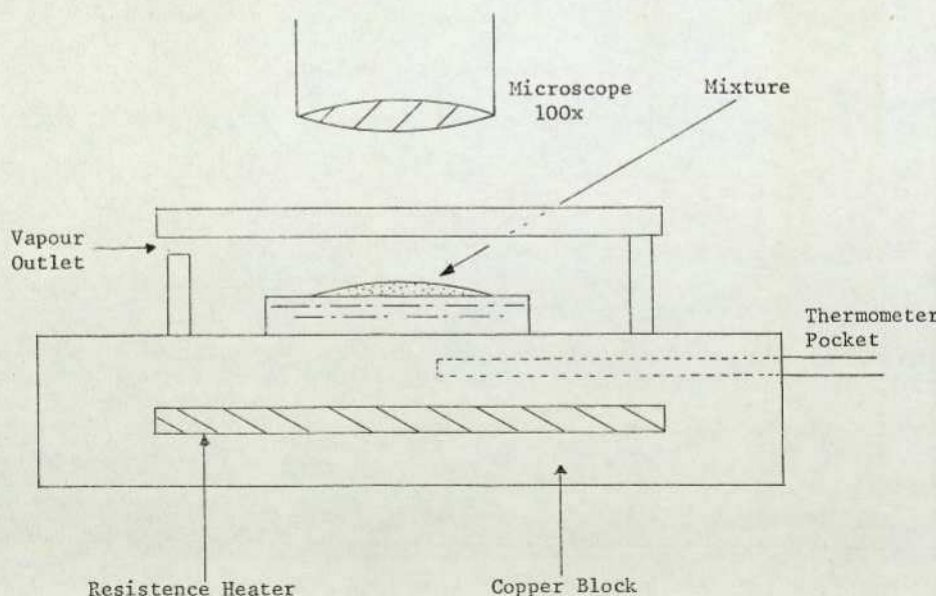


Figure 11

Microscope Heating Stage

The temperature of the substrate was slowly raised up to 60°C , within this temperature region a great deal of the water evaporated leaving normal solid deposits. Of the liquid remaining a noticeable change in the shapes of the drops occurred within the range of $60 - 80^{\circ}\text{C}$, some completely disappearing due to evaporation. Rather surprisingly some liquid remained at temperatures greater than 130°C , and although observation was difficult due to a liquid on the underside of the glass cover, and the fact that only low magnification could be used due to the very short focal lengths of the higher objective lens, some solid deposit could be observed inside some of the drops by observation with reflected polarised light. Some liquid remained up to temperatures of $150 - 160^{\circ}\text{C}$ however no optical effects were observed, which may have been due to the limitations of the optical system rather than the non-existence of any effects. At temperatures greater than 160° all the liquid disappeared leaving only crystalline solids.

This experiment was repeated several times, using different heating rates, typically $5^{\circ}/\text{min} - 3^{\circ}/\text{min}$ and allowing longer times for temperature equilibrium to be set up. But the same effects were always observed. These are shown on plates 48 and 49.

The sodium chloride crystal was also replaced by a thermocouple and a careful assessment of the temperature measurement was made. This showed the sodium chloride crystal could be at about a 10% lower temperature than that shown on the thermometer. But even assuming a 15% error, some liquid remained at temperatures far in excess of the boiling point of the solvent.

The deposits shown on plates 48 and 49 clearly show that something rather unexpected is occurring.

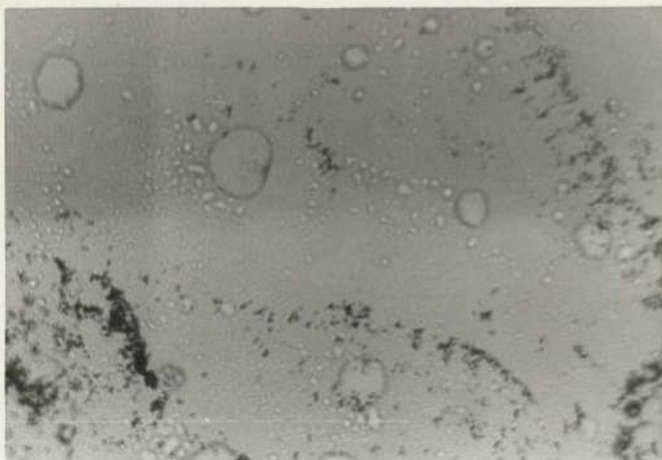


PLATE 48

Liquid Aspartic Acid deposit observed with
the Heating stage experiments
100X

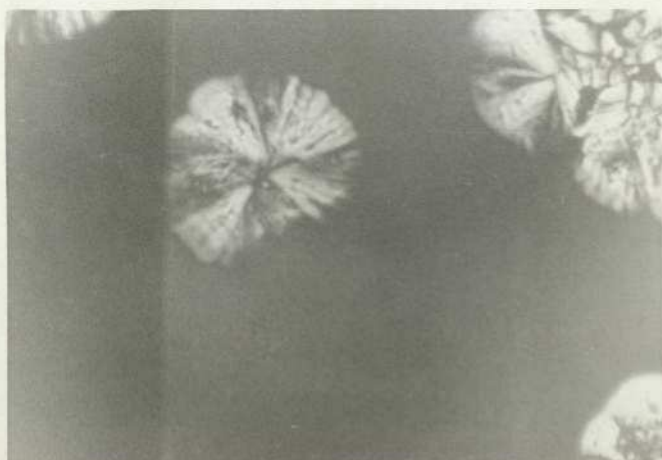


PLATE 49

The resultant crystallisation of
the deposit shown above

Summary

The results from the heating stage experiments are far from conclusive, as the bulk of the solid crystallised on the surface by the normal evaporation of the solvent, however, at temperatures of at least between 120 - 140°C some liquid did remain on the surface.

A mechanism for this interaction could possibly be the formation of a gel between the aspartic acid and water, when mixed in the correct quantities at a specific temperature. The substrate may change the surface wetting of the gel at the interface and lead to the solvent being able in some way to hydrate the solute.

Confirmation of the existence of a new mesomeric phase was not found in this study although it could not be confidentially refuted. A far more rigorous investigation would be required to determine the mechanism of the water interaction, and consequently the behaviour of L-Aspartic acid on a sodium chloride substrate remains rather a mystery.

As will be seen later in this chapter a similar behaviour is observed with deposits of L-Arginine under almost identical conditions.

3.18 L-Valine, L-Phenylalanine, L-Arginine, L-Leucine, L-Cysteine and L-Cystine on sodium chloride

Valine, Cysteine, Leucine and Phenylalanine all interacted with water when deposited on the surface of sodium chloride. It would be expected that with the use of the coolant technique, the water interaction could be eliminated and crystalline deposits observed.

The water interaction was only slight with deposits of L-Valine, consisting of a film being adsorbed on to the surface, and the only effect of this was to obscure observation. This effect can be seen on plates 50 and 51. It would be possible to grow an epitaxial deposit of this material as it grows readily as single crystals, and would be a matter of obtaining the correct growth conditions. This would not be expected with deposits of phenylalanine because although a number of growth conditions were attempted this material always grew as a polycrystalline film. It was found that the water interaction with phenylalanine could be easily eliminated, and enabled very thin films to be grown and replicated for observation with the electron microscope. The electron microscope investigation of deposits in an early stage of growth confirmed that this material grows as polycrystalline film at all stages of growth. The electron micrograph of this type of growth can be seen on plate 53.

L-Cysteine and L-Leucine behaved in a way similar to L-Valine deposits and no evidence was found to suggest that epitaxial deposits could not be grown.

L-Arginine behaved in many ways similar to deposits of L-Aspartic acid. A number of samples when observed only showed a series of drops (see plate 54) and no crystalline deposit. These drops were quite stable and no crystallisation was observed.



PLATE 50

Deposit of
L-Valine showing
Single Crystal Growth
100X



PLATE 51

Same as 50
in normal light

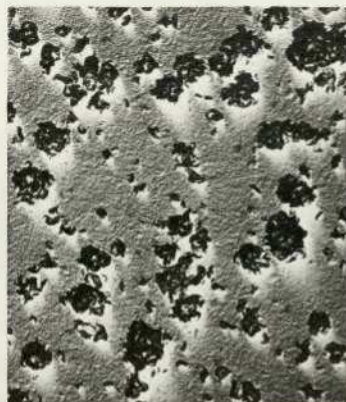


PLATE 52

6000X



PLATE 53

10,000X

ELECTRON MICROGRAPHS OF PHENYLALANINE
SHOWING POLYCRYSTALLINE GROWTH FROM THE
FIRST STAGES OF GROWTH

The malteze cross patterns were observed with some deposits of L-Arginine but not the grain type structure. The deposits exhibiting these effects are shown on plates 54 - 56. The deposition of this material was found to be as difficult as that experienced with L-Aspartic acid. A very high sublimate temperature (240°C) was required, and on no occasion could a thick film be deposited. (This was also observed by Gross, 226)

Very little could be concluded from the experiments with deposits of L-Arginine, because in many cases the results were not reproducible and there remained the possibility that the sublimed material was a decomposition product. For these reasons no further investigations were undertaken.

L-Cystine was the only compound of this series that grew epitaxially with no water interaction. Crystals were found to be oriented under a variety of conditions (typically sublimate 120° substrate 50°C) on the surface of sodium chloride. The orientation obtained is shown on plate 57.

L-Cystine has a hexagonal crystal structure (242) containing 6 molecules per unit cell, and the lattice parameters are $a = 5.422$ and $c = 56.275$. An examination of the orientated deposit, was found to correspond with the epitaxial relationship of:-

$$(1100)\text{CYSTINE}[0001]//[001]\text{NaCl}(001)$$



PLATE 54

Liquid deposit of Arginine
40X



PLATE 55

Malteze Cross effect
observed with Arginine
deposits



PLATE 56

Same as 55



PLATE 57

Oriented deposit of
Cystine

3.19 Summary

The deposition of Amino-acids on a sodium chloride substrates

The most dominating feature of this study was the discovery of the unexpected interaction of some of the deposits with atmospheric moisture. The interaction of water with a freshly formed surface is not a new phenomena, and has been observed with many compounds. A new surface of quartz is extremely active towards water (243), because the adsorption of the water is a means of reducing its surface energy. The importance of water is clearly demonstrated when a fresh surface of quartz is formed in a dry atmosphere, the surface distorts to such an extent as to produce ozone. Fresh deposits of SiO_2 are slightly active towards water, but the most striking example is that of silver deposits which can undergo agglomeration changes, and recrystallisation enhancing the growth of the (111) face (244, 245) as a result of exposure to moist air.

Organic compounds do not possess the high surface energies which would predict this behaviour, and materials remain stable to atmospheric moisture. The deliquescent tendencies of some organic compounds have been previously observed, and some substituted urea compound behave in this manner when deposited on crystalline substrates (84).

The most dramatic interaction with water amongst those compounds used in this study was that of L-Aspartic acid, where a different form of crystallisation, quite unusual for amino acids was observed. The situation with aspartic acid and water is not clearly understood, and although some indications of a new mesomeric phase were found, no conclusive evidence was obtained.

Deposits of L-Proline were found to be uniquely well defined and a rather strange dissolving re-crystallisation cyclic process was observed around each individual crystallite.

The initial and the recrystallised deposit were both, however, well oriented with a crystallographic plane of the substrate.

A technique was found to eliminate the water interaction with some of the deposit materials by cooling the surface prior to exposure to moist air. This was found to be highly successful with GABA and DL-Alanine as well as phenylalanine. By the use of this technique very well defined and oriented deposits of GABA and DL-Alanine were obtained. The reason for the success of the coolant technique is thought to occur by lowering the surface energy of the deposit by reducing the thermal energy of the sample. In all the water interactions the presence of the substrate was of prime importance as the effects were not observed in its absence.

The importance of the growth conditions in obtaining an epitaxial deposit was very well demonstrated by the deposition of β -Alanine, where a number of separate growth stages were observed. Each stage was found to be dependant on the rate of growth and the temperature of the substrate.

A good epitaxial deposit was obtained with β -Alanine, GABA, DL-Alanine, L-Proline and L-Cystine. These orientations together with the orientation of glycine are discussed in detail in Chapter Five, where the orientations are compared with the predictions of an epitaxial model.

3.2 A study of the growth of Glycine and Anthraquinone on Sodium chloride, Mica and Quartz substrates

To obtain a better understanding of the relevant parameters involved in the growth of epitaxial deposits, a comparative study was made on the deposition of two different organic materials, on three quite different substrates.

In the vacuum system previously described (chapter 2) the pressure could only be reduced to 10^{-3} Torr, at this residual pressure the mean free path of particles in the vapour is approximately of the order of 0.5cm. As a result of this, a number of particle collisions, and subsequent changes in energy would occur prior to the depositing vapour impinging on the substrate surface. Although it was not known if this property has a critical effect on the deposition and growth of organic epitaxial layers, it was decided to use a vacuum deposition chamber capable of a pressure better than 10^{-5} Torr. The two most important factors of the reduced residual pressure are, the substrate is likely to be cleaner prior to deposition, and the mean free path of the depositing vapour particle is now of the order of 50cm. This is also in keeping with most of the published work where a high vacuum system is nearly exclusively used.

3.21 Modifications to the Vacuum System

In order to obtain reduced pressures of better than 10^{-5} Torr a glass mercury diffusion pump was incorporated into the system. With the inclusion of a mercury pump, the positions of vapour traps are now critical to ensure the substrate or sublimate vapour are not contaminated by mercury vapour backing streaming from the pump.

The operation of the vacuum line is largely self explanatory from figures 12 and 13.

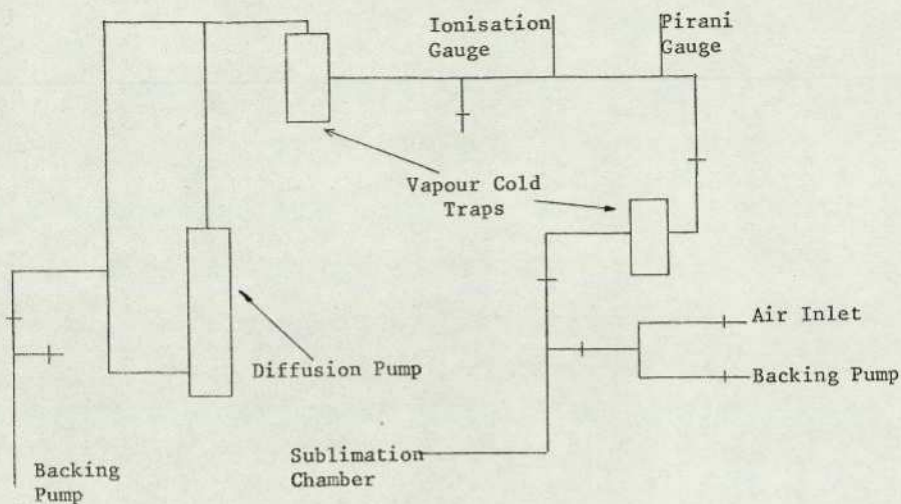


Figure 12
High Vacuum Line

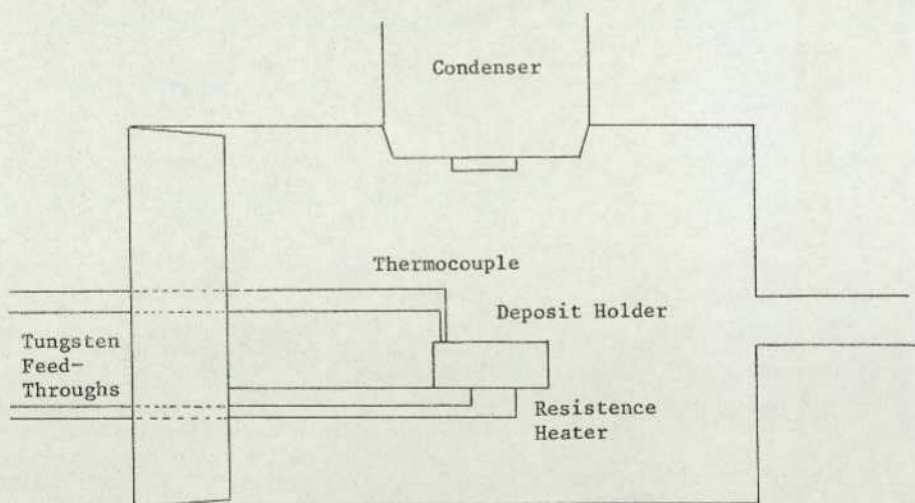


Figure 13
Sublimation Chamber

A simple shield was fitted on to the substrate condenser, which operated by rotation of the glass seal, this ensured that no premature deposition or contamination occurred while the temperature and pressure conditions were being reached. The sublimation chamber and substrate were evacuated for 30 - 40 mins prior to deposition to allow the removal of any contaminants. As the crystal growth was to be studied, all depositions were done as slowly as possible, and the temperature and pressure conditions remained quite stable over the long deposition periods.

3.22 Deposition of Anthraquinone and Glycine on Sodium Chloride

Anthraquinone has frequently been used as a depositing material, because of the ease of obtaining an epitaxial deposit, under a variety of conditions, (125, 84). Darling (84) conducted a thorough investigation of the deposition of anthraquinone on sodium chloride, and clearly demonstrated the relationship between depositing conditions and the degree of crystal perfection obtained.

The deposition of this material under high vacuum conditions confirmed Darling's observations, that by depositing very slowly on to a substrate held at a low temperature (typically 40 - 45°C) very well defined, and well oriented single crystals can be obtained. Typical deposits can be seen on plates 58 and 59.

There was no difference in the growth of glycine on sodium chloride under high vacuum conditions to the growth described earlier (section 3.11) and even under the very slow deposition rates used in this study large single well separated crystals could not be grown.

With both anthraquinone and glycine, good epitaxial layers could be easily obtained, the only difference being the orientation, both materials deposit on their (010) faces but are aligned differently: Glycine the [100] direction is parallel to the [100] direction of sodium chloride, and anthraquinone the [100] direction is parallel to the [110] direction of sodium chloride.

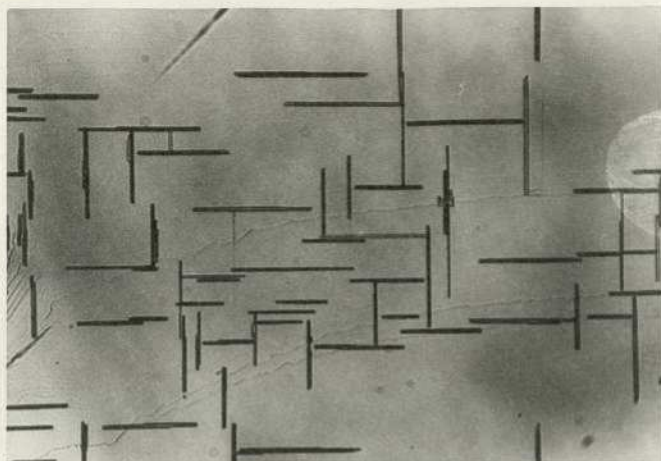


PLATE 58

Oriented Anthraquinone deposit grown
very slowly on Sodium Chloride



PLATE 59

Anthraquinone deposit grown rapidly

In addition to this main orientation, some deposit is orientated parallel to the $[100]$ direction of NaCl. The reasons for these orientations are discussed further in Chapter Five.

The major difference between these deposits, were the observed nucleation densities, Glycine deposits show a very high nucleation density under all conditions of growth. Which indicates a very low mobility over the surface and most nucleation and crystal growth occur by direct impingement. With anthraquinone this is not observed, where well separated crystals were obtained indicating a high mobility on a sodium chloride surface. Also the best defined and perfected crystals were probably due to the very slow rates of growth possible at these pressures, and obviously this effects the crystal growth stage rather than the nucleus/orientation stage.

3.23 Deposition of Anthraquinone and Glycine on Muscovite Mica

Muscovite Mica has cleavage properties which make it very suitable for studying phenomena which occur on surfaces. The excellent cleavage along the (001) plane produces surfaces which can be molecularly smooth over very large areas (246), and free from any surface inhomogenities.

Epitaxial deposits of anthraquinone on this surface could be easily grown under a variety of depositing conditions. Best deposits were obtained at low substrate temperatures (typically $35 - 40^{\circ}\text{C}$) (see plates 60 and 61). At higher temperatures although orientation was still obtained a marked reduction in the perfection of the deposit was observed. With much of the deposit, a curving and splintering effect was observed at the ends of crystallites.

Anthraquinone grows with its (010) face in contact with the substrate and its $[010]$ direction parallel to the equivalent $[011]$ directions of the mica substrate.



PLATE 60

100X

ORIENTED ANTHRAQUINONE DEPOSITS
ON A MICA SUBSTRATE

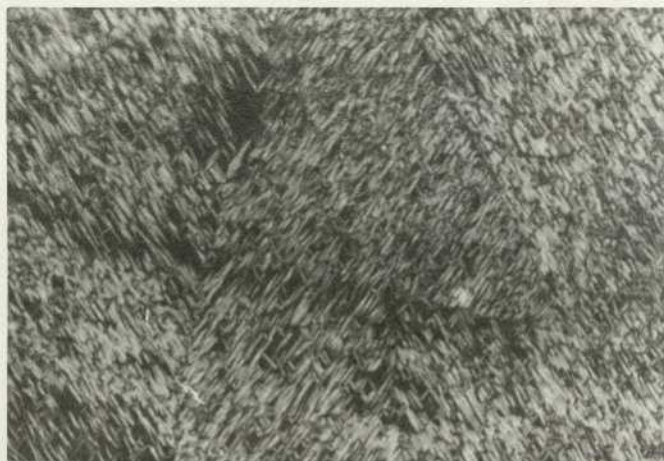


PLATE 61

100X

Anthraquinone proved to be a very good decorating agent for the study of various surface effects induced onto the surface of mica. These effects on the observed orientation of anthraquinone will be discussed in detail later in this chapter.

The deposition of Glycine on mica was found to change quite appreciably with different vacuum conditions. As with the deposition of this compound on the surface of sodium chloride, a high nucleation density was observed with the deposition on a mica surface at pressures of 10^{-3} Torr. A wide variety of substrate and sublimate temperatures were used but always the deposit coalesced at an early stage of growth.

This was not encountered when the deposition was conducted at a pressure of 10^{-6} Torr. A relatively high substrate temperature of $70 - 75^{\circ}\text{C}$ and a sublimate temperature of $100 - 110^{\circ}\text{C}$ were used, and because of the difference being quite small ($30 - 35^{\circ}$) long deposition times of 2 - 3 hours were required. Under these conditions very well defined and perfectly well oriented deposits were obtained. (See plates 62 - 64.) The individual crystals were also so well formed and separated that interfacial angles were measured with the optical microscope, to determine the crystallographic orientation. The (010) face of Glycine was in contact with the mica surface, and the [100] direction parallel to the [110] directions of the substrate.

A typical deposit obtained under the higher pressure conditions can be seen on plate 65.

The observation of such perfectly aligned and well defined crystals is a direct result of the improved vacuum conditions. As discussed earlier the improved vacuum conditions result in the depositing vapour losing less energy by collisions, prior to deposition (some collisions will still occur within the mean free path distance because a point source was not used) this in turn means that the particles arriving at the deposit surface will possess energy more in relation to that of the sublimate heating.



PLATE 62

100X

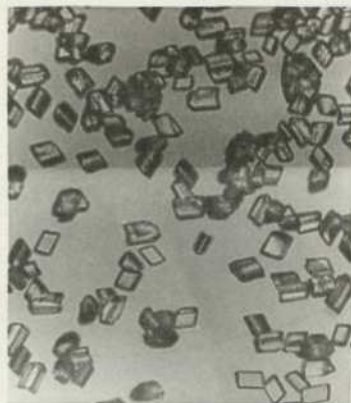


PLATE 63

400X

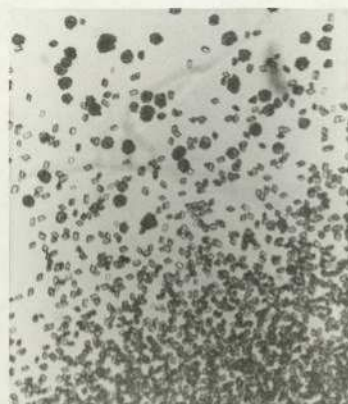


PLATE 64

100X



PLATE 65

Glycine Deposit obtained
under high pressure
conditions
100X

EPITAXIAL DEPOSITS OF GLYCINE
ON THE SURFACE OF MICA

This will permit a greater surface mobility and together with the thermal energy of the substrate allow more preferential nucleation. All these parameters taken together result in a well defined well oriented deposit, because once the nucleation and orientation event has taken place further growth only occurs at these epitaxial nuclei.

These conditions would not be arrived at solely by sublimate substrate temperature variations, because a limit exists on the thermal energy of the substrate. At a very high temperature the difference between epitaxial and random nucleation would be proportionately less, and also resublimation of the deposit from the substrate would become significant.

This aspect of epitaxial growth is extremely important for many organic deposits which grow as single crystals and do not possess the ability to reorient and recrystallize on coalescence as many metal deposits can (39, 40). Many workers (247 - 249) studying the phenomena of epitaxy have often assumed that the observation of misaligned overgrowths purely results from the inability of the substrate to influence deposit growths. When the observation of misaligned overgrowth has repeatedly occurred due to improper crystal growth conditions. (A very clear example of this was observed in the deposition of β -Alanine in section 3.13.)

These inaccurate assumptions has led to a great deal of confusion in the study of Distlers work, and this will be discussed in detail in Chapter Six.

3.24 The Deposition of Glycine and Anthraquinone on Quartz

The crystals of low temperature Quartz are prismatic ($10\bar{1}0$) terminated by two rhombohedrons ($10\bar{1}1$) and ($01\bar{1}1$) (250). The crystal habit of Quartz is shown on figure 14.

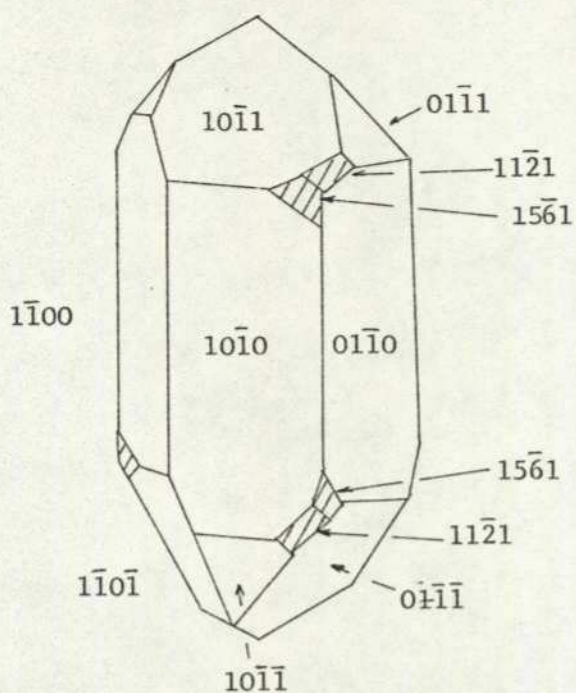


Figure 14
Crystal Habit of Quartz

The lattice parameters are, $a = 4.903$ and $c = 5.393$ and the unit cell contains 3 molecules. Only the faces represented by shaded areas on figure 14 are different in the two optical antipodes of Quartz. In this study only the natural (1010) face was used, and this face contains oxygen atoms sticking out of the plane, these atoms would be unsaturated and should be the predominant influence on any epitaxial deposits. The arrangements of the atoms on this face are shown on figure 15.

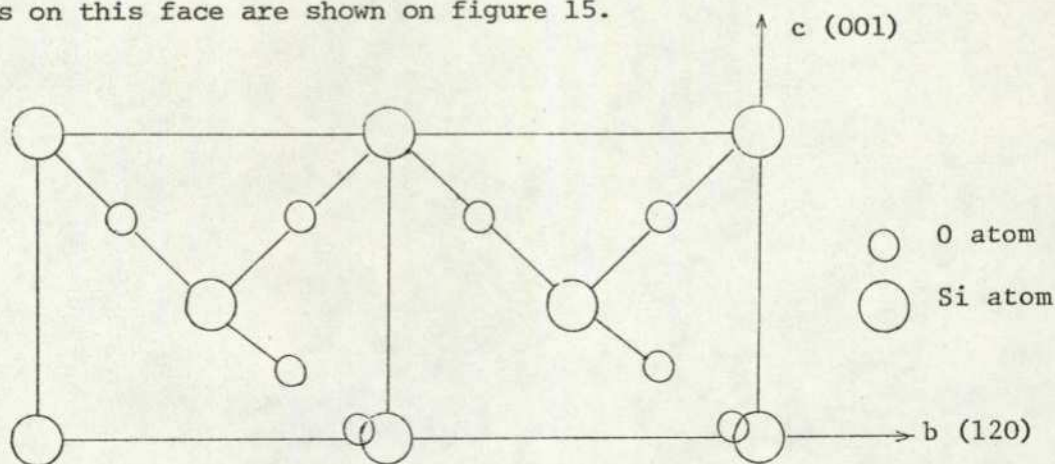


Figure 15

Quartz crystals contain no natural cleavage plane, which necessitates the mechanical preparation of a fresh surface prior to deposition. When a fresh surface of any material is produced, the surface will distort in some way as a means of reducing the surface energy, the extent of this distorting largely depends on the polarisability, and the only mechanism to reduce the surface energy available to a quartz surface is by the adsorption of foreign substances. In the grinding process during the preparation of fresh surfaces the lubricant is often strongly adsorbed on to the surface.

The process of grinding and polishing also leads to the formation of a surface layer of different structure to that of the bulk. This disturbed layer is often referred to as the amorphous Beilby layer (251). The change in surface geometry led earlier workers (243) to conclude that an oriented overgrowth could not be grown on the surface of Quartz. Oriented overgrowths were only deposited after this surface layer was removed by the action of hydrofluoric acid. This layer was subsequently calculated to be of the order of 300 - 500 angstroms thick (252, 253).

Although the etching process removes the amorphous layer the resulting surface structure is likely to be different from the bulk structure and further complicated by the presence of chemisorbed ions of the etching medium. (For further information concerning the surface preparation the reader is referred to Faust's publications (260) on the subject.)

H. Seifert and K.F. Seifert (254) have reported a systematic study of the growth of a series of amino acids on a Quartz substrate, and obtained positive results for most amino acids. Epitaxial orientation have also been obtained with, the co-crystallisation of Glycine and L-Glutamic acid (134), L(-)-Oxyproline (256) several di- and tri-peptides (254, 133), Vitamin B₁₂ crystals (257) and some homopolypeptides (139, 258, 259). K. Seifert (255) extended the work of glycine on quartz by depositing glycine on all natural and also several artificial cut faces of Quartz.

The impetus of the research on the epitaxial crystallisation of biologically related materials on mineral and inorganic crystal faces, has been to obtain an understanding of diseases like silicosis, which is the direct result of inhaling extremely reactive quartz dust, and Seifert (138) has suggested this may be due to the orientational effects on amino acids of the quartz surface.

The growth of both anthraquinone and glycine on quartz were extremely sensitive to the time of etching used on the substrate, and to obtain an epitaxial deposit of glycine very high substrate temperatures were required.

Anthraquinone initially deposited on to a quartz surface which had previously been washed and vacuum dried but not exposed to the etching process, grew as single crystals but of no preferred orientation. Orientation could only be obtained if the surface was previously etched for times varying between 45 - 75 seconds using a 48% v/v solution of hydrofluoric acid in water. Various lower concentrations of the hydrofluoric acid were used, to increase the etching times for practical convenience.

No difference was observed between the deposits grown at pressures of 10^{-3} Torr and 10^{-6} Torr and this was to be expected as the mobility of the deposit on the substrate was largely determined by the condition of surface of the substrate. A serious problem concerning this, was encountered with the etching process because after the initial easily soluble layer was removed from the quartz, the hydrofluoric acid continued to attack the surface preferentially at defects. This often led to a very inhomogeneous surface, and the holes acted as nucleation centres for the depositing material. The preferential nucleation at these defects led to the growth of polycrystalline clusters (see plate 66). But by very careful etching of the surface these defects could be avoided, and epitaxial growth was obtained (see plate 67).



PLATE 67

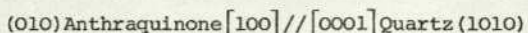
Partially Oriented Anthraquinone Deposit
on the surface of Quartz



PLATE 66

Anthraquinone deposit on the surface
of Quartz
400X

The conditions necessary for epitaxial growth were a substrate temperature of 60°C and sublimate temperature of 80°C. The orientation obtained corresponded to:



Glycine did not readily grow epitaxially on quartz and under normal substrate/sublimate temperature conditions, the overgrowth coalesced at a very early stage of growth. This coalescence took place before the deposit was large enough to be observed with the optical microscope, and consequently observation with the electron microscope was attempted.

Unfortunately the size of samples which could be inserted into the scanning electron microscope were too small, and it was not practical to handle such small samples of quartz at the grinding and polishing stage. The normal replica method was attempted but no suitable technique could be discovered for the detachment of the replica. Because very thin deposits were present on the quartz surface the technique of floating the replica off in both water and hydrofluoric acid were unsuccessful. A limited degree of success was, however, achieved by fixing the replica onto a cellulose acetate film with acetone, and then physically stripping the replica from the surface. The cellulose acetate film was subsequently dissolved in acetone and the replica mounted and observed. No definite orientation could be observed by this method, largely due to the damage sustained by the replica, but it was possible to confirm that the glycine had grown as single crystals.

After a number of temperature variations had been employed suitable conditions were obtained to grow slightly larger single crystals of glycine, but very high substrate temperatures were required. To obtain temperatures in excess of 100°C, the hot water circulation method could not be used, and an electrical method of heating was required. A simple resistance heating method however, was not suitable as without a large conduction block the temperature would not remain stable over the long deposition times.

The method finally decided upon, was the use of an immersion resistance heater, which raised the temperature of a large volume of high boiling silicone fluid. Although this system required a long time to reach thermal equilibrium once it had done so, the temperature remained quite stable over long periods.

Using this method, good epitaxial deposits were grown, but again great care was required at the etching stage to avoid the possibly random nucleation at surface defects. Typical temperatures required were $120 - 130^{\circ}\text{C}$ for the substrate and $150 - 160^{\circ}\text{C}$ for the sublimate, and times of 3 - 4 hours were allowed for deposition. The epitaxial growth obtained under these conditions are shown on plates 68 - 70.

Under these conditions, the long deposition times required were the result of a type of equilibrium being set up on the substrate. Due to the greatly reduced mobility of both anthraquinone and glycine on the surface of quartz, high substrate temperatures were employed, this permitted some of the random deposit to resublime off the surface and increased the probability of further growth occurring on the oriented nuclei.

If the surface preparation is considered in a very idealised way, the process of dissolving the amorphous layer, produced by polishing will result in the surface being covered with strongly adsorbed ions. It is almost certain that these ions would drastically effect epitaxial orientation of a subsequent deposit. It was thought that if these ions could be replaced by other contaminants, one may be found that would enhance the orienting ability of the substrate.

To change the contaminants, the quartz was heated to 250°C in high vacuum for 2 hours, and then the vacuum released with known vapours. In this vapour environment the substrate was allowed to cool, and left for a further 2 hours.



PLATE 68

100X



PLATE 69

100X



PLATE 70

100X

ORIENTED GLYCINE DEPOSITS ON THE SURFACE OF QUARTZ

A further modification was made to the sublimation chamber to accommodate this process. This consisted of the introduction of a large glass bulb which would act as a vapour reservoir between two vacuum taps and a liquid container, as shown in figure 16.

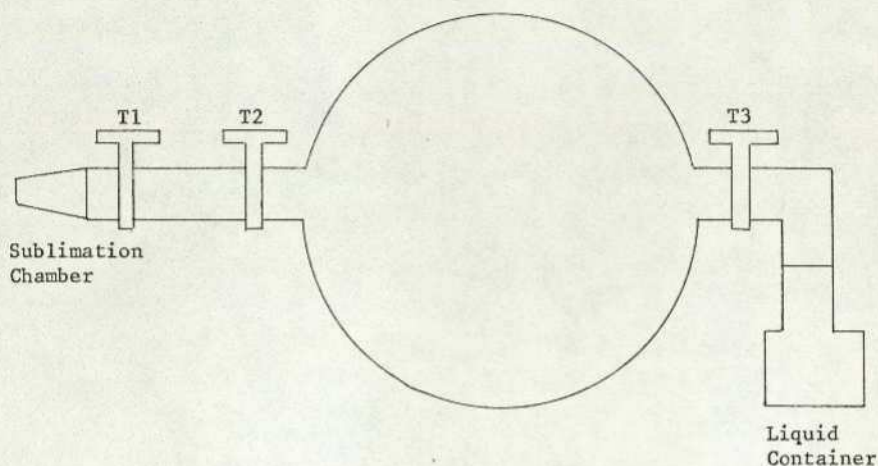


Figure 16

By careful adjustment of taps T_1 , T_2 and T_3 a continuous stream of vapour could be leaked into the chamber. The liquids used in this study were acetone, ether, aqueous ammonia, butyl acetate, hydrogen chloride and water.

Unfortunately none of these materials had any marked effect on the orientational ability of the substrate, this could either mean the initial layer had not been replaced, or the newly adsorbed vapours acted in the same way as the initial layer.

Reflectance infra-red was attempted as a method of determining the contaminants but because of the small sample, and the resolution limit of the instrument no useful information could be extracted.

The observation of an oriented overgrowth on a quartz surface is almost totally dependant on the surface treatment, and because of the

complicated effects of this treatment it is almost impossible to prepare two identical surfaces. This has been revealed several times by the fact that a suitable etching time for one polished surface was very often unsuitable for another. This was largely due to all the substrate specimens being prepared by hand and time was not available to obtain the necessary expertise for the perfection of this process.

It was concluded that without precise crystal cutting and grinding facilities, quartz is not a suitable substrate for any fundamental study of epitaxy. The difficulty experienced in obtaining epitaxial growth with quartz makes it appear improbable that the effect of quartz in the lungs, occurs solely by an orientation mechanism, and the quartz is more likely to act as some sort of catalyst to the modification of cell structures.

3.25 A Detailed study of the Growth of Anthraquinone on a mica substrate

Distler and his school have made an enormous contribution to the study of crystalline surfaces, but because much of their work has not been reproduced by other workers, a great deal of controversy surrounds Distler's interpretations. Because of the significance of Distler's work, some of his experiments have been repeated to determine if any of Distler's observations are open to more conventional interpretation. (see chapter 6)

The basis for Distler's theory of epitaxy is the electrical structure of the substrate, and one of his less controversial experiments was the investigation of the electrical structure of the matching faces of freshly cleaved single crystals, by the decoration with anthraquinone (261). By this technique Distler concluded that large regions (several thousand microns) of different electrical potential existed on the surface of freshly cleaved crystals. Because these effects were not observed during the course of experiments done in this laboratory, a more rigorous investigation was undertaken.

The structural conditions of the cleavability of a crystal, is the existence of definite directions in the ideal lattice where the weakest cohesion of elemental crystal components occurs caused, both by lattice geometry and the nature of the binding forces between the particles (262, 263). The (100) cleave obtained with alkali halides, produces a chequered layer pattern of positive and negative charges. Weyl (243) has suggested that this surface will distort to lower the surface energy of the surface, and calculations by Dundon (264) are consistent with this. (See figure 17)

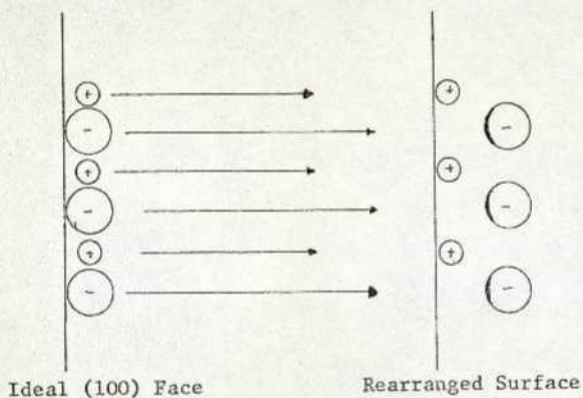


Figure 17

Rearrangement of the NaCl Surface

As a result of the (100) cleavage and subsequent rearrangement a strongly negative surface will exist on both cleavage faces, and decoration with anthraquinone should yield identical orientation on both faces.

By the simultaneous deposition of anthraquinone on the matching faces of sodium chloride, identical orientation was observed, although there did exist some lower density regions.

These regions of reduced deposit on surface one, could not be correlated with any effects observed on the other surface, except where major cracks or large crystal defects existed.

A detailed study of the (100) face of alkali halide has been made by Gallon et al (265 - 267), and they concluded that simple surface experiments would often be unreliable, because the surface structure and stoichiometry of alkali halide surface depended on many uncontrollable parameters. Among these, gaseous bulk impurities diffusing to the surface, and major changes in the stoichiometry of the surface brought about by the cleaving process.

The observation of local differences in the deposit were attributed by Distler, to the existence of oppositely charged areas, or areas of different charge magnitude. These effects should be mirrored on the opposite cleavage face.

This was not observed with sodium chloride, and it was concluded that any inhomogenities in the growth of the deposit were more likely to be due to differences in the surface structure and stoichiometry rather than solely the difference in the electrical structure.

The growth of anthraquinone on a mica substrate shows a number of interesting features, and variations in crystal habit, and because the surface of mica is ideal for surface studies, detailed observations were made of the overgrowth, enabling a proper assessment of Distler's interpretations to be made.

One of the most important features of any such study is the separation of those true surface effects, and those caused by the deposition or temperature conditions. As mentioned earlier, the overgrowth deposited under different vacuum conditions, vary in the number and final size of the crystals, this is primarily due to changes in the depositing material and not the substrate.

In all experiments using mica, the method of cleaving, was always the same, and the rate of cleaving kept as uniform as practically possible.

The anthraquinone was sublimed at temperatures between 80° - 110°C and deposition times were of the order of 15 mins.

At substrate temperatures of 25° - 30°C , the overgrowth consisted of three main types. The majority of deposit had grown as well oriented single crystals, although a very inhomogenous covering was obtained. Some deposit had grown as partially oriented single crystals, but with considerable curving at the edges, this type of deposit was often found close to or inside visible line defects on the surface. The final type of deposit was very well oriented single crystals all aligned to one orientation, and in amongst this material that had grown in the form of polycrystalline clusters. Examples of these different modes of growth are shown on plates 71 - 73. All these different growth modes were reproducible, and although the actual proportions differed to some extent, these main features were always observed. An exception to this was the polycrystalline cluster growth, which was observed on only some of the prepared specimens. It was concluded that this was due to some uncontrollable unknown parameter, and not considered again.

When slightly higher substrate temperatures were used (typically 30° - 50°C) a reduction in the quantity of deposit occurs, so longer deposition times were used. The most dominant feature of the overgrowth under these conditions was the appearance of much more of the deposit being curved, and showing definite signs of 'splintering' at the ends. All the deposit had grown as single crystals, and most of the deposit well orientated. Some of this deposit had preferentially grown at line defects, and where this had occurred some misalignment was observed.

The rounding of ends of the deposit had previously been observed with overgrowths on heated sodium chloride, and appears to be a feature of the anthraquinone when deposited on hot substrates. A similar effect was also observed on a heated quartz surface.

Examples of this growth can be seen on plates 74 - 77.

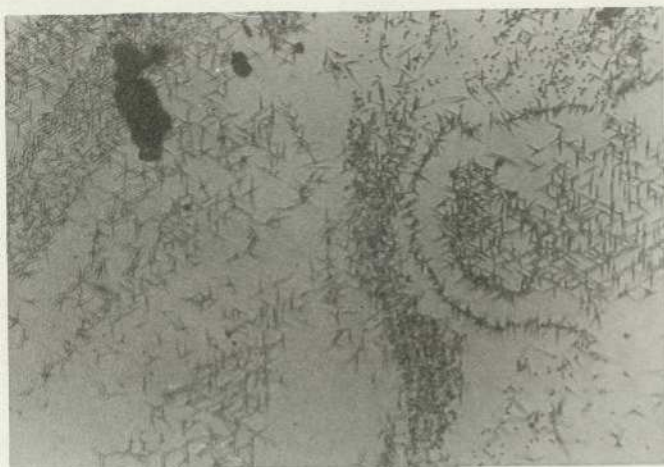


PLATE 71

40X

THE DIFFERENT MODES OF GROWTH OBSERVED WITH
ANTHRAQUINONE DEPOSITS ON A MICA SURFACE



PLATE 72

Cluster Growth
100X



PLATE 73

Preferential Growth
at Line Defects
100X

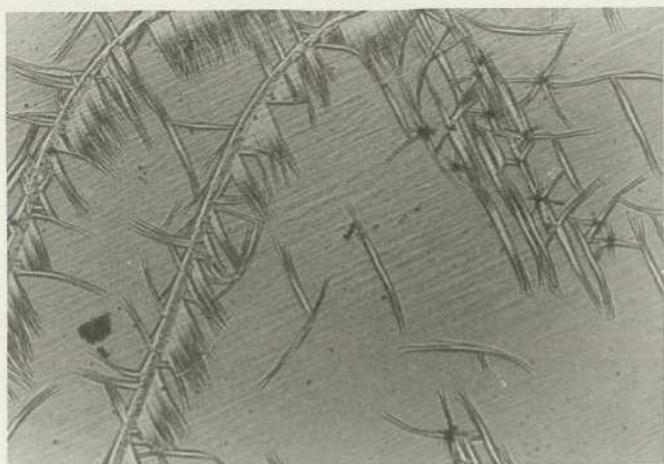


PLATE 74

400X

EXAMPLES OF THE CURVED DEPOSIT OFTEN
OBSERVED WITH DEPOSITION ON HOT SUBSTRATES



PLATE 75

100X



PLATE 76

100X

Another very interesting feature was observed in small quantities on all the specimens, was the presence of biaxial deposits oriented at 90° to each other, but with no particular orientation to the substrate surface. No reason could be found why this deposit occurs, as no visible effects on the substrate near the deposit were observed. As no connection could be found between this deposit and the substrate it is more likely the growth resulted from the substrate having no orientational influence but acting only as an inert nucleating base. A very good example of this growth is shown on plate 78.

An inhomogenous covering was obtained with all the specimens discussed so far, and with all of these deposition took place immediately after cleaving. However, if the cleaved surface is exposed to the atmosphere for long periods prior to deposition, only one mode of growth is observed.

Samples of mica were cleaved, and kept in a dust free atmosphere at room temperature for periods of 1 - 3 hours prior to deposition. This led to the preparation of a well oriented deposit, covering most of the substrate. The deposits grown under these conditions also showed no preferential growth at line defects, and no curving at the ends, it was, however, much thinner than previous deposits and contained large regions of crystals aligned all in one direction, and 120° to crystals in other regions, plates 79 and 81 clearly show these regions. As a result of the thinner overgrowth a much earlier transformation of single crystals to a coalesced film occurred and this can be seen on plate 81.

There did remain some regions of the substrate surface which contained a much lower concentration of deposit, as can be seen on plate 80 but these were few and only constituted a small proportion of the deposit.

Under these conditions, deposition on both cleavage faces, were not identical, and areas of one orientation on one surface, were aligned 120° to the orientation of the deposit on the opposite surface.

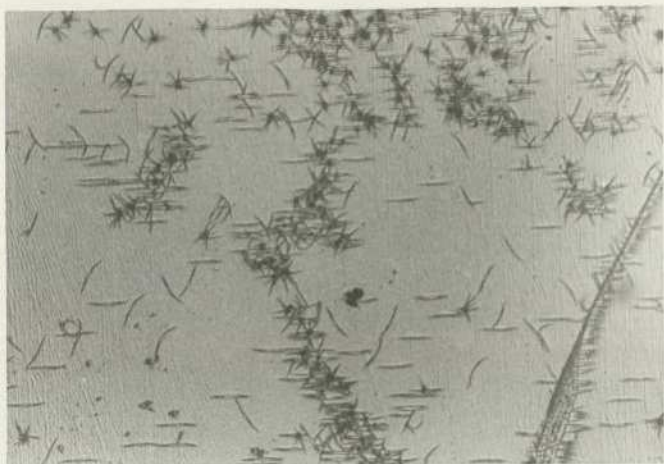


PLATE 77

A mixture of Oriented, Curved and Cluster
deposits on a Mica surface
100X

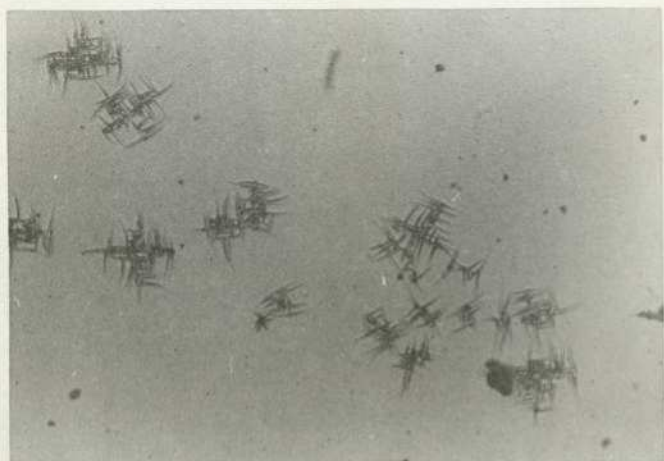


PLATE 78

Deposit grown in an ordered manner but with
no particular orientation to the substrate



PLATE 79

400X



PLATE 80

400X



PLATE 81

100X

DEPOSITS OF ANTHRAQUINONE
AT VARIOUS STAGES OF FILM GROWTH

The principle reason for the change in growth characteristics of anthraquinone deposited on air exposed mica, is thought to be the adsorption of a thin water film on the surface. It is known that one of the main differences between vacuum and air cleaved crystals of sodium chloride is the production of a hydroxide surface on the latter (268). This has the effect of increasing the probability of an epitaxial deposit. To examine the effect of water on the surface of mica, crystals were cleaved under water prior to deposition.

The cleaved crystals were vacuum dried, and kept at a constant temperature of 25°C , and deposition times of 10 - 15 mins were used.

The overgrowths prepared under these conditions consisted of very well oriented single crystals, very similar to the deposit obtained previously on air exposed surfaces. The most dominant feature of the deposit on water cleaved substrates, were the large areas of uniaxial deposit, abruptly changing in orientation, this can be seen on plate 82.

Another interesting feature was the very early transformation into a coalesced film, but only in certain areas of the substrate. A good example of this is shown on plate 83 where the large bright area indicated is in fact a well oriented film. Observation of this area under high magnification (700x) showed it to be a completely coalesced film with no visible defects brought about by any misalignment of the constituent crystals. On the surface of this film, some well developed faceted crystals could be observed which were perfectly orientated. Optical Interferometry was used on the film, which showed it to be only 500 angstroms high from the substrate surface, which is much thinner than the bulk of the deposit.

Very short deposition times were used, and samples prepared with a much reduced overgrowth, in an attempt to discover at what stage film growth occurred. Samples containing very little deposit, contained no film growth whatsoever, (see plate 84) and film formation could have only occurred by a very earlier coalescence. The only explanation for the film observed on



PLATE 82

100X



PLATE 83

Single crystal and film growth
100X

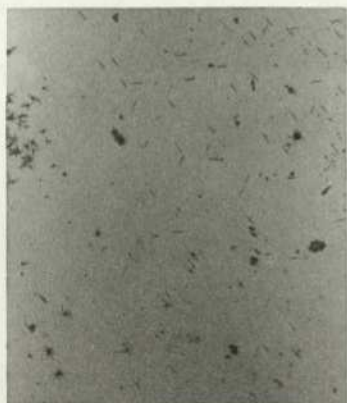


PLATE 84

100X

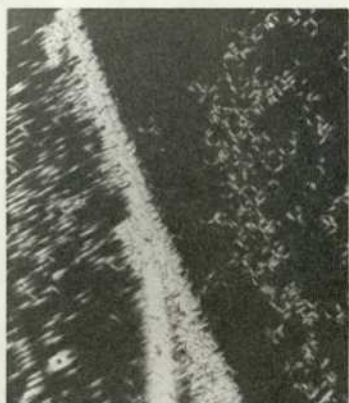


PLATE 85

100X

VARIOUS DEPOSITS GROWN ON THE SURFACE OF
MICA WHICH HAD BEEN CLEAVED IN WATER

plate 83, is that at the coalescence stage some spreading over the substrate surface occurred, to produce such a thin covering. No evidence from all the previous deposits of anthraquinone would suggest that film growth occurred from the initial nucleation, so a coalescence mechanism is assumed. The spreading phenomenon is likely to result when the correct surface energy at the interface is obtained, and this allows the deposit to 'wet' the surface, however, the mechanism for this process is not known. The film growth observed with other deposits, as seen on plate 85, have resulted from the normal coalescence without spreading, as the film is of the same thickness as the surrounding deposit. Also on plate 85 the peculiar biaxial deposit, discussed earlier, is present and appears on an area of the substrate where no oriented growth has occurred. This would confirm the suggestion made earlier that this type of deposit results only on areas of the substrate which have no orientational activity.

The close similarity between the deposits obtained on water cleaved, and substrates which had previously been air exposed, suggest that the principle contaminant on air exposed surfaces in water. This greatly smooths out the deposit and has an enhancing effect on epitaxy.

As another method of studying the electrical nature of the substrate, an induction coil was employed to charge or discharge areas of the surface. Because of the insulator properties of mica the effects of a water film could be the result of smoothing the charges on the surface which were formed at the cleaving stage.

The two possible ways of using the induction coil, was to discharge over the surface or discharge through the surface. This was done by either surrounding the mica with a conductor, or placing the conductor under the mica as shown in figure 18.

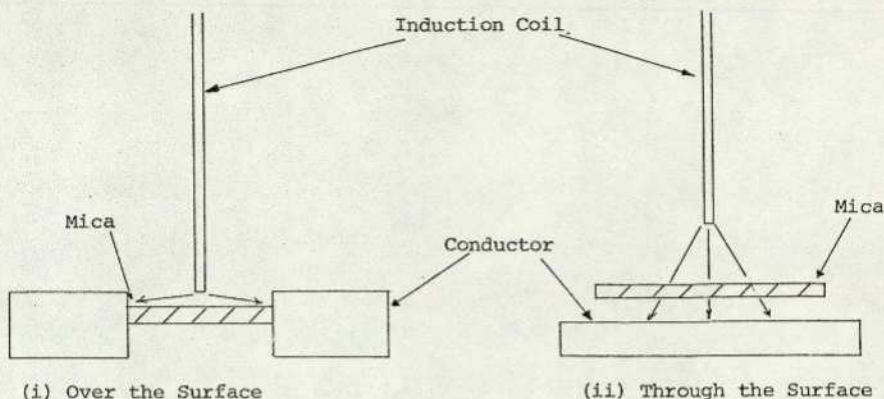


Figure 18
Methods of Discharging Mica

Great care had to be exercised when doing this operation because the surface, attracted dust etc., which would then affect the nucleating ability of the substrate. Unfortunately, the only way of determining which way the discharge proceeded, was by observation of the arcing process, and the effect of discharging through the surface seemed to have exactly the same effect as discharging over the surface.

Deposition on to these prepared surfaces resulted in the growth of well defined and separated triaxially oriented crystals. No growth was observed at cracks, or large defects on the surface. A reduced quantity of deposit was obtained, even though the same deposition times were used as with other preparations, and as most crystals were well separated, no coalescence into film growth occurred.

An effect which was not observed in any of the previous preparations, was the appearance of large domains containing no deposit at all, examples of this can be seen on plates 86 - 90.



PLATE 86

40X



PLATE 87

40X

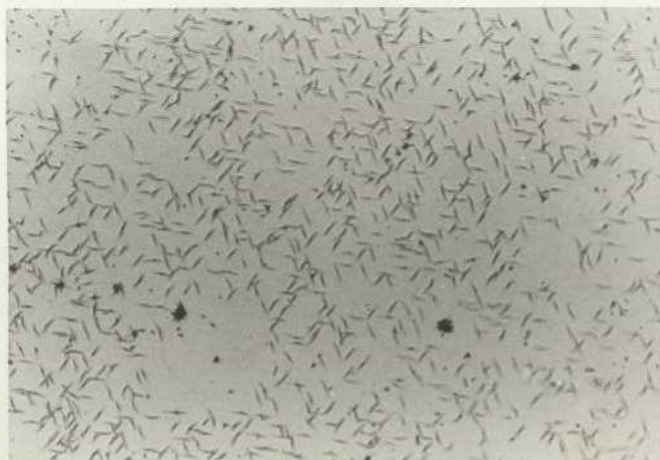


PLATE 88

100X

ORIENTED DEPOSITS ON THE SURFACE OF MICA, WHICH HAD
PREVIOUSLY UNDERGONE THE INDUCTION COIL TREATMENT

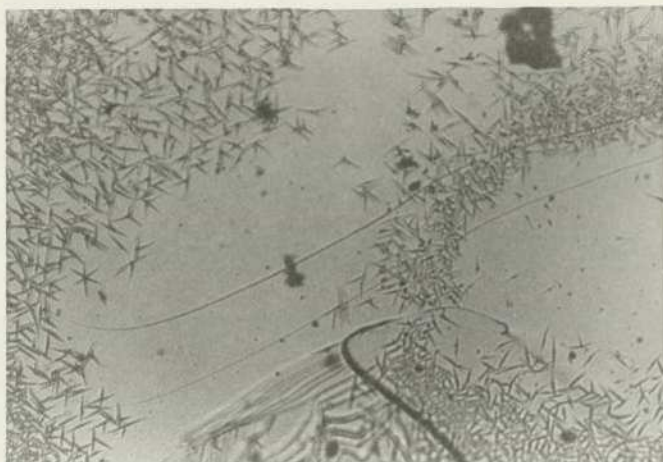


PLATE 89

400X

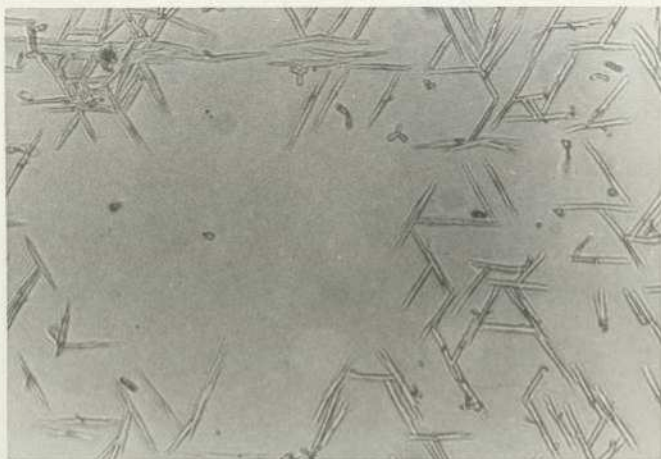


PLATE 90

400X

ANTHRAQUINONE DEPOSITS ON THE SURFACE OF MICA, WHICH
HAD PREVIOUSLY UNDERGONE THE INDUCTION COIL TREATMENT

Although areas of bare substrate have been observed previously, never such distinct 'holes' surrounded with identical well oriented deposit. Another major difference in these deposits, is that no large regions of uniaxial deposits are found, but an even number of triaxially oriented deposit in the same region.

To what extent the induction coil effects the substrate, and whether it introduces any major defects, is not known, but the most likely reason for the areas of no deposit, is the build up of a preferential negative charge on the surface. These areas would from a simple point charge approach, repel the oxygen dominated (010) surface of the anthraquinone deposit, and more deposit would grow outside these areas.

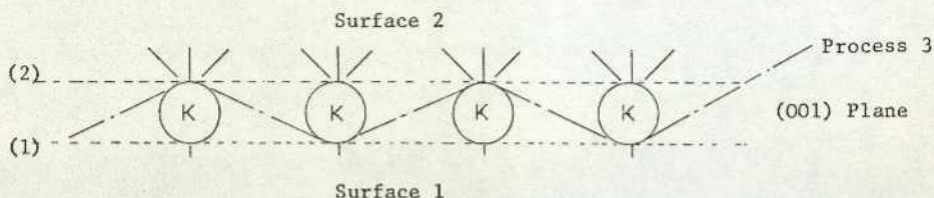
3.26 Summary

The deposition of anthraquinone onto the surface of mica has proved to be an ideal method of studying the forces responsible for epitaxial growth. The main features of this study were the differences in the behaviour of anthraquinone on air cleaved mica which were largely dependant on how long the surface has been exposed prior to deposition. These differences were a result of the different growth conditions and the presence of curved or rounded deposits were a feature observed only on substrates where exposure to the atmosphere was short. The condition of the substrate at the moment of cleaving is far from ideal, and effects dependant on uncontrollable parameters, like the rate of cleaving, the local atmosphere surrounding the new surface, the exact chemical composition of the new surface would be present. These could give rise to the different forms of growth observed, cluster, rounded, inhomogenous covering etc. Because the situation is complicated at the moment of cleaving, and many of the electrical forces cannot be experimentally determined, the behaviour of the deposit cannot be easily attributed to specific surface forces.

I believe this to be the case with the curved deposit, and find it hard to explain this deposit being due to small negatively charged areas as suggested by Distler.

After a long period of air exposure, or cleaving under water a general smoothing out of the surface effects occurs, which results in a more homogenous deposit being obtained. Under these conditions changes in the orientation could be specifically attributed to the electrical structure of the surface. In both cases large regions of uniaxial deposit were observed, and the areas of reduced deposits would correspond with regions of low electrical activity on the substrate surface.

When a crystal of mica is cleaved it does so along the (001) plane containing the potassium ions, this allows the two possible positions for the splitting, above or below the potassium ion.



The effect of this is to leave either positively charged or negatively charged regions on both surfaces. In addition the surface could cleave at alternative potassium ions to give both overall neutral surfaces.

The presence of areas of different charge signs on the surface of mica have been revealed by means of electrometer studies (269) and the presence of electrical 'domains' with the electrical field parallel to the surface, and displaced by 120° relative to the two cleavage faces have been found by LEED examinations (270).

As splitting at both positions around the potassium ion are equally likely, it would be expected that the process would be controlled statistically, and large areas of positive or negative charges would not be obtained. Recent calculations on the cleavage process, however, suggest that the rate of cleaving effects the surface energy and overall charge distribution of the resulting surfaces (271). By taking into account the lattice imperfections in real crystals, and summation of the electrostatic forces, the probability of obtaining locally ordered regions of potassium ions were greatest when the cleaving rate is high. It is due to these effects, that the anomolous domains of electrical activity are possible.

The effect of cleaving under water will reduce considerably the surface energy of the prepared mica surface and therefore a more uniform covering would be expected. The film of water acts as a polarised film, and smooths out any surface electrical irregularities, even those present at cracks and steps, although not changing them, resulting in regions of perfect orientation and the observation of only one type of growth. The water does not change the charged regions, because the oppositely charged regions are observed on the matching cleavage face with correspondingly different orientations.

The observation of large regions of uniaxial deposit with their texture axes displaced by 120° to other regions are consistent with the observations made by Distler. Also the domain regions of electrical activity, resulting from the presence of potassium ions yielding a high concentration of positive charge, and its absence results in a more diffuse negative region is consistent with Distlers interpretations. The regions of low electrically activity at any position a corresponding low concentration of the deposit would be expected.

The results obtained with those samples of mica exposed to the induction coil prior to deposition are consistent to the predicted effects due to different charge distributions.

The effect of the discharge of the induction coil would be to ionise the vapour around the mica surface, this would then have a similar effect as water by smoothing the resultant deposit. Also the existance of predominantly triaxial deposit would be expected from an ideal substrate which had cleaved at alternative potassium ions. The effect of the induction coil is to remove and change the charge distribution on the surface of mica, to that which would be setting up of large regions of charge would not be expected. The exception to this are the areas observed which contain no deposit, and these would be the result of a build up of negative charge, but even these areas are situated at regular intervals over the substrate and further demonstrating the effect of the induction coil to produce a symmetrical charge distribution.

(Calculations using various charge distributions, and the resulting predicted orientations are presented later in chapter 5.)

The result of the study of Glycine on mica confirm the importance of the electrical structure of substrate. The glycine contact face contains arrays of oxygen and nitrogen atoms, and the nitrogen atoms reduce the mobility of this species on negatively charged substrates, and because of this many effects observed with anthraquinone on mica are not observed with deposits of glycine.

Distlers observations and interpretations have been confirmed by this study, but some of his interpretations on the rather minor growth irregularities, which are more likely to result from the many unknown parameters of a surface, are thought to be largely speculation.

3.26 Summary - The growth of Epitaxial deposits on Sodium Chloride, Mica and Quartz

A comparison of the behaviour of both deposits of anthraquinone and glycine on the surfaces of the three substrates used, indicate the importance of the growth conditions, electrical structure and lattice parameters necessary to obtain an epitaxial deposit.

Both materials easily grew as epitaxial deposits on the surface of sodium chloride, the size of the crystals obtained however, were quite different. The reason for this difference was the differing mobility and nucleation properties of the two deposits and not the orienting ability of the substrate. The positions of the chlorine ions on the surface of sodium chloride exert the most important orientation influence, and growth occurred easily with anthraquinone because it is negatively biased and therefore possesses a high mobility on this surface. Glycine is not so negatively biased, and its mobility had to be increased by increasing the thermal energy of the substrate in order to observe an epitaxial deposit.

Because of the surface rearrangements and changes in stoichiometry of sodium chloride evidence exists to show the surface is far from ideal, and growth irregularities most probably occur as a result of these imperfections.

The mobility of both these deposits were far greater on the surface of mica, and the increased mobility of anthraquinone demonstrates that not only surface charges are responsible for surface mobility. Mica is a better substrate in many ways than sodium chloride, because of the increased mobility an epitaxial deposit was easily obtained. Results of this study did however, show that in cleaving a statistical distribution of charges did not occur, and the rate of cleaving and time of exposure to air were extremely important. If the mica surface is cleaved and the matching surfaces allowed to 'settle' subsequent deposition indicates the existence of mirror effects on the two surfaces. These effects are seen by the rotation by 120° of the electrical axes and consequently the deposit orientation of the two matching faces.

The surface of Quartz is far from an ideal substrate, as the surface treatment prior to deposition is lengthy, and leaves the surface in largely an unknown state.

As a result of the complicated surface of quartz the exact orientational forces are not clearly understood. Both deposits have a very low mobility on the surface and high substrate temperatures were required to obtain epitaxy. Epitaxy was only observed, however, if the amorphous surface layer had been completely removed and under no circumstances could an epitaxial deposit be obtained if any of this layer remained. This observation seriously questions Distler's hypothesis of the existence of long-range epitaxial forces in the substrate, although it is possible that the amorphous layer on quartz does not permit transmission of these forces.

Because an acceptable experimental technique in the preparation of quartz surfaces, could not be obtained in the time available, a thorough investigations of the amorphous layer and orientational forces could not be made. A further discussion on the orientation of both these deposits on all three substrates, and the different lattice parameters is considered in detail in chapter five.

The importance of the growth parameters, and the difference between obtaining an epitaxial deposit and actually observing it, has been stressed so far in this study because it is of considerable importance when attempting to reproduce Distlers long-range force observations, (Chapter 6) a fact that other workers have often neglected to consider.

A MATHEMATICAL MODEL TO DESCRIBE EPITAXIAL PHENOMENA

4.1 Introduction

The orientational results obtained in the previous chapter demonstrate the importance of both growth conditions and the electrical structure of the surface. Nearly all models and theories of epitaxy have neglected to consider these parameters, the reasons for this is largely due to most theories being formulated as a result of observation of metal deposits on metal or alkali halide substrates, where these parameters appear not to be of great importance. Because of this there still exists today no comprehensive theory of epitaxy. The exception to this is the Distler mechanism of long-range forces, which if correct would explain many observations, but this model still only considers the orientation of crystals and makes no account of growth parameters, and the electrical structure of the surface. The origin of the long range forces is thought to be a result of effects within the substrate, and remains largely a speculative deduction.

In an attempt to explain the behaviour of organic deposits Field and Darling (276, 277) formulated a very simple approach to epitaxy. The basis of their model was to consider the ideal electrical structure of both the deposit surface and substrate surface. This was done by defining the two surfaces as consisting of arrays of positive and negative species, and determining the overall coulombic interaction. (A complete description of this approach can be found in reference 84.)

With the Field-Darling model it should be possible to extend the coulombic interactions to include electron density values, and hence extend this approach to non-ionic substrates. The following section describes this model and its subsequent development together with the computer programming techniques used for the calculations. The latter is extremely important

because by the nature of this approach, it includes a very large number of calculations, and the programme must be designed as efficiently as possible, to avoid impossibly long computer operation times.

4.2 Model Description

The events leading to the growth of an epitaxial deposit can be summarised as follows:

- A) Atoms from the depositing vapour, condense on to the surface of the substrate without the loss of mobility.
- B) By a process of diffusion and collisions a stable three dimensional nucleus is formed, this subsequently is trapped at a lattice defect or other surface inhomogeneity, and retains its rotational freedom.

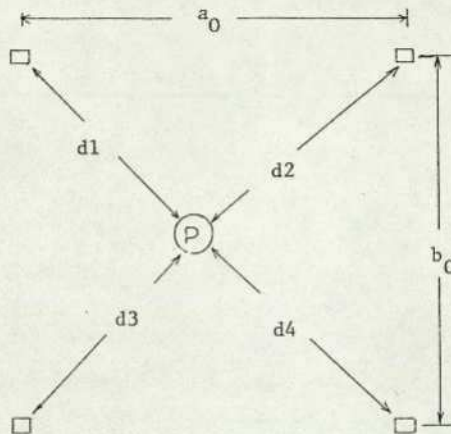
Events A and B are much the same as described for the fluid cluster concept discussed earlier (section 1.66).

- C) The stable three dimensional nucleus, rotates until the energetically most favourable orientation is found.
- D) The nucleus continues to grow by the various normal crystal growth mechanisms.

This model was concerned only with event C, and the criterion used for defining the most favourable orientation was that position which contains the lowest coulombic energy. The total coulombic energy being found by summing the attractive and repulsive energies of the most dominant species on the substrate and deposit surfaces.

4.21 Simple Point Charge Approach

A homopolar surface can be described as an array of charges with the dimensions defined by the lattice parameters.



The electrostatic interaction of a point P on the surface will be given from the expression:-

$$E = \frac{Kq_1q_2}{d}$$

where d = distance

q_1q_2 = the charge of the species

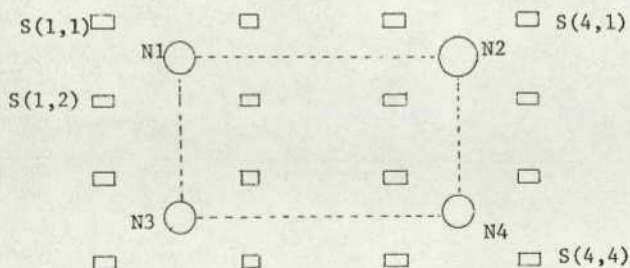
K = constant of proportionality

therefore the total interaction for identically charges species

$$E = K\left(\frac{1}{d_1} + \frac{1}{d_2} + \frac{1}{d_3} + \frac{1}{d_4}\right)$$

Clearly if $d_1 = d_2 = d_3 = d_4$ there is no resultant force on the point P, and under these conditions, the most stable position.

Similarly for a 4 point nucleus.



N1 N4 denotes the nucleus points
S(1,1) S(4,4) denotes the substrate points

The electrostatic interaction is found for each nucleus and nearest substrate point, and the resultant sum is determined for each possible position of the nucleus.

Using this approach, the most stable nucleus orientation of the nucleus is found. When this is applied to a real system for example the sodium chloride (100) face (figure 19) all the charge is assumed to be located at the centre point of each ion.

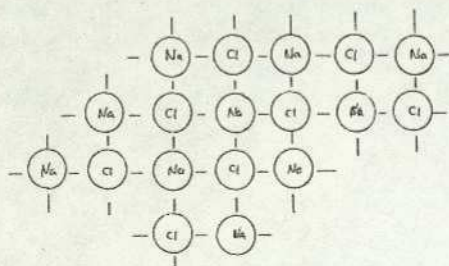
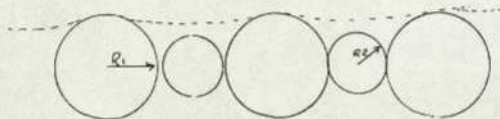


Figure 19

Sodium Chloride (100) Face

A comparison of the ionic radii of both species is used to determine which ion will exert the most dominating effect.



If $R_1 \gg R_2$ then the smaller ion in most cases need not be considered.

As the chloride ions are much larger than the sodium ions, together with the surface distortion occurring on this surface, the effect of the sodium ions would be negligible for a negative deposit. Therefore the surface is considered as consisting of an array of negative point charges.

The deposit surface is treated in a similar way, and the position of a deposit nucleus, on the substrate is defined by the three parameters X , Y and θ . X and Y are displacements in the x - and y - directions and θ the rotation of the nucleus about its centre of gravity. The magnitude of the electrostatic energy is determined for all the possible combinations of these variables, and the lowest value corresponding to the most favourable orientation.

The size of each separate iteration movement of x and y should be as small as possible, to improve the probability of determining the absolute minimum electrostatic energy. In practice however, very small iterative movements require excessive computer time and a compromise situation was necessary. As a result of the large number of repetitive calculations involved in this method a digital computer was employed. To achieve this objective the problem needed to be separated into a number of simple steps which could be easily converted to the high level Fortran IV computer language.

A co-ordinate system defining the positions of all the substrate and nucleus points is given from the expression:

$$X_I = I a_O S \quad X_J = J a_O N$$

$$Y_I = I b_O S \quad Y_J = J b_O N$$

The subscripts I and S denote a substrate point, and J and N a nucleus point. $a_O S$, $b_O S$ and $a_O N$, $b_O N$ are the respective lattice parameters of the substrate and deposit surfaces.

X_I, Y_I and X_J, Y_J co-ordinates were calculated until $I = M$ and $J = N$ where M and N are the number of points taken for the substrate and nucleus, respectively.

The distance squared between each nucleus and substrate point is determined from:-

$$d^2 = (X_I - X_J)^2 + (Y_I - Y_J)^2$$

Because only the nearest substrate points will exert the predominant influence on the nucleus, a limit is set on d^2 values, values greater than the limit are not considered further.

The reciprocal of d^2 is determined and assigned S , and the total sum of all the individual S values is calculated.

$$S = \frac{1}{(d^2)^{\frac{1}{2}}}$$

$$SSUM = S_1 + S_2 + \dots S_n$$

The total value $SSUM$ represents the overall stability of the whole nucleus for any one position, this nucleus is then displaced and the process repeated until all the possible positions have been used. The values of $SSUM$ are then compared and the most stable orientation found.

The degree of agreement between any predictions made with this model and the orientation observed experimentally will depend to a large extent on the relative importance of the electronic interaction in determining the orientation. It is desirable that the model should be refined to an extent for the occasions when no agreement between prediction and practice is found, the difference can be confidently attributed to the lack of importance of the electrostatic interaction. This will enable an assessment of the relative importance of the many variable parameters involved in epitaxial deposition to be made.

Any aspects in the model where possible errors would lead to errors in orientation prediction, should be eliminated, or the orientations disregarded.

One of the most important of these is deciding on the size and shape of the deposit nucleus. Inherent in the model's assumptions is the stable three-dimensional nucleus is of normal crystallographic habit, and the normal bulk lattice parameters are in no way changed. As discussed earlier (chapter one) the lattice parameters are identical in the nucleus and the bulk crystal habit modification at the nucleation stage. The size of the nucleus, however, was not readily determined, and it was in this stage where the introduction of an error was possible. Much of the past and present work has been restricted to metal deposits where the size of a critical nucleus can be a cluster of only a few atoms. With organic deposits, nucleus dimensions are not well documented, but it is likely that quite large clusters could exist prior to crystallisation. For the purpose of computation with this model, nucleus sizes were determined from a comparison of the substrate, nucleus lattice parameters. When these parameters are similar, a small nucleus was used, the contact face consisting of 4 - 9 points. This was decided upon because the largest difference in the stabilities of individual orientations occurred when small nuclei were used in the calculations. The effect of using larger nuclei, was to decrease these differences, and no overall favourable orientation could be predicted. Because there is no large difference between the lattice parameters of the substrate deposit pairs used in this study, small nuclei have been used in the calculations.

Further errors can be introduced into the model calculations, as a result of the determination of the number of positions of the nucleus. The total displacement of the nucleus, must account for nearly all the possible positions, to ensure that the most stable position is not omitted from the calculations.

The method of x-, y- displacement can be seen from figure 20.

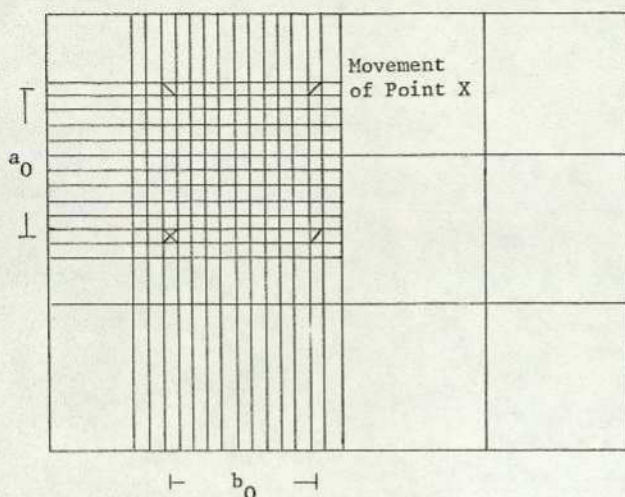


Figure 20

A point p_1 of the nucleus is moved in the x- direction until all the possible positions are considered, once a total displacement of a_0 has been completed, further movement will only result in the duplication of positions, the nucleus is moved back and moved in the y- direction. The unit cell of the substrate is divided into a number of sub-divisions, and every point of the nucleus is displaced by the magnitude of these sub-divisions.

The assigned value for each iterative movement is defined by:-

$$\text{ITERATION in x- direction} = \frac{a_0}{T} \quad \text{in y- direction} = \frac{b_0}{T}$$

In practice the most stable position was found using at least two different values of T , when quite different positions were predicted further values of T were used, until it was sure that the most stable position was not missed.

In addition to the translation of the nucleus, it is also rotated about its centre of gravity, and the most stable position found for each rotation. The orientation of the deposit with respect to the substrate is defined by the crystallographic planes of the substrate, and any orientation θ is defined by the expression

$$\tan \theta = \frac{Na_0}{Mb_0}$$

where N and M correspond to the number of unit cell lengths in the x and y directions.

For example where $N = 1$ and $M = 2$ this corresponds to the $[102]$ direction (see figure 21).

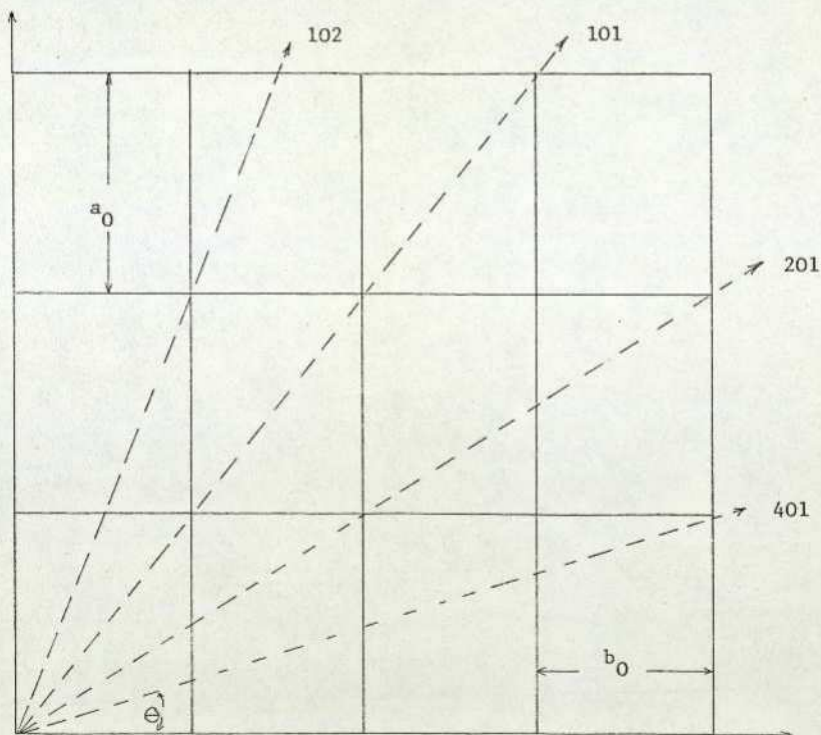


Figure 21

4.22 More Complex Surfaces

To enable this model to be used for more complex surfaces, it must be modified only in ways that do not introduce extra possible errors in the final predictions.

For a surface which contains similar ionic species but of opposite charge, the determination of the stability value must include a mechanism to differentiate between attraction and repulsion. This is achieved by the addition of simple logical comparison statements prior to the summing stage in the program. For a nucleus consisting of two different species, for instance, one which is the same charge as the substrate species and one of opposite charge, each nucleus point would correspond to either attraction or repulsion. These points are initially uniquely defined for example if nucleation points 1 and 4 positive and 2 and 3 negative the comparison statements after the determination of the distance from a substrate point are:-

IF (J = 1 or 4) S1 = -1

IF NOT S1 = +1

$$S = \frac{1}{(d)^{1/2}}$$

$$S_2 = S \times S_1$$

Therefore when the distance between like charges is found, a repulsion energy is indicated by a negative S1 and consequently a negative S₂.

This method assumes that both species interact in opposite but equal ways, this is often not the case and a method of weighting the calculation to account for the different electron density values is required. It is not sufficient just to use electron density values, as these would be different after surface distortion etc., although they can be used as an initial guide.

A technique was devised to overcome this difficulty and although empirical in its approach good agreement between prediction and experimentally observed orientation was obtained.

The method used was to determine the calculated orientations, initially with both species exerting equal but opposite charge effects. If a negatively biased substrate was being used, the relative importance of the positive species was increased, this resulted in larger differences between the predicted stabilities of orientations being obtained. The importance of this species was then progressively reduced until very little difference between the stabilities of orientations was obtained, or a new stable orientation predicted. At this stage the difference in the specific weighting of both species was compared to the difference expected from the electron density values. Normally the difference observed was far greater than the difference expected from electron density values, and it was concluded that the orientations predicted from the calculations using unity weighting would be those observed.

This was particularly true for most of the amino acids because of the large charge separation resulting from their zwitterion properties in the solid state. The method used for weighting was simply to assign fractional numbers to the values of S_1 , the actual value of these depend on the particular species being considered.

Although this model in no way describes fully the phenomena of epitaxy it can with certain reservations produce useful predictions concerning the relative importance of the electrical structure of particular substrate-deposit pairs. Using this method, useful predictions were made concerning the electrical structure of mica and quartz surfaces.

4.3 Computer programming methods

4.31 Introduction

In this section the two basic types of programs used are described in detail. The actual program efficiency is extremely important, as the degree of flexibility possible with this model is largely dependant on the computer calculation time needed. The computer used for the majority of calculations was the ICL 1900, and where a larger store, and longer calculations were required the faster London University computer was used.

4.32 The Basic Program

The stages involved in this calculation were, initially to set up a rectangular array for both the substrate and nucleus points, and then calculate the total interaction. The nucleus was then displaced and the new interaction calculated, this was repeated until all the desired positions of the nucleus were used. All the resultant values of interaction were compared and the most stable position determined.

The flow diagram for this process is summarised in figures 22 and 23 and is largely self explanatory.

The method used for determining the new lattice point co-ordinates for a rotation of θ

$$X^1 = X \cos \theta + Y \sin \theta$$

$$Y^1 = Y \cos \theta - X \sin \theta$$

where X and Y are the starting positions and X^1 , Y^1 the position after rotation.

To determine the most stable position for a particular orientation, a store and comparison technique was used. This involved the setting up of an interger counter to determine at what particular displacement corresponded to the stable position. Initially this counter IC was set to zero and the first stability value was stored under the label of TEST.

Subsequent stability values were compared with the value in the store TEST, and if a greater stability was present it replaced the value in TEST.

This process can be summarised as follows:-

IC = 0 (Starting Condition)

IF (IC equal 0) Go to store statement 18

IF (IC $\neq$ 0) Compare stability value with that in TEST

IF (STABILITY LESS THAN TEST) PROCEED

IF (STABILITY GREATER THAN TEST) STORE NEW VALUE

18 TEST = NEW STABILITY VALUE

PROCEED

After all the positions have been used, the value present in store TEST, is recorded, and the process repeated for all the rotations.

The method of itteration in the x- and y- directions was achieved by adding successive fractions of the total displacement to the co-ordinates of all the nucleus lattice points. The total displacement is also added to a particular point and compared with the gradual itterative value, when these two values are identical the itteration is halted in that direction, reset to zero displacement, and displaced in the other direction by the same method. This process can be summarised by the following:-

$A(J), B(J)$ = initial co-ordinates of the lattice points

$A_1(J), B_1(J)$ = displaced lattice co-ordinates

$A_2(J), B_2(J)$ = Rotated lattice co-ordinates

The test for completion of the displacement were set up using symbols AT and BT.

$AT = A_2(1) + \text{ALPHA}$ (ALPHA = TOTAL x- DISPLACEMENT)

$BT = B_2(1) + \text{BETA}$ (BETA = TOTAL y- DISPLACEMENT)

T_1 = Number of itterations

ITTERATION $A_1(J) = A_1(J) + \text{ALPHA}/T_1$

IF ($A_1(1)$ is less than AT) Proceed with program

IF ($A_1(1)$ is greater than AT) Stop Iteration

RESET to original value $A_1(J) = A_2(J)$

$B_1(J) = B_1(J) + \text{BETA}/T_1$

And again test for completion etc.

The rotation is done in an identical way using the symbols DELTA and DEG, where DEG is the actual value of the rotation and DELTA the fractional increase.

Using these symbols a more detailed flow diagram is shown in figures 24 and 25.

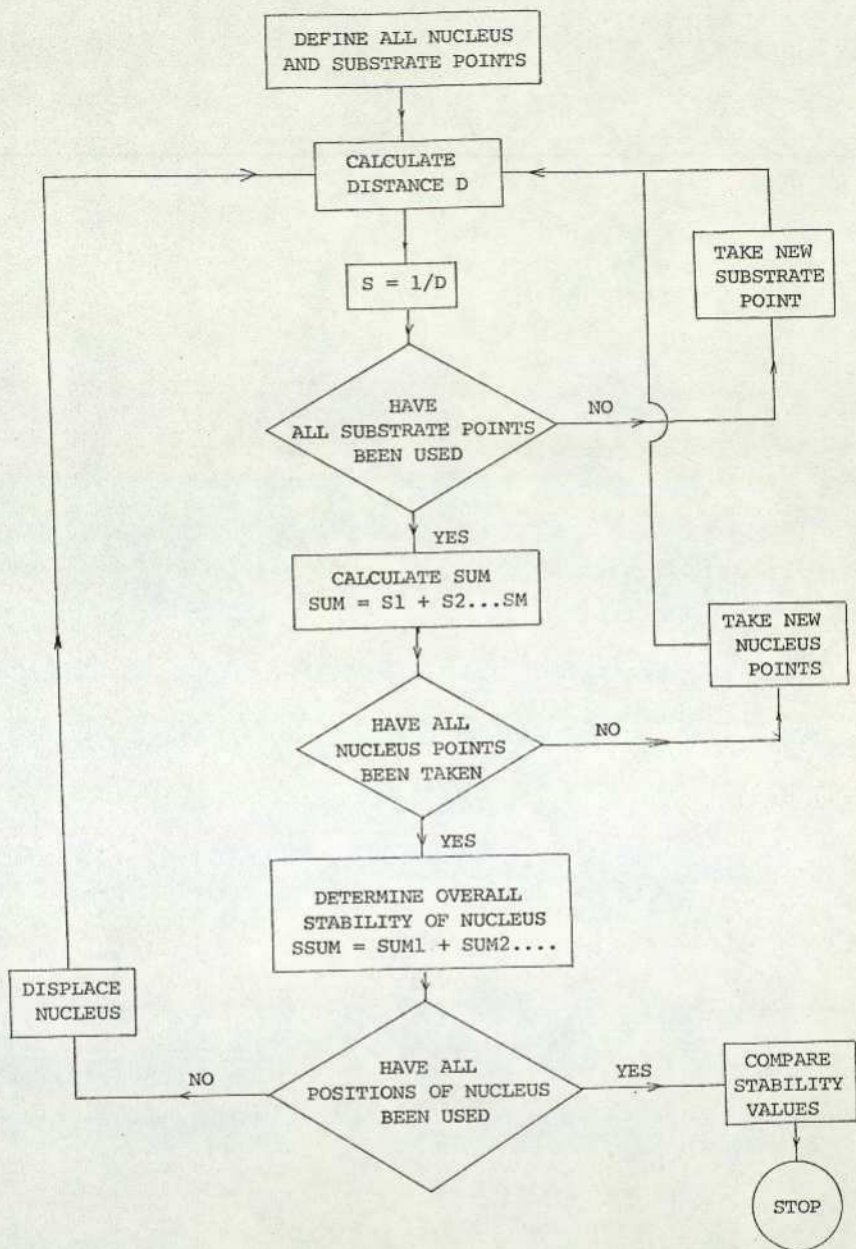


Figure 22

DISPLACEMENT FLOW DIAGRAM

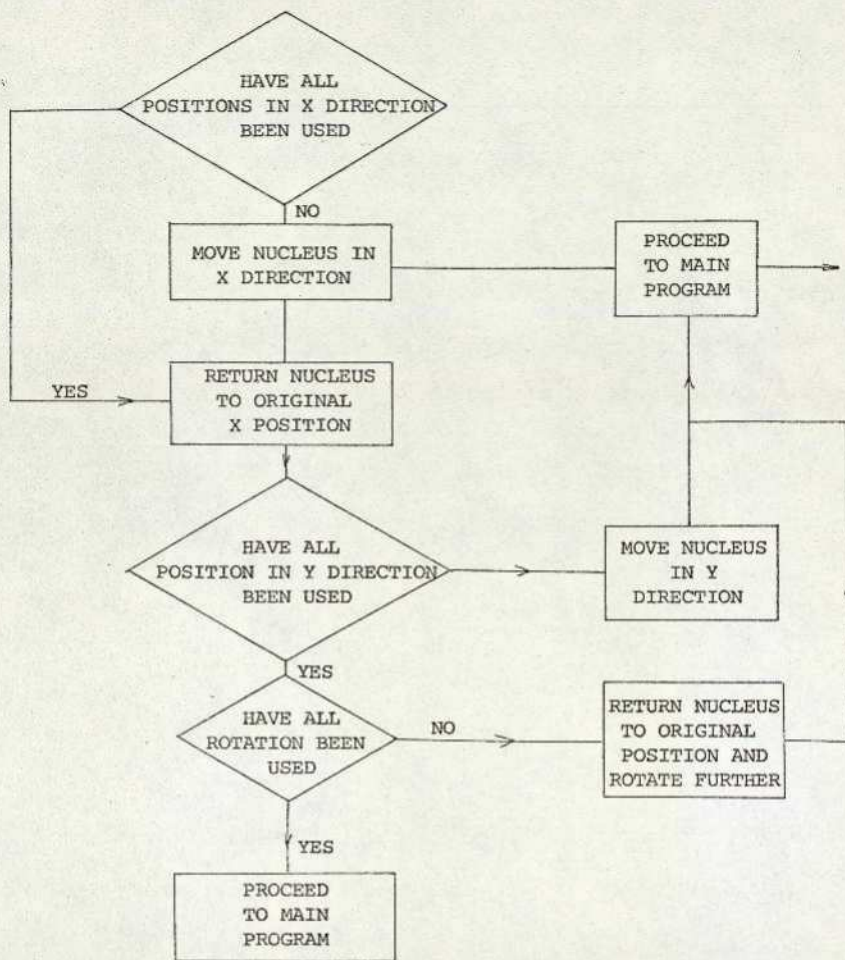


Figure 23

MAIN PROGRAM

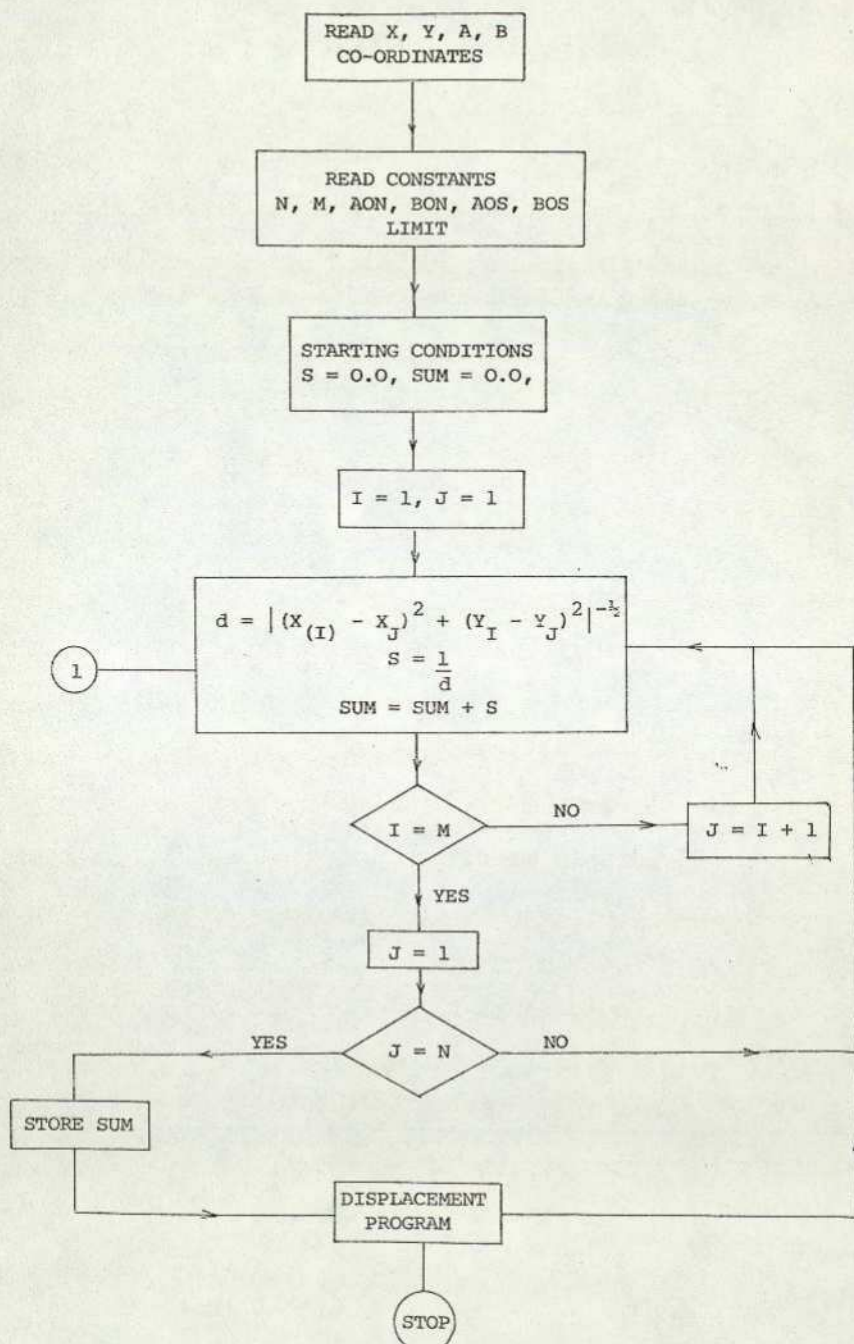


Figure 24

DISPLACEMENT PROGRAM

ITT1 = iteration in x direction
 ITT2 = iteration in y direction
 LIM 1 = Limit in x direction
 LIM 2 = Limit in y direction

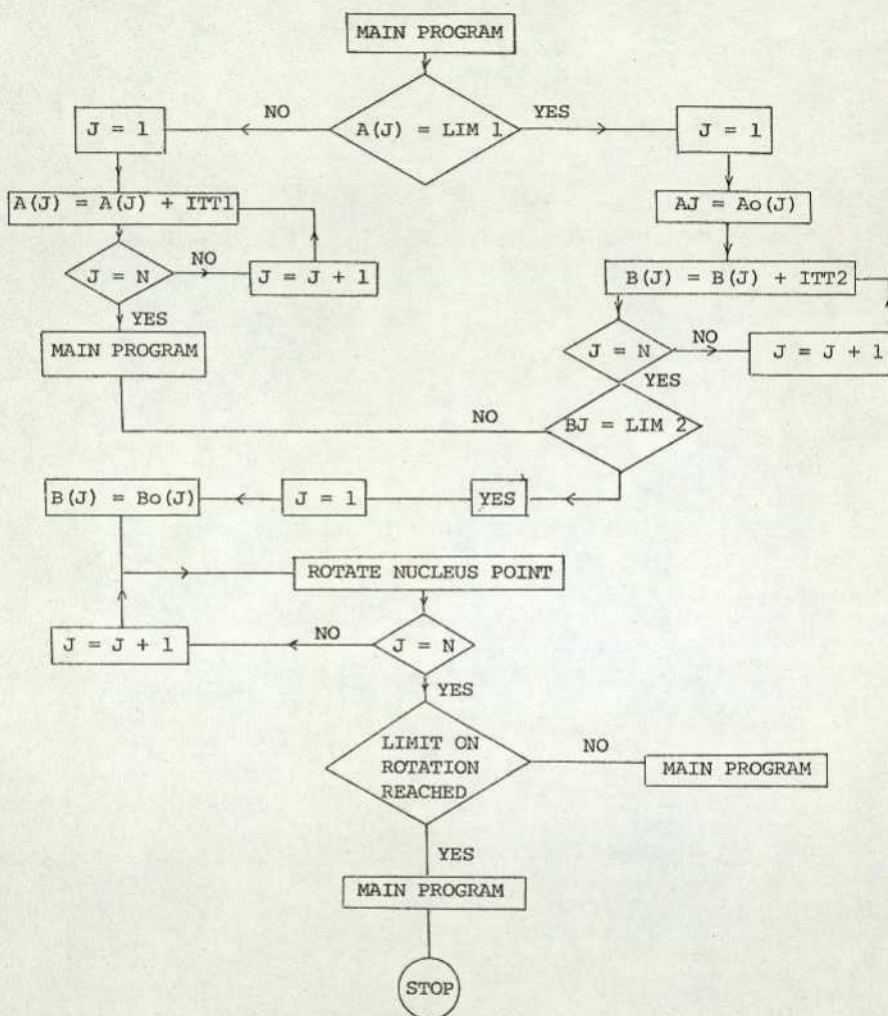


Figure 25

To illustrate the use of this program, it has been used to determine the most favourable orientation of an anthraquinone deposit on the (001) face of sodium chloride.

The arrangement of the species on the (001) face of sodium chloride is shown in figure 26.

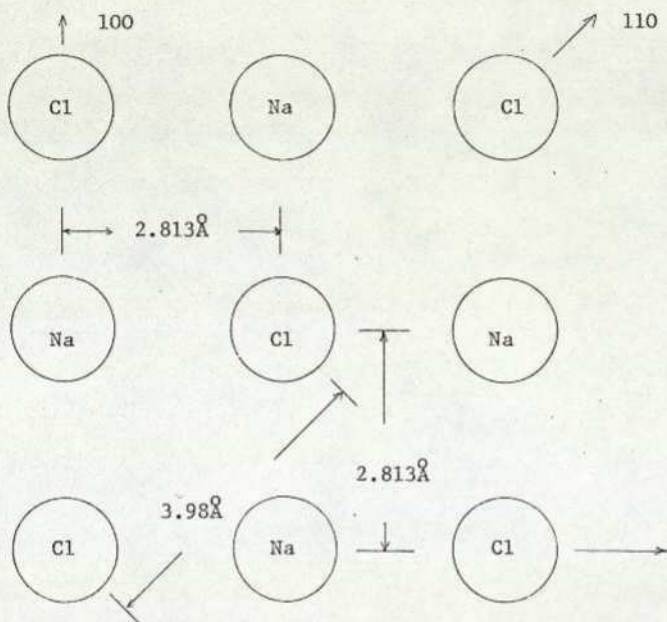


Figure 26

Arrangement of ions on the (001) face of Sodium Chloride

Because of the reasons discussed earlier the negatively charged chlorine ions are taken to be the most dominant species on the substrate, and for the purpose of computation and ease of handling the surface has been rotated by 45° to set up a simple square array in the $[110]$ direction, as shown in figure 27.

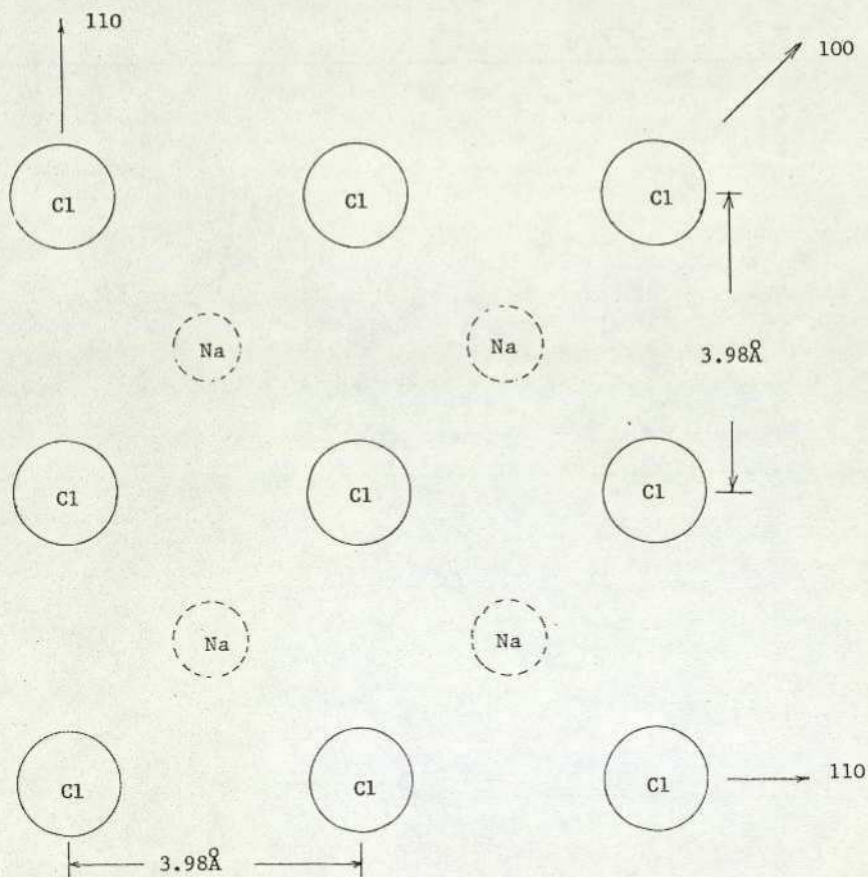


Figure 27

The array of Chlorine ions used in the Program

The crystal structure of anthraquinone was investigated by Sen (278), and is shown in figure 28. The contact face used in epitaxial deposition, is the (010) face which contains an array of oxygen atoms. This array of atoms will determine the orientation on the surface because they are the only charged species present on this face.

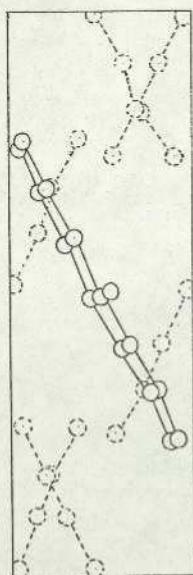
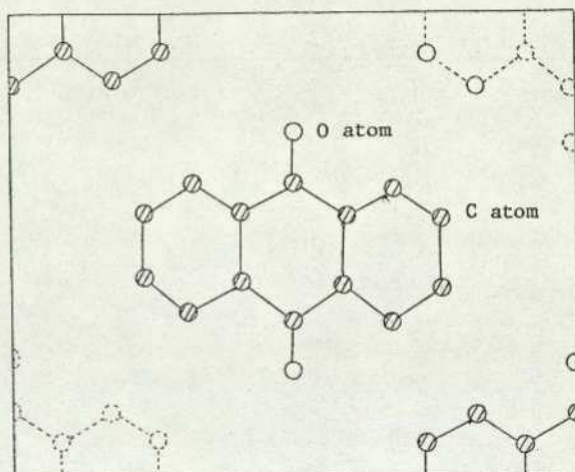
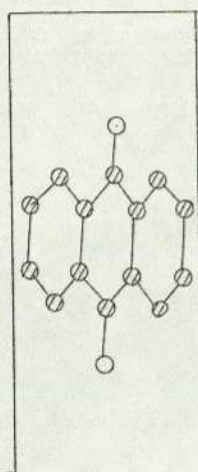


Figure 28
Structure of Anthraquinone based on a
Pseudo-orthorhombic System

Using the array of oxygen atoms in the array shown on Figure 29 the orientation was determined.

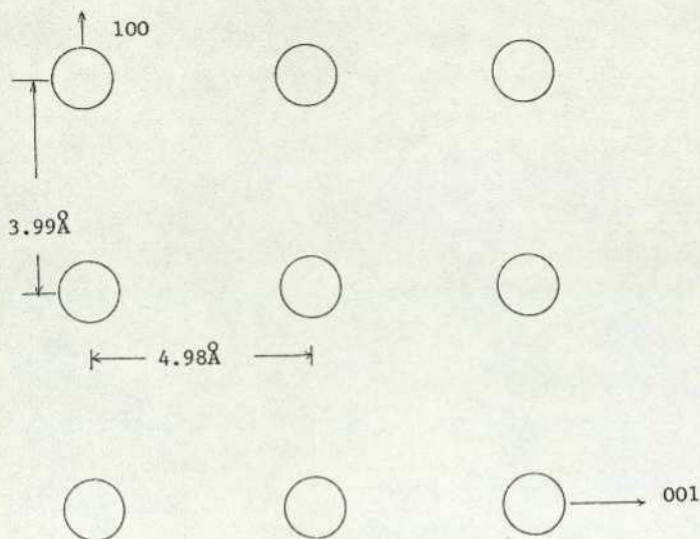


Figure 29
(010) face of Anthraquinone

4.33 Program to determine the orientation of anthraquinone crystals on the (100) face of sodium chloride

PROGRAM 1

```

C ANTHRAQUINONE ON SODIUM CHLORIDE
C DEFINE THE NUCLEUS AND SUBSTRATE SIZE
  DIMENSION X(36),Y(36),A(4),B(4),A1(4),B1(4),A2(4),B2(4)
  DEG=0.0
  ALPHA=3.98
  BETA=3.98
  SETVAL=18.0
  N=4
  M=36
  DELTA=5.0
C STARTING CONDITIONS
  READ(1,10) (X(1),Y(1),1=1,M)
  READ(1,10) (A(J),B(J),J=1,N)
10 FORMAT(2F10.3)
  WRITE(2,10) (X(1),Y(1),1=1,M)
  WRITE(2,10) (A(J),B(J),J=1,N)
12 THETA=DEG*3.14159/180.0
  IC=0
  R=COS(THETA)

```

```

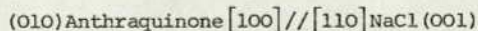
Q=SIN(THETA)
DO17J=1,N
A2(J)=A(J)*R+B(J)*Q
B2(J)=B(J)*R-A(J)*Q
A1(J)=A2(J)
B1(J)=B2(J)
17 CONTINUE
BT=B2(1)+BETA
AT=A2(1)+ALPHA
SSUM=0.0
SUM=0.0
DO11J=1,N
DO16I=1,M
DSQ=(X(1)-A1(J))**2+(Y(1)-B1(J))**2
IF(DSQ.GT.SETVAL)GOTO16
S=1.0/SQRT(DSQ)
SUM=SUM+S
16 CONTINUE
11 SSUM=SSUM+SUM
IF(IC.EQ.0)GOTO18
IF(SSUM.GT.TEST)GOTO19
18 TEST=SSUM
19 IC=IC+1
192 DO20J=1,N
20 A1(J)=A1(J)+ALPHA/10.0
IF(A1(1).GT.AT)GOTO22
GOTO13
22 DO23J=1,N
A1(J)=A2(J)
23 B1(J)=B1(J)+BETA/10.0
IF(B1(1).GT.BT)GOTO25
GOTO13
25 WRITE(2,26)DEG,TEST
26 FORMAT(1H,F7,1,1PE20.4)
DO21J=1,N
A1(J)=A2(J)
B1(J)=B2(J)
21 CONTINUE
DEG=DEG+DELTA
IF(DEG.GT.90.0)GOTO28
GOTO12
28 STOP
END

```

The Results of the program 1

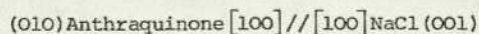
DEGREES OF ROTATION	VALUE OF REPULSION
0.0	1.0652 E 01
5.0	1.2216 E 01
10.0	1.2393 E 01
15.0	1.3092 E 01
20.0	1.3447 E 01
25.0	1.3655 E 01
30.0	1.3335 E 01
35.0	1.3336 E 01
40.0	1.2976 E 01
45.0	1.2148 E 01
50.0	1.2788 E 01
55.0	1.3193 E 01
60.0	1.3161 E 01
65.0	1.3937 E 01
70.0	1.3626 E 01
75.0	1.2831 E 01
80.0	1.2682 E 01
85.0	1.2471 E 01
90.0	1.0652 E 01

From these results the orientation with the lowest repulsion is 0.0 degrees and 90 degrees. This corresponds to the orientation.



It is also interesting that a second minimum repulsion value is obtained at a rotation of 45 degrees.

This corresponds to the orientation



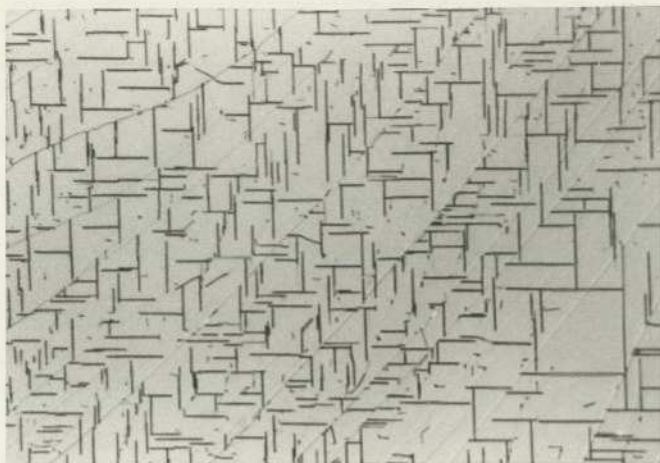


PLATE 91

40X

Orientations of Anthraquinone
on Sodium Chloride

The two orientations predicted from the computer calculations, are indeed those experimentally observed, especially gratifying is the prediction of a second possible orientation which is confirmed by observation (see plate 91).

The rate determining stage of this program, is in the calculation of the distance between the substrate and nucleus points, this distance is calculated for every point on the nucleus and substrate, and then recalculated for each iterative movement and rotation. Although not every distance is used in the calculation of the stability value, very little computer time is infact saved because long distances are only eliminated after their determination. A second program was written to reduce the number of calculations and make full use of the computer store and memory.

A negligible amount of time is used in data storage, but a significant reduction in operation time would be possible by a reduction in the number of calculations.

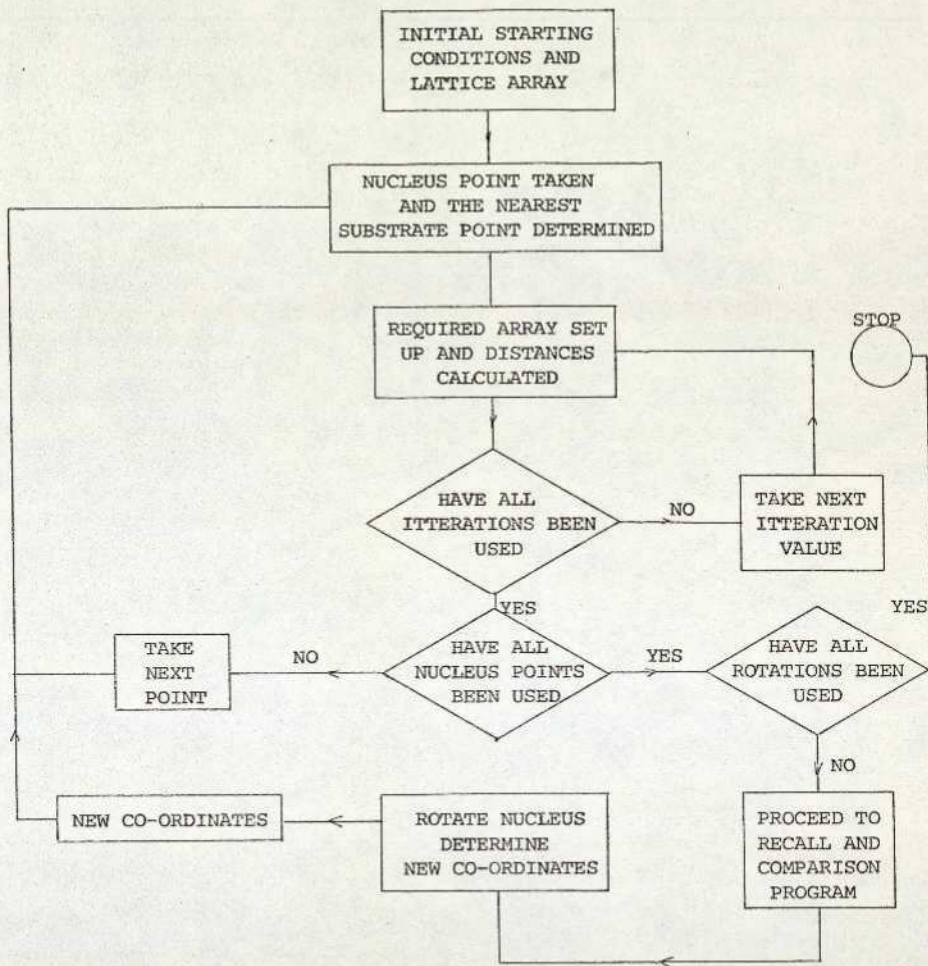
This method required the same arrays being set up for the substrate and deposit nucleus surfaces, but calculates the distances by a different method.

The basis to this approach is that each nucleus point is considered in isolation, the nearest substrate point being determined by a comparison of the lattice co-ordinates. Once the nearest substrate point is located, an array of substrate points are set up around the nucleus point. The distance between each of these and the nucleus point is calculated, summed and finally stored. The nucleus point is then iterated over a restricted area within this array, and for each iteration the total value stored. On completion of the iteration process, a second point was used and the process repeated, until all the nucleus points had been used. The nucleus is then rotated and the new lattice co-ordinates determined, and the total process repeated for all the orientations. The stability values determined by this process were then compared, and the most stable position found.

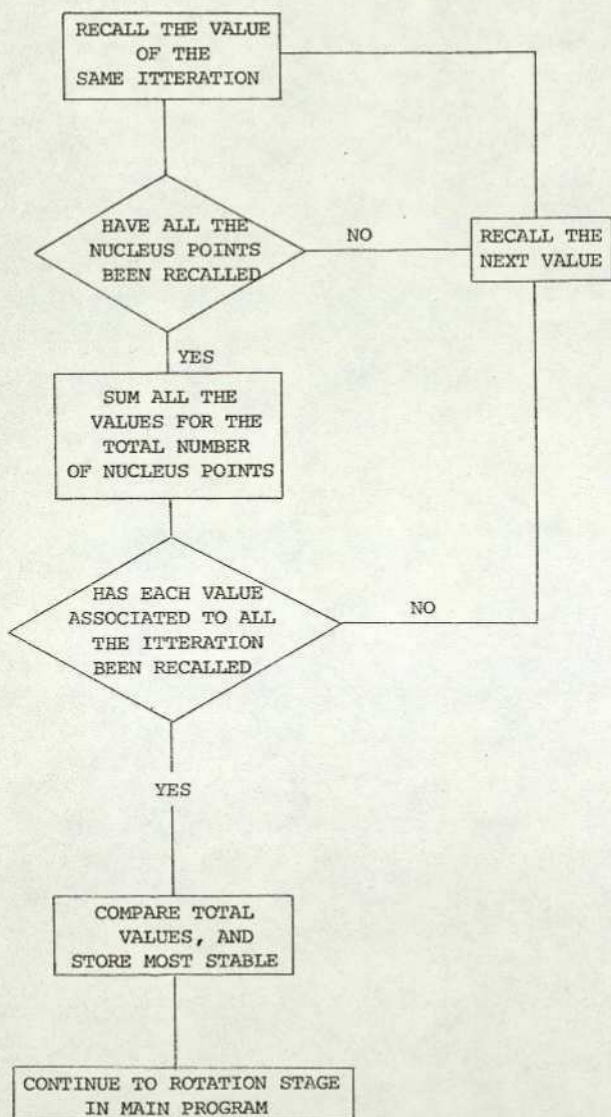
Using this method the number of calculations are considerably reduced, and because of the significant reduction in computer time more variables could be introduced making the process far more flexible.

The following section describes the flow diagram of this program which has been labelled the Logical Program.

LOGICAL FLOW DIAGRAM



RECALL AND COMPARISON PROGRAM



To locate the nearest substrate point to a particular substrate point a simple comparison stage was introduced into the program. This was done by comparing the distance between the substrate and nucleus point, separately along both the x and y axes. The nearest point will be that whose difference is less than half the separation between adjacent substrate points. This process may be summarised by the following:-

if X = substrate x, co-ordinate

A = nucleus x, co-ordinate

a_0 = separation of substrate points in the x- direction

then the distance (D_1)

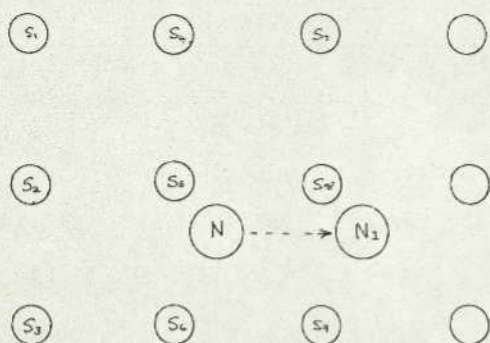
$D_1 = X - A$

IF (MODULUS OF $D_1 < \frac{1}{2}a_0$) STORE AND PROCEED TO 20

IF (MODULUS OF $D_1 > \frac{1}{2}a_0$) MOVE TO NEXT SUBSTRATE POINT

20 Calculate D_2 in the Y direction by the same method.

When the nearest substrate is located, an eight point array of substrate points is constructed around this point. To construct this array the position of the nucleus relative to the substrate point must be known, because there are four possible positions, and consequently four possible arrays. If the array was set up using the nearest substrate point as the centre, this would result, after complete iteration, in moving the nucleus point out of the constructed array. This can be seen more clearly from figure 30.



S_5 = Nearest Substrate Point

N = Nucleus Point

N_1 = Nucleus Point after complete displacement

Figure 30

The four possible arrays, depending on the position of the nearest substrate point relative to the nucleus point is shown in figure 31. The intersection of the two axes is the position of the nearest substrate point in all cases.

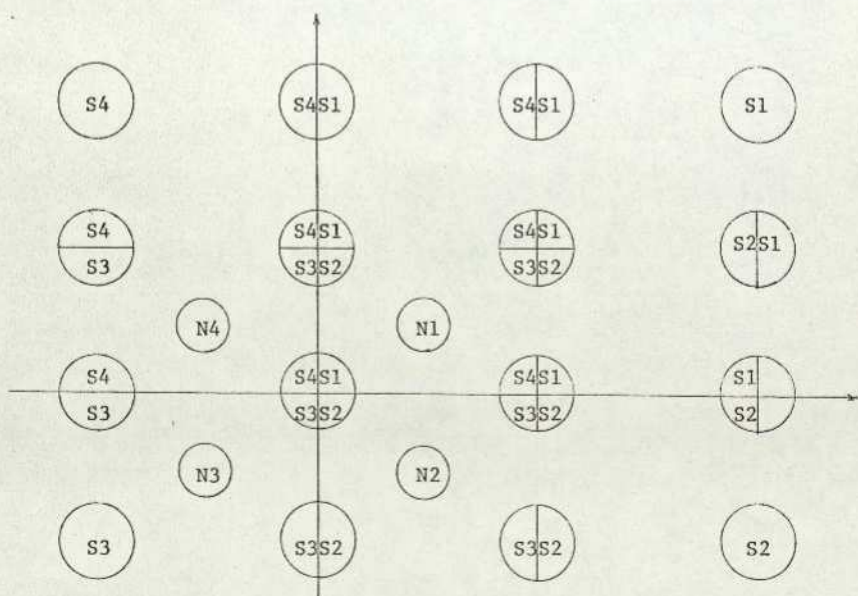
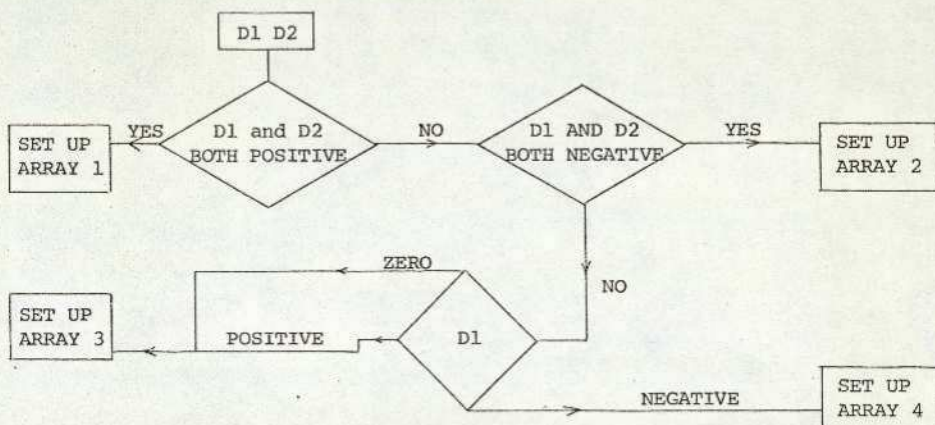


Figure 31

The method of constructing these arrays is to determine the sign of the difference, that is if the substrate point is to the left of the nucleus point, a positive distance will result, and conversly if it is to the right a negative distance will result; similarly in the y- direction. By determining the sign of both distances the unique array may be set up. This is achieved in the program by two logical comparison statements and one arithmetic comparison statement.

If D_1 and D_2 are the distances to the nearest substrate point in both directions then:-



After the required array has been set up, the distance is calculated between the nucleus point and each element of the array. These values are summed and stored in another two dimensional array.

If nucleus point 1 was used with no iteration the value is stored as element (1,1), with the first iteration (1,2) and so on up to (1,T) where T is the total number of iterations. The same process is used for all the nucleus points. Once this stage is completed the values associated with the total nucleus at the same iteration is determined by summing the respective elements 1,1 + 2,1 + 3,1N,1. This sum represents the total stability of the nucleus at position one. This is done for all the positions, and the stabilities compared and the lowest recorded. The new lattice co-ordinates after a rotation is determined and the whole process repeated.

Using this method the predicted orientation of anthraquinone on sodium chloride was determined. See program 2

PROGRAM 2

C INITIAL STARTING CONDITIONS

```

N=4
M=36
HXO=1.989
HYO=1.989
XO=3.978
YO=3.978
ALPHA=3.98
BETA=3.98
DELTA=5.0
SETVAL=18.0
DIMENSION X(36),Y(36),A(4),B(4),A1(4),B1(4),A2(4),B2(4)
DIMENSION SSUM (100,4),XT(9),YT(9)
READ(1,25) (X(1),Y(1),1=1,M)
READ(1,25) (A(J),B(J),J=1,N)
25 FORMAT(2F10.3)
WRITE(2,25) (X(1),Y(1),1=1,M)
WRITE(2,25) (A(J),B(J),J=1,N)
DEG=0.0
24 THETA=DEG*3.14159/180.0
IC=0
H=COS(THETA)
Q=SIN(THETA)
DO3J=1,N
A1(J)=A(J)
B1(J)=B(J)
A2(J)=A(J)*R+B(J)*Q
B2(J)=B(J)*R-A(J)*Q

```

```

      3 CONTINUE
C   TO DETERMINE THE ARRAY PRODUCED
      J=1
19   I=1
      LIMIT=A2(J)+ALPHA-(ALPHA/10.0)
      D1=X(I)-A2(J)
      D3=ABS(D1)
      IF(D3.LE.HXO)GOTO4
      I=I+1
      IF(I.LE.M)GOTO5
      4   I=1
      7   D2=Y(I)-B2(J)
      D4=ABS(D2)
      IF(D4.LE.HYO)GOTO6
      I=I+1
      IF(I.LE.M)GOTO7
      6   IF(D1)11,11,10
10   TX=A2(J)+D1-XO
      GOTO34
11   TX=A2(J)+D1
34   XT(1)=TX
      XT(2)=TX+XO
      XT(3)=TX+XO+XO
      XT(4)=TX
      XT(5)=YX+XO
      XT(6)=TX+XO+XO
      XT(7)=TX
      XT(8)=TX+XO
      XT(9)=TX+XO+XO
      IF(D2)31,31,30
30   TY=B2(J)+D2+YO
      GOTO35
31   TY=B2(J)+D2+YO+YO
35   YT(1)=TY
      YT(2)=TY
      YT(3)=TY
      YT(4)=TY-YO
      YT(5)=TY-YO
      YT(6)=TY-YO
      YT(7)=TY-YO-YO
      YT(8)=TY-YO-YO
      A1(J)=A2(J)
      B1(J)=B2(J)
      WRITE(2,41)(XT(I),YT(I),I=1,9)
41   FORMAT(2F10.3)
      WRITE(2,42)A2(J),B2(J),D1,D2,J
42   FORMAT(4F10.3,I5)
12   DO18J1=1,100
      SSUM(J1,J)=0.0
      DO13I1=1.9
      DSQ=(XT(I1)-A1(J)**2+(YT(I1)-B1(J))**2
      IF(DSQ.LT.SETVAL)GOTO14
      GOTO13
14   S=1.0/SQRT(DSQ)
      SSUM(J1,J)=SSUM(J1,J)+S
13   CONTINUE

```



```

      A1(J)=A1(J)+ALPHA/10.0
      IF (A1(J).GT.LIMIT)GOTO17
      GOTO18
17  A1(J)=A2(J)
      B1(J)=B1(J)*BETA/10.0
18  CONTINUE
      J=J+1
      IF (J.GT.N)GOTO20
      GOTO19
C  PROGRAM TO COMPUTE SUM
20  DO21J1=1,100
      SUM=0.0
      DO22J=1,N
22  SUM=SSUM(J1,J)+SUM
      IF (IC.EQ.0)GOTO23
      IF (SUM.GT.TEST)GOTO21
23  TEST=SUM
      IC=IC+1
21  CONTINUE
      WRITE (2,26) DEG,TEST
26  FORMAT(1H,F7.1,1PE20.4)
      DEG=DEG+DELTA
      IF (DEG.LE.90.0)GOTO24
      STOP
      END

```

Comparison of the Programs

The results obtained with program 2 (Logical Program) show excellent agreement with the orientations predicted from the first program and although the second logical program is more complicated and uses far more storage space, the time required for operation is considerably reduced. The logical program is of the order of four times faster than program one, and because each nucleus point is treated in isolation, it is readily adaptable to handle deposits with more than one dominant species present, and also when a large number of nucleus point need to be considered. It does, however, require a very symmetric substrate to work efficiently, and although it is ideal for the sodium chloride surface, when more complicated surfaces need to be considered the longer program one has been used. This is because the modification to the logical program, increase the operation time, and the relatively less time saved did not outweigh the added complications of programming.

In the following chapter the logical program has been used extensively with the amino acid deposits on sodium chloride and program one has been used when considering mica or quartz substrates.

The Computational predictions on the epitaxial deposits obtained in this study

In this section, the computer programs discussed in the previous chapter are used to predict the orientations of amino acid and anthraquinone deposits on the surface of sodium chloride, mica and quartz substrates. These predicted orientations are examined and discussed with relation to the experimentally observed overgrowths.

The results obtained in this section divide broadly into two categories, and are discussed accordingly. The first of these is the amino acid deposits of which Glycine, β -Alanine, DL Alanine, L-Proline and γ -amino-butyric acid (GABA), were found to grow epitaxially. The second is the orientation of deposits of anthraquinone and glycine on mica and quartz substrates.

5.1 Glycine on sodium chloride

From the molecular arrangement projected along the y axis of glycine, (figure 32) the oxygen atom O_1 , and the nitrogen atom N lie in the plane and would be incorporated in the (010) face, (227, 228). The (010) plane of glycine exhibits the highest reticular density in electro-negative atoms within the glycine structure, and from this observation, it is deduced that this plane will influence the epitaxial orientation.

For the purpose of computer calculations, the oxygen atoms have been assumed negatively biased, and the nitrogen atoms positively biased, this will result in a repulsive energy for the former and an attractive energy for the latter. The most stable orientation of the nucleus is that which corresponds to the greatest attractive energy between the growing crystal nucleus and its substrate.

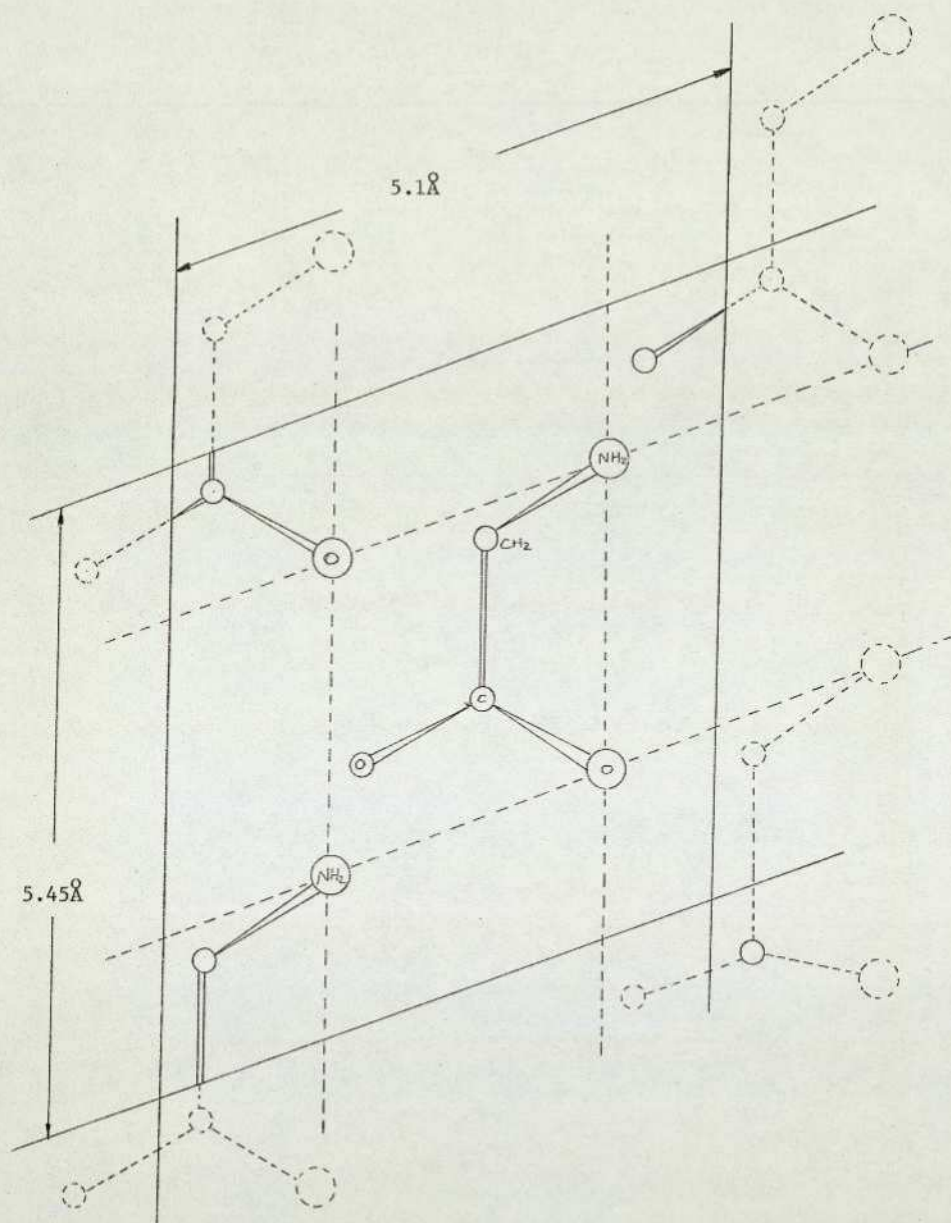


Figure 32
 Crystal Structure of Glycine Projected
 along the (y) axis

Three calculations have been carried out, assuming different relative importance of the two species, the first using equal importance the second the nitrogen atom 10% more important, and finally the oxygen atom 10% more important. The results of these calculations are summarised in table two.

<u>Rotation of the Nucleus in Degrees</u>	<u>Value of Attraction</u>			<u>Orientation</u>
	O=N	N+10%	O+10%	
0.0	23.22	23.93	19.58	[100]//[110]
5.0	20.52	21.26	17.21	
10.0	39.52	40.22	33.87	
15.0	38.80	39.62	33.12	
20.0	20.94	21.63	17.62	
25.0	23.49	24.20	19.82	
30.0	24.40	25.17	20.57	
35.0	20.54	21.31	17.20	
40.0	43.57	44.31	37.38	
45.0	84.29	85.02	73.01	[100]//[100]
50.0	29.14	29.87	24.76	
55.0	57.31	58.02	49.42	
60.0	56.07	56.78	48.33	
65.0	22.34	23.06	18.82	
70.0	79.85	80.57	69.15	[001]//[100]
75.0	40.12	40.85	34.37	
80.0	20.57	21.31	17.25	
85.0	24.89	25.62	21.03	
90.0	23.12	23.85	19.50	

TABLE 2

Predicted Orientations of the (010) face of Glycine

From table 2 it can be seen that the most stable orientation predicted corresponds to $[100]$ Glycine $//$ $[100]$ sodium chloride, which is the observed orientation of epitaxial deposits. (010) Glycine $[100]//[100]$ NaCl(001)

In addition to this orientation, the $[001]$ direction of glycine is observed, the reason why this is not identical to the $[100]$ direction is because these are at an angle of 69° to each other and not 70° which is used in the computation.

5.2 β -Alanine on sodium chloride

β -Alanine forms orthorhombic crystals with unit cell dimensions of $a = 9.865$, $b = 13.81$, $c = 6.07$, containing eight molecules / unit cell (272). The crystals grown naturally from aqueous solution grow as platlets parallel to the (100) face and show a cleavage parallel to the (010) plane. The existence of the cleavage plane can be seen from the molecular arrangement show on figure 33.

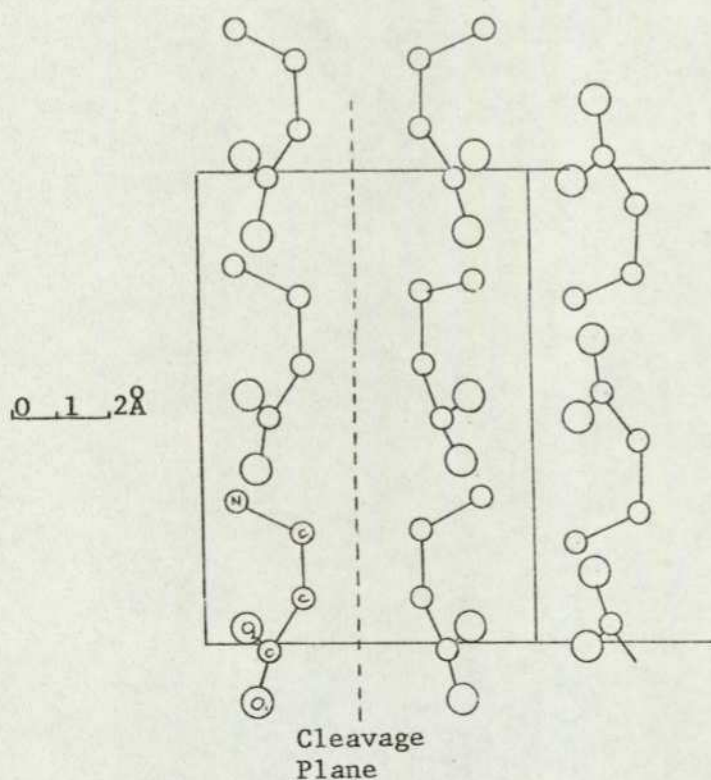


Figure 33
Structure projected on (001) face

The orientations of the (100) face have been determined using an array of oxygen atoms, which are the only species on this face likely to influence epitaxy, and the calculated stabilities are summarised in table 3.

<u>Rotation in Degrees</u>	<u>Repulsion Energy</u>	<u>Orientation</u>
0.0	12.91	[001]//[110]
5.0	12.60	
10.0	12.84	
15.0	12.59	
20.0	12.94	
25.0	11.78	
30.0	12.85	
35.0	12.86	
40.0	11.62	
45.0	11.31	
50.0	11.84	
55.0	12.75	
60.0	13.46	
65.0	12.49	
70.0	12.72	[001]//[100]
75.0	12.34	
80.0	12.50	
85.0	12.64	
90.0	12.92	

TABLE 3

Predicted Orientations of β -Alanine (100) face

The most striking feature of the calculated repulsion energies is the close similarity in their values, the most stable position predicted corresponds to the orientation $[001]//[100]$, but the rotations of 5° and 20° to this orientation are also likely to occur. The presence of these secondary orientations is consistent with the several orientations observed experimentally (see section 3.13).

The presence of both oxygen and nitrogen species in the (010) plane is complicated by the fact that these species are not exactly co-planar, (the nitrogen atom being $0.20\text{\AA}$ out of the plane). Because of this, three calculations, using the oxygen array, the nitrogen array, and the oxygen-nitrogen array (taking account of the divergence of the nitrogen atoms) have been performed and the results are summarised in table four.

<u>Rotation in Degrees</u>	<u>Attractive Energies</u>		
	<u>'O'</u>	<u>'N'</u>	<u>'O AND N'</u>
0.0	-12.79	37.86	11.65
5.0	-12.96	56.91	22.87
10.0	-12.23	35.27	35.90
15.0	-12.34	347.6	11.74
20.0	-12.12	41.66	50.10
25.0	-12.42	35.59	12.56
30.0	-12.89	30.59	32.17
35.0	-12.33	41.90	21.30
40.0	-11.69	77.53	20.57
45.0	-10.93	60.71	45.37
50.0	-11.97	59.29	28.74
55.0	-12.12	35.12	14.19
60.0	-12.59	31.56	22.08
65.0	-12.47	42.41	18.08
70.0	-12.05	36.45	33.20
75.0	-12.81	305.82	15.16
80.0	-12.77	30.28	54.01
85.0	-12.56	68.75	29.22
90.0	-12.78	38.12	11.72

TABLE 4

From these calculations, only the orientation predicted from the oxygen atom dominated face corresponds to the parallel orientation with the $[100]$ direction of the sodium chloride substrate. Rotations of 15° and 20° , and 45° are predicted from the nitrogen, and nitrogen/oxygen arrays respectively.

A similar situation is encountered with the (001) face, which although dominated by the presence of the nitrogen atoms, is complicated by the non-regular array present. (see figure 34)

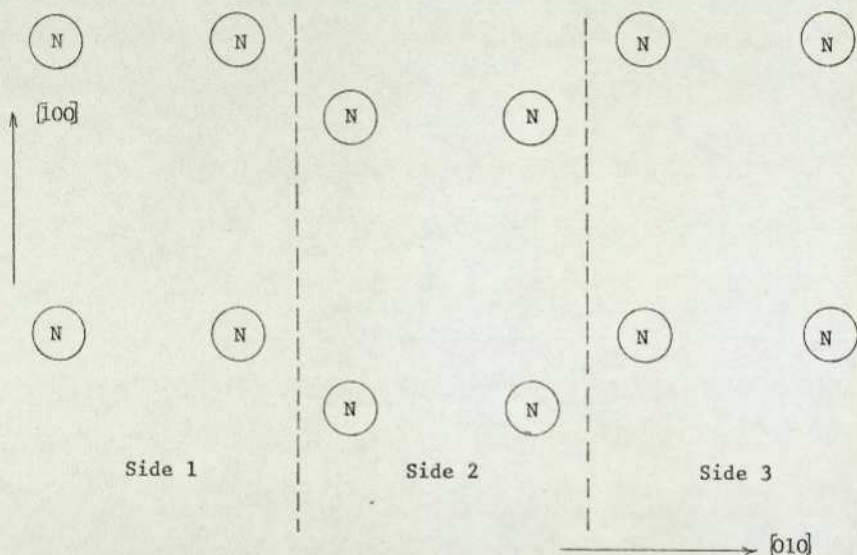


Figure 34

Projection of Nitrogen Atoms on the (001) face

The atoms present on side 2 are above the surface of the paper (001) and those on side 1 are below, which requires results in only $\frac{1}{2}$ a unit cell being used in the $[010]$ direction for each unit cell in the $[100]$ direction.

Calculation using just those atoms present on one side (1) together with the array using side 1 then missing side 2, to side 3 were performed and the results are summarised in table five.

<u>Rotation in Degrees</u>	<u>Attractive Energy</u>		<u>Orientation</u>
	<u>Side 1 + 3</u>	<u>Side 1 only</u>	
0.0	48.39	34.81	[100]//[110]
5.0	32.59	45.95	
10.0	52.42	50.78	
15.0	36.18	52.08	
20.0	41.79	34.20	[100]//[100]
25.0	35.15	35.00	
30.0	58.56	91.93	
35.0	34.33	32.89	
40.0	44.57	55.39	
45.0	36.40	96.06	
50.0	36.63	40.89	
55.0	37.50	68.84	
60.0	71.30	67.63	
65.0	41.60	33.86	
70.0	36.27	91.43	[010]//[110]
75.0	36.97	51.79	
80.0	42.59	32.51	
85.0	38.44	36.66	
90.0	47.93	34.72	

TABLE 5

From these calculations the parallel orientation is only predicted using a small nucleus, and a larger nucleus cannot easily be handled using this program due to the fact that large gaps must be left within the array used for computation.

The existence of the cleavage plane, parallel to the (010) face would suggest that this face would be incorporated in an epitaxial deposit, but this likelihood may be reduced by the dominant repulsive energy of the oxygen atoms with the substrate. No clear orientation was predicted using the (100) face although the parallel orientation would seem likely from the results, and the orientations of the (001) face was complicated by the fact that only a small nucleus could be used in the computer calculations.

Although some estimation of the orientation of particular faces was possible using this model, no unambiguous assignment could be made. This would be consistent with the many orientations experimentally observed, but this would require several contact faces being incorporated in the deposit overgrowth, and further experimental investigation would be required to confirm this possibility.

5.3 DL Alanine on sodium chloride

The unit cell of DL Alanine is orthorhombic, with dimensions of $a_0 = 12.04$, $b_0 = 6.04$ and $c_0 = 5.81$ (232, 233). Because the planes are inclined at 90° to each other, there is no easy way of determining the contact plane involved in epitaxy. As a result of this the three natural planes have been considered individually, and on all three faces the oxygen atoms present are the dominant species used in computer calculations.

The molecular arrangement on each of the faces can be seen from figure 35.

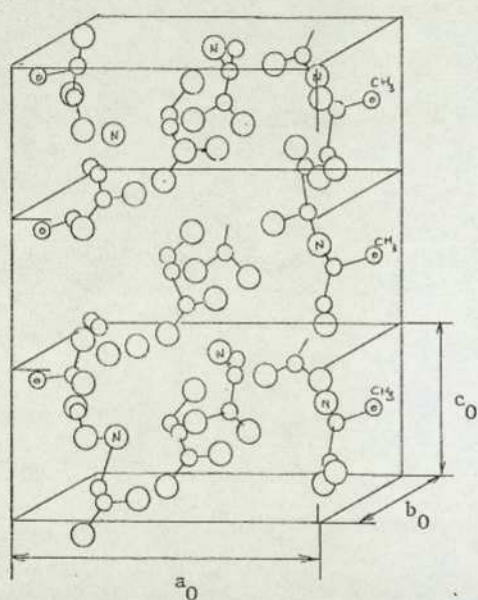


Figure 35

An oblique projection of the
molecular arrangement in D1-Alanine

The predicted orientations of the three faces of DL Alanine are summarised in table 6.

<u>Rotation in Degrees</u>	<u>Repulsion Energy</u>			<u>Orientation</u>
	<u>(100) face</u>	<u>(010) face</u>	<u>(001) face</u>	
0.0	13.58	13.71	13.66	[100]//[110]
5.0	13.45	13.52	13.40	
10.0	13.02	13.33	12.85	
15.0	11.31	11.33	12.17	
20.0	12.28	12.30	10.12	
25.0	12.55	12.55	12.66	
30.0	13.17	13.10	12.82	
35.0	12.77	12.97	12.86	
40.0	12.21	12.14	12.63	
45.0	11.00	11.05	12.04	[100]//[100]
50.0	12.02	12.15	12.39	
55.0	12.37	12.39	12.55	
60.0	12.76	12.86	12.50	
65.0	12.69	12.70	12.68	
70.0	12.40	12.41	10.12	
75.0	11.82	11.92	12.06	
80.0	12.97	13.05	12.85	
85.0	12.51	12.53	13.40	
90.0	13.58	13.61	13.66	[100]//[-110]

TABLE 6
Predicted orientations of DL Alanine

From table 6, the most stable orientation predicted for both the (100) and (010) faces of DL Alanine correspond to a parallel orientation with sodium chloride, which is the experimentally observed orientation. The orientation predicted from the (001) face is aligned 20° to this which does not correspond to a natural sodium chloride plane, and therefore it is concluded that this plane is not involved in epitaxy.

Because of the very close repulsive energies observed with the (100) and (010) planes, it is not possible to decide which of these is involved in epitaxy, as they both give the observed orientation. However, crystals of DL Alanine normally grow with an elongated C axis, and as no obvious long axis is observed with the epitaxial deposit, the (010) plane is most likely the plane involved in epitaxy.

5.4 L-Proline on sodium chloride

L-Proline forms orthorhombic crystals with unit cell dimensions $a_0 = 11.55$, $b_0 = 9.02$ and $c_0 = 5.20$ and containing four molecules (236).

From the molecular arrangement of L-Proline, (see also figure 36), the dominant species on both the (100) face and (001) face is an array of oxygen atoms. For the (100) face a rectangular array of atoms was used to represent the surface, but this could not be done for the (001) face, where the array shown in figure 36(1) was used.

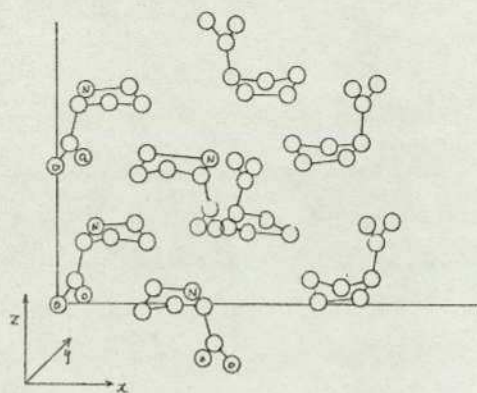


Figure 36

Molecular arrangements of L-Proline on the (100) face

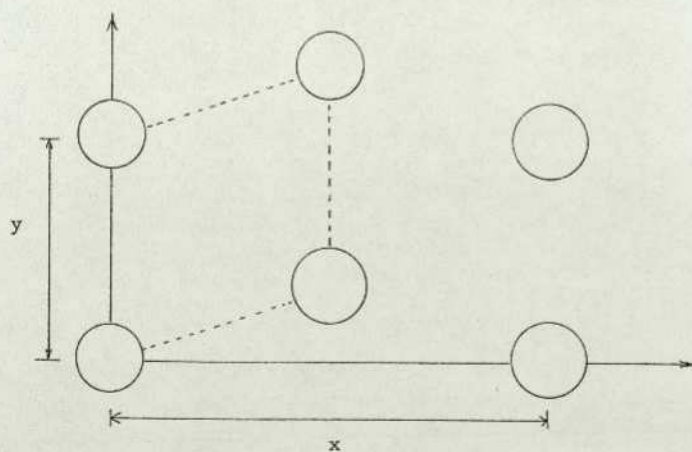


Figure 36(1)

Arrangement on (001) face

The predicted orientation of both these faces is summarised in table seven.

<u>Rotation in Degrees</u>	<u>Repulsion Energy</u>		<u>Orientation</u>
	<u>(100) Face</u>	<u>(001) Face</u>	
0.0	13.23	12.90	[010]//[110]
5.0	13.00	12.45	
10.0	12.89	13.37	
15.0	12.88	12.68	
20.0	12.31	13.43	
25.0	12.53	12.34	
30.0	12.57	12.13	
35.0	12.94	12.52	
40.0	12.03	12.45	
45.0	11.06	11.28	[010]//[100]
50.0	12.30	12.85	
55.0	12.67	12.82	
60.0	12.91	12.08	[001]//[100]
65.0	12.74	11.31	
70.0	12.71	12.84	
75.0	13.16	12.79	
80.0	13.07	12.01	
85.0	13.57	12.47	[010]//[110]
90.0	13.23	12.90	

TABLE 7
Predicted Orientation of L-Proline

The most stable orientation predicted for both the (100) and the (001) face corresponds to the experimentally observed orientation which is the deposit parallel to the [100] direction of the sodium chloride.

The reason that the 65° rotation of the (001) face corresponds to the [001] direction is the result of the non-rectangular array used to represent this face. This is shown in figure 36(1) where the two directions used are 70° to each other therefore the rotation expected would be $(90-70^\circ) + 45^\circ = 65^\circ$ instead of $(90+45^\circ)$ expected for a rectangular array.

In the (010) plane of L-Proline both oxygen and nitrogen species exist, but unlike glycine where both the species were exactly co-planer, the oxygen atoms stick out slightly ($0.004\text{\AA}$) from this plane, and this departure from planarity has been taken into account in subsequent calculations.

The predicted orientations of this face are summarised in table 8.

<u>Rotation in Degrees</u>	<u>Attractive Energy</u>	<u>Orientation</u>
0.0	9.98	
5.0	69.12	[001]//[110]
10.0	8.67	
15.0	22.15	
20.0	13.88	
25.0	16.74	
30.0	10.39	
35.0	14.00	
40.0	15.42	
45.0	-1.04	[100]//[100]
50.0	13.25	
55.0	10.85	
60.0	17.32	
70.0	10.86	
80.0	13.11	
85.0	34.53	
90.0	10.05	
95.0	67.62	[001]//[-110]

TABLE 8

The most stable orientation predicted for the (010) face corresponds to the deposit oriented to the $[110]$ direction of sodium chloride, this orientation is not experimentally observed. This result is rather unexpected as the attractive energy of the nitrogen atoms on the chlorine dominated substrate would have been expected to influence epitaxy as with glycine.

As a result of these calculations, the oxygen dominated (100) and (001) planes would be those incorporated in an epitaxial deposit, because the orientation predicted from these corresponds to that which is experimentally observed. In the crystal state molecular double layers are formed parallel to the (100) plane the separate layers being held together by hydrogen bonds, and because of this the (100) face is thought to be the most favourable plane to be involved in epitaxy.

5.5 γ -amino-butyric acid (GABA) on sodium chloride

GABA crystals grow with a monoclinic unit cell, containing four molecules, with the unit cell dimensions of $a = 8.228$, $b = 10.036$, $c = 7.210$ and the angle $\beta = 110.63^\circ$ (298).

With many well defined crystals, in an epitaxial deposit, the faces were of sufficient definition to enable the interfacial angles to be measured, these measurements corresponded to the (010) plane being incorporated as the contact plane with the substrate. The molecular arrangement on this plane is shown in figure 37.

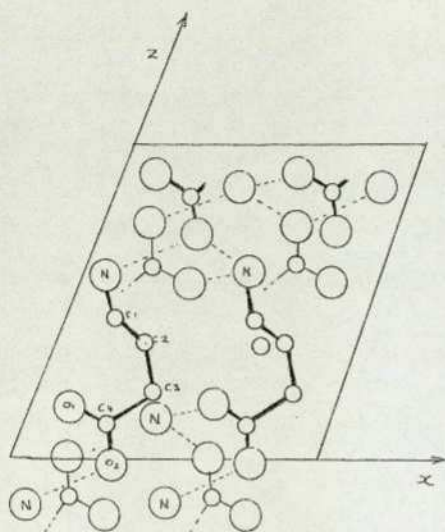


Figure 37

Molecular arrangement of γ -amino
butyric acid projected on the (010) face

Because on several occasions a unique interfacial angle was not obtained calculations using all three natural faces have been carried out, and the dominant species on all faces was found to be nitrogen atoms. The results of these calculations are summarised in table 9.

<u>Rotation in Degrees</u>	<u>Attractive Energy</u>		
	<u>(100) face</u>	<u>(010) face</u>	<u>(001) face</u>
0.0	42.43	60.48	34.81
5.0	56.11	46.00	45.95
10.0	39.15	35.50	50.78
15.0	45.07	41.96	52.08
20.0	86.37	59.09	34.20
25.0	35.30	33.72	35.00
30.0	47.35	51.08	90.93
35.0	51.16	36.19	32.89
40.0	44.66	45.03	55.39
45.0	39.66	73.80	96.09
50.0	52.27	32.01	40.89
55.0	62.56	60.34	68.84
60.0	57.23	35.48	67.63
65.0	41.54	42.97	33.86
70.0	67.49	60.49	90.43
75.0	56.70	42.01	51.79
80.0	50.90	39.95	32.51
85.0	44.92	39.73	36.63
90.0	42.11	60.28	34.72

TABLE 9

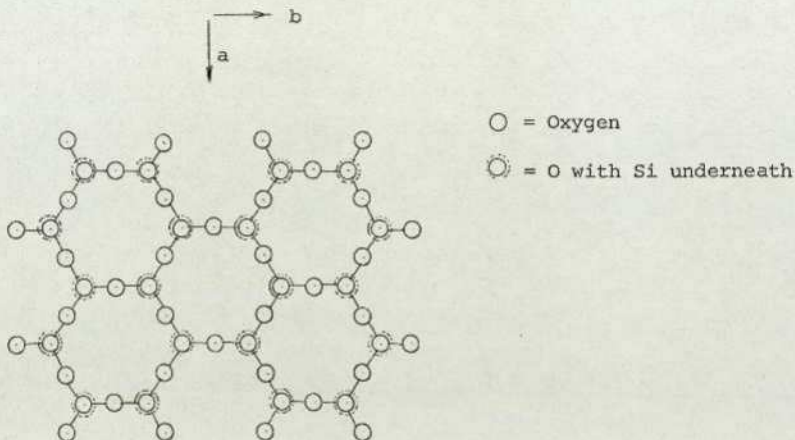
Predicted Orientations of γ -Amino-butyric acid

The predicted orientation of the (010) face, is consistent with the orientation experimentally observed, which corresponds to the orientation (010)GABA[100]//[100]NaCl(001). In addition to the main orientation, orientations of 10° , 25° and 45° to this might also be expected, and this would explain the misalignment experimentally observed on occasions.

The orientation of the (001) face predicted from the computation also corresponds to the [100]//[100] orientation, and demonstrates that some of the epitaxial deposit could incorporate the (001) face. However, when the deposit is carefully prepared, the majority of crystals are of sufficient definition to enable interfacial measurements to confirm the presence of the (010) contact face.

5.6 Anthraquinone on Mica

The first structural investigation of muscovite mica $[KAl_2(AlSi_3O_{10})(OH)_2]$ was made by Jackson et al. (273, 274), the structure and lattice parameters have since been refined by Radoslovich (275). Muscovite mica is one of the many layer silicates growing in sheets parallel to the (001) plane.



The dimensions of the monoclinic unit cell are $a = 5.19$, $b = 9.00$, $c = 20.10\text{\AA}$ and $\beta = 95.18^\circ$. Each layer of the (001) cleavage face is held together by potassium ions co-ordinated to the oxygen atoms of the silica oxygen rings. For reasons discussed earlier (3.25) cleavage can result in either a positive or negative site. For the purpose of computer calculations an array of substrate points as shown in figure 38 have been used.

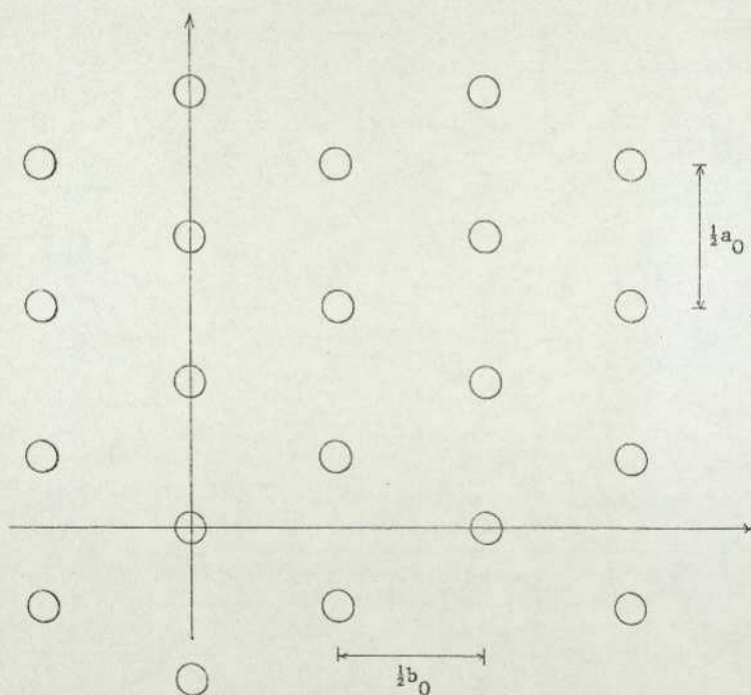


Figure 38

The predicted stabilities of an anthraquinone nucleus have been determined on both a positive region (potassium ions present) and a negative region. These are summarised in table 10.

<u>Rotation in Degrees</u>	<u>Attractive Energy</u>		<u>Orientation</u>
	<u>-ve environment</u>	<u>+ve environment</u>	
0.0	-42.31	63.94	[100]//[100]
5.0	-42.61	111.15	
10.0	-42.43	67.98	
15.0	-42.72	80.65	
20.0	-41.83	91.15	
25.0	-41.58	61.83	
30.0	-41.82	105.30	
35.0	-42.00	66.59	
40.0	-41.95	87.86	
45.0	-41.51	92.21	
50.0	-42.64	106.61	
55.0	-41.61	139.68	
60.0	-41.28	158.74	[100]//[110]
65.0	-42.77	115.68	
70.0	-43.35	64.26	
75.0	-42.46	81.72	
80.0	-41.53	92.83	
85.0	-41.33	83.21	

TABLE 10

Predicted Orientations of Anthraquinone on Mica

In a negative environment, there is a very small range of energies, covering all the possible orientations, and only a small preference for the 60° rotation.

This could be interpreted as areas of very low electrical activity as all the orientations correspond to only very small differences in an overall repulsive term. The situation with positive environment is quite different, where a large spread of energies are observed. A comparison of these show a strong preference for the rotation of 60° which is experimentally observed corresponding to the orientation of $[100]//[110]$.

These programs were extended to include further rotations up to 160° , the results of which are shown in table 11.

<u>Rotation in Degrees</u>	<u>-ve environment</u>	<u>+ve environment</u>	<u>Orientation</u>
60.0	-41.28	158.74	$[100]//[110]$
70.0	-43.35	64.26	
80.0	-41.53	92.32	
90.0	-41.13	61.76	$[100]//[010]$
100.0	-41.58	80.75	
110.0	-42.01	59.45	
120.0	-41.36	128.77	$[100]//[-110]$
130.0	-41.83	92.26	
140.0	-41.43	92.21	
150.0	-42.21	120.12	
160.0	-42.20	79.79	

TABLE 11

Extended Orientations of Anthraquinone on Mica

These results show that the most favourable orientation on a negative environment corresponds to $[100]//[010]$, this would correspond to the orientation of a small proportion of misaligned deposit relative to the $[110]$ deposit sometimes observed. However, in a positive environment no preference is observed for this orientation, and only the expected rotation of 120° is further predicted. The orientation of an anthraquinone deposit on a mica substrate is shown in figure 39.

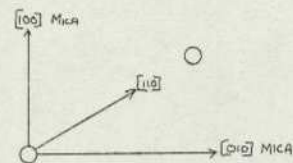
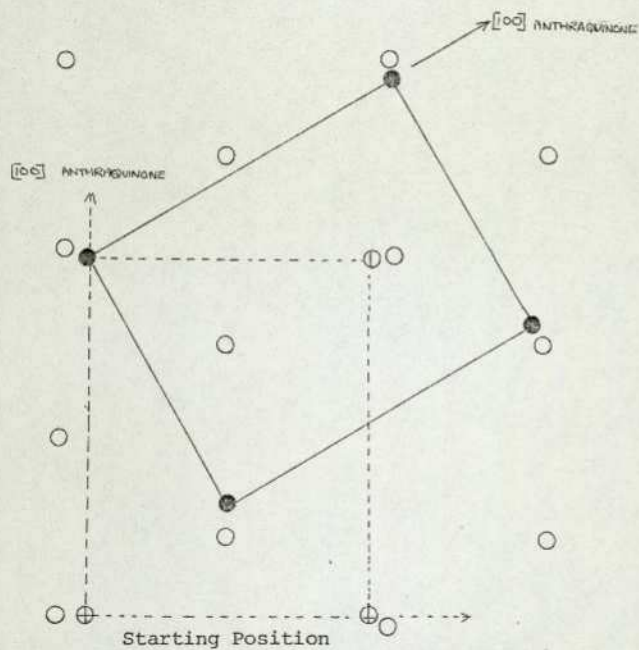


Figure 39

Orientation of Anthraquinone on a Mica Surface

From these calculations it is clear, that in areas where good orientation is observed, with a high density of deposit corresponds to areas of the substrate surface which is predominantly positively charged. Areas which contain a low density of deposit and some misalignment correspond to negatively charged regions of the substrate. These predictions are consistent with the interpretations of an unhomogenous covering of overgrowth propounded by Distler (261).

In addition to the two main positive and negative environments so far considered, there exists other possible charge distributions which could influence the deposit. The most important of these, are the various statistically predicted alternative charged regions. Three main types of alternating charge patterns immediately around the deposit nucleus have been used, and these are shown in figure 40.

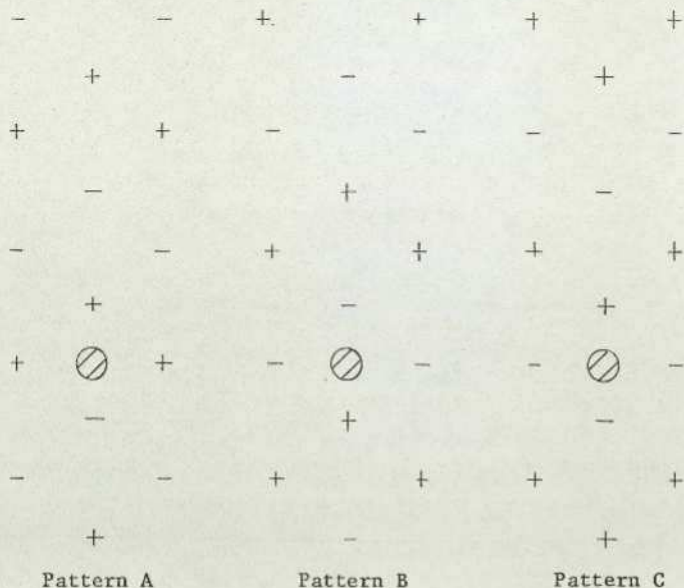


Figure 40

The predicted orientations of a nucleus within these patterns are summarised in table 12.

<u>Rotation in Degrees</u>	<u>Attractive Energy</u>			<u>Orientation</u>
	<u>Pattern A</u>	<u>Pattern B</u>	<u>Pattern C</u>	
0.0	29.56	27.19	27.82	[100]//[100]
10.0	15.10	29.79	30.64	
20.0	13.26	49.78	50.84	
30.0	66.53	64.77	45.57	
40.0	44.01	39.67	42.58	
50.0	70.00	59.93	70.40	
60.0	109.69	24.65	100.87	[100]//[110]
70.0	24.30	12.83	21.15	
80.0	54.62	54.59	19.96	
90.0	25.56	23.82	19.42	[100]//[010]
100.0	22.76	40.56	40.71	
110.0	17.70	19.42	20.52	
120.0	73.00	83.82	85.56	[100]//[110]
130.0	53.92	53.60	52.23	

TABLE 12

The most interesting feature of these results is the relative importance of the two rotations of 60° and 120° . In the case of patterns A and C the 60° is the most favourable orientation with the 120° rotation also likely, but with the distribution pattern B, only the 120° rotation is important and the second is the rotation of 30° which corresponds to the orientation [100]//[210].

Only a limited amount of information can be extracted from these calculations using the various charge patterns, however, the importance lies in the fact that the various proportions of particular orientations observed

on a mica surface, may be related to particular charge distribution patterns existing in micro regions of the substrate surface.

5.7 Glycine on Mica

The crystal structure and molecular arrangement of glycine has been previously discussed (section 5.1) and from this it was concluded that the (010) face of glycine would be incorporated in an epitaxial deposit. The predicted orientations of this face are presented in table 13. This includes the stabilities obtained with a deposit using oxygen and nitrogen of equal importance, and a deposit with the oxygen atom more important. All these stabilities were calculated using a positive mica substrate.

<u>Rotation in Degrees</u>	<u>Attractive Energy</u>		<u>Orientation</u>
	<u>'N' = 'O'</u>	<u>'O' more important</u>	
0.0	7.86	9.03	[001]//[010]
5.0	-1.04	1.84	
10.0	9.56	10.90	
15.0	14.49	14.66	
20.0	-1.32	1.63	
25.0	6.79	8.26	
30.0	7.40	8.69	[001]//[110]
35.0	6.50	7.94	
40.0	34.79	30.56	
45.0	-0.37	2.35	
50.0	17.97	17.02	
55.0	3.67	5.59	
60.0	8.93	9.85	[100]//[110]
65.0	22.28	21.14	
70.0	0.58	3.24	
75.0	10.13	1.13	

TABLE 13

Predicted Orientations of Glycine (010) face

As many of the deposit types obtained with anthraquinone deposits were not observed with glycine deposits, calculations were not carried out using the various mica charge patterns. The predicted orientations were, however, determined for glycine deposits on a negatively charged mica surface. This is shown in table 14 together with the predictions obtained with a positive substrate, in both calculations a greater importance has been placed on the nitrogen atoms on the glycine surface.

<u>Rotation in Degrees</u>	<u>Attractive Energy</u>		<u>Orientation</u>
	<u>Negative Surface</u>	<u>Positive Surface</u>	
0.0	40.13	2.76	[010]//[010]
5.0	33.58	-3.42	
10.0	18.12	3.44	
15.0	9.72	7.68	
20.0	29.14	-3.63	
25.0	29.32	1.92	
30.0	32.05	2.41	[001]//[110]
35.0	16.21	1.81	
40.0	15.13	21.62	
45.0	22.18	-2.90	
50.0	18.37	9.90	
55.0	15.52	-0.90	
60.0	15.48	3.5	[100]//[110]
65.0	13.68	13.12	
70.0	1.89	-2.37	
75.0	2.81	3.81	

TABLE 14

Predicted Orientations of Glycine (010)

The predicted orientations agree well with the experimentally observed orientation, which corresponds to the (010)Glycine[100]//[110]mica(001). This orientation of glycine on mica is shown in figure 41.

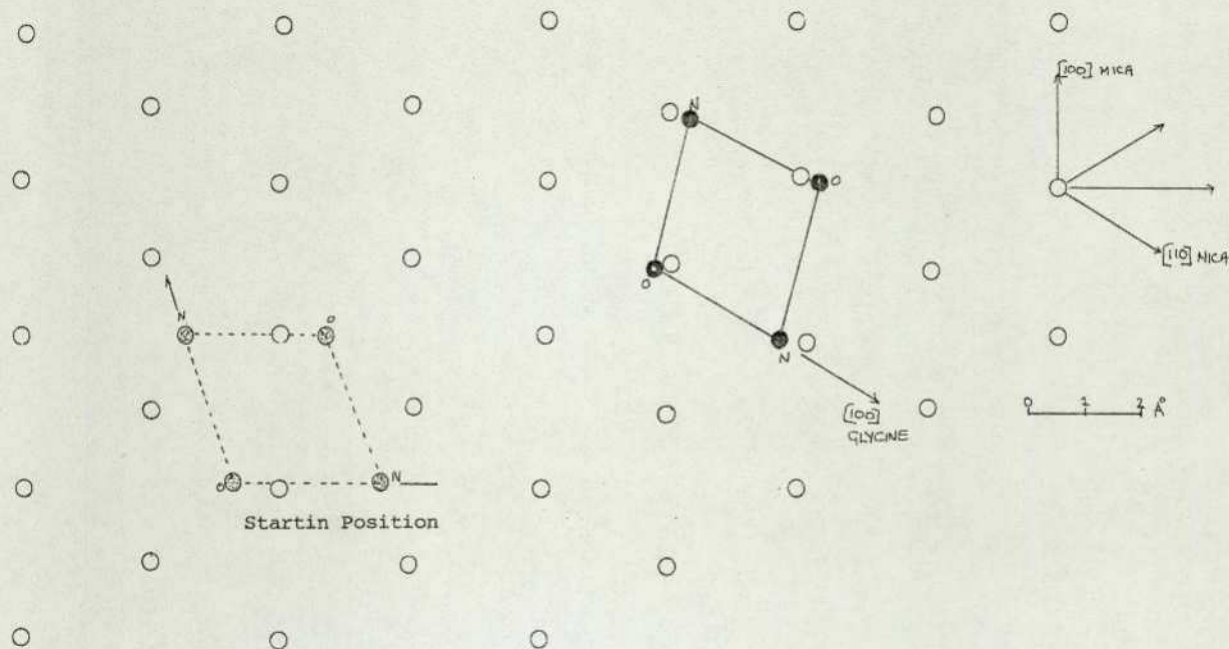


Figure 41
Orientation of Glycine on a Mica Surface

5.8 Anthraquinone and Glycine on Quartz

The crystal structure of both deposits, and the substrate have been discussed previously (chapter 3), and it was concluded that quartz was not a good substrate for any fundamental epitaxial study. For the purpose of computation, an ideal surface of quartz has been used, using negatively biased centres at the positions of the unsaturated oxygen atoms (see section 3.2). The orientational predictions, obtained from the computational model are summarised in tables 15 and 16 for anthraquinone and glycine deposits respectively.

<u>Rotation in Degrees</u>	<u>Repulsive Energy</u>	<u>Orientation</u>
0.0	9.14	[100]//[0001]
5.0	10.07	
10.0	10.07	
15.0	10.43	
20.0	10.68	
25.0	10.81	
30.0	10.35	
35.0	10.64	
40.0	10.26	
45.0	9.91	$\approx$ [100]//[0101]
50.0	10.26	
55.0	10.38	
60.0	9.93	
65.0	10.72	
70.0	10.23	
75.0	10.15	
80.0	10.28	
85.0	9.93	
90.0	9.19	[100]//[000-1]

TABLE 15
Anthraquinone on Quartz

<u>Rotation in Degrees</u>	<u>Attractive Energy</u>	<u>Orientation</u>
0.0	7.56	[100]//[0001]
5.0	25.99	
10.0	30.49	
15.0	7.51	
20.0	8.70	
25.0	18.39	
30.0	10.82	
35.0	24.55	
40.0	30.58	
45.0	9.74	$\approx$ [100]//[0101]
50.0	29.45	
55.0	14.81	
60.0	15.21	
65.0	73.28	[001]//[0001]
70.0	10.47	
75.0	17.71	
80.0	11.77	
85.0	5.62	
90.0	15.16	[100]//[000 $\bar{1}$]
100.0	10.47	
110.0	20.34	
120.0	8.37	

TABLE 16

Glycine on Quartz

From table 15 the predicted orientation corresponds to that which is experimentally observed, but in addition to this orientation, as a result of the very small range of repulsive energies, a number of other orientations would be likely, which are not observed.

A similar situation exists with the predicted orientations of glycine (table 16). These orientations do not correspond to those which are experimentally observed. This result is not totally unexpected, as it is difficult to visualize how electrostatic charges could remain on the contaminated quartz surface to influence the orientation of glycine or anthraquinone.

The orientation influence of a quartz surface is not understood but clearly any possible ideal charge distribution on its surface does not solely influence epitaxial growth. As suggested earlier the surface of quartz is rather too complex for it to be used in a simple epitaxial model, and further information concerning the nature of the surface would be required before it could be used in any epitaxial model.

Conclusions

The computational model used throughout these calculations, has worked well, and the majority of its predicted orientations are those which are experimentally observed. As a result of the extensions and modifications to the basic point charge approach, the model has been successfully used with polar surfaces containing more than one dominant species. It is thought that this approach has been extended to its limit, and although limited in its predictive capabilities the model can adequately describe the many observed orientations on polar surfaces. The major drawback of this approach is that much of the data is empirically determined (nucleus size etc.). The next extension envisaged would be to use a more comprehensive approach which, as well as determining the coulombic interactions would also include provision for when the electrostatic interaction is negligible, the orientation corresponding to the position of least misfit could be determined.

Even with this extension, however, this approach can only determine the orientation of a single crystal. Most evidence (see chapter one) suggests that an epitaxial relationship is decided at the nucleation stage, and the most important fact is whether the deposit grows as a single crystal on the particular substrate. This approach can explain why a crystal assumes a particular orientation, but is very limited in predicting which particular contact plane would be incorporated in an epitaxial deposit.

With this limitation, this model, including the extension to determine the position of least lattice misfit, would be a very useful approach, to gain an understanding of particular epitaxial relationships.

THE CONCEPT OF LONG RANGE FORCES

6.1 Introduction

The inability of current theories of epitaxy to explain all the observed orientational phenomena of different systems is not surprising, because of the enormous structural differences and surface properties of substrate deposit pairs. A hypothesis suggested by a worker in the field, using totally new concepts, and capable of explaining most of the experimental observations is always susceptible to scepticism. This is the current situation in the study of epitaxy. Totally new mechanisms to account for orientations have been suggested by G.I. Distler and his school. Their ideas are now over a decade old and still virilient opposition to this concept of long range forces is present (249). However, Distler has not been deviated by this opposition and continues to produce more startling observations in the epitaxial and crystal growth field.

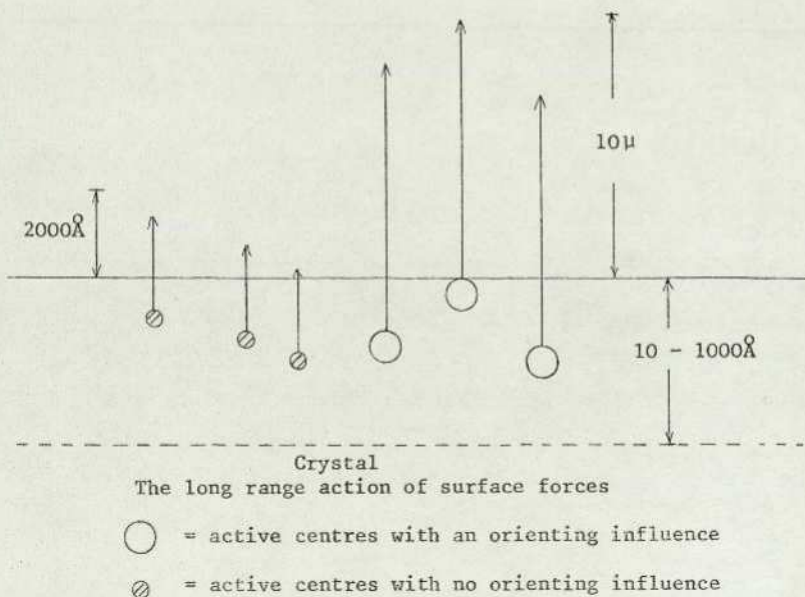
In the following sections, Distler's work will be reviewed together with the work of other experimenters in the field who have been unable to reproduce his results, or who disagree with his interpretations. Because of the controversey surrounding Distler's work, and its significance to crystal growth, a detailed study of his work has been made in an attempt to understand his interpretations and the reasons why other workers have found it so difficult to reproduce his results.

6.2 The Concept of long range forces

In 1958 Bassett (71) and Pashley et al (176) introduced a new method of surface decoration, as a means of studying surface defects. This technique consisted of the vacuum deposition of gold on the cleavage surface of alkali halide crystals, in such quantity to produce a continuous film of approximately $5\text{\AA}^0$ thick. It was found that under certain conditions gold

grew in the form of particles decorating the surface. Such decoration revealed elementary growth steps, slip lines, dislocations and defects of atomic dimensions, which were previously inaccessible to conventional methods of electron microscopy. Distler et al (177) extended this technique by the decoration of mica using the chemical precipitation of lead sulphide. By this method they discovered the phenomenon of secondary decoration, in which decoration did not occur directly on the mica surface but on a previously precipitated polycrystalline lead sulphide layer. In a series of publications (178 - 182) Distler and his school studied the decoration phenomena on many surfaces, by various deposition techniques. By deposition from a colloidal solution they studied directly the electrical micro-relief of various surfaces (183). The proposed mechanism for the secondary decoration process was the initial active sites present on the surface were blocked by primary decoration, and at higher supersaturations, after the surface was uniformly covered, deposition took place on the original active sites. The activity of these sites being accurately reproduced through the initial layer (184). Distler and Zuyagin (185) extended this concept to normal crystal growth, and suggested that active sites on the growing crystal would continue to influence crystal growth after covering and thereby not requiring a dislocation mechanism for crystal growth.

To discover the range of the proposed active centres, decoration reactions were carried out via intermediate amorphous plastic layers deposited on the surface of silicon, quartz, mica, sodalite and a number of other crystals (186 - 189). Evidence was found to suggest two quite distinct forces, the active centres discussed earlier and a second type of active centre which possessed an orientation influence (Epitaxy) see figure 42.



The origin of the active centres were thought to be defect aggregates, mainly vacancies and impurity atoms. The long range effect of these centres being determined by a complex combination of electrostatic and molecular forces.

A number of experiments were conducted to check the active centre hypothesis, these included; on semiconductor materials (190), a study of the memory effect and domain structures of ferroelectric triglycine sulphate crystals (191), and the use of amorphous carbon as the interfacial layer on a sodium chloride cleavage surface (192).

To demonstrate the importance of the electrical structure of the surface, amorphous carbon was deposited on silicon single crystals which had previously been doped with boron.

Subsequent decoration with silver chloride, onto the n-p junction region resulted in a monocrystalline film being observed in the n-region and a polycrystalline film on the p-region (193, 194). It was concluded that only the vacancy region of the surface contained epitaxial information with transference capabilities.

The mechanism for the transference of the forces originating from active centres depend on the material used as the interlayer. When electro optical materials such as anthracene, selenium etc., are used, the transference of information is said to occur via photoelectrets. Selenium layers deposited onto sodium chloride crystals, and subsequent decoration with anthraquinone resulted in orientation of the anthraquinone deposit only if the selenium layer had been subjected to visible radiation. The detached layer of selenium also contained orientational information, but if this layer was illuminated after removal, depolarisation of the layer occurred and random crystallisation was obtained (195). Similar studies have been made using zinc oxide (196), anthracene (197) and a variety of other photoelectret materials. The behaviour of semiconductors which have been previously illuminated have been studied, and different polarisation structures have been observed (198, 199), which in turn modified the orientation of the decorating agent (200).

Much work has been carried out on a second type of interlayer which can transfer epitaxial information. Amorphous plastic films have been deposited from solution on to the freshly cleaved surface of sodium chloride, the substrate and plastic interlayer are then heated to the softening point of the plastic to produce a thermoelectret state. The plastic film of upto 1500 Å⁰ thick is removed, by dissolving the substrate in water, and the decorating agent vacuum deposited on to the surface. Orientation of a silver chloride deposit has been observed, using this method with a heated polyvinyl chloride interlayer (201, 202).

P.V.C. has also been successfully used on mica surfaces, where anthraquinone was used as the decorating agent (203). The suggested mechanism for the memory of orientational information, is the induced polarisation by defect centres occurring in the substrate, which in turn transmits to the polymer layer through local orientation of dipole groups of the plastics molecular chains. The polymer film is heated to the softening point to permit the mobility and subsequent orientation of the molecular chains. Heating in excess of the softening point of the plastic after removal from the substrate destroys any memory effect, and random crystallisation is observed (204).

Metallic polycrystalline and single crystal interfacial layers have also been used, the metal layers were prepared, and the outer side of the layer decorated with anthraquinone. The metals used as interfacial layers were Bi, Ni, Ag, Au, Zn, Pb and Sn (205, 206). For nickel and gold (205, 208), layers up to $100\text{\AA}$ thick showed transmission of the structural information, thicker layers resulted in the rotation of the deposit by 45° , from the $[110]$ orientation of anthraquinone to the $[100]$ orientation (207). Gold layers of up to $1000\text{\AA}$ thick however were found to transmit some epitaxial information. Deposition of anthraquinone on the detached films of gold and silver, on the contact side also resulted in epitaxial growth, demonstrating a memory effect being present in these interfacial layers (207, 209).

Chemical transport reactions have been used to deposit cadmium sulphide single crystal films. These films were deposited on to mica via an amorphous interfacial film of carbon or SiO_2 upto $1000\text{\AA}$ thick, and the same epitaxial relationship was observed both in the presence and absence of the amorphous film (210, 211, 212). Homoepitaxy (deposit and substrate identical) can be observed by the normal technique of seeding the liquid phase.

Crystals of naturally occurring hydrosilicate $[\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\cdot\text{OH}\cdot 2\text{H}_2\text{O}]$ were coated with a polycrystalline film of silver or gold, and used for seeding the crystal growth of hydrosilicate from the liquid phase. The resulting crystals had a more perfect crystal structure, than those grown by the normal seeding methods, and the reason suggested for this improvement was the elimination of defects in the seed being transferred to the growing crystal, and consequently no misalignment would be observed (213).

As discussed earlier, the transmission of active centres in the crystal surface, is thought to be electrical in nature and Distler and his school, suggest that the only important force in epitaxial deposition is the presence of electrical active centres. A detailed study has been made of the electrical structure of many surfaces, in an attempt to gain a better understanding of epitaxy. Direct observation is seldom possible, and consequently most evidence is found by the interpretation of secondary effects, the most popular method is by the observation of deposited anthraquinone crystals.

By this method, a new fine structure has been shown to exist on γ -irradiated triglycine sulphate crystals, and also the changes in the domain regions have been identified (214, 215). The selective crystallisation of anthraquinone on the cleaved surfaces of sodium chloride and mica (216 - 218) has resulted in the identification of polarised states existing on the surface at the moment of cleaving (219). These states rapidly change and decay over a period of 15 sec. due to the neutralization of the charged surface by the surrounding species present in the residual vapour. The electrical structure of surfaces of CaF_2 , alkali halides, MgO and mica have been demonstrated by the deposition of anthraquinone on the matching cleavage faces of the crystals (220 - 222), and any irregularities in the growth of the deposit on surfaces showed a mirror effect on the matching cleavage face.

The active centres, and the electrical structure of the surface, have also been applied to crystal growth mechanisms, and crystallisation discussed in terms of a replication process of the electrical structure of the surface (223 - 225).

Summary

The underlying basis for the work carried out by Distler and his school is to establish the existence of active centres within the surface, and the presence of a definite electrical structure on the surface. The validity of this hypothesis depends on the capability of some materials to transmit these forces over long ranges (up to $1000\text{\AA}$); this has been shown by observation of epitaxial deposits, on interfacial films, which show no orientational properties by themselves. This concept suggests that epitaxy is not a surface phenomena, but results from forces under the surface of the substrate. Outside of the Distler school, very little confirmatory evidence has been found to suggest epitaxy is not purely a surface phenomena. Infact many workers have not been able to reproduce the results, and have found no evidence for the existence of long range forces; their work is considered in detail in the following section.

6.3 Observation by other workers

Resulting from a discussion of Distler's papers (279) many workers agreed that a carbon deposit on a single crystal substrate would destroy the epitaxial growth of a superimposed layer. To confirm this, Chopra (247) conducted a series of careful and systematic experiments, using amorphous carbon films as the interlayer. The epitaxial growth of vacuum deposited films of Au, Ag, PbS and SnS were studied on rocksalt and mica substrates. Parts of the substrates were coated with amorphous deposits of carbon and SiO to thicknesses ranging from a few angstroms up to about $200\text{\AA}$. Various deposition rates and substrate temperatures were used, but all resulted in randomly oriented overgrowths. Although Chopra admitted the exact deposition conditions used by Distler would not be reproduced, every effort

was made to use the experimental conditions reported in the literature by Distler. Chopra concluded that the negative results obtained in his laboratory were due to a homogenous interlayer being produced, but if poorly cleaved rocksalt substrates were used, which contained a high density of ledges and cleavage steps an unhomogenous carbon film with the possibility of holes would result. The presence of such holes would explain Distler's observations.

Hayek and Schwabe (280) studied in detail the nucleation and growth of gold films on rocksalt with an amorphous intermediate layer. They reported the disappearance of gold orientation with amorphous films of $10-12\text{\AA}$, and also the presence of porous or island structures in the interfacial film. The island and texture structure of the film was detected by tantalum-tungsten shadowing with subsequent platinum decoration, and the type of film produced was found to be dependant on the residual water vapour pressure at the time of evaporation. Further experiments of Chopra confirmed these results (248).

A study of the growth of vacuum deposited ZnS, and PbS on sodium chloride with $(\text{SiO})_x$ or carbon interlayers was made by Barna et al (281). They obtained an epitaxial orientation of the deposit using films of up to $130\text{\AA}$ and discovered the importance of the temperature of the substrate, when depositing the intermediate layer. A temperature of lower than 230°C being used resulted in a random deposit on films greater than $10\text{\AA}$ thick, however, films prepared at 230° permitted the transmission of epitaxial information. They suggest that the intermediate dielectric layer grows in the effective surface potential field of the basic single crystal and consequently forms within itself a built-in electric field corresponding more or less to this potential and to the disturbances of potential on the surface. The thickness of this layer is determined by the electrical forces at the surface, and is dependant on the substrate temperature during its deposition.

Bethge (282) confirmed this hypothesis, by considering the electric forces at the surface of the sodium chloride substrate. Methods of Kliever (283) enabling the electrical double layer theory to be applied to solids, were used by Bethge to calculate the potential difference of a surface layer of a thousand angstroms. He concluded that at temperatures of between 300 and 500°C a potential of 0.2 - 0.3V exists between the surface and volume. If the amorphous layer was prepared under the correct conditions, the film would be a continuation of the double layer. The correct conditions are those necessary to produce the Debye-Frenkle layer of adequate efficiency to influence the amorphous carbon film and subsequent epitaxial overgrowth.

Henning (284) studied the gold/carbon/rocksalt system and obtained partial confirmation of Distler's results. He found that an epitaxial deposit of gold could be grown on amorphous carbon films prepared on vacuum cleaved rocksalts. Films prepared on air cleaved crystals resulted in polycrystalline growth of the deposit if the films were greater than 30 - 40Å⁰, and concluded the surface of the air cleaved crystals were changed by the adsorption of a thin water film, which in some way limited the ability of the interlayer to transmit surface information.

The interaction of copper and gold to form well defined solid solutions was utilized by Ackerman et al (285) to study the homogeneity of prepared carbon films. They deposited the films of carbon on to previously prepared gold (111) platlets, and then evaporated copper on to the carbon surface.

Characteristic selected area diffraction patterns of the copper-gold solid solution were observed in the electron microscope. These observations confirmed the earlier predictions by Chopra (247) that epitaxy was only observed when there was direct contact between overgrowth and substrate. Carbon films of up to 80Å⁰ prepared at room temperature were found to contain bare patches, enabling direct contact between deposit and substrate to take place.

As part of a wide study on the influence of defects and impurities on the nucleation and growth of evaporated films Green (249) studied the possibility of orientation through amorphous layers. He studied the orientation of f.c.c. metals on alkali halide surfaces, which has previously undergone various surface treatments. These included, exposure of the surface to contaminant vapours, electron bombardment, doping materials and X-ray and ion radiation. Under no circumstances was orientation observed through amorphous carbon layers even when major electrical as well as structural changes had occurred in the substrate.

A study using plastic interfacial layers, has been made by Darling (277) who deposited anthraquinone on rocksalt via films of P.V.C. Darling did observe partial epitaxy but concluded that this was due to the primary orientation of the P.V.C. layer, therefore the interfacial layer was not in fact transmitting epitaxial information from the rocksalt surface.

The only other study using plastic layers was made by Sheftal et al (286) who deposited bismuth on to muscovite mica. They used various thicknesses of 70 -150 Å of celluloid film and observed orientation of the bismuth deposit, on these films, with the normal orientation as on virgin mica.

An ingenious experiment was conducted by Zhdanov (290), who studied the migration of copper on carbon replicas which contained gold particles on the underside. Tungsten disks coated with copper were used as support grids for the carbon film, and by electron beam heating copper migrated over the carbon replica. Although epitaxial nucleation was not observed the gold particles under the carbon film did act as active centres for the nucleation of the copper, and subsequent growth occurred over gold particles.

From the many conflicting reports and arguments submitted by other workers it is impossible to assess the true merit of Distler's hypothesis, and many workers have not correctly reproduced his conditions.

An example of this is the condition where some workers find holes in the interfacial films (285, 280) and others do not (281, 284). It was thought improbable considering the enormous output of evidence for this theory from Distler's school that their results could not be repeated by this laboratory, and once this confirmation had been achieved an explanation could be found as to why other workers encountered such difficulty. It would also be possible to determine if Distler's observations were open to any other interpretations.

6.4 Growth of Deposits through amorphous interlayers

From the experience obtained with the growth of organic deposits, it was decided that anthraquinone would be used as the decorating agent because it was known to respond to the electrical structure of the substrate. The two substrates used were sodium chloride and mica, two were used to enable a comparison of the growth behaviour of the deposit to be made which is extremely important as all observations were to be made with the optical microscope.

A new apparatus was designed and built to enable the continuous deposition of film and decorating agent, without exposure to air. Further requirements of the apparatus were the inclusion of vacuum cleaving facilities provision for several samples to be prepared under identical conditions, and a residual pressure at evaporation of better than 10^{-6} Torr. (The basic construction of this deposition chamber is included here, but the more technical details are described in appendix one for further reference.)

6.41 Deposition Chamber

The basic vacuum chamber consisted of a 12" dia x 14" x $\frac{1}{4}$ " glass cylinder, 6" dia oil diffusion pump, 2-stage rotary backing pump, a water cooled chevron baffle and a 6" dia water cooled baffle valve. Two 12" Viton 'O' rings were fitted to the glass cylinder and the residual pressure was measured by Pirani and Penning vacuum gauges. A large Ballast tank, and a magnetically operated isolation valve were included in the backing line to enable deposition under vibration free conditions, and this necessitated the inclusion of a second pirani gauge to continuously monitor the backing pressure. The basic deposition chamber and the positions of the high vacuum valves, gauges etc. are shown in figures 43 and 43.1 respectively.

The substrate and decorating material were both heated by resistance heating, and their temperatures measured by attached thermocouples. The substrate heater and substrate were fixed on a rotary feed-through, this permitted the preparation of several specimens in the one vacuum cycle. The technique of electron beam heating was employed for the carbon evaporation as this was far more controllable than the alternative resistance heating method, used in replication for the electron microscope (see chapter two).

The thickness of prepared carbon films were measured by a previously calibrated quartz crystal. Both the electron beam source and the quartz calibration are discussed in detail in appendix one.

All electrical connections were made via feed-throughs in the top-plate, with the exception of the high current/high voltage connections to the electron gun which were made through feed-throughs in the side of the baffle valve, (for further details see appendix one).

The relative position of the components within the vacuum chamber are shown in figure 43.2.

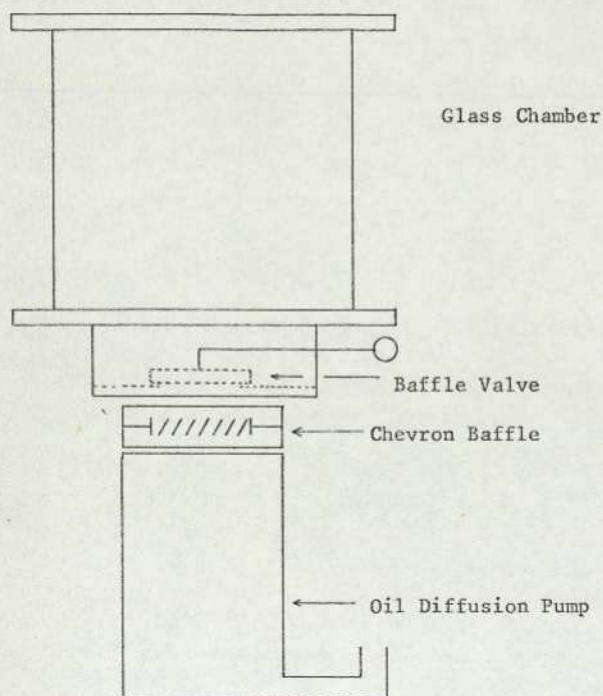


Figure 43

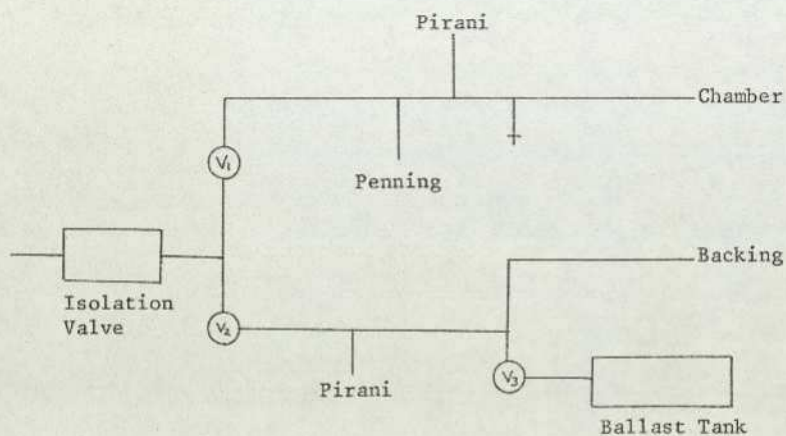


Figure 43.1

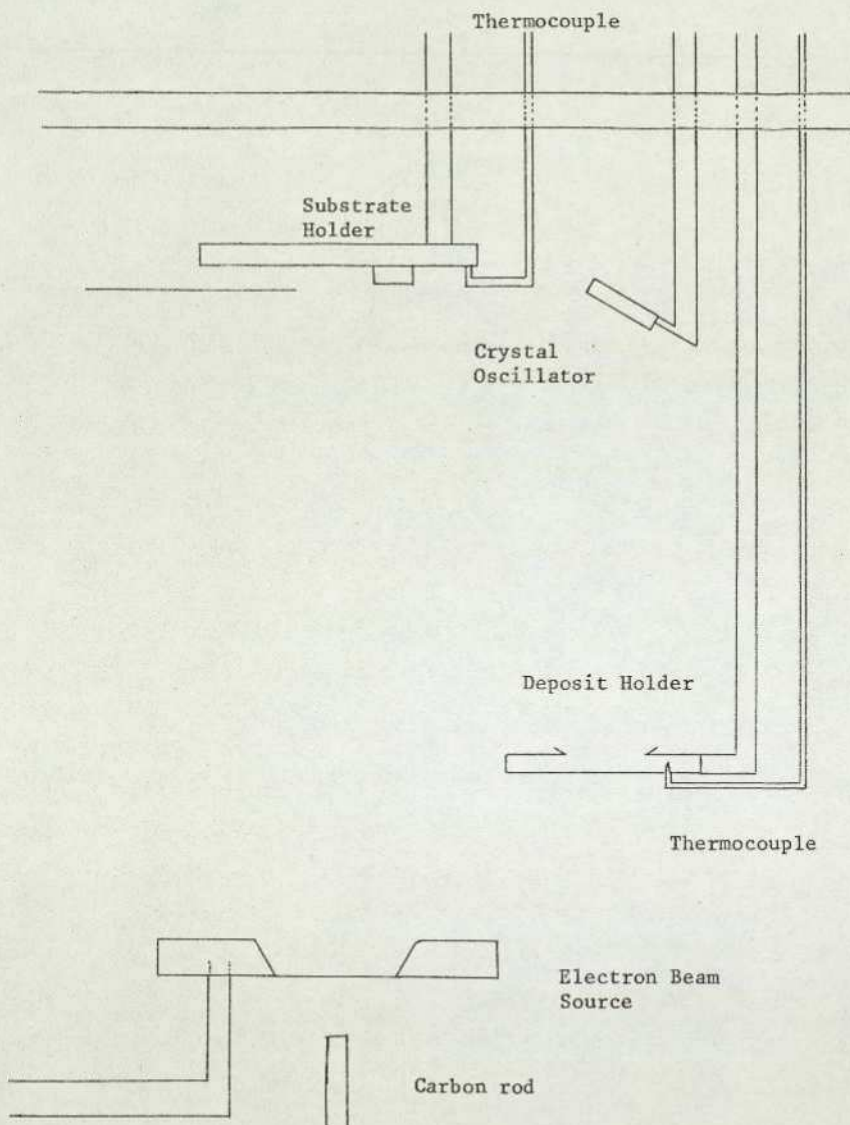


Figure 43.2

6.42 Results and Discussion

To determine whether the radiation from the carbon deposition source had any marked effect on the growth of anthraquinone on rocksalt three samples were prepared and examined. The first sample was prepared in the normal way with the direct deposition of anthraquinone on to the sodium chloride, with the second sample the deposition of anthraquinone took place simultaneously with the visible and UV radiation of the heated carbon tip, and with sample three deposition took place after the radiation treatment to the substrate. This was achieved by magnetically operated shutters, and although it was impossible to be absolutely sure no impurity species from the hot carbon arrived at the substrate, it was possible to eliminate carbon evaporation. This was achieved by using a very small carbon rod held in a large heat sink, and this inhibited the temperature rising at the tip sufficiently high to cause significant carbon evaporation. During all operations the substrate was held at 40°C . Examination of the three samples showed there was no marked difference in the deposits obtained with the exception that the radiation treated sample contained a slightly thinner covering. Because there existed no clear cut differences in the deposits it was concluded that any radiation from the carbon evaporation source had a negligible effect on epitaxial deposition. The same tests were carried out on mica substrates with similar results.

A series of carbon films were deposited on a freshly cleaved mica surface (early carbon depositions showed there to be no difference between air and vacuum cleaved mica specimens) at room temperature; any temperature fluctuations on the surface were recorded by means of a thermocouple held on its face.

At a thickness of approximately $10^{\circ}\text{\AA}$ of carbon orientation of the anthraquinone deposit became random and a noticeable change in the anthraquinone deposit was also observed at this stage.

The separation between growing crystallites showed a marked reduction, and coalescence occurred at a very early stage of growth. This would be expected due to the reduced mobility of the deposit on the surface of carbon, unfortunately accurate density measurements could not be made because of the unhomogeneity of the covering.

Carbon layers of 50, 70, 100, 120, 150, 200, 250 and 300 Å⁰ were prepared and the subsequent deposition of anthraquinone studied.

The growth of anthraquinone became rather uncontrollable, and irreproducible at carbon film thicknesses over 100 Å⁰, on several occasions, even though identical deposition times were used the quantity of overgrowth varied enormously. The reasons for this phenomena are not known but is probably due to the complicated surface changes in various carbon films, for example the island effect reported by Hayck and Schwabe (280). At this stage no attention was paid to the time between the end of carbon evaporation, and the commencement of anthraquinone deposition. This time varied from a few seconds to up to an hour depending only on the current practical circumstances. Although it is not known how this parameter would effect the deposition, a standard time of 10 mins was employed, to eliminate any possible ageing effects, and the results repeated. This was used for all evaporations of carbon up to 100 Å⁰, where deposition rates of 5 - 10 Å⁰/min were used, for thicker layers, and longer evaporation periods, a longer time interval was allowed before the commencement of the anthraquinone deposition.

In all cases single crystal growth occurred and at a carbon film thickness of 120 Å⁰ partial epitaxy of anthraquinone deposits was observed, some of the deposit being aligned to the 110 directions of the mica substrate. These deposits are shown on plates 91 - 94.

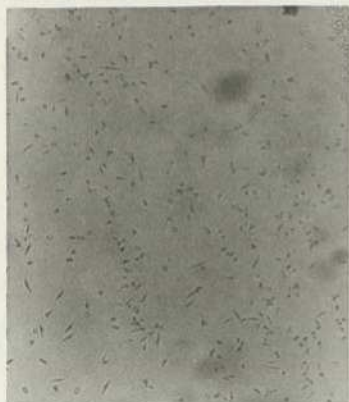


PLATE 91

400X



PLATE 92

400X



PLATE 93

400X



PLATE 94

400X

THE PARTIAL ORIENTATIONS OF AN ANTHRAQUINONE DEPOSIT
ON THE SURFACE OF A CARBON INTERFACIAL BARRIER WHICH
HAD BEEN PREPARED AT ROOM TEMPERATURE ON A MICA SURFACE

The proportion of the anthraquinone deposit oriented shown on plate 93 was determined and corresponds to approximately 51% orientation. This result is highly significant, because a sudden change over from random to epitaxial deposit would not be expected. Infact on the Distler long range forces mechanism the fraction of epitaxial deposit would be expected to decrease as the thickness of the interfacial carbon film increased.

A check was made on the homogeneity of the prepared carbon films by an electron microscope examination. Some damage did occur as a result of the detachment and mounting of these films, but this damage could easily be differentiated from any major inhomogenities originally present in the film. No evidence was found to suggest the presence of any holes or major defects in the films.

The orientation and the thickness of the carbon films were to a large extent irreproducible, and although some fraction of deposit on films ranging from $80 - 150^{\circ}$ were oriented, no consistent fraction was maintained. Indeed epitaxial deposits seldom exceeded 30 -45%. Various refinements were made to the technique in an attempt to improve the reproducibility of the results, among these were to carry out all depositions under identical pressures, and the deposition rate kept as consistent as practically possible. However, even with these precautions there was no marked increase in the reproducibility. (A range of substrate temperatures were used ($20 - 70^{\circ}\text{C}$) when depositing the anthraquinone but little change was achieved.)

An elevated substrate temperature at the carbon deposition stage was employed in an attempt to improve the irreproducibility, temperatures of $50, 100, 150$ and 250°C were used. Subsequent deposits of anthraquinone again showed marked changes in the growth, variations in the extent of covering, size of crystallites, and separation of individual crystallites were the major changes obtained. This observation confirmed that some changes in the prepared carbon films were being transferred to the surface of the film, and modifying the growth characteristics of the decorating material.

At temperatures greater than 200°C a second marked change in the subsequent deposit of anthraquinone took place. Deposits prepared on the surface of mica containing an interfacial layer of $120\text{\AA}$ of carbon grew epitaxially. Difficulty in obtaining the correct quantity of deposit was again experienced but once this had been achieved the majority of the deposit (60 - 80%) grew epitaxially.

The degree of crystal perfection showed a marked decrease, and in some instances a definite crystal centre could be identified. Any epitaxial deposit at large surface defects were ignored because direct contact between the overgrowth and substrate could possibly occur at these defect emergent points. The epitaxial deposits obtained can be seen on plates 95 - 98.

To ensure that the epitaxial orientation was due to the substrate, and not just the result in change in the carbon films, these experiments were repeated using a freshly cleaved sodium chloride surface.

The many conditions used with mica were not repeated for sodium chloride and carbon films were only deposited on to the substrate at room temperature and 230° .

Orientation was only observed within the same carbon film thickness range of between $80 - 120\text{\AA}$. When thicker carbon films were used no orientation was observed and the anthraquinone deposit grew in the same way on a carbon coated rocksalt surface as it did on a carbon coated glass surface.

The carbon films were deposited at the same rates as used with a mica substrate, at 230°C , and although difficulties in obtaining the correct quantity of anthraquinone deposit were again experienced, it was to a much lesser extent than on a carbon covered mica substrate. Once the correct quantity of anthraquinone was obtained, a good epitaxial deposit was observed on carbon coated rocksalt surface which was heated to 230° whilst carbon deposition occurred.



PLATE 95

100X



PLATE 96

100X



PLATE 97

400X



PLATE 98

400X

ORIENTED DEPOSITS OF ANTHRAQUINONE ON A CARBON INTERFACIAL
BARRIER WHICH HAD BEEN PREPARED AT 200° ON A MICA SURFACE

An interesting difference between the anthraquinone deposits grown on sodium chloride with interfacial carbon films, and those grown on the virgin sodium chloride surface is the larger proportion of crystals observed on the former substrate which grew with the orientation corresponding to (010) anthraquinone $[100]//[100]$ sodium chloride (001). This orientation was only observed in a small proportion of the deposit grown on a virgin rock-salt surface.

With the deposits obtained on carbon covered surfaces, a homogenous covering was very seldomly obtained, and normally small areas of relatively densely populated crystallites were separated by regions containing very little deposit. This can only be the result of local differences on the carbon surface, causing differing mobilities, and nucleation properties, as the irregularities in the deposition would not account for these different regions of overgrowth.

The epitaxial deposit obtained is shown on plates 99 - 103, the main orientation corresponds to (010) anthraquinone $[100]//[110]$ sodium chloride (001) and on plate 99 some of the deposit is oriented with the secondary relationship previously described. The existence of definite crystal centres can be observed, especially on plates 101 and 103.

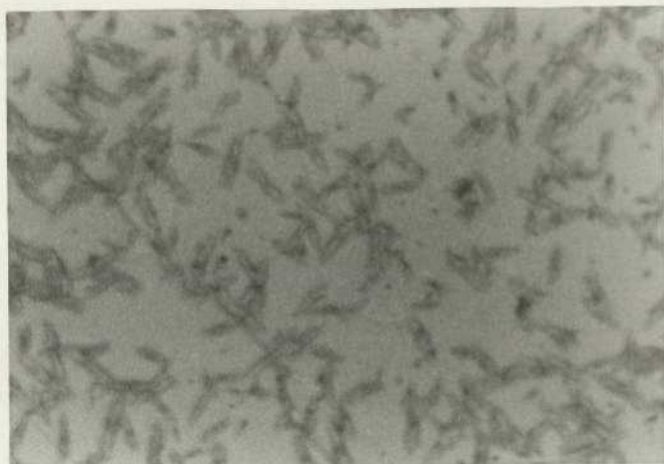


PLATE 99

400X



PLATE 100

400X

ORIENTED DEPOSITS OF ANTHRAQUINONE ON A CARBON INTERFACIAL
BARRIER PREPARED AT 230° ON A SODIUM CHLORIDE SURFACE

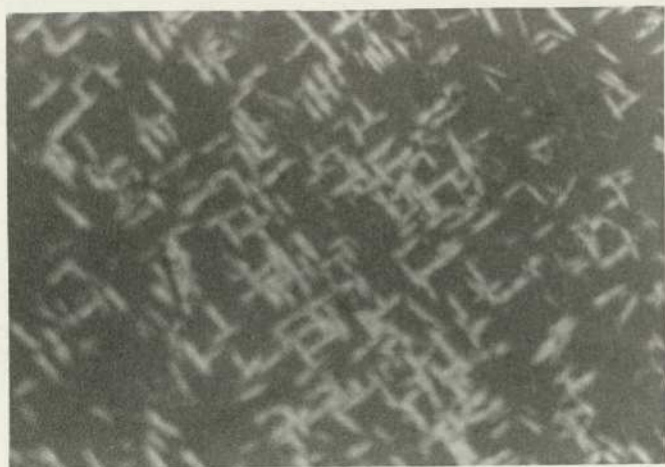


PLATE 101

400X



PLATE 102

400X



PLATE 103

400X

ORIENTED DEPOSITS OF ANTHRAQUINONE ON A CARBON INTERFACIAL
BARRIER PREPARED AT 230° ON A SODIUM CHLORIDE SURFACE

6.5 Summary

Epitaxial deposits of anthraquinone were grown on both sodium chloride and mica substrates, which were coated with carbon layers of $80 - 120\text{\AA}$ thick, and the orientations observed were identical to those observed on the virgin surfaces. This orientation, however, was only obtained if the substrate was heated to above 200°C whilst the carbon deposition took place. There were many irregularities observed in the growth of anthraquinone on the carbon covered surfaces, and among these the most significant was the variations in deposition times required to obtain a suitable overgrowth. On the virgin surfaces a suitable deposition time for a mica substrate was 15 mins, and 5 - 8 mins for a sodium chloride substrate. Using similar distances, and evaporation rates, times of 8 - 10 mins were sufficient for a carbon covered mica surface, indicating reduced mobility of the deposit, but the opposite effect was observed with a carbon covered sodium chloride surface where deposition times of 15 - 20 mins were required. The prepared carbon films were examined for the existence of holes and major defects, with the electron microscope, and these were shown not to be present.

The observation of epitaxial growth, only on carbon films between $80 - 120\text{\AA}$ thick is not consistent with a long range force mechanism, where no change over from random to epitaxial growth would be predicted as the interfacial film increased in thickness. However, the behaviour of anthraquinone on differently prepared carbon films, does confirm that some information of the surface of the substrate is modifying and influencing the surface of the carbon film.

The different behaviour of anthraquinone on the prepared carbon surfaces, would explain the wide divergence of observations reported by other workers. Normally anthraquinone is thought to be an ideal decorating agent for the observation of epitaxy, as it grows as well oriented crystals under a variety of conditions, (with substrate temperatures of between $20 - 70^{\circ}\text{C}$ and under a wide range of sublimation rates).

This does not occur on carbon covered substrates, where anthraquinone will only grow epitaxially under well defined experimental conditions.

The reasons for the observed behaviour on carbon surfaces is not clearly understood. One possible explanation would be the existence, under certain conditions, of a definite crystal structure in the carbon film, and the epitaxial growth is dependant on the existence of this structure. Crystal structure in the carbon films would also explain the islands (280), and the variations in the film with the residual water vapour pressure observed by some workers (280, 248). The existence of a defined crystal structure in carbon films has not been observed with transmission electron diffraction studies, which is the reason why these films are so often used as support materials in electron microscopy. But as these films are normally prepared rapidly and onto substrates at room temperature, structure may be avoided. Also the resolution of transmission electron diffraction of very thin films is not very high, and normally films of at least $180 - 200^{\circ}\text{\AA}$ are required before structure can easily be identified.

This does not, however, eliminate the possibility of structure resulting from a surface crystallisation of the amorphous film, which is in some way induced by the presence of the sodium chloride or mica substrate. The only direct method to examine this possibility is by the technique of low energy electron diffraction which is ideally suited for an investigation of surface crystallisation. To examine this possibility carbon films were prepared on heated and unheated mica surfaces in the same chamber where a L.E.E.D. study could be made, the results of which are described in chapter 7.

LOW ENERGY ELECTRON DIFFRACTION (L.E.E.D.) AND AUGER ELECTRON SPECTROSCOPY
STUDY OF CARBON FILMS

7.1 Introduction

The object of this study was to discover the possible existence of a regular crystal structure in the surface layers of thin carbon films. Due to the limitations of time and the complexity of both L.E.E.D. and Auger spectroscopy, the comprehensive understanding necessary for a complete interpretation of the results could not be obtained. In spite of this, however, a number of important conclusions can be made with a very limited fundamental understanding of both techniques. In the foregoing sections only the very essential aspects necessary for obtaining meaningful results are described.

7.2 Low Energy Electron Diffraction

A beam of low energy electrons striking a single crystal surface, produces a reflection diffraction pattern. Although the original work by Davisson and Germer (287) demonstrated the extreme sensitivity of low energy electrons for surface studies, the experimental technique only became feasible with improved vacuum conditions, a method of recording. Because the electrons interact strongly with the surface atoms, they are unlikely to penetrate further than the first few atomic layers, consequently examination of the surface must be conducted under clean, very high vacuum conditions. The introduction of a fluorescent screen which was excited by the diffracted electrons (288) made direct photographic recording possible. This technique coupled with advances in vacuum technology enabled the wide application of L.E.E.D. to be used as a means of surface study.

Conditions for Diffraction

The amplitude (A) of a wave incident on a crystal surface at a given point r is given by the expression:-

$$A(r) = A(o) \exp[ikr - \omega t]$$

where A(o) is the amplitude at the origin $r = o$ and k is the wave vector of the travelling wave which has an angular frequency ω . The magnitude of k is given by $|k| = 2\pi/\lambda$ where λ is the wavelength.

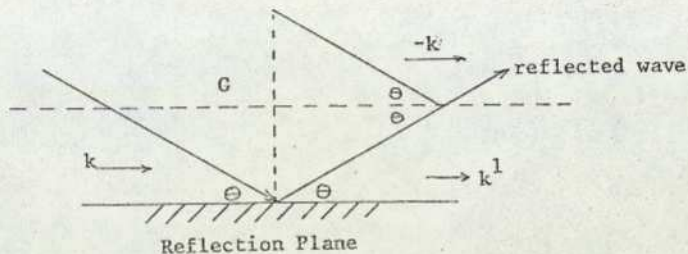
If $|k^1|$ is the magnitude of the scattered beam, diffraction can only occur if the magnitude of the incident and scattered wave vectors remain the same.

$$|k^1| = |k|$$

The magnitude of any reciprocal lattice vector $|G(hkl)|$ is related to the real lattice by expression 2.

$$2. \quad |G(hkl)| = \frac{2\pi n}{d(hkl)}$$

where d is the spacing between lattice plane (hkl) of the crystal.



$$\text{From } G = k^1(hkl) = 2|k| \sin \theta$$

$$\text{and since } |k| = 2\pi/\lambda$$

The Bragg reflection law is arrived at $n\lambda = 2d \sin \theta$

For L.E.E.D. the wave vector k in units of $\text{\AA}^{-1}$ and is uniquely defined by the electron beam energy, as

$$\begin{aligned} |k| &= 2\pi/\lambda = 2\pi[E(\text{eV})/150.4]^{1/2} \\ &= 0.512\sqrt{E(\text{eV})} \end{aligned}$$

In practise this model does not adequately describe the observed intensity of diffraction spots, and various theoretical studies have been carried out to explain the observed spot intensities, these have recently been reviewed by Fierman et al (289). As the theoretical treatment of the diffraction pattern is largely irrelevant to this study, it has not been considered further.

Low-energy electrons are produced by heating a metal or an oxide filament (cathode) in vacuum. The emitted electrons are accelerated towards the anode by a suitable potential, a small fraction escapes through a hole in the anode and are electrostatically or magnetically focused and allowed to impinge on the surface of the target crystal. The majority of the electrons back scattered from the crystal have undergone inelastic scattering and contain no diffraction information. These electrons are separated from the diffracted electrons by using a retarding potential on grids prior to the screen. Only electrons which have not undergone energy loss can penetrate these grids. The elastically scattered electrons are post accelerated by a large positive potential and impinge on a spherical fluorescent screen where the diffraction pattern is displayed. Typically for a 100eV incident beam only about 5% of the scattered electrons suffer no energy loss, and contain diffraction information.

To ensure the crystal surface remains clean whilst under study ultra-high vacuum conditions must be employed (pressures below 10^{-8} Torr). (For further information on the L.E.E.D. system the reader is referred to the work of Duckworth (296).)

7.3 Auger Electron Spectroscopy (A.E.S.)

Auger spectroscopy is a means of probing the electronic energy levels of an ion, and is part of the broader field of secondary electron energy spectroscopy. A.E.S. is capable of uniquely identifying elements present at very low concentrations. Under ideal conditions elements present on the surface, down to minute quantities of 10^{12} atomic/cm² may be identified. It is essentially a surface probe and the data coming from the first five atomic layers or so, depending on the material and its ionisation energy.

The ejection of an auger electron is essentially a three electron process. The atom is irradiated from an X-ray or electron beam, which excites an electron from an inner level causing ionisation. After an interval this level is filled by an electron from a less tightly bound state from an outer level. The excess energy is removed by the ejection of another electron, the so-called Auger electron. As a result of the electronic rearrangement the auger electron contains information characteristic of the electronic environment and hence the element from which it came. The energy of the total auger current is analysed by the same set of grids utilized in the low energy diffraction process, and information concerning the valence state or chemical environment can be obtained.

Auger electron spectroscopy has only been used in this work, as a finger printing technique of the contaminants on the crystal surface. As a result of work by Somarjai et al (291) and Grant (292), the shape and position of a characteristic auger peak has been used to detect the particular chemical environment of the atom.

This work has been extended by Grant and Maas (293) who have reported that the carbon 272eV peak is sensitive to the form in which the carbon is present, and illustrated the changing shape of this peak in various carbon structures. As a result of their work the shape of the carbon 272 peak obtained in this study has been compared to the shape published by them and

this comparison used as a method of determining the structure of the carbon present. The auger spectra obtained in this study have only been compared with published data, and no fundamental interpretation has been attempted on any occasion.

For further details of A.E.S. excellent reviews have been published by Chuan (294), Somorjai (295) and for the most recent review concerning applications by Duckworth (296).

7.4 Experimental

The basic system used in this investigation was a commercial unit supplied by Vacuum Generators Ltd. Pressures of below 10^{-10} Torr were achieved by cooling 2 sorption pumps to liquid nitrogen temperature. A Titanium sputter ion pump capable of $140 \text{ litres-sec}^{-1}$ pumping speed was then used evacuating down to the ultimate pressure of below 10^{-10} Torr.

Electron beam heating as described earlier was used for carbon evaporation, but certain geometric modifications to the electron beam source were necessary to eliminate gross contamination of the vacuum chamber and electron optics by carbon.

The electron gun was fixed in the horizontal position to an 8" demountable flange, this flange incorporated a 2" dia stainless steel bellows terminating to a 2" dia demountable flange, and the carbon rod was held via a stainless steel connecting bar to this flange.

Two stainless steel plates were used to restrict the carbon vapour, and to collimate the beam on to the target crystal. The geometry of this arrangement is shown in figure 44.

Plate one, contained a $\frac{1}{4}$ " x $\frac{1}{4}$ " slit and was held at the same high positive potential as the electron deflector of the gun, and the second plate was designed to fit tightly into the evaporation port.

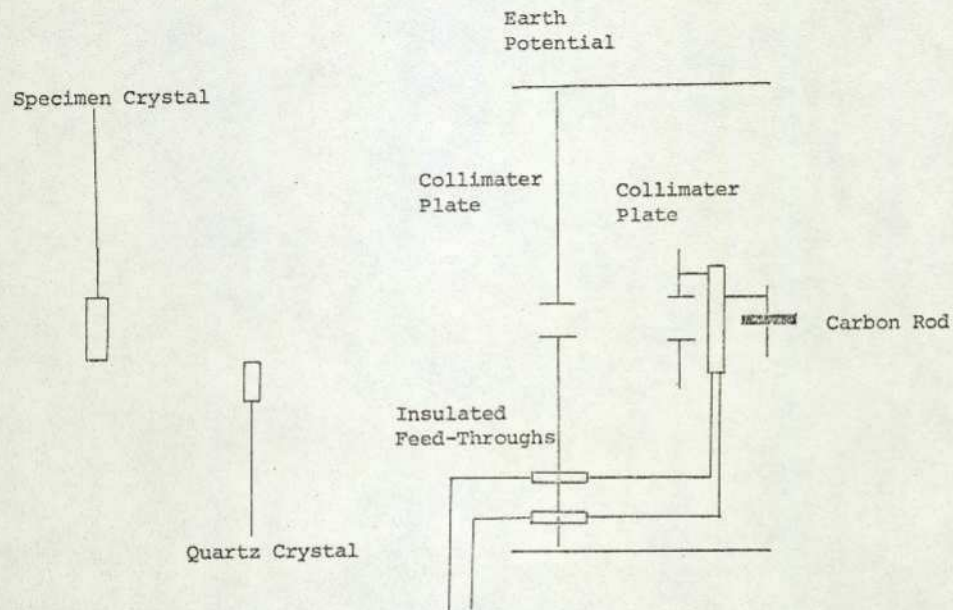


Figure 44

Electron Beam Arrangement inside L.E.E.D. Chamber

The second plate contained a $1" \times \frac{1}{16}"$ slit, and was held at earth potential, electrical connection to the electron gun were made via constructed electrical feed throughs, to this plate.

The collimator arrangement was calculated from the geometry of the electron gun, to produce a $2" \times \frac{1}{2}"$ beam at the crystal, and the crystal oscillator was held in this beam. The position of the oscillator was determined by evaporating a thick carbon film on to a previously light adsorption calibrated glass slide. The homogeneity of the prepared carbon film was then determined by spot photometer measurements on the intensity of light transmitted through the film, and the crystal oscillator placed in a position where it would receive a homogenous covering of carbon.

An extension to the crystal manipulator was constructed to include facilities for resistance heating and temperature measurement of the substrate, this is shown in figure 45.

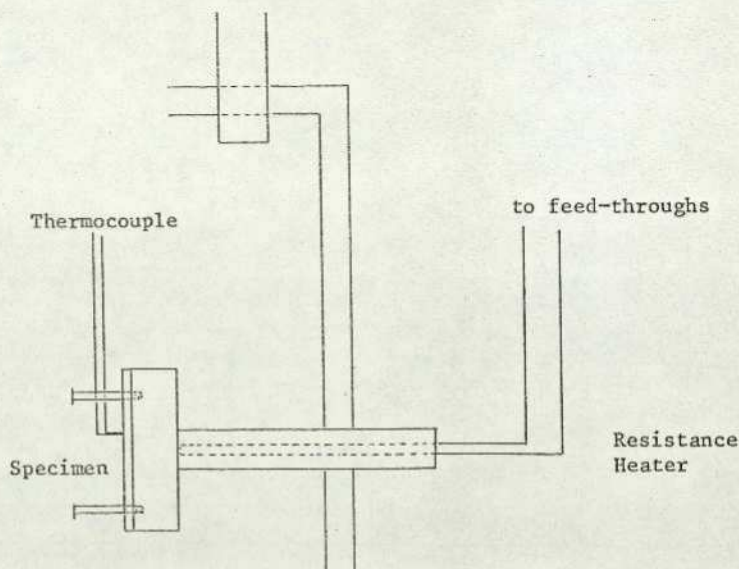


Figure 45

Sample Holder

Connections of both heater wires and thermocouple leads were made to the electrical feed through at the top of the plate via copper wire, and 4" length of spiraled flexible copper braid which were covered with insulator beads to allow 280° rotation of the sample and 3" vertical movement.

Due to the surface activity of carbon, the carbon rods used were capable of outgassing for very long periods, and to eliminate this the rods were kept as short as possible and heated by the electron beam for 20mins prior to the baking stage of the pressure reduction.

A tripod arrangement (shown in figure 46) fixed to the carbon holder, permitted the fine alignment of the rod required to obtain the optimum position with the electron beam for evaporation. Also this allowed the rod to be inserted further into the beam, to compensate for the material lost through evaporation, to enable further evaporation without removal and realignment of the carbon rod.

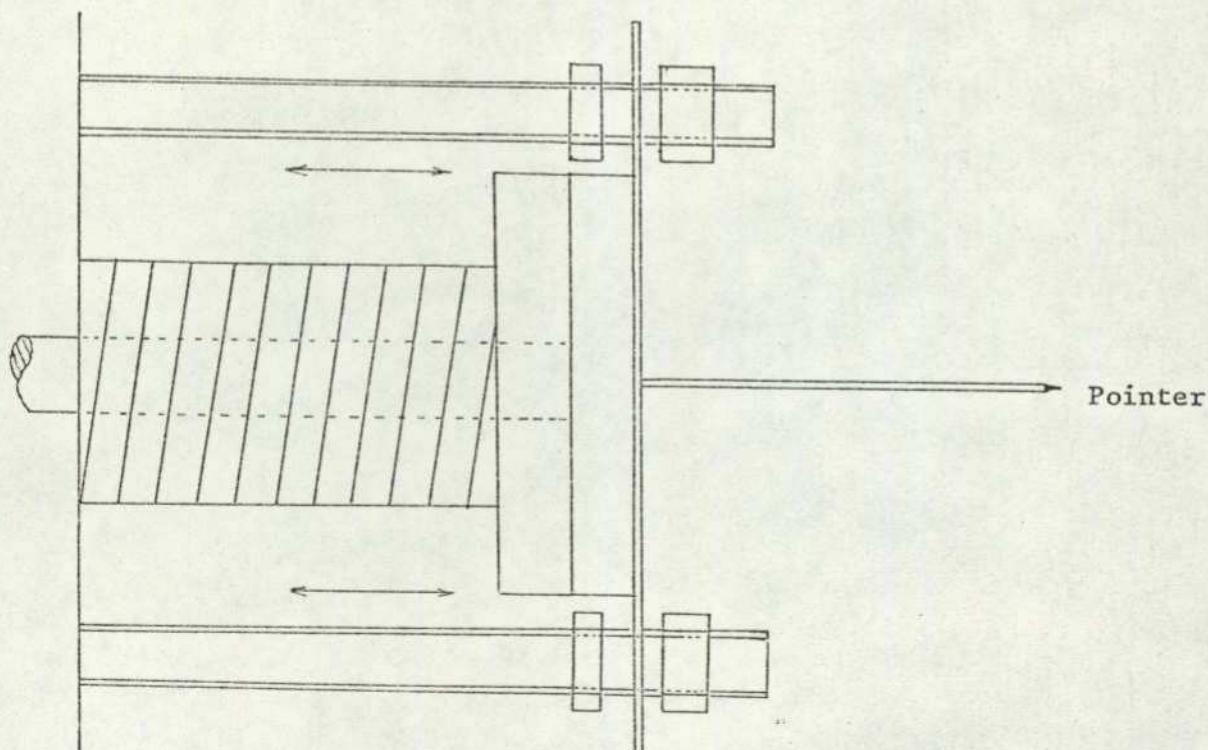


Figure 46

Carbon Rod Holder

When either L.E.E.D. or A.E.S. investigations are to be carried out the crystal must be kept at earth potential, and this was achieved by earthing the crystal through the thermocouple connection.

As the carbon deposition was to take place in stages interpreted by a L.E.E.D. and A.E.S. investigation, great care was exercised in the repositioning of the crystal prior to a deposition to avoid inaccuracies in the film thickness estimation.

7.5 Results and discussion

The diffraction pattern from a mica surface is usually readily observed but suffers from the complication of surface charging. As an extra precaution to limit this charging, the contact of the earthing connection was increased. This was done by the evaporation of a small quantity of gold onto the surface of mica, and the substrate holder, with the centre area being covered by a detachable mask. This procedure was used prior to the insertion of the sample onto the vacuum chamber, and subsequent A.E.S. investigations confirmed that no gold had diffused onto the clean substrate centre.

The charging process of the surface can be further reduced by using a specified range of beam energies, this is because under certain conditions, the secondary electron emission from the surface is sufficiently adequate to remove any built up charge. The recommended electron beam energy range is between 65 - 150eV (297). The electron beam energy is obtained directly from the potential on anode four, and a good diffraction pattern was obtained under the following conditions:-

Anode one (A1) = +567 volts

Anode two (A2) = +39 volts

Anode three (A3) = +537

Anode four (A4) = +114

The diffraction pattern obtained is shown on plates 104 and 105.

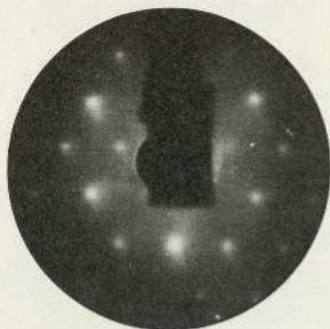


PLATE 104



PLATE 105

THE DIFFRACTION PATTERNS FROM A MICA SURFACE

The Auger spectrum of the virgin mica surface was obtained which identified the principle elements on the surface to be carbon, oxygen, fluorine, calcium, potassium and iron.

A current of 3.4 amps was sufficient to raise the temperature of the surface to 230°C , and once a steady temperature was obtained carbon was slowly deposited. A film of $8\text{\AA}$ was deposited over a period of 2 mins, no particular relevance could be associated with this thickness on such a small quantity is outside the accuracy of the thickness monitor. However, it was sufficient to completely obscure the mica diffraction pattern.

A further Auger spectrum confirmed a total covering of carbon on the surface, and also an increase in the quantity of oxygen present. Carbon was deposited on to the heated surface of mica in successive layers of approximately $20\text{\AA}$ thick and a L.E.E.D. and A.E.S. investigation carried out after each stage.

At an approximate thickness of $100\text{\AA}$ a diffraction pattern was observed, but it was of too low intensity for photographic recording. The method employed to discover the presence of a very faint pattern, was to constantly change the beam volts around the value which is suspected to produce a diffraction pattern. As the correct energy of the beam is reached, the illumination on the screen increases, and as the energy is further increased so the illumination gradually decreases. By using this method the presence of very diffuse spots were suspected around the beam energy of 140 - 180. Spots of sufficient definition and intensity were only observed after a further layer of carbon was deposited. These were obtained with the conditions:-

$$A1 = +990, A2 = +16, A3 = 269, A4 = 160-170$$

with a total carbon film thickness of $120\text{\AA}$.

The diffraction spots observed were recorded with a Praktica AB single lens reflex camera with an additional 2 diopetre close up lens. Exposure times of 20 - 30 mins were required to record the weak patterns on Ilford HP4 film. The long exposure times that were found necessary, are nearly ten times longer than those that would be expected, and give an indication of the efficiency of the screen. Unfortunately, the premature ageing of the screen resulting from adsorbed contaminants etc., is a serious limitation in a study of this nature, and the reduced light intensity may have contributed to the difficulty in observing patterns with thinner carbon films, and also explains the poor quality of the diffraction pattern obtained, shown on plates 106 and 107.



PLATE 106



PLATE 107

THE VERY WEAK DIFFUSE DIFFRACTION PATTERNS
OBTAINED FROM A CARBON FILM $120\text{\AA}$ THICK

To confirm the presence of structure in the carbon film, the Auger spectrum was recorded, and as discussed earlier a change in shape of the carbon 270 peak would be expected. The changes observed by Grant et al (293) are reproduced in figure 48.

In order to observe such changes in the auger peak, the electron energy detector must be functioning at maximum resolution. The method used to improve the resolutions of auger peaks is by reducing the beam energy to approximately 4 times the energy of the peak under investigation. This does, however, also reduce the auger electron yield, and a suitable compromise beam energy was only found by a trial and error procedure. To ensure that any changing shape of the peak, could be wholly attributed to a changing structure all other effects must be minimised. In practise it was found that electrical noise in the recording system, especially the x-y recorder, could change the shape of a wide peak. To eliminate this effect, the carbon 272 peak was recorded many times under a variety of conditions and the average peak shapes were compared. A number of these can be observed in figure 49.

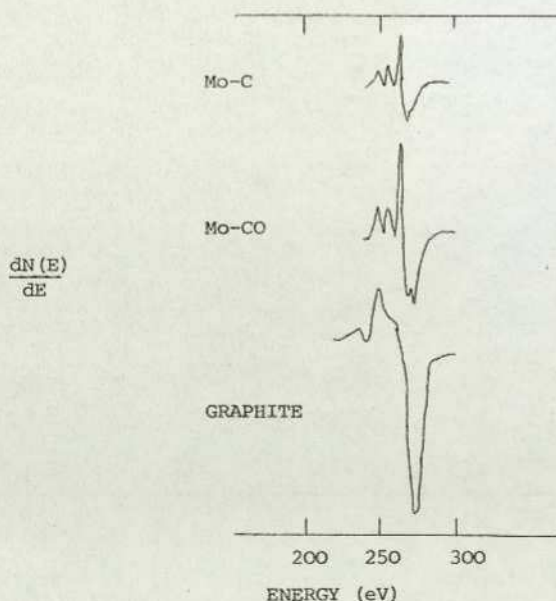


Figure 48
Auger Electron Spectra of Carbon

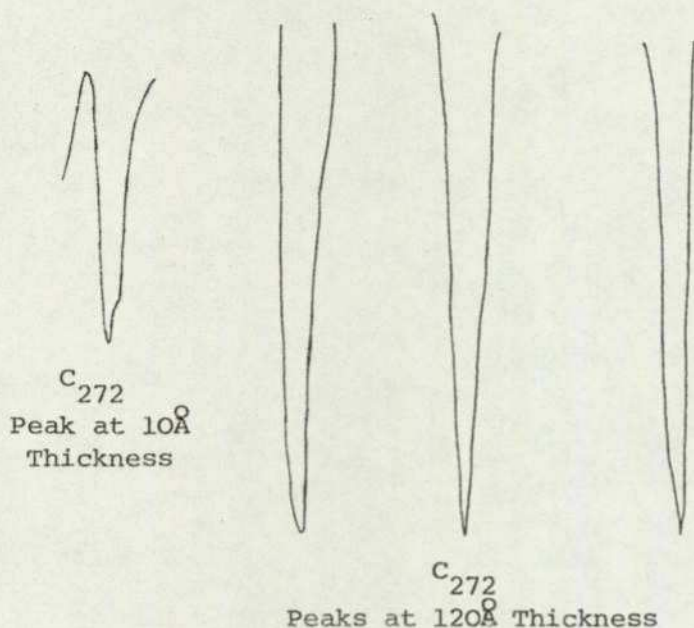


Figure 49

As can be seen from the auger peaks no firm confirmatory evidence is present to demonstrate the existence of structure in the carbon film. Although sufficient change is observed to suggest that some difference in the films is present. Due to the limitations of time and expertise the maximum resolution from the A.E.S. system could not be obtained, and without this it is impossible to observe unambiguously the small changes in peak shapes resulting from various environments.

In order to confirm that structure would not occur when the carbon films are deposited on to an unheated substrate, the same procedure described was repeated on a mica substrate held at room temperature. Carbon was deposited in identical stages but only a L.E.E.D. investigation was carried out as very little information could be obtained from an A.E.S. study.

A carbon film of total thickness of approximately $150\text{\AA}$ was deposited, and although many variations in anode potentials were employed, on no occasion could a diffraction pattern be observed. However, an interesting secondary effect was unexpectedly observed with the carbon film prepared on an unheated mica substrate, which was the quite different charging properties. A beam of energy of only 100 - 130v was sufficient to cause charging with the low energy electron gun. This effect was also observed with an auger examination, where the instability of peak positions is characteristic of early charging. The processes involved in charging and conductivity of thin films are extremely complicated, but are likely to be dependant to some extent, on the structure of the films, and the charging properties of the film prepared on an unheated substrate, together with the lack of structural evidence from the L.E.E.D. examination, would suggest that films prepared under these conditions differ quite considerably from those deposited on a heated substrate.

A second carbon film was deposited on a mica surface at 230° and each stage was again examined for structure. Weak diffraction patterns, like those discussed earlier were again observed but at a film thickness of approximately 140 - $150\text{\AA}$.

Summary

Because of the nature of L.E.E.D. and A.E.S. investigations, these techniques are not suitable for experiments involving the inserting and removal of samples from the vacuum chamber, for this reason conclusions have to be deduced from a limited experimental study. Three investigations were undertaken in this study, two on the surface of a carbon film prepared on a heated mica surface and one on the surface of a carbon film deposited on to a mica surface at room temperature, and although each separate film was largely unique in its properties certain similarities were present.

The most important of these, is the observation of weak diffuse diffraction patterns only with carbon films prepared as a heated substrate, and although the patterns were not of sufficient definition for a thorough investigation, their existence can only be explained by the presence of structure on the surface of the carbon film. This structure was only detected within the film thickness region of 80 - 150A°.

No diffraction pattern was observed with the carbon film prepared on an unheated mica surface, and this together with the different charging characteristics of this film indicated that no structure was present. Unfortunately sufficient time and expertise was not available to investigate the A.E.S. results, but early indications would suggest that the films prepared on unheated and heated substrates do contain fundamental differences.

The results of this study are discussed in relation to the long range concept in the next chapter.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1 The Long-Range Forces Concept

The phenomena of epitaxial deposits on substrates, through interfacial carbon barriers, reported by Distler have been substantiated in this study. Orientation of the deposit was only obtained if two conditions of carbon deposition were satisfied. These were, (i) the carbon films were deposited on substrates raised to above 200°C and (ii) the carbon films were between $80 - 150\text{\AA}$ thick. Using Distler's long-range forces concept the existence of the first condition could be understood by a number of explanations, among which, a minimum temperature would be required to allow the mobility for epitaxial nucleation, the heated substrate could remove adsorbed contaminants, and the heated substrate would be required to set up an electrical double layer of sufficient efficiency to transmit the surface forces, (see section 6.3). The existence of the second condition, the critical interfacial carbon film thickness, however, could not be explained using Distler's concepts. The presence of both an upper and lower film thickness limit, would suggest a unique change in the carbon film at certain thicknesses. The actual values of the thickness limits would be expected to vary with specific deposition parameters, and under the correct conditions an upper limit would be expected to vary with specific deposition parameters, and under the correct conditions an upper limit of several hundred angstroms (reported by Distler) could be possible. One explanation for the lower limit would be the development of structure in the carbon films, the lower limit is the stage at which surface crystallisation occurs and the upper limit where the crystallisation of the carbon film is not influenced in anyway by the substrate surface.

This mechanism was confirmed, by the Low Energy Electron Diffraction examination of the carbon films, and surface structure was observed for films prepared on heated substrates only. The method by which this crystallisation would effect the growth of the deposit is by the substrates initially orienting the carbon film, which subsequently orients the decorating material. This would explain why the unique orientations of anthraquinone are obtained on carbon coated rocksalt and mica substrates. At the upper carbon film thickness limit, the normal crystallisation process occurs in the film, which then does not epitaxially orient the decorating material.

The reason why other workers have not been successful in repeating Distler's results are twofold, primarily because even with the good decorating characteristics of anthraquinone the growth properties are considerably modified on the carbon surface, therefore with deposits of gold and lead sulphide the conditions for crystal growth on carbon films would initially have to be determined before any epitaxial investigation on carbon coated substrates should be attempted. The second reason is that no worker who obtained negative results with very thin carbon films 5 - 40Å^o on heated substrates continued to investigate thicker carbon films. This deficiency in carbon film thickness in not reaching the critical dimension for crystallinity to be produced by the substrate coupled with inadequate control in the deposition of the interfacial carbon films (as described for the replication process, section 2) has led other workers to prematurely doubt the validity of the ability of carbon films to transmit surface characteristics.

The observation of epitaxial growth only with a high residual water vapour pressure, is also consistent with the structure hypothesis, as water vapour, growth conditions etc. would be expected to modify the crystallisation of the carbon film. We consider therefore the existence of epitaxial deposits through interfacial layers is now confirmed, although the major contribution to its occurrence is thought to be the existence of structure in the prepared interfacial film.

8.2 Epitaxial Growth

The motivation for this study was to assess the contribution of the various parameters involved in the epitaxial growth of an organic deposit. All current theories have been restricted primarily to metal or metal salt deposits and consequently inherent in previous theories is an overdependence on the substrate-deposit relative lattice dimensions.

For many organic deposits, a very simple consideration of the electrostatic forces resulting from the polarity of the dominant species in the surfaces of both the deposit and substrate can be used to predict the orientation of a single crystal deposit.

The conditions required to obtain an epitaxial deposit may be broadly divided into two categories, which are (i) the growth of a single crystal deposit on the substrate and (ii) the existence of an energetically favourable orientation of the deposit. Much is known now about the latter condition from various models, whether these consider lattice dimensions or electrostatic forces, but very little is known concerning the former condition. The results of the study of amino acids and anthraquinone on mica substrates which had undergone different surface treatments, illustrate the complex mechanisms involved in obtaining a single crystal deposit on the surface of a particular substrate. It is the lack of understanding of exactly how a single crystal deposit grows on a specific substrate which limits the completion of a mechanistic study of the phenomena of epitaxy. Pashley in his 1956 review concluded that information on heteronucleation studies was restricting the development of epitaxial theories and this situation is still applicable today.

As a result of the current work, any definitive model for epitaxy must include a parameter that would explain both the single crystal growth and its subsequent orientation.

The model envisaged would describe both surfaces in terms of a surface energy parameter which contains provisions for the positions and residual charge of the atoms on the surface and how this surface energy would change with temperature. By considering both these surfaces the predicted orientation corresponding to the position of lowest energy could be determined at a particular substrate temperature.

8.3 Suggestions for further work

The observations of epitaxial growth through interfacial layers has important ramifications in the catalyst and semiconductor fields, and far more work would be required in this area. The important preliminary studies would be a more rigorous investigation into the structure of carbon films, prepared under different conditions, and the determination of the exact nature of the upper and lower thickness limits for epitaxial transmission found in this study.

In the light of the existence of structure in the previously thought amorphous interfacial films, the metal films used in some of Distler's investigations (205 - 209) should be re-examined for structural inhomogenities. Also the area of electro-optical materials (195 - 200) has not been considered and an investigation in this field could open exciting possibilities in the understanding and production of optical properties of many materials. For example an understanding of Distlers photo electret properties of anthracene would open up new areas in solid state chemistry.

The unexpected behaviour of many of the amino acids on a sodium chloride substrate, with atmospheric moisture, at specific minimum temperatures requires further investigation, especially with aspartic acid. This compound was found to interact very strongly with water on a rocksalt substrate and the existence of a new mesomeric phase is suggested. Further experiments using larger quantities of materials should be undertaken to examine the possibilities of this new liquid-crystalline phase.

Specific epitaxial orientation of molecules on active substrates may provide a route to the synthesis of stereospecific molecules. Glycine epitaxially deposited onto mica and onto sodium chloride has been chlorinated using chlorine gas and U.V. irradiation. The resulting material was examined for optical activity in water solution (298, 299) and shown to be active. This result is encouraging in suggesting the potential of epitaxy in assymmetric synthesis; and gives some credence to early suggestions by H.C. Urey and others that the first proteins were produced using quartz templates in a primeaval soup, and would also account for the stereo specificity of biologically active molecules.

APPENDIX ONE

(i) Electron Beam Carbon Evaporation

The method of electron beam heating is used for evaporation of carbon when a control on the rate of carbon deposition is required. A beam of electrons are emitted from a hot tungsten cathode and focussed by a positively charged deflector plate onto the end of a 5mm thick carbon rod. The temperature of the carbon rod is controlled either by the charge on the deflector plate or the electron emission from the cathode.

The electron gun used during the course of this study consisted of a tungsten ring cathode with a stainless steel deflector plate held at a 2.5kV negative potential, and control on the temperature of the carbon rod was obtained by a variable cathode current. The construction of the gun is shown in figure A1.

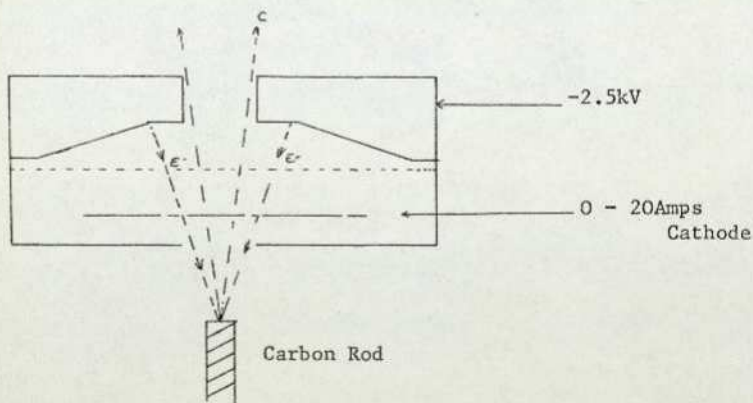


Figure A1

A current of approximately 18 amps was required to produce an electron beam current of 90mA which was sufficient for carbon evaporation.

(ii) Electrical Feed-Throughs

The top-plate of the deposition chamber was designed and constructed in this laboratory. It contained one rotary feed-through, seven high current feed-throughs were designed and constructed by Noakes and Ryan, the basic insulator section was obtained from Vacuum Generators Ltd. The insulator component was silver soldered on to retaining bolts and $\frac{1}{8}$ " copper rod was used for the conductor. This construction is shown in figure A2.

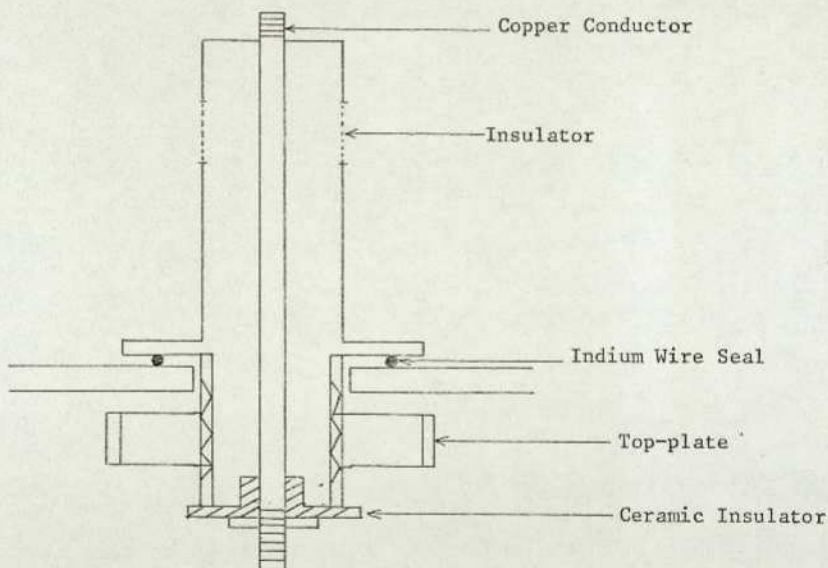


Figure A2

The electrical feedthroughs used for the electron beam source were held on 2" demountable flanges, fixed via coppering seals on previously constructed ports in the side of the baffle valve. These ports were designed in this laboratory and argon welded by Vacuum Generators Ltd.

(iii) Quartz Crystal Film Thickness monitor

This consisted of oscillating two quartz crystals of similar frequency and measuring their frequency difference. One crystal was held in the vacuum chamber, and its oscillator frequency changed with the mass of the crystal and consequently the mass of deposited material.

For calibration, highly pure (99.999%) copper was evaporated from an electron beam heater (shown in figure A3) simultaneously on to the surface of the quartz crystal, and a small piece of (2cm x ½cm) tantalum foil. The new oscillating frequency was recorded, and the copper removed from the tantalum foil, by dissolving it in a known quantity of analar concentrated nitric acid. The copper content of the nitric acid solution was subsequently determined by atomic adsorption spectroscopy.

This process was repeated many times with different amounts of deposited copper. The surface area of the tantalum foil was determined by two independent methods, the first of which was to determine its weight and as its density and mean thickness were known the surface area could be calculated. The second method was to project a shadow of the foil from a photographic enlarger onto the surface of graph paper and knowing the magnification factor the surface area was determined.

A comparison of the densities of carbon and copper yielded a carbon calibration of a frequency change of 100C/S corresponded to a mean carbon thickness of $10\text{\AA}$. An assessment of possible errors at the various stages of calibration resulted in an overall error of between 10 - 20% for films of less than $100\text{\AA}$ thick and between 10 - 15% with films greater than $100\text{\AA}$ thick. The total thickness error, although rather high is well within the limits necessary for a study of this nature.

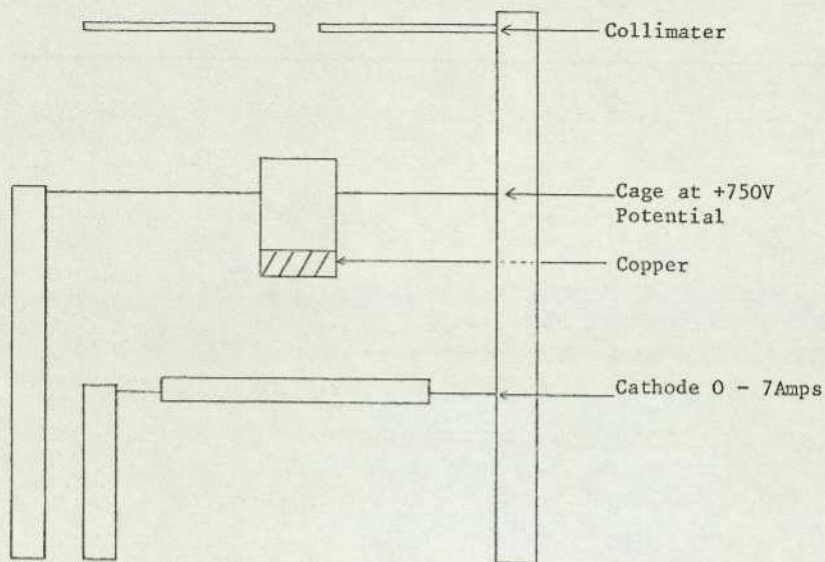
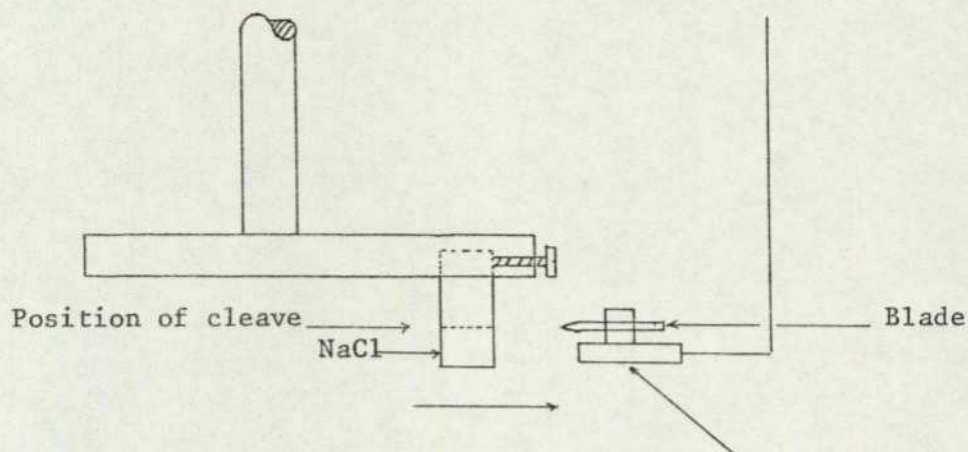


Figure A3

(iv) Vacuum cleaving

This was achieved for crystals of sodium chloride by replacing the shield used in front of the substrate holder (see figure 43(ii)) with a blade, and the sodium chloride crystal was rotated into the blade with sufficient force to produce a clean cleave. This arrangement is shown in figure A4.

For mica specimens the cleave was initiated outside the vacuum chamber, and a piece of cellulose acetate fixed to the upper surface and to a stationary point inside the chamber. On rotation of the specimen the mica cleaved readily and a fresh surface could be prepared.



On rotation the crystal hits the blade, and the STOP ensures that the bottom side breaks off before the blade can come in contact with the majority of the new surface.

Figure A4

(v) Optical Intensity Measurements

To determine the thickness distribution of a carbon covering with the particular electron beam source and collimator arrangement the carbon was evaporated on to the surface of an optically calibrated microscope slide. This was then illuminated from a homogenous source, and the transmitted light intensity measured with a spot photometer. As the light intensity would only vary with the thickness of carbon, and proved to be very sensitive to this, it acted as an excellent indicator for the unhomogenous areas of a deposited carbon film, and only the collimator arrangement which produced a homogenous covering over the desired area was used in subsequent experiments.

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