

THE EPITAXIAL DEPOSITION OF  
CADMIUM SULPHIDE

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### ABSTRACT

Thin films of CdS have been deposited in high vacuum on a variety of single-crystal substrates. They were NaCl(100) and BaF<sub>2</sub>(111) cleaved faces and NaCl(110), NaCl(111), Ge(111) and Si(111) chemically polished faces. The substrate temperature range over which the films were epitaxial was determined by electron microscopy.

A structural analysis of the films showed that they grew with the stable hexagonal wurtzite structure on substrates in (111) orientation whereas substrates in (100) and (110) orientation produced films having the metastable sphalerite structure.

Films containing included grains of a second phase were analysed and the structure and distribution of the grains were determined.

Over certain temperature ranges, epitaxial films with either structure could be prepared free of included grains. According to their temperature of preparation, these films contained a varying number of dislocations, planar defects and vacancy loops.

Some films were annealed in order to determine the effect on their defect content. The content was reduced in films having either structure but a simultaneous transition to the wurtzite structure was promoted in films deposited with the sphalerite structure. Photographic evidence and a brief description of this process are presented.

Epitaxial layers of CdS were readily deposited on Ge(111) substrates but no success was achieved when using Si(111) substrates. It is believed that this may have been due to contamination of the silicon surface whilst under vacuum. The moiré fringe system produced by the CdS(0001)/Ge(111) heterojunction interface is illustrated and the spacing is shown to be that predicted by theory.

Finally, some recommendations are made concerning the course which future work on this subject should take.

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## CHAPTER 1

### INTRODUCTION

The most widely used semiconducting materials are the two group IVb elements, silicon and germanium, and certain members of the two sets of binary compounds formed between the elements of groups IIIb and Vb and between the elements of groups IIb and VIb of the periodic table.

The II-VI compounds are the least exploited of these although an extensive literature exists on their physical and chemical properties. A general review of this has been compiled by AVEN and FRENNER (1967). Many applications require that the material be in the form of a high quality single crystal and it is largely because the II-VI compounds in general are difficult to grow as good single-crystals that they are still only to be found in applications using polycrystalline material. In this context wide use is made of ZnS for phosphors and CdS for photoconducting layers and more recently for field-effect transistors (e.g. NEUGEBAUER et al. 1967).

There are several potential applications for single crystals of the II-VI compounds. Their band gaps lie between 0.02 e.v. (HgTe) and 3.7 e.v. (ZnS) (BUBE, 1969). Some of these (e.g. CdS, ZnS, ZnSe and ZnTe) should, in theory, be suitable for making devices producing visible radiation (MOREHEAD, 1967). This is particularly the case since electron transitions within the band structure of the II-VI compounds are believed to be direct (SEGALL, 1967). This implies that the process of radiative recombination should be more efficient in these semiconductors than in those in which it takes place as a result of an indirect transition. Gallium phosphide, silicon and germanium are semiconductors of the latter type. The piezoelectric properties of the II-VI compounds in general and ZnO and CdS in particular make them suitable for applications using the acoustoelectric effect (section 2.2). Neither Si nor Ge is

Piezoelectric and cannot, therefore, be used.

The development of microcircuitry has resulted in the successful industrial production of thin film single-crystal silicon devices. These films are "epitaxial", a term which describes the situation where there is a simple orientation relationship between the crystal lattices of the film and its substrate. Although several II-VI compounds have been epitaxially deposited on a variety of substrates (section 2.5) the work, generally, has not been well-coordinated. In particular, a great proportion of the studies of these epitaxial films has been concerned with their electrical or optical properties without reference to their crystal structure. Crystalline faults, particularly when associated with impurity atoms, provide traps of varying depths for charge carriers. These greatly affect the electronic properties of the material (BUBE, 1960; 1967). The reverse dependency, that of the structural properties on the electronic properties is, by comparison, very weak. A satisfactory structural analysis which is independent of the electrical character of the material is therefore quite possible. For this reason it is advantageous to begin by studying the crystal and defect structures of these materials and subsequent electrical measurements may then be interpreted in the light of this knowledge. Very little systematic work of this kind has been published. The only detailed structural analyses of defects in thin epitaxial films of II-VI compounds published so far refer to ZnTe (HOLT, 1969a and b), ZnS (WOODCOCK and HOLT, 1969; HOLT and WOODCOCK, 1970) and CdS (WILCOX and HOLT, 1969). Both the zinc compounds are stable in the cubic sphalerite structure (section 2.1) in the temperature range of deposition. This thesis is mainly concerned with such an analysis of epitaxial CdS films which are stable in the hexagonal wurtzite structure (section 2.1) over a similar temperature range. No structural analyses of epitaxial films of II-VI compounds

stable in the hexagonal wurtzite structure have so far been published.

The work reported here was directed towards the production of single-crystal thin films suitable for making devices operating in the acoustoelectric mode. The layers were deposited in high vacuum and the source was heated by an electron beam. ZnO and CdS are two of the most promising materials for this application. Some experiments were initially carried out using ZnO but it became apparent that the apparatus was not suitable for use with this compound. This was because the layers produced from ZnO powder were found to be nearly devoid of oxygen when grown in vacua below  $10^{-3}$  torr, a condition necessary for the operation of the electron beam evaporator. It was therefore decided to use CdS instead as a source material.

Thin CdS layers were epitaxially grown on a variety of single crystal substrate faces and their structural properties were studied by transmission electron microscopy. The crystal faces used were the (100), (110) and (111) faces of sodium chloride (NaCl), the (111) cleavage face of barium fluoride ( $\text{BaF}_2$ ) and also the (111) faces of both germanium (Ge) and silicon (Si). A very few layers were also grown on the (0001) face of CdS but, owing to a lack of suitable substrate material and the difficulty of obtaining specimens for transmission electron microscopy, no significant results were obtained.

It has already been reported that CdS films have the sphalerite structure if grown on (100) oriented NaCl substrates and the wurtzite structure if grown on (111) oriented mica and Ag substrates (CHOPRA and KHAN, 1967). It was decided to determine whether this result applied to films grown on the NaCl and  $\text{BaF}_2$  substrates mentioned above and, if so, to compare the defect content of films having the two different structures.

The  $\text{BaF}_2$  (111) substrates were used for two reasons; a) they can be prepared by cleaving in vacuo producing very clean (111) oriented substrates, and b) they enable the substrate temperature range investigated to be extended to about  $550^\circ\text{C}$ . which is beyond that possible for NaCl.

The difference between the interatomic distances of atoms in the (0001) plane of wurtzite CdS and atoms in the (111) plane of  $\text{BaF}_2$ , expressed as a percentage of the mean of these two values, is 5.8% and for CdS (0001) and Si (111) it is 7.4%. The corresponding figures for CdS (0001) on NaCl (111) and Ge (111) are 3.8% and 3.6% respectively. All these values are based on measurements made at room temperature. The  $\text{BaF}_2$  and Si and the NaCl and Ge thus form two pairs each having a similar value for the misfit with respect to the (0001) plane of CdS. Because of this and since all the substrate materials have cubic symmetry, (although they do have different crystal structures) it was hoped that the information obtained from the structural analysis of the epitaxial films grown on the ionic substrates could be usefully compared with those grown on the two semiconductors Ge and Si.

Transmission electron microscopy was used exclusively for all the structural analysis since this technique is capable of great resolution at high magnification. The associated technique of dark field electron microscopy also provides a means of removing ambiguities in the interpretation of bright field images (section 2.6).

The work is presented in five parts. Chapter 2 which follows is a survey of the most relevant literature and also includes a brief statement of some of the more important parameters which have been found to influence the growth of thin films. A section is also devoted to a discussion of diffraction patterns. This is intended to make possible a more concise analysis of results in Chapter 5. Chapters 3, 4 and 5 are concerned with the experimental procedure used,

the results obtained and to a discussion of these results. Finally a short chapter deals with general conclusions and recommendations for further work.

## CHAPTER 2

### BACKGROUND INFORMATION AND A SURVEY OF RECENT WORK

The literature of the II-VI compounds covers a very wide range. Much of this information has been gathered over the last twenty years during which time, interest has been mainly devoted to the synthesis of large single crystals and to the numerous electrical properties which these compounds display. AVEN and PRENNER (1967) have compiled a comprehensive review of the information concerning the physics and chemistry of the II-VI compounds. Consequently, this survey is confined to those topics which are most pertinent to the work reported here.

#### 2.1. THE CRYSTAL STRUCTURE OF THE II-VI COMPOUNDS

Many of the useful semiconducting materials have closely related crystal structures. These structures are built up in such a way that each atom is tetrahedrally co-ordinated by four others. The basic structural unit is a tetrahedron of four atoms containing one atom at its centre as is shown in fig. 2.1. By joining other tetrahedra to one another in a particular way, the assembly of atoms can be extended to form the diamond structure which has cubic symmetry. It can be seen from fig. 2.2 that it is an f.c.c. structure containing four extra atoms at positions within the unit cell. Apart from diamond, both germanium and silicon have this structure.

The "adamantine structures" are closely related to the diamond structure. These are the sphalerite and wurtzite structures which contain equal numbers of two types of atom and are constructed from the basic tetrahedron shown in fig. 2.1. The sphalerite structure has its atoms at the same positions as the diamond structure and therefore also has cubic symmetry. In this case, however, each atom of one kind is tetrahedrally co-ordinated by atoms of the other kind. This is illustrated in fig. 2.4. The wurtzite structure differs

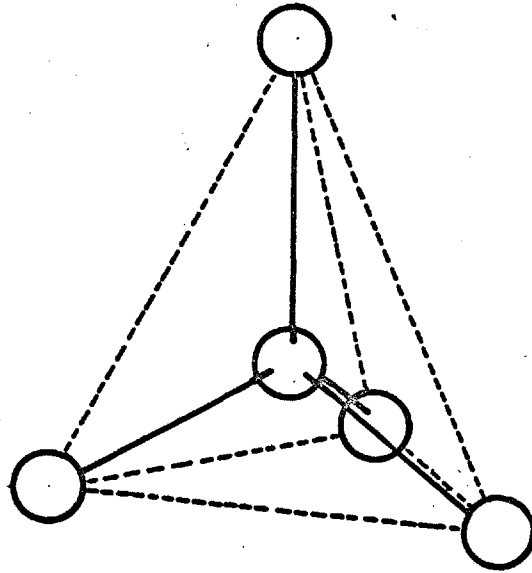


Fig. 2.1 A diagram showing the tetrahedral co-ordination of one atom by its four neighbours.

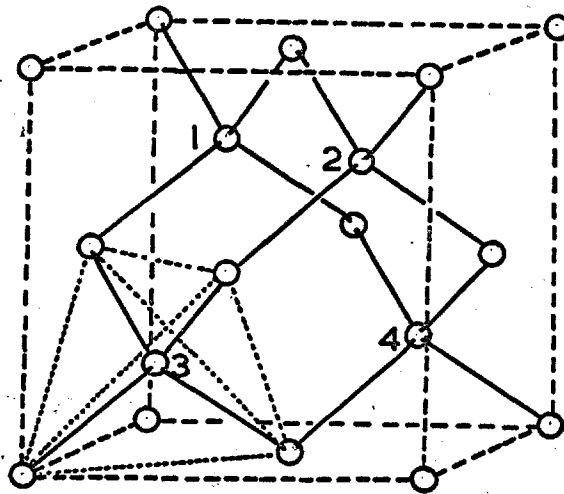


Fig. 2.2 The unit cell of the diamond structure. A tetrahedron of atoms like that shown in Fig. 2.1 is outlined. The atom in the center of the tetrahedron is marked '3'. The atoms 1, 2, 3 and 4 all lie inside the cube. The rest of the atoms occupy the f.c.c. positions.

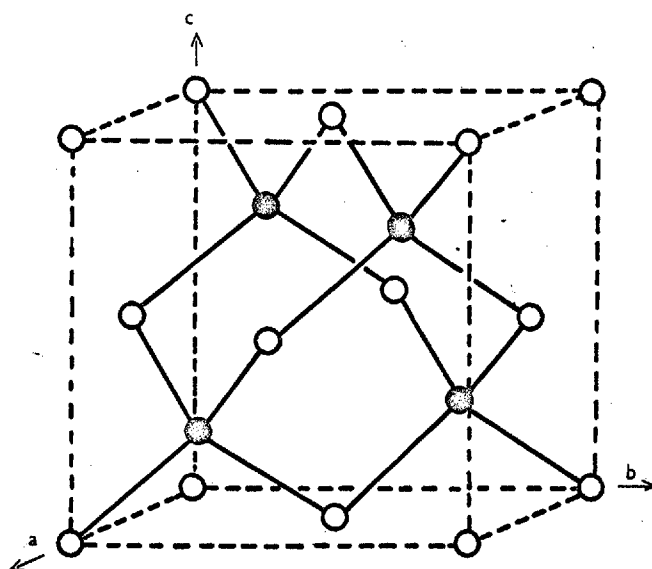


Fig. 2.3 THE UNIT CELL OF THE SPHALERITE STRUCTURE

Open circles represent metal atoms and solid circles represent non-metal atoms. The orthogonal crystallographic axes are denoted by a, b and c.

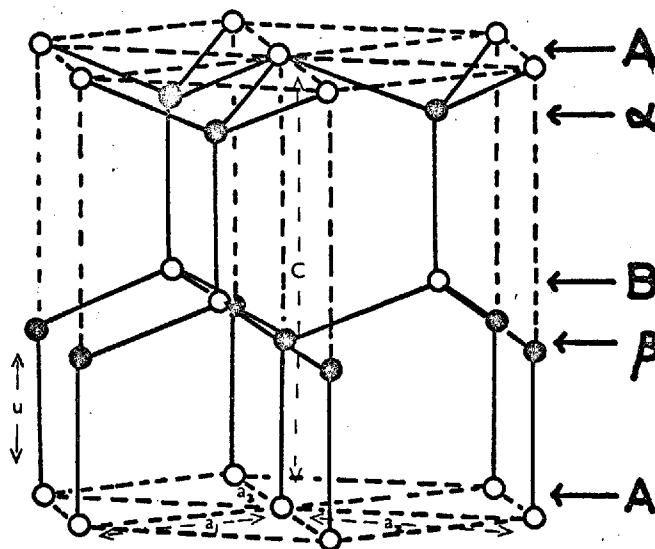


Fig. 2.4 THE UNIT CELL OF THE WURTZITE STRUCTURE

Open circles represent metal atoms and solid circles represent non-metal atoms. Roman letters indicate layers of metal atoms and Greek letters indicate layers of non-metal atoms. The crystallographic axes are denoted by  $a_1$ ,  $a_2$  and  $c$ , and the interatomic spacing of atoms of different types is denoted by  $u$ .

from the sphalerite structure only when next-nearest neighbours of the same atom type are considered. The wurtzite structure has hexagonal symmetry and is illustrated in fig. 2.3 and it can be seen that it is based upon the h.c.p. lattice.

The relationship between the diamond and the adamantine structures is discussed by EVANS (1964).

### 2.1.1. THE ATOMIC ARRANGEMENT IN II-VI COMPOUNDS

All the II-VI compounds in their stable state at room temperature have one of the two crystal structures illustrated in figs. 2.3 and 2.4. Either structure can be considered as two interpenetrating h.c.p. or f.c.c. lattices and, in a perfect crystal, each lattice is occupied entirely by the atoms of one element.

In the wurtzite structure of CdS, the atoms occupy the following positions:-

$$\text{Cd at } (0,0,0); \left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$$

$$\text{and S at } (0,0,u); \left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2} + u\right)$$

where  $u$  is almost exactly  $\frac{3}{8}$ . The co-ordinates are given in terms of  $a$  and  $c$  along the  $a_1$ ,  $a_2$  and  $c$  axes. The two sublattices are seen to be separated by the lattice vector  $(0,0,u)$ . The lattice parameters for this structure are  $a = 4.1368 \text{ \AA}$  and  $c = 6.7163 \text{ \AA}$  (ROTH, 1967).

The atoms in the CdS sphalerite structure lie at the following sites:-

$$\text{Cd at } (0,0,0); \left(0, \frac{1}{2}, \frac{1}{2}\right); \left(\frac{1}{2}, 0, \frac{1}{2}\right); \left(\frac{1}{2}, \frac{1}{2}, 0\right)$$

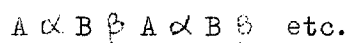
$$\text{and S at } \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right); \left(\frac{1}{4}, \frac{3}{4}, \frac{3}{4}\right); \left(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}\right); \left(\frac{3}{4}, \frac{3}{4}, \frac{1}{4}\right)$$

The co-ordinates are given as fractions of the lattice parameter along the  $a, b$  and  $c$  axes. In this case, the sublattices are separated by the lattice vector  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$  and the lattice parameter is  $a = 5.818 \text{ \AA}$  (A.S.T.M. index).

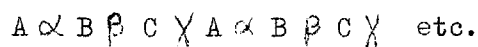
The magnitude of the lattice vectors separating the two sublattices in the sphalerite and the wurtzite structures are identical

if  $u$  is exactly  $\frac{3}{8}$ . For all the II-VI compounds, the vector is very close to the ideal value of  $\frac{3}{8}$  which corresponds to regular tetrahedral co-ordination (ROTH, 1967).

A more convenient description of the two structures is that based upon the stacking of double layers. Each double layer consists of one layer from each of the sublattices. The possible positions for atoms in the layers stacked one on top of the other can be denoted by the letters A, B and C (or  $\alpha$ ,  $\beta$  and  $\gamma$  depending on which atom species is being considered). All the atoms in a particular layer occupy either an A site a B site or a C site. The relative positions of these atomic sites is shown in fig. 2.5. Simple, regular alternating sequences may be constructed from layers occupying either of two positions, e.g. ABABAB etc., or from layers in all three positions e.g. ABCABC etc. On this basis, the wurtzite structure may be represented by the following sequence:-



where the Roman letters represent the atoms from one sublattice and the Greek letters represent those from the other sublattice. The sphalerite structure can be represented in the same way, but in this case the layer sequence repeats itself after three double layers:-



These layers are the  $\{0001\}$  planes in the wurtzite structure and the  $\{111\}$  planes in the sphalerite structure.

The bonding between one layer of atoms and its two adjacent layers is divided unequally. By referring to fig. 2.3, it can be seen that the tetrahedral bonding of an atom in the  $\alpha$  layer is obtained from bonds to three atoms in the A layer and to only one atom in the B layer. It is surmised that cleavage cracks always propagate between layers joined by only one bond per atom and that chemical attack invariably leaves a layer of atoms at the surface each having

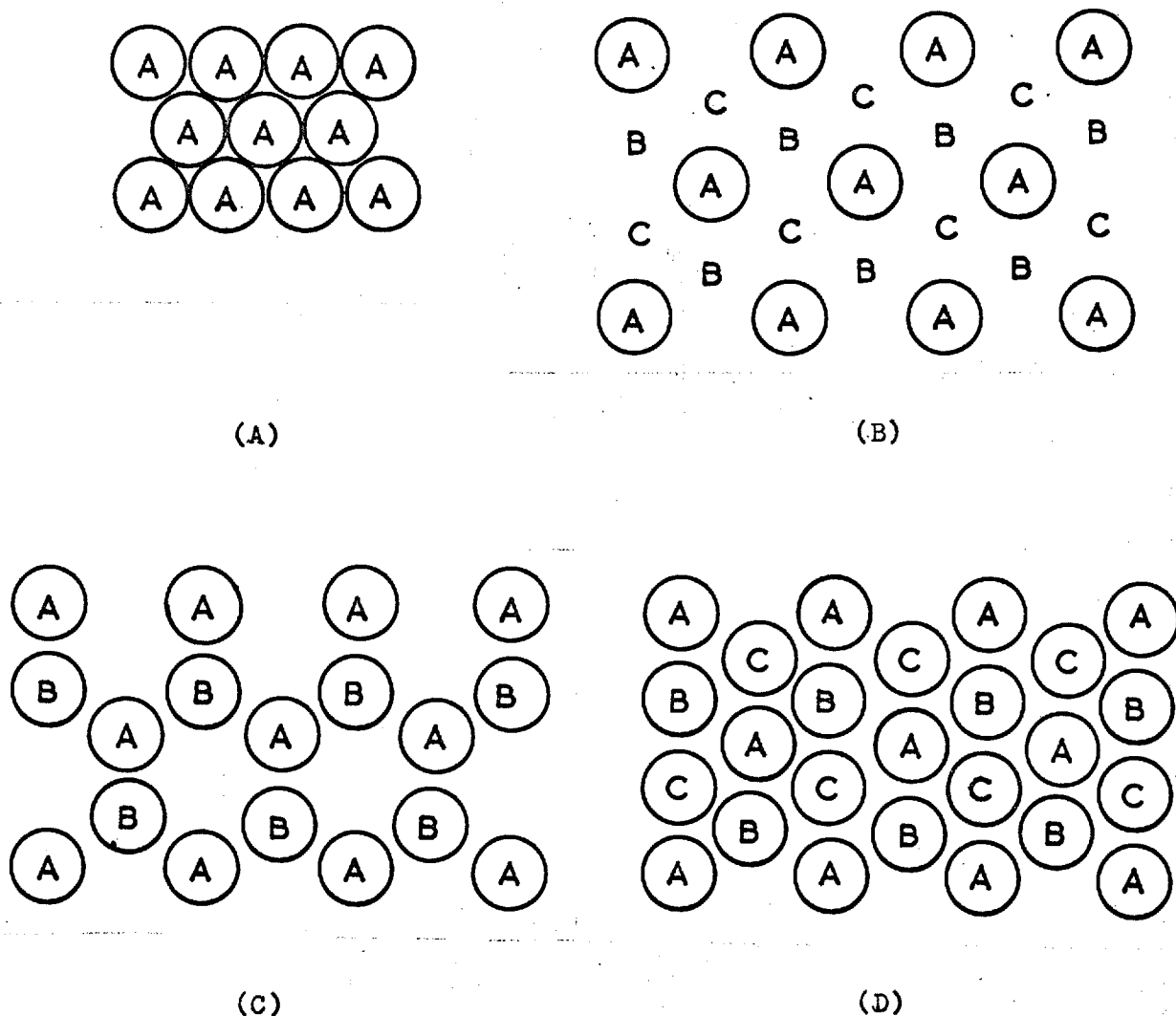


Fig. 2.5 EXPLANATION OF NOMENCLATURE USED IN DESCRIBING STACKING SEQUENCES.

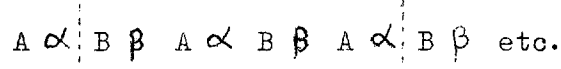
- (A) Close packed array of atoms on A sites.
- (B) Relative positions of the A, B and C sites.
- (C) Double layer stacking sequence on A and B sites only. The wurtzite structure.
- (D) Triple layer stacking sequence on A, B and C sites. The sphalerite structure.

three bonds to atoms in the layer beneath.

The spacings of nearest neighbour atoms in material with either the wurtzite or the sphalerite structure are very nearly the same for those II-VI compounds which can be prepared in both forms (ROTH, 1967). Consequently the fraction of the space available which is occupied by the atoms of the material (or "packing fraction") is nearly identical for each structure. A further consequence of this is that the binding energy for crystals of the same material with either structure is nearly equal. The occurrence of crystals having structures with repeat distances longer than the two shown above is believed to be partly due to this small difference in binding energy (ROTH, 1967). These structures are known as polytypes and ZnS has been found to form polytypes with very large unit cells. In some cases the structures have been found to repeat after as many as a hundred layers (STEINBERGER and MARDIX, 1967). Also related to the small difference in binding energy is the fact that a number of II-VI compounds undergo a phase transformation from one structure to the other at high temperature (ROTH, 1967).

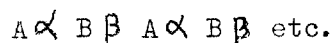
#### 2.1.2. THE POLAR CHARACTER OF THE II-VI COMPOUNDS

An important property of these compounds is the absence of a centre of symmetry in both crystal structures. A defect which is peculiar to non-centrosymmetric crystals is that of "polarity reversal". The stacking sequence of the wurtzite structure is represented, as shown in section 2.1.1., by the sequence:-

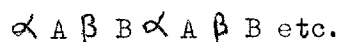


The Roman letters now stand for metal layers and the Greek letters for non-metal layers. The dotted lines represent the intersection of  $\{0001\}$  planes with the plane of the page. It can be seen that if the crystal were to be cleaved on these planes, the face exposed to the right of the first dotted line would consist of metal atoms and the

face to the left of the second dotted line would consist of non-metal atoms. A "polarity reversal" from one region of a crystal to another results in the stacking sequence changing from:-



to:-



It can be seen that the stacking sequence in the two regions are in antiphase with one another. A section through a crystal on an (0001) plane containing regions stacked in antiphase would reveal a face containing areas of metal atoms and areas of non-metal atoms. The boundary between these regions and the matrix is called an "antiphase domain boundary" and the volume of crystal in which the stacking sequence is reversed is the "antiphase domain". The same terminology applies to the sphalerite structure. An analysis of the geometry of this situation has been made by HOLT (1969a) in which it is pointed out that two antiphase domain boundaries (A.P.Bs.) cannot meet. This arises from the fact that the junction of two A.P.Bs. defines three regions of crystal, each stacked in antiphase with respect to its neighbours. Since there are only two possible stacking modes for the II-VI compounds, it follows immediately that two of these three regions thus defined must be stacked "in phase", hence there can be no A.P.B. between them. This implies that A.P.Bs. form continuous loops at a free surface or else pass out of the sides of a crystal. The antiphase domains can be easily detected at (0001) or (111) surfaces by almost any etch (WILSON 1966) since the metallic and non-metallic faces have very different corrosion characteristics (WAREKOIS et al, 1962; REYNOLDS and CZYZAK, 1960; BAKHRADZE and ROM-KRICHEVSKAYA, 1963; WOLFF et al, 1964). The metallic and non-metallic faces at the ends of the  $[0001]$  and  $[111]$  polar axes are normally distinguished by the use of (0001) or (111) indices for the metallic face and (000 $\bar{1}$ ) and

( $\bar{1}\bar{1}\bar{1}$ ) for the non-metallic face.

It is possible to correlate the etching behaviour with the atom species at the face by means of x-ray diffraction (WAREKOIS et al. 1962). Having obtained this correlation, the orientation of a crystal can then be determined by observing the etching characteristics over its surface. This technique has been commonly used on bulk single crystals, for example by WAREKOIS et al. (1962), BAKRADZE AND ROM-KRICHEVSKAYA (1963) and HEMMAT and WEINSTEIN (1967). It has also been used for determining the polarity of thin films of CdS by VECHT et al. (1966) and ROZGONYI and FOSTER (1967).

### 2.1.3. THE PROPERTIES OF THE INTERFACE BETWEEN A FILM AND ITS SUBSTRATES.

The geometry of the interface between the substrate and the thin film is of particular interest where the thin film and the substrate are different semiconducting materials. The interface in this case is called a heterojunction to distinguish it from a homojunction which exists between two differently doped regions of the same semiconductor. Heterojunctions formed with CdS as one of the components have been prepared by several people including AVEN and GARWACKI, CdS/ZnTe (1963), MUELLER and ZULEEG, CdS/CdTe (1964), AVEN and COOK, CdS/ZnTe (1961) and KANDILAROV and ANDREYITCHIN, CdS/CdSe (1965).

In general there is a lattice mismatch between the two components at the interface which is accommodated by a network of dislocations. The dislocations have charged cores where the unpaired, or "dangling", bonds terminate. An analysis of the geometry of the crystal structure at the interface between two materials with the sphalerite structure has been made by HOLT (1966a) for the (100), (110) and (111) planes. The equilibrium configuration for the dislocations is a network whose mesh size is inversely proportional to the lattice mismatch.

The direct observation of these networks by electron microscopy

is possible. However, it is frequently rendered rather difficult by the superposition of moiré fringes caused by the electron beam being diffracted by each crystal lattice in turn. This fringe spacing is also dependent upon the lattice mismatch. Moiré patterns are similarly generated when there is a slight angular displacement between the lattices of the two crystals although only those produced by two lattices in parallel alignment are relevant here. A complete analysis of the contrast obtained with both misfit dislocations and moiré patterns in electron micrographs is given by HIRSCH et al. (1965) and BASSETT et al. (1958 a and b).

The spacing of a moiré fringe system, where there is no rotation between the two lattices, is given by:-

$$D_m = \frac{d_1 d_2}{|d_1 - d_2|} \quad (1)$$

where  $d_1$  and  $d_2$  are the spacings of the electron diffracting planes in the two crystal structures which are giving the moiré pattern. If  $\delta$  is the misfit between the two lattices then  $\delta$  is given by the relation:-

$$\delta = \frac{2(d_1 - d_2)}{d_1 + d_2} \approx \frac{d_1 - d_2}{d_1} \text{ if } d_1 \approx d_2 \quad (2)$$

The spacings of the misfit dislocations is given by:-

$$D_d = \frac{|b|}{\delta} \quad (3)$$

where  $b$  is the burgers vector of the dislocations.

It can also be seen that:-

$$D_m = \frac{d}{\delta} \quad (4)$$

where  $d$  is either  $d_1$  or  $d_2$  depending upon the approximation made in (2). This means that if  $|b| = d$ , then the spacing of the misfit dislocation network and the moiré fringe systems will be the same.

They will also be coincident only if, in addition, the lattice planes giving the moiré pattern are parallel to the dislocation lines.

## 2.2. THE ACOUSTOELECTRIC EFFECT

When a lattice vibration, or acoustic wave passes through a material, it is coupled with a localised variation in the electric field which moves in phase with, and in the same direction as the acoustic wave.

The electrical effect which this field variation causes depends upon the electrical conductivity of the material. If the free electron concentration is high, as it is in a metallic conductor, the field variations are immediately nullified by the movement of charge and no net field variation can be detected. In other words, the field inside a conductor is zero. If the free electron concentration is zero or very low, as in an insulator, the electrons are tightly bound and hence there is no variation in the charge distribution in the material as the wave moves by, i.e. the divergence of charge in an insulator is zero. However, at intermediate values of free electron concentration, the electrons are bunched together to form high field regions by the acoustic waves and they move through the crystal in phase with them. This "electro-mechanical" coupling of acoustic waves and electron bunches is greatly enhanced if the material is "piezoelectric". A piezoelectric material is one whose crystals exhibit electric charges over their surface when subjected to mechanical stresses, and undergo dimensional changes along certain crystallographic directions when placed in an electric field (CADY 1946).

By applying a D.C. electric field across the material in the direction in which the acoustic wave is travelling, the electrons are accelerated. If the electron velocities in the direction of propagations of the wave are less than the velocity of sound in the material, energy is drained from the acoustic wave and given to the

electrons, but if the electrons are accelerated to a speed greater than the local speed of sound, energy is fed from the electric wave to the acoustic wave. Net amplification of the acoustic wave takes place when the energy transferred to it from the electric wave exceeds the losses it incurs in passing through the material. This is known as the "acoustoelectric" effect.

A number of mathematical treatments of this effect exist (WHITE, 1962; HUTTON and WHITE, 1962; EINSBRUCH, 1965; WANG, 1966). They are all based on a model first applied to oscillating fields in media by KYAME (1949) who subsequently modified it to take account of conductivity (KYAME, 1954). The mathematical treatments listed above all make simplifying assumptions, one of which is that there is a linear relationship between the acoustic and the electric components. This restricts the model to small signal cases only. Another simplification is that only one dimensional models are considered. Unfortunately, a number of the observed effects are nonlinear since, under acoustic gain conditions, the signals generated are frequently very large. A nonlinear analysis was used by MOORE (1967) when studying current fluctuations in the saturation current of a CdS crystal.

All the II-VI and III-V semiconducting compounds are piezoelectric and are therefore capable of generating an acoustoelectric effect. The II-VI compounds, CdS and ZnO, have high piezoelectric constants ( $e = 11.6 \text{ coulombs/m}^2$  for CdS and up to  $36 \text{ coulombs/m}^2$  for ZnO) which means that the electromechanical coupling referred to above is efficient. ZnO is theoretically the better material since both the piezoelectric constant and the speed of sound are higher in this than in CdS. Material problems with ZnO have restricted most of the research to CdS which is, by comparison, easy to obtain in a suitable form. However, McFEE (1963) made some measurements on single crystals of

ZnO and MICKELSEN and KINGERY (1966) and FOSTER and ROZGONYI (1966) have prepared some fibre textured thin films of ZnO which exhibit acoustoelectric properties.

An effect akin to the acoustoelectric effect was predicted by WEINREICH (1956) who attempted, unsuccessfully, to amplify ultrasonic waves in a non-piezoelectric semiconductor. It was hoped that the energy transfer would take place between the electric field and the acoustic wave using the deformation caused by the electric potential to couple them.

In 1961, HUTSON et al. succeeded in amplifying ultrasonic waves in CdS. It was found that the threshold field between acoustic loss and acoustic gain did in fact exist. A saturation current which was unstable, was also found. The instability began as the threshold field was reached and consisted of rapid current fluctuations. MOORE (1967) and HAYDL (1967) have studied these current oscillations. HAYDL analysed large-scale fluctuations which were attributed to the passage of electron bunches and their associated acoustic flux domains from the cathode, where they were created, to the anode where they were destroyed. MOORE (1967) pointed out that there are two types of current fluctuations one of which is that investigated by HAYDL. The other is due to amplification of components in the "white noise" spectrum existing inside the crystal. MOORE investigated this and decided that the domains of acoustic flux and electron bunching associated with the random noise were very small by comparison with the larger kind investigated by HAYDL. They were continually being created by the acoustoelectric effect and destroyed by lattice scattering. Like the large scale fluctuations, they drift towards the anode at the velocity of sound in the crystal.

Unfortunately, this ability to amplify random noise is a disadvantage when wishing to use these devices as wide-band width

amplifiers. However, a very promising application is the amplification of surface waves. This is ideally suited to thin films and microcircuit technology since the useful signals are transmitted in the surface layers of the semiconductor. The relatively poor semiconducting properties so far obtainable with CdS as compared with Si or Ge can be partly overcome by using a composite device. In theory a layer of CdS is deposited on a thin Si substrate. The electric field of a signal passing across the Si penetrates the CdS interface and piezoelectric coupling occurs between the electric waves in the Si and the corresponding stimulated acoustic waves in the CdS. In practice the disadvantage is that the voltages required to operate the Si part and the CdS part are very different. For a device about 1 cm long the voltages are about 10 volts for the Si and 2 kilovolts for the CdS. This may be overcome by insulating the CdS from the Si by a narrow layer of insulator. A better solution to these problems would be to improve the properties of the CdS so that either the CdS and Si have the same operating voltages or the Si substrate is unnecessary. These devices have other advantages, particularly the ease with which wave guides and delay lines may be constructed. Their potential uses are discussed in some detail by COLLINS and HAGON (1969).

Since the magnitude of the acoustoelectric effect depends upon the free electron concentration, any factor which affects this concentration will also affect the acoustic gain. Differences in the behaviour of semiconducting and photoconducting CdS have been observed by HAYDL (1967) and MOORE (1967). GREEBE (1966) and KIKUCHI et al. (1966) have investigated the effect of illumination on the acoustoelectric properties of photoconducting CdS. KIKUCHI et al. (1966) also investigated the effect of temperature on the gain of a CdS device and it was found that this reached a maximum at a particular temperature.

Devices made from material containing antiphase domains exhibit reduced gain. This is because the polarity of the crystal structure reverses across the boundary and produces discontinuity in the electromechanical coupling as the acoustoelectric wave front passes through it. As a result, a percentage of the wave is reflected at the boundary and consequently a crystal containing antiphase domains has an effective piezoelectric constant which is less than that for a perfect crystal. This has been observed by WILSON (1966) and ROZGONYI and FOSTER (1967).

Other crystallographic defects like dislocations and stacking faults, also destroy the electrical homogeneity of the material. They provide trapping centres of varying depths for charge carriers and the characteristics of any device dependent upon the carrier density are thereby rendered very temperature-dependent and photosensitive (BUBE, 1960, 1967). The effect of charge carrier trapping on the acoustoelectric effect in CdS has been studied by GREEBE (1966).

Thus, the elimination of as many defects as possible is very important if a crystal is to be suitable for use as an acoustoelectric device. The intrinsic conductivity is also a parameter which must be controlled if reproducible results are required. These criteria are most easily reached with bulk crystals and for this reason the majority of the work with acoustoelectric devices has been performed with these. Little progress has yet been made with single-crystal thin-film devices since their properties have not been reproducible. In general, thin films of II-VI compounds contain many faults and this is one of their shortcomings which must be overcome before good quality thin-film devices can be produced.

### 2.3. GROWTH OF THE II-VI COMPOUNDS FROM THE VAPOUR PHASE

The growth of crystals from the vapour phase involves the two important physical processes of evaporation of the source material and

condensation of the crystal material. In the case of II-VI compounds the processes are complicated by the fact that they dissociate when vaporised.

The vapours of the group II metals are always monatomic whereas the vapours of the group VI non-metals usually exist as diatomic molecules. Species other than the diatomic molecule are only found in quantity at high temperatures and pressures (GOLDFINGER and JEUNEHOMME, 1963).

The transition from the solid to the vapour state for CdS obeys the reaction:



The law of mass action applies to this reaction and it is possible to suppress evaporation of the solid by increasing the relative vapour pressures of either gaseous component (SOMORJAI and JEPSEN, 1964; SOMORJAI, 1962; SOMORJAI and STEMPLE, 1964; SOMORJAI and LESTER, 1965; KROGER, 1964).

It is found that the equilibrium composition of II-VI compounds is a function of the partial pressures of the two elements and of the temperature during crystal growth (GOLDFINGER and JEUNEHOMME 1963).

A deficiency in one or other of the component elements is usually accommodated by vacancies on the appropriate sub-lattice (sec. 2.1) but can also be compensated for by incorporating the extra atoms of the excess element as interstitials within the crystal structure.

The general formula for the compounds can be written as  $\text{MX}_{(1-x)}$  or  $\text{M}_{(1-x)}\text{X}$  where  $x$  is the fractional deficiency in either X or M. Crystals which have the exact composition, MX, are said to be stoichiometric.

Conversely, the relative vapour pressures of the elements over a crystal are functions of the crystal temperature. Thus, in a crystal growing system in which the source and substrate temperatures

are different and where, for example, the vapours are carried along by an inert gas, the composition of the growing crystal will differ from that of the source and the excess of one of the two elements is carried away by the transport gas. Systems in which the vapour pressures can be altered by the removal or addition of the active gases may be described as "open" systems. The vacuum deposition of thin films is a technique using an open system. The pressures are never allowed to reach equilibrium since the vapours are continually being pumped away. In a completely enclosed system, like the technique for growing crystal boules in sealed quartz envelopes, the relative vapour pressures adjust themselves until the source material and the depositing crystal material have the same composition.

If the crystal composition is to be controlled during growth, it must be possible to regulate the partial pressures of the two elements. This is achieved in closed systems by ensuring that the initial charge is of the required composition. In open systems using vapour transport techniques, the vapour pressures can be controlled directly and continuously. This can also be achieved during vacuum evaporation of thin films by co-evaporating the compound together with an excess of the appropriate element. This can be done from a single source, or, more controllably, from two separate sources. Thin films of CdS have been prepared in both ways. A mixed source of CdS and S was used by WEBER (1966) and two separate sources were used by PIZZARELLO (1964) and FOSTER and ROZGONYI (1966). It was found possible to control the resistivity and, therefore, by implication, the stoichiometry of the film using either technique. The non-stoichiometry of CdS thin films was investigated by READEY (1966). A direct correlation between the excess Cd in the film and their electrical resistivities was established.

## 2.4. SOME PARAMETERS WHICH AFFECT THE GROWTH OF EPITAXIAL FILMS

### 2.4.1. GEOMETRICAL CONSIDERATIONS

The early stages of growth of epitaxial metal films have been studied in detail, particularly in the cases of gold deposited on ionic crystals, molybdenite and mica substrates (MATTHEWS, 1959 and 1965; MATTHEWS and ALLISON, 1965; MATTHEWS and GRUNBAUM, 1965; NEUGEBAUER C.A., 1969). Continuous observations of the nucleation and growth of thin films were made by PASHLEY et al (1963; 1964; 1965 a and b); CHOPRA (1966) and NEUGEBAUER (1969) which enabled the mechanisms to be identified by which defects are introduced into a growing film. It was found that, although the initial nuclei were defect free, dislocations were formed at an early stage of growth principally as a result of the mismatch between the nuclei and between the substrate and the film structures. In theory, only films epitaxially grown on substrates with the same lattice parameters can be defect free. Practical examples of this have only been obtained for Si deposited on Si substrates (BOOKER and UNVALA, 1965).

Films deposited from the vapour phase begin their growth from many points on the substrate at once and other defects besides dislocations may arise from geometrical considerations when these separately growing regions meet. The work of MATTHEWS et al. referred to above, deals with defects produced in f.c.c. structured films by this means. The most important of these in relation to the II-VI compounds are the twins formed by the process of double positioning when a material with the f.c.c. structure is deposited on a substrate with the f.c.c. lattice in (111) orientation. The (111) face of the substrate has a 6-fold axis of symmetry perpendicular to the surface whereas the  $[111]$  direction in the f.c.c. structure of the film is only a 3-fold axis of symmetry. This enables the cubic film to grow

in two non-equivalent orientations which have an angular separation of  $180^\circ$  and are therefore twin-related with the substrate normal as the twin axis.

A similar type of double positioning may occur in thin films with a hexagonal crystal structure when deposited on a (100) oriented substrate with f.c.c. structure. The structurally symmetrical positions of the substrate lie  $90^\circ$  apart since the  $[100]$  direction is a 4-fold axis of symmetry. Material with a hexagonal crystal structure commonly grows with the (0001) basal plane parallel to the (100) substrate surface with close packed directions in both the thin films and the substrate lying parallel to one another. Since the close packed  $\langle 11\bar{2}0 \rangle$  directions in the hexagonal structures are  $60^\circ$  apart and the close packed  $\langle 110 \rangle$  directions in the f.c.c. structure are  $90^\circ$  apart, there are two non-equivalent epitaxial orientations which are separated by a rotation of  $90^\circ$  about the substrate normal. In this case the two orientations are not twin-related (WOODCOCK and HOLT, 1969). Both types of double positioning are discussed in greater detail in sec. 2.6. since they are often found in epitaxial layers of II-VI compounds.

#### 2.4.2. THE EFFECT OF THE SUBSTRATE TEMPERATURE AND THE RATE OF DEPOSITION

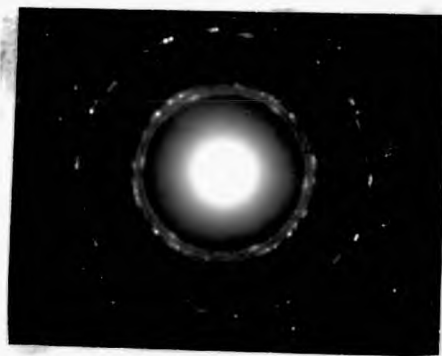
It has frequently been found that an increase in the growth rate causes a decrease in the degree of orientation of a thin film (KALINKIN et al., 1962; SLOOPE and TILLER, 1962; KRIKORIAN and SNEED, 1966). The rate of elimination by a process of annealing of defects incorporated into the film during growth is temperature dependent and the arrival of new material will tend to bury these defects in the film unless their movement to a free surface is sufficiently rapid. (MATTHEWS, 1959; NEUGEBAUER, 1969). In apparent contradiction to this, MATTHEWS (1959) found that the quality of Au, Ag and Cu films.

deteriorated if the deposition rate onto NaCl (100) substrates was too slow. It was found that under these conditions, the nucleation density is low and each nucleus reaches on appreciable size before coalescence begins. Reorientation and recrystallisation is more difficult in this case, since the quantities of material and the distances over which diffusion must take place are large. This means that for metals, at least, a high nucleation density and a high surface mobility of atoms, implying high deposition rates and high substrate temperatures, are conducive to good epitaxy.

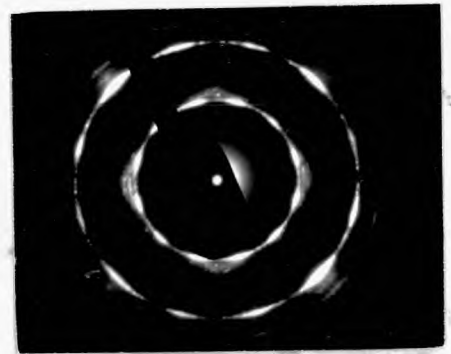
An increase in the substrate temperature should therefore be accompanied by an improvement in the structural quality of the epitaxial layer. Generally, the temperature range over which an improvement may be obtained is limited at the upper end, either by volatilisation of the substrate or by the re-evaporation of the depositing material. This situation is further complicated for II-VI compounds by the possibility of obtaining mixtures of both the sphalerite and the wurtzite phases in particular substrate temperature ranges.

#### 2.4.3. THE "R" VALUE

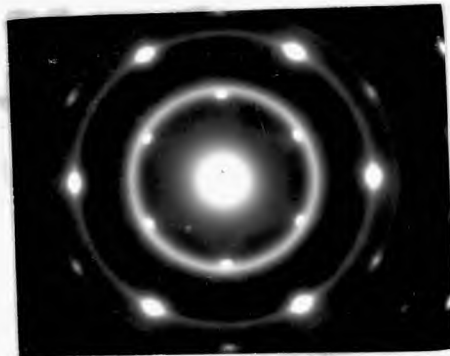
A convenient way of plotting film structures as a function of substrate temperature was devised by INO et al. (1964). A parameter, R, was defined, which roughly represents the fraction of epitaxial material. The values for R are assessed by eye from diffraction patterns of the thin films. The R-value for any film is given one of five values which lie between 0 and 100 and are 25 apart (fig. 2.6). As will be seen in the results to be presented below, values of R different from 0 and 100 only occur in narrow ranges of temperature when the film structure is changing rapidly. Therefore the poor definition of the degree of orientation in partially oriented films does not significantly affect the conclusions drawn from the experiments.



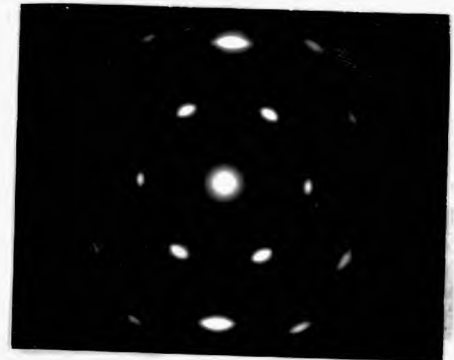
R = 0



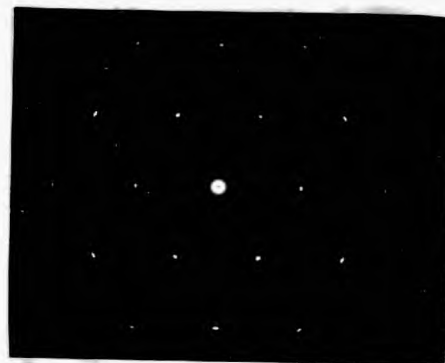
R = 25



R = 50



R = 75



R = 100

Fig. 2.6 THE FIVE "R-VALUES" FROM 0 TO 100

The diffraction patterns illustrate the standards applied when assessing the degree of monocrystallinity.

If a more quantitative assessment of film structure is required in regions where R is varying dark field observations may be used (WOODCOCK and HOLT, 1969).

Film structure (R values) versus substrate temperature graphs have been obtained for gold on NaCl (INO et al. 1964); for Ge on Ge (KRIKORIAN and SNEED, 1966) and also for Ge on  $\text{CaF}_2$  (SCHALLA et al, 1964). Similar graphs have been obtained for ZnTe, on a number of ionic substrates (HOLT, 1966; HOLT and PORTER, 1970) and for ZnS on NaCl (100) (WOODCOCK and HOLT, 1969) and ZnSe on NaCl (100) (HOLT and PORTER, 1970).

#### 2.4.4. THE EFFECT OF CONTAMINATION OF THE SUBSTRATE SURFACE

The effect of contamination of the substrate surface on the growth of thin films is not certain. MATTHEWS and GRUNBAUM (1964, 1965) showed that the best quality Au films grown on NaCl (100) were obtained if the substrate was exposed to air before deposition. MATTHEWS (1965) then showed that although the orientation of the initial nuclei was better in films grown on vacuum-cleaved substrates than it was on substrates exposed to air, the nucleation density on the contaminated substrates was much greater. The latter led to earlier coalescence which had already been shown to promote good epitaxy (MATTHEWS, 1959).

HARSDORFF (1963 and 1964) studied the effect of adsorbed layers on NaCl (100) substrate surfaces upon the zenithal misalignment of crystallites in epitaxial layers of Ag, Au and Cu. The angular displacement of crystallites about an axis lying in the film was plotted as a function of the substrate temperature. The curve obtained by HARSDORFF was an oscillating function. This was accounted for by supposing that different contaminants were volatilising from the substrate surface at different temperatures. Contamination by water vapour alone was found to give an oscillating

function which suggested that successive layers of water molecules were increasingly tightly bound to the substrate surface. The last layer did not begin to disappear until the substrate temperature went above  $350^{\circ}\text{C}$ . HARSDORFF found that the effect was destroyed if the NaCl substrates were heated to above  $450^{\circ}\text{C}$ . for a short time. It was supposed that this removed not only the contamination but also the surface layers of the substrate. The angular displacements for Ag on NaCl oscillated between  $4^{\circ}$  and  $14^{\circ}$ . This is a sufficiently large displacement from the normal to give the characteristic "buckling" contrast frequently seen in the electron micrographs of evaporated films.

The effects of oil and water vapour contamination of NaCl (100) substrates upon the epitaxy of ZnS has been investigated by UNVALA et al. (1968) and WOODCOCK and HOLT (1969). The results which they obtained from films grown on substrates purposely contaminated with these two substances, were compared with those obtained using an ordinary high vacuum system equipped with a nitrogen trap and also with some results obtained in ultra high vacuum. The conclusion was that the quality of the films improved with increasing cleanliness of both the vacuum and the substrate. No determination of nucleation densities was made and it is therefore not possible to establish whether there was any difference in the nucleation and growth patterns of these ZnS films and the metal films deposited by MATTHEWS et al.

However, the effects of contamination in the two cases appear to be opposed. Contamination promoted epitaxy in the case of gold on NaCl whereas it prevented it in certain temperature ranges in the case of ZnS on NaCl. The different effects of improving the apparent cleanliness of the conditions of deposition have also been observed by HOLT and PORTER (1970) with layers of ZnTe and ZnSe deposited on various ionic substrates.

#### 2.4.5. THE EFFECT OF THE MODE OF SOURCE EVAPORATION

One of the conditions of film growth which can have a marked effect upon the quality of films grown on ionic crystals is the means by which the source material is evaporated. There are several ways in which this can be done. The most common technique is that of evaporation from a resistance heated crucible. Most of the films studied in the papers referred to in section 2.5 were produced in this way.

It is now apparent that the structural quality of films is often improved and the temperature range over which they are epitaxial is increased if other techniques for heating the source are used. UNVALA et al. (1968) found that single crystal ZnS films deposited on NaCl (100) using an electron beam heated source were structurally more perfect and could be obtained over a wider substrate temperature range than those deposited using a source heated by radiation from a hot tantalum spiral. CdS layers produced from a cathode sputtered source were found by BEPMEENKOVA and LURASOVA (1968) to have better structural quality and require a lower minimum substrate temperature for epitaxy than those grown from a source in a resistance heated crucible.

Conversely, it has been found that in some cases, changing from resistance heating to electron beam heating of the source does not improve the quality of epitaxial growth. For example HOLT and PORTER (1970) found that no improvement was produced in ZnTe layers deposited on cleaved  $\text{CaF}_2(111)$  faces and that reproducible epitaxy was even eliminated in the case of ZnTe on cleaved  $\text{BaF}_2(111)$  faces.

It therefore appears that the method used for evaporating the source can have a significant effect on the structural quality of the epitaxial layer. The effect may or may not be beneficial but it is likely to be quite specific to the thin film - substrate system in question. Because of this and the lack of empirical data, no

predictions can yet be made of the effects which a particular evaporation technique may have on the epitaxy of a particular thin film - substrate pair.

#### 2.4.6. THE EFFECT OF ELECTRIC FIELDS AND CHARGES

Recently, it has been found that an electric field in the vicinity of the substrate can affect the epitaxial growth of a thin film. It has also been found that the presence of charged particles either in the condensing vapour or on the substrate surface can also modify their growth.

The first example of an electric field affecting epitaxial growth was reported by CHOPRA (1965). CHOPRA has since observed the effect of a transverse field in the plane of the substrate upon the nucleation and coalescence of low melting point metals (1965) and also of gold and silver (1966). In a more recent paper (CHOPRA and KHAN, 1967), the same effect was observed with CdS films grown on NaCl(100) substrates. Results have also been obtained by HAYES et al. (1966, 1967), STIRLAND, (1966) and HILL (1966, 1967). HAYES et al., found that the application of an electric field across the substrate face, or removing the charge from the vapour stream, produced similar results. STIRLAND bombarded cleaved rocksalt substrates with electrons during the deposition of gold and found that the minimum epitaxial temperature was reduced. Films deposited immediately after electron bombardment of the substrate did not possess an improved crystal structure. HILL likewise found that gold deposited onto glass substrates after electron bombardment did not have an improved structure. However, it was found that after positive ion bombardment of the glass substrate, gold films were deposited having improved crystal structures.

These effects have only been reported in cases where the films were deposited on insulating substrates. CHOPRA (1965) suggested that charges residing on the surface of the condensing nuclei interfere

with their coalescence by making them mutually repulsive and the moment at which continuity in the thin film is achieved is thereby delayed. This process could only occur on an insulating substrate. It is also supposed that the various methods involving electric fields, ion bombardment or extraction of charge from the vapour stream all result in the elimination of charge arriving in the condensing material thereby reducing the mutual repulsion between the growing nuclei. As a result, continuity in the epitaxial layer is achieved at an earlier stage of growth. It is thought that this enables the recrystallisation of the coalescing nuclei to occur more quickly since the quantity of material involved is smaller. In view of the observations made by the above authors, WOODCOCK and HOLT (1969) investigated the possibility that charged particles emanating from an electron beam evaporator were affecting the epitaxial growth of ZnS films grown on cleaved NaCl(100) substrates. It was found that no effect was produced in the thin film structure when all the charges were extracted from the vapour stream and it was concluded that charge effects were not playing a significant part in the epitaxy of these layers. The relatively good quality of the ZnS films as compared with those produced from resistance heated sources was considered to be mainly due to the extreme cleanliness of this mode of evaporation. The claim by EFREMEKOVA and YURASOVA (1968) that charges in the cathode sputtered CdS vapour from which they grew epitaxial layers were partially responsible for their good structure was not substantiated by any experimental evidence.

The role played by charges during the growth of epitaxial films is still not well understood although it is known that epitaxial growth in conditions other than electrical neutrality can exhibit a modified behaviour.

## 2.5. THE DEPOSITION OF THIN SINGLE CRYSTAL FILMS OF THE II-VI COMPOUNDS

### 2.5.1. VARIATIONS OF THE EPITAXIAL FILM STRUCTURE WITH SUBSTRATE ORIENTATION

A number of studies have been made of the properties of thin films of the II-VI compounds but few of these have been concerned with their detailed structural analysis. However, certain structural observations are common to many of the thin film substrate systems. For example, considerable evidence now exists to show that, under certain conditions, it is possible to obtain single crystal layers of some II-VI compounds either with the wurtzite structure or with the sphalerite structure by using substrates with appropriate cubic orientations. This is most likely for II-VI compounds for which the wurtzite structure is stable at the growth temperatures and appears to be because the  $\{111\}$  sphalerite planes have the same symmetry as the  $\{0001\}$  wurtzite planes. In this case, when a (111) oriented substrate is used, the film usually grows with the wurtzite structure whereas if substrates are used with symmetries peculiar to the cubic system like (100) or (110) then the film frequently adopts the less stable sphalerite structure. II-VI compounds stable with the sphalerite structure tend to give epitaxial layers with cubic symmetry if grown on substrates with cubic symmetry whatever their orientation. The polymorphic behaviour has been observed in the following cases:

ZnS on NaCl(100) and NaCl(111) AGGARWAL and GOSWAMI (1963)

CdTe on the (100) faces of NaCl, KCl and KBr, and on the

(111) faces of NaCl and mica RUMSH et al, 1963 a and b.

CdS on Mo(100) and mica (111) ESCOFFERY (1964).

CdS on NaCl(100) and the (111) faces of Ag and mica

CHOPRA and KHAN (1967).

ZnTe and ZnSe on NaCl(100) and NaCl(111) (DHERE and GOSWAMI, 1969).

In some cases these orientation dependencies have not been observed. For example, HOLLOWAY and WILKES (1968) found that films of CdS with

the sphalerite structure were obtained on InSb substrates regardless of their orientation and WEINSTEIN et al. (1965) found that a rhombohedral form of CdS was obtained on the ( $\bar{1}\bar{1}\bar{1}$ ) phosphorus face of GaP whereas CdS with the wurtzite structure grew on the (111) gallium face. VAN DIJK (1967) reported that films grown on Ge(110) surfaces had the wurtzite structure and were invariably polycrystalline. These deviations from the more common polymorphic growth of CdS as exemplified in the references above and in the work reported here, usually occur on substrates which are **either** non-centrosymmetric or semiconducting. The electrical conditions associated with the ends of a polar axis or with the interface between a semiconductor and a semiconducting thin film, may be responsible for this.

#### 2.5.2. THE DEFECT CONTENT OF EPITAXIAL FILMS OF II-VI COMPOUNDS

Defects lying parallel to the  $\{\bar{1}\bar{1}\bar{1}\}$  planes in thin films with the sphalerite structure have frequently been reported. The defects have generally been thought to be stacking faults, but owing to their great profusion and very small size, an unambiguous identification has not been made. WOODCOCK (1968) and HOLT and WOODCOCK (1969) reported the presence of many such planar defects in ZnS films with the sphalerite structure grown on NaCl(100) substrates. While the contrast arising from the planar defects could be explained, it was not possible to determine the nature of these defects.

Holt (1966b) deposited ZnTe onto a variety of ionic crystal substrates with (100) and (111) orientation. All the epitaxial films obtained had the sphalerite structure. The best of these were grown in (111) orientation and not only contained stacking faults but also a large number of double-positioning twins (sec. 2.4.1 and sec. 2.6.4.) a detailed analysis of the diffraction patterns produced by these films was subsequently published (HOLT, 1969b).

A mixture of both the wurtzite and the sphalerite structures was obtained in CdTe layers deposited on NaCl(111) substrates (RUMSH et al. 1963a). The two structures grew with either the  $\{0001\}$  or the  $\{111\}$  planes parallel to the substrate surface. In the substrate temperature range of 200°C. to 300°C, diffraction spots associated with material having the sphalerite structure were streaked in  $\langle 111 \rangle$  directions. It was supposed that stacking faults lying parallel to the  $\langle 111 \rangle$  planes were the most likely cause of the streaks. Extra reflections were also seen in the diffraction pattern which were attributed to material within the film having a polytype structure. In a further study of CdTe films deposited on the (100) faces of NaCl, KCl and KBr (RUMSH et al. 1963b), it was found that a structural transformation took place which was dependent upon the substrate temperature. The cubic sphalerite structure predominated at low substrate temperatures and as this temperature was increased, the film structure became highly faulted until, finally, a pure wurtzite structure was obtained at the highest temperatures.

Films with a sphalerite matrix structure containing included grains of doubly-positioned material with the wurtzite structure are common. The geometry required to produce material in this form is that described in section 2.3. This mode of growth in II-VI compounds has been reported by a number of workers (KALINKIN et al, 1963; AGGARWAL and GOSWAMI, 1963; HOLT, 1966b; CHOPRA and KHAN, 1967 and WOODCOCK and HOLT, 1969). It has been analysed in detail by WOODCOCK and HOLT (1969) for films of ZnS. The percentage of doubly-positioned material having the wurtzite structure was found to decrease with rising substrate temperature. It was also reduced by co-evaporating either Zn or S with the source material. Grains having the wurtzite structure with single positioning only were, however, sometimes seen in films produced by co-evaporating ZnS with either Zn or S but never

in films grown from ZnS alone.

### 2.5.3. THE POLARITY OF CdS THIN FILMS WITH RESPECT TO THEIR SUBSTRATES

Examples have been found where the epitaxial growth of CdS has been affected by the polar properties of the substrate crystal structure (sec. 2.5.1). The polarity of the CdS film itself with respect to its substrate has not received so much attention. VECHT et al. (1961) and ROZGONYI and FOSTER (1967) have both made etch pit studies on thin fibre-textured CdS films deposited on glass substrates. In both cases, it was found necessary to recrystallise the films before etching in order to increase the grain size. The etch pits were otherwise too small to be identified. A second technique employing the piezoelectric effect, was used by ROZGONYI and FOSTER.

VECHT et al. found that the "C" axis was perpendicular to the glass substrate and that the sulphur face was bonded to the glass. The results of ROZGONYI and FOSTER suggested that thin films with one of two structures could be deposited. One type grew with the (0001) sulphur face next to the glass which confirmed VECHT's findings, the second type contained grains of both polarities and therefore gave a much reduced piezoelectric voltage when compressed along the "C" axis. No mention has been made in the literature of the polarity relationship between CdS and the ionic crystal substrates or between CdS and the elemental semiconductors Si and Ge. WILSON (1966) demonstrated that the presence of areas of reverse polarity reduced the efficiency of devices dependant for their action on the piezoelectric effect and that they were therefore of considerable practical importance.

## 2.6. THE DIFFRACTION PATTERNS OF EPITAXIAL FILMS OF II-VI COMPOUNDS

### 2.6.1. THE ATOMIC SCATTERING FACTOR AND THE STRUCTURE FACTOR

The atomic scattering factor,  $f$ , is a measure of the efficiency with which an atom elastically scatters electrons. By definition,  $f$  is 1 for an isolated electron scattering other electrons. Each element has a different value of  $f$  which is a constant for all atoms of the same element. The constant is not usually affected by the environment of the atom so that the value is similar for the same element in different compounds.

The elastically scattered electrons from a crystal, which is a regular array of atoms, undergo interference effects similar to those for light passing through a diffraction grating. If the electrons arrive as a monochromatic, parallel beam (as occurs in an electron microscope) their wave properties cause those which are elastically scattered to undergo constructive interference in well defined directions. The directions are determined by the interplanar spacings of the crystal and the energy of the electrons.

Not all possible sets of planes need give rise to a diffracted beam. The positions where destructive and constructive interference take place also depend on the spatial distribution of the atoms, i.e. the crystal structure. It was stated above that a crystal is a regular array of atoms. The array is produced by the repetition of a fundamental unit which may contain more than one atom. This unit is called the "unit cell" which is the smallest element of the crystal that still preserves the symmetry properties of the whole crystal. This implies that the atoms within the unit cell occupy non-equivalent positions in space. As a result, the electrons diffracted by each atom within the unit cell will not have the same phase. To determine the total contribution from the unit cell, for a particular set of reflecting planes,  $hkl$ , the amplitudes of the waves from each atom in

the unit cell must be summed taking account of both the atomic scattering factors and the phase differences. The summed effect is called the structure factor, denoted by  $F(hkl)$ , and is the amplitude of the resultant reflection. The intensity of the reflection is proportional to the square of  $F(hkl)$  and the total intensity diffracted by the crystal therefore depends on the number of unit cells involved.

In section 2.1, the relationship between the diamond, sphalerite and wurtzite structures was discussed. It was stated that the diamond structure is based upon the f.c.c. lattice and that it differs from the f.c.c. structure by having four extra atoms inside the unit cell at positions indicated in fig. 2.2. As a result of the structural effects indicated above, the presence of the extra atoms causes destructive interference to occur between electrons scattered from certain sets of planes. The diffraction patterns from a material with the diamond structure therefore have some reflections missing when compared with those from a material with the f.c.c. structure. The selection rule which determines the reflections which are present in an f.c.c. diffraction pattern states that the indices,  $h, k, l$ , of a particular reflection must be either all odd or all even. This means that reflections which have a mixture of even and odd indices are not present. Besides these, reflections, for which  $(h+k+l) = 4n + 2$ , are also not found in diffraction patterns from materials with the diamond structure (CULLITY, 1956). These are the absences which occur as a result of destructive interference between electrons scattered by the four atoms inside the unit cell and those scattered by the atoms at the f.c.c. positions. In the case of the sphalerite structure, however, the atoms inside the unit cell are not of the same element as those at the f.c.c. positions. Since the scattering factors for electrons are different for the two atom types complete destructive interference does not occur and reflections of the type  $h + k + l = 4n + 2$  are still present. This means that the diffraction patterns

obtained from materials with the sphalerite structure are like f.c.c. structure diffraction patterns and not like diamond structure diffraction patterns (CULLITY 1956).

None of the  $(h + k + l) = 4n + 2$  reflections lie in the (111) plane, however, so it is not possible to determine whether a material has the f.c.c. structure or the diamond structure from a diffraction pattern in this orientation, since in both cases the pattern is the same.

The wurtzite structure also contains two atom types and for similar reasons to those given above for the sphalerite structure, no extra absences will occur when diffraction patterns from this structure are compared with those from the hcp structure.

#### 2.6.2. SINGLE AND DOUBLE DIFFRACTION FROM A TWO-PHASE MATERIAL

The diffraction patterns obtained from metal films with the f.c.c. structure have been studied in detail (e.g. PASHLEY and STOWELL, 1963; PASHLEY, STOWELL and LAW, 1965; JACOBS and STOWELL, 1965). Twins or grains of a second phase included within the thin film matrix gives rise to more complicated diffraction patterns. The extra spots which occur in diffraction patterns from some of these more complex structures have also been analysed.

The pattern which the spots form is often a reliable indication of the crystal structure which is being studied. In other cases, however, the origin of certain spots in the diffraction pattern may be uncertain. Sometimes this is because two possible mechanisms may give rise to a spot at the same position, in which case an ambiguity exists, and at other times the spot may have irrational indices based on the indexing system applied to the rest of the diffraction pattern. In the latter case, the spot evidently does not arise from single diffraction within the thin film matrix. When they are present, spots with irrational indices frequently form subsidiary patterns around

each matrix spot and are therefore usually referred to as "satellite spots". The technique of dark-field electron microscopy, in which any diffracted beam may be used to form an image may be used to establish conclusively the origin of a particular spot.

Extra spots may occur in diffraction patterns either as a result of single diffraction within second phase material such as included grains or twins, or as a result of double diffraction, first in the thin film matrix and then in the second phase material or vice-versa. Electrons suffering such a double diffraction must evidently be those which enter the material close to the matrix/second phase material boundary so that on being diffracted on one side they pass across the boundary and subsequently undergo the second diffraction on the other side (fig. 2.7). If electrons diffracted in this way are used to form an image, the boundary between the second phase material and the matrix shows up brightly in dark-field. This is known as "outline contrast" (fig. 2.8A). If electrons which are singly diffracted by the second phase material are used to form a dark-field image, then the area covered by this material is illuminated. This is known as "domain contrast" (fig. 2.8B).

Not all possible reciprocal lattice points resulting from double diffraction are necessarily permissible reflections. Certain conditions must be fulfilled before a doubly diffracted beam is excited. The doubly diffracted beam can only arise from a primary diffracted beam (from either the matrix or the included grain) which undergoes a second diffraction in the other material. The sphere of reflection must therefore pass through the reciprocal lattice point corresponding to the primary diffracted beam. It need not pass through the spot corresponding to the second reflection although this must be an allowed reflection in the second phase. If the double diffraction spot is in the same plane as the primary diffraction spot,

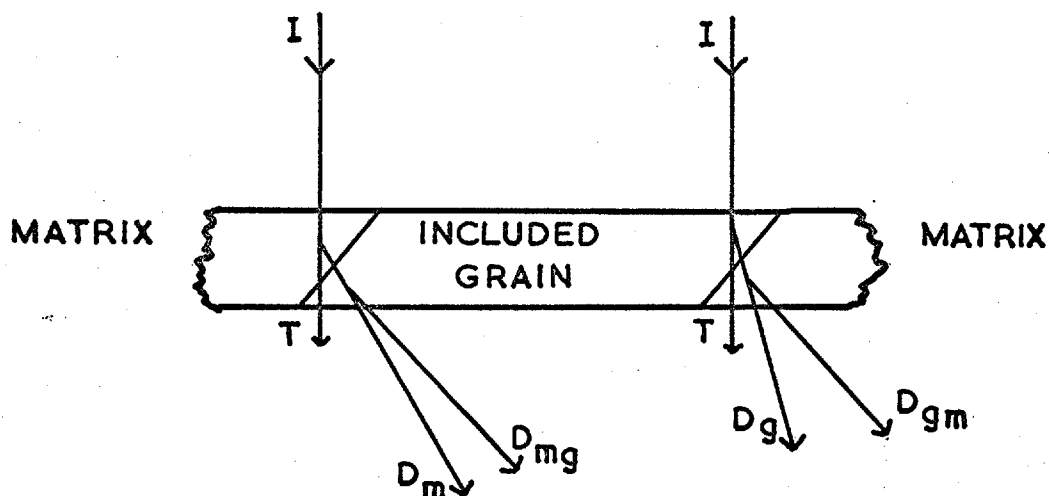


Fig. 2.7 SINGLE AND DOUBLE DIFFRACTION IN A CRYSTAL CONTAINING AN INCLUDED GRAIN.

I - Incident beam; T - Transmitted beam;  
 Dm - Singly diffracted beam from the matrix;  
 Dg - Singly diffracted beam from the included grain; Dmg and Dgm - Beams doubly diffracted first by the matrix and then by the grain or vice versa.

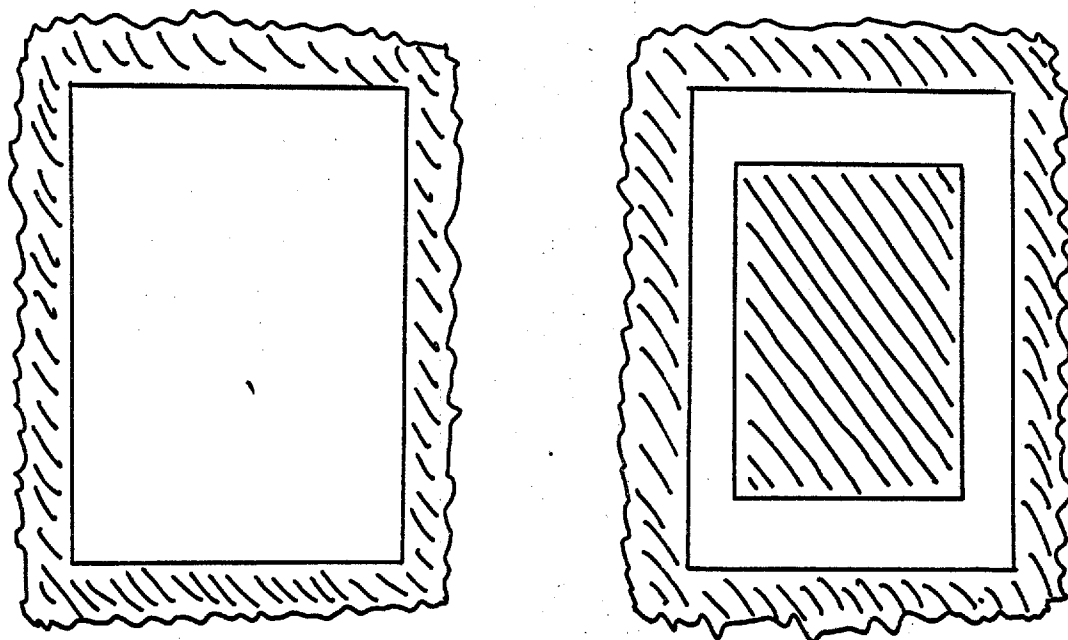


Fig. 2.8

(A)

(B)

#### CONTRAST SEEN IN DARK FIELD

- (A) Outline contrast obtained in dark field by imaging Dmg or Dgm.
- (B) Domain contrast obtained in dark field by imaging Dg.

then the spot corresponding to the second diffraction is also in the same plane.

A complete account of the electron diffraction phenomena in thin crystals is given by HIRSCH et al. (1965) in which this technique is discussed and where much of the analysis is illustrated using results applicable to material with the f.c.c. structure.

### 2.6.3. DIFFRACTION EFFECTS FROM FILMS CONTAINING NO IMPERFECTIONS

The diffraction patterns produced by the sphalerite structure in (100) and (110) orientation and the wurtzite structure in (0001) orientation are plotted in fig. 2.9. They are identical to the reciprocal lattice plots for these planes except that certain of the spots are missing owing to destructive interference between the diffracted electrons. For example, the only spots present in diffraction patterns from the f.c.c. structure (and therefore the sphalerite structure (sec. 2.6.1)) are those whose indices are either all odd or all even. The (010) and (011) spots are therefore not seen in the (100) diffraction pattern although they lie in the (100) plane.

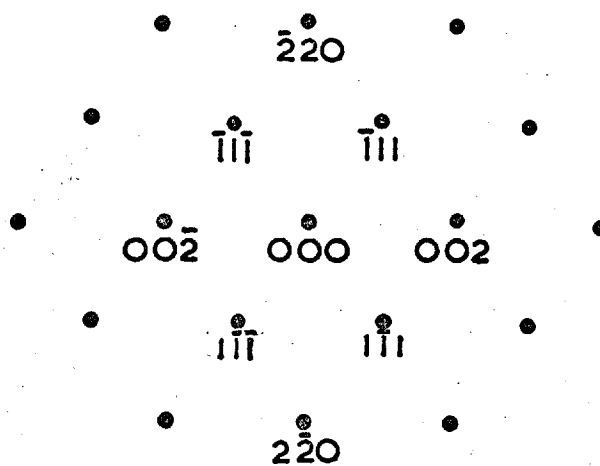
Small dimensions in real space correspond to large dimensions in reciprocal space. Since the crystal films are very thin in the direction of the electron beam, and relatively broad in the two directions at right angles to the beam, the reciprocal lattice representations of the thin film are arrays of long thin spikes whose axes lie normal to the film and therefore close to the beam directions. These spikes project through the Ewald sphere of reflection and so it is possible to observe a diffraction pattern at tilts other than that required for the exact Bragg condition for the particular pattern (fig. 2.10). The pattern is made by the points of intersection of the spikes and the sphere of reflection. The maximum tilt that can be given before the pattern is lost depends

$0\bar{2}2$     $0\bar{0}2$     $022$

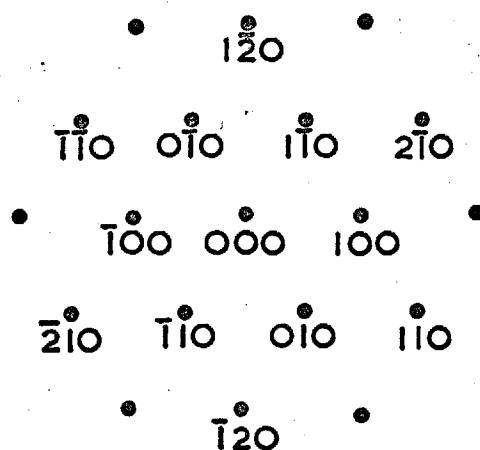
$0\bar{2}0$     $0\bar{0}0$     $020$

$0\bar{2}\bar{2}$     $0\bar{0}\bar{2}$     $02\bar{2}$

(A) (100) cubic orientation



(B) (110) cubic orientation



(C) (0001) hexagonal orientation

Fig. 2.9 SINGLE CRYSTAL DIFFRACTION PATTERNS FROM FILMS CONTAINING NO INCLUDED GRAINS.

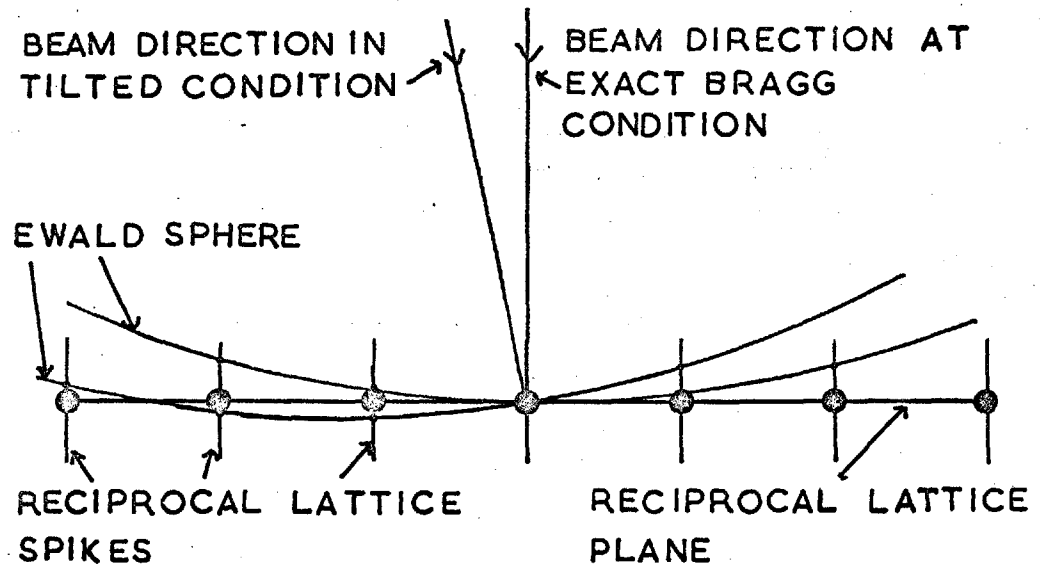


Fig. 2.10 Diagram illustrating the way in which a diffraction pattern can be produced at positions other than at the exact Bragg condition. The reciprocal lattice spikes pierce the Ewald Sphere to provide diffraction spots over a range of specimen or beam tilts.

upon the length of the spikes and therefore on the thickness of the film. In practice thin films are frequently not well enough supported to avoid buckling. This causes some parts of the imaged specimen to be tilted into an appropriate orientation for strong diffraction, even if the specimen as a whole is tilted away from the exact position. The maximum tilt is, therefore, somewhat larger than might be expected and is usually several degrees to either side of the exact Bragg condition.

The intensity of the diffracted beam falls off quickly as the angle to which the crystal is tilted is increased. Regions of the crystal which diffract strongly, i.e. which are at, or near to, the exact Bragg condition appear dark in the image of the crystal formed by the transmitted beam. Consequently, when the crystal is buckled, the parts which are bent into the appropriate orientation for strong diffraction show up as dark contours running through areas of equal tilt. If the whole crystal is tilted further, these contours or "bend extinction contours" are seen to move across the film to regions which have newly acquired the appropriate orientation for strong diffraction.

#### 2.6.4. DIFFRACTION PATTERNS FROM FILMS CONTAINING INCLUDED GRAINS

The term "included grains" is used here to describe small volumes of material contained within the body of the film which have either a different crystal structure from the matrix or the same crystal structure as the matrix and which lie in an orientation other than that of the matrix.

Included grains may be divided into two classes. The first comprises all grains whose crystal lattices have a simple orientation relationship with respect to the crystal lattice of the matrix and the second comprises those grains which do not have such an orientation relationship. The latter type do not occur in good

epitaxial films and when they occur in films of lesser quality, their precise orientations are of no particular significance since they will be random. For this reason, the effects of such included grains on the diffraction patterns of otherwise epitaxial films are not discussed here in detail. It should, however, be mentioned that continuous rings concentric with the central spot of the diffraction pattern show the presence of crystallites with random orientations.

Included grains having a simple orientation relationship with respect to the matrix give rise to extra spots in the diffraction pattern. Some occur as a result of single diffraction within the bulk of the grains and some by the process of double diffraction across the boundary between the included grains and the matrix (sec. 2.6.2.). The positions of these spots characterise the structure and orientation of the included grains from which they arise.

There are two particular types of oriented included grain which are found in thin films of the II-VI compounds. One consists of grains with the same crystal structure as the matrix and in a twin orientation with respect to the matrix. The other type consists of grains of material with the wurtzite structure in films having the sphalerite structure or vice versa. A few of these configurations which have particular relevance to the work reported here are now discussed.

#### 2.6.4.1. GRAINS IN TWIN ORIENTATION IN FILMS WITH THE SPHALERITE STRUCTURE.

It has been shown above (sec. 2.6.1) that the diffraction patterns from films with the sphalerite structure may be directly compared with those from films with the f.c.c. structure. PASHLEY and STOWELL (1963) have analysed the diffraction patterns of f.c.c. structure single crystal films and established that material twinned about all the  $\langle 111 \rangle$  crystal axes gives rise to spots either at positions already occupied by matrix spots or at positions removed

from them by reciprocal lattice vectors of the type  $\pm \frac{1}{3} \langle 111 \rangle$ . Some of the spots occur as a result of single diffraction and the rest are due to double diffraction. The array of spots which is obtained in a diffraction pattern from a film in (001) orientation containing twins is plotted in fig. 2.11. None of the extra spots lie exactly in the (001) reciprocal lattice plane since all the  $\langle 111 \rangle$  directions lie outside the plane. However the twin spots "spike through" the (001) plane as a result of the mechanism described in sec. 2.6.3. at positions displaced by  $\pm \frac{1}{3} \langle 110 \rangle$  from the matrix spots of the (001) diffraction pattern.

The diffraction pattern produced by the same twinned structure in (111) orientation is plotted in fig. 2.12. Again the extra spots show up as a result of spiking through since none of the  $\langle 111 \rangle$  directions lie in the (111) plane.

#### 2.6.4.2. DOUBLE-POSITIONING TWINS

A particular type of twinned structure is sometimes found in films with a cubic structure grown on substrates in the (111) orientation. In this case, the matrix and twinned material are rotated by  $180^\circ$  relative to one another about the normal to the substrate. These twins are called double-positioning twins since the matrix and twins each occupy one of only two possible orientations. The twins give rise to single diffraction spots coincident with the matrix spots and double diffraction spots having fractional indices of the type  $\frac{1}{3} \langle 422 \rangle$ . These spots, unlike those of the form  $\pm \frac{1}{3} \langle 111 \rangle$ , lie in the plane of the (111) diffraction pattern and are produced by electrons doubly diffracted at the incoherent boundaries between the twins and the matrix. The spots lie at the centers of triangles formed by the central spot and two neighbouring  $\{220\}$  type matrix spots (fig. 2.12). They can therefore be confused with  $\{1010\}$  matrix spots of the hexagonal structure in (0001) orientation which lie at

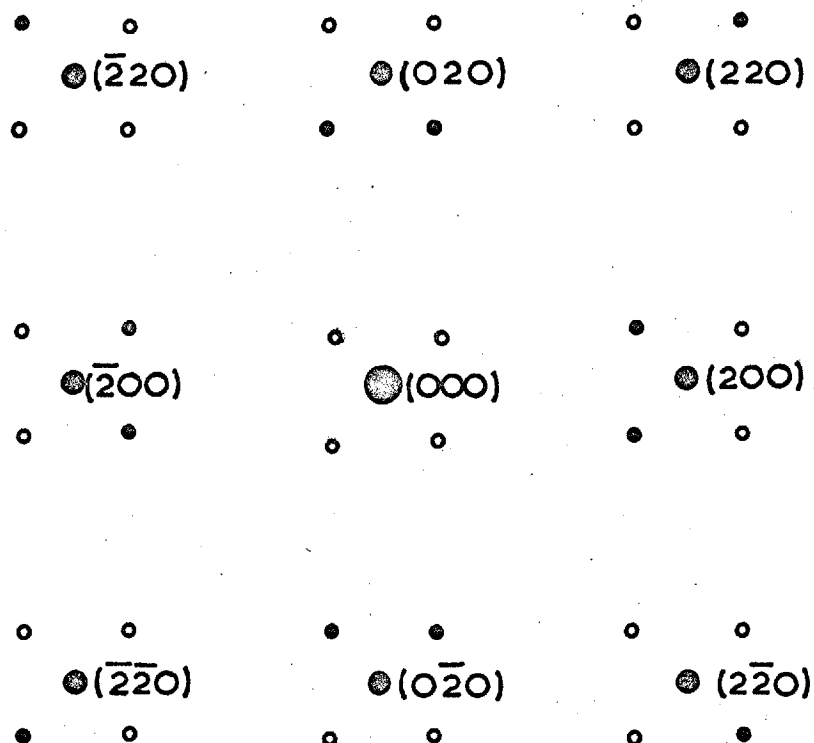


Fig. 2.11

DIFFRACTION PATTERN FROM TWINNED SPHALERITE STRUCTURE  
IN (001) ORIENTATION.

- represents a matrix spot.
- ⊗ represents a twin spot.
- represents a spot due to double diffraction between the matrix and the twins.



the same positions, unless dark-field microscopy is used.

#### 2.6.4.3. DIFFRACTION PATTERNS FROM FILMS HAVING THE SPHALERITE STRUCTURE CONTAINING GRAINS WITH THE WURTZITE STRUCTURE

There are two situations which are of particular relevance to this work. The first concerns thin films in (100) orientation containing grains with the wurtzite structure having the (0001) plane parallel to (100). The second concerns films with the sphalerite structure containing grains with the wurtzite structure oriented with their {0001} planes parallel to the {111} planes of the matrix. These two situations are discussed in turn.

#### 2.6.4.4. FILMS WITH THE SPHALERITE STRUCTURE IN (100) ORIENTATION CONTAINING GRAINS WITH THE WURTZITE STRUCTURE WITH (0001) PARALLEL TO (100)

This type of growth provides another example of double positioning. This is commonly found in epitaxially grown films of II-VI compounds (sec. 2.5.2). The films are deposited on a (100) oriented substrate and the film matrix grows in parallel orientation. The included grains, however, may grow in either of two orientations each with (0001) parallel to (100) (fig. 2.13a). The two orientations have either  $[2\bar{1}10] \parallel [011]$  or  $[2\bar{1}10] \parallel [\bar{0}11]$  (fig. 2.13b) which are separated by a rotation of  $90^\circ$  about the substrate normal. They each give rise to six diffraction spots of the type  $\{10\bar{1}0\}$  and the two sets of spots appear as twelve spots angularly spaced by  $30^\circ$  from one another about the central spot. The pattern is plotted in fig. 2.14. No double diffraction spots are included in this figure.

#### 2.6.4.5. FILMS WITH THE SPHALERITE STRUCTURE IN (100) ORIENTATION CONTAINING GRAINS WITH THE WURTZITE STRUCTURE WITH (0001) PARALLEL TO (111)

The situation where material with the h.c.p. structure occurs in an f.c.c. matrix with the (0001) basal plane parallel to the (111) planes of the matrix and the  $[11\bar{2}0]$  and  $[\bar{1}10]$  directions parallel, has been considered by PASHLEY and STOWELL (1963). It was found that satellite spots due to single diffraction within the h.c.p. material

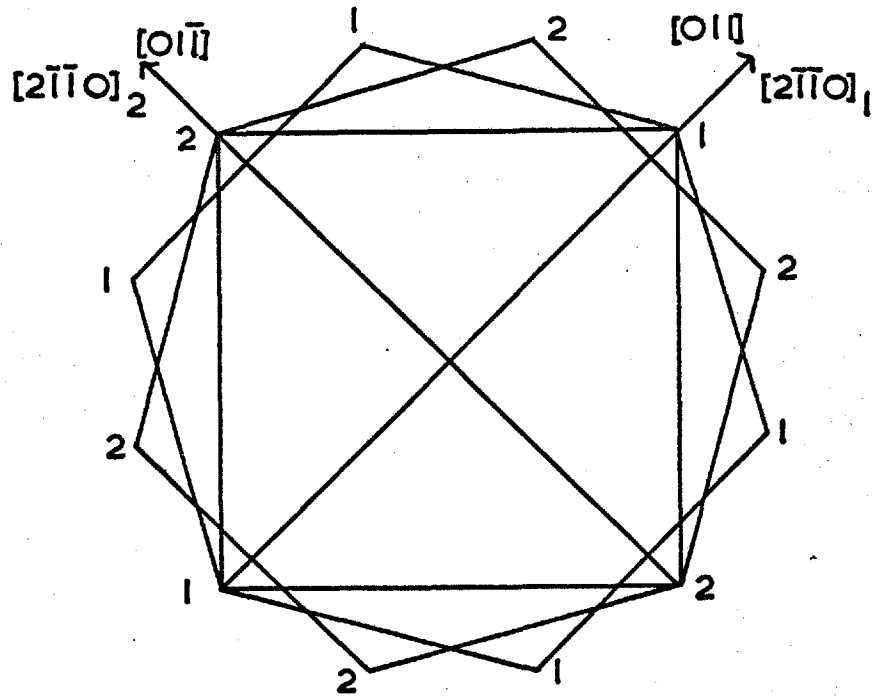


Fig. 2.13 a) Diagram showing the two symmetrical positions (1 and 2) of a hexagon on a square.

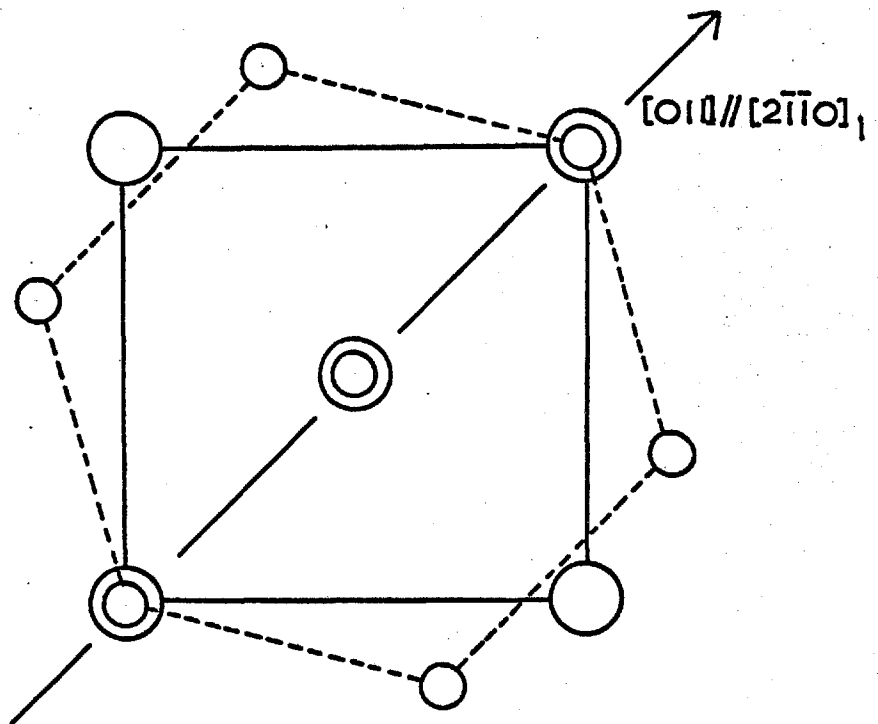


Fig. 2.13 b) Diagram showing the relative positions of atoms in the (0001) plane of the wurtzite structure and the atoms in the (100) plane of the substrate surface for position 1 of Fig. 2.13 a).

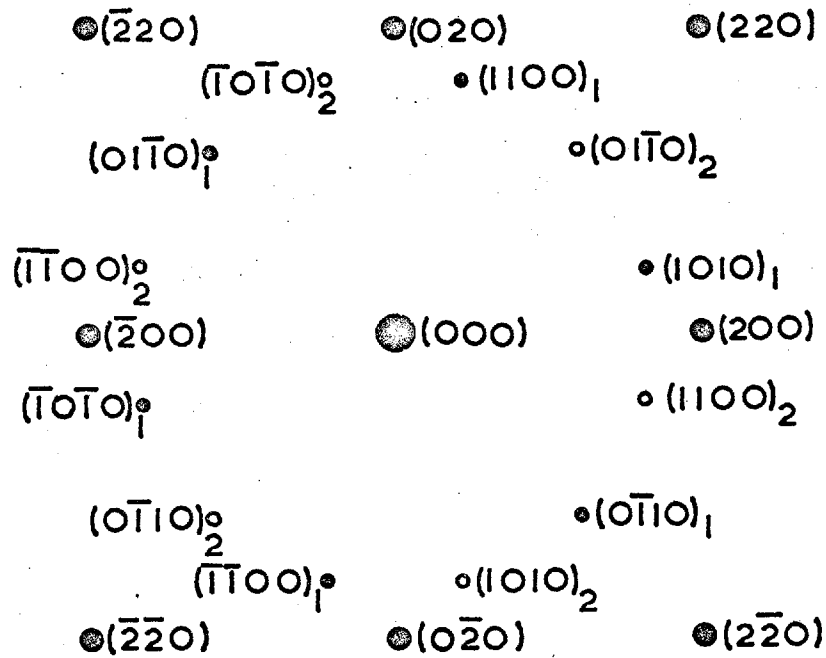


Fig. 2.14 The diffraction pattern obtained from a thin film with the sphalerite structure in (001) orientation containing included grains with the wurtzite structure having their  $\{0001\}$  planes parallel to (001).

- $\bullet$  represents a cubic matrix spot.
- $\bullet$  represents a wurtzite matrix spot in the first position (labelled 1).
- $\bullet$  represents a wurtzite matrix spot in the second position (labelled 2).

and double diffraction between this and the f.c.c. matrix should lie either at the same positions as f.c.c. matrix spots or at distances from these of  $\pm \frac{1}{3} \langle 111 \rangle$  and  $\pm \frac{1}{6} \langle 111 \rangle$ . There should therefore be two squares of four spots round each matrix spot of the (100) diffraction pattern. The theoretical plot of this diffraction pattern is shown in fig. 2.15. The pattern expected from a film with the sphalerite structure containing included grains with the wurtzite structure is identical to this one. The extra spots also included are reflections which are forbidden as primary diffracted beams but occur as a result of multiple diffraction within the wurtzite lattice (sec. 5.1.1.3a)

#### 2.6.5. THE STREAKING OF DIFFRACTION SPOTS

Many of the diffraction patterns from CdS films illustrated in this work contain spots which are smeared out or streaked in certain well defined crystallographic directions. The streaks are produced by planar defects within the material. If the streaks lie in the  $\langle hkl \rangle$  directions, this shows that the lamellae are parallel to the  $\{hkl\}$  planes.

The theory of diffraction streaks due to stacking faults in f.c.c. crystals has been given by PATTERSON (1952) and WIEBLAN and HIRSCH (1957). THOMAS et al. (1965) have discussed the formation of streaks by planar defects and precipitates.

The theory predicts that for f.c.c. crystals the diffraction spots which are streaked when stacking faults are present have indices for which  $h+k+l = 3N+1$  where  $h$ ,  $k$  and  $l$  are the indices and  $N$  is an integer. Spots unaffected are (000), (111) and (220). In fact, all these spots are streaked in the diffraction patterns from the CdS films. This comes about as a result of multiple diffraction within the crystal. For example, a streak associated with a (200) spot can be taken to a position near a (220) spot by a second diffraction through an (020) reciprocal lattice vector. An instance of double diffraction is illustrated in fig. 5.2. of section 5.1.1.3a, where a diffraction pattern

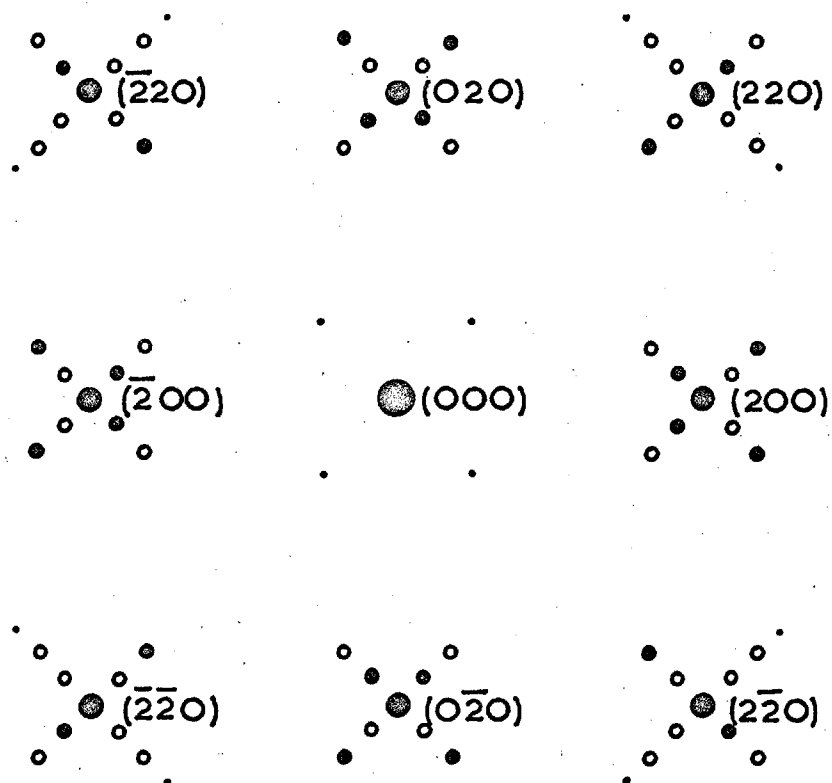


Fig. 2.15

A diffraction pattern from material with the sphalerite structure in (001) orientation containing wurtzite structure included grains having  $\{0001\}$  planes parallel to the  $\{111\}$  cubic planes.

- represents a sphalerite matrix spot.
- represents a wurtzite matrix spot from the included grains.
- represents a spot due to double diffraction between the two structures.
- represents a "forbidden" wurtzite matrix spot which appears as a result of multiple diffraction within the wurtzite lattice (secs. 5.1.13a and A1).

from a film containing both sphalerite and wurtzite structure material is analysed.

The planar defects causing the streaks may vary in thickness but cannot be thicker than a few atomic layers otherwise they give rise to their own diffraction spots.

Under special circumstances, stacking fault defects do not produce streaking. If they occur regularly spaced throughout the matrix, they give rise to a region of polytype with a superlattice (sec.2.1). In this case, both matrix and superlattice spots will be seen in the diffraction pattern (HIRSCH et al. 1965). Regular spacing of thin defects in this way does not occur in these CdS films, and the faults must therefore be randomly distributed on the  $\{111\}$  planes.

#### 2.6.5.1. THE OBSERVATION OF STREAKS IN DIFFRACTION PATTERNS

The streaks will only show up on the diffraction pattern as streaked matrix spots if they lie either parallel or nearly parallel to the sphere of reflection. This corresponds to the defects lying nearly parallel to the beam direction. Otherwise, they appear as satellite "pseudo" spots around the matrix spots, whose positions are determined by the point of intersection of the streaks with the sphere of reflection. In cases where none of the streaks lies in this plane, for example as in the (100) sphalerite diffraction patterns, evidence of streaking will be detected only when the film is tilted or buckled away from the exact Bragg condition. If the film is slowly tilted, the image of the intersection of the streak and the sphere of reflection is seen to run away from the matrix spots in directions corresponding to the projections of the  $\langle 111 \rangle$  directions on the (100) plane, i.e. in  $\langle 011 \rangle$  directions. This is illustrated in Fig. 2.16 A.

Diffraction patterns from films in (110) orientation exhibit well-defined streaks, since two  $\langle 111 \rangle$  directions lie in the (110) plane. At the exact Bragg condition these streaks are continuous

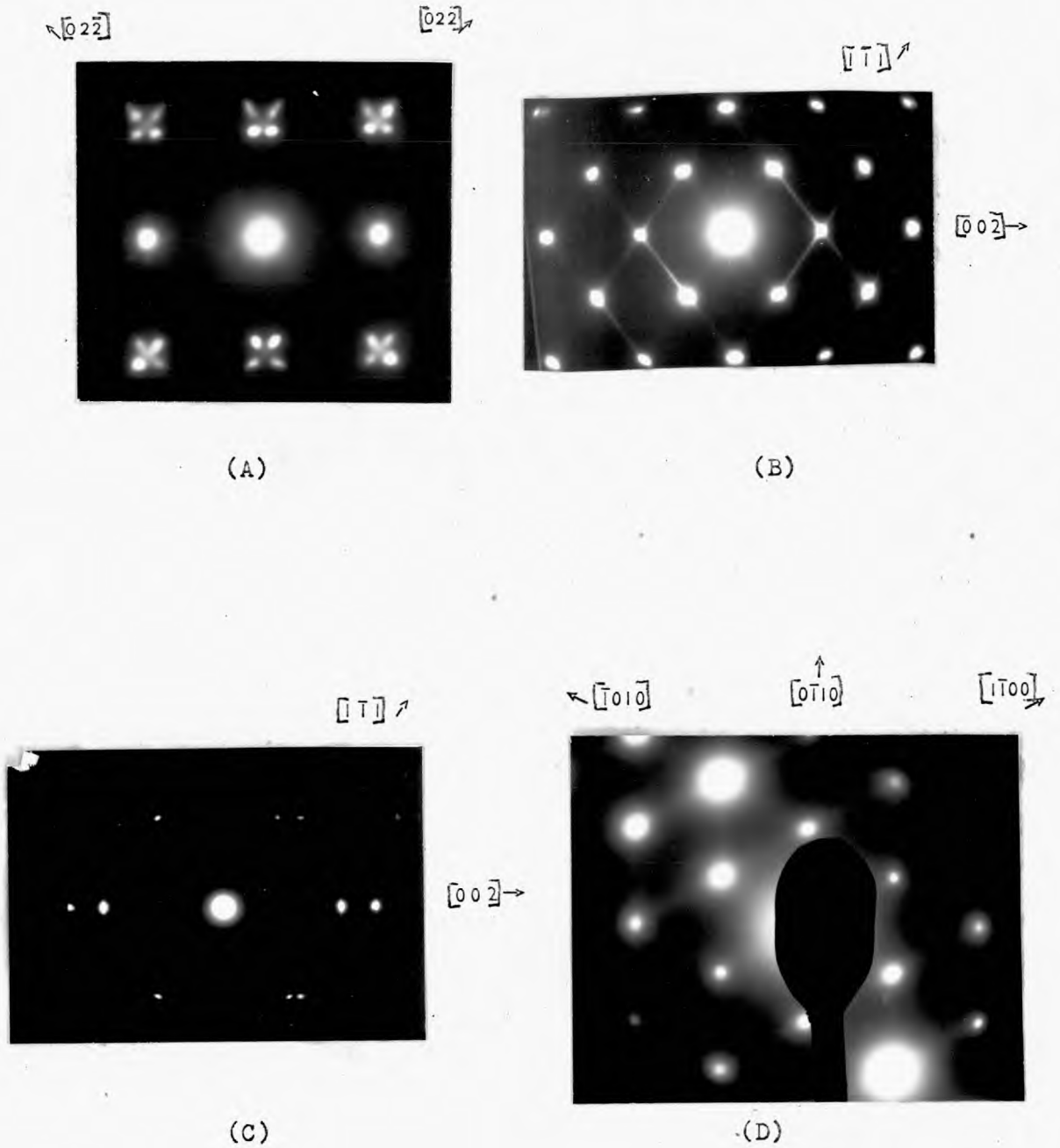


Fig. 2.16 STREAKING IN DIFFRACTION PATTERNS.

- (A) Streaks observed in (100) diffraction patterns.
- (B) Streaks observed in (110) diffraction patterns.
- (C) Extra spots due to streaks in near (110) orientation diffraction patterns.
- (D) Streaks observed in (0001) diffraction patterns.

between neighbouring diffraction spots and lie along the  $[\bar{1}\bar{1}\bar{1}]$  and the  $[\bar{1}\bar{1}\bar{1}]$  directions, as shown in Fig. 2.16B. When the film is tilted, these streaks gradually disappear. If a film in (110) orientation is tilted about the  $[\bar{1}\bar{1}\bar{0}]$  axis, the diffraction spots split in two along a direction corresponding to the projection on the (110) plane of the other two  $\langle 111 \rangle$  directions which lie outside the plane. These are the  $[\bar{1}\bar{1}\bar{1}]$  and the  $[\bar{1}\bar{1}\bar{1}]$  directions and  $[\bar{0}\bar{0}\bar{1}]$  is the projected direction. The two spots formed from each matrix spot are not streaked, because the  $[\bar{1}\bar{1}\bar{1}]$  and  $[\bar{1}\bar{1}\bar{1}]$  directions intersect the (110) plane at a steep angle. This is shown in Fig. 2.16C.

Some of the diffraction patterns from films with the wurtzite structure in (0001) orientation also contain streaks. The streaks, which lie in the (0001) plane along  $\langle 10\bar{1}0 \rangle$  directions, indicate that there are faults in the wurtzite structure on the  $\{10\bar{1}0\}$  planes. This is shown in Fig. 2.16D. The streaking in the diffraction patterns of films with the wurtzite structure is discussed in detail in sections 5.1.3. and 5.2.4.

### CHAPTER 3

#### EXPERIMENTAL APPARATUS AND PROCEDURE

##### 3.1. APPARATUS FOR GROWING THIN FILMS

###### 3.1.1. THE VACUUM SYSTEM Fig. 3.1.

The thin films were grown in a high vacuum system operating between  $10^{-6}$   $\tau$  and  $10^{-5}$   $\tau$ . It was evacuated by a 2" oil diffusion pump backed by a rotary oil pump. The normal pumping speed of the diffusion pump was 75 litres per second using a silicone oil type M.S. 704. A liquid nitrogen trap was also fitted and was always used during experiments. The pumping speed of the assembled system was estimated to be about 30 litres per second for gases not condensed by the nitrogen trap.

###### 3.1.2. THE ELECTRON BEAM EVAPORATOR Fig. 3.2.

An electron beam evaporator of the type developed by UNVALA (1963) was used for heating the source material. The crucible containing the source material was made of stainless steel and was plugged into a watercooled copper pedestal. The electron beam could be focussed so that the heating effect was localised well away from the crucible walls. This minimised the possibility of contamination from the crucible.

The furnace was constructed so that the filament was out of line-of-sight of both the source and the substrate. Direct radiation from the filament when run at very high temperature was the only means by which the evaporator assembly could be heated for outgassing.

The power input to the source was varied either by changing the filament temperature, thereby altering the emission current, or by changing the potential between the source and the filament. Both of these adjustments were made with variable A.C. transformers. The power was computed from the accelerating voltage and the electron beam current. The evaporator provided a very stable power input to the source and only occasional readjustments of the control settings

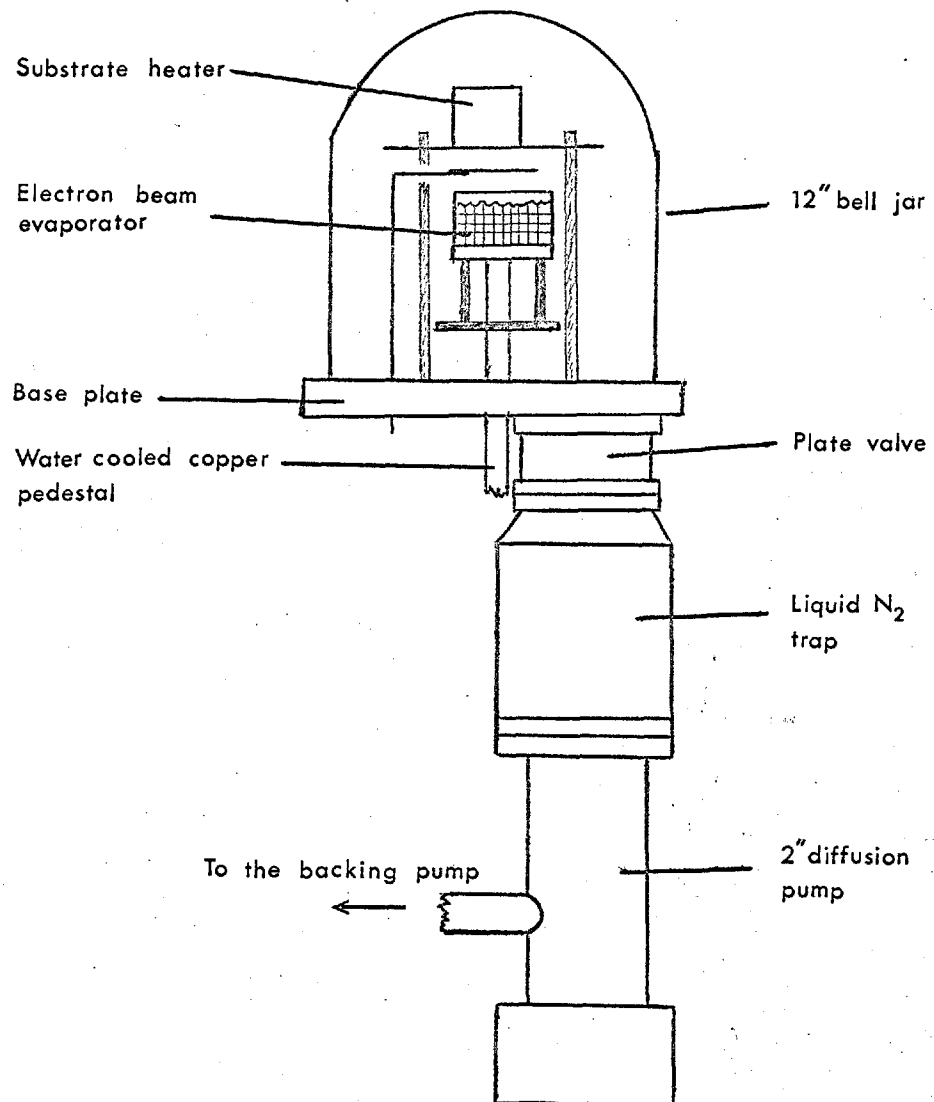


Fig. 3.1 THE VACUUM SYSTEM

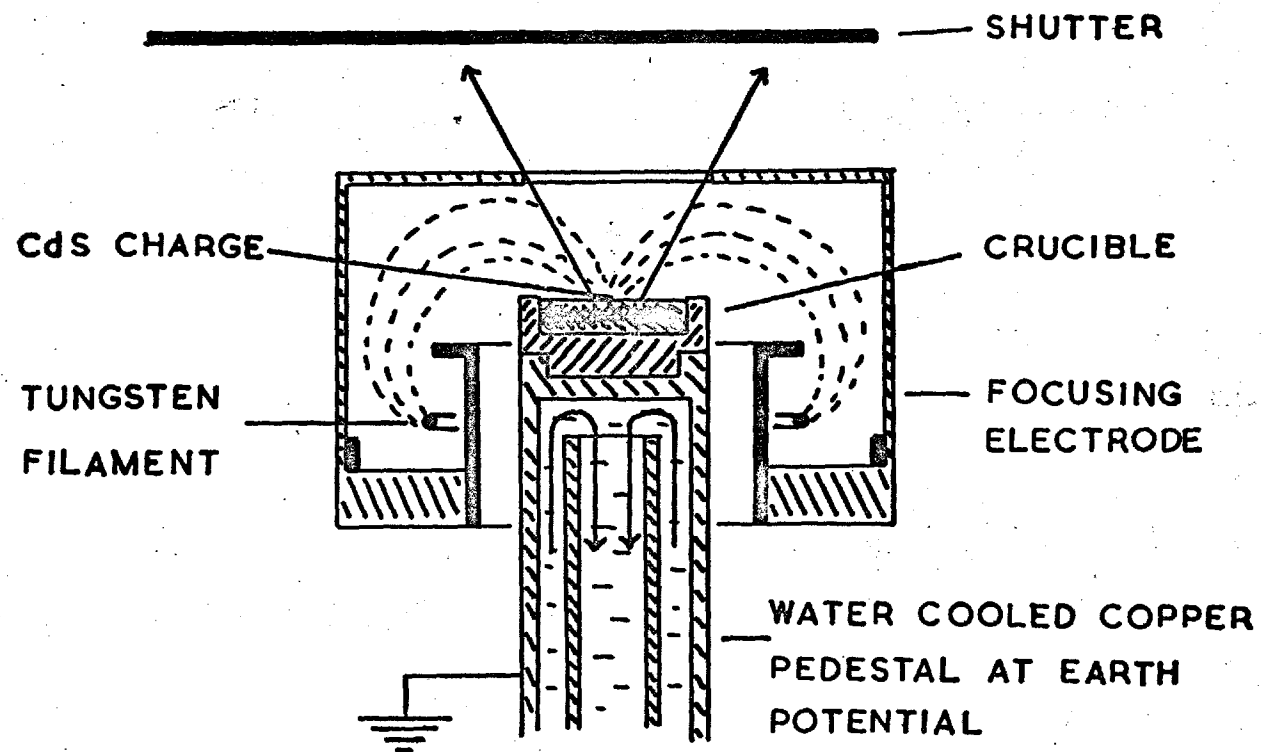


Fig. 3.2 THE ELECTRON BEAM EVAPORATOR

were necessary.

A shutter was situated between the evaporator and the substrate heater assembly. This was in position during the outgassing procedure to prevent contamination of the source with material volatilised from the substrate assembly or vice versa. The shutter could be turned to one side from outside the vacuum system when deposition commenced.

### 3.1.3. THE SUBSTRATE HEATER ASSEMBLY Fig. 3.3.

The substrate heater assembly was built on a stainless steel disc which was held rigid on three lengths of mild steel studding screwed into the base plate of the vacuum system. The substrate to source distance was adjusted by clamping the disc at the appropriate level on the studding and this distance was kept constant (7 cms.) for all experiments. The power supply to the substrate heater provided a variable voltage up to 25 volts and was fitted with coarse and fine controls.

Substrates were heated by radiation from a hot tantalum coil. To improve the temperature distribution in the substrate region, a heat diffuser made of molybdenum sheet was placed between the substrate holder and the coil. A double-walled heat shield, also made of molybdenum, was placed outside the coil.

It was possible to obtain temperatures in excess of  $1000^{\circ}\text{C}$ . and this provided a means of cleaning the substrate region efficiently.

Temperature measurements were made with two chromel-alumel thermocouples placed just beneath and on either side of the substrate holder. These were led into the substrate region through silicon tubing.

The thermocouples, heater coil and two substrate holder pins were mounted rigidly on a small insulated stainless steel plate. This in turn was mounted on the stainless steel disc, previously referred to, with ceramic insulating bushes. Both the heat shield

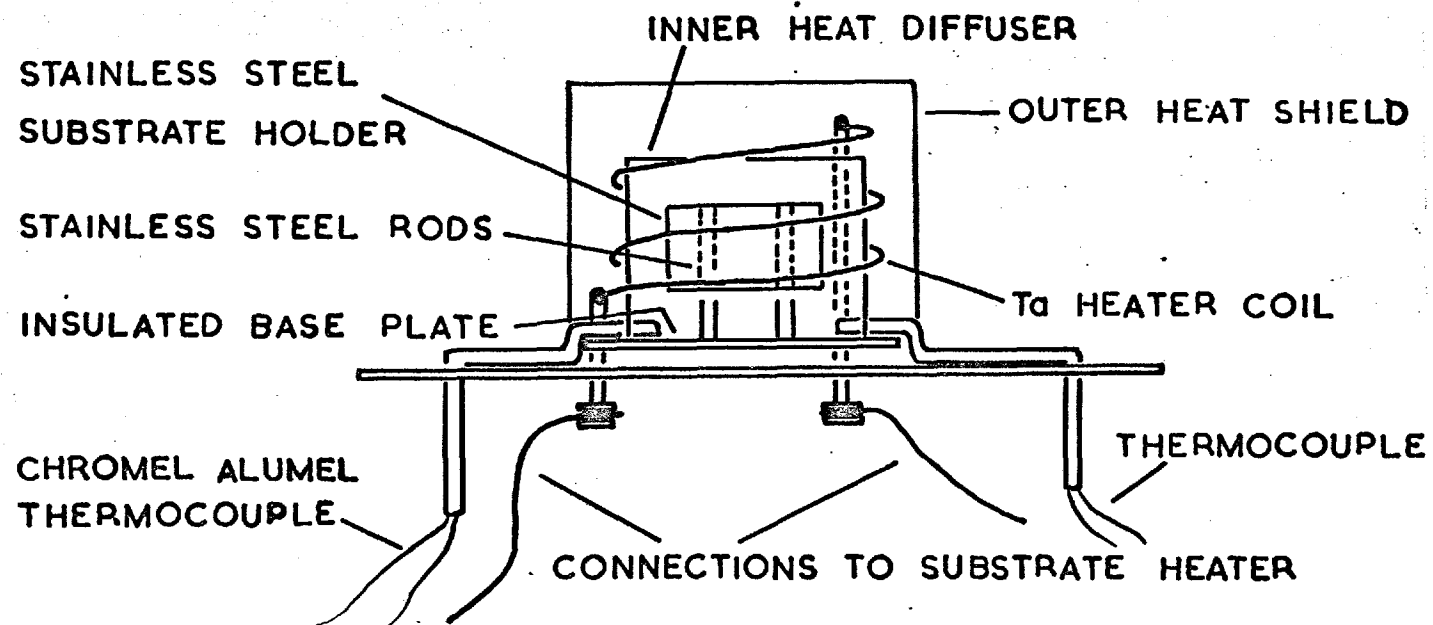


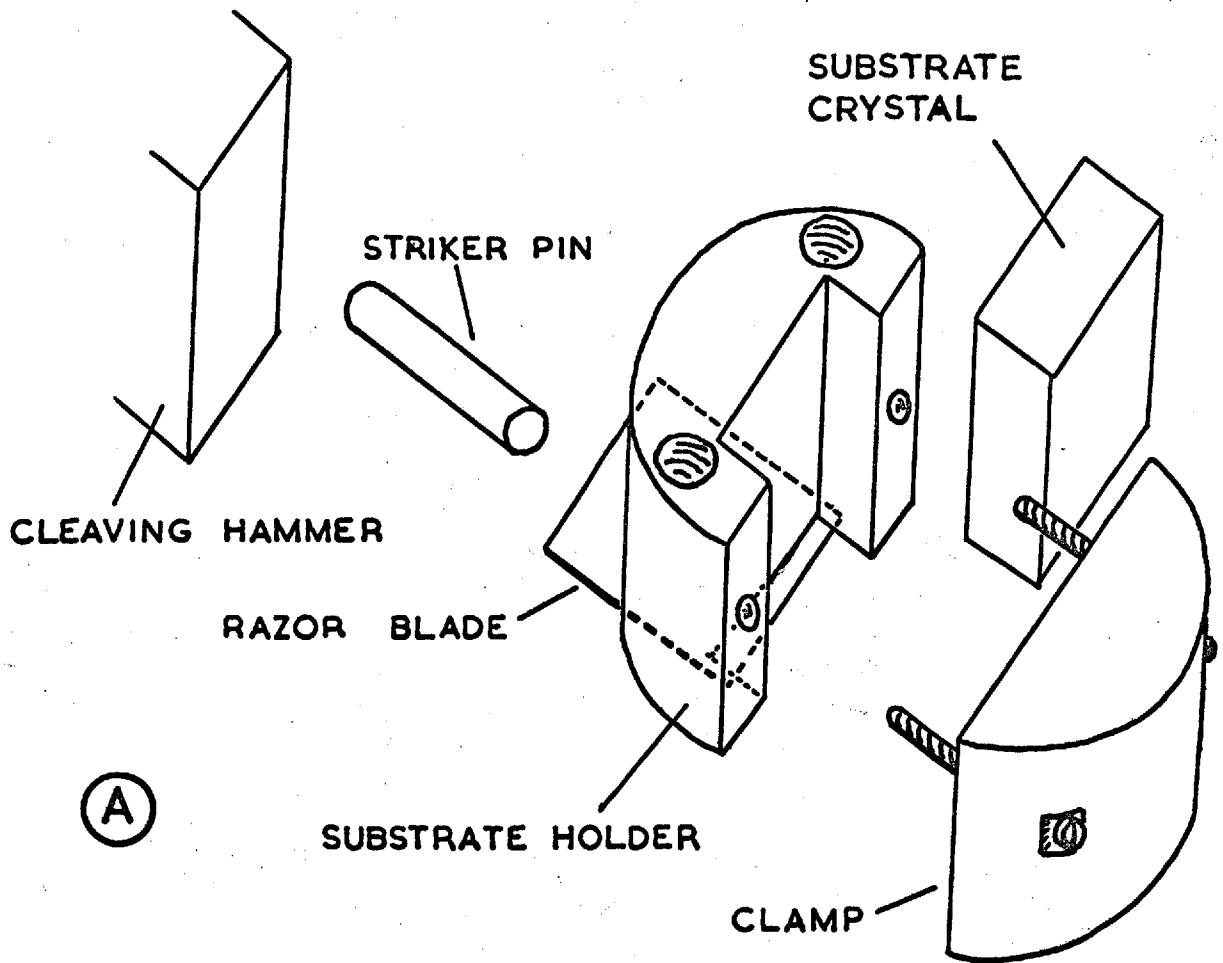
Fig. 3.3 THE SUBSTRATE HEATER ASSEMBLY

and the heat diffuser plugged onto the insulated disc.

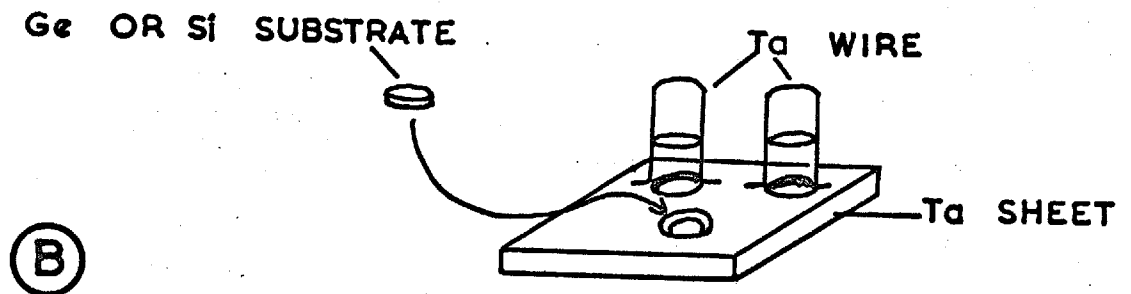
#### 3.1.4. THE SUBSTRATE HOLDERS Figs. 3.4 and 3.5

The substrate holder used with NaCl(100) and BaF<sub>2</sub>(111) substrates was made from a short length of stainless steel rod cut into two unequal portions parallel to the rod axis (fig. 3.3.A.). The substrate crystal was held in a rectangular-sectioned groove milled in the larger portion and the two segments could be screwed back together to provide a clamp for the crystal. Two holes were drilled in the larger segment so that the holder could slip over the two pins on the insulated base plate and the upper ends of the holes were blocked so as to limit the downward movement of the holder. A shallow groove was milled in the underside of the holder leading back between the support holes. A flat plate was then spot welded across the bottom of the holder to locate a small razor blade in the groove. The razor was used to cleave the substrate while in vacuo. The blade was struck by a pin which ran in a guide and passed between the heater coils and through the heat shields. This pin was in turn struck by a hammer actuated from outside the system.

A cooled substrate holder was made so that the lower end of the epitaxial temperature range for CdS deposited on vacuum-cleaved BaF<sub>2</sub>(111) substrates could be investigated. This was constructed from two small copper blocks, which screwed together as is shown in fig. 3.5. and a length of copper tubing. The ends of the copper tube were taken through a blanking plate on the vacuum system. The substrate holder was held in position by two screws which bolted it rigidly to an aluminium plate held above the evaporator. As in the case of the substrate holder described above, a slot was made to accommodate a small razor blade so that the cooled substrate could be cleaved immediately before deposition was commenced. One end of the copper tube was connected to a pump and the other was dipped in a dewar of liquid nitrogen. The temperature of the substrate holder could

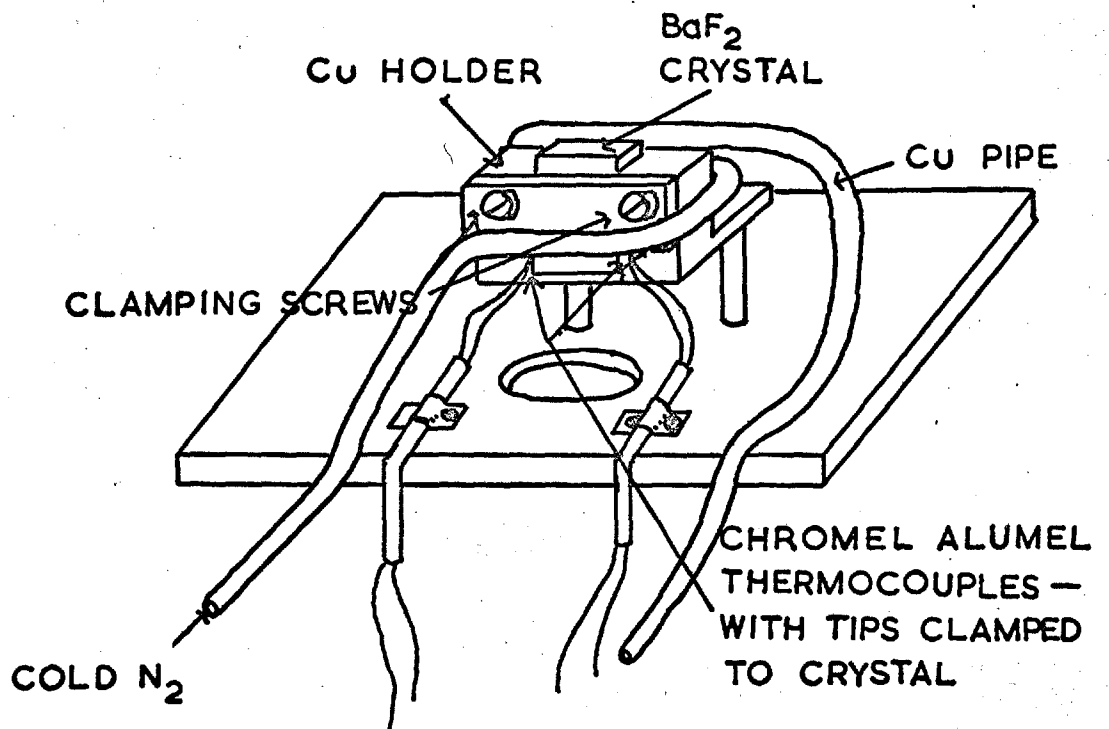


The substrate holder used for holding  $\text{NaCl}(100)$  and  $\text{BaF}_2$  rods. This had to be rigidly constructed to enable the crystals to be cleaved cleanly.



The substrate holder used for Ge and Si substrates. A similar one was used for  $\text{NaCl}(111)$  and  $\text{NaCl}(110)$  substrates.

Fig. 3.4 THE SUBSTRATE HOLDERS



COOLED SUBSTRATE HOLDER

Fig. 3.5 THE COOLED SUBSTRATE HOLDER

be lowered to about  $-100^{\circ}\text{C}$ . and maintained at this temperature indefinitely by sucking cold nitrogen gas through the tube.

The substrate holders for the other substrates were made from tantalum sheet and tantalum wire. They are illustrated in fig. 3.4.B. The substrates were simply laid over a hole in the substrate holders.

### 3.2. PREPARATION OF SUBSTRATES

#### 3.2.1. PREPARATION OF NaCl(110) AND NaCl(111) SUBSTRATES

A perspex holder was made in two halves fig. 3.6. Both halves had a groove of rectangular cross-section milled down the centre. When glued together, the two halves made a cylinder containing an axial hole of rectangular cross-section. The hole was such that a standard size rod of NaCl (manufactured by the HARSILAW CHEMICAL Co Ltd) having (100) faces was a close fit when pushed inside. Nylon screws through the side served to clamp the crystal. Two holders were made. They were mounted in a milling machine and a (111) face was cut on one holder and a (110) face cut on the other.

By pushing a crystal through to the end of the holder where the faces had been milled, the portion projecting could be ground off on emery paper thus exposing either a (111) face or a (110) face. The face was then polished using  $15\mu$  and  $1\mu$  pastes. Finally, the shaped part of the crystal was cleaved off and chemically polished in a solution containing two parts of concentrated HCl to one part of deionised water (STEARNS, 1965). The substrate was washed in ethyl alcohol. If the alcohol was at all damp, the crystal surfaces became dull when the alcohol evaporated. This was commonly the case, but the problem could be overcome by swilling the substrate in a beaker of  $\text{CCl}_4$ . This is not prone to water contamination and has the added

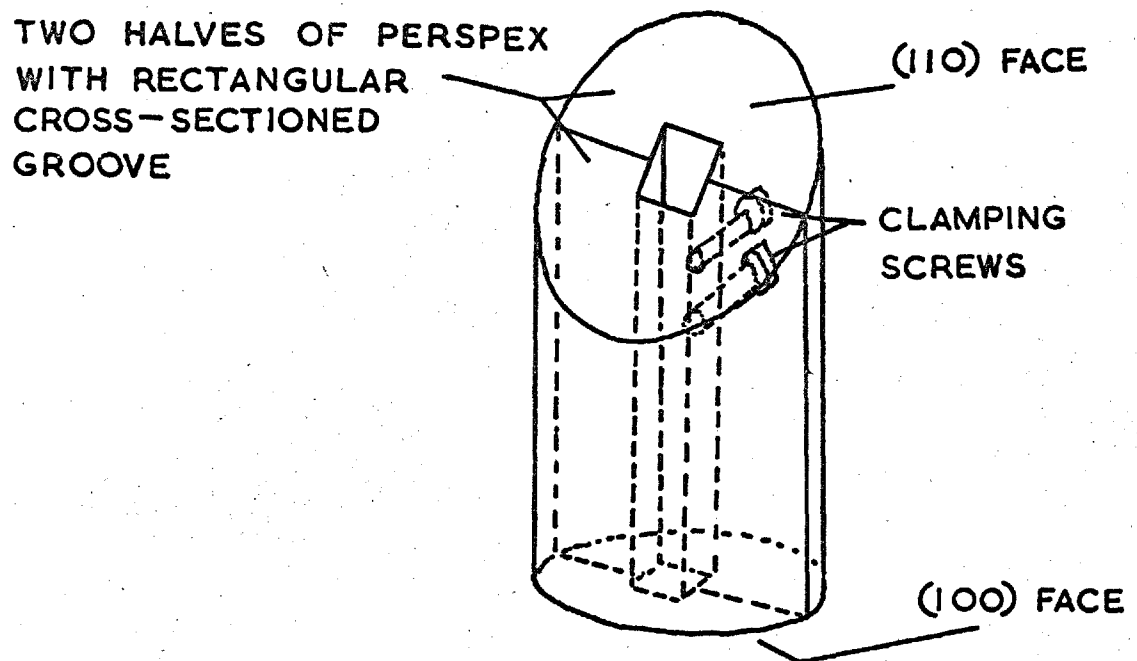


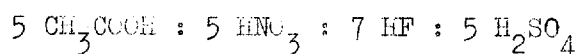
fig. 3.6 A polishing jig for making (110) oriented NaCl substrates.

advantage of not wetting the NaCl surface. The  $\text{CCl}_4$  did not appear to contaminate the substrate surfaces. The substrates were stored under  $\text{CCl}_4$  until immediately before placing in the vacuum system because it was found that the surfaces were etched by the humidity in the atmosphere.

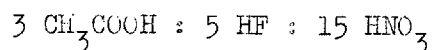
### 3.2.2. PREPARATION OF Ge(111) AND Si(111) SUBSTRATES

Both substrates were prepared in similar ways. A large mechanically polished (111) oriented slice was mounted on a glass slide with picene wax and discs 3 mm in diameter were cut out using an ultrasonic drill and a fine abrasive. The wax was removed in boiling trichlorethylene in three stages to ensure that the surface of the discs was completely clean. The discs were then washed in methyl alcohol and stored in deionised water.

The Ge(111) substrates were prepared for the evaporation by chemically polishing for two minutes in a solution of the following composition:-



Si(111) discs were prepared by chemically polishing them for one minute in the following solution:-



All the acids were of technical grade and were concentrated.

The substrates were then washed repeatedly in deionised water and finally rinsed in methyl alcohol before being stored in  $\text{CCl}_4$ .

### 3.2.3. PREPARATION OF THIN FILM Ge(111) SUBSTRATES

Some preliminary experiments were performed to establish the optimum growth conditions for Ge on air-cleaved  $\text{CaF}_2(111)$  substrates. This substrate material was used as it had already been shown to give reasonable results by SLOOPE and TILLER (1962) and CATLIN and BELLEMORE (1966). The thin films produced in this way were studied in the electron microscope to determine their crystal structure and

thickness variation. The best results were obtained using the following procedure:-

The  $\text{CaF}_2$  substrate was cleaved in air and placed in the vacuum system. It was outgassed for five minutes at  $700^\circ\text{C}$ . and then cooled to  $550^\circ\text{C}$ . The germanium was then evaporated from a molten button heated by an electron beam. The button was held in a carbon crucible which plugged into the watercooled pedestal.

The films were allowed to cool to  $60^\circ\text{C}$ . and were floated off in boiling deionised water. Occasionally, if the film was particularly adherent, hot  $\text{NH}_4\text{Cl}$  solution was used.

The films which were used as substrates were left on the  $\text{CaF}_2$  crystal in the vacuum system and the Ge source exchanged for the CdS source. This was a weakness in the procedure as it entailed opening the system to the atmosphere. A certain amount of contamination of the Ge surface was inevitably incurred. The system was re-evacuated and the crystal and Ge layer outgassed at  $600^\circ\text{C}$ . Deposition of CdS was carried out after the substrate had been cooled to  $400^\circ\text{C}$ .

The total thickness of the composite film was such that it was transparent in the electron microscope. These films were also removed in one of the ways mentioned above, and collected on copper grids.

### 3.3. EXPERIMENTAL PROCEDURE FOR GROWING THIN FILMS

When the substrates to be used were chemically polished or air-cleaved, the substrate heater was outgassed under vacuum, without the substrate in position, at about  $1000^\circ\text{C}$ . for a few minutes. The temperature was then allowed to drop below  $100^\circ\text{C}$ . and the system opened to air. This preliminary outgassing procedure was omitted when vacuum-cleaved substrates were being used. The crucible was then filled with an electronic grade of CdS powder (DERBY LUMINESCENT Co. LTD.) and this and the substrate placed in position. The belljar

was evacuated and when the pressure had fallen into the  $10^{-5}$   $\gamma$  range, the substrate was heated to its outgassing temperature. This was about 500°C. for NaCl, 650°C. for BaF<sub>2</sub>, 750°C. for Ge and 1000°C. for Si. At these temperatures, not only was adsorbed material removed from the substrate but also the vapour pressures of the materials at these temperatures indicate that the first few atomic layers of the substrate itself should sublime. The substrate was held at the appropriate high temperature for about five minutes while the source was outgassed. This was done by defocussing the electron beam until the whole surface of the charge was being heated. The evaporator was then switched off and the substrate cooled to the deposition temperature. This was allowed to stabilise for several minutes before beginning deposition.

Stable evaporation conditions were established immediately with the electron beam evaporator. The time of deposition was standardised at three minutes and the deposition rate (section 3.7) was maintained at about 10<sup>0</sup>Å per second.

As soon as the three minutes had passed, the evaporator and the substrate heater were switched off. When the substrate had cooled to 60°C, it was removed from the system.

Films grown on the ionic crystals were floated off and collected on 400 mesh copper microscope grids. The films used for annealing experiments were collected on gold grids. Films deposited on NaCl came off easily in deionised water but those deposited on BaF<sub>2</sub> were more difficult to remove. Hot NH<sub>4</sub>Cl solution removed small pieces from most of the layers and these were washed to remove the solution. This was done by collecting the specimen from the surface of the solution and transferring it immediately to a dish of deionised water. Films washed in this way rarely showed signs of contamination when viewed in the electron microscope.

The silicon and germanium substrates were thinned down from the side opposite to the film using the techniques described below in section 3.5 until the undersides of the films were exposed.

The layers were studied by transmission in an A.E.I. EM6G electron microscope operating at 100 Kv and plots were made of "R" value (sec. 2.4.3) versus substrate temperature for each kind of substrate.

#### 3.4. PROCEDURE FOR ANNEALING THIN FILMS

A small nickel box was made which fitted over the substrate holder pins shown in fig. 3.3. The bell jar and its contents were cleaned and the vacuum system thoroughly outgassed.

The thin films, which were collected on gold grids, were annealed one at a time in the nickel box using the substrate assembly as an annealing furnace. No contamination of the films was ever detected by microscopy. The films were annealed for times of between ten minutes and one hour. The maximum annealing temperature which could be used for the one hour anneals was about  $450^{\circ}\text{C}$ . whereas  $500^{\circ}\text{C}$ . could be tolerated for annealing times of thirty minutes or less. The annealing furnace took no more than thirty seconds to reach the required temperature. The rate of cooling however was considerably lower. The furnace temperature dropped only about  $200^{\circ}\text{C}$ . in the first minute of cooling. Despite this, the true annealing time was probably no more than 10% wrong in the worst case (i.e. the 10 minute anneal at  $500^{\circ}\text{C}$ ).

#### 3.5. APPARATUS AND METHOD USED FOR THINNING Ge(111) AND Si(111)

The electrochemical thinning technique is based upon that used by BLANKENBURGS AND WHEELER (1963-64). Fig. 3.7. is a schematic diagram of the thinning apparatus. This comprised a lamp, a transparent jet, the specimen holder and moveable carriage and also a microscope. These were mounted in line on an optical bench so that light from the lamp passed through the jet and fell onto the

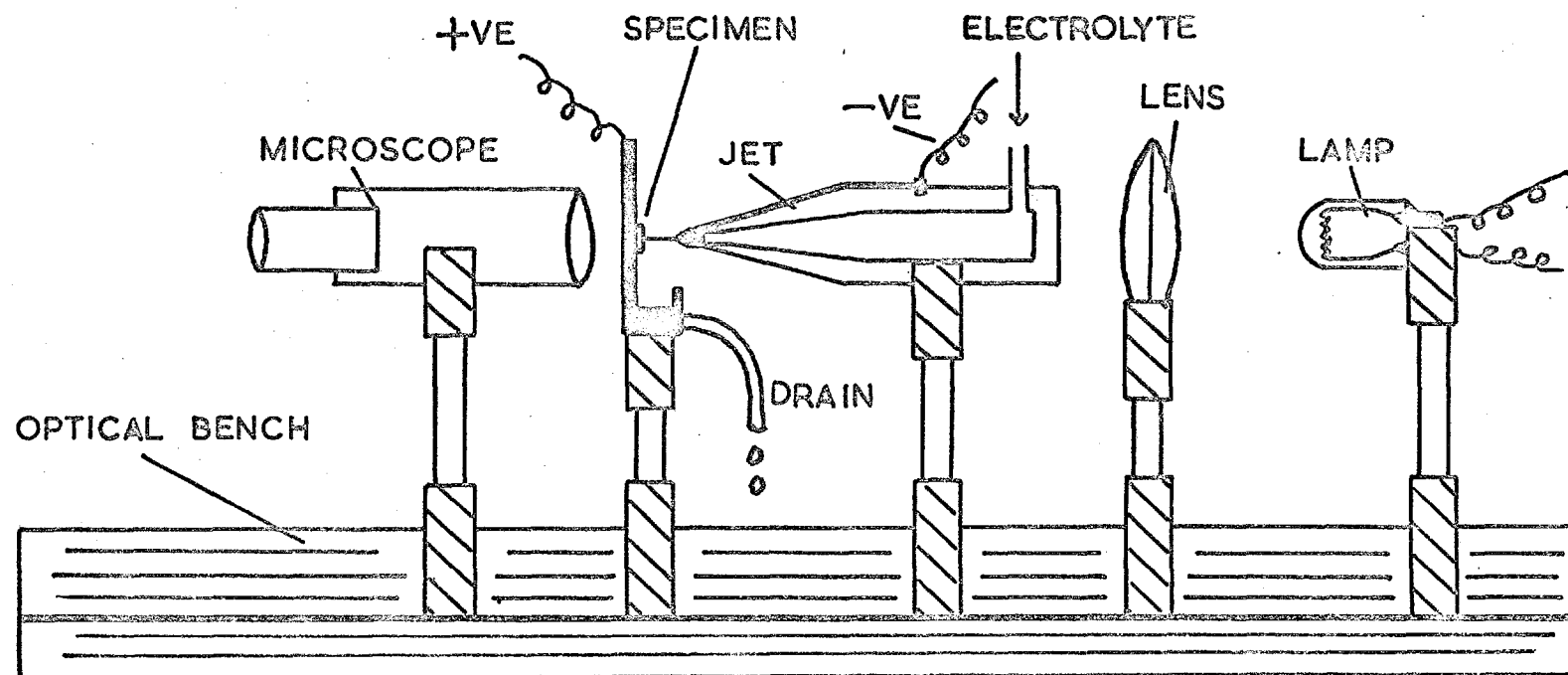


Fig. 3.7. THE ELECTROCHEMICAL JET-THINNER

specimen. Any light transmitted by the specimen could be observed through the microscope. The thinning solution was fed to the jet through flexible plastic tubing from a header tank and the flow rate was regulated by an adjustable clip which constricted the tube. The distance between the jet nozzle and the specimen was adjustable and the microscope could be focussed on the specimen after it and the jet had been placed in the correct positions.

Specimens were mounted over a hole in a copper plate. The hole was slightly smaller than the specimens and no light was visible through the microscope after it had been stuck over the hole with "lacomit" varnish. The plate was covered with the varnish wherever the reagent could reach.

Electrical connections were made to the plate (positive) and the metal nozzle (negative). Current was supplied by high voltage dry batteries and a bell-push was placed in series with them so that a polishing current passed only when the button was depressed.

The flow conditions at the specimen face were found to be critical. The correct conditions are very easily recognised. For satisfactory "dimpling" of the specimen, the jet has to strike the surface so that the liquid shoots away radially from the point of impingement as a very thin and therefore a highly **resistive** disc. When this occurs, the corrosion current is concentrated at the point where the jet strikes the specimen surface and dissolution is restricted to this small region. Provided that the flow conditions at the specimen surface are correct, the flow rate is not critical.

The only other significant parameter is the current density. It was found that this had to be above a certain minimum value otherwise pitting of the specimen surface occurred. The current density was calculated to be about 30 amps/cm<sup>2</sup> for Ge(111) and

45 amps/cm<sup>2</sup> for Si(111).

The solution used for thinning Ge was approximately 0.1N KOH containing about 5 gms/litre of NH<sub>4</sub>Cl and that used for thinning Si was a 0.6N HF solution.

The silicon was not attacked by the dilute HF if there was no current flowing. Consequently, the final stages of thinning could be accurately controlled. Even when the current was flowing, the CdS layer would not dissolve and this enabled a hole to be made right through the Si substrates without destroying the thin CdS film which was left unsupported across the hole.

Since Ge absorbs visible light more strongly than Si, it was not quite so easy to judge the moment at which the Ge became transparent. However, the CdS was quite insoluble in KOH and it did not matter if the Ge thinned right through. In fact this was always purposely done so that some of the film could be studied without interference from the substrate.

### 3.6. DETERMINATION OF THE ORIENTATION RELATIONSHIP BETWEEN THE THIN FILMS AND THEIR SUBSTRATES

When the thin film was viewed in the electron microscope whilst still on the substrate, as was the case with thin films on thinned Ge and Si substrates, the orientation relationship was determined directly from the diffraction patterns.

In cases where the thin film was removed from the substrate and placed on grids, the following technique was used. Well-defined cleavage steps lying in [100] direction on NaCl substrates or [110] direction on BaF<sub>2</sub> substrates were occasionally replicated by the CdS film. The orientation relationship between the thin film and its substrate could then be determined from the real image and the diffraction pattern.

The same technique was used for thin films on NaCl(110) and (111) substrates except that in this case, replicated etch pits whose edges

lie along  $\langle 110 \rangle$  directions, could be aligned with directions in the CdS lattice. The orientation relationship between the etch pits and the substrate crystal was determined with an optical microscope.

### 3.7. MEASUREMENT OF FILM THICKNESS

The film thickness was measured directly by using the Nomarski interferometric method. This could be used at the edge of the film where the substrate had been masked by the cleaving blade.

Most of the film thicknesses were obtained indirectly by observing the interference colour produced by the film in light at normal incidence. The wavelength of the interference colour was estimated and the film thickness,  $t$ , determined from the formula:-

$$(m + \frac{1}{2})\lambda = 2nt$$

Where  $n$  is the refractive index of CdS ( $n$  for CdS is 2.5 HANDBOOK OF PHYSICS AND CHEMISTRY),  $\lambda$  is the wavelength of the interference colour and  $m$  is the order of the interference colour. A factor of  $\frac{1}{2}$  is added since there is a phase change of  $\pi$  in the light reflected at the interface between the air and the CdS but not at the interface between the CdS and the NaCl or BaF<sub>2</sub> since neither of these has a refractive index as high as that of CdS. There is therefore a phase difference of  $\pi$  between the light reflected from the top surface of the film and that reflected from the bottom surface (JENKINS and WHITE, 1951).

All the continuous films which were transparent to the electron beam gave interference colours which ranged between green and red. This corresponded to wavelengths between about 4000Å and 6000Å.

The formula above may be rearranged to give the film thickness directly. If the value of 2.5 for  $n$  is inserted, then  $t$  is given by:-

$$t = \frac{m + \frac{1}{2}}{5} \lambda$$

If  $m$  is 1,  $t$  lies between  $1200\overset{\circ}{\text{A}}$  and  $1800\overset{\circ}{\text{A}}$  for wavelengths corresponding to colours from red to green and if  $m$  is 2,  $t$  lies between  $2400\overset{\circ}{\text{A}}$  and  $3600\overset{\circ}{\text{A}}$  for the same colour range. Since films giving second and higher order interference colours were too thick for useful observations to be made in the electron microscope, the interference colour uniquely defined the film thickness for electron transparent specimens.

It was estimated that the accuracy of thickness measurement by the Nomarski technique was no better than  $\pm 100\overset{\circ}{\text{A}}$  and the accuracy obtainable by observing the interference colour of the film no better than  $\pm 25\overset{\circ}{\text{A}}$ .

The deposition rate was obtained by dividing the final film thickness by the time of deposition. The rate so obtained lay between  $7\overset{\circ}{\text{A}}$  and  $10\overset{\circ}{\text{A}}$  per second. The constancy of the deposition rate was not determined. However, the average deposition rates could not have varied by as much as a factor of 2 otherwise thicker films showing second order interference colours or thinner films showing no colours at all would have been produced at apparently similar power settings for the evaporator. This criterion was considered to be perfectly adequate since an increase of 10 times in the deposition rate had the effect of increasing the minimum epitaxial temperature by only about  $100^{\circ}\text{C}$ . (sec. 4.2.2).

## CHAPTER 4

### EXPERIMENTAL RESULTS

#### 4.1. THE EPITAXIAL TEMPERATURE RANGES

##### 4.1.1. FILMS DEPOSITED ON AIR-AND VACUUM-CLEAVED NaCl(100) SUBSTRATES

Fig. 4.1.A shows the "R" value versus substrate temperature curves for air-and vacuum-cleaved substrates. Films grown on either substrate at room temperature were polycrystalline with mainly random orientations. CdS with both the hexagonal wurtzite structure and the cubic sphalerite structure was present and as the substrate temperature was increased, both structures became oriented with respect to the substrate. No polycrystalline material was detected in thin films grown on air-cleaved substrates above 125°C. and on vacuum-cleaved substrates above 100°C. The following are the orientation relationships between the substrate and the two structures in the thin film which were determined.

CdS with the wurtzite structure:-

$$\begin{aligned} & (0001) \text{ CdS} // (100) \text{ NaCl} \\ & \text{and } [\bar{1}120] \text{ CdS} // [011] \text{ NaCl} \\ & \text{or } [\bar{1}0\bar{1}0] \text{ CdS} // [011] \text{ NaCl} \end{aligned}$$

This represents a double-positioning of the material with respect to the substrate as discussed in section 2.6 and gives an inner ring of twelve diffraction spots angularly separated by 30°. This is illustrated in Fig. 4.2.A.

CdS with the sphalerite structure had the parallel orientation relationship:-

$$\begin{aligned} & (100) \text{ CdS} // (100) \text{ NaCl} \\ & [011] \text{ CdS} // [011] \text{ NaCl} \end{aligned}$$

Above substrate temperatures of 125°C. for vacuum-cleaved substrates and 150°C. for air-cleaved substrates, the thin films were single-phase and had the cubic structure with the orientation relationship just specified.

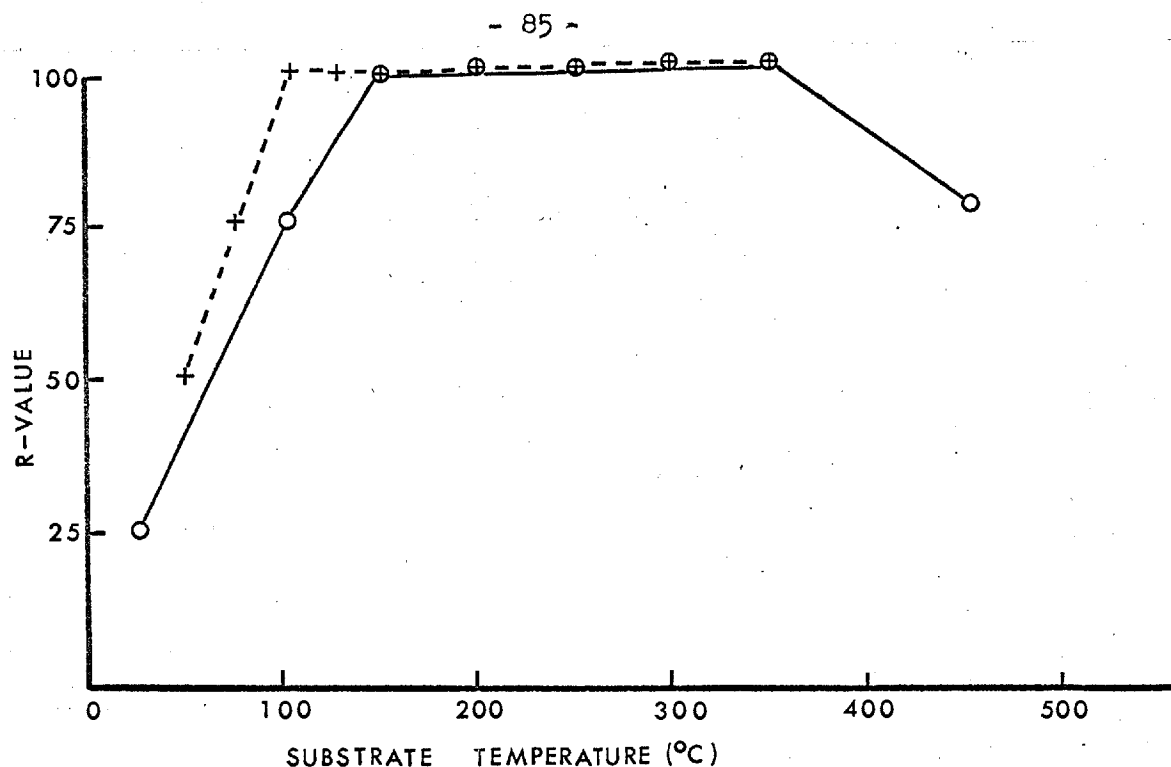


Fig. 4.1.A. THE R-VALUE VERSUS SUBSTRATE TEMPERATURE CURVE FOR CdS DEPOSITED ON AIR-AND VACUUM-CLEAVED NaCl(100)

- o represents a result for air-cleaved substrates.
- + represents a result for vacuum-cleaved substrates.

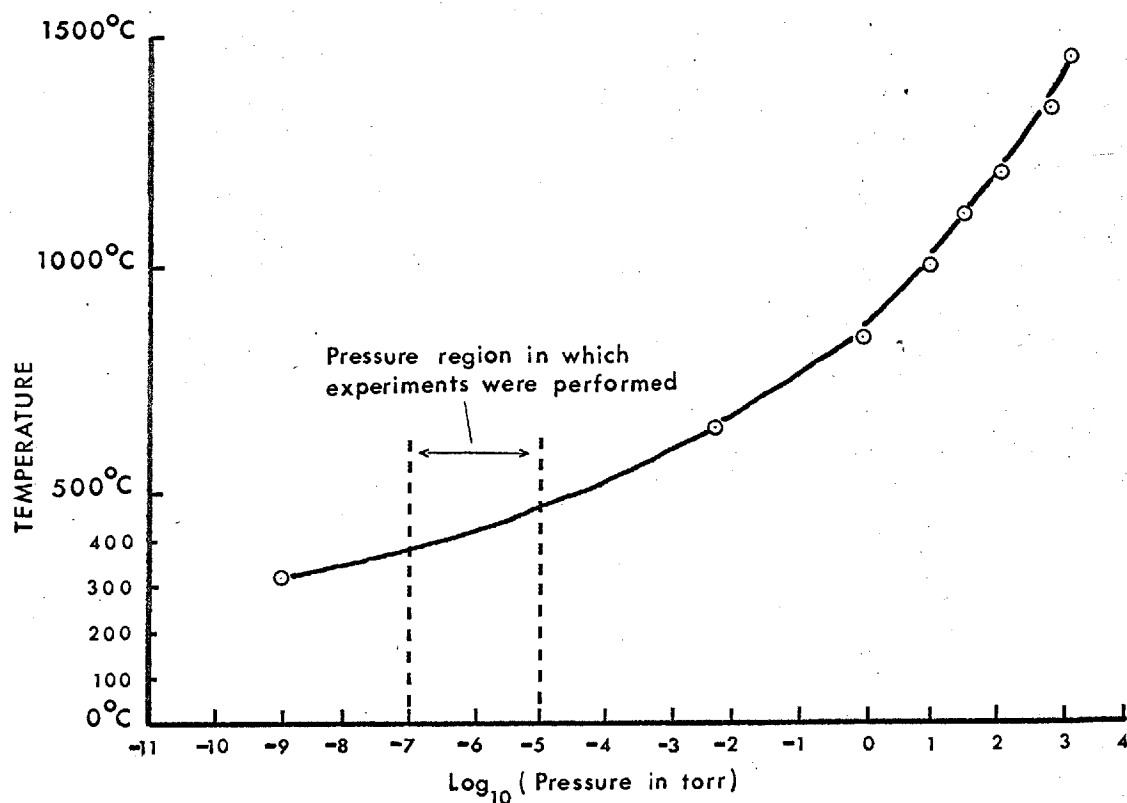
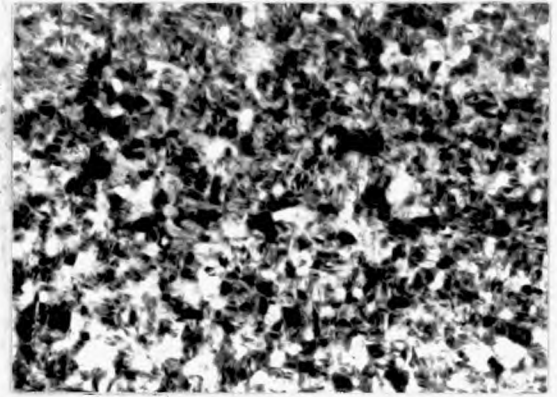
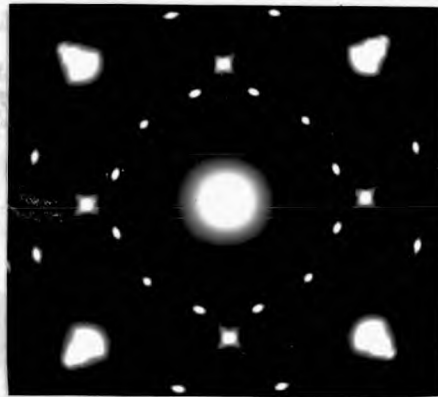
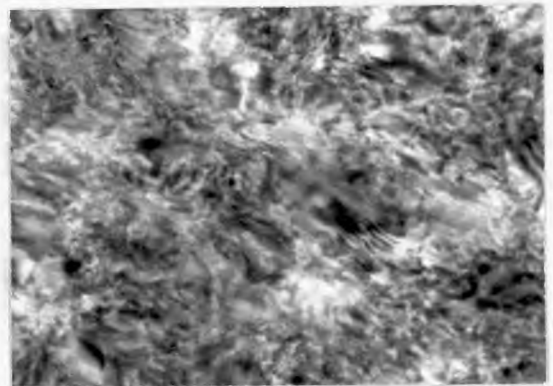


Fig. 4.1.B. THE VAPOUR PRESSURE VERSUS TEMPERATURE GRAPH FOR NaCl



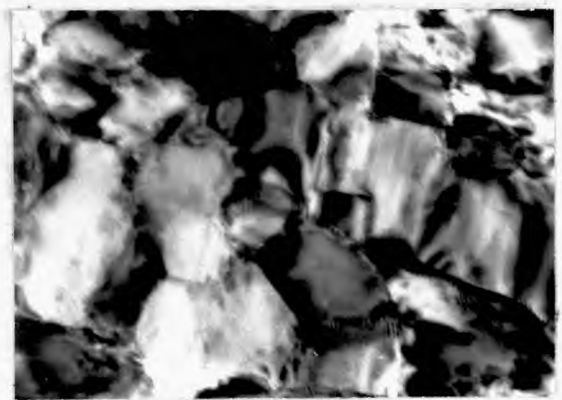
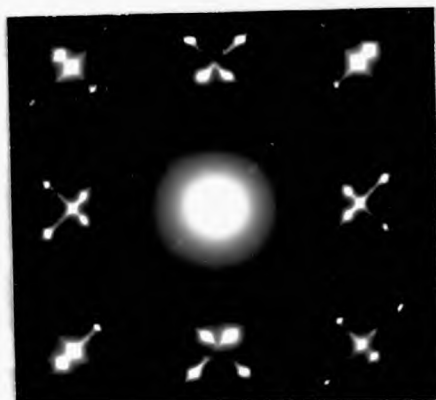
(A) SUBSTRATE TEMPERATURE =  $100^{\circ}\text{C}$ .

$\overline{0.1 \mu}$



(B) SUBSTRATE TEMPERATURE =  $300^{\circ}\text{C}$ .

$\overline{0.1 \mu}$



(C) SUBSTRATE TEMPERATURE =  $350^{\circ}\text{C}$ .

$\overline{0.1 \mu}$

Fig. 4.2. DIFFRACTION PATTERNS AND MICROGRAPHS FOR EPITAXIAL LAYERS OF CdS DEPOSITED ON VACUUM CLEAVED NaCl(100) SUBSTRATES.

Fig. 4.2.B shows a diffraction pattern and a micrograph of a film grown on vacuum-cleaved NaCl(100) at a temperature of 300°C.

Included grains of CdS with the wurtzite structure were again present in films grown on both air-and vacuum-cleaved substrates at 350°C. The orientation relationship with respect to the sphalerite matrix was different from that for the doubly positioned grains.

Fig. 4.2.C shows a diffraction pattern and a micrograph of a film grown on a vacuum-cleaved substrate at 350°C. The extra spots in the diffraction pattern are due to the included grains. By comparing the diffraction pattern with the one discussed in section 2.6.4.5. it can be seen that they are identical. The included grains with the wurtzite structure therefore had the following orientation relationship:-

$$(0001) \text{ wurtzite CdS} // (111) \text{ sphalerite CdS} \\ \text{with } [\bar{1}120] // [\bar{1}01]$$

This diffraction pattern is analysed in some detail in section 5.1.1.4 and appendix A.1.

At a substrate temperature of 400°C. the film structure was polycrystalline and at 450°C. no layers could be deposited using even the highest evaporation rates. This was presumably due to the evaporation of the substrate (HARSDORF, 1963 and 1964). This view is substantiated by fig. 4.1.B which shows a graph of the vapour pressure of NaCl as a function of temperature. It can be seen that the vapour pressure of NaCl at the temperature above which it was found that no epitaxial layer could be deposited (450°C.) is close to the background pressure of the vacuum system during evaporation. That is, NaCl sublimates at 450°C. to generate a vapour pressure of  $10^{-6}$  Torr.

The data for this graph was obtained from ROWE and BROCKWAY (1966) and HANDBOOK OF CHEMISTRY AND PHYSICS 45th EDITION.

#### 4.1.2. FILMS DEPOSITED ON NaCl(110) SUBSTRATES

Fig. 4.3 shows the "R" value versus substrate temperature curve for films evaporated onto chemically polished NaCl(110) substrates. The structure of the films grown at room temperature consisted of a mixture of oriented CdS with both the wurtzite and sphalerite structures together with some polycrystalline material. This is shown in fig. 4.4.A. The absence of satellite spots in diffraction patterns from films deposited at substrate temperatures of 50°C. and above showed that they consisted of entirely sphalerite structure material.

The material with the wurtzite structure obtained in films grown at room temperature was mainly polycrystalline with random orientations. Some of it was also oriented with respect to the substrate and its epitaxial relationship was

$$\begin{aligned} & (0001) \text{ CdS} // (110) \text{ NaCl} \\ & \text{with } [\bar{1}1\bar{2}0] // [\bar{0}01] \end{aligned}$$

CdS with the sphalerite structure had the epitaxial relationship:-

$$\begin{aligned} & (110) \text{ CdS} // (110) \text{ NaCl} \\ & \text{with } [\bar{0}01] \text{ CdS} // [\bar{0}01] \text{ NaCl} \end{aligned}$$

A diffraction pattern and micrograph of a film grown at 300°C. is shown in fig. 4.4.B. The film consists entirely of material with the sphalerite structure. The epitaxial relationship for this film is the same as that stated above for the sphalerite structure.

#### 4.1.3. FILMS DEPOSITED ON CHEMICALLY POLISHED NaCl(111) AND VACUUM-CLEAVED BaF<sub>2</sub>(111) SUBSTRATES

The "R" value curves for films grown on these two substrates are shown in Fig. 4.5.

Thin films grown at all temperatures on both kinds of substrate had the hexagonal wurtzite structure. At room temperature, single-crystal films were obtained on BaF<sub>2</sub> only. Fig. 4.6.A shows a diffraction pattern and micrograph of a layer grown on BaF<sub>2</sub>(111) at

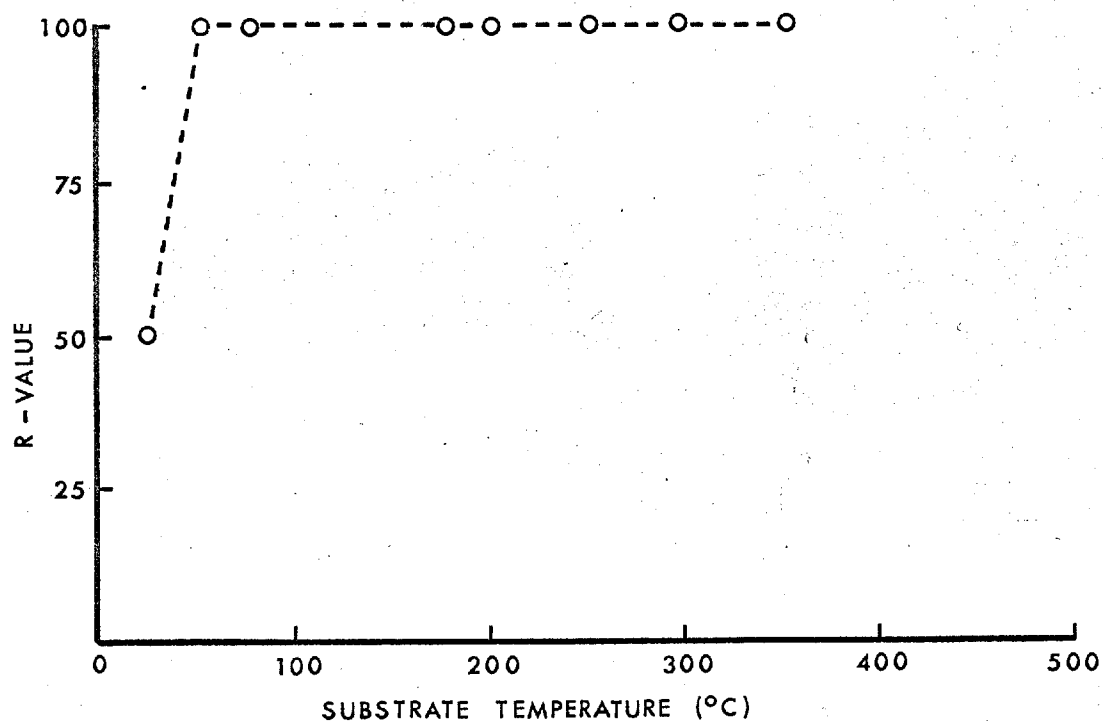
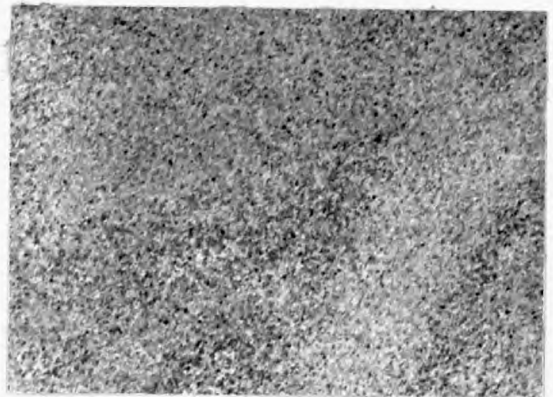
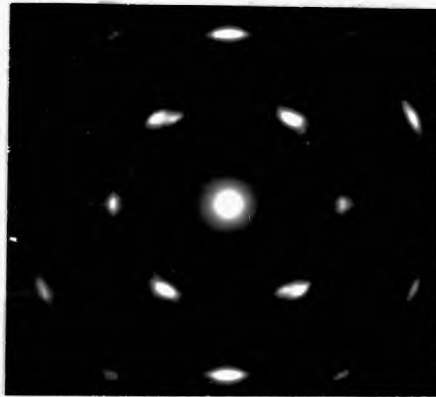
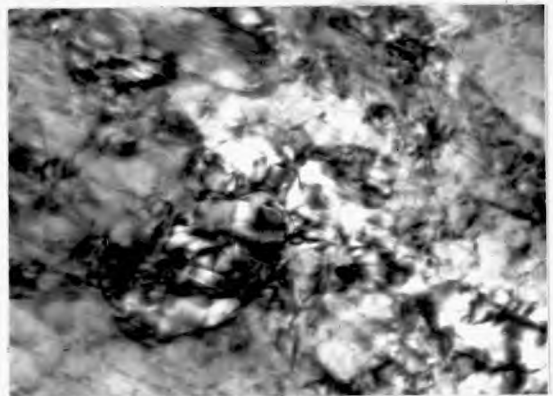
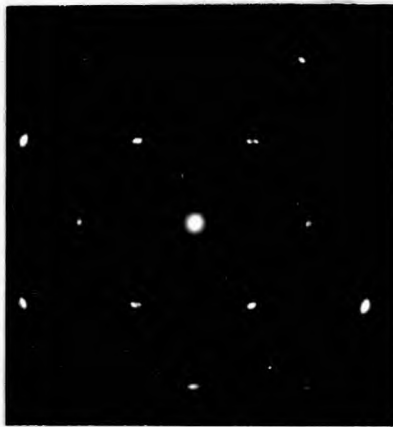


Fig. 4.3. THE R-VALUE VERSUS SUBSTRATE TEMPERATURE CURVE FOR CdS DEPOSITED ON CHEMICALLY POLISHED NaCl(110)



(A) SUBSTRATE TEMPERATURE =  $25^{\circ}\text{C}$ .  $\overline{0.25\mu}$



(B) SUBSTRATE TEMPERATURE =  $300^{\circ}\text{C}$ .  $\overline{0.25\mu}$

Fig. 4.4. DIFFRACTION PATTERNS AND MICROGRAPHS FOR EPITAXIAL LAYERS OF CdS DEPOSITED ON CHEMICALLY POLISHED NaCl(110) SUBSTRATES.

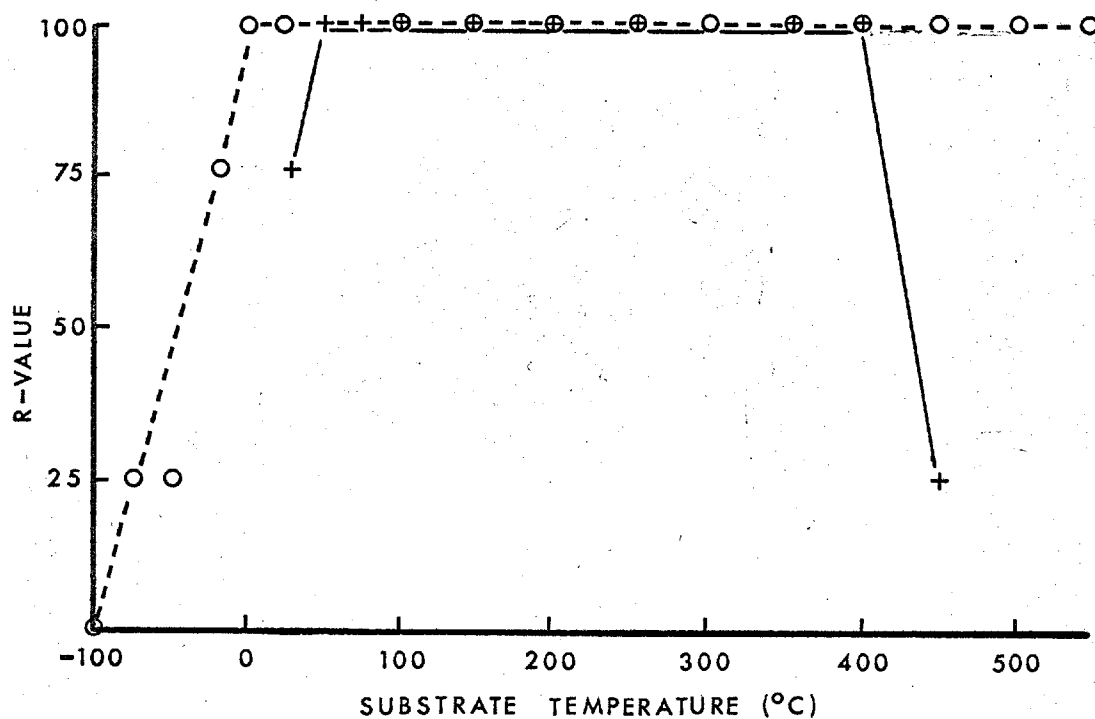
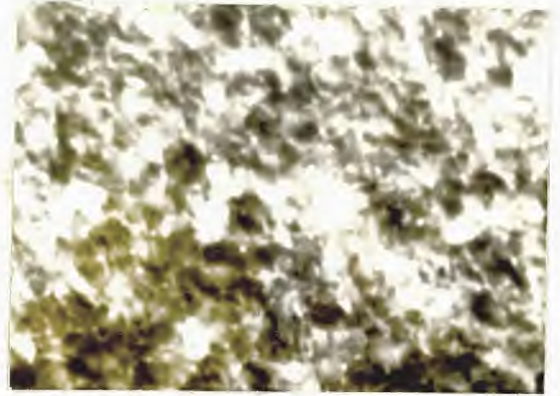


Fig. 4.5. THE R-VALUE VERSUS SUBSTRATE TEMPERATURE CURVE FOR CdS DEPOSITED ON CHEMICALLY POLISHED NaCl(111) AND VACUUM CLEAVED BaF<sub>2</sub>(111)

+ represents a result for NaCl(111) substrates.

o represents a result for BaF<sub>2</sub>(111) substrates.



(A) SUBSTRATE TEMPERATURE =  $25^{\circ}\text{C}$ .  $\overline{0.1\mu}$



(B) SUBSTRATE TEMPERATURE =  $200^{\circ}\text{C}$ .  $\overline{0.1\mu}$



(C) SUBSTRATE TEMPERATURE =  $300^{\circ}\text{C}$ .  $\overline{0.1\mu}$

Fig. 4.6. DIFFRACTION PATTERNS AND MICROGRAPHS FOR EPITAXIAL LAYERS OF CdS DEPOSITED ON VACUUM CLEAVED  $\text{BaF}_2(111)$  SUBSTRATES (A and B) AND CHEMICALLY POLISHED  $\text{NaCl}^2(111)$  (C).

room temperature. Raising the substrate temperature to 50°C. enabled single crystal films to be grown on NaCl(111) faces as well. Below this substrate temperature, some polycrystalline CdS was present in films grown on NaCl(111).

The number of visible defects decreased markedly in thin films grown on both substrates above a certain temperature. This was about 200°C. for BaF<sub>2</sub> and 250°C. for NaCl. Fig. 4.6.B and 4.6.C show diffraction patterns and micrographs from films grown on BaF<sub>2</sub> at 200°C. and on NaCl at 300°C.

Single crystal layers were obtained on NaCl up to a substrate temperature of 400°C. At 450°C. the layer was polycrystalline and no film at all could be obtained at 500°C. It was possible to obtain single crystal layers at 550°C. on BaF<sub>2</sub> but at 600°C. either the CdS or the BaF<sub>2</sub> was too volatile to allow deposition to take place.

In all cases, the orientation relationship between the substrate and the thin film was found to be:-

$$(0001) \text{ CdS} // (111) \text{ NaCl or BaF}_2 \text{ with } [\bar{1}120] // [\bar{1}1\bar{0}]$$

The lower end of the epitaxial temperature range for CdS deposited on BaF<sub>2</sub>(111) substrates was investigated using the cooled substrate holder shown in fig.3.5. The layers were deposited at temperature intervals of 25°C. from room temperature (25°C.) down to -100°C. The orientation of the layers began to randomise at -25°C. A hexagonal array of intensity maxima was visible in the diffraction rings of patterns obtained from layers deposited at -100°C. This indicated that the substrate was still maintaining an orienting effect on the growing film. The deterioration in the crystal structure could have been genuinely due to the layer being deposited at temperatures below the epitaxial temperature range. However it could also have been due to the incorporation into the layer of impurity material which was being given off from the warmer parts of the system.

#### 4.1.4. FILMS DEPOSITED ON CHEMICALLY-POLISHED Ge(111) AND Si(111) SUBSTRATES

##### 4.1.4.1. FILMS GROWN ON Ge(111) SUBSTRATES

Fig. 4.7. shows the "R" value versus substrate temperature curves for CdS deposited on Ge(111). Polycrystalline layers were found to grown on Ge(111) up to a substrate temperature of 250°C. At 250°C, however, the layers had the wurtzite structure with the "C" axis perpendicular to the substrate surface and only the azimuthal distribution of the crystallites about the "C" axis was random.

Fig. 4.8.A.

At 300°C. the layers were single-crystal but the diffraction spots were slightly arced showing that the crystallites were still misaligned about the C axis (film normal) to a small extent. At substrate temperatures of 400°C. and above, the layers gave diffraction patterns with sharp diffraction spots.

The epitaxial relationship between the films and the substrate was:-

$$\begin{array}{l} (0001) \text{ CdS } // (111) \text{ Ge} \\ \text{with } [\bar{1}120] // [\bar{1}10] \end{array}$$

Fig. 4.8.B shows a diffraction pattern and micrograph of a layer grown on Ge(111) at 300°C.

##### 4.1.4.2. FILMS GROWN ON Si(111)

In no case was a layer produced which was epitaxial. Throughout the entire substrate temperature range (between room temperature and 500°C.) the CdS layers were polycrystalline (fig. 4.8.C). It is believed that this was due to contamination of the substrate surface. When the Si substrates were placed under vacuum, heated to a high temperature of the order of 1000°C. and cooled, the surface appeared to have become slightly dull. This indicated the presence of a surface layer which may have been responsible for the poor results. It was therefore concluded that

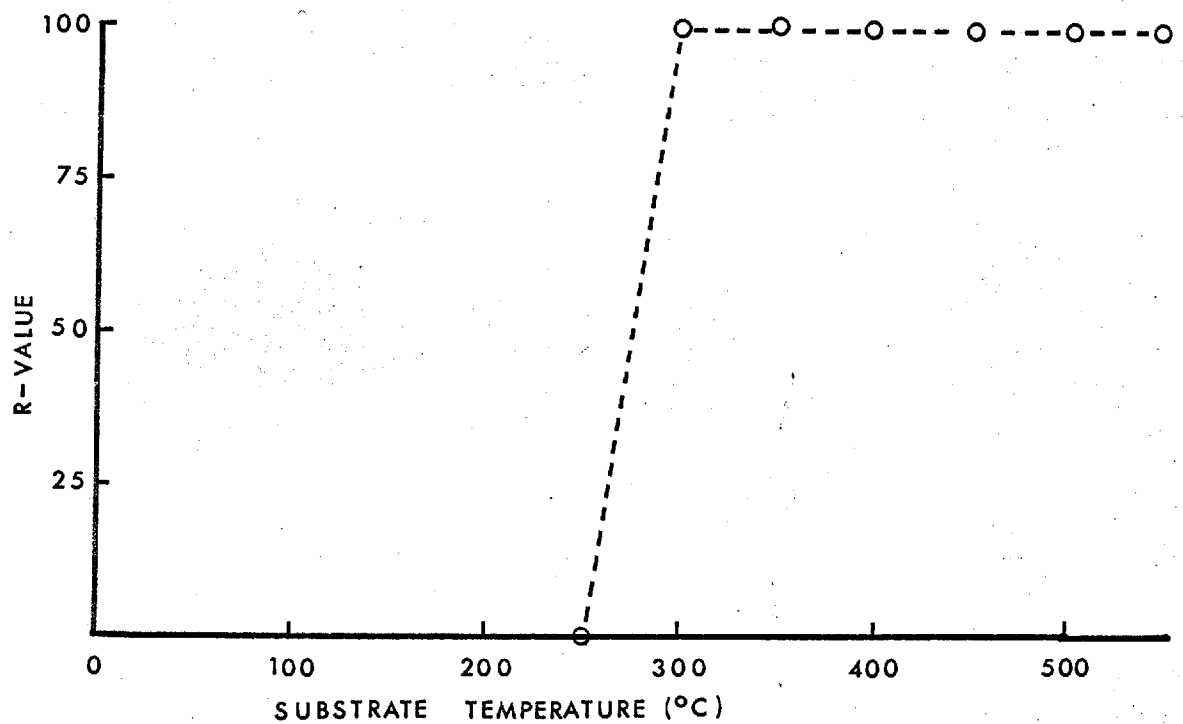
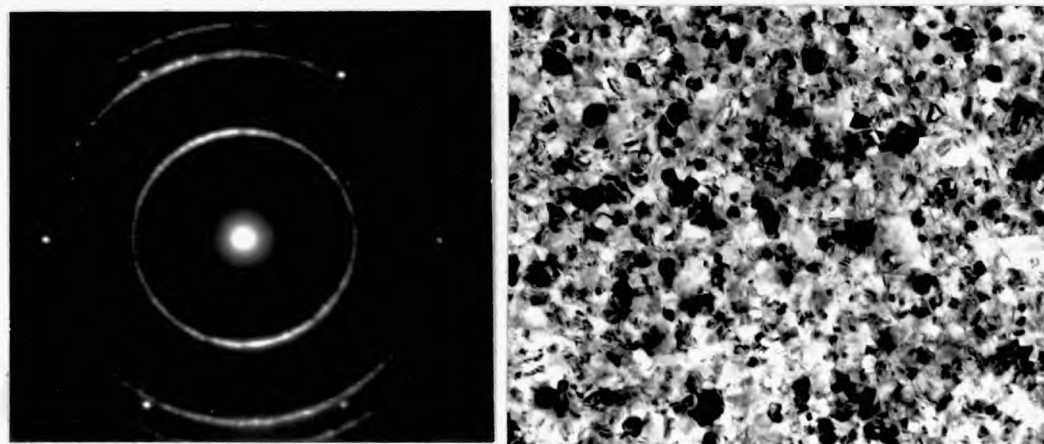
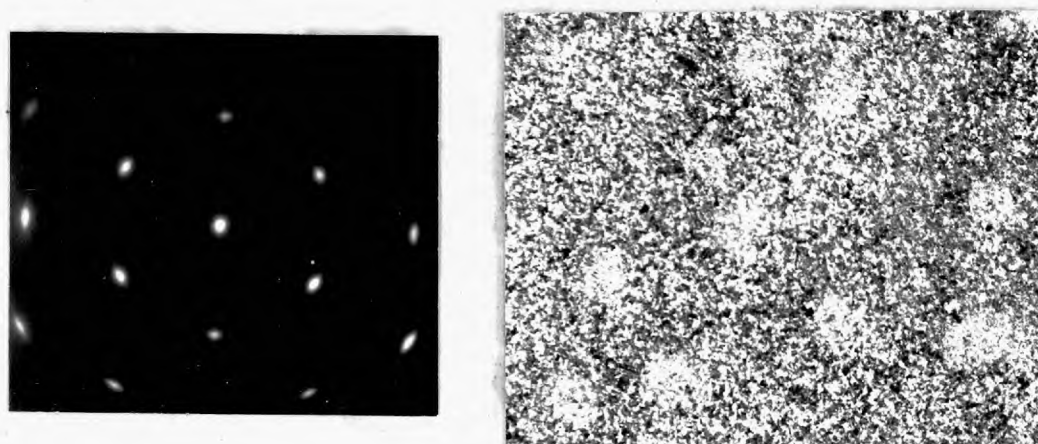


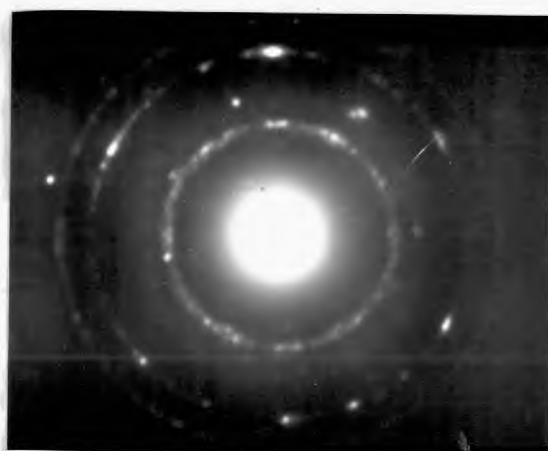
Fig. 4.7. THE R-VALUE VERSUS SUBSTRATE TEMPERATURE CURVE FOR CdS DEPOSITED ON CHEMICALLY POLISHED Ge(111)



(A) SUBSTRATE TEMPERATURE =  $150^{\circ}\text{C}$ .



(B) SUBSTRATE TEMPERATURE =  $300^{\circ}\text{C}$ .



(C) SUBSTRATE TEMPERATURE =  $300^{\circ}\text{C}$ .

Fig. 4.8. DIFFRACTION PATTERNS AND MICROGRAPHS FOR EPITAXIAL LAYERS OF CdS DEPOSITED ON CHEMICALLY POLISHED Ge(111) SUBSTRATES (A and B) AND Si(111) (C - DIFFRACTION PATTERN ONLY)

the investigation of the CdS/Si(111) system should only be continued using a vacuum system pumped by sorption and ion pumps operating in the  $10^{-9}$  pressure region,

#### 4.2. MISCELLANEOUS EXPERIMENTS

##### 4.2.1. FILMS GROWN ON THIN Ge(111) FILMS USED AS SUBSTRATES

The thin films of Ge were grown on air-cleaved  $\text{CaF}_2(111)$  at  $550^\circ\text{C}$ . as described in section 3.2.3. Although the films were epitaxial, they contained many twins as comparison of the diffraction pattern of fig. 4.9. with fig. 2.12 shows. Such a comparison between a (111) oriented diffraction pattern of Ge with a theoretical plot of that for a (111) oriented f.c.c. structure is valid. This is because the absent reflections in the diamond reciprocal lattice of Ge which do occur in the f.c.c. reciprocal lattice are not reflections lying in the (111) plane.

Fig. 4.10.A. shows a micrograph and diffraction pattern of a typical Ge(111) thin film substrate. It can be seen that the film is not uniform in thickness.

A few of these Ge(111) films were used as substrates for the deposition of CdS as described in section 3.2.3. The composite layers gave fibre textured diffraction patterns for the CdS part. Fig. 4.10.B. shows a diffraction pattern and micrograph of a composite layer. The CdS was deposited at  $400^\circ\text{C}$ .

##### 4.2.2. THIN FILMS GROWN AT TEN TIMES THE STANDARD RATE OF EVAPORATION

Two films were grown at about 100 Å per second on vacuum-cleaved  $\text{NaCl}(100)$ . Fig. 4.10 shows diffraction patterns and micrographs of two films grown at  $200^\circ\text{C}$ . on vacuum-cleaved  $\text{NaCl}(100)$  one of which was grown at the standard rate of 10 Å per second, fig. 4.10.B, and the other at the higher rate, fig. 4.10.A. Fig. 4.2.A. shows a diffraction pattern from a film grown at the slower rate of 10 Å per second on an  $\text{NaCl}(100)$  substrate at  $100^\circ\text{C}$ . Comparison between

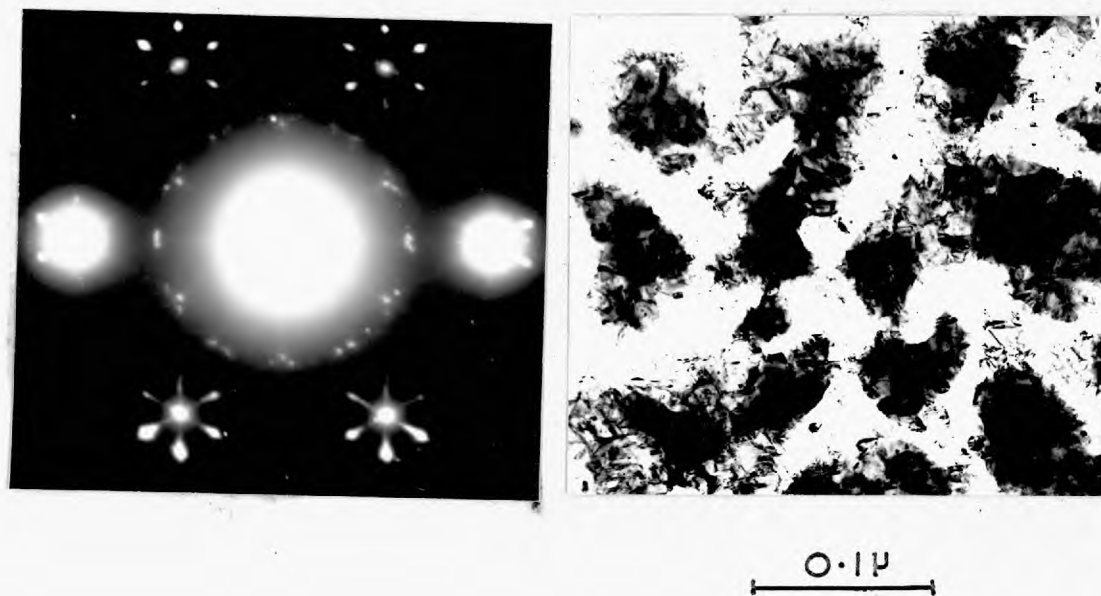


Fig. 4.9.A. DIFFRACTION PATTERN AND MICROGRAPH OF A Ge(111) LAYER DEPOSITED ON AN AIR-CLEAVED  $\text{CaF}_2(111)$  SUBSTRATE.

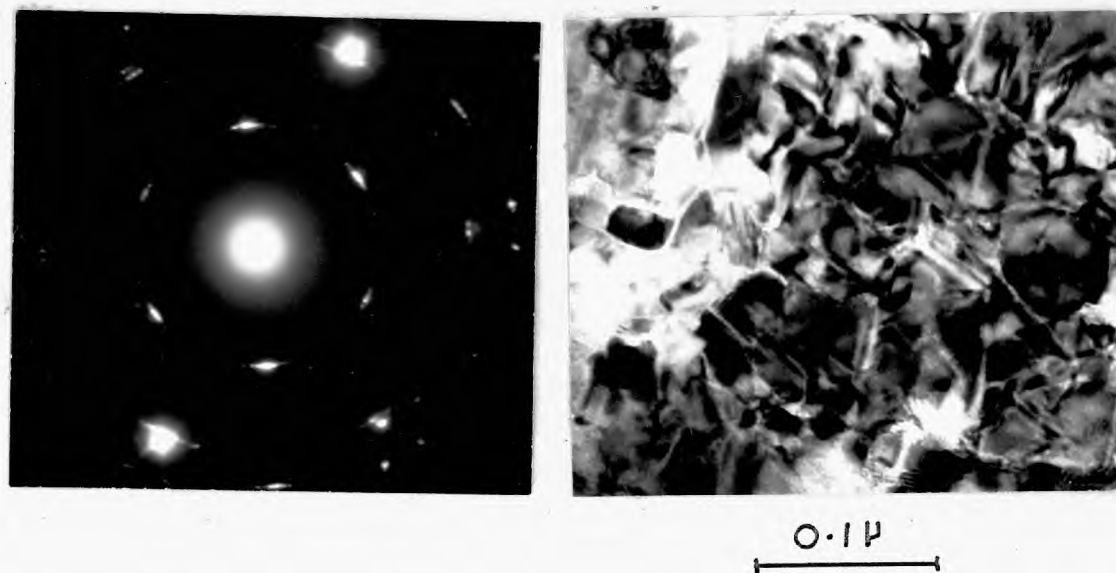
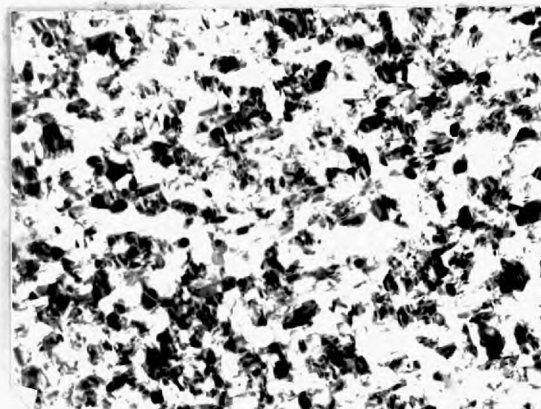
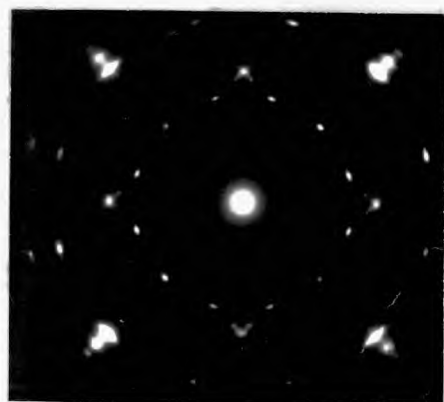
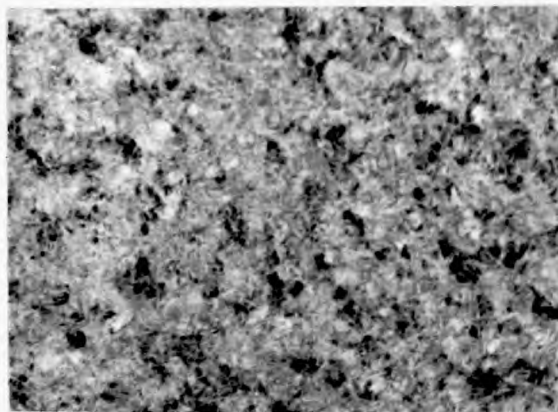


Fig. 4.9.B. DIFFRACTION PATTERN AND MICROGRAPH OF A CdS/Ge(111) COMPOSITE LAYER DEPOSITED ON AN AIR-CLEAVED  $\text{CaF}_2(111)$  SUBSTRATE.



(A) A CdS layer deposited at 100 Å/sec. on a vacuum-cleaved NaCl(100) substrate at 200°C.



(B) A CdS layer deposited at 10 Å/sec. on a vacuum-cleaved NaCl(100) substrate at 200°C.

Fig. 4.10. THE EFFECT OF THE DEPOSITION RATE ON THE CRYSTAL STRUCTURE OF AN EPITAXIAL CdS FILM WITH A SPHALERITE STRUCTURE MATRIX

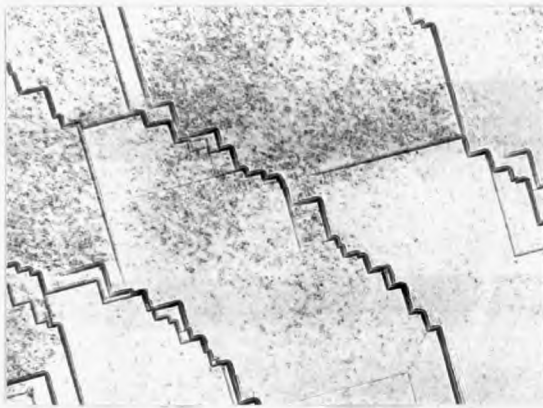
Figs. 4.10.A and 4.2.A shows that an increase in the evaporation rate has an equivalent effect on film structure to that produced by a reduction in the substrate temperature.

#### 4.2.3. REPLICATION OF DEFECTS ON THE SUBSTRATE SURFACE

Several of the substrates had surface topographical features which were replicated by the CdS layers. The surface features, cleavage steps or etch pits, were useful for determining the epitaxial orientation relationships between the thin films and their substrates (sec. 3.6.). Fig. 4.11 shows a number of micrographs of films grown on defective surfaces.

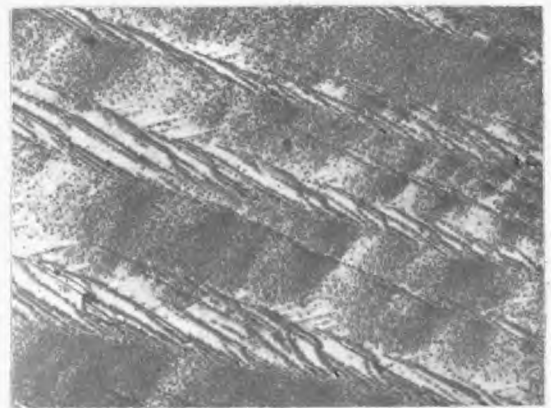
Occasionally, the diffraction patterns from films grown on (111) oriented substrates contained extra diffraction spots. When they were imaged in dark field, they were always found to arise from material which had grown inside an etch pit as shown in figs.

4.11 (C) - (E). These figures are the real image, the dark field image and the diffraction pattern from an (0001) oriented film grown on a Ge(111) substrate surface covered with etch pits.



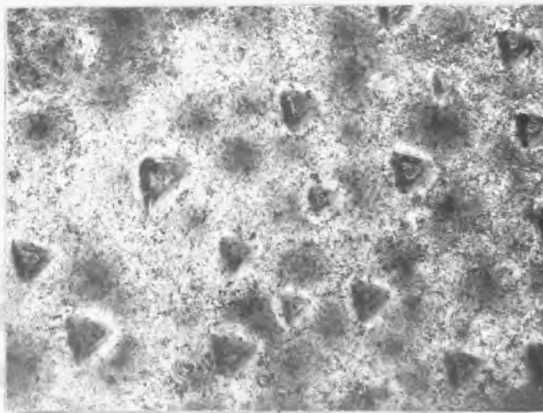
1  $\mu$

(A) AIR-CLEAVED  $\text{NaCl}(100)$



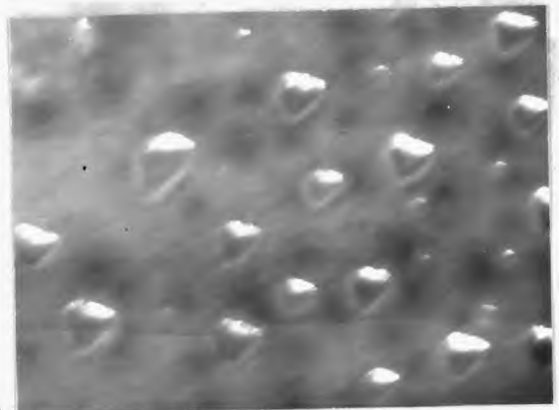
10  $\mu$

(B) VACUUM-CLEAVED  $\text{BaF}_2(111)$



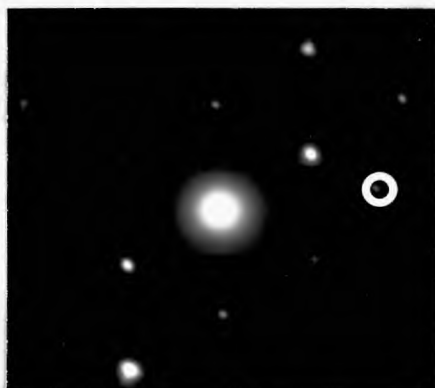
1  $\mu$

(C) BRIGHT FIELD



1  $\mu$

(D) DARK FIELD



(E) DIFFRACTION PATTERN

A diffraction pattern showing the spot imaged to obtain D.

## CHAPTER 5

### DISCUSSION

CHOPRA and KHAN (1967) showed that epitaxial layers of CdS deposited on (100) NaCl surfaces grew with a sphalerite structure matrix and that those deposited on (111) oriented mica and Ag surfaces grew with a wurtzite structure matrix. This dependence of the matrix structure of CdS films on the substrate orientation has been confirmed in this work. The results obtained by CHOPRA and KHAN are not in themselves conclusive. Different materials were used to make substrates with the two different orientations. There still remained the possibility that it was the substrate material rather than its orientation which was causing the epitaxial CdS films to vary their matrix structures. This possibility was investigated here by studying the epitaxy of CdS on the (100), (110) and (111) faces of a single material, NaCl. The polymorphic growth of CdS on these three substrates shows that, for NaCl at least, the effect on the film structure is due to the orientation and not the material of the substrate. A similar series of experiments was performed by AGGARWAL and GOSWAMI (1963). Their results are at considerable variance with those shown here, but it is not possible to determine exactly why since they presented insufficient information on their experimental procedure. The photographic illustrations contained in the paper suggest that the structural quality of their best films was very much worse than those produced in this work. Neither they nor VAN DIJK (1967) were able to produce epitaxial CdS layers on a (110) oriented substrate. The layers deposited on NaCl(110) in this work were of good quality and so this thesis presents the only account of both the epitaxy and the defect content of CdS layers grown on the three principal faces of a cubic structure substrate.

The defect content of films with the two structures varies considerably and the structural analysis of these defects forms the

bulk of this discussion. Three main kinds of defect have been observed. They are the included grains found in sphalerite structure films, the planar defects found in all the sphalerite structure films and in some of the wurtzite structure films, and dislocations.

Most of these defects have already been detected in thin films of other II-VI compounds. In particular, streaks in diffraction patterns arising from planar defects have frequently been mentioned (references to other work given in section 2.5.2.) although no direct evidence has been published to show whether these defects are precipitates or stacking faults. Considerable circumstantial evidence has been obtained in this work which favours the stacking fault interpretation.

Dislocations are undoubtedly present in all the films but they can only be resolved in those of the best quality in which the defect content is sufficiently low. Individual dislocations have therefore only been observed in films deposited with the wurtzite structure or in sphalerite structure films which had been annealed. Defects associated with high temperatures of deposition have also been seen. These appear to be dislocation loops associated with vacancy discs. Again, they are only resolved in the better quality films.

None of these defects appear to have been introduced as a direct result of the chemical composition of the substrate. The same defects might therefore be expected to exist in layers grown on either Ge or Si substrates. The epitaxial temperature range determined for layers of CdS(0001) on Ge(111) substrates extends into the region where the best results are obtained with ionic crystal substrates. It should, therefore, be possible to produce layers of CdS on Ge(111) having a structural quality comparable with those deposited on NaCl(111) or BaF<sub>2</sub>(111) substrates.

5.1. THE ANALYSIS OF RESULTS OBTAINED FROM FILMS WITH THE SPHALERITE STRUCTURE.

5.1.1. FILMS GROWN ON AIR-CLEAVED AND VACUUM-CLEAVED NaCl(100) SUBSTRATES

The differences which there were between the structures of films grown on air-cleaved and vacuum-cleaved surfaces in otherwise similar conditions were probably due to the substrate condition immediately prior to deposition. The air-cleaved surfaces could have been affected in several ways of which the following are perhaps the most important:-

- a) by contamination of the air-cleaved surfaces while exposed to the atmosphere (e.g. by adsorption of air, moisture or dust particles);
- b) by contamination of the surface with volatile materials boiled off inside the substrate region during outgassing.
- c) by exposing the air-cleaved surfaces to vacuum at elevated temperature during outgassing.  
(evaporation of the substrate might be significant here (sec. 4.1.1)).

The only practical difference appeared to be that the temperature required to produce R=100 films on vacuum-cleaved substrates was slightly lower than that required for air-cleaved substrates.

Similar small effects were detected by WOODCOCK and HOLT (1969) who investigated the influence of a number of contaminants likely to be present in an oil diffusion pump system on the epitaxial growth of ZnS films. They found that contamination induced the growth of included grains in the films which occupied a maximum volume of only 10% of the total volume. Contamination of this kind does not, therefore, have a great influence over the included grain content of the films when compared with the effect of the

substrate temperature. A variation in this of as little as  $25^{\circ}\text{C}$ . can induce an equivalent change in the included grain content of the film (fig. 5.1.C). A direct comparison between the results obtained here and those obtained by other researchers for CdS on NaCl(100) substrates is not really meaningful. Many other considerations like the rate of deposition used, the purity of the source material and even the mode of source evaporation can have a greater effect on the minimum epitaxial temperature than that of cleaving the substrates in air rather than in vacuo. The variation in the results obtained by AGGARWAL and GOSWAMI (1963) WEINSTEIN et al. (1965) CHOPRA and KHAN (1967), EFREMENKOVA and YURASOVA (1968) and DISTLER (1968) serves to illustrate this point.

The epitaxial temperature range which is achieved appears to be the net result of many variables not all of which are necessarily under experimental control. Since it is virtually impossible to optimise every variable, the range obtained is partly determined by the particular experimental arrangement and is therefore not a fundamental property of the thin film/substrate system. This is a further justification for using the very rough R-value estimation of the degree of orientation in non-epitaxial films.

#### 5.1.1.1. FILMS GROWN AT LOW SUBSTRATE TEMPERATURES WHICH CONTAINED INCLUDED GRAINS OF MATERIAL WITH THE WURTZITE STRUCTURE

Included grains of CdS with the wurtzite structure were present in films grown both on air-cleaved substrates below  $150^{\circ}\text{C}$ . and on vacuum-cleaved substrates below  $125^{\circ}\text{C}$ . The included grains were epitaxial to the substrate surface and had the doubly-positioned symmetry recorded in section 4.1.1. and discussed in sec. 2.6.4.4. The proportion of doubly-positioned material decreased as the substrate temperature was increased. Fig. 5.1A shows a diffraction pattern from a film grown on vacuum-cleaved NaCl(100) at  $50^{\circ}\text{C}$ . The double-

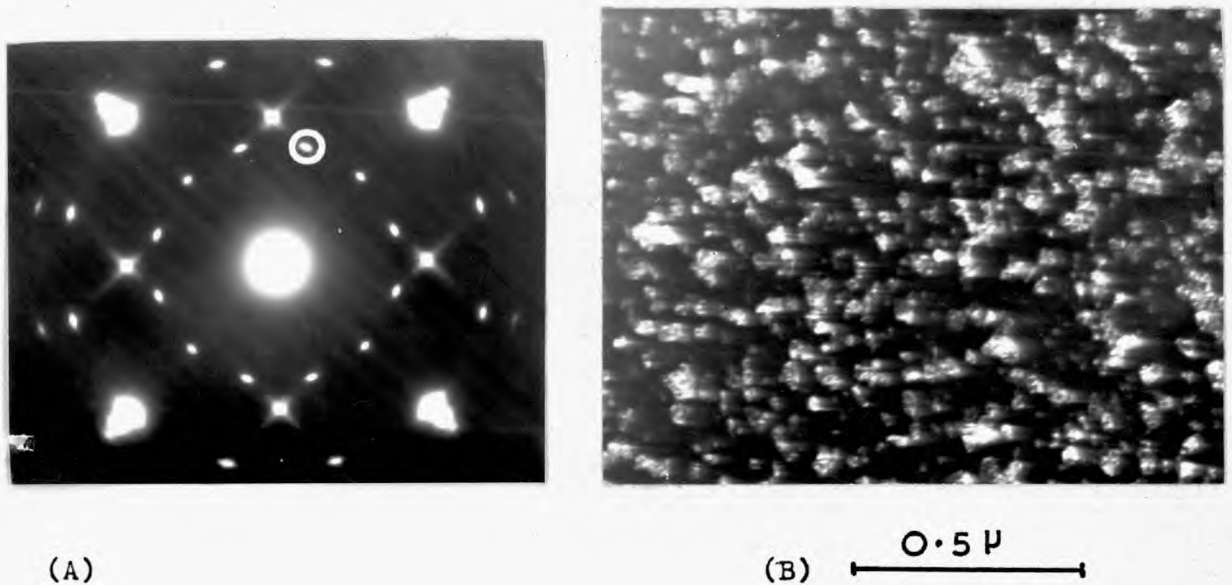
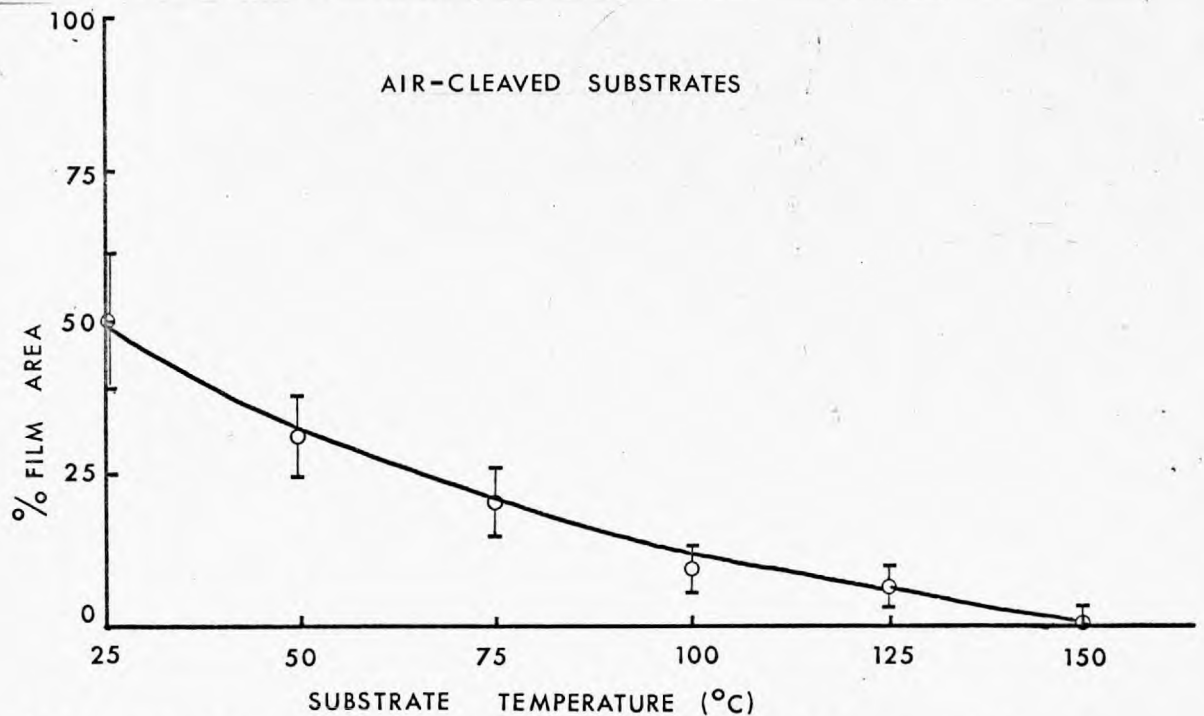


Fig. 5.1.A shows a diffraction pattern produced by a sphalerite structure layer deposited on vacuum-cleaved NaCl(100) at 50°C. Fig. 5.1.B shows the dark field image produced by the spot circled in the diffraction pattern.



(C) The variation with substrate temperature of the percentage of film area covered with material having the doubly-positioned wurtzite structure.

Fig. 5.1 DOUBLY-POSITIONED GRAINS WITH THE WURTZITE STRUCTURE IN SPHALERITE STRUCTURE FILMS.

positioning spot indicated, was used to give the dark-field image shown in fig. 5.1.B. A plot is shown in fig. 5.4.C. of the percentage film area covered by doubly-positioned grains versus the substrate temperature for films grown on air-cleaved NaCl(100) substrates. The plot is obtained by measuring the areas which light up in dark field when a spot due to material in each position is imaged, The two areas are summed together and expressed as a percentage of the total. Included grains in this orientation were seen by CHOPRA and KHAN (1967). The doubly positioned grains did not disappear until a substrate temperature in excess of  $280^{\circ}\text{C}$ . was used. In their case the CdS was deposited at a very much slower rate and the results are therefore not strictly comparable. EFREMEKOVA and YURASOVA (1968) and DISTLER (1968) also found included grains of this type in CdS layers deposited on NaCl(100) substrates. The variation of their concentration with substrate temperature was not investigated in either case.

WOODCOCK and HOLT (1969) and HOLT and WOODCOCK (1970) have investigated the temperature distribution of this type of defect in ZnS films. Under similar conditions of cleanliness, ZnS with the doubly-positioned wurtzite structure was still detectable in films deposited at  $250^{\circ}\text{C}$ . Even when prepared in ultra high vacuum, the volume of included grains was considerably higher than that observed in CdS films at corresponding temperatures. Since the experimental conditions under which the CdS films and ZnS films were prepared were nearly identical, it is likely that the contrasting results reflect a genuine difference in the epitaxial growth of CdS and ZnS.

#### 5.1.1.2. THE STRUCTURE OF CdS FILMS GROWN ON NaCl(100) SUBSTRATES AT INTERMEDIATE TEMPERATURES

Within a certain range of substrate temperatures, the structure of the films was single-crystal and single-phase for both air-cleaved and vacuum-cleaved substrates. This range lay between  $150^{\circ}\text{C}$ . and

300°C. for air-cleaved substrates and between 125°C. and 300°C. for vacuum-cleaved substrates. The films always gave diffraction patterns whose spots were streaked along  $\langle 111 \rangle$  directions.

A detailed explanation of the bright-field contrast seen in (100) oriented films containing large numbers of planar defects has been given by WOODCOCK (1968) and HOLT and WOODCOCK (1970). The analysis was made for epitaxial ZnS films deposited on (100) oriented NaCl substrates and is directly applicable here. The fringe and dotted contrast, examples of which can be seen in the micrographs of 4.2.B and 4.10.B, was found to be due to interaction between the direct transmitted beam and beams of satellite pseudo-spots (sec. 2.6.5.1). The satellite pseudo-spots occur near the matrix spots as a result of primary diffraction. They are then brought to positions close to the direct beam by double diffraction. These doubly diffracted satellite pseudo-spots are relatively weak in intensity and as they lie near to the direct beam spot, they are not often visible since their images are usually swamped by that of the direct beam. CHOPRA and KHAN (1967) found that their films were not free of included grains unless they were deposited above 200°C. They also did not observe the high temperature orientation for wurtzite structure included grains but claimed to have produced completely sphalerite structure layers at 400°C. which contained a large number of twins. The diffraction pattern which they show to illustrate the structure obtained at this temperature contains maxima at both  $\pm \frac{1}{6} \langle 111 \rangle$  and  $\pm \frac{1}{3} \langle 111 \rangle$  which suggests that the included grains contain wurtzite structure material rather than twinned material. This would then conform with the results obtained in this work.

5.1.1.3. THE STRUCTURE OF CdS FILMS GROWN ON NaCl(100) SUBSTRATES AT 350°C.

At a substrate temperature of 350°C. the films grown on both air- and vacuum-cleaved substrates contained CdS with the wurtzite structure having the epitaxial relationship:-

$$\text{CdS (0001)} // \text{NaCl(111)}$$

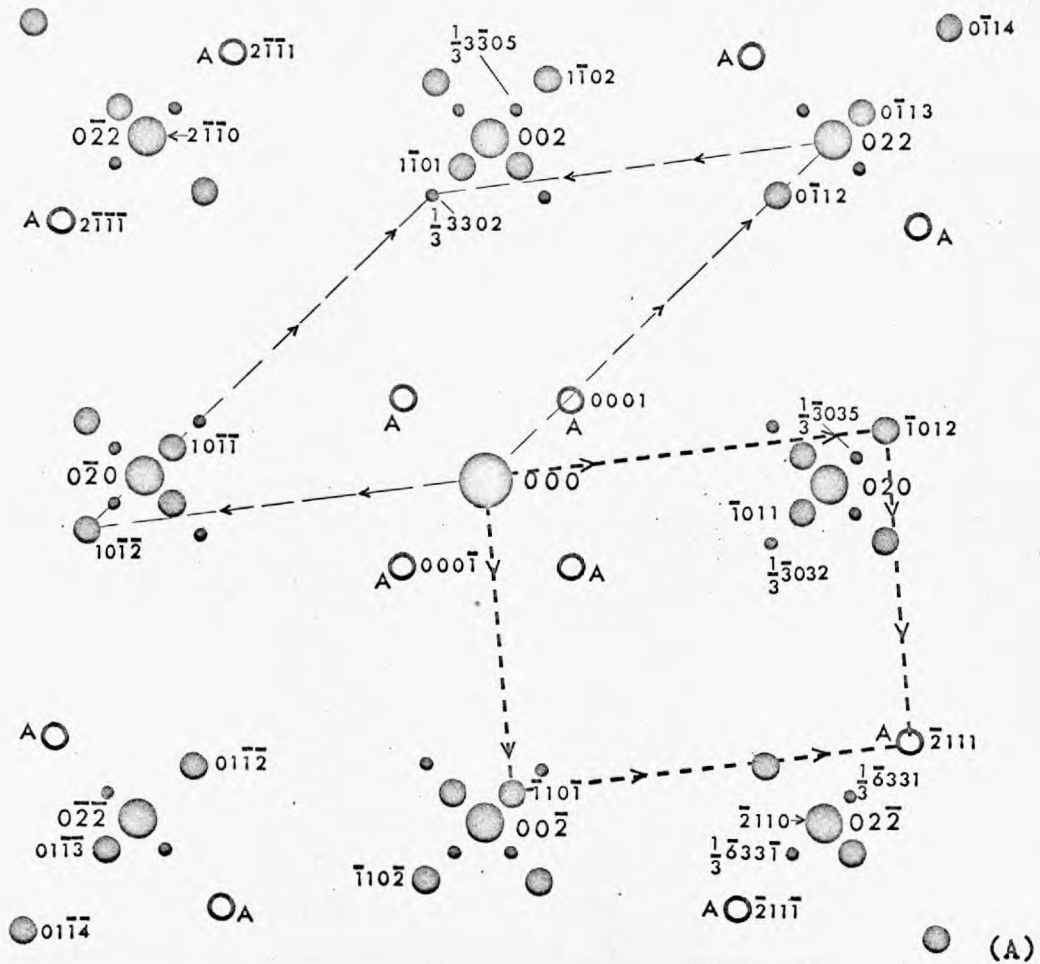
$$\text{with } [11\bar{2}0] // [110] \quad (\text{secs. 2.6.4.5. and 4.1.1.})$$

No doubly-positioned wurtzite CdS with the low substrate temperature orientation was detected.

5.1.1.3a. ANALYSIS OF THE DIFFRACTION PATTERN FROM SPHALERITE STRUCTURE FILMS CONTAINING WURTZITE STRUCTURE GRAINS WITH (0001) //(111)

Although the films grown on (100) oriented substrates at certain temperatures contained material with both the wurtzite and the sphalerite structures, double diffraction between the two structures was nearly always too weak to be detected on the photographic plates. However, multiple diffraction within the same crystal structure does appear to take place quite strongly. This can be seen in fig. 5.2. where the diffraction pattern from a CdS layer grown at 350°C. can be compared with the theoretical plot. Comparison shows the presence of material with the wurtzite structure lying with the  $\{0001\}$  basal planes parallel to the sphalerite  $\{111\}$  planes. The spots labelled "A" are forbidden reflections from the wurtzite structure which can only appear as a result of multiple diffraction through two allowed lattice vectors (PASHLEY and STOWELL, 1963, and section 2.6.2). The heavy broken lines illustrate the mechanism in fig. 5.2.A. Since these spots show up quite strongly, it is evident that strong multiple diffraction occurs within the wurtzite matrix.

Double diffraction between the wurtzite and sphalerite structures is very much weaker but some spots due to this can also be detected in the diffraction pattern of fig. 5.2.B. The double diffraction spots and the matrix spots which give rise to them are marked on the



- - sphalerite matrix spot.
- - wurtzite matrix spot.
- - forbidden wurtzite matrix spot which appears as a result of double diffraction
- - wurtzite/sphalerite double diffraction spots.

(B)

Fig. 5.2. (A) is a theoretical plot and (B) is a diffraction pattern both showing the presence of included grains with the wurtzite structure having  $\{0001\}$  planes parallel to the  $\{11\bar{1}\}$  matrix planes.

theoretical plot. Most of the wurtzite spots do not lie in the (100) reciprocal lattice plane but show up in the diffraction pattern as the intersection of a reciprocal lattice spike with the sphere of reflection (section 2.6.4.5). This is to be expected since the dimensions of the wurtzite grains are still rather small.

Indices are given to all the cubic spots, to all the wurtzite matrix spots due to grains with the  $\{0001\}$  planes parallel to the  $(111)$  sphalerite planes, and to some double diffraction spots due to these two structures. Since diffraction patterns are centrosymmetric, a rotation through  $180^\circ$  of the structure about the beam direction will bring the diffraction pattern into coincidence with itself again. The beam direction is along  $[100]$  and such a rotation would take the  $(111)$  sphalerite planes to positions previously occupied by the  $(\bar{1}\bar{1}\bar{1})$  planes. This means that grains with the wurtzite structure having (0001) parallel to either  $(111)$  or  $(\bar{1}\bar{1}\bar{1})$  produce the same array of diffraction spots. The indices assigned to the spots in fig. 5.2.A. are for the first of these orientations only. The remaining spots which are not indexed are due to wurtzite structure grains with (0001) parallel to  $(\bar{1}11)$  and  $(1\bar{1}\bar{1})$ . Thus there are only two sets of diffraction spots although there are four orientations for the included grains.

The indices were obtained by measurements from the diffraction pattern followed by matrix manipulation. This procedure is summarised in appendix A1 at the end of chapter 6.

The observation by CHOPRA and KHAN (1967) of twin spots in a diffraction pattern from a film deposited at  $400^\circ\text{C}$ . on NaCl(100) has already been disputed in the previous section. It appears to be more likely that their films deposited at high temperature contain wurtzite structure grains in the same orientation as that reported here. This is a more satisfactory interpretation since the

orientation relationships determined here are quite unambiguous and the possibility of two quite contrary growth characteristics existing in the same temperature region is unlikely.

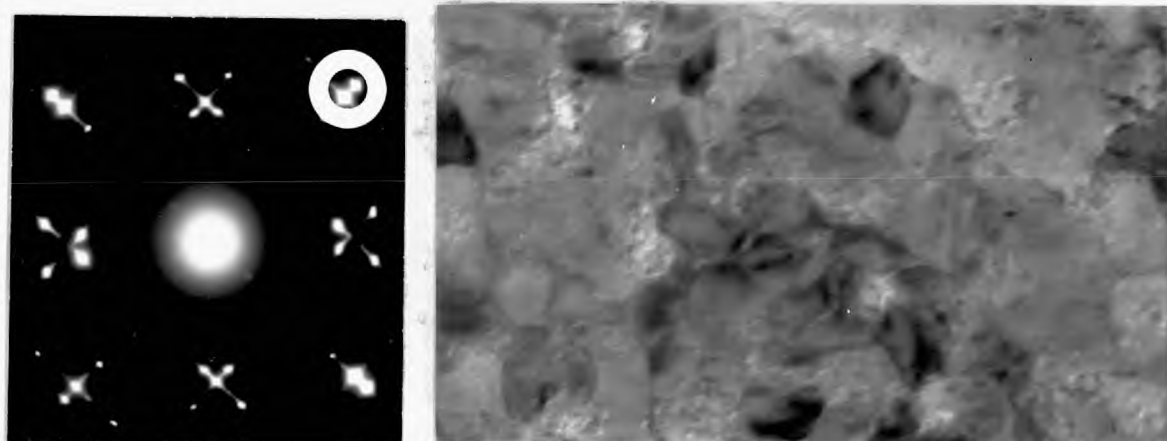
AGGARWAL and GOSWAMI (1963) obtained the doubly-positioned included grain structure at high substrate temperatures in contradiction to the results obtained both here and by CHOPRA and KHAN. The reasons for this are obscured by the fact that the overall structural quality of their layers of CdS appear to have been very poor.

#### 5.1.1.3b. OBSERVATION OF INCLUDED GRAINS IN DARK FIELD

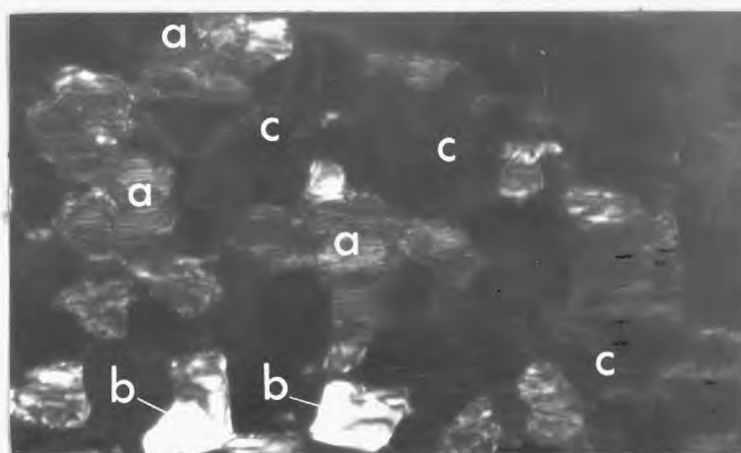
Fig. 5.3.A shows a real image and diffraction pattern of a film at high magnification. Fig. 5.3.B is a dark field image formed from the matrix and wurtzite structure spots ringed in the diffraction pattern.

If reference is made to fig. 5.2 and the associated discussion, it can be seen that the diffraction spots imaged by the objective aperture are the (022) sphalerite reflection, the  $(0\bar{1}13)$  and  $(0\bar{1}\bar{1}\bar{3})$  wurtzite reflections from grains with (0001) parallel to (111) and  $(\bar{1}\bar{1}\bar{1})$  respectively and also the  $(2\bar{1}\bar{1}0)$  and  $(\bar{2}110)$  spots which are coincident with (022) and are due to grains with (0001) parallel to  $(\bar{1}\bar{1}\bar{1})$  and  $(1\bar{1}1)$  respectively. Also imaged because of the size of the objective aperture is at least one of the two  $\frac{1}{3}\{6331\}$  type double diffraction spots which lie close to (022). These are due to double diffraction between the sphalerite matrix and grains with (0001) parallel to  $(\bar{1}\bar{1}\bar{1})$  and  $(1\bar{1}1)$  (fig. 5.3.A).

The dark field micrograph of fig. 5.3 shows systems of parallel moiré fringes ("A") produced by interference between the (022) and  $(0\bar{1}13)$  reflections. Other regions containing no fringes show up brightly ("B"). These could be regions which are entirely of just one structure which, therefore, cannot give rise to any moiré fringes



(A) A real image and diffraction pattern from a CdS film grown on a vacuum-cleaved NaCl(100) substrate at a temperature of  $350^{\circ}\text{C}$ .



(B) Dark field micrograph obtained from imaging the (220) and (0113) spots circled in the diffraction pattern of (A).

Fig. 5.3. Moiré fringes due to interference between the two beams are labelled A. Grains in which only one of the above reflections is excited are labelled B. Boundaries between grains showing up weakly as a result of double diffraction can be seen at C. Further details are contained in the text.

or they could be regions in which the (220) and the (2 $\bar{1}\bar{1}$ 0) reflections only are excited. The interplanar spacings corresponding to these two reflections are identical and again no moiré fringes are produced.

Outline contrast (sec. 2.6.2) labelled "C" can be seen in several instances. This is formed from the  $\frac{1}{3}$  ( $\bar{6}\bar{3}\bar{3}$ 1) double diffraction spots and the outlines define the boundaries between areas with the two different crystal structures. None of the imaged single diffraction spots is excited within the volume of the crystal between the outlines and therefore the background is dark. The outlines are not very bright because the intensity of the doubly diffracted beam is low.

5.1.1.4. A POSSIBLE REASON FOR THE POLYMORPHIC GROWTH OF CdS ON (100) ORIENTED SUBSTRATES.

The processes which occur during the nucleation and coalescence of thin films have been studied in some detail by a number of authors (sec. 2.4.1). An interesting aspect of these studies is the transition of the crystal structure of a thin film from polycrystalline to epitaxial single crystal as the substrate temperature is increased. It has been shown that although there may be a preferred orientation for the depositing nuclei, there is rarely a unique orientation. The proportion of nuclei in each observed orientation can be related to their activation energy for formation on the substrate surface and the orientation which has the lowest activation energy is the preferred one. The rate at which the nuclei are formed and also their size depends upon the energy available for nucleation. This available energy increases as the substrate temperature is decreased and is thus a function of the degree of supersaturation of the vapour with respect to the substrate surface. At the same time, the difference in activation energy for the various orientations becomes less significant by comparison. It can therefore be expected that the proportion of nuclei in orientations other than the epitaxial one

will increase as the substrate temperature is decreased. Another consequence of lowering the temperature of deposition is that there is a reduction in the size at which a nucleus becomes stable. This means that layers deposited at low temperatures have a finer grain structure than those deposited at a high temperature.

Where CdS is concerned, these are not the only considerations to be taken into account. Changes in the crystal structure occur at high substrate temperatures where the mechanism based on nucleation theory expressed above is inoperative. The other important factor is the polymorphic nature of CdS. The stability of the wurtzite structure with respect to the sphalerite structure can be expected to have an influence on the crystal growth at temperatures where atomic movement in the crystal structure is possible.

The structural variations discussed in the foregoing sections obtained with (100) oriented substrates can be explained to a first approximation in terms of nucleation and structural stability considerations.

At low substrate temperatures, the surface mobility of atoms is low. The elimination of nuclei in non-epitaxial orientations by a process of recrystallisation cannot proceed sufficiently quickly to keep pace with the arrival of new material. These nuclei give rise to grains with non-epitaxial orientations and the film is polycrystalline.

Surface energy and surface mobility have been shown by several authors to be of great importance in the formation of epitaxial layers. The work of MATTHEWS et al. and PASHLEY et al. referred to in section 2.4.1 is of particular significance here.

By increasing the substrate temperature, both of these quantities are increased and in the case of the CdS layers with the sphalerite structure, complete epitaxy was achieved at about 100°C. on NaCl(100).

The presence of the doubly-positioned wurtzite structure at low substrate temperatures indicates that nuclei in this orientation have a low activation energy for formation. It is common to find CdS growing with the wurtzite structure and having the "C" axis perpendicular to the substrate. All the layers grown on the NaCl(111) and BaF<sub>2</sub>(111) substrates grew with this geometry at temperatures down to room temperature and crystallites in this orientation were visible in CdS layers deposited on BaF<sub>2</sub>(111) substrates at temperatures as low as -100°C. (section 4.1.3). Layers grown on glass substrates have also been found to have the "C" axis perpendicular to the substrate (VECHT et al., 1966; ROZGONYI and FOSTER, 1967; NEUGEBAUER et al., 1967). It is therefore evident that little or no substrate orienting effect is necessary to induce growth with this orientation. However, the (100) oriented substrates do have some orienting effect on this growth morphology since low index directions in the substrate surface and in the thin film lie parallel to one another.

As the temperature of the substrate is raised, its influence becomes paramount and only the sphalerite structure is found in the films. This condition prevails throughout the temperature region in which surface diffusion is significant and diffusion within the bulk of the film is still too sluggish to allow for rearrangement inside the film.

At the highest substrate temperature of 350°C. the mobility of atoms in the bulk material may be sufficient to allow ordering to take place under the influence of thermodynamic forces. This would result in a reversion to the stable wurtzite structure. Any stacking faults on the {111} planes of the sphalerite structure could provide ideal sites for the nucleation and growth of this phase at the expense of the matrix. This may account for the structure of films obtained at this substrate temperature in which the planar defects appear to

have been greatly reduced in favour of discrete regions with the wurtzite structure large enough to give their own diffraction pattern.

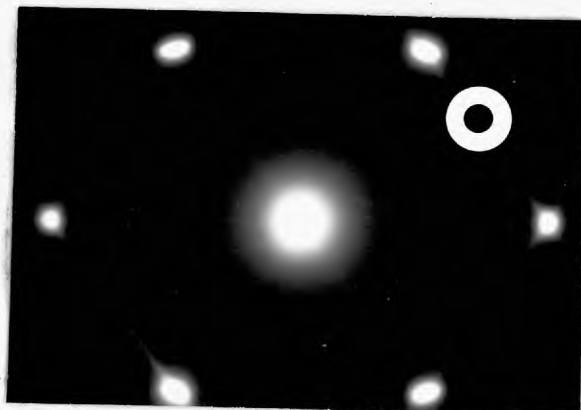
The instability of the sphalerite structure with respect to the wurtzite structure is very likely to be responsible for the high planar defect density in the sphalerite structure films throughout the whole epitaxial temperature range. At 450°C., however, the mobility of the atoms becomes sufficiently great to allow the phase transformation to proceed fairly quickly in the grown film with the simultaneous elimination of most of these defects (sec. 5.1.2.2).

#### 5.1.2. FILMS GROWN ON CHEMICALLY POLISHED NaCl(110) SUBSTRATES

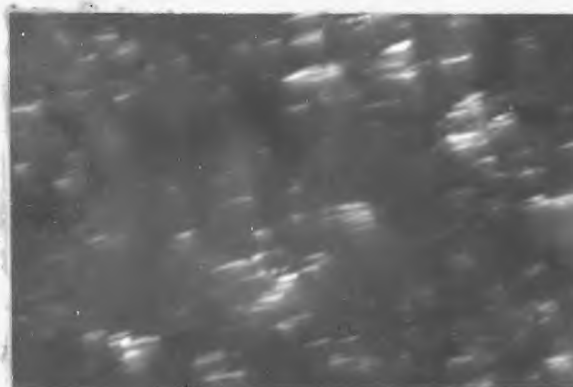
All the epitaxial films had the sphalerite structure and contained no included grains giving rise to satellite spots in their diffraction patterns although the matrix spots were always streaked along  $\langle 111 \rangle$  directions.

##### 5.1.2.1. THE OBSERVATION OF THE PLANAR DEFECTS IN DARK FIELD

In section 2.6.5.1 it is explained how streaks lying along the  $\langle 111 \rangle$  directions in the plane of the film are due to thin defects lying at right angles to the plane of the film on  $\{111\}$  planes. Consequently when a streak was imaged in dark field, thin bright lines could be seen which ran at right angles to the direction of the streak (allowing for the rotation of the diffraction pattern relative to the real image in the microscope). Since the defects were being viewed edge-on, they could be resolved, whereas the images of those viewed along a  $[100]$  direction in (100) oriented films overlapped and therefore could not be resolved. Fig. 5.4.A shows a diffraction pattern and a dark field image from a (110) oriented film. The portion of the streak being imaged arises from the defects which show up as thin, bright lines about 100Å long and 10Å or so thick in the dark field micrograph. Similar defects have been observed in ZnS (HOLT and WOODCOCK, 1970). The dimensions of the defects were



(A) Diffraction pattern from (110) oriented film showing streaks. The portion of streak circled was imaged to give the dark field micrograph below.



0.1  $\mu$

(B) A dark field micrograph showing the planar defects lying on one set of  $\{111\}$  planes. Their dimensions are about  $10\text{\AA}$  thick and  $100\text{\AA}$  long.

Fig. 5.4. THE OBSERVATION OF PLANAR DEFECTS IN DARK FIELD

much the same as those seen in fig. 5.4.A. The streaks in the diffraction patterns caused by the defects have been more widely observed. KALINKIN et al. (1961 and 1963) detected strong streaks along  $\langle 111 \rangle$  directions in diffraction patterns from CdSe films deposited in (100), (110) and (111) orientations, RUMSH et al. (1963) and NOVIK et al. (1963) obtained streaked diffraction patterns from CdTe layers in (100) and (111) orientations. They deduced that the planar defects must be stacking faults introduced during the growth of the films. Thin films of ZnSe (DHIRE and GOSWAMI, 1969) and ZnTe (DHIRE and GOSWAMI, 1969 and HOLT, 1969) also exhibit streaked diffraction patterns. This phenomenon is evidently common to all the compounds mentioned above and points very strongly towards an explanation based on faulting of the structure during growth. This is all the more likely since the compounds all exhibit polymorphism (ROTH, 1967). A more detailed argument favouring this explanation is given in section 5.1.3.

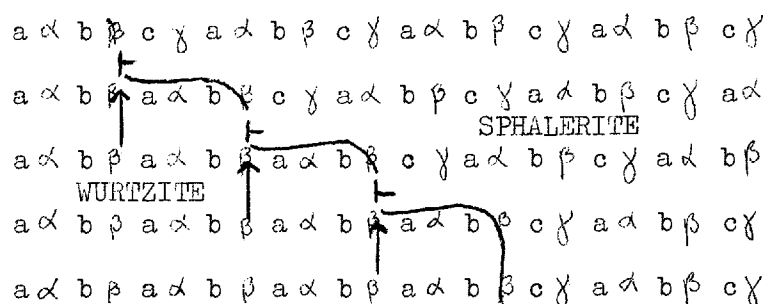
#### 5.1.2.2. THE STRUCTURE OF (110) ORIENTED FILMS WHICH HAD BEEN ANNEALED

The reversion to the wurtzite structure observed in (100) oriented films deposited at 350°C. (sec. 5.1.1.3) was not observed in (110) oriented films grown at the same temperature. However, if (110) oriented films were annealed at about 450°C. for 30 minutes, evidence of a transformation from the sphalerite structure to the wurtzite structure could be seen. If the film was annealed for a further 30 minutes, an almost complete transformation from the sphalerite to the wurtzite structure occurred. The micrographs of the partially transformed regions show very similar features to those seen in some martensitically transformed alloy steels.

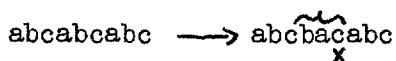
The phase transformation from the wurtzite structure to the sphalerite structure has been observed in ZnS by SECCO D'ARRAGONA et al. (1966). In this case the transformation proceeds in the

reverse direction to that observed in the annealed CdS films because the sphalerite structure is the stable one for ZnS below 1020°C.

The model which they proposed was one of slip on alternate closest-packed planes and can be illustrated in the following manner:-



stainless steels containing a high chromium or manganese content (KELLY and NUTTING, 1961; LAGNEBORG, 1964; MANGONON and THOMAS, 1969; and a theoretical discussion by CHRISTIAN, 1965). The  $\gamma$  to  $\epsilon$  transformation is understood to occur as a result of successive slip on the f.c.c.  $\{111\}$  planes giving an orientation relationship between the two structures of (0001) h.c.p.  $\parallel$  (111) f.c.c. with  $[11\bar{2}0] \parallel [\bar{1}10]$  for each set of  $\{111\}$  planes (this is also the high substrate temperature orientation of included grains with the wurtzite structure in (100) oriented CdS films (sec. 5.1.1.3)). The microstructure which this transformation produces consists of thin laths of  $\epsilon$  phase parallel to the  $\{111\}$  planes of the austenite matrix. Fig. 5.5 is a micrograph showing similar features in an annealed CdS film in (110) orientation. Fig. 5.6.A shows a diffraction pattern from another partially transformed region in which the transformation is taking place on only one set of  $\{111\}$  planes. The array of spots is due to the material being in an intermediate stage of transformation. The theoretical plot in fig. 5.6.A. shows the (1 $\bar{1}$ 0) oriented sphalerite diffraction pattern and the (11 $\bar{2}$ 0) diffraction pattern of the wurtzite structure superimposed. Comparison between this and the diffraction pattern below (fig. 5.6.B.) indicates that only spots at (hkl) cubic  $\pm \frac{1}{3}(111)$  are prominent which suggests that the structure at this stage of the transformation approximates to a twinned cubic structure. A transitional structure is to be expected since stacking faults passing through the sphalerite matrix initially produce a twinned sphalerite structure. This can be illustrated by the following sequence of stacking symbols:-



where the microtwin is bracketed. A further stacking fault passing across the "c" layer (marked x) taking this to a "b" position is required before a lath of the wurtzite structure is formed. Similar transitional structures have been seen in ZnS films (RAI et al., 1970) In Fig. 5.7.A., a dark field micrograph is shown of

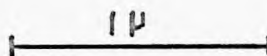
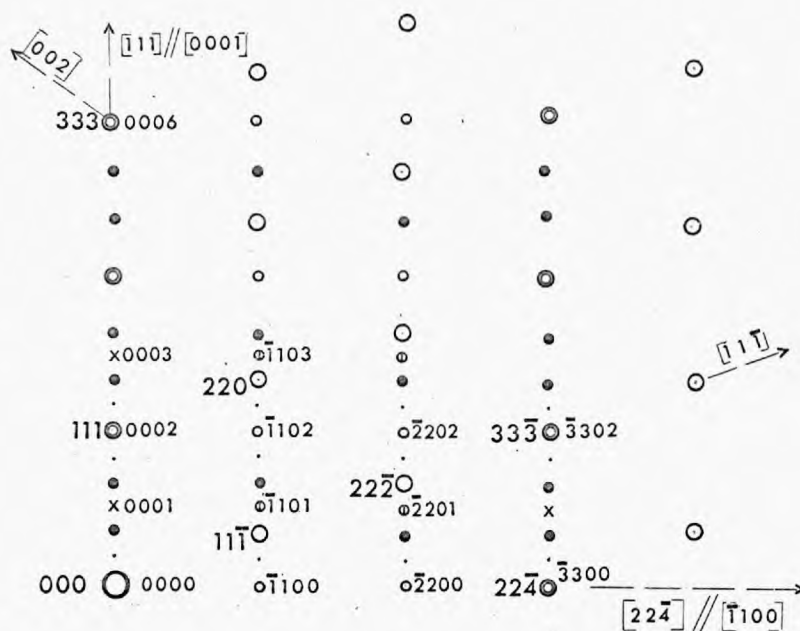
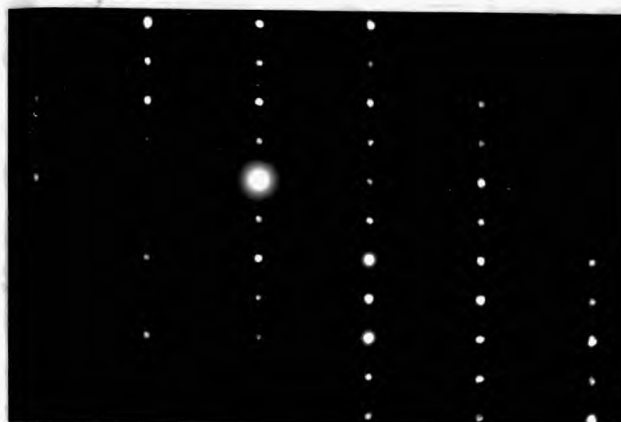


Fig. 5.5. Annealed film showing laths of material transformed to the wurtzite structure (B) lying on the two sets of  $\{11\bar{1}\}$  planes perpendicular to the film. The diffuse area at the lower left corner contains material transformed on the other two  $\{11\bar{1}\}$  planes. "A" is a low angle grain boundary running right across the field of view. The wurtzite structure laths kink at the boundary by about  $2^\circ$ . Areas of sphalerite structure material are labelled "C". It can be seen that these areas are relatively very free of defects compared with the unannealed films.



(A) Theoretical plot of a quadrant of the superimposed diffraction patterns from the  $(1\bar{1}0)$  sphalerite structure and the  $(11\bar{2}0)$  wurtzite structure. Spots at  $(hkl)$  cubic  $\pm \frac{1}{2}$  and  $\pm \frac{1}{6}$   $(111)$  are included only near the origin so that comparison between this and the diffraction pattern below is more easy.

- $\bigcirc$  represents a sphalerite matrix spot.
- $\bullet$  represents a wurtzite matrix spot or a sphalerite twin spot.
- $\circ$  represents a wurtzite matrix spot only.
- $\times$  represents a forbidden wurtzite matrix spot which can appear as a result of double diffraction.
- $\bigodot$  represents either a sphalerite/wurtzite double diffraction spot or a sphalerite twin spot.
- $\bullet$  represents a sphalerite/wurtzite double diffraction spot only.



(B) Diffraction pattern from a region of material which is transforming on only one set of  $111$  planes.

Fig. 5.6.

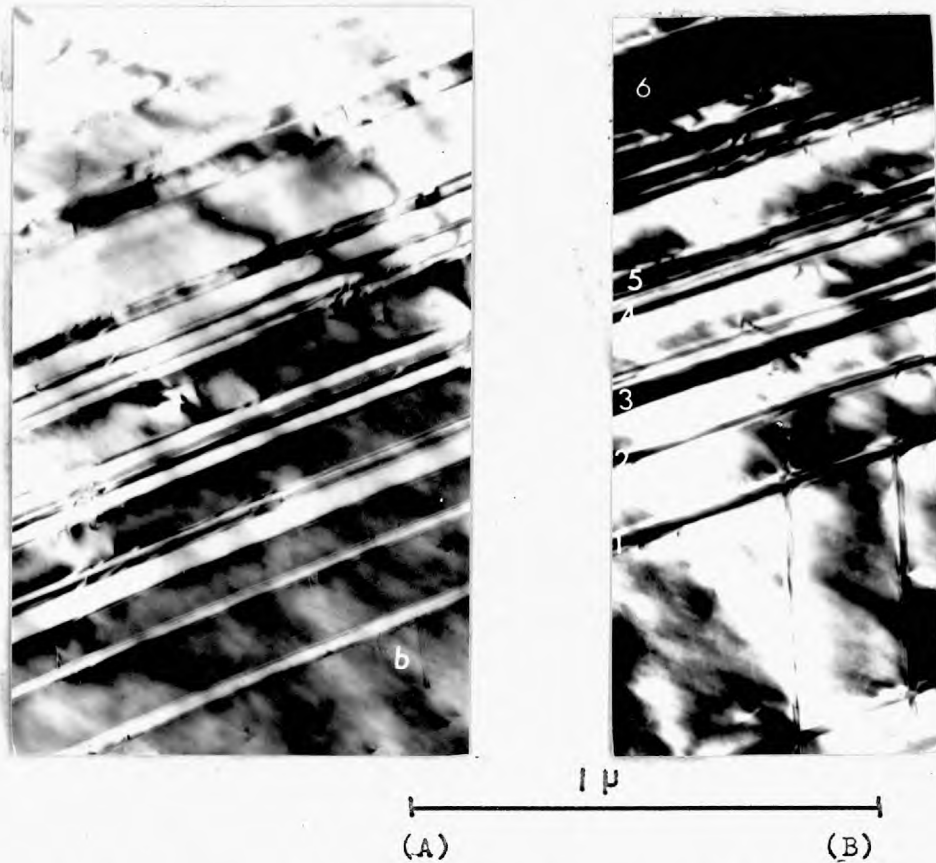


Fig. 5.7. Dark field micrographs showing (A) wurtzite structure laths (spot imaged is  $(\bar{1}100)$ ), and (B) the sphalerite structure matrix in the neighbouring region (spot imaged is  $(11\bar{1})$ ).

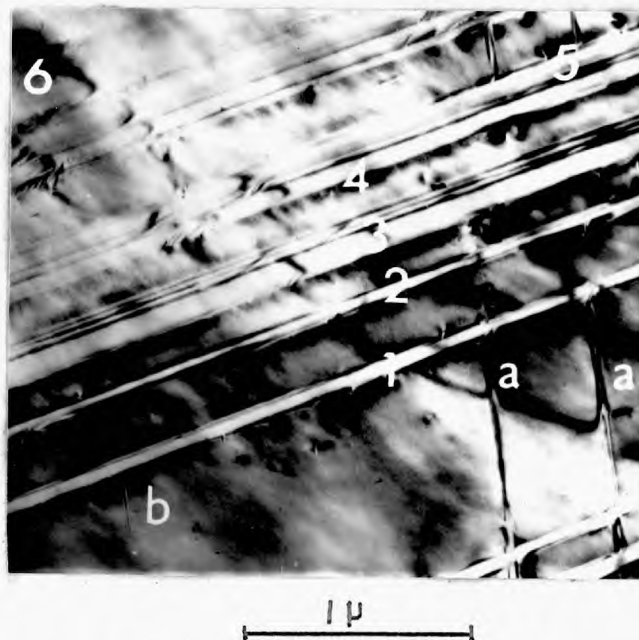


Fig. 5.7. (cont.) (C)

Bright field micrograph covering both areas shown in (A) and (B). Corresponding features are numbered or lettered in the three micrographs.

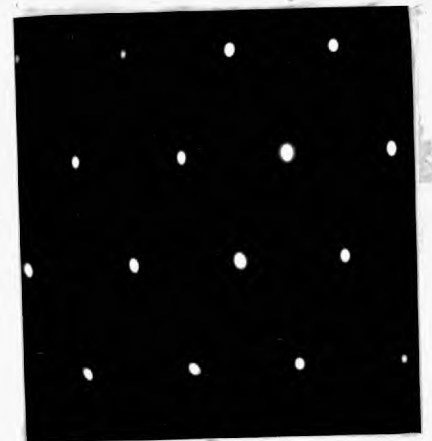


Fig. 5.8.

Diffraction pattern from a transformed region in  $(\bar{1}101)$  orientation.

the transforming laths. The spot used was  $(\bar{1}100)$ . Fig. 5.7.B is another dark field micrograph of the adjoining area of the film. In this case the imaged spot was the  $(11\bar{1})$  sphalerite spot. As can be seen from the theoretical plot, the two spots which are imaged in dark field lie next to one another in the diffraction pattern. Fig. 5.7.C is a bright field micrograph of the same region at lower magnification. Corresponding features in the three micrographs are labelled according to the captions beneath.

It is evident that the laths of transformed material lie at right angles to the  $\langle 111 \rangle$  directions and that the interface between the sphalerite matrix and the laths lies between the  $\{111\}$  sphalerite and the  $\{0001\}$  wurtzite planes. If this is so, then the sphalerite to wurtzite and the  $\chi$  to  $\epsilon$  transitions are probably identical.

The hexagonal  $\epsilon$  phase is an intermediate phase in the  $\chi$  to  $\alpha$  transition of the stainless steels and only a small fraction of the alloy will have the  $\epsilon$  structure at any instant. The sphalerite to wurtzite transition can be taken to completion however. Fig. 5.8. shows a diffraction pattern from a completely transformed region in  $(\bar{1}101)$  orientation. The absence of satellite spots indicates that the transformation has occurred almost exclusively on one set of  $\{111\}$  planes. The diffraction spots did not streak when the film was tilted and therefore the film contained very few, if any, planar defects.

It is also of interest to note that in the partially transformed films illustrated in fig. 5.5 and 5.7, the regions with the sphalerite structure contained a greatly reduced number of the small planar defects which are always found in the unannealed films. These defects are evidently removed by annealing before transformation begins. The processes of planar defect removal and

phase transition therefore appear to proceed independently of one another. The absence of planar defects in the crystal structure immediately before transition may account for the great length of the transformed bands of material when compared with all other structural features. The planar defects, whatever their nature, would undoubtedly impede the movement of stacking faults on the  $\{111\}$  planes and therefore reduce the size of individual volumes of transformed material.

Since the planar defects can be annealed out, it is almost certain that they are structural faults. Furthermore, they lie on  $\{111\}$  planes in the sphalerite structure and this strongly suggests that they are very small areas of stacking fault.

Another point of interest is that over large areas of the film, transformation has occurred preferentially on one set of  $\{111\}$  planes only. This cannot be explained in terms of the transformation beginning on all the  $\{111\}$  planes at random. Some other agency must be having a selective effect on the sets of planes on which transformation begins. It may be that internal stresses in the film have a large shear component on one set of  $\{111\}$  planes and only a small component on the others. Since slip is induced by shear stresses, the slip planes already subject to a shear stress would be favoured for the transformation. The stresses may be caused by the film bending between the grid bars during annealing, or internal stresses present before annealing. Another possibility is that the transformation itself may polarise the internal stresses so that the transformation continues on one set of planes only. This type of stress system may well exist at the matrix/lath interfaces since it is well known that martensitic transformations can generate high internal stresses. However, whichever agency is operating must have an effect over large distances. The regions of

preferential nucleation can cover areas at least as large as a grid square since bands of wurtzite structure material have frequently been seen which pass from one side of the grid square to the other (i.e. about 75 microns).

Very few results have yet been published on the structure of annealed epitaxial films of II-VI compounds. HOLT and WOODCOCK (1970) found that no effect was produced in ZnS films when annealed under vacuum at temperatures between 350°C. and 550°C. The planar defects remained unaltered both in size and numbers. Annealing the films in H<sub>2</sub>S at the same temperatures produced intensity maxima at  $\pm \frac{1}{3} \langle 111 \rangle$  in their diffraction patterns although no changes were observed in the micrographs. This implies that annealing twins may have formed in the matrix of the ZnS films. As it is pointed out above, a transformation from the sphalerite to the wurtzite structure should not occur because of stability considerations. The removal of planar defects with the resultant formation of twinned regions is a very likely process, particularly if the defects are stacking faults. This interpretation of the diffraction pattern data was not confirmed although the implications are that this is another manifestation of the difference between the stable structures of CdS and ZnS.

#### 5.1.2.3. CONCLUSIONS ON THE WORK WITH FILMS IN (110) ORIENTATION

Although the structural properties of the (110) oriented films are apparently very similar to those grown in (100) orientation across the centre of the epitaxial temperature range, certain differences in the epitaxial growth exist towards both ends of the range. No included grains of material with the wurtzite structure were found in any epitaxial layers deposited on (110) substrates. This contrasts with the presence of doubly positioned grains with the wurtzite structure in (100) oriented films grown below about 150°C. and also with the growth of wurtzite structure material on the  $\{111\}$  sphalerite planes at a substrate temperature of 350°C. It

could be expected that included grains would form in (110) oriented films grown at higher substrate temperatures. The annealing experiments suggest that included grains would be present in films grown on substrates at about 450°C. Chemically polished  $\text{BaF}_2(110)$  faces would make suitable substrates for investigating the epitaxial growth of CdS at temperatures up to about 550°C.

Owing to the relative difficulty of obtaining (110) oriented substrates, very little has been published on the epitaxy of II-VI compounds in this orientation. AGGARWAL and GOSWAMI (1963) deposited ZnS and CdS on (110) oriented NaCl substrates. At no substrate temperature did they obtain films which gave sharp diffraction patterns. The best of their CdS layers consisted mainly of material with the wurtzite structure having (0001) CdS // (110) NaCl and  $[11\bar{2}0] // [\bar{1}\bar{1}1]$ . The substrate temperature which they used was about 300°C., well within the epitaxial temperature region determined here. In this work, material with the above orientation was found only in the partially oriented (110) films deposited at room temperature (sec. 4.1.2). The ZnS layers which AGGARWAL and GOSWAMI produced were of better quality than their CdS layers and were predominantly in (110) orientation. Even these, however, were not of comparable quality to those studied here. VAN DIJK (1967) deposited CdS on Ge (110) and invariably obtained polycrystalline layers with the wurtzite structure.

The (110) orientation is potentially a convenient one from an analytical point of view since it contains the  $[001]$ ,  $[1\bar{1}0]$  and  $[\bar{1}\bar{1}1]$  low index directions. This enables features associated with the corresponding low index planes to be observed in dark field microscopy with little or no tilting. It is perhaps surprising, therefore, that more use has not been made of substrates with this orientation.

### 5.1.3. THE INTERPRETATION OF THE PLANAR DEFECTS WHICH CAUSE THE DIFFRACTION SPOTS TO STREAK

The streaking of the diffraction spots observed in diffraction patterns of films with the sphalerite structure is due to defects lying parallel to the  $\{111\}$  planes. The defects could be either stacking faults or thin, plate-like precipitates of impurities but for the following reasons it was concluded that they are in fact stacking faults.

Films with the wurtzite structure containing no planar defects were grown using (111) oriented substrates, whereas all the sphalerite structure films grown on (100) or (110) oriented substrates contained many such defects even though the conditions under which they were prepared were very similar. The defect content of these films was therefore dependant upon the structure of the film and its orientation. This has rather unlikely implications if it is assumed that the defects are precipitates. For example, the impurity content of the material condensed from the vapour would also have to be structure and orientation dependant. Moreover, in films having the sphalerite structure, the defects all lie on the  $\{111\}$  planes which are the most closely packed planes whereas in films with the wurtzite structure, when defects are seen, they lie at right angles to the  $\{0001\}$  closest-packed planes. One would expect that the defects would lie parallel to the closest-packed planes in both structures where the interfacial energy between them and the matrix is likely to be at a minimum. This situation is even more probable in this case since the closest-packed planes have identical symmetry in both structures. Furthermore, it was found that the defects could be annealed out from both structures (secs. 5.1.2.2. and 5.2.3). It is most likely that precipitates going into solution at a high temperature would precipitate again on cooling through the temperature range in which they were originally formed. No

precipitates or defects similar to those present in the as-grown films were ever detected in annealed films

The observations made above can all be explained quite simply in terms of stacking faults on the  $\{111\}$  planes. Consequently it was decided that structures other than the two CdS structures do not occur at a detectable level. Unfortunately, the thin faults cannot be resolved with sufficient detail by the E M 6 G microscope to enable a conclusive interpretation to be made.

## 5.2. FILMS WITH THE WURTZITE STRUCTURE GROWN ON CHEMICALLY POLISHED NaCl(111) AND VACUUM-CLEAVED BaF<sub>2</sub>(111) SUBSTRATES

Whereas the films deposited on substrates with (100) and (110) orientation had the sphalerite structure those deposited on the (111) oriented substrates had the wurtzite structure. The temperature range over which epitaxy could be achieved was considerably wider for films with the wurtzite structure than it was for those with the sphalerite structure. It was possible to produce epitaxial films from 550°C. down to 0°C. on vacuum-cleaved BaF<sub>2</sub>(111) substrates. CHOPRA and KHAN (1967) also obtained an epitaxial layer of CdS at room temperature with an (0001) oriented mica substrate but they did not investigate the epitaxial properties of CdS at lower temperatures.

### 5.2.1. THE DETERMINATION OF THE CRYSTAL STRUCTURE OF CdS FILMS GROWN ON (111) ORIENTED SUBSTRATES.

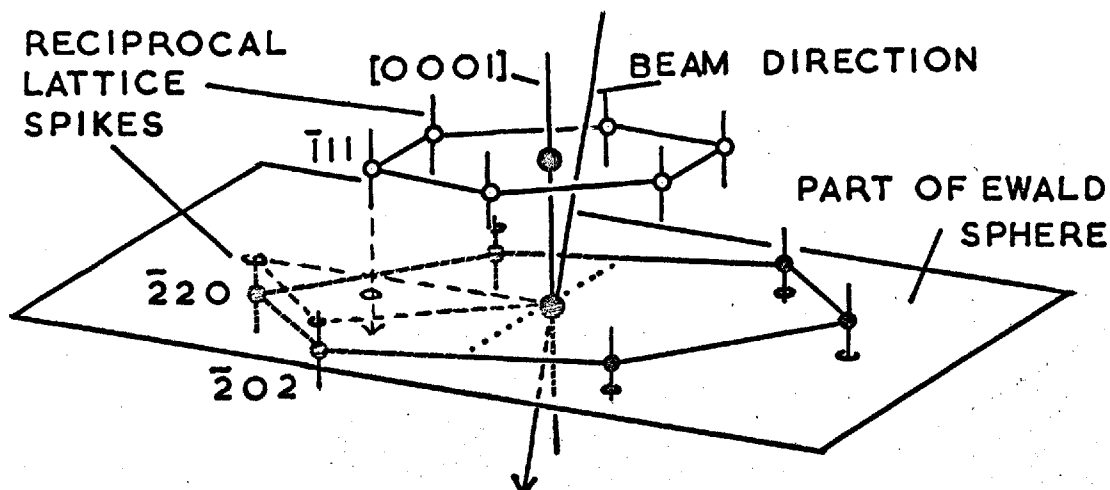
It was possible to determine that the diffraction patterns from CdS films grown on (111) oriented substrates were due to the material having the wurtzite structure by using dark field electron microscopy. Section 2.6.4.1. and Fig. 2.12 show that the innermost hexagon of spots in the diffraction patterns from these films can be due a) to double-positioning twins in the sphalerite matrix; b) to "spiking through" of the (111) spots which lie outside the plane of the (111) diffraction pattern or c) to (10 $\bar{1}$ 0) matrix reflections from material with the wurtzite structure. These possibilities may be distinguished

by observing in dark field, the image formed by one of the spots and by noting the intensity variations of these spots relative to the hexagon of spots immediately outside. The outer hexagon of spots are  $\{02\bar{2}\}$  reflections (Fig. 5.9.B) if cubic indexing is used.

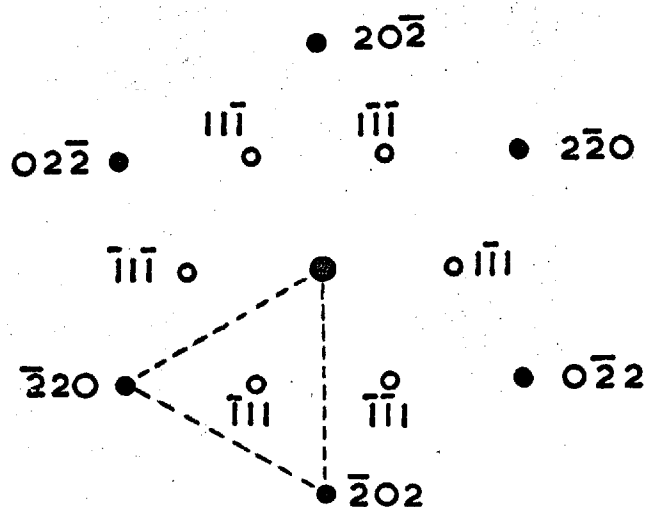
a) If double-positioning twins are present then one of three situations should occur when the spots are imaged in dark field (sec. 2.6.2). The twins can show up either as bright areas against a dark background or vice versa according to whether the spot is of the  $(111)$  type belonging to the twin or the matrix. Otherwise the boundaries between the twins and the matrix light up if the spot is the double diffraction spot due to the two  $\{11\bar{1}\}$  type spots of the matrix and the twins. In this case the spot is of the type  $\frac{1}{3}(\bar{2}\bar{2}4)$  (PASHLEY and STOWELL, 1963). In no case was domain or outline contrast seen when imaging these spots.

b) If the film is buckled, it is possible for the  $\{111\}$  reflections to be sufficiently near to the sphere of reflection for them to "spike through" (Fig. 5.9.A). If a selected area diffraction pattern is observed as the film is moved about the  $(111)$  spots will wink on and off as the film orientation in the selected area passes through positions for which these beams are and are not excited. The  $\{02\bar{2}\}$  spots, on the other hand, would not extinguish although they might dim, since the orientation changes are not likely to be great enough to carry the  $(111)$  plane right out of the diffraction condition. Furthermore, the  $(\bar{1}11)$  spot would be seen to increase in intensity as its two neighbours,  $(\bar{2}20)$  and  $(\bar{2}02)$ , decreased in intensity (Fig. 5.9.B). The dark field image of the  $\{\bar{1}11\}$  spots would, however, give the normal bend extinction contour contrast associated with matrix reflections.

c) If, on the other hand, the imaged spot is a  $\{10\bar{1}0\}$  type matrix reflection from material with the wurtzite structure, the dark field image will reveal the bend extinction contours corresponding to



(A) A diagram showing the  $(\bar{1}11)$  spot spiking through the Ewald sphere which is at an angle to the  $(111)$  plane.



(B) Diffraction pattern showing positions at which  $\{111\}$  reflections spike through. Triangle formed by the central spot and the  $(\bar{2}20)$  and  $(\bar{2}02)$  spots is the same as that outlined in the diagram above.

Fig. 5.9

this reflection and the image of the contour should appear uniformly bright apart from intensity variations due to buckling. In addition, if the film is tilted continuously, the contour will move across the image of the film thereby lighting the whole film up during its passage. By observing the selected area diffraction pattern, this situation can be distinguished from the one due to "spiking through" of  $\{111\}$  spots. If the spots are  $\{10\bar{1}0\}$  type, their intensities and those of the  $\{11\bar{2}0\}$  spots (i.e. the  $\{02\bar{2}\}$  spots as indexed above) will increase and decrease together as the film is tilted. This condition was found to prevail in all the films which gave diffraction patterns with a regular hexagonal symmetry. Thus it was concluded that the matrix of all films deposited on (111) oriented substrates had the wurtzite structure. Fig. 5.10 shows micrographs of a film with the wurtzite structure. The bend extinction contours associated with the  $\{10\bar{1}0\}$  spots can be seen both in dark field as bright bands and also in bright field as dark bands.

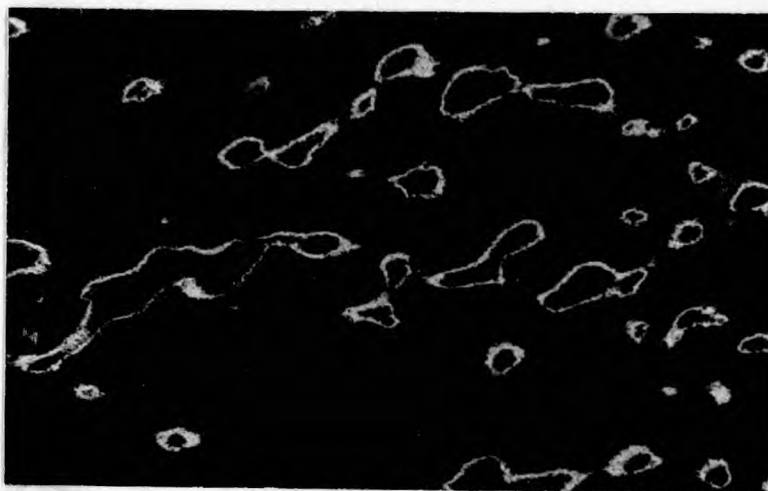
Material with the sphalerite structure lying with the (111) plane parallel to the substrate surface cannot be detected solely by observation of the diffraction pattern since the sphalerite matrix spots lie in the same positions as the  $\{11\bar{2}0\}$  wurtzite matrix spots. However, any material with the sphalerite structure would appear dark in a dark field image formed from a  $\{10\bar{1}0\}$  wurtzite reflection. No such areas were seen in dark field which could be ascribed to material having the sphalerite structure and it was, therefore, concluded that the films were indeed single phase.

#### 5.2.2. THE DEFECT CONTENT OF THE FILMS

No included grains with the sphalerite structure were ever detected in these films. However, streaking of the diffraction spots was apparent, particularly in the diffraction patterns from films grown at low substrate temperatures. The streaking disappeared from the diffraction patterns of films grown on  $\text{BaF}_2(111)$  above  $170^\circ\text{C}$ .



(A)  $10\mu$



(B)  $10\mu$

Fig. 5.10. Micrographs of a CdS film with the wurtzite structure showing  $\{10\bar{1}0\}$  type bend extinction contours.

(A) Bright field micrograph.

(B) Dark field micrograph using a  $(10\bar{1}0)$  spot.

while for films grown on NaCl(111), the relevant temperature was about 250°C.

The reciprocal lattice plane in which these streaks lay was determined by tilting the thin films in the electron beam. It was observed that the streaks disappeared as the matrix spots disappeared and there were no intensity maxima that moved along the streaks, which might suggest that they were intersecting the sphere of reflection at an angle. Thus it was concluded that the streaks lay in the (0001) reciprocal lattice plane. All matrix spots were streaked in  $\langle 10\bar{1}0 \rangle$  directions which indicated the presence of planar defects lying parallel to the  $\{10\bar{1}0\}$  planes.

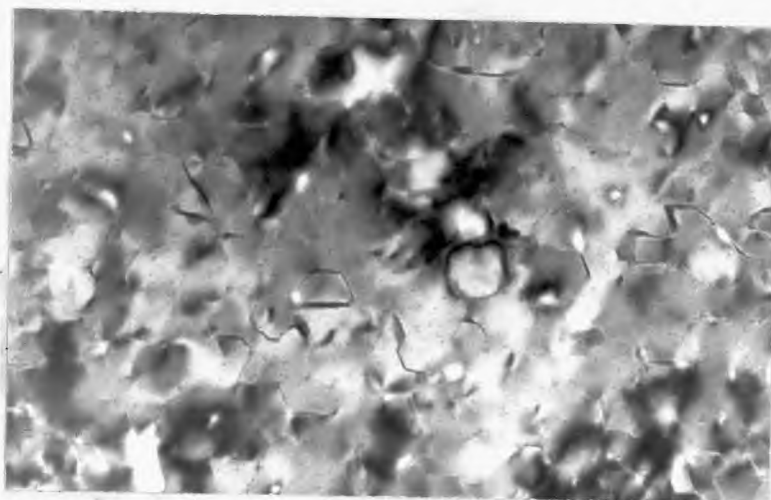
Unlike the defects lying on the  $\{11\bar{1}\}$  planes in the films with the sphalerite structure, those on the  $\{10\bar{1}0\}$  planes could be eliminated together with the corresponding streaking of the diffraction spots by raising the substrate temperature. At the same time, the micrographs of films grown on substrates at the higher temperatures were seen to contain far fewer defects. Fig. 4.6 shows micrographs and diffraction patterns of two films, one of which was grown at 300°C. and the other at 25°C. This illustrates the change in defect density produced by an increase in the substrate temperature. It is possible that substrate temperatures of 170°C. for BaF<sub>2</sub>(111) and 250°C. for NaCl(111) are the minimum temperatures which allow the removal by annealing of defects generated by nucleation and coalescence before they are buried by depositing material. Once the film has become continuous, it is reasonable to suppose that the growth properties of films deposited on the two substrates are the same. This model would account both for the high defect density of films deposited below these two temperatures and also for their good overall orientation despite these defects. A model such as this must be proposed in order to account for the substantial degree of orientation

seen in films grown on cooled  $\text{BaF}_2(111)$  substrates. The considerable difference between the minimum epitaxial temperature for  $\text{BaF}_2(111)$  substrates and the minimum temperature quoted above for the removal of growth defects from the depositing film suggests that epitaxy need not necessarily be accompanied by the removal of "grown in" defects.

Above the two substrate temperatures quoted, most of the defects appeared to be dislocations and only a few of them were planar defects. At higher temperatures still, defects with the appearance of dislocation loops associated with collapsed vacancy discs were seen. No other study of the variation with substrate temperature of the defect content of wurtzite structure epitaxial layers has been published although the subject is briefly mentioned in WILCOX and HOLT (1969).

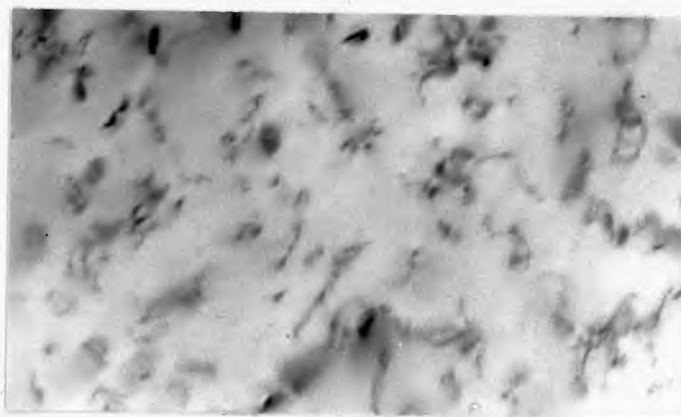
### 5.2.3. THE EFFECT OF ANNEALING ON THIN FILMS WITH THE WURTZITE STRUCTURE

A further reduction in the defect density of thin films with the wurtzite structure could be obtained by annealing for 30 minutes at  $450^\circ\text{C}$ . Fig. 5.11.A shows a micrograph of a film grown on  $\text{NaCl}(111)$  at  $300^\circ\text{C}$ . Since the material is relatively free of defects, it is possible to pick out the individual defects on the  $\{10\bar{1}0\}$  planes. The  $\{10\bar{1}0\}$  planes lie normal to the plane of the film so the defects are seen edge-on lying along directions separated by  $60^\circ$  which corresponds to the angular separation of the  $\{10\bar{1}0\}$  planes. Fig. 5.11.B shows a micrograph of a film grown under the same conditions and then annealed. The planar defects have all but disappeared to leave behind a number of other defects which appear to be dislocations. The net effect, however, is that the planar defects are completely removed by annealing whereas the dislocations are only partially removed and an overall improvement in the structural quality of the films is achieved. This contrasts with the more dramatic effect of annealing on films with the sphalerite structure.



0.1  $\mu$

- (A) A micrograph of a CdS film grown on NaCl(111) at 300°C. The planar defects can be seen clearly.



0.1  $\mu$

- (B) Diffraction pattern and micrograph of a CdS film grown on NaCl(111) at 300°C. followed by annealing for 30 minutes at 450°C. on a gold grid.

Fig. 5.11



sequence 1.:-

1a.      $\underbrace{abca\ BA}_{\text{hexagonal}}$      and     1b.      $\underbrace{abca\ BC}_{\text{cubic}}$

and for sequence 2.:-

2a.      $\underbrace{abca\ CA}_{\text{hexagonal}}$      and     2b.      $\underbrace{abca\ CB}_{\text{cubic}}$

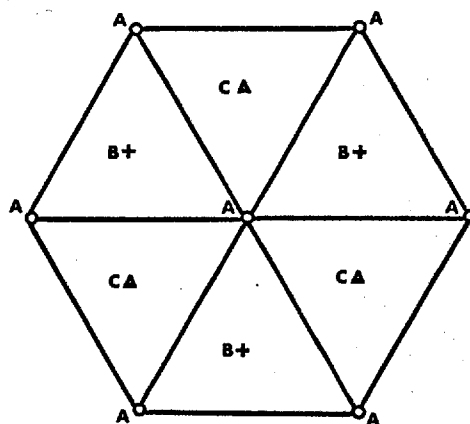
Of these, 2a. appears to be the most favourable having already four layers in hexagonal array and 1b. the least favourable, all the layers so far being in cubic array. 1a. and 2b. are sequences which lie somewhere between the two extremes.

If the stacking of the first two layers strongly favours hexagonal sequences, then one can expect to find stacking sequences mainly of the type 1a. and 2a. The conclusions in the following argument are in no way altered if any two or more of the stacking sequences occur on the substrate surface. For simplicity, it is assumed that only nuclei with types 1a. and 2a. stacking deposit on the substrate.

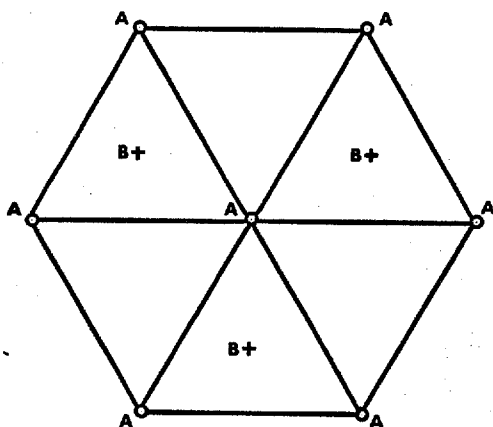
#### 5.2.4.2. THE FORMATION OF STACKING FAULTS ON $\{10\bar{1}0\}$ PLANES DURING COALESCENCE

A kind of multiple positioning of the original nuclei could provide a mechanism for the formation of faults on the  $\{10\bar{1}0\}$  planes. It should be mentioned here that these faults cannot be antiphase domain boundaries since many instances of three faults meeting at a point can be seen in the micrographs of Figs. 5.11.A and 4.6.C. It was mentioned in section 2.1 that antiphase boundaries in II-VI compounds cannot meet (HOLT, 1969). One would also not expect to see antiphase boundaries show up strongly in bright field since the crystal structure remains the same across an antiphase boundary and only the occupancy of the two sublattices is reversed.

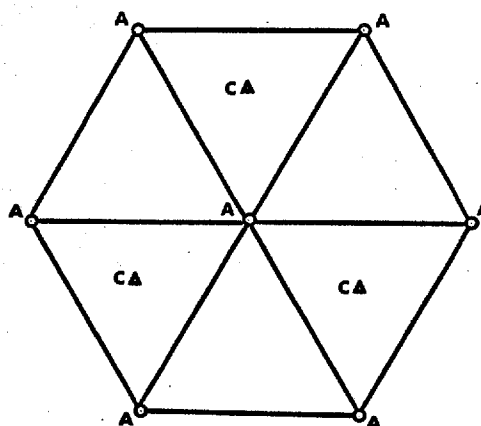
Fig. 5.12.A. shows the three possible positions of the close packed layers. In the following analysis, the "A" sites lie in the



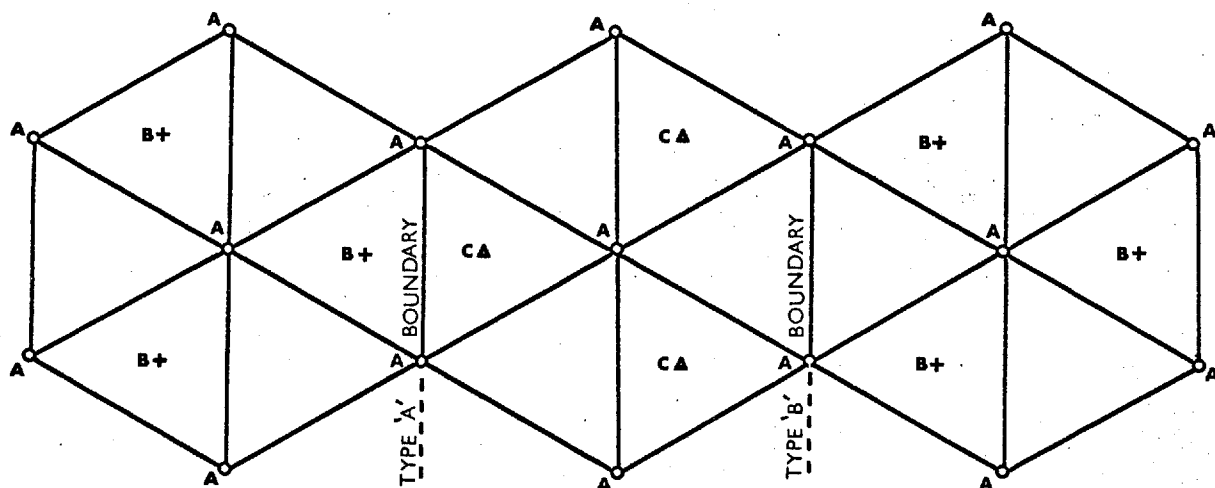
(A) The three possible positions for atoms in a close-packed structure.



(B) 1a - stacking



2a - stacking

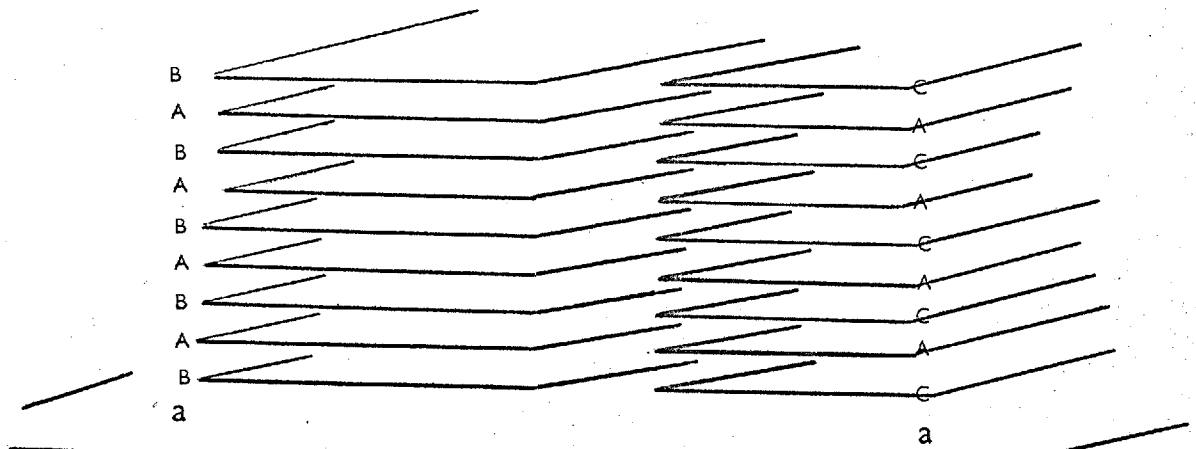


(C) Two hexagonal regions with 1a - stacking having boundaries with a hexagonal region with 2a - stacking. Type "A" boundary contains an excess of atoms and type "B" boundary contains a dearth of atoms.

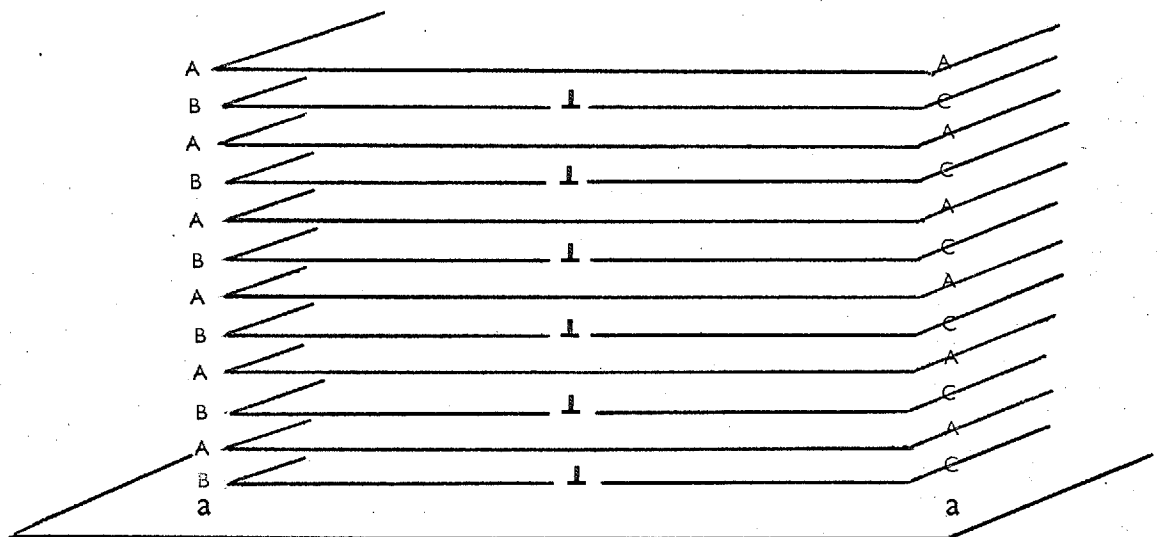
Fig. 5.12

substrate surface and the atoms of the first layer of the film are situated either at "B" sites or at "C" sites. Following the same system of symbols used in the previous section, the layers in the thin film are denoted by capital letters. Fig. 5.12.B shows the two modes of stacking, 1a and 2a. In both cases, the atoms in the substrate surface lie at "A" sites. The first layer of deposited atoms go into "B" sites for 1a and into "C" sites for 2a. The second layer goes back into "A" sites and the two structures may then be represented by the sequences BABA etc. and CACA etc. Fig. 5.12.C. shows an idealised situation where three nuclei have grown together. Two kinds of boundary are seen to exist. In type "A", the atomic-packing fraction at the boundary is higher than average whereas in type "B" the atomic-packing fraction is lower than average. It can be expected that strain is associated with both of these boundaries and could give rise to the contrast seen in the micrographs. A three dimensional representation of the situation is shown in Fig. 5.13.A. and the boundary is seen to consist of a vertical wall of partial dislocations (represented in Fig. 5.13.B) as the two nuclei join together. According to BLANK et al. (1964), this should be a stable configuration since the movement of one of the partial dislocations away from the boundary would create a stacking fault in its wake. On the other hand, there should be a repelling force between the partial dislocations of the same kind on alternate planes and the equilibrium configuration for the dislocation wall may be a zig-zag rather than a plane. In other words, the total energy is reduced by storing some of the energy in small areas of stacking fault parallel to the basal plane in order to lower, by a greater amount, the strain field energy of the dislocations.

The simple situation discussed above based on only two stacking sequences leads to the same criterion as for antiphase boundaries namely that the analysis does not allow three intersecting faults on



(A) A three dimensional representation of two nuclei growing together on the substrate surface. The stacking sequence in the nucleus on the left is BABA etc. and in that on the right it is CACA etc.



(B) The two nuclei shown in (A) have joined up to form a wall of partial dislocations at their boundary. The boundary is thus a particular type of stacking fault.

$\{10\bar{1}0\}$  planes to exist. Therefore, more than two stacking sequences must be present to account for the intersection of faults seen in the films. The possibility that faults of this type could be annealed out at 450°C. is quite high since slip on the  $\{0001\}$  basal planes is relatively easy. Partial dislocations with burgers vectors of the type  $\frac{1}{3} [10\bar{1}0]$  take atoms from "B" sites to "C" sites. This would enable the stacking sequence of one volume of material to transform progressively to that of a neighbouring volume by a process of slip on alternate or successive  $\{0001\}$  planes. This is similar to the slip process proposed by SECCO D'ARAGONA et al. (1966) for the ZnS phase transformation discussed in section 5.1.2.2.

#### 5.2.5. DEFECTS WHICH REMAINED IN FILMS HAVING THE WURTZITE STRUCTURE GROWN AT HIGH SUBSTRATE TEMPERATURES

Once the stacking faults had been eliminated either by growing the films at high substrate temperature or by annealing, numerous other defects remained. It was not possible to remove these completely either by raising the substrate temperature or by annealing in the manner described in section 3.4. These defects appeared to be dislocations and could only be observed at the higher end of the magnification range.

Their origin has not yet been determined. The work of MATTHEWS, PASHLEY and NEUGEBAUER referred to in section 2.3 has established that during the last stages of coalescence of a thin film, dislocations are frequently generated at points where the holes in the growing film have finally filled in. The mismatch between the thin film and substrate crystal structures is important in this (JACOBS et al., 1966). The mismatch has to be accommodated by strain and dislocations in the growing film.

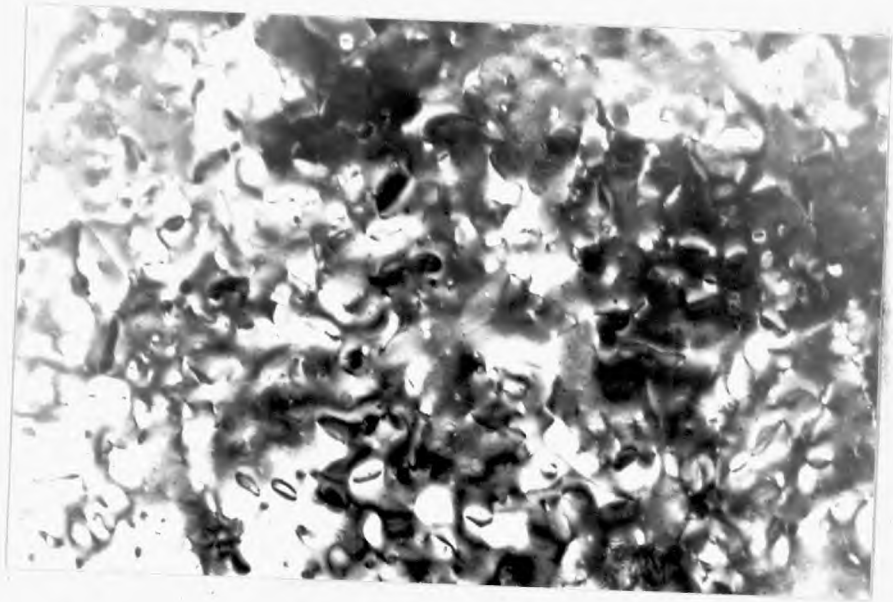
Another possible source of dislocations is that due to the annealing out of stacking faults on the  $\{10\bar{1}0\}$  planes which could lead to the formation of dislocations threading the film.

Dislocations which thread the films can only be removed either by reaction between two of opposite signs or by passing out through the sides of the films. Since the mobility of dislocations in the wurtzite structure is low, especially on planes other than the basal plane, annealing of the films cannot be expected to lead to a great reduction in the dislocation density. This was found to be so in the case of a film which had been annealed twice. No change in the visible number of dislocations was detected.

A fundamental limitation to the growth of thin layers of CdS by the process of vacuum evaporation is that nucleation inevitably takes place at many separate sites before coalescence begins. This guarantees that a certain minimum dislocation density will be present in an epitaxial layer whenever there is a mismatch between the film and substrate crystal structures.

A quite different class of defects having the appearance of dislocation loops can be seen clearly in the micrograph of Fig. 5.14. These are particularly characteristic of films grown at high substrate temperatures. The film illustrated in Fig. 5.14 was grown at 500°C. They are very similar in appearance to dislocation loops which are seen in thin metal films (as illustrated for example in HIRSCH et al., 1965) and in irradiated metals (RAU R.C., 1968; MEAKIN and GREENFIELD 1965). These had been formed either by condensation of vacancies or, in the case of irradiated metals, by the aggregation of interstitial atoms.

Most of the loops were less than 200Å across and were probably formed by the condensation of vacancies either during growth at high temperature or during cooling. Since CdS has a sulphur-deficient structure when heated in the absence of a sulphur-rich atmosphere, (SCMORJAL and JEPSEN 1964), the loops may be formed by condensation of sulphur vacancies.



0.1  $\mu$

Fig. 5.14. A bright field micrograph taken near a bend extinction contour showing many loop-like structures. The film was deposited on a  $\text{BaF}_2(111)$  substrate at  $500^\circ\text{C}$ .

5.3. THE NUMBER AND CLASSIFICATION OF DEFECTS FOUND IN SOME OF THE EPITAXIAL FILMS

Table 5.1 shows the estimated defect density in a number of the epitaxial films deposited in the three orientations. The density measurements were determined by counting the number of defects visible in areas of the micrographs 5 cms square. The arithmetic average of three such counts was taken for each specimen. The question marks indicate that it was not possible to determine whether the particular fault was present or not because of the confusion in the image caused by so many other defects. It was estimated that if planar defects were present in numbers greater than about  $10^{13}/\text{cm}^2$ , then it would not be possible to distinguish one from the next and the true number could therefore not be determined.

TABLE 5.1

THE DEFECT DENSITY IN EPITAXIAL CdS LAYERS

TYPE OF DEFECT AND THEIR NUMBERS PER  $\text{CM}^2$

FOR NaCl(100) SUBSTRATES - MATRIX SPIHALERITE STRUCTURE  
(VACUUM-CLEAVED)

| SUBSTRATE<br>TEMPERATURE | PLANAR<br>DEFECTS                     | DISLOCATIONS | LOOPS | OTHER<br>DEFECTS             |
|--------------------------|---------------------------------------|--------------|-------|------------------------------|
| 25°C.                    | $>10^{13}$<br>N O T E P I T A X I A L | ?            | NONE  | POLYCRYSTALLINE<br>TWO PHASE |
| 100°C.                   | $>10^{13}$                            | ?            | NONE  | 12 % WURTZITE                |
| 200°C.                   | $>10^{13}$                            | ?            | NONE  | NONE                         |
| 350°C.                   | ?                                     | ?            | NONE  | ~50 % WURTZITE               |

Table 5.1 (cont.)

FOR NaCl(110) SUBSTRATES - MATRIX SPHALERITE STRUCTURE

| SUBSTRATE<br>TEMPERATURE             | PLANAR<br>DEFECTS           | DISLOCATIONS    | LOOPS | OTHER<br>DEFECTS             |
|--------------------------------------|-----------------------------|-----------------|-------|------------------------------|
| 25°C.                                | $>10^{13}$<br>NOT EPITAXIAL | ?               | NONE  | POLYCRYSTALLINE<br>TWO PHASE |
| 300°C.                               | $>10^{13}$                  | ?               | NONE  | NONE                         |
| Annealed at<br>450°C. for<br>1 hour. | NONE                        | $2 \times 10^8$ | NONE  | TWO PHASE                    |

FOR NaCl(111) SUBSTRATES - MATRIX WURTZITE STRUCTURE

| SUBSTRATE<br>TEMPERATURE                        | PLANAR<br>DEFECTS  | DISLOCATIONS       | LOOPS | OTHER<br>DEFECTS |
|-------------------------------------------------|--------------------|--------------------|-------|------------------|
| 25°C.                                           | $>10^{13}$         | ? NOT EPITAXIAL    | NONE  | POLYCRYSTALLINE  |
| 300°C.                                          | $2 \times 10^{11}$ | $2 \times 10^{11}$ | NONE  | NONE             |
| Annealed at<br>450°C. for<br>$\frac{1}{2}$ hour | NONE               | $8 \times 10^{10}$ | NONE  | NONE             |

FOR BaF<sub>2</sub>(111) SUBSTRATES - MATRIX WURTZITE STRUCTURE

| SUBSTRATE<br>TEMPERATURE | PLANAR<br>DEFECTS | DISLOCATIONS           | LOOPS              | OTHER<br>DEFECTS                |
|--------------------------|-------------------|------------------------|--------------------|---------------------------------|
| -100°C.                  | $>10^{13}$        | NOT EPITAXIAL          | NONE               | POLYCRYSTALLINE<br>SINGLE PHASE |
| 0°C.                     | $>10^{13}$        | ?                      | NONE               | NONE                            |
| 200°C.                   | NONE              | $3 \times 10^{10}$     | NONE               | NONE                            |
| 400°C.                   | NONE              | $3 \times 10^{10}$     | $8 \times 10^{10}$ | NONE                            |
| 500°C.                   | NONE              | $1 \times 10^{10} (?)$ | $5 \times 10^{11}$ | NONE                            |

The best quality layers were those with the wurtzite structure which had been annealed. These contained a comparatively low number of dislocations and were single phase. A lower dislocation density is given for the annealed (110) oriented sphalerite structure layers. However, these were two phase and it was not possible to determine the defect density at the interfaces between the two structures.

The results for CdS in table 5.1 are consistent with the fact that the wurtzite structure is stable in the temperature range investigated. The only aspect which is a little unexpected is the low defect density of the untransformed sphalerite structure material in the annealed (110) oriented films. It must be deduced from this that the highly faulted as-grown sphalerite structure is energetically less favourable than the unstable, unfaulted sphalerite structure and that the latter is a transitional stage in the transformation to the stable wurtzite structure.

Few other figures have been quoted for the defect density of epitaxial semiconductor layers on ionic crystal substrates. MATTHEWS and ISEBECK (1963) found between  $10^{10}$  and  $10^{11}$  dislocations per  $\text{cm}^2$  in PbS layers deposited on NaCl(100) and CATLIN et al. (1964) found about  $10^{11}$  faults per  $\text{cm}^2$  in Ge layers deposited on  $\text{CaF}_2$ (111) substrates. Both results are very much in line with the figures found here for CdS on  $\text{B}\text{F}_3$ (111) substrates.

#### 5.4. CdS LAYERS DEPOSITED ON Ge(111) SUBSTRATES

The results obtained with the ionic crystal substrates suggested that Ge substrates in the (111) orientation would provide the most fault-free layers. The results of VAN DIJK (1967) showed that single crystal films could be deposited on Ge(111) substrates but results with other orientations, especially (110), might prove erratic. The few results obtained here, which amount to about thirty films, confirm that epitaxy can be achieved on Ge(111) although the minimum.

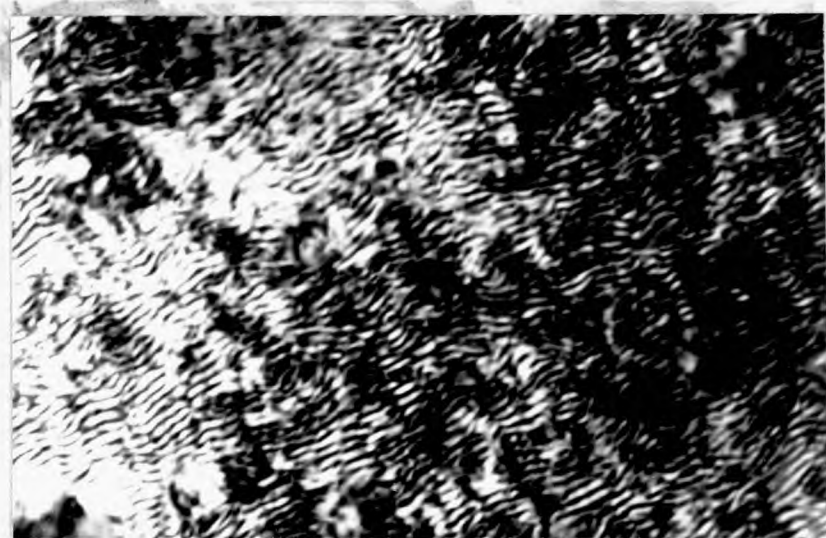
epitaxial temperature is higher for this than it is for the ionic crystal substrates.

#### 5.4.1. STRUCTURAL OBSERVATIONS OF CdS FILMS DEPOSITED ON Ge(111) SUBSTRATES

The contrast in the micrographs was generally more complex for these films than it was for those floated off the ionic crystal substrates. Effects due to diffraction, first in the film then in the substrate, gave strong fringe contrast when the specimen was tilted to the correct angle. Fig. 5.15 shows such a fringe system. These are parallel moiré fringes of the type discussed in 2.1 whose spacing corresponds to diffraction from the  $\{2\bar{1}\bar{1}0\}$  planes of CdS and the  $\{220\}$  planes of Ge. The measured spacing is  $61.0\text{\AA}$ . The spacing predicted by equation (1) defined in section 2.1.3 is  $61.6\text{\AA}$ . The discrepancy between these two is no greater than might be expected due to errors in the calibration of magnification in the electron microscope. The determination of both the theoretical and the observed values of the fringe spacing is contained in the appendix section A.2.

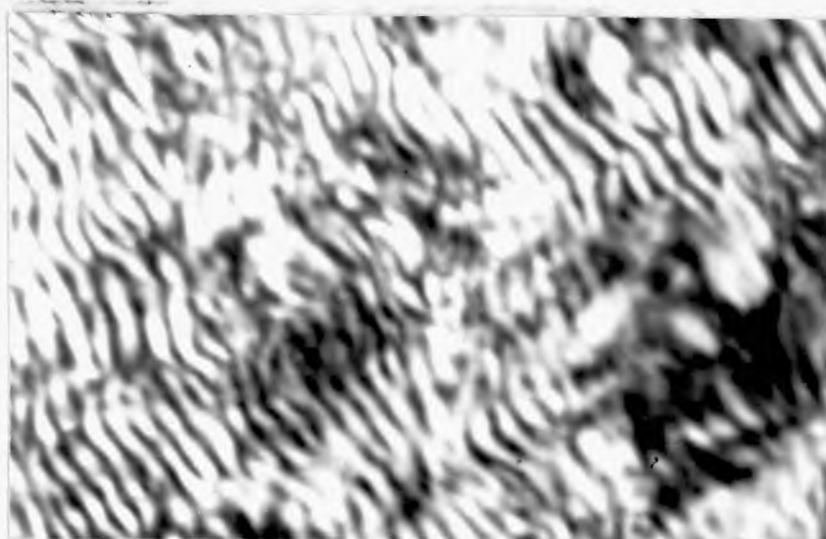
Both the diffraction patterns and the presence of wide areas of moiré systems indicate that the CdS layers are of a reasonably good structural quality. Although results as detailed as those presented in the previous sections have not yet been obtained for the CdS/Ge(111) system, the observations so far indicate that a study of the electronic properties of these heterojunction would give useful results capable of being correlated with their crystal structures.

The CdS/Si(111) system has been investigated with the same apparatus used for the rest of the work and no useful positive results have been obtained. The literature on silicon epitaxy contains many references to carbon contamination of the substrate surface adversely affecting epitaxial growth. This is one of the most likely contaminants in an oil diffusion pumped system and it has been



(A)

0.1  $\mu$



(B)

0.1  $\mu$

Fig. 5.15. Two micrographs of the moiré fringe pattern seen in a CdS/Ge(111) layer grown at 450°C. The fringes are due to the  $\{220\}$  Ge planes and the  $\{11\bar{2}0\}$  CdS planes. (B) is an enlargement of part of (A)

concluded that further work would need to be done in a vacuum system using ion pumps.

#### 5.5. SOME COMMENTS ON EPITAXY AT LOW SUBSTRATE TEMPERATURES

KALDIS (1969) has investigated the growth of bulk single crystals of CdS from the supersaturated vapour. The crystal morphology and growth rates were studied as a function of the degree of supersaturation of the vapour with respect to the growing crystal. It was found that single crystals could not be grown if the undercooling of the crystal with respect to the vapour was greater than about  $20^{\circ}\text{C}$ . because at greater temperature differences, nucleation could not be controlled and a polycrystal was produced. No similar investigation has been made of crystal growth on single crystal substrates.

The essential difference between the growth of a bulk single crystal and an epitaxial film is that in the former case, nucleation and growth can be allowed to occur at only one site whereas in the latter case, the single crystal substrate ensures that all nuclei are aligned and so form part of the same single crystal. By keeping the degree of undercooling small, it can be ensured that only one nucleus grows. If the number of nuclei formed is of no particular consequence, the degree of undercooling becomes less significant and very large values of undercooling may be tolerated.

The degree of undercooling permissible in epitaxial growth (i.e. the minimum epitaxial temperature) is at least partly determined by the strength of the orienting effect of the substrate over the depositing film. In the case of CdS deposited on vacuum-cleaved  $\text{BaF}_2(111)$  substrates the effect is sizeable even at temperatures below  $0^{\circ}\text{C}$ .

A further point of interest is that the surface reaction at the substrate in which the Cd atoms and  $\text{S}_2$  molecules combine to form CdS must be capable of proceeding at these low temperatures. It is possible that the heat of reaction between the two atom species

provides the energy to give them enough mobility on the growing surface to find their proper positions. Alternatively, it has been suggested that the vapour consists of a number of cadmium-sulphur complexes of the type  $\text{Cd}_n\text{S}_m$  (where  $n$  and  $m$  are integers) whose structures dictate the mode of growth of the crystal (BULAKH, 1969). BULAKH's work, however, was based upon measurements made with non-stoichiometric vapours at near-atmospheric pressures in which many atomic collisions would occur in the vapour phase before the vapour had reached the growing crystal surface. This would provide an opportunity for complexes to form. In the case of sublimation of the source in vacuo, the vapour is given off as a diverging beam in which atomic collisions are much less likely. A surface reaction between the elements seems to be a more probable process in these circumstances rather than the condensation of molecular complexes. A further drawback to the molecular complex model is that their mobility at low temperatures would be very much less than that of the atoms. This would render epitaxy less rather than more likely on substrates at low temperatures.

A model describing the chemical reaction at the epitaxial growth surface would be a great help in understanding the way in which epitaxy can still occur at such low temperatures. The models presently available which describe crystal growth at high temperatures are inadequate. Such a model would also have to account for the fact that the minimum epitaxial temperature on Ge(111) is at least  $250^\circ\text{C}$ . higher than that for  $\text{BaF}_2(111)$  i.e. about twice the absolute temperature. There are many great differences between these two substrate materials, but there are two which may be of particular significance in this context. The first is that the Ge(111) surface contains only Ge atoms whereas the  $\text{BaF}_2(111)$  surface contains both  $\text{Ba}^{++}$  and  $\text{F}^-$  ions. Since CdS is to some extent ionic, there may be a

beneficially stronger orienting effect from the ionic crystal substrate surface. The second difference is that Ge is a conductor of electrons and the ionic crystals are insulators. If the process of condensation and chemical combination at the substrate surface is in any way electronic, the presence of an alternative path for electrons through the substrate rather than across its surface may retard the epitaxial process, particularly at low temperatures where thermal surface diffusion of atoms is slow.

## CHAPTER 6

### CONCLUSIONS AND PROPOSALS FOR FURTHER WORK

The technique of deposition of CdS in vacuo to form thin epitaxial layers has been shown to work very well. For the first time, good quality epitaxial layers of CdS have been produced on the three principal low index cubic substrate faces.

The work reported here indicates that although thin films of CdS may be grown with either the sphalerite structure or the wurtzite structure, only the latter type contain comparatively few defects. Annealing removes planar defects from films with the sphalerite structure while at the same time promoting a phase transformation to the wurtzite structure. By comparison, all the planar defects and some of the dislocations are removed from films with the wurtzite structure. These results are compatible with the fact that CdS is stable in the wurtzite structure at the temperatures investigated.

The phase transformation should be investigated more thoroughly. In particular, the preferential transformation on one set of closest-packed planes, which seems to be a general feature of the annealed films, should be looked in to. If this property can be exploited, the possibility exists of producing wurtzite structure films in unusual orientations by annealing films with the sphalerite structure in other orientations besides (110). The application of this technique to the (100) orientation was not investigated. Such a film may transform into an approximately (01 $\bar{1}$ 1) wurtzite orientation.

Another interesting feature not explained by this work is the epitaxy of CdS at very low substrate temperatures. The need for a satisfactory model for the nucleation and growth of CdS at these temperatures was expressed in section 5.5 as this may give some clues as to why the epitaxial growth of CdS can vary so greatly from one substrate to the next.

At the other extreme, the presence of what appear to be collapsed vacancy discs in films grown at about  $400^{\circ}\text{C}$ . upwards suggests that useful epitaxial layers should be deposited below this temperature with this technique. No doubt, these defects could be suppressed if a suitable background pressure of sulphur were maintained during growth, assuming that the discs are due to sulphur vacancies.

For the experimental set-up used in this work, it can be stated that the best layers are obtained in the temperature range between  $200^{\circ}\text{C}$ . and about  $400^{\circ}\text{C}$ . on (111) oriented substrates. It is on these layers that electrical measurements should first be made. The measurements should be an investigation of the simple electrical properties (e.g. voltage-current characteristics and Hall mobility) as a function of the structural quality of the layers. This could be extended to include the effects of annealing and the electrical properties of films transformed from the sphalerite structure. The structural complexity of the films with the sphalerite structure in the unannealed condition would probably render a similar study of their electrical properties impracticable because of the difficulty of interpretation.

A way of removing the remaining faults in the best quality films might yet be devised once their exact analysis is complete. Therefore a continued programme of fault analysis in CdS layers is advocated.

The work planned for the immediate future in this laboratory concerns the growth of CdS layers on Ge(111) and Si(111) substrates and the assessment of their electrical properties.

A P P E N D I X

A.1. THE ANALYSIS OF THE DIFFRACTION PATTERN OBTAINED FROM FILMS GROWN ON NaCl(100) SUBSTRATES AT 350°C.

A.1.1. THE TRANSFORMATION MATRIX

Fig. A.1 shows a hexagonal prism representing one unit cell of the wurtzite structure lying with its basal plane on a (111) plane of a unit cell of the sphalerite structure. The orientation of the crystal axes is shown.

By simple geometry it can be shown that:-

$$(100)_{\text{HEX}} = \frac{1}{3} (2\bar{4}2)_{\text{CUB}}$$

$$(010)_{\text{HEX}} = \frac{1}{3} (4\bar{2}\bar{2})_{\text{CUB}}$$

$$(001)_{\text{HEX}} = \frac{1}{2} (111)_{\text{CUB}}$$

The transformation matrix to obtain the equivalent cubic lattice vector from a given hexagonal lattice vector is:-

$$(hkl)_{\text{CUB}} = \frac{1}{6} \begin{pmatrix} 4 & 8 & 3 \\ \bar{8} & \bar{4} & 3 \\ 4 & \bar{4} & 3 \end{pmatrix} \begin{pmatrix} H \\ K \\ L \end{pmatrix}_{\text{HEX}}$$

To obtain the equivalent hexagonal lattice vector from a given cubic lattice vector, one must multiply both sides of the above matrix, which shall be called A, by its reciprocal matrix,  $A^{-1}$ , to obtain the appropriate transformation matrix.

Thus:-

$$(hkl)_{\text{CUB}} A^{-1} = \frac{1}{6} A A^{-1} (HKL)_{\text{HEX}}$$

$$\text{i.e. Since } A A^{-1} = 1$$

$$(HKL)_{\text{HEX}} = 6 A^{-1} (hkl)_{\text{CUB}}$$

$A^{-1}$  is defined as  $\frac{\text{adj } A}{|A|}$  where adj A is the adjoint matrix formed from the cofactors of A and |A| is the determinant of A.

This gives the following identity:-

$$(HKL)_{\text{HEX}} = \frac{1}{6} \begin{pmatrix} 0 & \bar{3} & 3 \\ 3 & 0 & \bar{3} \\ 4 & 4 & 4 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}_{\text{CUB}}$$

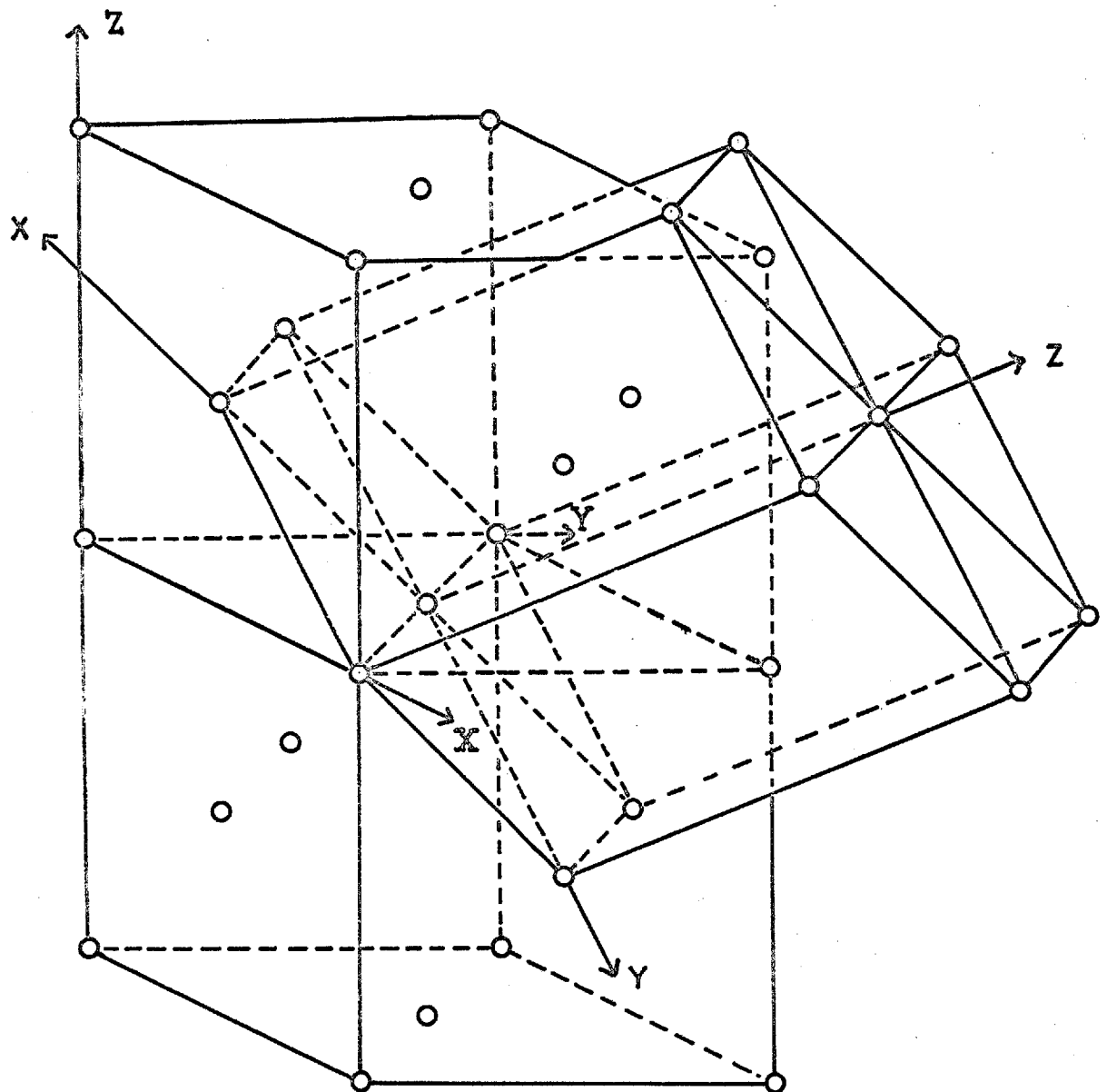


Fig. A.1. A hexagonal prism representing one unit cell of the wurtzite structure lying with the (0001) plane in contact with the cubic (111) plane of the two f.c.c. unit cells which represent the sphalerite structure. The open circles represent metal atoms but, for the sake of clarity, solid circles representing non-metal atoms have not been included.

This matrix was used to determine the hexagonal indices of spots lying along the  $[111]$  direction from sphalerite matrix spots. An equivalent matrix exists for determining the indices of spots due to material with the wurtzite structure lying on the  $\{1\bar{1}1\}$  planes.

#### A.1.2. SATELLITE SPOTS DUE TO WURTZITE MATRIX DIFFRACTION

Satellite spots due to material with the wurtzite structure were found at the following positions:-

About the 022 spot:-

$$1) (022) + \frac{1}{6}(111), \quad 2) (022) + \frac{2}{3}(111), \quad 3) (022) - \frac{1}{3}(111) \\ \text{and } 4) \frac{1}{2}(111).$$

About the 020 spot:-

$$5) (020) + \frac{1}{3}(111) \text{ and } 6) (020) - \frac{1}{6}(111)$$

The hexagonal indices associated with these spots are determined below and plotted in the diagram of Fig. 5.2. The first spot is worked in detail.

$$1) (022) + \frac{1}{6}(111) \equiv \frac{1}{6}(1 \ 13 \ 13) \\ \text{i.e. (HKL)} \equiv \frac{1}{6} \begin{pmatrix} 0 & \bar{3} & 3 \\ 3 & 0 & \bar{3} \\ 4 & 4 & 4 \end{pmatrix} \begin{pmatrix} 1 \\ 13 \\ 13 \end{pmatrix} \frac{1}{6} \\ \equiv \frac{1}{36} (0 \ \bar{3}6 \ 108) \\ \equiv (0\bar{1}3)$$

i.e. Spot 1) has the indices  $(0\bar{1}13)$

$$2) (022) + \frac{2}{3}(111) \equiv \frac{1}{3}(288)$$

This has the hexagonal indices  $(0\bar{1}14)$

$$3) (022) - \frac{1}{3}(111) \equiv \frac{1}{3}(\bar{1}55) \equiv (0\bar{1}12)$$

$$4) \frac{1}{2}(111) \equiv (0001)$$

$$5) (020) + \frac{1}{3}(111) \equiv \frac{1}{3}(171) \equiv (\bar{1}012)$$

$$6) (020) - \frac{1}{6}(111) \equiv \frac{1}{6}(\bar{1}11\bar{1}) \equiv (\bar{1}011)$$

A bright spot is also seen at positions of the kind  
 $(02\bar{2}) + \frac{1}{2}(111) = \frac{1}{2}(15\bar{3}) = (\bar{2}111)$  - spot 7)  
 Other spots at similar positions about the rest of the sphalerite matrix spots are also plotted in Fig. 5.2.

All of the spots plotted so far are wurtzite matrix spots. Some of these, however, are forbidden reflections but show up as a result of multiple diffraction through allowed lattice vectors (PASHLEY et al., 1963). The condition for forbidden reflections in the h.c.p. structure is that  $h + 2k = 3n$ ,  $n$  being an integer including zero, and  $l$  must be odd. The spots  $(\bar{2}111)$  and  $(0001)$  are of this type. The spot  $(\bar{2}111)$  appears as a result of diffraction through the two allowed vectors  $(\bar{1}10\bar{1})$  and  $(\bar{1}012)$ . Double diffraction between the  $(10\bar{1}\bar{1})$  spots and  $(\bar{1}012)$  gives the  $(0001)$  spot. Thus  $(10\bar{1}\bar{1}) + (\bar{1}012) = (0001)$

#### A.1.3. DOUBLE DIFFRACTION BETWEEN THE WURTZITE AND SPHALERITE MATRICES

Some weak spots can be seen in the diffraction pattern of Fig. 5.2 at the following positions:-

- 1)  $DD_a(02\bar{2}) + \frac{1}{6}(111)$  and 1)  $DD_b(02\bar{2}) - \frac{1}{6}(111)$ ,
- 2)  $DD(002) + \frac{1}{6}(111)$  and 3)  $DD(002) - \frac{1}{3}(111)$

The spot in position 1)  $DD_a$  is due to diffraction through an  $(02\bar{2})$  vector in the sphalerite structure followed by diffraction through a  $(\bar{1}10\bar{1})$  vector in the wurtzite structure. This can be illustrated as follows:

The fractional hexagonal indices of the double diffraction spot are given by  $(02\bar{2}) + \frac{1}{6}(111) = \frac{1}{6}(1\ 13\ \bar{1}\bar{1}) = \frac{1}{3}(\bar{6}331)$ .  
 The two diffraction vectors are  $(020) = \frac{1}{3}(\bar{3}034)$  and  $(\bar{1}10\bar{1})$ .  
 Their sum is  $\frac{1}{3}(\bar{6}331)$  which is evidently the double diffraction spot.

Similarly  $(02\bar{2}) - \frac{1}{6}(111) = (00\bar{2}) + (\bar{1}011)$

Spot 2)  $DD$  is due to diffraction through the vectors  $(0\bar{2}0) + (0\bar{1}13)$  and spot 3)  $DD$  is due to diffraction through the vectors  $(0\bar{2}0) + (0\bar{1}12)$ .  
 The double diffraction spots are also plotted in Fig. 5.2.

A.2. DETERMINATION OF THE MOIRÉ FRINGE SPACING DUE TO THE LATTICE MISMATCH BETWEEN CdS AND Ge.

Fig. A.2 shows, superimposed, plots of the diffraction patterns of (111) Ge and (0001) CdS. It can be seen that spots of the  $\{0\bar{2}2\}$  type due to the Ge structure are near spots of the type  $\{2\bar{1}\bar{1}0\}$  due to the CdS structure. No Ge spots are found near CdS spots of the type  $\{10\bar{1}0\}$ . Thus, the moiré fringe system seen when viewing along the  $[111]$  direction is due to the  $\{0\bar{2}2\}$  Ge planes and the  $\{2\bar{1}\bar{1}0\}$  CdS planes. Fig. 5.13 illustrates such a fringe system. Due to the tilt of the specimen at the time when the micrograph was taken, only fringes lying along one of the three possible directions are seen.

The lattice parameters of Ge and CdS with the wurtzite structure are:-

$$\begin{array}{lcl} \text{Ge ; a cubic} & = & 5.6576 \overset{\circ}{\text{A}} \\ \text{CdS; a hexagonal} & = & 4.136 \overset{\circ}{\text{A}} \end{array}$$

The formula for the fringe spacing, M, is:-

$$M = \frac{d_1 d_2}{|d_1 - d_2|}$$

where  $d_1$  and  $d_2$  are the relevant interplanar distances. For CdS this is  $\frac{\text{a hexagonal}}{2}$  and for Ge it is  $\frac{\text{a cubic}}{2\sqrt{2}}$

$$\begin{aligned} \text{Thus:- } M &= \frac{1}{2} \left( \frac{5.6576 \times 4.136}{5.6576 - \sqrt{2} \times 4.136} \right) \\ \text{i.e. } M &= 61.6 \overset{\circ}{\text{A}} \end{aligned}$$

Fig. 5.13.B shows an enlargement from the micrograph shown above it. 41 fringes occupy a distance of 12 cms. The total magnification of the enlargement is 490,000 and this gives a value for the fringe spacing of  $61.0 \overset{\circ}{\text{A}}$ . The measured and the predicted value are closer than one should expect since the calibration of the microscope is not guaranteed to be within such close limits. It is also not reasonable to expect the lattice spacings of the thin films to be identical with those of bulk crystals.

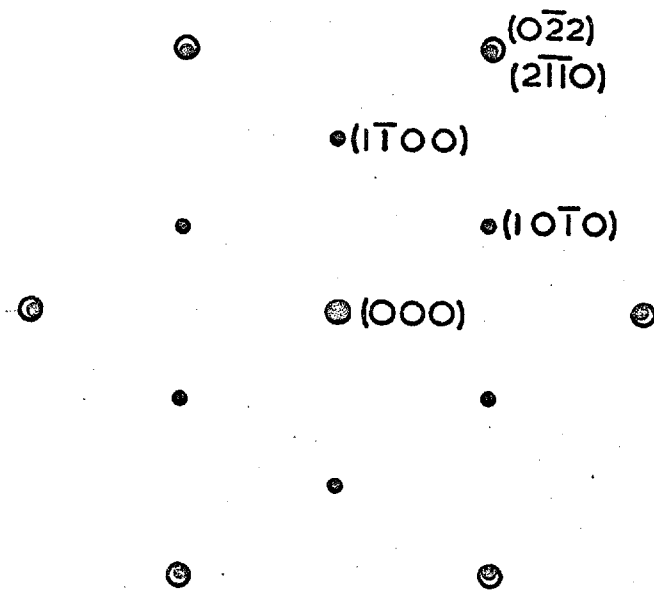


Fig. A.2 The superimposed diffraction patterns of Ge(111) and CdS(0001).

- - represents a spot due to Ge
- - represents a spot due to CdS

BASSETT et al. (1958) have discussed the variation in the spacing of Moiré fringes obtained from a single set of planes and concluded that a deviation of up to 10% from the theoretical spacing could be expected.

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