

STRUCTURAL AND ELECTRICAL PROPERTIES
OF ZnTe - Ge HETEROJUNCTIONS

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ABSTRACT

ZnTe was evaporated by electron-beam heating in high vacuum on to (111) and (100) surfaces of Ge. In both cases the epitaxial range of substrate temperatures was from 300 to about 430° C. In both cases the films had the sphalerite structure and grew in parallel alignment with the substrate. Some (111) films grown at temperatures in the upper portion of the epitaxial range gave diffraction patterns containing satellite spots showing that these films contained twins. Most films grown in the lower portion of the epitaxial temperature range for (111) substrates and films grown on (100) substrates at all epitaxial temperatures, however, were free of twins and included grains and their diffraction patterns contained no satellite spots. Moire fringe observations of these more perfect specimens showed that any misalignments of portions of the films with the substrates were 0.5° or less. The best (111) films contained about 10^{10} bent stacking faults per cm^2 .

In the second phase of the project films of ZnTe about 1 μm thick were grown on n-type Ge (111) substrates and the I-V characteristics of these p-n heterojunctions were measured at room temperature. It was found that the epitaxial ZnTe/Ge heterojunctions showed rectifying behaviour while the polycrystalline ZnTe/Ge heterojunctions showed less assymmetric characteristics. The forward I-V characteristics were found to be linear when they were plotted on a

log I scale versus $V^{\frac{1}{2}}$. This is the form of the Schottky or Poole-Frenkel effects. Switching from low to high conductivity states was observed. This was similar to phenomena observed in related heterojunctions by Hovel et al (1971) , Ota et al (1971) and Newbury et al (1972).

Some preliminary observations on the electrical and luminescent properties of these heterojunctions were also made using the scanning electron microscope.

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PART I

" STRUCTURAL PROPERTIES OF ZnTe
EVAPORATED ON TO Ge IN VACUUM "

CHAPTER I

1.1. INTRODUCTION

The group of materials known as II-VI Compounds, consists of fifty per cent each of elements of group II-B and VI-B of the Periodic Table. Generally the semiconductor oxides, selenides, sulphides and tellurides of magnesium, beryllium, mercury, zinc and cadmium, and their solid solutions are included in this family.

Due to their great potential and increasing applications in science and industry for their photo-conductive, photo-voltaic and luminescence effects, the interest in these compounds is on the increase. For instance due to their wide forbidden energy bands (3.8 ev for ZnS, 2.4 ev for CdS and 2.23 ev for ZnTe) the red edge and the maximum of their photo-sensitivity lie in the visible part of spectrum or in the ultra-violet and infrared. Some of these(e.g. CdS, ZnS, ZnTe and ZnSe) should in theory, be suitable for making devices producing visible radiation (Morehead 1967). Their nature makes them suitable to form continuous series of solid solutions. The absence of a centre of symmetry is responsible for strong piezoelectric effect and the list of technical applications like photoresistors, D.C. electroluminescent display panels, microelectronic devices such as acousto-electric and surface wave devices, CdS solar cells,

switches, electrical signal convertors etc. is on the increase.

The use of these materials in such devices requires considerable knowledge of, and control over, their physical and electrical behaviour. Unfortunately the research work on these materials was very slow, but with considerable improvement of technology, such as micro-analytical techniques to determine the composition of microstructures, electron microscopy and improved vacuum systems, the pace of research has increased.

More and more information is being gathered from different branches of research using diverse type of techniques, and the limitations of the unsatisfactory state of purity, stoichiometry and perfection of the II-VI crystalline compounds are being overcome. Most of these methods for the study of their properties can be broadly classified under two main heads. Firstly, methods for the study of crystals in bulk form, and secondly, methods for the study of thin films. In bulk form the single crystals are grown from ^{the} vapour phase by static methods (based on Reynolds and Czyzack's method 1950), by dynamic methods (Frerich's method 1947), from melts (Stockbarger method) and by the hydrothermal processes (Landise and Ballman 1960).

Most of the information about the electrical properties of II-VI compounds have been obtained from the materials in the bulk form, but in accordance with the modern trends toward miniaturization, thin films are

becoming more important. So far thin films have not been able to reproduce the bulk properties exactly, but efforts are being made to reach that end. Most important problems encountered in these efforts concern the perfection of the crystals and the non-preservation of stoichiometry. Although quite a number of compounds have been prepared in epitaxial form of films, the vast majority of electrical and optical studies reported in the literature were made on polycrystalline films. Because for several device applications such as photo detectors, thin film transistors etc. the polycrystalline films were quite suitable and easy to make. Epitaxial films are, however, getting increasing attention. Several II-VI compounds have been epitaxially deposited on a variety of substrates,^{but} 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. So far this reason it is advantageous to begin by studying the crystal and defect structure of ZnTe on Ge and subsequent electrical measurements may then be interpreted in the light of this knowledge. It may be pointed out that no published work of this systematic kind is yet seen in the literature published on II-VI compounds.

A multitude of techniques have been developed to prepare polycrystalline and nearly single crystal films of all types of materials. Deposition rates may range from

a fraction of an angstrom to thousands of angstroms per second. Among these deposition techniques, those of thermal evaporation by resistance and electron bombardment heating, sputtering by means of glow discharge, rf. and ion beam sputtering and vapour deposition by a variety of chemical reactions have been perfected. The details of the various methods are given in most of the modern books such as those written by Holland (1956), Berry, Hall and Harris(1968) Ray (1969) and Chopra(1969). The choice of any one of the many available methods for growing thin films of II-VI compounds is a function of the required crystalline order, perfection and the impurity concentration of the films.

A programme of research on the epitaxial growth of II-VI compounds has been carried out in this laboratory for some years. The films were evaporated in vacuum on to ionic crystal substrates at first. These substrates were chosen for ease of removal of the films for examination by means of transmission electron microscopy. This work showed that the minimum substrate temperature for epitaxial growth can be improved by the systematic minimisation of contamination from all sources in the system (Woodcock et al 1969 and Holt et al 1971).

It has always been one objective of this work to employ the growth techniques that were developed in order to produce II-VI epitaxial films in useful forms. This means among other things growing the films on semiconductor substrates. Initial work showed that ZnSe

(unpublished work), and CdS (Holt et al 1971, Wilcox 1970) could readily be grown on germanium substrates in vacua in the 10^{-5} to 10^{-6} torr range but CdS could not be grown on Si substrates in vacua in this range (Wilcox 1970).

The epitaxial growth and structure of ZnTe evaporated on to ionic substrates was previously investigated (Holt 1966, 1969). It was pointed out by Holt(1966) that ZnTe grew epitaxially, over broad ranges of substrate temperature, when evaporated in high vacua from hot metal crucibles on to (111) cleavage faces of BaF_2 and CaF_2 . The epitaxial films appeared monocrystalline but with many small included grains which were identified as second phase material, or microtwins or both. It was also reported that epitaxial growth of ZnTe could not be obtained reproducibly on (100) cleaved faces of NaCl at any temperature. Subsequently it was found that by changing from conventional hot metal evaporators to focussed electron beam evaporation epitaxial growth of ZnS (Unvala et al 1968, Woodcock 1969), CdS (Wilcox et al 1969) and ZnTe (Holt 1969) could be obtained on NaCl over a wide range of substrate temperatures. So from this past experience *the* vacuum evaporation technique was also chosen for the present work.

As the present work is based on the vacuum evaporation technique, so no details of the other methods will be given here. The basic principle involved in the

formation of evaporated films is to evaporate the charge in a vacuum chamber. Due to the low density of residual gas molecules in the chamber, the molecules of the charge are allowed to travel almost collision free. They are then transmitted to a substrate kept at a definite temperature. A fraction of the incident atoms and molecules stick to the substrate to form a thin film thus making a heterojunction.

Due to the difficulty in preparing the II-VI compounds with high conductivities both n type and p type and ^{the}consequent impossibility of making well controlled p-n homojunctions, an alternative approach of preparing heterojunctions has attractions. Heterojunctions, unlike the conventional p-n and n-p junctions separating differently doped regions of the same semiconductor material (homojunction), are the interfaces between two different semiconductor materials. They are usually the sites of discontinuities in all the significant semiconductor parameters such as energy gap, effective mass, lattice parameters etc. These junctions can be prepared from two different compounds one of which can be made "n" type and the other "p" type with suitable carrier concentration and transport properties. The varied choice of combinations of these heterojunctions has made it an extensive field of research.

It may be pointed out here, that meaningful studies of electrical and optical properties of semiconductor

heterojunctions can only be made if the material on either side of the junction approximates to the ideal of pure single crystal with the minimum of crystallographic defects. Bube(1960, 1967) pointed out that the crystalline faults, particularly when associated with impurity atoms, provide traps of varying depths for charge carriers and greatly affect the electronic properties of the material. Since the transport properties of semiconductor materials in general can be dominated by crystal perfection, so emphasis has to be placed on the growth of high quality single crystal films. For this project it was desired to prepare and study the properties of the heterojunctions between ZnTe (energy band gap 2.23 ev) and Germanium (energy band gap 0.67 ev). So obviously the first objective was to grow epitaxial films of ZnTe with a minimum defect density on germanium substrates and the second was to investigate the electrical properties of these heterojunctions.

"Vactran" type ZnTe from B.D.H. having a purity of 99.999% was used in this work. Germanium, used as substrate, was available as technological developed material in the form of slices of single crystal of known orientation, resistivity and doping. The facilities for preparing the substrate for epitaxial growth, growing of films and the study of their growth and electrical properties were developed in this laboratory.

This presentation is divided into two

self-contained parts. The first part contains the account of the preparation of epitaxial films of ZnTe on Ge single crystal substrates with the vacuum evaporation technique. The various parameters of growth and the defects of the films are discussed. Films of ZnTe of the order of 1000 Å to 3000 Å ^{thick} were grown for this work. Their structural analysis was done with the help of transmission electron microscopy, as this technique is capable of great resolution at high magnification. The associated technique of dark field electron microscopy provided a means for removing any ambiguities in the interpretation of bright field images. Line, planar and volume defects have been observed in ZnTe films and the volume defects were successfully eliminated.

The second part deals with the electrical properties of ZnTe/Ge heterojunctions. For this work the logical starting point is the study of I-V characteristics which contain a lot of information about the transport mechanism etc. Thicker films were needed for this work, and with the facilities available in this laboratory ZnTe films were grown up to 1 μm thick.

The present work is another step forward in the comparative studies of II-VI compounds which is going on in this laboratory for the last eight years.

1.2. STRUCTURE OF II-VI COMPOUNDS

The crystallography of II-VI compounds is somewhat complicated by their propensity to crystallize in a variety of polymorphic modifications, but the principle types are Sphalerite(Zinc blende) and Wurtzite. Both these types, on the average, have four valence electrons per atom, which is conducive to the formation of tetrahedral coordinated atom sites. A compound AB having a tetrahedrally coordinated structure has the A atom surrounded symmetrically by four nearest neighbour B atoms, which sit on the corners of a tetrahedron. The A atom occupies the geometrical centre of it. A and B sites are identical as far as their tetrahedral nature is concerned.

There are two different types of tetrahedrally coordinated structures relevant to the present work. In Fig. 1(a) the bases of the tetrahedra are parallel to each other but rotated through 60° about the vertical axis through their centres relative to one another. This arrangement gives rise to the zinc blende or sphalerite structure. In Fig 2(a) the bases of the tetrahedra are parallel to each other and the corners are in line vertically. This pattern gives rise to the structure known as wurtzite which is based on hexagonal close packed space lattice.

Figs 1(b) and 2(b) represent their unit cells and the positions of the atoms.

1.2.1 Sphalerite Structure

This structure has a close relationship to the diamond structure and belongs to the cubic system. Sphalerite lattices are made up of a network of tetrahedral, essentially covalent bonds, which link atoms of group II of the periodic table to atoms of group VI by sharing electron pairs between valence orbitals of neighbouring atoms. This lattice structure may be regarded as formed by two inter-penetrating fcc lattices, one for each type of atoms, mutually displaced along their body diagonal by one quarter of its length. Each atom of a sublattice is thus in a tetrahedral environment of its four nearest neighbours of the opposite sublattice. The nearest neighbour distance is $\frac{\sqrt{3}}{4} a$ where "a" is the cubic lattice parameter. There are twelve next nearest neighbours of atoms of the same kind at a distance of $\frac{\sqrt{3}}{2} a$.

There are four ZnTe molecules in a unit cell and the atoms occupy the positions:

Zn at $000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$

Te at $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}$

If all the B lattice positions are also occupied by A atoms then the structure will be converted to diamond structure.

Crystals with the zinc blende structure are characterised by the absence of a centre of symmetry i.e.

they show polar character, and opposed (hkl) and ($\bar{h}\bar{k}\bar{l}$) faces and opposed [hkl] and [$\bar{h}\bar{k}\bar{l}$] directions have different physical and chemical properties. Consequently they also

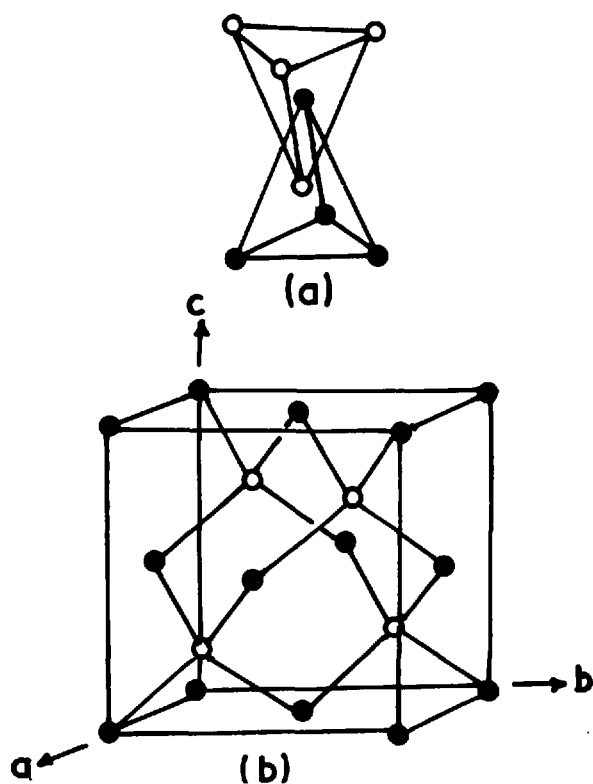


Fig. 1

(a) Tetrahedral sites for sphalerite structure compound. The bases of the tetrahedra are parallel and 60° out of line vertically.

(b) 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.

possess the property of being Piezoelectric. Their Madelung Constant is 1.638 (Sherman 1932).

Zinc Telluride has generally been observed to grow in the sphalerite structure but Pashinkin et al 1960 and Chistyakov and Krucheanu (1961) have reported to have ZnTe grown in the wurtzite form.

1.2.2. The wurtzite structure

This structure belongs to the hexagonal class and composed of two inter-penetrating h.c.p. lattices displaced with respect to each other by a distance $\frac{3}{8}c$ along the hexagonal c-axis. The nearest neighbour distance is $\frac{3}{8}c$ in crystals having the ideal c/a ratio 1.633 (Wyckoff 1960).

There are two molecules in a hexagonal unit cell with two Zn atoms at 000 and $1/3 \ 2/3 \ 1/2$ and two Te atoms at 00u and $1/3 \ 2/3 \ 1/2 + u$ where $u \approx \frac{3}{8}c$.

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 coordination (Roth 1967). The two structures can be compared in terms of the $[111]$ three-fold axis of Zinc blende and the $[00.1]$ hexad axis of wurtzite. Rotation of ^{one of} the inter-penetrating tetrahedra in Zinc blende about the $[111]$ axis converts the structure into wurtzite and the symmetry axis becomes an $[00.1]$ axis.

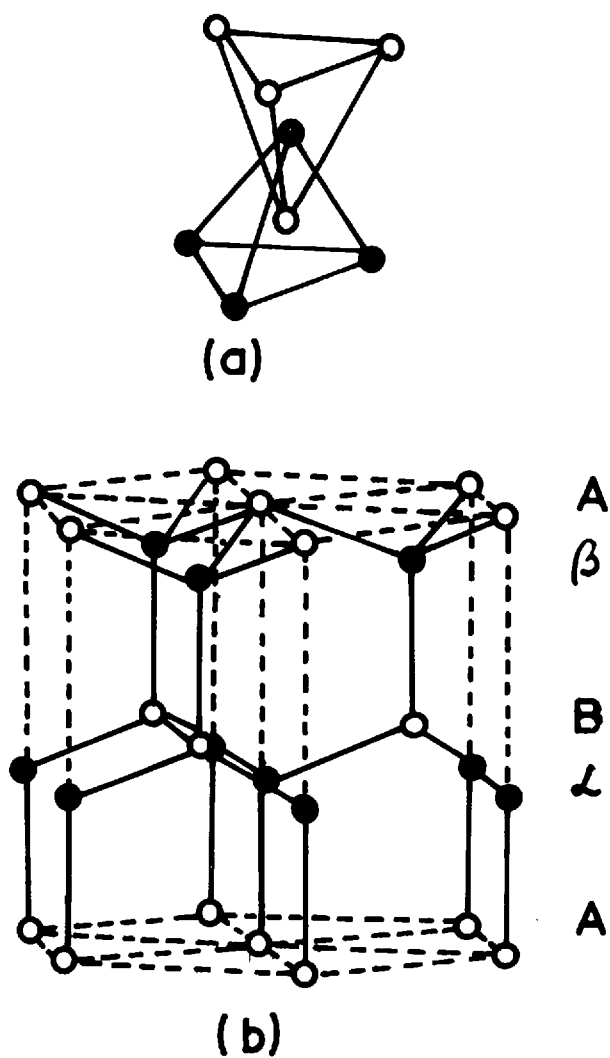


Fig. 2

(a) Tetrahedral sites for a wurtzite structure compound. The bases of the tetrahedra are parallel and in line vertically.

(b) 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.

1.2.3. Structure Description Based On Stacking Of Layers

Sphalerite and wurtzite structures can be described by noting the sequence of the stacking of layers. This can be very easily explained in a two dimensional diagram which can be subsequently visualised in three dimensions.

If a number of equal spheres are packed together as tightly as possible, then we get the arrangement shown in Fig. 3(a). The spheres are centered at the points "A" of equilateral triangular network. Now the same arrangement is repeated in Fig. 3(b), but for clarity the spheres are ^{farther apart} shown/smaller in size. We start first with the lowest most layer shown in Fig. 3(b), and call these spheres as "A". The upper surface of such a single layer of spheres results in a series of triangular depressions or "dimples" which can be divided into two sets centered at B and C respectively. The pattern of B's alone or of C's alone, is exactly the same (except for a translation) as that of A's alone, and there is no fundamental distinction between C and B.

Now to place a second close packed layer there are two choices either B positions can be filled or C. If B positions are taken up then the upper surface shows two sets of dimples centered about A and C. For a single layer these two sets are indistinguishable, but for the assemblage of two layers they are different. So the third layer can be placed either at A or at C. If C positions

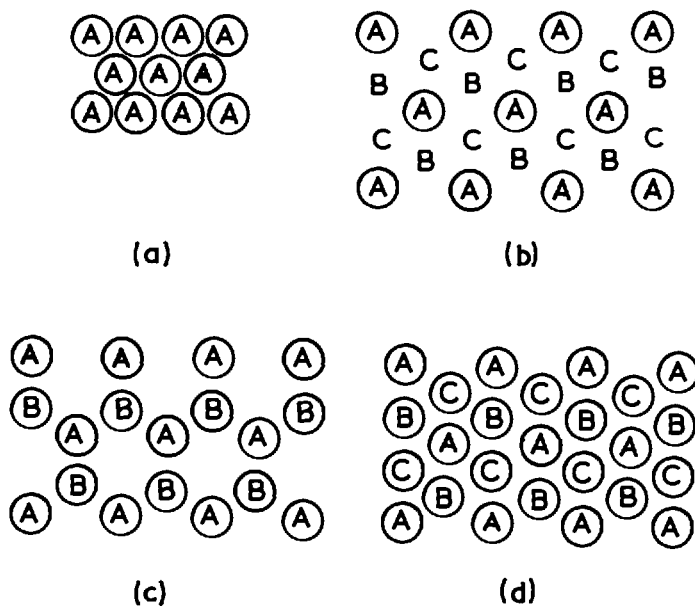


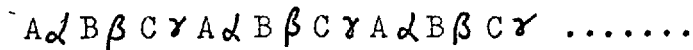
Fig. 3

SEQUENCE OF STACKING LAYERS

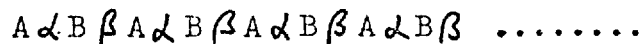
- (a) Close packed array of atoms on A sites.
- (b) Relative positions of the A, B and C sites.
- (c) Double layer stacking sequence on A and B sites only. The wurtzite structure.
- (d) Triple layer stacking sequence on A, B and C sites. The sphalerite structure.

are filled in then the arrangement has the sequence ABC and this can be continued to give the cyclic sequence ABCABCABC..... On the other hand if A positions are filled then the ABABABAB..... arrangement results. The former sequence results in the cubic close packed arrangement and the latter produces hexagonal close packing.

With the help of this picture of stacking layers the description of sphalerite and wurtzite structures can be based upon the stacking of double layers. Each double layer consists one layer from each of the sublattices placed vertically above one another i.e. in the same stacking position. On the basis of this arrangement the sphalerite structure can be represented as



where Roman letters represent the atoms from one sublattice and the Greek letters represent those from the other sublattice. Similarly the wurtzite structure can be represented by the following notation:



CHAPTER II

CONSIDERATION OF PARAMETERS OF EPITAXIAL GROWTH

2.1. EPITAXY

Different types of films or layers have been developed for different kind of studies. They may be broadly classified as single crystal films, polycrystalline films with considerable degree of preferred orientation, polycrystalline films of randomly oriented small crystals and amorphous films. A good deal of literature has been published during recent years on all these four types of films. An upto date review of the published literature can be found in Aven and Prenner (1967), Ray (1969) and Chopra (1969). But in the present work, we will be concerned only with the first two kinds of films, with much more stress on the first kind only, which are commonly known as epitaxially grown films.

The term " Epitaxy ", originally used by Royer (1928), is a general term used for the phenomenon of growth of one crystal on another so that there is an orientation relationship between the two crystals. Usually the overgrowth is a thin film on a single crystal substrate. Since then a good deal of study had been done on different combinations of overgrowths and substrates, and some comprehensive review articles such as Pashley (1956, 1965) were published. ZnTe has also been studied in epitaxial form to a limited extent by Holt (1966,69), Dhere and

Goswami (1969) and Mufti and Holt (1972).

Although the details of the processes involved in epitaxial growth are still far from clear, yet a number of important points have been observed by different research workers. It has been pointed out that certain factors, such as nucleation mechanism, misfit parameter, substrate cleanliness and temperature, rate and mode of evaporation, contamination of the vacuum system and the substrate, geometrical arrangement of the apparatus, electrostatic and illumination effects etc. have some influence on the epitaxial growth. So in order to grow epitaxial films of ZnTe on germanium it was quite important to know all the parameters suggested so far, and make use of them in the present work. In this chapter these influencing parameters are discussed very briefly along with the modifications and observations connected with the present work of epitaxial growth of ZnTe on germanium.

2.1.1 Growth Mechanism Of Films

Before a comprehensive theory of epitaxy can be formulated a certain amount of knowledge of the mode of growth of oriented layers is essential. The study of the growth sequence dates back to Andrade's work on silver films in 1938. But electron microscope studies in situ were first done by Bassett (1958). Poor vacuum inside the microscope, uncertain effects due to contamination by decomposed hydrocarbons, and due to the electron beam, and difficulties in controlling

the deposition parameters hampered this technique to a great extent. However, Poppa (1964,67) improved this technique by using ultra high vacuum and rate monitors etc. under controllable conditions. Fortunately, the growth sequence observed in an in situ experiment is not significantly different from that obtained from micrographs of different growth stages of films prepared in a separate system and detached from the substrate for electron microscopy. A summary of the results of in situ studies of Bassett(1958) and Pashley and coworkers (1964,65) and a comprehensive review of the whole subject is give by Pashley (1965).

The growth of continous films, in order of sequence, occurs in the following four stages:

1.Nucleation: At first randomly, three dimensional nuclei are formed that rapidly approach a saturation density with a small amount of deposit. For gold evaporated on NaCl at three hundred degrees centigrade, Pashley reported about 10^{11} nuclei per square centimeter with a distance of about $20 \text{ \AA}$ across a nucleus. Thus the mean separation between nuclei is around $300 \text{ \AA}$. Although these nuclei are ordinarily distributed at random, the nucleation is occasionally observed at preferred sites.

These nuclei then grow to form observable islands whose shapes are determined by interfacial energies and deposition conditions. The growth is diffusion controlled; that is adatoms around subcritical clusters diffuse over the substrate surface and are captured by stable islands. This

is known as the " gradual nucleation " mechanism. However, some research workers favour the idea of " spontaneous nucleation " mechanism. In this process when the amount of deposit material is increased to a certain value a crystallization process occurs, and the nuclei are formed spontaneously via an intermediate stage which could be an amorphous or liquid state. Again it is assumed that the nuclei can be oriented. This type of process might form

a large number of nuclei of almost the same size, so that for a certain period of growth the number of nuclei would not increase, but their sizes would increase appreciably. It may be pointed out that the nucleation theory does not always apply. A monolayer deposit theory instead of three dimensional nuclei was advocated by Newman (1955), and others.

2. Growth and Coalescence of the Nuclei: Continued deposition leads to an increase in the size of the nuclei without any appreciable increase in number. On the other hand they become closer to each other and the larger ones appear to grow by coalescence of the smaller. This suggests that the incident atoms move freely on the surface and join existing nuclei, or those atoms which strike other than a nucleation site are reflected or desorbed. When the nuclei have grown to the point that they touch, coalescence begins and rapid changes in geometry and orientation occur.

3. The Channel Stage: When the island distribution reaches a " critical " state a rapid large scale coalescence

of the islands results in a connected network structure, and the islands are flattened to increase surface coverage. This process is very rapid initially but slows down considerably on formation of the network. The network contains a large number of empty channels, which in some cases of epitaxial growth are holes of crystallographic profiles. Occasionally they are long, uniformly wide, homogeneously distributed and possess approximately matching curvatures over small areas.

4. Formation of Continuous Film By Filling In Of Holes:

The final stage of the growth process is a slow filling of the empty channels requiring a considerable amount of deposit. The incident evaporant atoms now strike like atoms, the binding energies are high, and little reflection or desorption is observed.

It may be pointed out that the above sequence is qualitatively common to other types of vapour deposited films prepared by a variety of techniques. The kinetics of each stage may, however, vary markedly depending on the deposition parameters and the deposit-substrate combination. So a knowledge of the other parameters of growth is quite essential and will be discussed in the following sections.

2.1.2. Misfit Parameter

Royer's hypothesis (1928) about the importance of the misfit parameter in epitaxy was accepted by many workers until 1960. The misfit parameter is defined as the percentage difference^e of the lattice spacings of the

two crystals along a particular crystallographic direction i.e. $\frac{b-a}{a} \times 100$, where "a" and "b" are the lattice spacings of the substrate and the overgrowth respectively. It was usually assumed that for good epitaxial growth the mismatch should be as small as possible (maximum misfit of 15 % for epitaxy was deduced by Royer (1928, 32) from his limited observations of Alkali Halide deposits on mica). Schulz (1951,52) showed that Royer Rule was not obeyed by many systems. Moreover, in the later work it was shown that the percentage misfit of the order of 90 (CsI/ LiF), 105 (RbBr/ Ag), -31 (Ag/ PbS) and -38 (Ni/ NaCl) was quite acceptable for epitaxial work. This does not mean that misfit is not an important parameter. On the contrary, this is expected to be the key to the understanding of epitaxy, as the relative positioning of the atoms rather than the best geometrical fit of the two lattices is a significant variable.

If there is a lattice mismatch between the two components at the interface then this is accommodated by a network of dislocations. Theoretically, defect free films could be grown with zero mismatch, and in fact Booker and Unvala(1965) and later workers were successful in growing fault free Si films on Si.

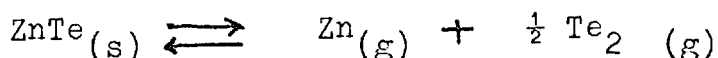
The mismatch between ZnTe and Ge is 7.8% (ZnTe $a = 6.1037$, Ge $a = 5.6575$), so due to this inherent limitation (presence of mismatch) , the project of growing fault free films of ZnTe on Ge, seemed to be an impossibility. However with the help of other growth

parameters the fault density in these films could be curtailed to a minimum extent.

2.1.3. Stoichiometry

The requirements for the growth of films for our project are that they should be pure, stoichiometric, single crystal, defect free and of required thickness. The purity of the films is to a large extent determined by the quality of the starting material. For this purpose 99.999 % pure "Vactran" type ZnTe from B.D.H. was used as the initial charge. My previous attempts to grow the films of ZnTe with less pure samples resulted in Zn rich films which gave irrational types of diffraction patterns.

Goldfinger and Jeunehomme (1963) pointed out that vapours of group II metals are always monoatomic, and vapours of group VI non-metals usually exist in diatomic molecules. ZnTe, like the other II-VI compounds, dissociate completely on sublimation according to the equation:



The vapour arriving at the substrate is therefore a mixture of vapours in the stoichiometric proportion, since the vapour pressure of either component is many order of magnitude greater than that of the compound at the same temperature and no enrichment of the source occurs. However the vapour pressures of zinc and tellurium differ so it was probable that their sticking coefficients on the substrate or growing films might also be different. Therefore there could be a likelihood of formation of zinc rich films.

Goldfinger and Jeunehomme (1963) also pointed out that the equilibrium composition of II-VI compounds is a function of the partial pressures of the two elements, and the temperature during crystal growth. A deficiency in one or other of the component elements is usually accomodated by vacancies on the appropriate sublattice and can also be compensated by incorporating the extra atoms of the excess element as interstitials within the crystal structure. 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 temperature 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 as the excess of one of the two elements is carried away by the transport gas.

The various approaches to this problem of non-stoichiometry can be tackled by the following techniques:

According to Somorjai (1962), Somorjai and Jepsen (1964), Somorjai and Stemple (1964), Somorjai and Lester (1965) and Kroger (1964) it is possible to supress evaporation of the solid by increasing the relative pressure of either gaseous component. This is achieved in closed systems by ensuring that the initial charge is of 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 the thin films by co-evaporating the compound together with an excess of the appropriate element.

The problem of producing stoichiometric films may be approached by two different routes. One possibility is to grow the film at the lowest possible substrate temperature in an attempt to condense all the incident vapour. An advantage of this method is that the films will have the maximum possible thickness. Such films, according to Hill and Rawlings^{et al} (1968), are usually not epitaxial. So for this reason this approach was not used in the present work of ZnTe on germanium. However, a second approach was considered more practical. This approach is to form the films at an elevated temperature with a vapour incidence rate such that neither component could form a stable film in the absence of the other. Under these conditions an adsorbed population of zinc and tellurium atoms will exist on the surface. These atoms will be loosely bound and probably mobile; the population density will be determined by the dynamic equilibrium between incident and re-evaporated material. These conditions should also be very favourable for large crystallite formation and thus epitaxial film growth.

For the compounds with one component markedly more volatile than the other (InSb, HgSe, HgTe) the vapour contains an excess of the volatile element. In this case it is necessary to keep the temperature of the substrate

high enough so that only the compound deposits on it. On the other hand, the evaporation velocity must be sufficient to over-compensate the re-evaporation from the substrate. However, by appropriate combination of these two parameters it is possible to evaporate from the bulk material and obtain relatively stoichiometric films.

In view of all these considerations and according to the observations of Cardona and Harbeke (1963), who claimed that in the cases of ZnTe and CdTe both the components evaporate approximately at the same rates, it was considered essential to use pure ZnTe at an elevated temperature of substrate without any co-evaporation. No traces of non-stoichiometry were observed in any of the ZnTe films by means of electron microscopy. This shows that non-stoichiometry in ZnTe films might be less than 1 % as below this limit no non-stoichiometric effects are usually observable.

2.1.4. Evaporation Source

Since the beginning of epitaxial work, in general, a number of different techniques have been used for providing the vapour source. The simplest of these is a tungsten or molybdenum spiral which was heated by passing an electric current through it with a small lump of the deposit material resting in it. This method was satisfactory if the material wetted the tungsten or molybdenum, and if no mutual solubility or chemical reaction occurred as the temperature was raised. For many deposit materials, one or other of these two conditions were not satisfied, and a

number of other sources involving crucibles of various kinds had been devised (Holland 1961).

It was observed that the structural quality of the films was often affected and the temperature range over which they grew epitaxially increased if cleaner sources were used. For making cleaner sources one had to dispense with the crucible and container. A satisfactory answer was found in the use of electron bombardment to melt a small region of a block of the deposit material. Various arrangements have been used for this purpose (Heavens 1959, Unvala 1962, and Chopra 1969).

Holt (1966) reported that ZnTe grew epitaxially over broad ranges of substrate temperature when evaporated in high vacua from hot metal crucibles on to (111) cleavage faces of BaF_2 and CaF_2 . The epitaxial films appeared monocrystalline but with small included grains. Moreover the films gave rise to electron diffraction spot patterns containing irrational satellite spots.

It was also reported that the epitaxial growth of ZnTe could not be obtained reproducibly on (100) cleavage faces of NaCl at any temperature. Subsequently it was found that by changing from conventional hot metal evaporators to focussed electron beam evaporation (Unvala 1962) epitaxial growth of ZnS could be obtained on NaCl over a very wide range of substrate temperature (Unvala ^{and Holt} Woodcock 1968, Woodcock and Holt 1969). The use of focussed electron beam evaporation was then found to result in epitaxial growth

of CdS (Wilcox and Holt 1969) and ZnTe (Holt 1969) on NaCl cleaved or polished faces over a wide range of substrate temperature.

In the light of all these observations it was decided to use an electron beam heating arrangement of the Unvala type as this system has the obvious advantages of being clean, reducing contamination and/out of sight of the Source ^{material} ~~having the filament~~ and substrate. It is also easily controllable and produces a well defined localised hot spot.

2.1.5. Contamination of Substrate Surface And Environment

Besides the other conditions referred ^{to} before, the surface cleanliness of the substrate has also been considered as an important influencing factor in the growth of epitaxial layers. A definite theory to explain these experimental observations is yet to come forward, while a good deal of literature is being published which puts forward conflicting observations. Most of the references found in literature concern ionic crystal substrates while very few references are concerned with the contamination effects of semiconductor substrates.

A number of workers such as Murr (1964 for Au Ag and Cu on NaCl), Catlin et al (1964 for Ge on CaF₂), Sloope and Tiller (1965 for Ge on polished CaF₂), Evans et al (1966 for GaAs on NaCl), Woodcock and Holt (1969 for ZnS on NaCl) have observed a reduction in the minimum substrate temperature for epitaxial growth by using an

ultra high vacuum system instead of an ordinary high vacuum system. On the other hand Ino et al (1964) found that the quality of films of Au, Ag, and Cu on NaCl was degraded by using an ultra high vacuum instead of high vacuum.

It has also been observed by Spinulescu-Carnaru (1969) that undue contamination of the system can be reduced by reducing the pressure in the working chamber. A minimum pressure of the order of 10^{-7} torr in the vacuum system was suggested for good epitaxial work as at higher pressures there is some possibility of trapping of residual gas molecules in the film. However, in our work on ZnTe on Ge it was found that pressures of the order of $2-4 \times 10^{-5}$ torr was quite adequate. Some films of ZnTe were prepared in the 10^{-6} torr range but no difference was observed in the structural quality of the films. Pressures in the evaporation chamber greater than 7×10^{-5} torr resulted in the deterioration of the quality of films producing polycrystalline films and greater double phase material content.

Matthews and Grunbaum (1964, 65) pointed out that the best quality of Au films grown on NaCl were obtained if the substrate was exposed to air before deposition. Woodcock and Holt (1969) observed that the epitaxial range of ZnS on vacuum cleaved NaCl was larger as compared to air cleaved substrate. Matthews(1965), however, showed that although the orientation of the initial nuclei was better in films grown on vacuum cleaved substrate than it was on the substrates exposed to air, the nucleation density on

the contaminated substrates was much greater. The latter effect led to earlier coalescence which had already been shown to promote good epitaxy.

Harsdorff (1963, 64) studied the epitaxial growth of silver and gold and the effects of adsorbed layers on NaCl. He plotted the angular displacement of crystallites about an axis lying in the film as a function of the substrate temperature which resulted in an oscillating plot. The oscillating nature of this function was interpreted by supposing that different contaminants were volatilising from the substrate surface at different temperatures.

Water vapour also played an important role. According to Harsdorff the contamination of the substrate (NaCl) by water also gave the angular displacement of crystallites as an oscillating function of substrate temperature which suggested that successive layers of water molecules were increasingly tightly bound to the substrate and that heating upto 450° C not only removed the contamination but even the surface layers of the substrate. So the result was that after heating upto 450° C this effect of adsorbed water was destroyed. On the other hand Sato (1965) observed that Fe films on NaCl grew in a single orientation of the substrate when exposed to water vapours.

In our present work on ZnTe on Ge, it was clearly established that thermal cleaning was an essential requirement for the growth of good epitaxial films. The Ge substrate was heated to a temperature of 600° C prior to deposition.

Excessive heating above 700°C and insufficient heating below 300°C resulted in a poor quality of ZnTe films. Spinulescu-Carnaru^{et al} (1969) also studied this effect on films of PbTe grown on mica. He also noted that the crystallites in PbTe thin films prepared on clean substrates well degassed in vacuum at sufficiently high temperature ($350^{\circ}\text{C} - 400^{\circ}\text{C}$) had a perfect crystalline structure in contrast to those prepared on dirty substrates previously not sufficiently outgassed in vacuum.

Several other papers have been published in which the effect of contaminants such as water and oil was studied by introducing them into the vacuum system (Unvala et al 1968, Woodcock and Holt 1969) and it was confirmed that generally a beneficial effect is achieved by minimising the contaminants on the II-VI compounds and other semiconductors.

2.1.6 Deposition Rate

The effects of this parameter are still under exploration. In 1949 Levinstein pointed out that at higher rates of arrival of atoms more atoms migrate across the surface per unit time and the rate of formation of nuclei is high. Films formed at higher rates of deposition, therefore, tend to have smaller grain sizes than films deposited slowly. A few years later Kalinkin (1962), Sloope and Tiller (1962) and Krikorian and Sneed (1966) observed that, for substrate temperatures near the end of the epitaxial range, an increase in the growth rate caused a decrease in the degree of orientation of thin films while low deposition rates favoured

epitaxial growth. This was also predicted indirectly by Nucleation theories (section 2.1.1.) that low vapour supersaturation favoured epitaxial growth (Pound et al 1964).

In contradiction to this Matthews (1959) studied Au, Ag and Cu on NaCl and found that in the case of too slow deposition rate nucleation density was low and each nucleus reached an appreciable size before coalescence began. Consequently due to large diffusion distances the re-orientation and recrystallization of grains in non-epitaxial orientations was more difficult. So a high nucleation density and high substrate temperature were the two preferable conditions for good epitaxial growth. But Sloope and Tiller (1961, 62) observed that low substrate temperature instead of high, and high deposition rates were preferable for Ag on NaCl and Ge on CaF_2 . Booker and Unvala (1965) while working with Si on Si concluded that a high deposition rate was essential for getting stacking fault free films.

However, Wilcox and Holt (1969) found, that in *the* case of CdS on NaCl the effect of increasing the deposition rate was to decrease the structural perfection of the films considerably. They examined the diffraction patterns and micrographs of films grown under the same conditions except for an order of magnitude difference in deposition rate. The slowly deposited films had diffraction patterns free of satellite spots and the micrographs showed only fine scale fringe (section 4.6.3) and dot contrast, characteristic

of planar defects in II-VI compound films. The rapidly deposited films, however, had gross included grain structures visible as large dark areas and giving rise to extra satellite spots.

In the present work on ZnTe on Ge various different deposition rates were tried. Except at very high evaporation rates the films were not affected by the evaporation rates. However at very high rates such as when the power applied to the evaporating furnace was 5 Watts (as compared to 2.75 Watts for normal work) some films were found to be polycrystalline. The whole responsibility for this polycrystalline nature of the films could not be put on the rate of evaporation as the rest of the growth parameters were also not exactly identical to any standard evaporation (section 3.3.). However, the repetition of so many films in polycrystalline form at very high evaporation rates clearly gave a convincing indication that very high evaporation rates were not suitable for ZnTe on Ge. Another point of importance was that at very high evaporation rates the time for evaporation was supposed to be curtailed to less than 1 minute, and it was found that with short time of evaporation the time for removal of the shutter became quite significant. So due to the non-uniform time of exposure of the substrate to the incoming vapour a wedge shaped film could result. Moreover, films grown for less than 1 minute were found to fail to achieve a well oriented, continuous and smooth film surface.

So by suitable adjustments it was found that with an evaporating power 2.75 Watts the rate of evaporation was between 30 to 40 Å / sec. depending upon the focussing of the beam furnace (section 3.3). With this rate of deposition continuous films of ZnTe of about 2000 to 3000 Å, suitable for electron microscopic work were produced with one minute of growth time.

2.1.7 Substrate Preparation

Pashley (1952) has shown that to define ^{the} orientation of an overgrowth involves the knowledge of contact planes between the two surfaces i.e. the overgrowth and the substrate, and a knowledge of the topography of the substrate is essential for the determination of the contact planes. If the substrate has an atomically smooth surface then the contact planes can be immediately inferred from the relative orientation. So in practice, for epitaxial work, the substrates used should have smooth and flat surfaces on an atomic scale and be free from etch pits or surface damage. Although it was observed (Wilcox and Holt 1969) that small scratches on the substrate surfaces were replicated and caused no damage to the epitaxial growth yet the uniformity of the film was disturbed by the unevenness of the substrate surface. They observed that nearly perfect orientation of the preferentially condensed nuclei at the cleavage steps suggest that the orienting influence of the substrate was not altered by such defects. An example of the uneven substrate surface is shown in

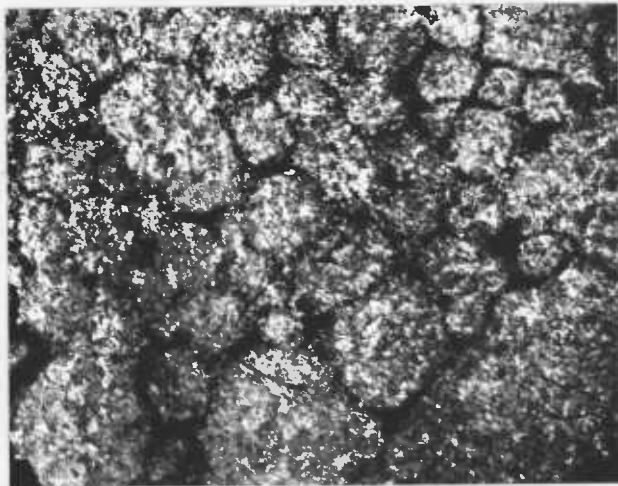


Fig. 4

2 μ

EFFECT OF NON SMOOTH SURFACE OF SUBSTRATE

Bright field micrograph of a ZnTe film grown on (111) oriented Ge. Due to the orange-peel type surface of the substrate the ZnTe film is replicated on it.

Fig 4. which shows the bright field micrograph of ZnTe film grown on an " orange-peel" type surface of Ge substrate. It may be noted that the ZnTe film is epitaxial yet is far from uniform for any practical purpose.

Usually the requirements for smooth surfaces of substrates are commercially met by cleaving the substrate crystal or by subjecting it to mechanical and chemical polishing. Cleaving (in air or vacuum) has some advantages and has been used successfully for ionic crystal substrates, but for substrates like germanium and silicon, only mechanical and chemical polishing techniques are practicable. So in our case too, for the growth of ZnTe on Ge, the latter techniques were employed (section 3.2).

There are many mechanical polishing methods ranging from simple grinding on a fine sand paper to the modern diamond wheel methods. Grinding on sand paper, due to obvious limitations of introducing microscopic damage, was replaced by a diamond knife (Reimer 1959, Philips 1960,61). But the main disadvantage of this technique was the introduction of deformation due to elastic and plastic strain caused by the geometry of the knife(Philips 1961, Glauert et al 1961). For the work on ZnTe on Ge the rotating wheel method was used. In this method the mechanical polishing was done by a rotating pad impregnated with diamond paste. The details are discussed in section 3.2.

After mechanical polishing the specimen had a smooth mirror surface and required the removal of the damaged

layer. This objective was achieved by chemical polishing. In its simplest form the specimen is dipped in a solution which, due to its dissolution action, removes the damaged layer. Various techniques and reagents for chemically polishing the III-V and II-VI compounds have been reported (Waekois et al 1962,66, Sullivan et al 1967, Maeda et al 1967 and Strehlow 1969). A comprehensive list of them is given by Hirsch/^{etal}(1968).

2.1.8 Substrate Temperature

The effect of substrate temperature has been well known since Bruck's work (1936) on the epitaxial growth of metals on metals and on non-metal substrates. It was well known that vacuum deposition onto relatively cold substrates/yields highly disordered layers of non-stoichiometric composition. Bruck (1936) pointed out that the temperature of the substrate has a significant effect on the quality of the grown layer in any particular environment. There was a particular temperature for each combination of deposit and substrate below which epitaxial growth was not possible. With further research work it is now well confirmed that the substrate temperature is, in fact, the most influential parameter for the growth of epitaxial films. In later work by studying the quality of grown layers on a substrate at different temperatures for Ge on Ge (Krikorian 1966),

ZnTe on ionic substrates (Holt 1966)

ZnTe on Mica (Dhere and Goswami 1969), PbTe on glass

(Spinulescu-Carnaru 1969), ZnS on NaCl (Woodcock and Holt

et al

1969), Ge on CaF_2 (Schalla/1969), CdS on NaCl (Wilcox 1970) it was confirmed that the improvement in the orientation with increasing substrate temperature is quite gradual from the polycrystalline state to the well oriented films. This marked improvement in the orientation can occur for certain deposit-substrate combinations upto a certain temperature after which the orientation is again lost leading to a completely mis-oriented state. This particular range of temperature for epitaxial growth is known as the " Epitaxial Range " . The reason for this limit at the upper edge of the epitaxial range is far from clear but it has come to our observations that the change of sticking coefficient and the increase of the rate of re-evaporation are responsible for this behaviour.

The energy of the incident atoms is already high and consists of two parts, the latent heat of evaporation and the thermal velocity attained from the hot vapour source. The energy retained by the molecules condensing on a surface depends upon the binding energy or heat of adsorption. If this is low compared with the latent heat of evaporation possessed by the condensing molecule, then the molecule retains high energy and may be mobile on the surface. A high substrate temperature provides additional kinetic energy, so that a molecule on the surface may migrate to sites of lower surface potential energy and form a preferred structure. At much higher substrate temperature there may be sufficient energy available for re-evaporation to occur.

Because of the importance of the dependance of the

epitaxial growth of films on the substrate temperature a substantial portion of this work was devoted to explore the epitaxial range of ZnTe on germanium and study the behaviour of their growth.

2.1.9 Effect Of Illumination

It is well known, that the structure of the evaporated metal and that of the semiconductor films depends upon many deposition variables such as , the deposition rate, the substrate temperature and its orientation, the electric field applied to the substrate etc. But lately a new parameter, the effect of illumination, is also getting some attention. Knight and Jha (1968) have observed a definite correlation between the structure of the films (Au / Melinex, an I.C.I. polymer, Silver / glass, Copper / Kapton, a Du Pont polymer) prepared under illuminated conditions, and their electrical conductivity. They observed that illumination conditions commonly encountered during vacuum deposition , such as strong sunlight or electrical light from a tungsten lamp, or light radiated from the evaporation source, are sufficient to influence the structure of the growing films. They concluded that the effect of illumination is not a nucleation effect, does occur if the substrate is illuminated only after the first $10^8 \text{ \AA}$ of deposition , but does not occur if the substrate is illuminated only before deposition or during the first $10^8 \text{ \AA}$ of deposition. They also observed that the illuminated regions of the films had more

discontinuous structure and higher resistance than the non-illuminated regions.

An attempt was made to observe the effect of illumination on the growth behaviour of ZnTe on germanium. During the growth of the films, light from an ordinary lamp and from a tungsten bulb was allowed to fall on the substrate. The application of the illumination to the substrate was repeated on several samples before, during and after the deposition of the films. No effect was seen in the electron microscope as far as the structure of the films were concerned. The ZnTe films grown under otherwise identical conditions with and without illumination showed the same structure and defect content. They also did not show any change of orientation or discontinuity.

2.2. THINNING OF SUBSTRATE

After the deposition of the film on the substrate, it was required to remove the substrate from a portion of the film without any damage to it so that the film could be examined in an electron microscope. This object may be achieved by using any of the well known chemical, electro-chemical or ion -bombardment methods (Hirsch et al 1965). Several chemical etching and polishing reagents have been developed to produce the required types of attack on a great variety of crystallographic faces of many semiconducting compounds in numerous conditions of doping (Faust 1962, Aven and Prenner 1967, Amelinckx 1964). Several of the reagents described in the literature could be used to thin samples of a number of III-V and II-VI compounds for transmission electron microscopy (Holt et al 1966).

The apparatus for using such solutions should be so devised, that the solution creates non-preferential thinning. The area to be examined in the electron microscope must be uniformly thin and in general must be less than 1 μm thick and in the case of more electron opaque materials, only a few thousands $\text{\AA}$ thick. The thin area should preferably, be produced by localised attack so that the remainder of the specimen, shaped to fit the electron microscope holder, is left in the form of a relatively thick and sturdy rim of a disc. This type of localised attack can be achieved by several techniques falling into two classes. Either the specimen disc is immersed in a bath of the reagent but has

the edges masked in some way, or a jet of a reagent is used to bring about contact only with the chosen central area of one face (Holt et al 1966). The latter techniques are referred to as jet polishing or thinning techniques and have been long and widely used, generally with the electro-polishing action. Riez and Bjorling (1961) have described a method for germanium in which a disc is electrolytically polished with a jet of KOH solution. Booker and Stickler (1962) have also described the details of an electro-chemical method for thinning Ge and Si samples. For our work the electro-chemical method of Blackenburgs and Wheeler (1963,64) was chosen for thinning the germanium substrate. The details are described in section 3.4.

2.3. MEASUREMENT OF THICKNESS OF EVAPORATED FILMS

Measurement of the thickness of the evaporated films is essential for quantitative work. In recent years a great deal of interest has been centred on the use of insulating and passivating films in the semiconductor industry and some of the characteristics of the devices largely depend upon their thickness.

There are two types of thickness measurements — firstly macroscopic measurements, when the average thickness over a large area is to be determined, secondly local measurements at specific points on the film. For our work on ZnTe we were only concerned with the first type of measurements as due to the uniformity of the film surface, the possibility

of point to point variation of the thickness was not taken into consideration.

There are several direct and indirect methods for these measurements which due to their obvious features can be classified as mechanical, electronic, visual, optical and chemical methods.

Mechanical methods include the Talysurf with which the variations in the movements of a mechanical stylus can be amplified electronically. Step heights and surface irregularities of $\sim 10 \text{ \AA}$ can be measured with this technique. The electronic methods, becoming more and more popular, include the measurement of the thickness either by in-situ monitoring of the rate of deposition by monitors such as capacitance monitors, film resistance, ionisation and quartz crystal monitors, or after the film is taken out of the deposition chamber, by microbalances.

Visual methods include metallurgical microscope measurements, and noting the colour of the reflected light with normally incident illumination. The wavelength of the interference colour and film thickness are related by $(m + \frac{1}{2}) \lambda = 2nt$, where λ is the wave length of incident light, m the order of the interference colour, t , the thickness of the film and $\frac{1}{2}$ is added due to the phase change at the reflecting surface. By putting the value of n for ZnTe as 2.68 (Marple 1964) and noting the colour of the primary reflection i.e. $m = 1$ a quick and rough idea of the thickness of the films was obtained for this

work. However, the accurate measurements were made with the help of Nomarski interferometry which is described later in this section.

While the ordinary microscope, the classic instrument of the metallurgist, is no longer sufficient in many cases, techniques based on the phenomenon of optical interference, today, offer promise of valuable assistance through their very high accuracy and sensitivity. The optical methods mostly depend upon the principle of destructive interference. Some of the most commonly used techniques are Multiple Beam Interferometry (Tolansky 1960, Kurtz 1969) and Nomarski Interferometry (Nomarski^{et al}/1955). The interferometric techniques can be divided into two general categories. A technique known as " Vamfo " has been developed by Pliskin and co-workers (Pliskin et al 1964, 65, Wessen^{et al} 1967, Popova/1970) . In this technique the interference fringes are formed by varying the angle of observation at constant wave length. In the other technique named " Caris " (Coil 1964) the angle of incidence is held fixed, but the wavelength is varied.

The Nomarski polarization interferometer^o produces interference fringes from two images of the object, which are formed as the light passes through a double quartz prism. The two images are slightly displaced, and tilted relative to each other, and thus give rise to interference fringes. In this way each point on the object surface is compared with a neighbouring point on the same surface, one

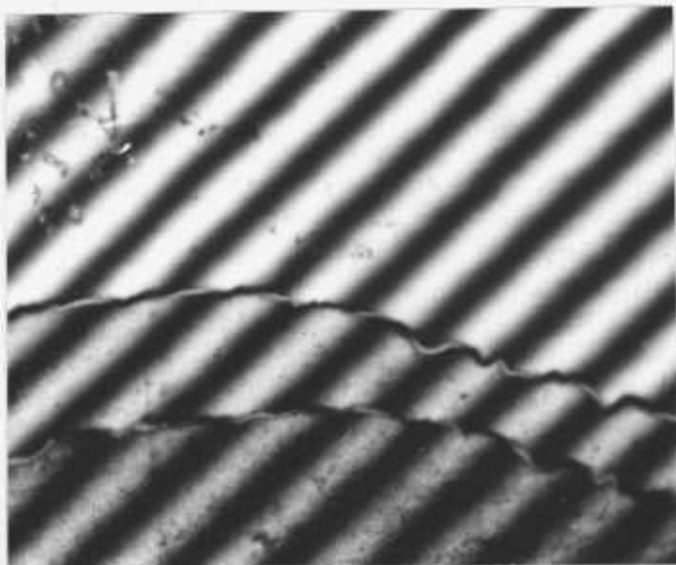


Fig. 5

THICKNESS MEASUREMENT OF A FILM

A picture of ZnTe / Ge taken near the edge of the film with a Nomarski Interferometry arrangement. The straightness of the fringes is an indication of the smoothness of the ZnTe film and Ge substrate surfaces.

image always acting as reference surface relative to the other image. The interference fringes are lines of equal path difference and therefore represent contour lines on the object with a height spacing of half the wave length of the light. A perfectly flat object would show accurately straight and parallel interference fringes. If one point of the surface departs from true flatness the interference fringes at that point show a displacement from the straight line. In this case a displacement of $1/n$ th of a fringe spacing corresponds to a depth of $\lambda / 2n$. These are the obvious reasons for choosing this technique for our present work. Fig 5 clearly shows that besides giving the measure of thickness of the film, the straightness of the fringes indicate the smoothness of the deposited layer and the substrate surface.

CHAPTER III

THE EXPERIMENTAL SET UP

The apparatus for growing thin films of ZnTe on to germanium substrates consisted of a vacuum system which provided a suitable environment for the evaporation process, a vapour source where the material to be evaporated was held and heated, and a substrate holder and heater stage.

3.1.1. The Vacuum System

The vacuum system used in this experimental work was a conventional vacuum system made by NGN. A schematic diagram of the system is shown in Fig 6(a). This consisted of a working chamber, a rotary oil vacuum pump RSR2 with a capacity of 99 liters per minute and a two inch diffusion pump with liquid Nitrogen^o trap. Appropriate high vacuum valves and inlets for Pirani and Penning gauges were provided. The system was successfully operated in high vacuum range of 10^{-6} torr.

3.1.2. The Evaporator

The evaporator used for heating the source was an Unvala type(1963) focussed electron beam evaporator, shown in Fig 6(b). It consisted of a water cooled copper pedestal into which a stainless steel crucible containing ZnTe could be plugged. The pedestal was surrounded by a tantalum filament and a focussing electrode. The electron beam could be focussed so as to create a concentrated localised heating

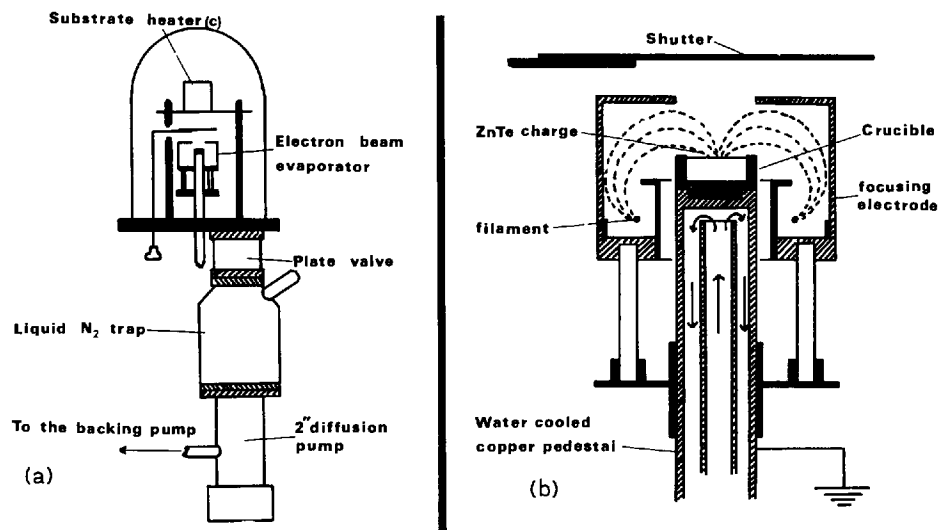


Fig. 6

THE VACUUM EVAPORATION SYSTEM

(a) The vacuum system.

(b) The electron beam evaporator.

effect in the centre of the crucible in a limited space of about 2 mm in diameter. This technique was quite helpful in minimising the contamination that might have arisen from heating the material of the crucible, and also by keeping the filament out of line of sight of both the source and the substrate.

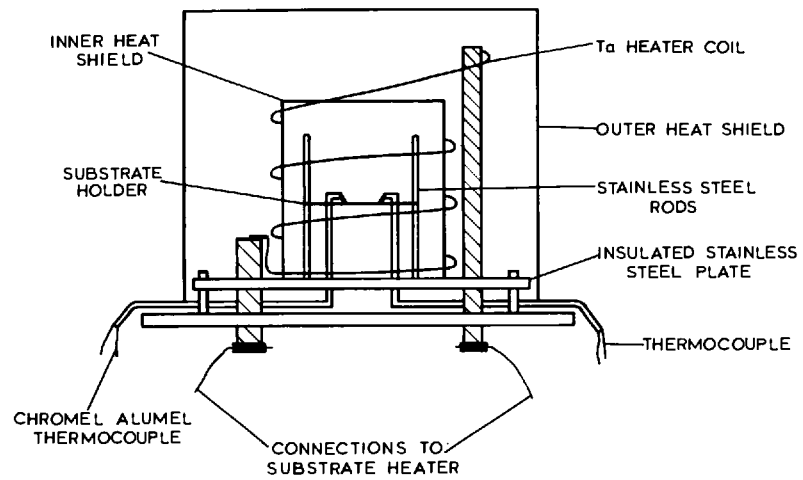
A movable shutter was also provided to isolate the substrate specimen from the incoming vapour. The shutter could be removed from outside the vacuum system to let the vapour deposit on the substrate for a specific time.

The input power was varied by changing either the accelerating voltage or emission current, but the adjustment of the emission current was more practical.

3.1.3. The Substrate Holder and Heater

A line diagram of the substrate holder and heater assembly is shown in Fig 7. The holder consisted of a stainless steel plate with a central hole in it. This plate was raised to its proper position (about 9 inches from the base of the working chamber) by means of three sturdy stainless steel pillars. In the middle of this platform there was another insulated stainless steel plate with a central hole for the vapour to pass through. The hole was surrounded by three stainless screws on which a molybdenum specimen holder rested.

The heating of the substrate was done by a tungsten coil filament which surrounded the holder system. In order to achieve uniform thermal equilibrium conditions



The Substrate Heater Assembly

Fig. 7

An enlarged view of the substrate holder and heater assembly.

around the substrate, a molybdenum diffuser was placed between the substrate and the heater. Another double walled molybdenum cylinder enclosed the whole holder and heater assembly. This ensured the uniformity of the temperature over the substrate and also meant that the thermocouple junction reached the same temperature as the substrate when placed near it. Thus the necessity for thermally conducting contact between the thermocouple and the heated substrate, which was difficult to achieve, was avoided. The heating filament was fed from an external power supply.

Two Chromel-Alumel thermocouples were placed in the diffuser very near to the substrate and the temperature was measured with the help of a potentiometer manufactured by Croydon Precision Instruments Co.

3.2. THE SUBSTRATE PREPARATION

During the course of the experiments it was realized that the quality of the polished surface had a marked effect on the degree of epitaxy, so substrates with scratch free finishes had to be used. In order to achieve this quality of substrate surface the commercial slices of germanium were first mechanically and then chemically polished.

Germanium slices (2 cms. in diameter and $\frac{1}{2}$ mm. thick) obtained from Metallurgie Hoboken were first mechanically polished on a wheel by using pads with diamond pastes of 15 μ , 1 μ , and 0.5 μ . The substitution of diamond paste by Silicon Carbide did not produce the desired effects

(section 2.1.7). The slices were then cleaned ultra-sonically and mounted on pyrex glass slides with picine wax. Three mililimeter discs were then cut out of these discs with the help of an ultra-sonic cutter using fine F2 silicon Carbide abrasive. All the traces of wax were removed from the prepared germanium discs by putting them into boiling Carbon Tetrachloride for at least three separate baths followed by dip in absolute alcohol. A final fifteen minutes ultrasonic bath in deionized water ensured that the surfaces of the discs were free from all contamination . The discs were then chemically polished for removing the damaged layer introduced in the material by mechanical lapping. The chemical polishing solution consisted of:

CH_3COOH			15 CC
HNO_3 (Specific Gravity 1.42)			25 CC
HF (40 %)			15 CC
Bromine			1 drop.

The solution was warmed to about 60°C in a PTFE beaker and was then placed in an eccentrically rotating beaker. The germanium discs were placed in the solution. A thirty seconds chemical polish was found to give an adequately smooth surface for successful epitaxial growth of ZnTe. The reaction of the chemical polish was stoped by pouring out the solution and dropping the discs into a beaker containing deionized water. From there the discs were transferred into another water beaker and ultimately to the third one. This quick and successive washing removed even the last traces

of chemical solution. A final thorough ultrasonic cleaning in deionized water was done and then the discs were stored in a beaker of deionized water before putting them in the vacuum evaporation apparatus.

3.3. THE GROWING OF THE FILMS

The ZnTe used in the preparation of the films was " Vactran " type bought from B.D.H. and was supposed to be 99.999 % pure. Before putting it into the evaporation machine, it was crushed to powder form, and then was charged in the crucible to its brim and placed on the pedestal. One germanium disc was taken out of the deionized water and after giving it a fresh ultrasonic bath and drying , it was placed in the substrate holder. The vacuum chamber was then sealed and pumped down for about five minutes. The substrate heater current was then switched on to about 12 amp. and the evaporating furnace was also put in the warming condition by switching on the emission current and accelerating voltage. The substrate temperature was allowed to rise to about 600° C for thermal cleaning, and then the substrate heater current was reduced to achieve steady thermal conditions at the required temperature. The temperature and pressure were monitored after every five minutes and usually after thirty minutes both these parameters stabilized to the required values. The emission current and accelerating voltage were then raised to the required power thus producing a well focussed spot in the middle of the ZnTe charge. The shutter was then removed for a known time and the vapour allowed to

deposit on the substrate. After the specified time the shutter was brought back to the closed position and all the power supplies were immediately switched off. A twenty minute cooling brought the chamber to about 50° C when the air could be let in and the grown film be removed for thinning purposes.

Efforts were made to grow the films to a constant thickness employing a constant deposition rate. This was done by operating the electron beam evaporator at a constant accelerating voltage and as nearly as possible a constant current. The currents and hence the power inputs varied about 10 % . However, it was not possible to obtain identically sharp focussing of the electron beam each time. Therefore the evaporation rates varied by considerably more than 10 % . In addition the sticking coefficient for ZnTe growth apparently varied with substrate temperature. The film thicknesses were measured by optical interferometry (section 2.2.) and varied from 1000 to 3000 Å. Growth times were constant (1 minute) so deposition rates also varied by a factor of three. The sticking coefficient of ZnTe on germanium fell rapidly above about 450° C so that at 500° C no film was deposited when the standard evaporator power level was employed. By increasing the evaporation rate films could be deposited at 500° C but they were polycrystalline.

3.4. THINNING OF THE SUBSTRATES

After deposition of the film, the substrate had to be thinned from the other side for transmission electron microscopy. The jet electro-polishing method of Blankenburgs

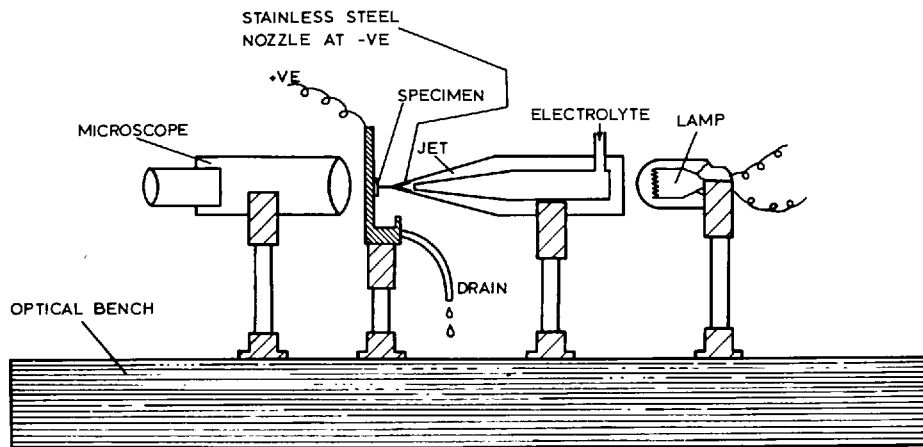


Fig. 8

THE ELECTRICAL JET THINNER

and Wheeler (1963-64) was used for thinning the germanium substrate and to get a free ZnTe film. A schematic diagram of the arrangement is shown in Fig. 8, which is basically the same as used by Booker and Stickler (1962), and Riesz and Bjorling (1961).

A well collimated and focussed beam of light from a lamp was adjusted to fall axially on a perspex jet and through a 0.5 mm. diameter stainless steel jet. Thinning solution was prepared by dissolving 5.5 gms of KOH and 1.5 gm of NH_4Cl in a litre of deionized water. This solution was allowed to flow from a tank through the jet on to the germanium discs which were mounted on a copper plate rigidly fixed on a movable specimen plate holder. The mounting of the germanium discs was managed with the help of Lacomit solution. A travelling microscope was focussed on the films to receive the light transmitted through them. The necessary power for electro-chemical polishing was obtained from a well stabilised D.C. power supply.

With this strength of KOH solution a current of 20 to 30 mili-ampere was sufficient to polish the Ge side in the well established polishing plateau (Hirsch *et al* 1965). A gradual removal of germanium resulted and the current could be stopped at the appropriate time when the light was visible through the microscope.

CHAPTER IV

ANALYSIS OF THE EXPERIMENTAL RESULTS

4.1. DIFFRACTION PATTERNS

Electron microscopy, with its ingenious manoeuvrability, high resolving power and well defined contrast effects, has proved to be a very useful technique for the analysis of the structure of thin films. Most of the structural analysis work of this project on ZnTe has been done with the help of AEI EM6G and Siemens Elmiskop I electron microscopes.

The basic principle of this technique is that a parallel beam of electrons, accelerated by a potential between 30 to 100 KV, is transmitted through a thin film usually 1000 to 5000 Å thick. This beam is deflected by parallel sets of atomic planes in a number of directions satisfying the Bragg's reflection conditions. The diffracted beams are then brought to a focus in the back focal plane of the objective lens, thus forming a diffraction pattern, which can be suitably magnified or photographed. The diffraction pattern whose size and geometry can be found, with the help of the reciprocal lattice and Ewald's Sphere construction (^{etal} Hirsch/1968), consists of an approximately two dimensional array of spots, where each spot corresponds to a particular set of reflecting planes. These diffraction patterns can be used to determine the orientation of the crystal relative to the electron beam.

By indexing the spot pattern not only the orientation of the diffracting medium is calculated but the zone axis calculated from any pair of sets of Miller indices represents the direction in the crystal which is collinear or almost so with the incident beam. In this technique the single crystal films will give spot patterns while the polycrystalline films, due to the superposition effect, will show ring patterns.

Pure and perfect single crystal films give diffraction patterns containing sharp spots free from any streaking effects or satellite spots. In practice, however, usually the spots are not sharp but have a fine structure such as broadening or elongation of spots, splitting of spots into groups of satellite spots, or the formation of continuous streaks. These fine structure effects arise from a number of causes such as the shape of the crystallite particles of the specimen, the presence of lattice strains due to imperfections, or to the presence of more than one crystallographic phase.

Pashley and Stowell (1963), Pashley, Stowell and Law (1965) and Jacobs and Stowell (1965) studied the diffraction patterns of some epitaxial metallic films and found that twins or grains of a second phase included within the film matrix were responsible for the complicated diffraction patterns observed. A number of other papers on II-VI compounds published in the last few years (Dhere and Goswami 1969, Holt 1969, Holt and Woodcock 1970

Wilcox and Holt 1969, Holt and Wilcox 1971) also suggest that the extra spots in the diffraction patterns of ZnSe, ZnTe, ZnS, CdS, were due to either a single diffraction within a second phase material such as included grains or twins or double diffraction first in the thin film matrix and then in the second phase material. All these possibilities will be discussed at a later stage for the analysis of ZnTe films.

In order to understand the diffraction patterns of a material, a knowledge of the structure factor and the size and shape of the unit cell of the crystal is essential.

4.2. STRUCTURE FACTOR

The atomic scattering factor " f " is defined as the amplitude scattered by an atom relative to that from a single electron. Each element has a different value of " f " which is a constant for all atoms of the same element and has the value one for an isolated electron scattering electrons.

A crystal, made up of so many small unit cells, scatters the electrons in all directions. The electrons act as waves which interfere and undergo constructive interference in certain well defined directions. These directions depend upon the interplanar spacings of the crystal, the energy of the electrons, and the symmetry of the unit cell. Due to the non-equivalent positions in space of the atoms in a unit cell the electrons

diffracted within the unit cell from different atoms will have different phases. So in order to find the total contribution from the unit cell for a particular set of reflecting planes the amplitudes of the waves scattered by atoms at different points in the unit cell are added together. Due account is taken of the atomic separation, and hence of the extent to which waves scattered by two atoms are out of phase. The summed effect is called the Structure Factor " F " and is the total amplitude of reflection. This summation includes each atom in the cell and its atomic scattering factor i.e. the relative strength of each atom contributing to "F". The resultant intensity depends upon $|F|^2$.

When $|F| = 0$, there is no Bragg's reflection. This shows that not all the reciprocal lattice points are associated with Bragg reflections because due to symmetry the structure factor for some reciprocal lattice points is zero. Since the amplitude of the Bragg reflection depends upon F_{hkl} , and as $|F|$ depends upon the arrangement of atoms within the unit cell, the amplitude of the Bragg reflection depends upon the crystal structure.

For a crystal with the F.C.C. structure the condition for $F_{hkl} \neq 0$ is that the indices hkl are either all even or all odd. The sphalerite structure has a F.C.C. space lattice with a basis of two atoms at each lattice point (section 1.2.1). In diamond, as both types of sites are occupied by the same type of atom, the destructive

interference between the diffracted atoms for the two F.C.C. sub-lattices can be complete, which results in certain reflections having zero structure factor, in addition to those having zero structure factor in the case of F.C.C. structure materials. Besides the latter reflections, according to Cullity (1956), the reflections for which $h+k+l = 4n+2$ are not found for diamond structure.

But in the sphalerite structure, due to the different atomic scattering factors of the atoms of the two F.C.C. sub-lattices, the destructive interference between atoms of the two sublattices cannot be complete and the only absent reflections are those that are also absent from the F.C.C. reciprocal lattice. So unlike diamond structure, $h+k+l = 4n+2$ type reflections are present for the sphalerite structure. Similar arguments apply to the analogous case for the wurtzite and hcp structures. It may be pointed out here that the amplitudes of the structure factors of the permitted reflections are not the same in the sphalerite and fcc cases. However, due to complications arising from the strong scattering of electrons, reliable intensity information is not available in electron diffraction work. So the sphalerite and fcc reciprocal lattices may be regarded as equivalent for the present purposes.

Another important point in this context is that as none of the $h+k+l = 4n+2$ type reflections lie in the (111) plane, so it is not possible to distinguish between the fcc and diamond structure from the diffraction

patterns in this orientation only.

By applying this technique of electron microscopy along with the relevant selection rules etc. a thorough analysis of the structure and growth habits of ZnTe has been done in the following sections.

4.3. EPITAXIAL RANGES OF GROWTH TEMPERATURES

Films of ZnTe were deposited on germanium substrates with polished surfaces in both (111) and (100) orientations at a number of substrate temperatures ranging from 100° C to 500° C, which was the highest temperature at which the films could be made to deposit under the experimental conditions outlined in chapters II and III.

As in the case of the II-VI deposit / substrate combinations studied previously in this laboratory it was found possible and convenient to represent the film structures in terms of their diffraction patterns by using the degree of orientation parameter introduced by Ino et al (1964). At the low temperatures the films grew with a fine grained polycrystalline structure giving rise to ring diffraction patterns which were given the value $R=0$. In the epitaxial temperature range the films grew with a single orientation or a few simply related orientations (double positioning, twinning etc.) and gave rise to spot diffraction patterns which were given the value $R=100$. Over a relatively narrow range of growth temperatures the film structure changed from polycrystalline to epitaxial through a series of intermediate structures which were given values of $R=25$,

50 or 75 on the basis of the relative intensities of the spot and ring patterns. Thus R gave an indication of the proportion of the film which had the epitaxial orientation. (Ino et al 1964, Holt 1966).

The results for (111) and (100) oriented Ge substrates were very similar. Fig. 9 for (111) substrate shows that the epitaxial growth range of substrate temperatures was 300° to about 430° C. A typical micrograph along with the diffraction pattern for this orientation of the substrate is given in Fig. 10. It may be pointed out that the diffraction pattern contains neither satellite spots nor streaks which means that the sample was free from any volume faults, such as second phase material or microtwins, and of high densities of planar defects.

The results for ZnTe on (100) oriented Ge substrates are represented in Fig. 11. Again the epitaxial range of growth temperatures was from 300° C to about 430° C. A typical bright field micrograph and diffraction pattern for this orientation is given in Fig. 12. Again the absence of satellite spots and streaks is noticeable.

The range of substrate temperature over which ZnTe grew epitaxially on (111) and (100) oriented germanium were the same. The minimum epitaxial growth temperature, 300° C is the same as that above which CdS evaporated under similar conditions was found to grow epitaxially on (111) surfaces of germanium (Holt and Wilcox 1971). However, Abdalla (private communication) found that CdTe grew on Ge down to

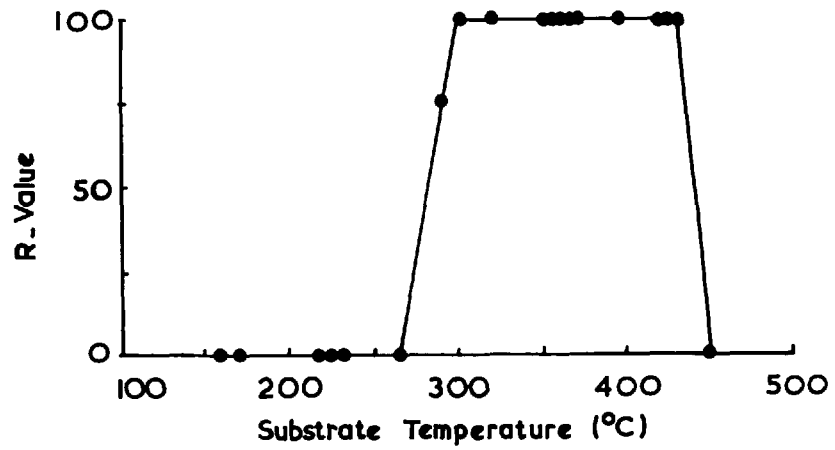


Fig. 9

THE EPITAXIAL RANGE

The degree of orientation against substrate temperature for ZnTe electron beam evaporated in high vacuum on to (111) oriented Ge discs. $R = 100$ indicates epitaxy.

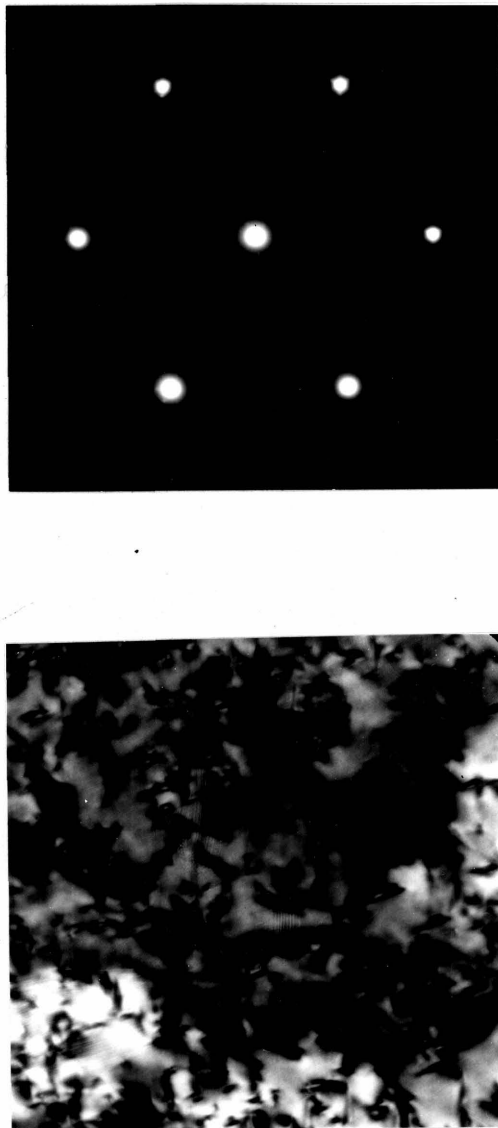


Fig. 10

$\overline{0.3\mu}$

Epitaxial film of ZnTe grown on (111) oriented germanium substrate at 370° C.

(Top) The diffraction pattern.

(Bottom) The micrograph.

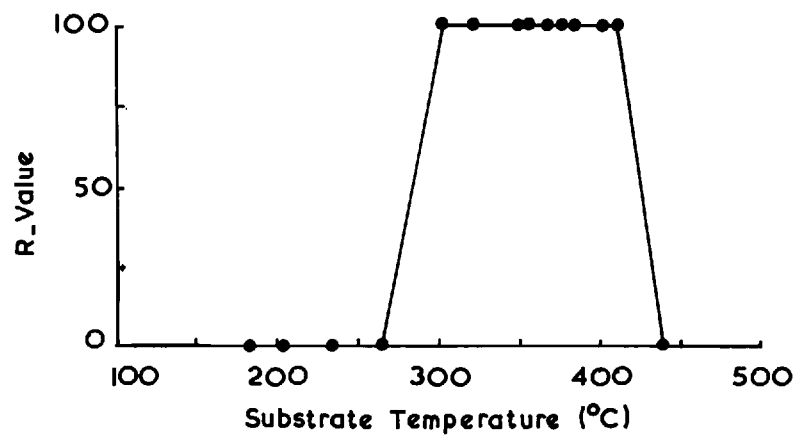
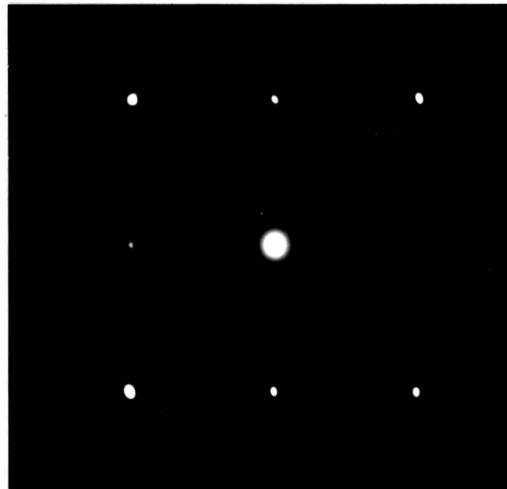


Fig. 11

THE EPITAXIAL RANGE

The degree of orientation against substrate temperature for ZnTe electron beam evaporated in high vacuum on to (100) oriented Ge discs. $R = 100$ indicates epitaxy.



0.2 μ

Fig. 12

Epitaxial film of ZnTe grown on (100) Ge
at 380° C.

(Top) Diffraction Pattern.

(Bottom) Micrograph.

200° C and 250° C.

The form of R versus T curves of fig 9 and 11 is similar^{to} those obtained previously for ZnTe (Holt 1966), ZnS (Woodcock and Holt 1969) and CdS (Wilcox and Holt 1969) evaporated in vacuum on to ionic crystals substrates. In all these case, at the highest temperatures, the degree of orientation of the films falls just before the films cease to deposit. In the case of ionic substrates this was due to the onset of the sublimation of the substrate. In the present case, however, the temperature concerned i.e 500° C is well below the sublimation temperature of Ge (1200° K) as shown by the vapour pressure data of Ge (fig 13). A lower limit for this temperature is also known from the work done in establishing the temperature for thermally cleaning the substrate prior to deposition. What is required for this purpose is that the substrates be raised to^a high temperature that does not produce thermal etch pitting due to sublimation or surface diffusion. For Ge in high vacuum it has been found by several workers in this laboratory that thermal pitting does not occur below 700° C. The cessation of film deposition on Ge at about 500° C in the case of ZnTe, at the evaporation rate that was used, must therefore be explained in terms of the properties of ZnTe or of the properties of the substrate other than its sublimation temperature.

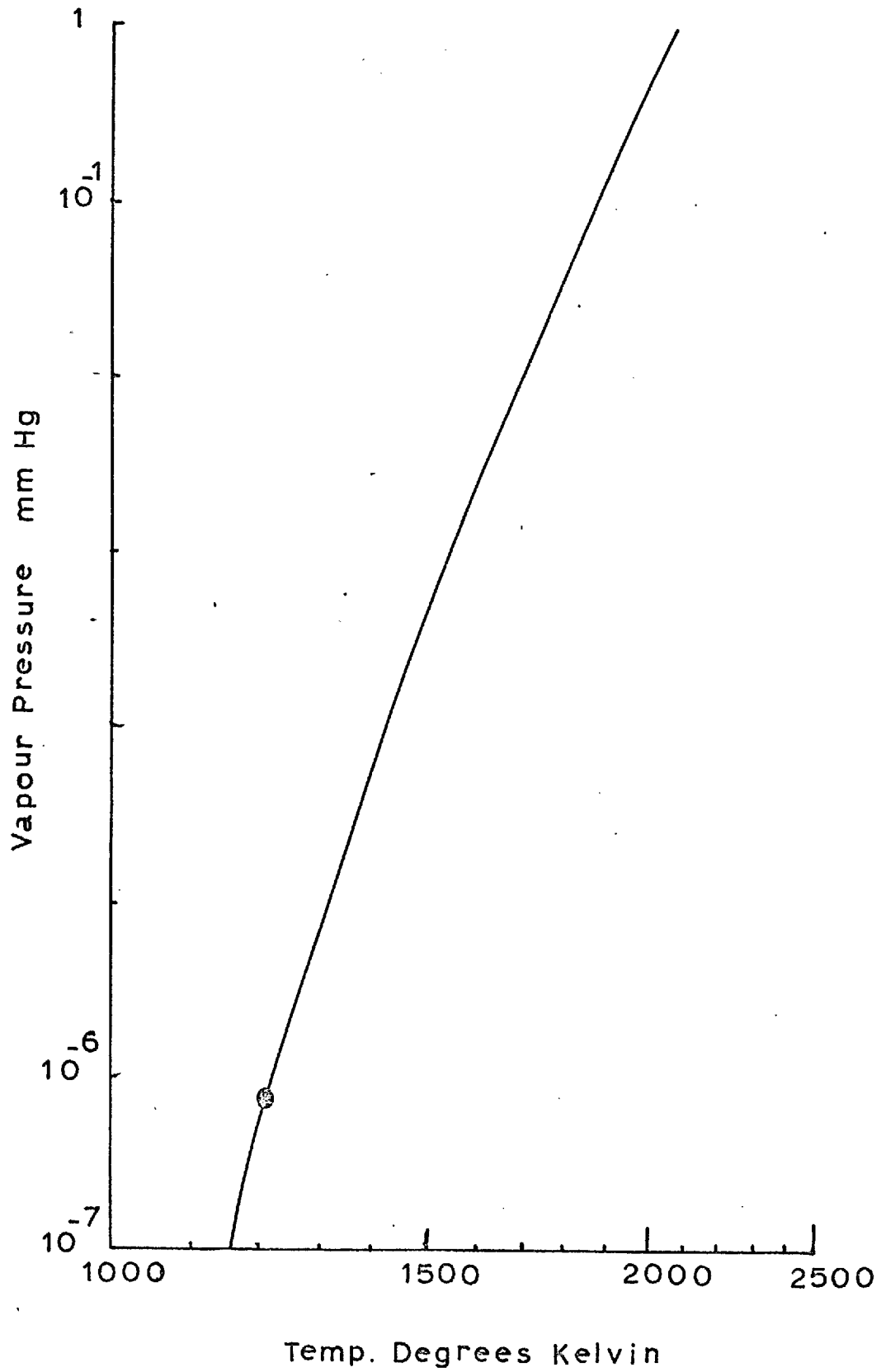


Fig. 13

Vapour pressure curve for Ge. Solid circle represent the melting point.

4.4. CRYSTAL STRUCTURE OF FILMS

4.4.1. Films Deposited on Ge (111).

The diffraction patterns as in the example given in Fig. 10 clearly showed that the ZnTe films contained neither three dimensional defects such as microtwins or included grains with the wurtzite structure in sufficient numbers to give rise to satellite spots nor planar defects in high densities that would produce streaks in the diffraction patterns (section 4.6.3).

The structure of ZnTe films grown on Ge(111) can be ascertained with the help of a typical diffraction pattern as shown in fig. 14. This diffraction pattern can be analysed with the help of Fig. 15. A part of the (111) diffraction pattern of ZnTe is shown in Fig. 15 (a). The $\langle 110 \rangle$ directions of the reciprocal lattice are indicated by broken lines. The projection of the $\langle 111 \rangle$ directions on the (111) plane are indicated by the dash-dot lines. If this pattern is superposed on the (111) germanium diffraction pattern then the resultant pattern is shown in Fig 15 (b). The central solid circles are ZnTe diffraction spots, the outer solid circles are the germanium diffraction spots and the open circles are Ge/ZnTe double diffraction spots. In this case the satellite spots are displaced a distance $(|d_{2\bar{2}0} - d'_{2\bar{2}0}|)^{-1}$ from the ZnTe spots in $\langle 110 \rangle$ directions, where $d_{2\bar{2}0}$ and $d'_{2\bar{2}0}$ are the $(2\bar{2}0)$ plane spacings in Ge and in ZnTe. In Fig. 14 the six satellite spots round each 220 ZnTe diffraction spot include one 220 germanium spot and five Ge / ZnTe



Fig. 14

A typical diffraction pattern from a ZnTe film grown epitaxially on (111) oriented Ge substrate at 370° C. The six satellite spots round each $2\bar{2}0$ ZnTe diffraction spot include one $2\bar{2}0$ Ge spot and five Ge / ZnTe double diffraction spots.

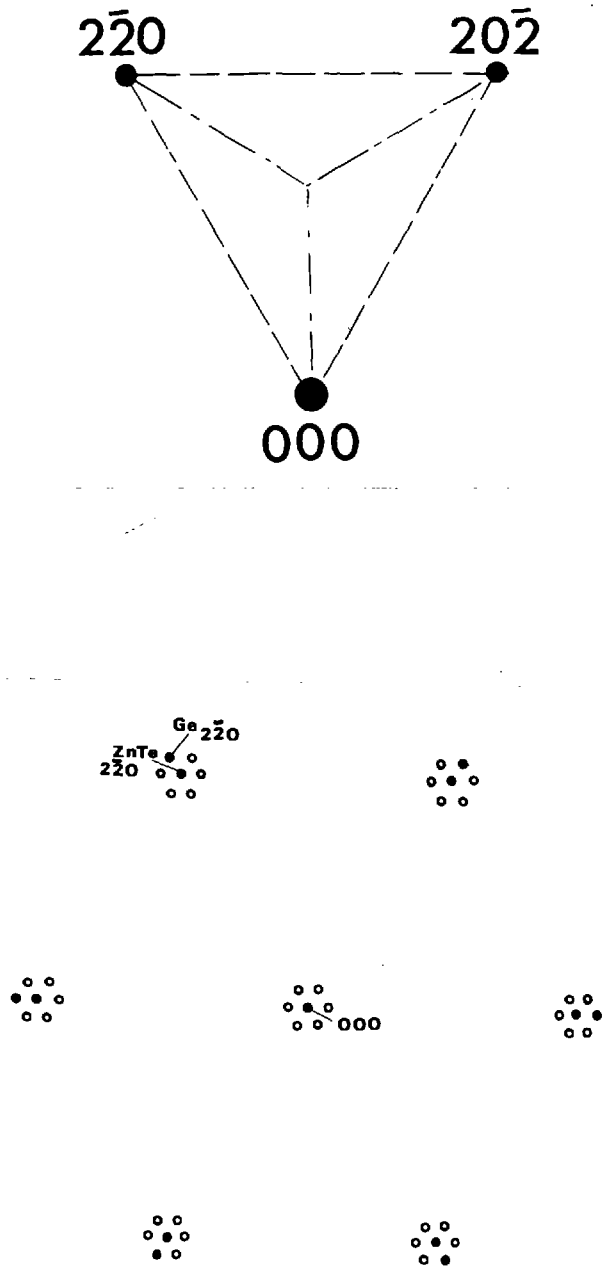


Fig. 15

Diagram showing the formation of double diffraction spots. The details are given on page 78 in the text.

double diffraction spots as indicated in fig. 15 (b). The interpretation of these spots as due to microtwins can be convincingly contradicted with the help of Fig. 16. In this figure the (111) diffraction pattern plus satellite spots due to twins on the $\{111\}$ planes other than (111) are shown by small solid circles and the small open circles represent the twin / matrix double diffraction spots. In this case the satellite spots are displaced from the matrix spots by $\pm 1/3 \langle 111 \rangle$ which is $1/3$ the distance to the centres of the triangles with 000 and two $\{220\}$ spots as specified by Pashley and Stowell(1965) and Holt (1969). The satellite spots arising from (111) double positioning spots occur at the mid-points of these triangles (Pashley and Stowell 1963) at the points marked by solid squares in Fig. 16

It is clear that the satellite spots due to $\{111\}$ twins in epitaxial ZnTe would lie at much greater distances and in the $\langle 111 \rangle$ directions, and not in the $\langle 110 \rangle$ directions from the matrix spots (comparison of figs.14, 15 b and 16). Thus the diffraction pattern of Fig.14 shows that ZnTe films had the cubic sphalerite structure and grew in parallel alignment on to germanium i.e. with (111) ZnTe parallel to (111) Ge and $[1\bar{1}0]$ ZnTe parallel to $[1\bar{1}0]$ Ge. This interpretation can be confirmed by the Moiré fringe observations as discussed below:

When the actual lattice periodicities of a crystal are below the resolution limit of the microscope then an indirect lattice resolution method known as the Moiré Pattern

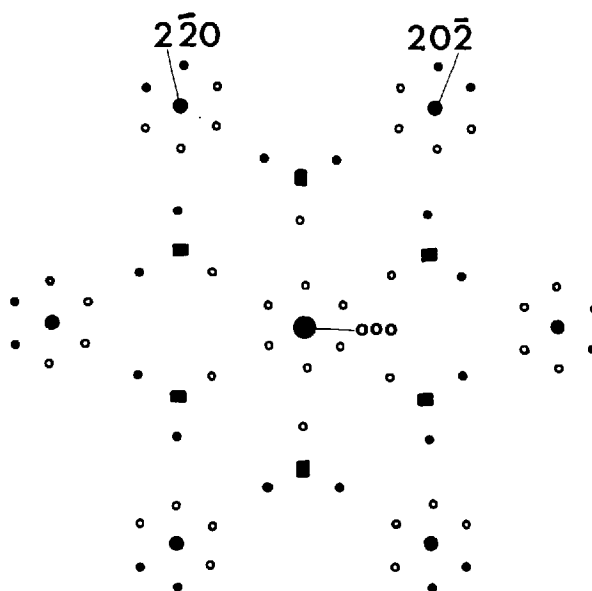


Fig. 16

The (111) diffraction pattern plus satellite spots due to twins on the $\{111\}$ planes other than (111) (small solid circles) and twin/ matrix double diffraction (small open circles). In this case the satellites are displaced from the matrix spots by $\pm \frac{1}{3} \langle 111 \rangle$ which is $\frac{1}{3}$ the distance to the centres of the triangles with 000 and two $\{220\}$ spots. The satellite spots arising from (111) double positioning spots occur at the mid points of these triangles at the points marked by solid squares.

method is quite effective. The basic principle of this technique is that when two parallel sets of lines, with spacings d_1 and d_2 are superimposed then an enlarged pattern of parallel fringes (beats) are produced with a spacing

$$\frac{d_1 d_2}{|d_2 - d_1|} \text{ thus giving magnification } M = \frac{d_1}{|d_2 - d_1|}$$

(The detailed treatment is given in Appendix I).

So when two crystals which have differences in lattice parameters or orientation overlap (as in epitaxial films) then an effective magnification of spacings between their atomic planes is produced in the form of uniformly spaced interference fringes known as Moiré patterns. These patterns can be formed in parallel pattern, rotation pattern or cross pattern form (Appendix I).

Figure 16 shows the parallel Moiré pattern produced by the interference between the $2\bar{2}0$ beams diffracted by overlapping germanium and ZnTe, having similar structure and in parallel alignment but differing in lattice parameter. For such Moiré fringes the spacing M is given by

$$M = \frac{d_1 d_2}{|d_2 - d_1|} \quad (\text{Appendix I})$$

Substituting for d_1 and d_2 the $2\bar{2}0$ spacings for ZnTe and Ge which can be obtained by substituting into the expression:

$$\frac{1}{d_{hkl}} = \frac{(h^2 + k^2 + l^2)^{1/2}}{a}$$

The values $a = 5.6575$ for germanium (Straumanis 1952) and

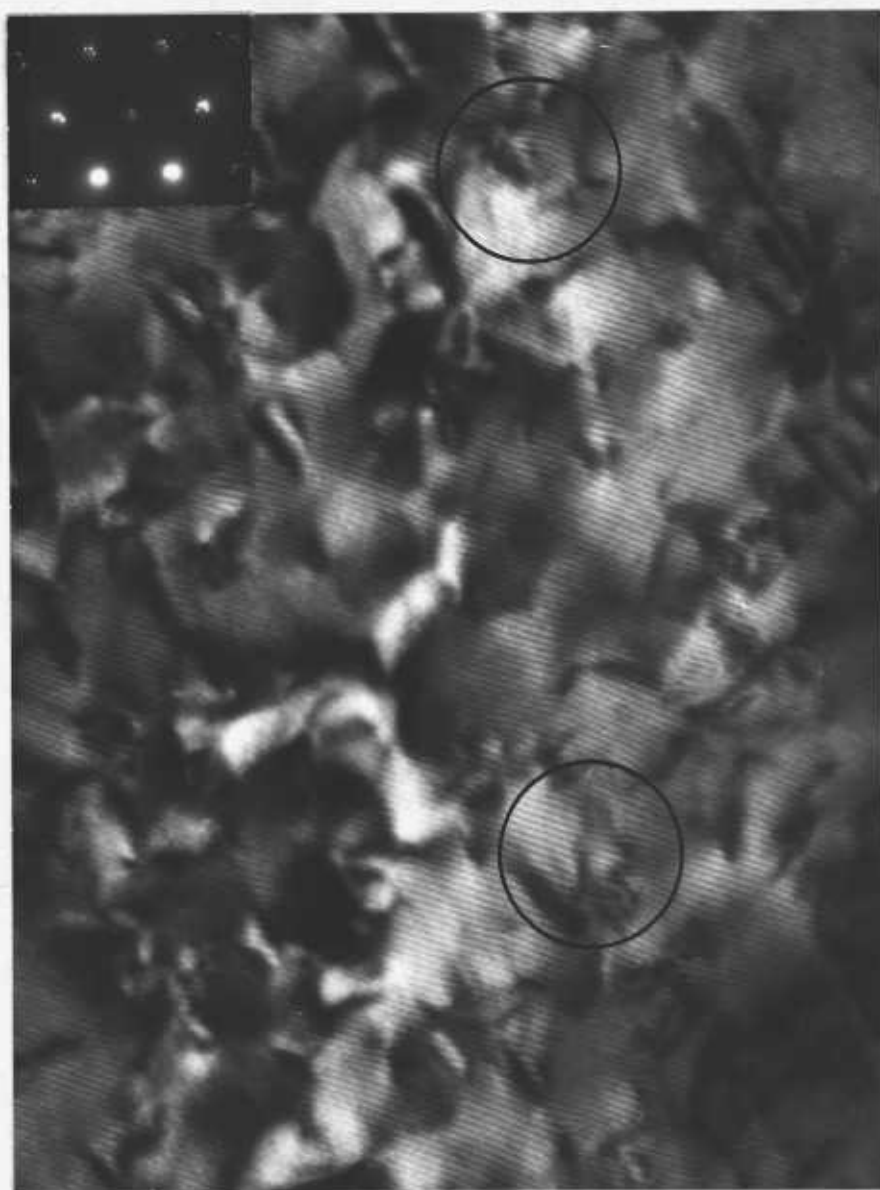


Fig. 17

0.1 μ

Transmission electron micrograph of film of ZnTe grown on Ge at 370⁰ C, showing the moire fringes and dislocations.

$a = 6.1037$ (Aven and Prenner 1967) gives a value for the fringe spacing of $27.6 \text{ \AA}$. The observed value is $25.0 \text{ \AA}$, in good agreement with the calculated value.

The indexing of the ring patterns obtained from ZnTe films grown on (111) Ge at temperature below the epitaxial limit showed that in these polycrystalline films too, the structure was sphalerite.

Some films grown on (111) Ge, unlike the more perfect films grown, gave diffraction patterns containing satellite spots indicating the presence of $\{111\}$ microtwins and (111) double positioning twins. These will be discussed in section 4.7.1

4.4.2. ZnTe Films Grown On Ge (100)

The best ZnTe films grown on (100) germanium in the epitaxial range gave diffraction patterns that were free of satellite spots and showed no streaks (Fig 12), which showed that they were free of high densities of both three and two dimensional defects. Indexing the diffraction patterns showed that the films had the sphalerite structure and grew in parallel orientation on the germanium i.e. the epitaxial orientation relationship was (100) ZnTe parallel to (100) Ge and $[0\bar{1}0]$ ZnTe parallel to $[0\bar{1}0]$ Ge.

4.4.3. Discussion

The growth of ZnTe films with the sphalerite structure was to be expected, as this is the stable structure for ZnTe and there is no difficulty in matching the symmetry

of the films to that of the substrate surface. In the case of CdS for which wurtzite is the stable structure, this structure could not be oriented to match the symmetry of (100) and (111) orientations of a cubic structure substrate and on those substrate surfaces CdS was found to grow with the sphalerite structure (Wilcox 1970). The degree of structural perfection of the films is relatively high as compared with the films of ZnTe grown on ionic substrates (Holt 1966). Three dimensional defects such as twins and wurtzite structure grains were far less common in epitaxial films grown on germanium and in the case of substrates in the (100) orientation did not appear at all. Two dimensional defects such as stacking faults were also present in far lower densities in the films grown on germanium as was shown by the absence of streaking in the diffraction patterns of ZnTe grown on (111) orientation of germanium. In fact as evidenced by both the relatively low density of stacking faults and the parallel alignment of the moire fringes, the best films of ZnTe on germanium were comparable in structural perfection with other heteroepitaxial films such as Au on NaCl (Matthews 1959) and recently reported films of Ge grown on Si in ultra high vacuum (Cullis and Booker 1970,71).

It has been reported in the case of CdTe, CdS (Weinstein, Wolff and Das 1965, Wilcox and Holt 1969) and CdSe(Ludeke and Paul 1967) that the structure of epitaxial films of II-VI compounds can be changed from cubic (sphalerite) to hexagonal(wurtzite) by changing the orientation of the

substrate surface. However this was found not to occur in the case of CdS/InSb in the work of Holloway and Wilkes (1968). In the present case also it was found that the structure of ZnTe did not change with the change of the orientation of the substrate. As a matter of fact the valid general rule is that at low temperature all the II-VI compounds grow on (100) and (110) with the cubic structure .

4.5.1 The Structural Quality Of The Films

I. Topography: All the ZnTe films showed extremely clean continuous, smooth and uniform surfaces in the optical microscopes, except that in a few cases the irregularities of the substrate such as pits or scratches were replicated by the ZnTe layer. Attempts to resolve the topography of the films in the Scanning Electron Microscope also proved unsuccessful as due to their flatness focussing was difficult. It may be pointed out that interference fringes run quite straight across epitaxial films of all the II-VI compounds that have been studied in this laboratory(ZnTe, ZnS and CdS on ionic substrates and ZnTe, ZnSe and CdS on germanium)(group observation). Moreover in a number of these cases films were examined by scanning electron microscope using the secondary electron emissive mode of operation and it was found that the film surfaces were so flat and featureless that it was difficult to focuss on them (Culpan, private communication).

The degree of smoothness of the films can also be inferred from the straightness of the Nomarski interferometric fringes as shown in Fig 5.

II. Alignement: In fig 17, here and there, at points such as those encircled, localized bends and terminations of individual moiré fringes can be seen. These are a form of image of dislocations in the specimens (Hirsch et al 1965), (Appendix I). Aside from these however, the fringes are straight and parallel over large areas of the specimen. Over distances of upto 1 or 2 μm these fringes were found to be parallel to within 8° .

If two overlapping crystals that differ in lattice spacing are rotated through an angle θ from parallel alignment, the Moire fringes will be rotated through a much larger angle ω given by

$$\omega = \frac{d_1}{|d_1 - d_2|} \theta \quad (\text{Hirsch et al 1965})$$

Observation that the fringes in fig 17 do not rotate through more than an angle of 8° , means on substituting the values of d_{220} for germanium and ZnTe that the lattice rotation angle θ cannot be more than about half a degree. That is the parallel alignement of ZnTe on (111) Ge is accurate to within this limit.

When the Moiré fringes are out of contrast the most prominent features to be seen are bent stacking faults as shown in fig. 18. The density of the faults in films grown at temperatures near 350°C was found to be about 8×10^9 per cm^2 . This is an order of magnitude higher than the density of bent stacking faults in the epitaxial films of gold, silver and copper grown on NaCl and reported by

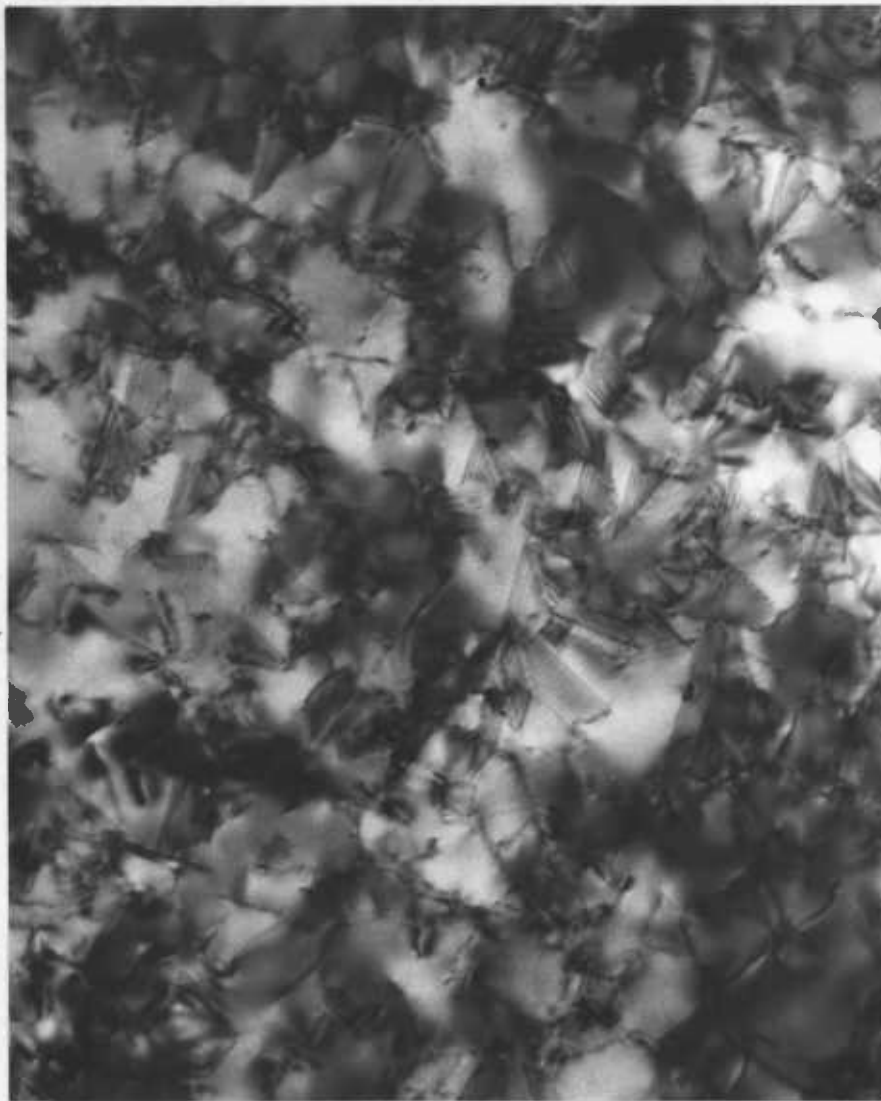


Fig 18

0.3 μ

Transmission electron micrograph of a film of ZnTe grown on (111) Ge at 350° C. The stacking fault fringes are clearly visible.

Matthews(1959). The projected widths of the faults are remarkably constant. In fig 18 for example, the widths correspond to a film thickness of $1200 \pm 200 \text{ \AA}$. This constancy of projected fault width indicates that the thickness of these films is also constant. This observation is in agreement with the results obtained with other methods of examination.

4.6. FAULTS AND DEFECTS IN THE ZnTe FILMS

The epitaxial films of II-VI compounds, in broad classification, contain the following four types of defects:

1. Three dimensional defects.
2. Planar defects.
3. Dislocations.
4. Point defects.

Three dimensional defects are usually present in structurally less perfect films, and are due to the presence of microtwins, doubly positioned twins and / or included grains with different crystal structure (Wilcox and Holt 1969, Holt 1969, Holt and Woodcock 1970). These defects give rise to irrational satellite spots in the electron diffraction patterns of the films. By optimising the growth conditions and starting with material of suitable quality (Holt and Wilcox 1972) the three dimensional defects can be eliminated, and then the largest defects left in the films are the planar defects.

The planar defects are probably stacking faults, but it is also just possible that they are thin flat precipitates. They give rise to the streaking effects in the electron

diffraction patterns (Holt and Woodcock 1970). The details are discussed in section 4.6.2.

As pointed out previously (sections 4.3 and 4.4) in the ZnTe films grown under the most favourable growth conditions, three dimensional defects were found to be absent and two dimensional defects were present in the high densities (near 10^{10} cm^{-2}). However to make the structural analysis portion of this work more complete, the defects which were observed in the ZnTe films, are discussed in the following sections.

In the analysis of the defects and faults, a well known and confirmed assumption is taken for granted. The II-VI compounds crystallize in the two structures— Sphalerite (Zinc blende) and Wurtzite (section 1.2). The structure factor for the sphalerite structure (section 4.2) allows the same set of reflections as that for the face centred cubic structure, and the structure factor for wurtzite allows the same set of reflections as that for the hexagonal close packed structure. Therefore the analysis of the satellite spots in electron diffraction patterns of epitaxial films of fcc metals (Pashley and Stowell 1963, Pashley, Stowell and Law 1965) and compounds (Holt 1969) due to twins and included grains with the hcp structure can also be applied to the satellite spots in the electron diffraction patterns of epitaxial films of II-VI compounds with sphalerite structure and containing three dimensional defects.

4.6.1 Included Grains of Second Phase, Twinning & Double Diffraction

The term "included grains" is usually used for the formation of a region within the film, which has either different crystal structure from the matrix or the same crystal structure as the matrix with a new and special orientation with respect to the matrix.

There are two types of included grains — firstly those, which have no orientation relationship with the matrix. These grains are formed in structurally less perfect films and are almost non-existent in good epitaxial films. Secondly those grains which have a simple orientation relationship with the matrix. Generally in II-VI compounds the oriented included grains are of two types. One consists of the grains with the same crystal structure as the matrix (for example sphalerite structure grains present in the sphalerite matrix structure) and are in twin orientation with respect to the matrix. The other type consists of grains of material of different structure (say wurtzite structure grains present in the sphalerite structure or vice versa). A particular type of twinned structure, known as double positioned twins, is found in the films with cubic structure grown on substrates in the (111) orientation. In this case the matrix and the film material are rotated by 180° relative to one another about the normal to the substrate. As this work mainly concerns epitaxial films of ZnTe, the latter type of grains i.e. oriented grains, will be dealt in a little more detail.

The basic crystallography of twinning is the formation of a region with a new and special orientation with respect to the matrix. The twin orientation is obtained by rotating the matrix orientation by 180° about a particular crystal direction known as twin axis. The plane perpendicular to the twin axis is called the twin plane. As a well known example, the $\{111\}$ planes of the fcc structure are normally the twinning planes. Twins can therefore form on several different planes (e.g. four $\{111\}$ planes), so that the electron diffraction patterns from the matrix plus its various twins is a composite diffraction pattern due to several related orientations. In some cases the extra spots give the appearance of being satellites around the matrix reflections. Further if the twin platelets are narrow, or if there is any elastic strain at a twin interface, the reciprocal lattice points can be elongated, giving rise to either streaks or subsidiary pseudo spots.

Pashley and Stowell (1963) showed that the reciprocal lattice points due to twins occurring on all the $\{111\}$ planes of a fcc matrix either coincided with the matrix points or were displaced from matrix points by vectors of $\pm 1/3 \langle 111 \rangle$. Points of the form $(pqr) = (uvw) \pm 1/3 [hkl]$, where (uvw) is a matrix point and $[hkl]$ is a twinning axis, represent permitted twin reflections if the distance of the spot from the undiffracted spot $R = \frac{\lambda_L}{d_{pqr}}$ is equal to that for an atomic plane, spacing d_{pqr} of the fcc structure. It was also pointed out that not all points of

this form are introduced into the reciprocal lattice and that the allowed cases are given by the selection rule

$$(hu + kv + lw) = \pm (3N + 1)$$

where N is an integer. Different methods of plotting and indexing the twin spots in the electron diffraction patterns are given by Hirsch et al (1968).

Included grains having a simple orientation relationship with respect to the matrix give rise to extra spots in the diffraction patterns. 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. So in order to understand the interpretation of the electron diffraction patterns with satellite spots, an understanding of the double diffraction phenomenon is quite essential.

If the specimen contains more than one crystalline component, such as regions of different orientations with in a single material or the co-existence of two or more phases and if it is geometrically possible for the diffraction beam produced in one component to pass into a second component, then the occurrence of double diffraction is to be expected and it is always necessary to consider that extra reflections can be formed in this way.

Consider fig 19(a) which shows a twin platelet passing through the specimen. It is geometrically favourable for electrons diffracted in the matrix to pass into the twin through the boundary AB, and for electrons diffracted in the

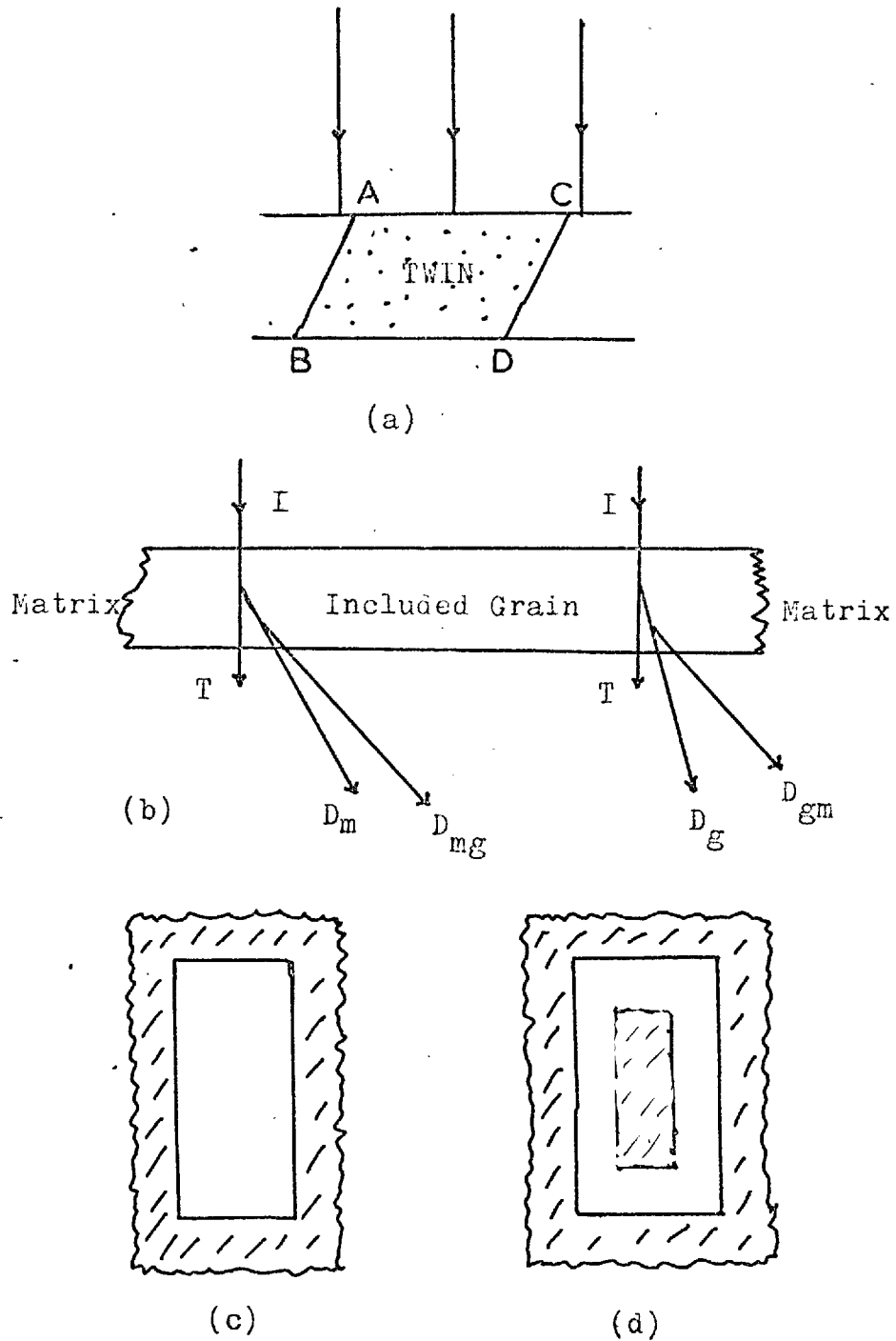


Fig. 19

(a) Presence of twin.

(b) I is the incident beam, T, the transmitted beam, D_m , singly diffracted beam from matrix, D_g , singly diffracted beam from included grain, D_{mg} and D_{gm} , beams doubly diffracted first by the matrix and then by the grain or v.v.

(d) Outline contrast obtained by imaging D_{mg} or D_{gm} (D.Field)

(c) Domain contrast obtained in dark field by imaging D_g .

twin to pass into the matrix through the boundary CD. Thus double diffraction is likely in the vicinity of the twin boundaries. In order to consider the effect of double diffraction we simply treat a primary diffracted beam from the matrix as a new source or origin for the twin diffraction pattern.

As pointed out earlier extra spots may occur in diffraction patterns either as a result of single diffraction within the 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 as shown in fig 19(b). If the 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 the dark field. This is shown in fig 19(c) and is known as " outline contrast ". If the 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 as shown in fig. 19(d).

It may be pointed out that not all possible reciprocal lattice points resulting from double diffraction are necessarily permissible reflection. 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 grains) 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, then the spot corresponding to the second diffraction is also in the same plane. Further details and methods of plotting double diffraction spots are given in the book by Hirsch et al (1968).

Double diffraction in the twins and matrix may be treated by adding the matrix vectors in the (111) reciprocal lattice plane to each of the twin reflections. This results in the appearance of many additional spots and a complete diffraction pattern is shown in fig 16 which was drawn by Holt (1966) by assuming the presence of sphalerite structured microtwins in the sphalerite structure. The prominent features of this pattern are the six pointed star with points at the 220 matrix reflections and the hexagonal arrays of satellite spots around each 220 matrix spot. Double positioning, that is the occurrence of twinning about the normal to the film, (which is a $\langle 111 \rangle$ direction) results in additional satellite spots (Dickson and Pashley 1962) as indicated by the squares in the fig 16.

The observed satellite spots in the electron diffraction patterns of the ZnTe films are shown in fig 20. A comparison between fig 16 and fig 20 clearly shows that the theoretical plot of fig 16 containing satellite spots due to the presence of twins and second phase material is identical to the experimentally observed diffraction pattern. The identification of these grains was checked with the help of dark field microscopy and the results are shown in fig 21.

The possibility of the presence of included grains of wurtzite structure material was ruled out after comparison of the observed diffraction patterns with the theoretical plots by Holt (1969) as shown in fig 22 for a sphalerite structure containing wurtzite structured included grains with basal planes parallel to each of the $\{111\}$ planes in the (111) film. It may also be noted that in fig 22 there is a six pointed star of the satellite spots but it contains more spots than in the case of fig 16. In fig 22 there are two hexagons of satellite spots around each matrix 220 spot, one at $\pm 1/3 \langle 111 \rangle$ and the other at $\pm 1/6 \langle 111 \rangle$ from it.

No indication of the presence of included grains was observed in the ZnTe grown on the (100) orientation of germanium. However, some streaking was observed in the diffraction patterns in this orientation. This streaking will be discussed in section 4.6.3.



Fig. 20

Diffraction pattern from a twinned sphalerite structure film showing the presence of satellite spots.

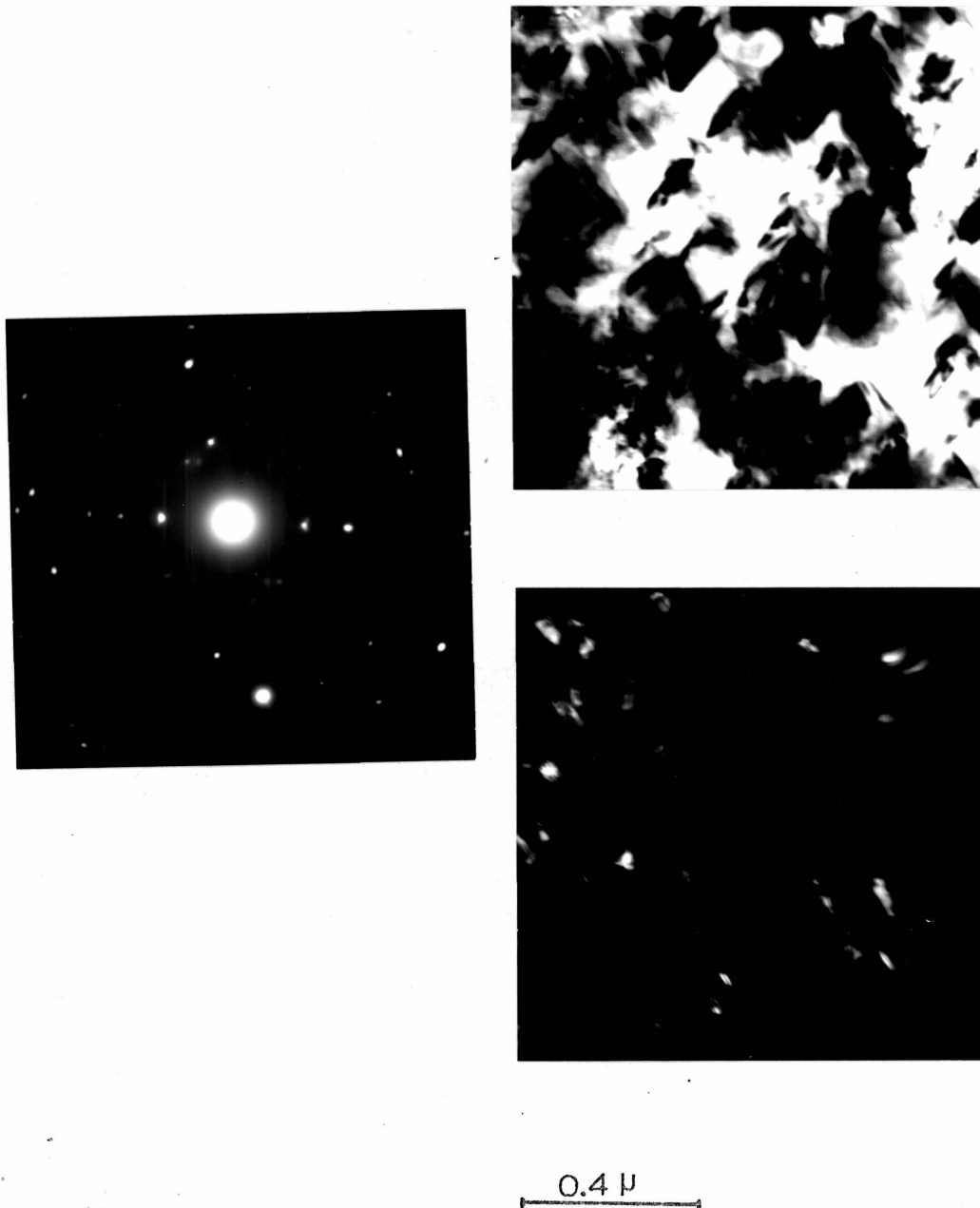


Fig. 21

Bright and dark field micrographs of a ZnTe film grown on Ge (111) showing the presence of second phase material/ included grains/ twins.

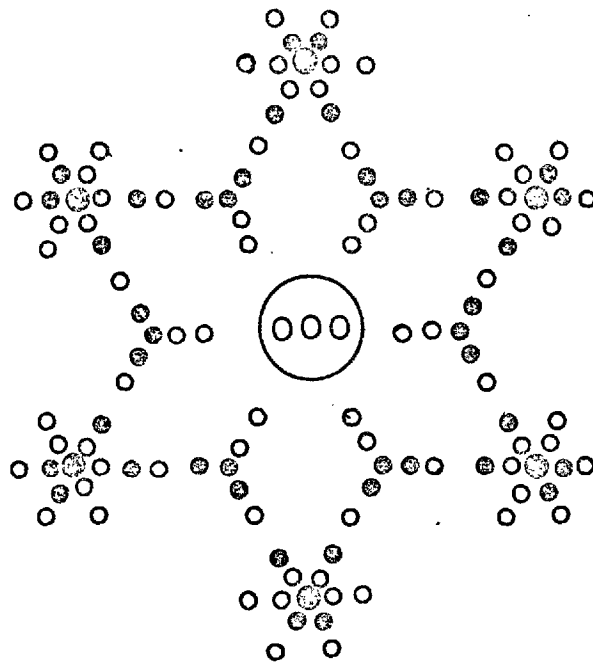


Fig. 22

Sphalerite-structure matrix spots (large solid circles), wurtzite spots(small solid circles) and wurtzite/matrix double diffraction spots(small open circles) in and near the sphalerite (111) reciprocal lattice plane. This is the diffraction pattern due to a sphalerite structure film containing wurtzite structure included grains oriented with basal planes parallel to each of the $\{111\}$ planes of the matrix.

4.6.2 Stacking Faults

Stacking faults are the simplest type of planar imperfection. The crystal below the fault is identical to that above the fault in spacing and orientation but is translated with respect to it by some constant vector $\vec{R}$ (fig 23). Thus the phase factor which determines the contrast (Hirsch *et al* 1968) changes abruptly from its value zero above the fault to the value $\Delta = 2 \pi \vec{g} \cdot \vec{R}$ below the fault. This means that if $\vec{R}$ is a lattice translation vector (so that the crystals are once more in perfect register) , the fault is invisible for all reflections $\vec{g}$ since Δ merely changes from zero to the equivalent value of $2 \pi n$ where n is an integer.

Stacking faults can be formed by shearing parallel to the fault, or by the expansion or collapse of the lattice in a direction perpendicular to the fault.

Frank pointed out that the simplest stacking fault in the fcc structure lies in the (111) planes and can be of two types, intrinsic stacking fault and extrinsic stacking fault. A schematic diagram of an intrinsic fault is given in fig 24. This type of fault can be formed by aggregation of pairs of vacancies to remove a slab of material from a double {111} plane. The subsequent inward collapse of the lattice on either side produces this kind of fault. They can also be visualized as generated by glide motion. For an intrinsic fault all that is needed is the passage of one Shockley partial with a Burger vector of the type $a/6 [112]$. The shear vectors, $\vec{R}_j$, for the formation of intrinsic stacking faults on the (111) plane are

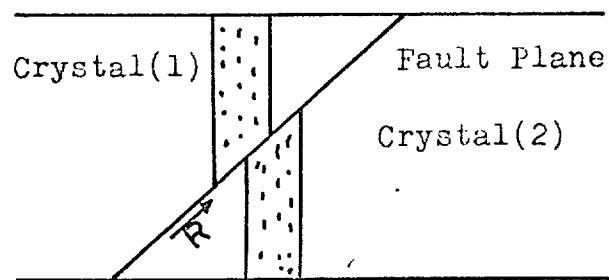
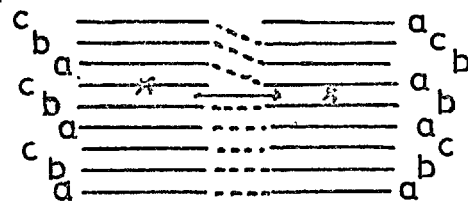
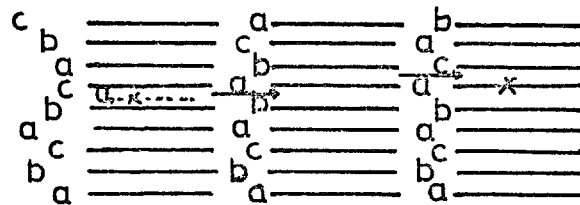


Fig. 23

Stacking fault running across a foil, causing the column to be displaced.



(a) (b)
INTRINSIC



(a) (b) (c)
EXTRINSIC

Fig. 24

Scheme indicating how an intrinsic fault can be created by a single glide:

(a) before and (b) after glide has taken place. The removed layer is marked by a cross.

(Bottom) :

Scheme indicating how an extrinsic fault can be created by glide in two successive layers:

(a) before, (b) after first glide and (c) after second glide. The insertion layer is marked by a cross.

faults on the (111) plane are

$$\vec{R}_1 = \frac{a}{6} [\bar{1}\bar{1}2] \quad \vec{R}_2 = \frac{a}{6} [\bar{1}2\bar{1}] \quad \text{and} \quad \vec{R}_3 = \frac{a}{6} [2\bar{1}\bar{1}]$$

As shown in section 1.2.3 the sphalerite structure can be represented by layers of the different atoms i.e. A α B β C γ where A and α represent the first layers of different atoms. So A α B β C γ : B β C γ : A α represents^{an} intrinsic fault.

Extrinsic faults are formed due to the aggregation of pairs of interstitial atoms to form an extra slab of material in an out-of-sequence position between double {111} planes, and a consequent outward movement of the double atom planes on either side to accomodate the slab. In simple terms this type of fault is formed by the insertion of an extra double layer of atoms which pushes the two crystals apart (fig 24). An extrinsic fault in terms of the structural layer scheme, (section 1.2.3) can be represented by A α B β C γ : B β : A α B β C γ .

The shear vectors of an extrinsic fault are the negative to that of the intrinsic fault i.e. $-\vec{R}_j$. This means that $\alpha = 2 \pi \vec{g} \cdot \vec{R}$ has opposite sign for the extrinsic and intrinsic fault with the same diffraction vector $\vec{g}$ operating. For a fault on (111) , $\vec{R}$ can take values $\pm \frac{1}{3} [111]$. One of these possibilities corresponds to the removal of a layer of atoms followed by a collapse of the two crystal on either side of the fault, and the other corresponds to the insertion of an extra layer of the atoms pushing the two crystals apart.

Matthews (1959) has also suggested a mechanism for the formation of growth faults in epitaxial films. He confirmed from his films of gold on NaCl that the majority of the gold nuclei in their early stage of growth were epitaxially aligned on the substrate. Due to the misfit between the lattices of metal and substrate, the lattice of one nucleus may be displaced from that of the other by a non-integral number of lattice spacings. So when the two nuclei meet they will not always do so in perfect register. The nuclei would be expected to grow with facets that coincide with low index crystal planes.

When two nuclei grow together the joint plane will probably be a $\{111\}$, a $\{110\}$ or a $\{100\}$ plane. If they meet on a $\{110\}$ or a $\{100\}$ plane then no stacking fault can form between them although the nuclei may have to strain slightly to get into perfect register. It is however, possible for a stacking fault to form between nuclei that join on a $\{111\}$ plane. It is clear from fig 25 that when the nuclei growing on a (100) substrate surface are of different height they can only meet on $\{111\}$ planes. So if a stacking fault is formed between nuclei A and B it will be on a $\{111\}$ plane. If B were larger than A the faulted plane would be $\{\bar{1}\bar{1}1\}$.

On the basis of kinematical and dynamical theories, detailed treatments of the stacking fault contrast have been formulated by Whelan and Hirsch (1957), Hirsch et al (1960), Hashimoto et al (1960-62), Gevers (1963)

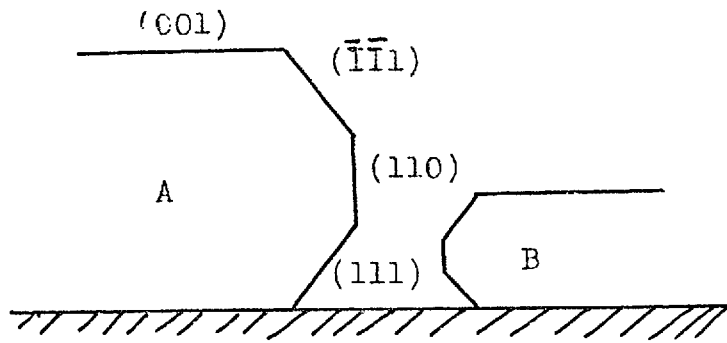


Fig. 25

When the nuclei are of different height then they can only meet on $\{111\}$ planes. If the stacking fault is formed between nuclei A and B it will be on the $\{111\}$ plane. If B were larger than A the faulted plane would be $\{\bar{1}\bar{1}1\}$.

and Gevers, Art and Amelinckx (1963) . But for the present work it is sufficient to point out that in very simple terms if a fault occurs in a foil at a depth t then by applying the column approximation the intensity is given by (Hirsch Chapter VII) :

$$I = \frac{1}{(\xi_g s)^2} \left[\sin^2 \left(\pi t s + \frac{\phi}{2} \right) + \sin^2 \frac{\phi}{2} - 2 \sin \frac{\phi}{2} \sin \left(\pi t s + \frac{\phi}{2} \right) \cos 2\pi s z \right]$$

where $z = \frac{1}{2} t - t_1 =$ distance to the fault measured from the centre of the foil. ξ_g and s are the extinction distance and deviation parameter from the exact Bragg condition respectively . From fig 26 it is clear that if the fault is inclined with respect to the foil surface, then the intensity distribution will become visible as cosine fringes parallel to the line of intersection of fault plane and surface having the depth periodicity s^{-1} . For a fault parallel to the foil plane, however, instead of fringes uniform intensity will be visible.

A micrograph of the Zinc Telluride film showing stacking fault fringes is reproduced in fig 18. It was found that the angle between the two arms containing parallel fringes was exactly equal to 60° .

Several authors (Cottrell 1952, Thomson 1953, Frank and Nicholas 1953, Friedel 1955, Whelan 1959, Matthews 1959) have discussed how it is possible that some stacking faults could have a part of their area on one plane and the remainder on another non-parallel plane. The bend itself would contain an imperfect dislocation called a " Stair rod "

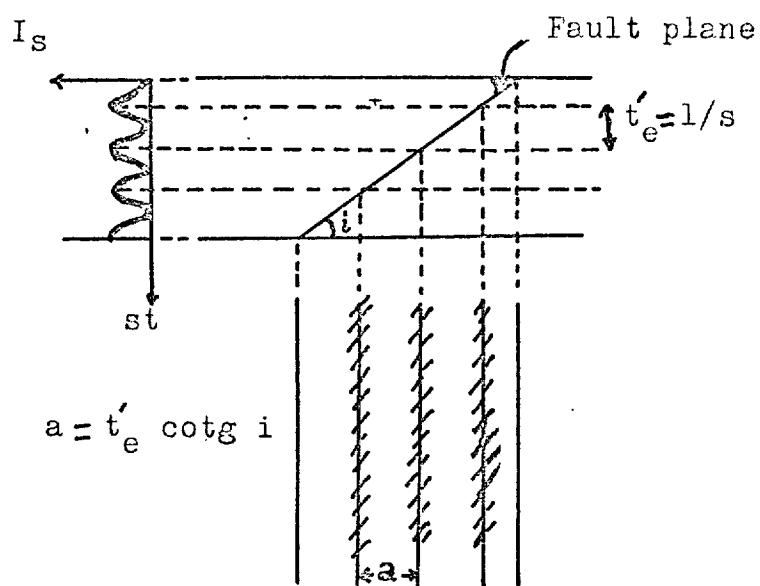


Fig. 26

Origin of the stacking fault fringes for an inclined fault plane. Where I_s has a maximum a dark fringe will be observed in the bright field image.

ZnTe being sphalerite in structure (section 4.4) could contain stacking faults on the $\{111\}$ planes. The possibility of the presence of stacking faults on the (111) and $(\bar{1}\bar{1}\bar{1})$ planes in the fig 18 can be ruled out as such faults would lie normal to the electron beam and would not show any fringes. However, the bent stacking faults in the $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$ and $(\bar{1}1\bar{1})$ planes could show up in the film in (111) orientation. If a line diagram of the bent stacking faults lying in the $(\bar{1}\bar{1}1)$ and $(\bar{1}\bar{1}1)$ plane is drawn then the resultant stacking fault fringes in the (111) plane are shown in fig. 27. The intersections of the stacking faults with the upper and lower surfaces of the foil are indicated by thick full and thick dotted lines respectively. Fine full lines represent the electron interference fringes caused by the fault and the fine dotted lines are imperfect dislocations. The angle between the two arms of the fringes is 60° . The identical form of fringes (fig 18 and fig 27) is an indication that ZnTe films contained bent stacking faults as discussed by Matthews (1959). However a few ZnTe films showing stacking fault fringes contained loops also. Their presence indicated that the stacking faults might be of tetrahedral type caused by the vacancy loops as discussed by De Jong and Koehler (1963). When a disk of vacancies collapses a triangular sessile loop such as CDB (fig 28) in the (111) plane could result. The partials bordering the loop would dissociate and the Shockely partials bow out in the other (111) planes (fig 28 b) causing a final

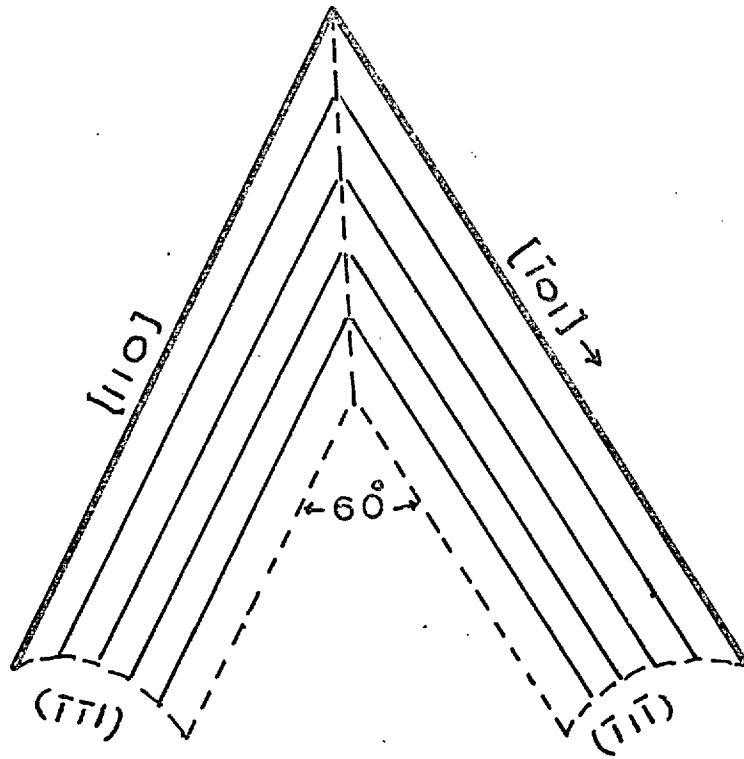


Fig. 27

Line drawing of a bent stacking fault. The intersections of the stacking fault with the upper and lower surfaces of the foil are indicated by thick full and thin dotted lines respectively. Fine full lines represent the electron interference fringes caused by the fault and other dotted line is the imperfect dislocation.

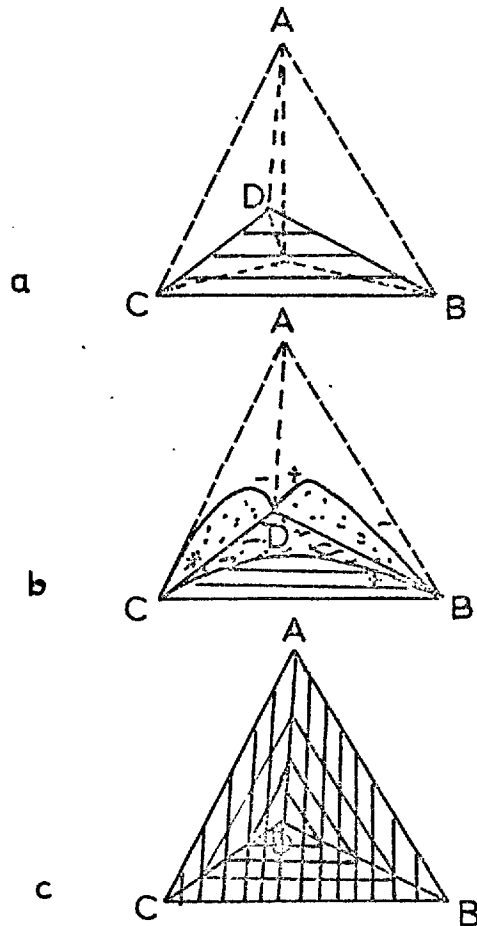


Fig. 28

FORMATION OF A STACKING FAULT TETRAHEDRON

- (a) Triangular sessile loop CDB in the (111) plane resulting from the collapse of a disk of vacancies.
- (b) The partials bordering the loop dissociate and the Shockley partials bow out in the other (111) planes.
- (c) Final shape of the tetrahedron. The edges are stair rod dislocations; the side faces contain stacking faults.

shape of a tetrahedron (fig 28 c). The edges would form the stair rod dislocations and the side faces would contain stacking faults. In (111) oriented films the projected shape of the bent stacking faults on $\{111\}$ planes of Matthews and of faults forming two sides of stacking fault tetrahedra would be the same. Therefore it is not easy to make a definite distinction between them. The following observations were however made:

1. By tilting the specimen from this orientation i.e. (111) no third side of the hypothetical tetrahedra could be observed.

2. As shown in fig 28 the angle CDB is 120° when the film is in the (untilted) (111) orientation. But in the micrograph of fig 18 it was observed that only a very small minority of the stacking faults were bounded by lines that made an angle of $120^\circ \pm 10^\circ$, while the rest of the fringe patterns showed a diversity of other values for this angle.

So from these observations it can be concluded that the stacking faults in ZnTe did not form tetrahedra.

4.6.3 Streaking of Diffraction Patterns & Planar Faults

As discussed in section 4.5. the ZnTe films grown on (100) orientated Ge under the cleanest conditions, were free of included grains and no satellite spots appeared in their diffraction patterns. However, the diffraction patterns from some ZnTe films grown on Ge (100) under less clean conditions were streaked in the $\langle 111 \rangle$ directions as shown

in fig 29. The $\langle 111 \rangle$ streaks manifested themselves in the presence of satellite pseudo spots in the diffraction patterns recorded with the film tilted off the exact $[100]$ beam direction. This kind of streaking of electron diffraction micrographs indicated the presence of a high density of $[111]$ planar defects. A brief account of the streaking effect is given below:

The theory of the diffraction streaks due to the stacking faults in fcc crystals has been given by Paterson (1952) and Whelan and Hirsch (1957). Thomas et al (1965) have also discussed the formation of streaks by planar defects and precipitates. Holt and Woodcock (1969) and Wilcox and Holt (1971) have also discussed the formation of streaks in the case of ZnS and CdS evaporated on to ionic crystal substrates.

From the definition of reciprocal space it is clear that 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, the reciprocal lattice representations of the thin films are arrays of long thin spikes whose axis lie normal to the film and therefore close to the beam direction.

Now if we consider a structure in the form of layers stacked on top of each other then the amplitude distribution from one layer will be in the form of streaks through the R.L. points. If the layers are packed in

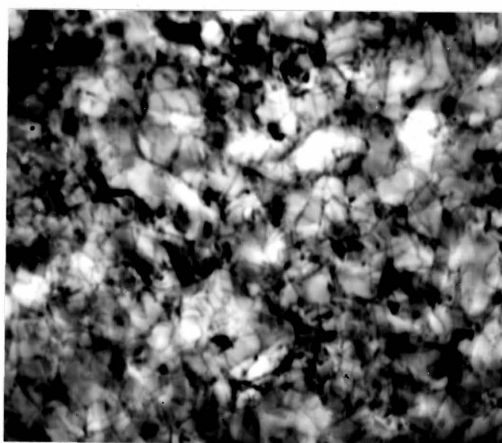
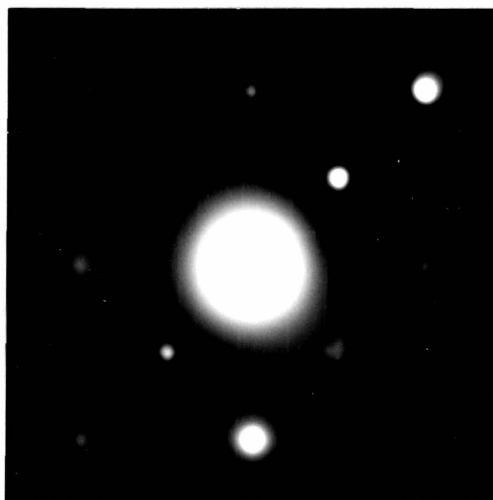


Fig 29

0.5 μ

Transmission electron micrograph of a ZnTe film grown on Ge(100). Showing streaking effect in the corresponding diffraction pattern on the top.

a regular way on top of each other, or crystals of greater thickness are built up then the streaks shorten. However, if the layers are not packed regularly i.e. if there are faults, then at least some of the spots will have streaks through them, the intensity of the streaks will increase with the number of faults. Such streaks can give rise either to streaks or to spots on the diffraction patterns. Consider for example fig 30 which shows a crystal with faults parallel to a plane which is not parallel to the plane of the foil. The intensity distribution will be in the form of two streaks one perpendicular to the plane of the foil and other perpendicular to the faults. These spikes project through the Ewald sphere of reflection and so it is possible to observe diffraction patterns at tilts other than that required for the exact Bragg condition for the particular pattern. The pattern is made by the points of intersection of the spikes and the sphere of reflection. So in this case two spots can occur.

The streaks will only show up in the diffraction patterns 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. The positions of the pseudo-spots are determined by the point of intersection of the streaks with the sphere of reflection. In cases where none of the streaks lie in the plane of the diffraction pattern, for example in (100) sphalerite diffraction patterns, evidence of streaking will

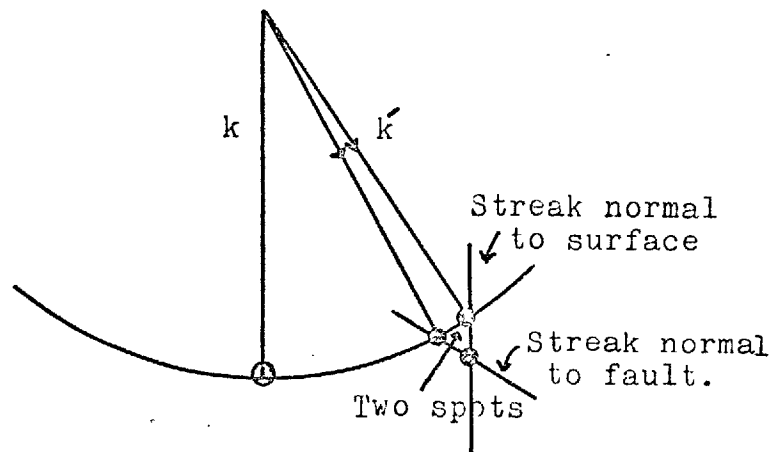
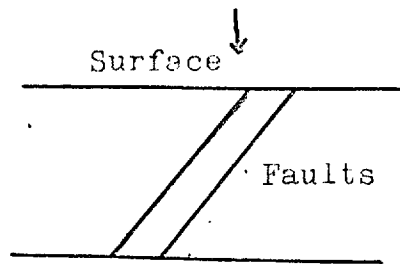


Fig.30

Effect of streaks from faulted crystal, showing how two spots can be produced by intersection of the reflecting sphere of the two streaks respectively normal to the crystal surface, and to the plane of the fault.

be detected only when the film is tilted or buckled away from the exact (100) position. If the film is slowly tilted, pseudo spots due to the intersection of the streaks and the sphere of reflection are seen to run away from or towards the matrix spots along the direction corresponding to the projection of the $\langle 111 \rangle$ directions on the (100) plane i.e. along the $\langle 011 \rangle$ directions.

Fig. 31 shows the reciprocal lattice near the (100) orientation along with the position of Ewald sphere and streaks. By visualising the change of orientation of the film or Ewald sphere a diffraction pattern similar to fig 29 results.

It may be pointed out that in fig 29 the groups of four intensity maxima consisted of pseudo spots and not real spots as shown by the following two facts. Firstly these spots are not circular but elliptical due to the fact that these correspond to positions where the sphere of reflection cuts through $\langle 111 \rangle$ streaks, which are of circular cylindrical form. Secondly the distances of the pseudo spots from the matrix spots (reciprocal lattice points) at the centres of the arrays was not constant as can be seen in the fig. The separation of the pseudo spots could be seen to vary continuously when the specimen was tilted so that the sphere of reflection cut the streaks at varying distances from the reciprocal lattice points. These pseudo spots have also been observed previously in films of ZnS (Woodcock and Holt 1969) and CdS (Wilcox and Holt 1971) grown on (100) surfaces of NaCl.

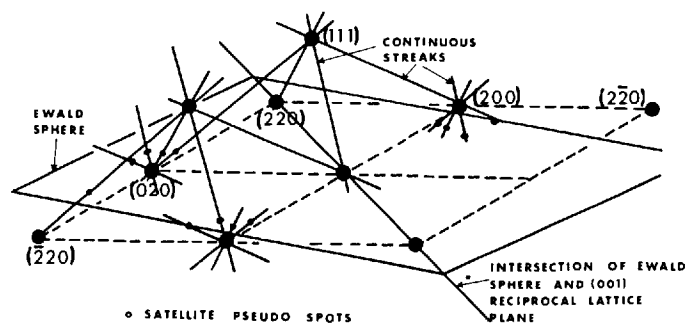


Fig. 31

Diagram showing how satellite pseudo-spots are formed where the Ewald sphere of reflection intersects the continuous $\langle 111 \rangle$ streaks in reciprocal space. These streaks are due to the defects lying on the $\{111\}$ planes in the film.



Fig. 32

0.5 μ

Bright field micrograph of a ZnTe film grown on Ge(100) showing the presence of fine fringes.

Another interesting feature is that the interference of the beams corresponding to satellite pseudo spots gives rise to characteristic contrast effects. In an area covered by one $\{111\}$ planar defects which might be a stacking fault, one of the satellite pseudo spot beams might be strongly excited. In such an area on the bright field micrograph interference between the pseudo spot beam and the direct transmitted beam would give rise to a set of fringes as shown in fig 32. In the cases of ZnS and CdS films grown on (100) faces of NaCl these fringes were shown to occur with variable spacings corresponding to the variable positions of the pseudo spots, and in varying contrast on a very fine scale and with a very high density corresponding to the presence of an estimated density of 10^{12} to 10^{13} planar defects cm^{-2} . This fine scale fringe contrast was the dominant and characteristic feature of the bright field micrographs of these films. The same fringe contrast was quite often observed in the bright field micrographs of ZnTe films grown on (100) oriented germanium in the present work.

4.6.4 Anti-Phase Domain Boundaries

The occurrence of anti-phase domains in crystals of semiconducting compounds with the wurtzite or the sphalerite structure is considered to affect the overall value for the sample of polarity-dependant properties, as certain physical parameters measured in polar directions reverse sign when the polarity is reversed. Examples of polarity dependent parameters

are the piezoelectric and pyroelectric constants. If the sample contains equal volumes of matrix and anti-phase material the averaged value of such a parameter will be zero. The effect of the presence of any volume percentage of anti-phase material is supposed to reduce the measured value of the parameter proportionally. Holt (1969) has suggested that the electrical and optical properties of APBs should resemble those of grain boundaries. As the periodicity of the lattice potential is disturbed by APBs, scattering of charge carriers can occur. Since the like-neighbour bonds occur across APBs the possibility of trapping and recombination of charge carriers arise. In compounds that are predominantly covalently bonded the wrong bonds that occur have either more or less than two electrons per sp^3 hybrid orbital and should be readily excited so that electrons may tend to be either lost (donor action) or gained (acceptor action). The resultant charges are likely to be less than in the case of grain boundaries containing dangling bonds which have been observed to have charges as great as 2.5×10^{12} electrons cm^{-2} or one per 10^3 atoms in the surface. Such surface charges in semiconductors would result in band bending and in extreme cases might result locally in majority charge carrier sign reversal (Holt 1964). In predominant ionically bonded compounds APBs would automatically have a charge of the sign of the ions involved and of the order of 10^{15} electrons cm^{-2} i.e. one per ion in the surface. Such surface charges are not energetically possible and may be avoided either by a change

in the valence state of atoms concerned, or by the incorporation of impurity atoms, or by adopting an atomically non-planar configuration for the APBs.

So in view of these reasons it was very essential that the sample prepared for the electrical measurements should be free of anti-phase material. As is clear in the section 4.3 and 4.4 that the best samples were free of all these types of defects so this purpose was achieved very successfully. However, a detailed study of the anti-phase material in ZnTe films could not be taken in hand for the reason that only an extremely small number of ZnTe films showed the presence of APBs in the electron microscopic studies in the concluding stages of this project. In view of the scanty data available for the following micrograph in fig 33 the results may be taken with reservations.

The sphalerite structure characteristic of most of the important III-V and II-VI compounds is an ordered superlattice. Each of the elements of the compound with this structure occupies the sites of a fcc superlattice. Each fcc superlattice is offset by a quarter of a body diagonal of the fcc structure cell from the sites of the other superlattice. It is possible either for the A atoms (those of lower valence element in the compound) to occur on the (000) (white atom) sites of fig. 34 and the B atoms therefore on the $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ (black atoms) sites or for the A atoms to occupy the $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ sites. Changing from one occupation scheme to the other creates anti-phase domains between which polarity is reversed.

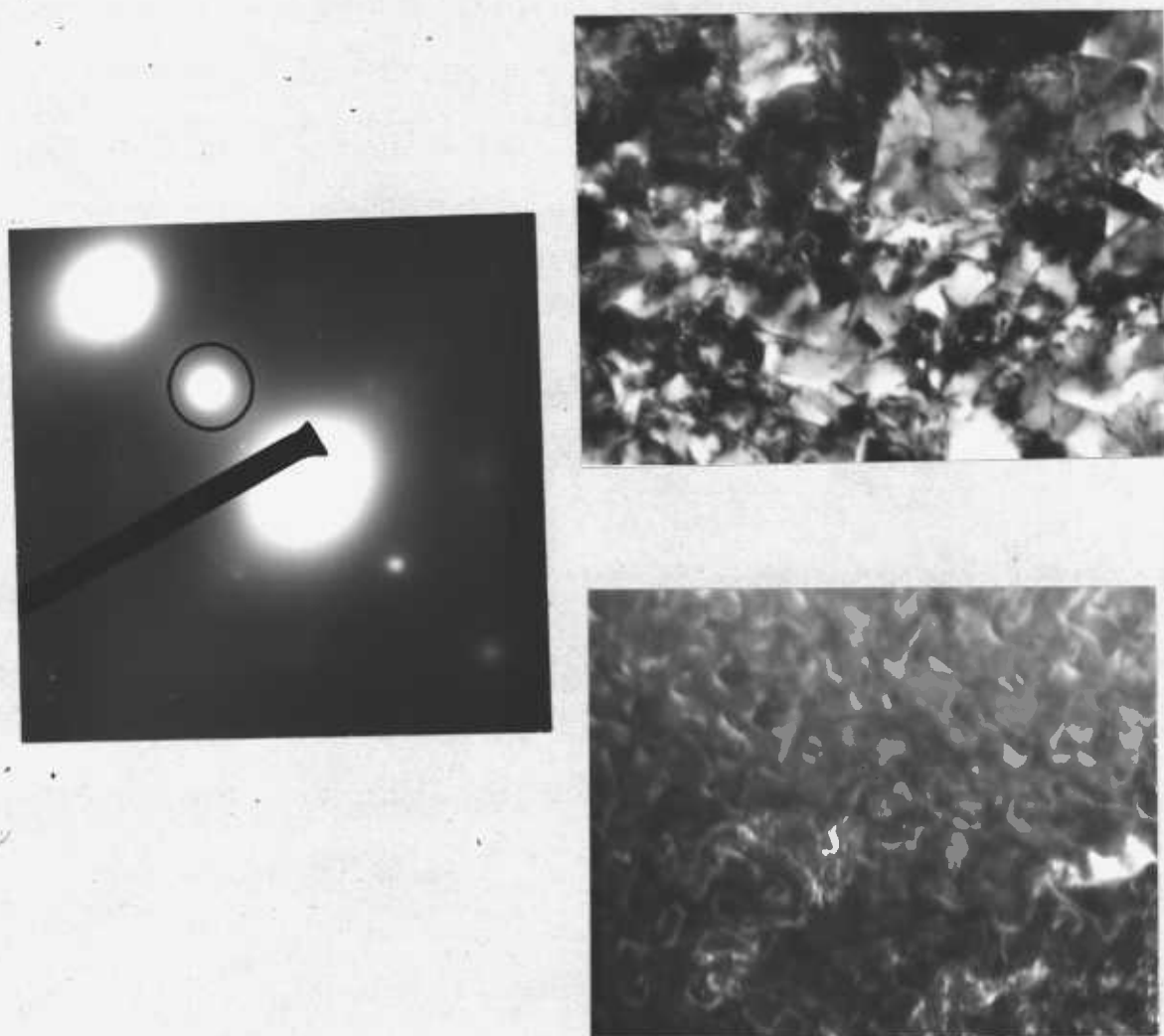


Fig. 33

Micrograph of a ZnTe film grown on Ge(100) showing anti-phase boundaries. (Top) Bright field micrograph. (Middle) Diffraction Pattern, spot for dark field micrograph is encircled. (Bottom) Dark field micrograph.

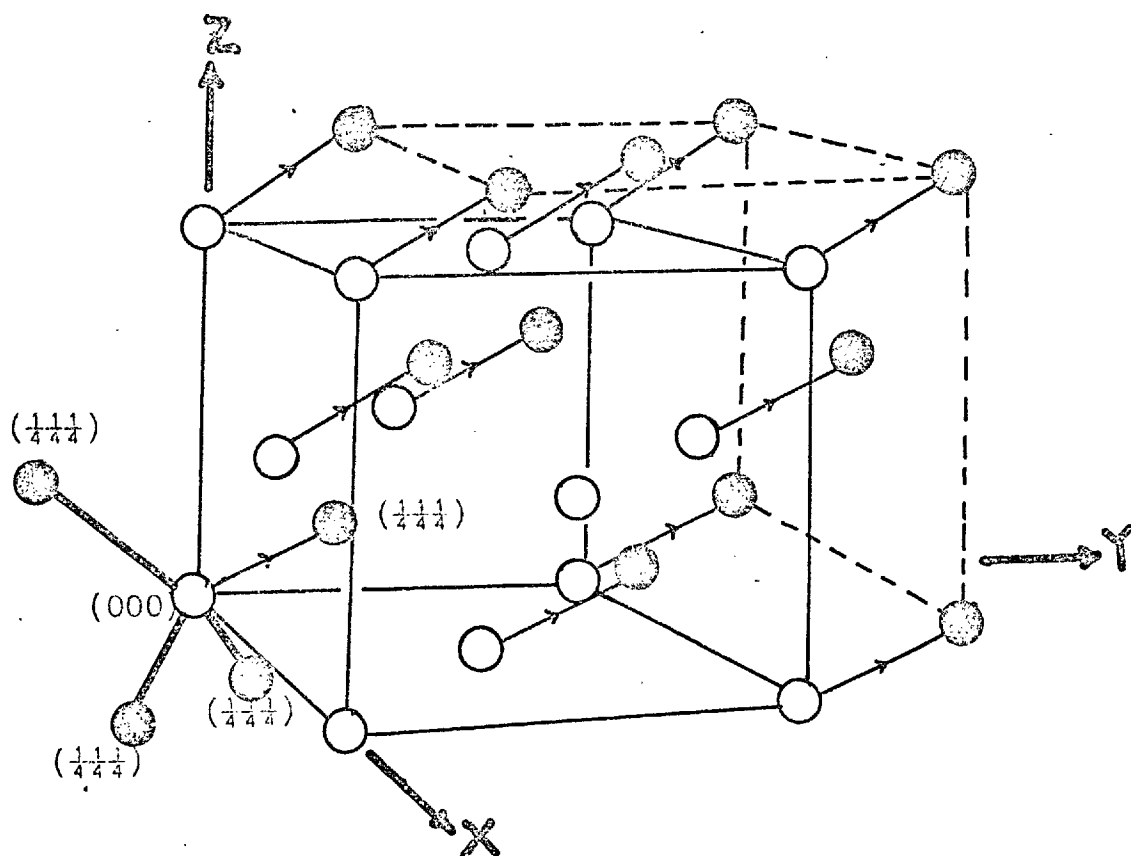


Fig. 34

A f.c.c unit cell of the sphalerite structure is drawn with fine solid lines. Part of another face centred cubic unit cell is shown by dotted lines. The latter cell is occupied by black atoms displaced by $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$ in terms of the lattice parameter along the three crystallographic axes from the white atoms of the first unit cell. The co-ordinates are given for the black atoms to which the white atom at the origin is bonded. The pairs of atoms connected by arrows are the basis of the structure.

The interface between anti-phase domains is an anti-phase boundary (APB). Holt (1969) has discussed the geometry of the anti-phase boundaries in the sphalerite structure and their connection with the grains of the material and dislocations. Without going into these details here only the method of observation of APBs is given below:

The positions of the atoms in sphalerite structure materials may be given in terms of their co-ordinates in an fcc unit cell (fig 34) as A atoms at $u_A \ v_A \ w_A = 000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$ and B atoms at $u_B \ v_B \ w_B = \frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}$. Substituting these values into the expression for the structure factor for hkl reflections

$$F_{hkl} = \sum_{uvw} f \ e^{2\pi i (hu + kv + lw)}$$

leads to the expression

$$F_{hkl} = \left[f_A + f_B e^{\frac{\pi i}{2} (h+k+l)} \right] \left[1 + e^{\pi i (h+k)} + e^{\pi i (k+l)} + e^{\pi i (h+l)} \right]$$

where f_A and f_B are the atomic scattering factors for the two constituent elements of the compound. The second factor in the structure factor is that for the fcc space lattice and is equal to 4 when h,k,l are all even or all odd and is equal to zero when h,k,l are mixed even and odd integers. The first term is the basis structure factor for permitted reflections (h,k,l all even and all odd) therefore

$$F_{hkl} = 4 \left(f_A + f_B \exp \frac{i\pi}{2} (h+k+l) \right)$$

which represents both the phase and the amplitude of the reflected wave. Holt (1969) has pointed out that there are four cases of permitted reflections in the sphalerite structure i.e when $h+k+l = 4n, 4n+1, 4n+2$ and $4n+3$ so that the structure factor $(F_{hkl}) = 4 (f_A + f_B), 4 (f_A + i f_B), 4 (f_A - f_B)$ and $4 (f_A - i f_B)$ respectively. Except in the third case i.e when $h+k+l = 4n+2$ and $F_{hkl} = 4(f_A - f_B)$ the type of reflection is due to superlattice while in the other three cases the reflections are fundamental.

The effect of interchanging the occupation of the sublattices across an APB is to interchange f_A and f_B in the structure factor. In the first case when f_A and f_B are interchanged then neither phase nor amplitude change is involved. So no APB contrast arises in the dark field electron micrograph using such reflections. In the second case $(f_A + i f_B)$ becomes $(f_B + i f_A)$ which does not alter the amplitude but involves a phase change. The fourth case i.e. $h+k+l = 4n+3$ and $F = 4(f_A - i f_B)$ is similar to the second except that the sign of the phase change is reversed. In the third case, however, when $h+k+l = 4n+2$ and $F = 4(f_A - f_B)$ the superlattice reflections undergo a phase change π across the APBs and strong APB contrast occurs in the dark field micrographs. Fig33 shows a micrograph of ZnTe film grown on (100) oriented Ge . When the 200 spot was used to get the dark field micrographs then a strong contrast of possible APBs was noticed. However without taking

more micrographs, both bright field and dark field, using fundamental reflections, it is not possible to be certain that these observations were of APBs. As very few films (two only) showed these kind of micrographs so detailed data could not be collected . This is an open branch for future work.

PART II

"ELECTRICAL PROPERTIES OF
ZnTe-Ge HETEROJUNCTIONS "

CHAPTER V

5.1. INTRODUCTION

Thin films of noble metals have been used for decorating glass and ceramics for over a thousand years and making of gold leaves is another ancient art of making thin films. But due to the potential technical value and scientific curiosity in the properties of two dimensional solids, thin films have been extensively studied for over a century. However, until this decade sufficient technological progress had not been made to give reasonable scientific confidence in the film research. The developments in the last two decades have made, directly or indirectly, significant contributions to many areas of basic and applied solid state research. Besides numerous other contributions the studies of thin films have also contributed some useful inventions such as the variety of active and passive, micro-miniaturized components and devices, cryotrons, bolometers, interface filters and reflection and anti-reflection coatings. In the last few years several books (Holland 1956, Anderson 1960, Berry et al 1969, Chopra 1969, Wieder 1970 etc.) have been written in order to collect the scattered literature in book form.

Much more recently, thin films have been used in the study of the relationship between the structure of solids and their physical properties. Practical applications include electrical circuits, optical instruments and magnetic information-storage devices. These more modern films are prepared by depositing material on to a clean supporting

substrates to build up the film to thickness rather than by thinning down the bulk material. Thin films for electronic circuit applications range from a few hundred Angstroms to tens of thousands of Angstroms in thickness. Extensive theoretical and experimental investigations of conduction in thin insulating films have led to an understanding of the various transport mechanisms involved and also to the determination of the barrier parameters and barrier profile for insulator-electrode interfaces.

For sometime past, it had been appreciated that vacuum deposition could play an important part in the manufacture of electronic components. In fact metallized paper and plastic foils had been used for more than a decade in the production of rolled foil capacitors. Evaporated selenium films were commonly used in the manufacture of selenium rectifiers and vacuum deposition had also been used extensively for making ultra-clean metallic contacts to a wide range of components. These included cathode ray tube screens, quartz crystal oscillators, transistors and diodes.

Vacuum deposition, as a technique of material preparation, has been shown to have many advantages for micro-miniaturization as seen in the success in the fabrication of passive devices such as resistors and capacitors. The technique would represent ^amajor contribution to the feasibility of production of complete circuits particularly for the needs of large scale computers of the future. So in view of these advantages this technique was

also selected for the present work of making ZnTe / Ge heterojunctions.

In recognition of the need of single crystal films, a good deal of work has been done on the various possible approaches. These fall into two broad areas, the one of epitaxy, or ordering of crystal growth by deposition on to a suitable single crystal surfaces, and the other of self ordered growth which is independent of substrate. As far as various types of transistors are concerned, only one, the field effect transistor, has been made wholly by vacuum deposition and been successfully demonstrated to have useful characteristics. As for other types, the bipolar transistor which depends upon single crystal material and the hot electron devices which depend upon $50 \text{ \AA}$ thickness films, it is believed that their success will depend upon the completion of sufficient fundamental research on the structure of thin films to make the necessary control of the various parameters practical.

The performance of ^a/thin film component depends upon its microstructure, which in turn depends upon the conditions existing during deposition. For example the electrical properties of semiconductors are affected by the type, the density and the distribution of dislocations within them. This is due partly to the interaction of charge carriers with the localized distortion in the lattice structure around a dislocation, and partly because of the migration of impurities to dislocation sites in order to

relieve the local strains. Thus heterogeneous regions may be formed within a semiconductor and these affect the concentration of the charge carrier and their mobility.

... So a thorough knowledge of the degree of reproducibility and purity of films and the effects of growth parameters is quite vital for the preparation of specimens for electrical and optical work. In fact the first portion of this thesis contains a detailed account of this study.

As a part of the programme of investigation of the epitaxial growth and structure of films of II-VI compounds, techniques were developed for the vacuum evaporation and transmission electron microscope examination of films of ZnTe deposited first on ionic crystal substrates (Holt 1966) and later on germanium (Mufti and Holt 1972). Systematic development of the growth technique to improve the structural perfection of the films resulted in the production of ZnTe films containing neither included grains of second phase material nor twins. Moiré fringe observation showed the ZnTe to be well oriented, i.e. within 1° of parallel alignment on germanium. The best films grown on (111) Ge had stacking fault densities below the values that would produce $\langle 111 \rangle$ streaking in the diffraction pattern and measurements showed that stacking fault densities to be about 10^{10} per cm^{-2} . The nature of the ZnTe films were ascertained by growing a few ZnTe films on " P " type Ge(111) substrates. It was observed from the I-V characteristics

of these heterojunctions that they behaved like " p-p " type diodes. By changing the substrate from " p " type to " n " type Ge (111) the I-V characteristics were altered the form for " p-n " type diodes. This "p" type growth of ZnTe films was checked to be a reproducible growth property of ZnTe. This was also confirmed by the previous observations in the literature, that ZnTe is unusual in being a wide band gap semiconductor (2.23 ev.) which is always "p" type due to a deviation from stoichiometry, when not intentionally doped. It has also been shown (Thomas et al 1964) that the "p" type conductivity is due to the presence of doubly ionisable native acceptors.

Before using any material for making electrically active or passive components it is always essential to find out the electrical behaviour and the limitations of that material. Usually the studies of I-V characteristics of the material are considered to be the most logical starting point, as the A.C. and D.C. I-V characteristics serve as the foundation for any advanced studies. A good deal of literature is being published now a days on the studies of I-V characteristics of dielectric thin films, and of isotype and anisotype heterojunctions. The greater part of the work on thin films capacitors and resistors has been concerned with the dependence of electrical properties on the method of preparation. Similarly the work reported on the structure of thin films has been concerned mainly with the relationship between structure and deposition parameters. There has been

only a limited effort to relate the electrical properties of films directly to the structure. This is the most fruitful field because it is essential to understand the basic properties of the material used in order to make satisfactory components. Mechanisms of failure, ⁿinstability, and break down in thin film components have the greatest chance of full interpretation by studying both cause and effects i.e. by investigating the changes of physical structure and chemical composition in relation to the changes of electrical parameters.

A list of the several papers on different combinations of II-VI compound heterojunctions will not serve any useful purpose here except that ZnS, ZnSe, CdTe and CdS have received much attention while ZnTe, as usual, has received the least of these compounds. In fact no paper on ZnTe heterojunctions had appeared prior to the present work. A few notable papers were published in the last few years which include Aven and Garwacki (1963), Ota and Moruzumi (1971,72), and Clevite group (1967), but not much definite and systematic information has been extracted out of these studies. For example Ota et al (1971) have studied the I-V characteristics of ZnTe on InAs and concentrated on the switching mechanism without any efforts to study the conduction mechanism or to obtain a mathematical expression for their electrical behaviour. Similarly Aven and Garwacki (1963) used ZnTe as a substrate for CdTe, and the Clevite group concentrated on the bulk properties of ZnTe, which

as pointed out before, may differ completely from those of the thin films.

So in order to bridge this gap a systematic study of the I-V characteristics of ZnTe on germanium was undertaken. With the experience of growing pure, stoichiometric and reproducible films of ZnTe on Ge with a minimum defect content (Mufti and Holt 1972), it was quite logical to start with the study of the I-V characteristics.

This portion of the project was divided into the following sections:

1. The growth of the desired quality of ZnTe films on Ge (part I of this thesis).
2. The making of low noise, low resistance ohmic contacts on the surfaces of the ZnTe and the Ge.
3. Plotting the I-V characteristics of the heterojunctions by manual and curve tracer methods.
4. The attempt to find the conduction mechanism of the devices.
5. A study of the properties of the interfacial junction with the help of a Cambridge Stereo-scan electron microscope.

Most of the results of this work could not be confirmed beyond my experimental observations as at the present, it is quite difficult to find any published data on the various properties of ZnTe. A few papers have been published recently (Smith 1971) in which parameters such as the Hall Coefficient, the resistivity and the carrier concentration have been measured but this work was done at

high temperature with "n" and "p" type doped ZnTe. Moreover these studies were done in Zinc rich or Tellurium rich atmospheres. However, the present systematic work on the structural and electrical properties of the ZnTe / Ge combination seems to be the first step in the understanding of this member of the family of II-VI compound heterojunctions. It is hoped that the observations and results in this thesis will not only act as a guideline for the future work but some of these results will be put on better footings with the discovery of more and more data about ZnTe.

CHAPTER VI

EXPERIMENTAL ARRANGEMENT

6.1. PREPARATION OF HETEROJUNCTIONS

As mentioned in chapter II and III, a good compromise between the different parameters of epitaxial growth was achieved so that reproducible films of good structural quality and desired thickness could be grown on germanium. In the electrical measurement work, however, bigger substrates could be used as there was no restriction to 3mm diameter as there was for the electron microscopy work. All the experimental set up and growth parameters such as rate of evaporation, pressure in the evacuating chamber, substrate preparation etc. were kept the same as for previous structural analysis work (Mufti and Holt 1972, and chapter II and III) except that the time for the growth of the films was increased upto 8 minutes. The substrates were 5mm diameter discs of germanium in the (111) orientation with "n" type conductivity of 0.03 to 0.05 Ω cm. The ZnTe films were grown to a thickness ranging from 3000 Å to 1 μ m i.e. 10,000 Å . The previous structural studies of ZnTe on Ge (Mufti and Holt 1972) had shown that epitaxial films of ZnTe were grown on Ge substrate kept at 350° C to 400° C, and fine grained randomly oriented polycrystalline films were grown when the substrate temperature was less than 200° C. So the two types of films were prepared for this work with the substrates held in these ranges of temperatures.

The nature and quality of the ZnTe films were ascertained with the help of an Electron Reflection Diffraction Camera, as owing to their thickness, they could not be studied in the Transmission Electron Microscope. The epitaxial films gave sharp spot diffraction patterns Fig 35 while the polycrystalline films showed ring patterns Fig 35

In the later part of this work it will be seen that the thickness of the heterojunctions plays a dominant part in the behaviour of the electrical conduction. The measurement of thickness to a great accuracy was therefore quite essential. Different techniques such as Talysurf, Watson Interferometry and Nomarski Interferometry were tried for this purpose (section 2.3.). It was found that the Nomarski Interferometric arrangement gave the best possible results. A photograph of Nomarski interference fringes is given in fig. 36 . A comparison of Fig. 5 and Fig. 36 clearly shows the difference in thickness of the films prepared for the structural analysis work and this work.

6.1.1 Making Of Contacts

In order to make electrical measurements on the heterojunctions these had to be provided with contacts and leads so that the device could be joined in the electrical measurement circuit.

At the start of the electrical measurement studies the making of good low noise, low resistance ohmic contacts was a difficult task. The great difficulty in making this kind of contact arises in part from the fact

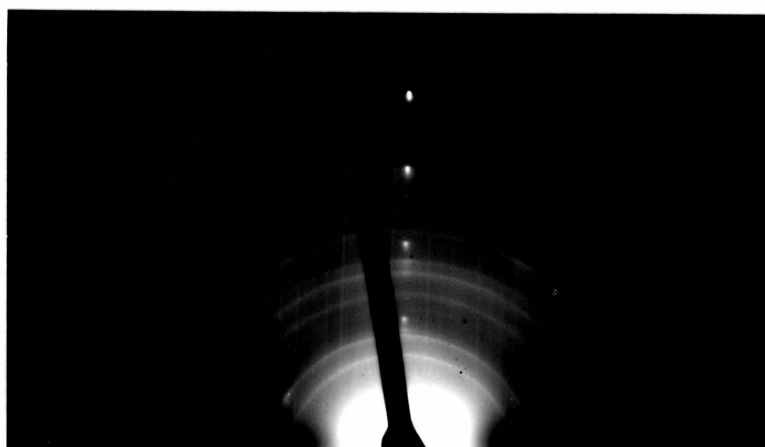


Fig 35

The nature of the grown layer of ZnTe in the ZnTe / Ge heterojunctions was ascertained with the help of electron reflection diffraction camera.

(Top) Diffraction pattern from an epitaxial film.

(Bottom) Diffraction pattern from a polycrystalline film.

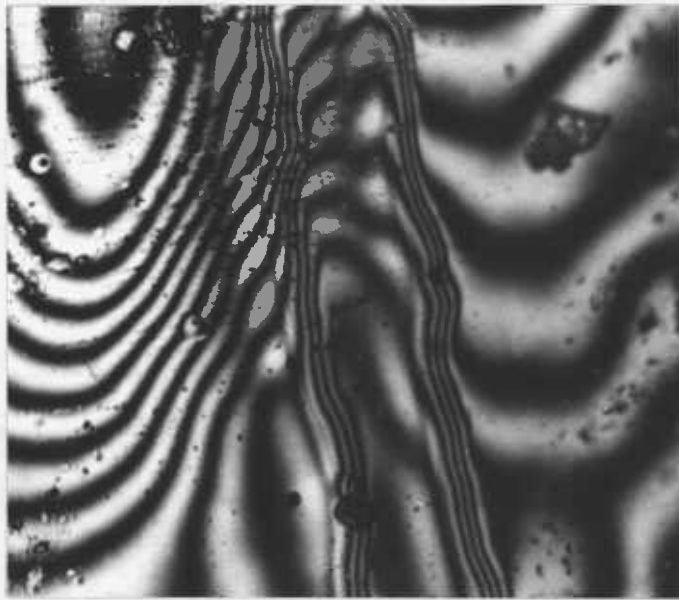


Fig. 36

THICKNESS MEASUREMENT OF A FILM

A picture of ZnTe / Ge heterojunction taken near the edge of the ZnTe film with a Nomarski Interferometry arrangement.

that at a contact, unlike the heterojunction, there are abrupt discontinuities of the lattice structure and surface effects sometimes override the properties of the contact. Further more it is not known what properties of the contact metal are needed in order to easily inject electrons into II-VI compounds. A good deal of research has been done to give this work of contact making a systematic footing, but still the situation is far from clear. Some papers (Blount et al 1966, Aven and Garawaki 1967) have put forward some useful hints, but they do not clarify the situation completely. Simmons (1971) in his review article has dealt with the three types of contacts i.e. neutral, ohmic and blocking contacts, and has given some mathematical expressions for each type of contact. For example for an ohmic contact he gave the condition:

$$\lambda = \frac{\pi}{2} \left(\frac{2kT K \epsilon_0}{e^2 N_t} \right)^{1/2} \exp \left(\frac{\psi_i - x - E_t}{2kT} \right)$$

Where ψ energy of the bottom of the conduction band,

x = distance from the interface,

N_t = number of shallow electron traps positioned at energy E_t below the bottom of the conduction band.

Unfortunately, at the present time, these types of expression are not of much help for the work of making contacts for II-VI compounds. For example the values of N_t and E_t are not yet known for ZnTe. So at this moment the best guidelines are to try the different techniques and materials used by other research workers. But this approach has again some limitations. Uptil now no concise specifications of

any combination of materials are given which will make good ohmic contacts. However, Blount et al (1966) have reviewed the requirements in general for obtaining such kind of ohmic contacts. In brief, these requirements call for a material for the contact electrode which has a smaller work function than that of the semiconductor if the semiconductor is "n" type, or larger, if the semiconductor is "p" type, and which when diffused into the semiconductor will act as a dopant providing majority carriers. Following these guidelines satisfactory ohmic contacts have been made with CdS, CdSe, CdTe, ZnS and ZnSe.

Low resistivity "p" type ZnTe was also contacted with moderate success with electroless gold (Crowder 1966, Aven and Gar wacki 1963 , Clevite group 1967). But the contacting in high or even moderate resistivity form, however, was found to be very difficult. Another problem is that the Aven and Gar wacki (1967) and Clevite group have used gold contacts on the bulk samples of ZnTe which can be easily etched, heated or diffused to a limited depth without any danger of diffusion of gold through the ZnTe to the contact on the other side of the film . For example Aven and Gar wacki (1967) pointed out that gold contacts to ZnTe have frequently displayed strongly non-ohmic behaviour even at room temperature. On investigations of the conditions which produce optimum room temperature gold contacts showed that 60 seconds of heating at 80° - 100° C after the forming step led to best results. No heating or heating at higher temperature

produced much inferior contacts. They improved their technique and introduced Li-diffused gold contacts to ZnTe which gave better performance. However, their method of first boiling the crystal with NaOH and putting on a dot of LiNO_3 to make a clean base for the gold contact, could not be tried in our case of ZnTe / Ge heterojunctions due to their unsuitability because of their small thickness for heating and possible diffusion.

In our work, Blount's suggestion was taken into consideration, and in view of the work functions of ZnTe (5.76 eV) and gold (5.1 eV), gold contacts were tried. Just after deposition of ZnTe on Ge the heterojunctions were transferred to another vacuum evaporation system in order to minimise the contamination on the surfaces of the heterojunctions. Gold contacts of about 1.5 mm diameter were evaporated on both sides of the heterojunctions i.e. one each on ZnTe and germanium. The reason for making a big area of contact was the suggestion of Aven and Garawacki (1963) that small size contacts have some definite resistance and hence can prove to be non-ohmic. In order to avoid any danger of diffusion of gold into ZnTe at high temperature and to comply with the suggestions of Aven and Garawacki the sample was allowed to receive a small quantity of radiant heat from the gold source after the deposition of gold.

6.1.2 Experimental Set up

In order to connect the specimen with the electrical measurement circuit the heterojunctions were mounted one at a

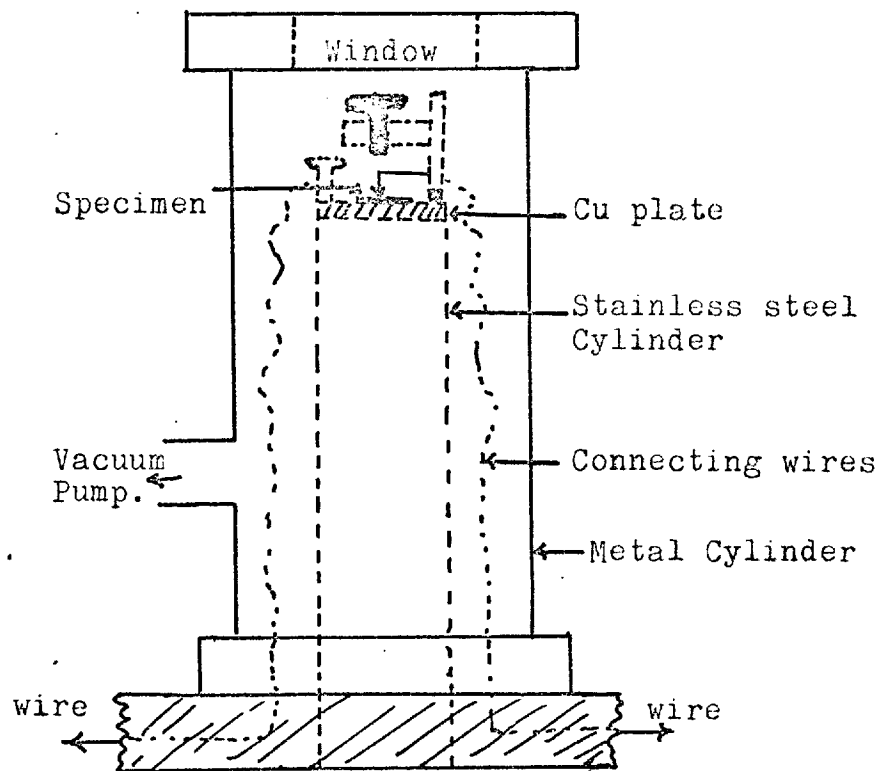


Fig. 37

The specimen mounting arrangement.

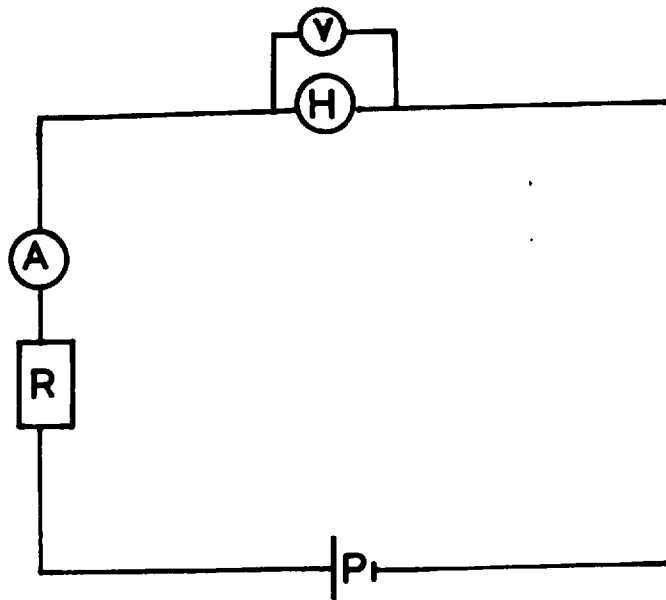


Fig. 38

The current-voltage characteristics measurements circuit. The various components are :

H .. Heterojunction.

A .. Ammeter.

V .. Voltmeter.

R .. Variable series resistance

P .. Stabilised DC power supply.

time in a special jig made in this laboratory and a line diagram is shown in Fig. 37 . In this jig the substrate gold contact was seated on a copper pedestal and a phosphor-bronze spring pressed down on the gold contact on the ZnTe film. The jig was fitted into a vacuum container with facilities for heating and cooling and for viewing the specimen. In order to make a better contact with the spring and gold, a drop of high conductivity silver dag solution was put on each of the gold contacts.

The electrical measurements were made by means of a simple circuit shown in Fig. 38 . The voltage from a stabilised D.C. power supply (P) could be varied in small steps and the corresponding current and voltage drop across the specimen were measured with an ammeter (A) and voltmeter (V). R was a variable series resistance.

I-V characteristics were also observed with the help of an Elliot Curve Tracer coupled to a cathode ray oscilloscope. It was found that no difference could be observed between the current-voltage characteristics obtained with slowly (manually) varied voltages and those obtained with rapid (50 Hz.) scanning across the same voltage range in the curve tracer.

CHAPTER VII

EXPERIMENTAL RESULTS

7.1. EXPERIMENTAL RESULTS

More-than twenty samples each^{of} epitaxial and polycrystalline ZnTe deposited on " n " type of germanium in (111) orientation were studied as regards their I-V characteristics. The following observations were made:

1. The I-V characteristics of all the epitaxial films, when plotted on a linear scale of current versus voltage, showed rectifying behaviour. The forward direction in which current rose rapidly with voltage was that for which " p " type ZnTe was biased positively and the " n " type germanium negatively. With the application of reverse bias (ZnTe negative) the current did not rise rapidly and an over all picture of the I-V characteristics showed a marked difference in the forward and reverse bias conditions (Fig. 39 and 40). For example the ratio between the forward and reverse bias currents for the same value of voltage often exceeded 10 and in some cases at low voltages this ratio was as high as 50.

2. All the heterojunctions containing polycrystalline ZnTe films showed less rectifying behaviour. A comparison of the I-V characteristics of epitaxial and polycrystalline structural heterojunctions is shown in Fig. 41.

7.1.1. The Initial Form Of I-V Characteristics

To gain an idea of the current transport mechanism involved in the observed I-V characteristics it is necessary to compare them quantitatively with the forms of the behaviour

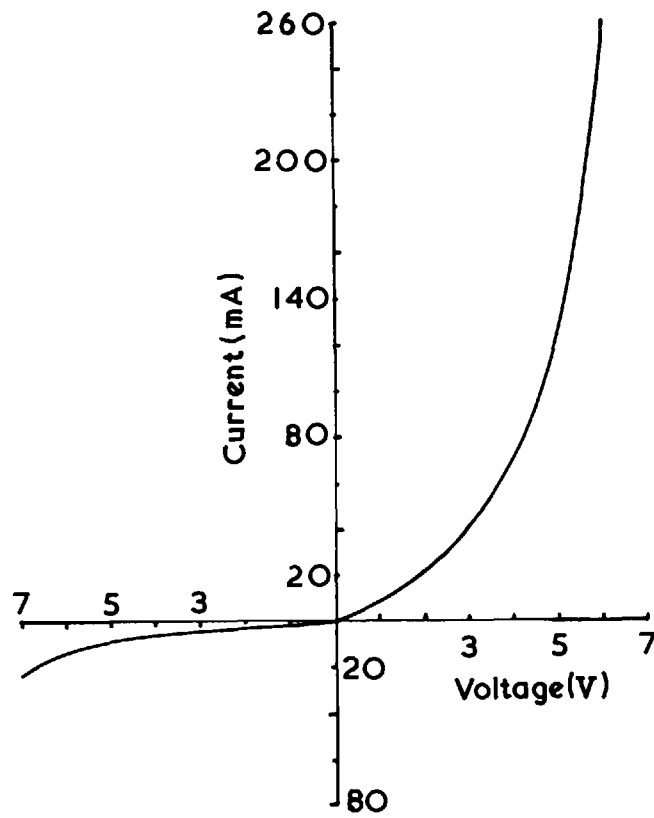


Fig. 39

Current-Voltage characteristics of an epitaxial
ZnTe / Ge heterojunction.

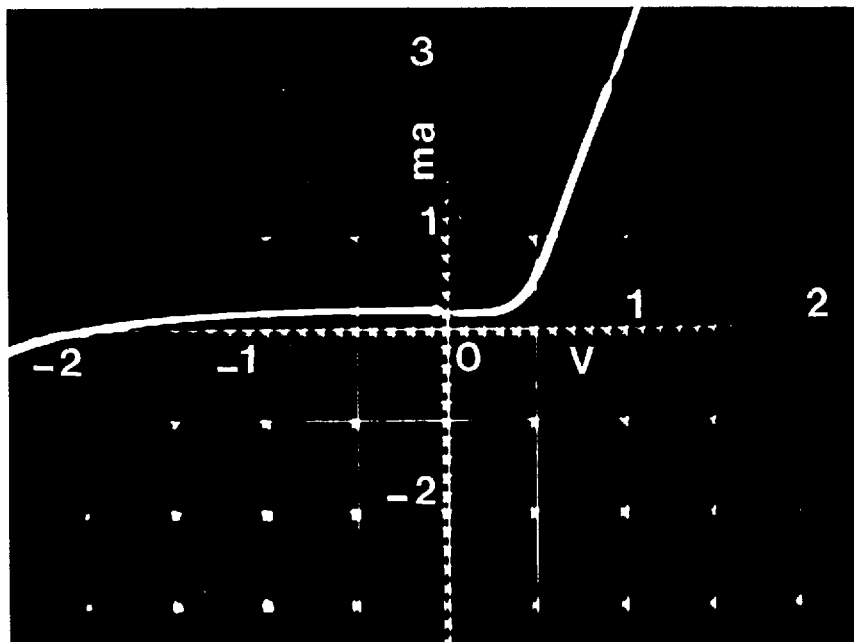


Fig. 40

Current-Voltage characteristics of an epitaxial ZnTe / Ge specimen. This picture was taken from the oscilloscope coupled with an Elliot Curve Tracer.

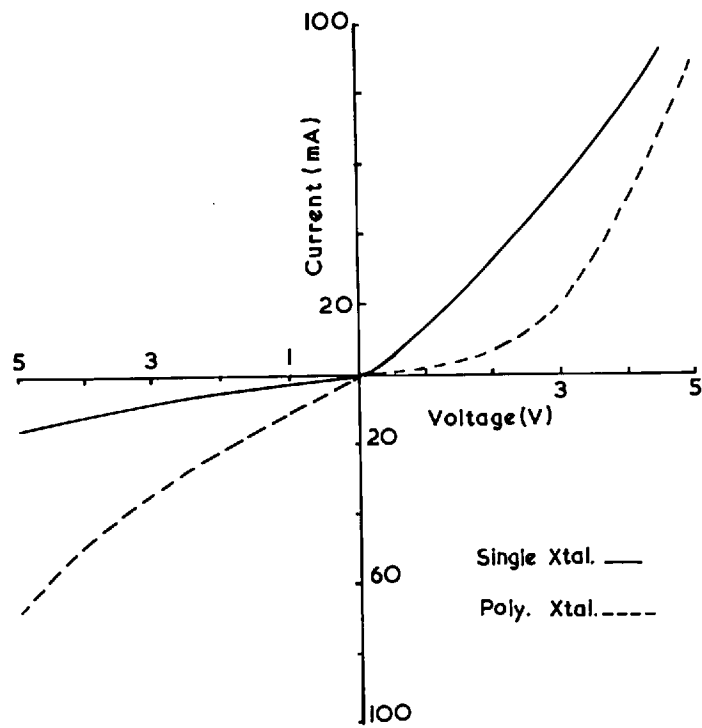


Fig. 41

Current- Voltage characteristics of epitaxial and polycrystalline ZnTe / Ge specimens.

predicted by the various theories of conduction through dielectric films and through barriers such as rectifying contacts and heterojunctions. The reviews of the literature (Jonscher 1967, 69, Simmons 1971, Callow et al 1968 and C. Van Opdorp 1969) indicate that three types of plots should be tried:

1. Van Opdorp(1969) reviewed the various models for anisotype heterojunctions. The energy band diagrams of Anderson,^{of} Oldham and Milnes and^{of} Van Ruyven and models for charge transport mechanisms such as ~~the~~ diffusion models of Anderson (1960) , Perlman and Feucht, tunneling model of Rediker, Stopeck and Ward (1964), tunneling recombination model of Riben and Feucht (1966) , and emission recombination model of Dolega (1963) led to characteristics of the form $I = I_0 \exp (CV)$, where C stands for characteristic constant for each model. To test whether the I-V characteristics of the ZnTe / Ge heterojunctions have this form, a plot of I-V characteristics of the devices should be tried on $\ln I$ versus V basis.

2. Basing their ideas on space charge limited currents and using the single and double injection of electrons Mott and Gurney (1948), Rose (1955) , Lampert (1956, 64) obtained relations of the form $I \propto V^2$ and higher powers. This suggested a suitable plot as $\ln I$ versus $\ln V$.

3. The Poole-Frenkel⁽¹⁹³⁸⁾ and Schottky effects (1914) which are forms of field assisted thermal ionisation lead to characteristics of the form $I \propto \exp (m V^{\frac{1}{2}})$. Therefore these results are also plotted as $\ln I$ versus $V^{\frac{1}{2}}$.

If a plot of the first type ($\ln I$ versus V) is linear, then conduction is controlled by the heterojunction (or one of the contacts) is indicated. If a plot of the second type ($\ln I$ versus $\ln V$) is linear with a definite slope over a wide range of voltages then space charge limited current theories for insulating materials may apply to the film. If the third type of plot is linear, either the Schottky or Poole-Frankel mechanism of conduction through insulating material is indicated as predominant in determining the form of I-V characteristics.

The forward I-V characteristics for the epitaxial ZnTe / Ge heterojunctions and polycrystalline ZnTe / Ge heterojunction specimens were plotted in all the above mentioned ways. It was found that as indicated in Fig. 42 the form of these forward characteristics was $I = I_0 \exp m V^{\frac{1}{2}}$. That is these characteristics were of the form to be expected on the assumption that the dominant process was Schottky or Poole-Frankel conduction through the ZnTe.

7.2.1 SCHOTTKY AND POOLE-FRANKEL EFFECTS

If an electron escapes to some distance from metal then the force acting on it at a distance x is

$$F = \frac{e^2}{4\pi\epsilon_0(2x)^2} \dots\dots (1) \quad (\text{From the method of Images})$$

and the potential energy is

$$U(x) = -\frac{e^2}{16\pi\epsilon_0 x} \dots\dots (2)$$

where ϵ_0 is the permittivity of free space.

As the electron approaches the metal surface to within a few atomic diameters, it is most strongly affected

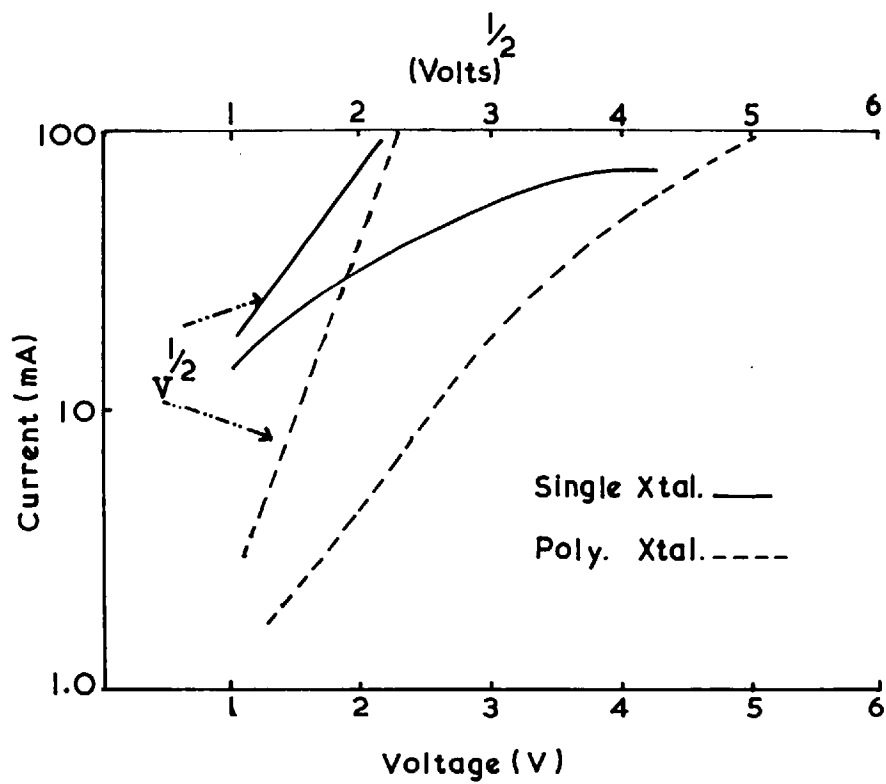


Fig. 42

Forward I-V characteristics of epitaxial and polycrystalline ZnTe / Ge specimens plotted as log I versus V and log I versus $V^{1/2}$.

by the ions closest to it. Therefore a more accurate model of the shape of the barrier is required at these distances. For example for a primitive cubic structure the total force on the electron is

$$F = \frac{e^2 \kappa}{4\pi\epsilon_0 (\kappa^2 + \frac{a^2}{z^2})^{3/2}} \dots\dots (3)$$

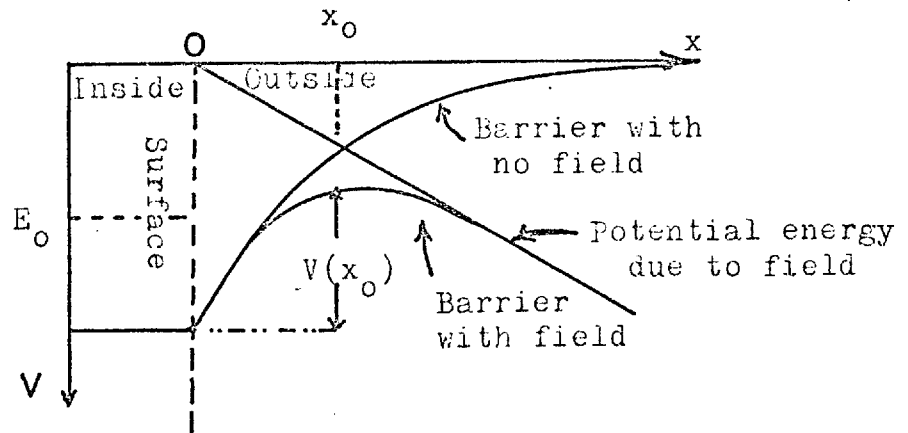
where "a" is the interatomic spacing and the potential energy is

$$U(x) = - \frac{e^2}{4\pi\epsilon_0 (\kappa^2 + \frac{a^2}{z^2})^{1/2}} \dots\dots (4) \quad \text{(Azaroff and Brophy)} \\ \text{(1963)}$$

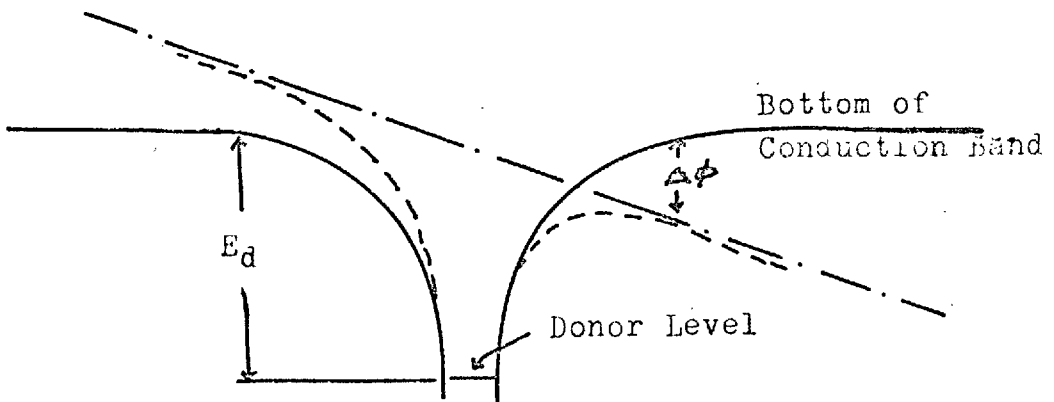
When an accelerating electric field is applied to the cathode surface then the emitted electrons are removed from the region of the cathode and are accelerated to the collector electrode. Here they constitute the measured thermionic emission current. The accelerating field also alters the potential energy barrier at the cathode surface and increases emission. This increase and its dependence upon the electric field is called the Schottky Effect.

7.2.2 Schottky Effect

The accelerating electric field produces a constant force on the escaping electron eE , where E is the electric field, and this results in a contribution to the potential energy of $-eEx$ at a distance x from the surface. The total energy of the escaping electron is then the sum of the surface potential barrier (equation 4) and that due to the field $-eEx$. As shown in the Fig. 43 the new potential energy curve has a maximum value, and the effective work function is reduced.



(a)



(b)

Fig. 43

(a) Reduction in the surface barrier due to an external electric field.

(b) Poole-Frenkel effect at a donor centre.

The point x_0 is the distance at which the effective force of the surface in the negative x direction is equal to the force, due to the external field, in the positive x direction.

Equating these forces

$$eE = \frac{e^2}{16\pi\epsilon_0 x_0^2}$$

and $x_0 = \left(\frac{e}{16\pi\epsilon_0 E} \right)^{1/2} \dots\dots (5)$

The effective potential energy in the presence of the field is that given by equation (2) less that resulting from the field.

$$U(x) = -\frac{e^2}{16\pi\epsilon_0 x} - eEx \dots\dots (6)$$

The height of the barrier at x_0 is found by substituting equations (5) and (6)

$$-U(x_0) = -e \left(\frac{eE}{4\pi\epsilon_0} \right)^{1/2} \dots\dots (7)$$

Since the work function is the difference between the barrier height and the position of the Fermi level, equation (7) represents the effective reduction in the work function due to the applied field. So the thermionic emission current of charge carriers over a potential barrier of height ϕ_0 , at a contact leads to the Richardson-Schottky current field relationship for a neutral contact i.e.

$$I = A_0 T^2 \exp\left(-\phi_0 - \frac{\beta_s F^{1/2}}{kT}\right) \quad \text{(Azaroff and Brophy) (8)} \\ \text{(1963)}$$

where A_0 is a universal constant which has the value

$$A_0 = 1.2 \times 10^6 \text{ A / m}^2 \text{ deg K}^2$$

and

$$\beta_s = \left(\frac{e^3}{4\pi\epsilon\epsilon_0} \right)^{\frac{1}{2}}$$

which shows that the observed thermionic emission at constant temperature increases with applied field and that a plot of $\ln (I / T^2)$ as a function of $E^{\frac{1}{2}}$ is a straight line.

7.2.3 Poole-Frenkel Effect

In the case of a point defect (such as a donor like centre in a crystalline lattice) which can be treated as an electron trapped in a Coulombic potential energy well when an external electric field is applied to the specimen then the situation is slightly different. The potential energy required for the electron to escape in the direction of the applied field F , is reduced by an amount $\beta_{P.F} F^{\frac{1}{2}}$ (Simmons 1971), where

$$\beta_{P.F} = \left(\frac{e^3}{\pi\epsilon\epsilon_0} \right)^{\frac{1}{2}}$$

e is the electronic charge and ϵ the dielectric constant of the material.

As a result the thermal release of the electron from the trap is facilitated so that the probability of thermal release becomes proportional to

$$\exp - \left(\phi - \frac{\beta_{P.F} F^{\frac{1}{2}}}{kT} \right)$$

where ϕ is the depth of the trap. This is known as the Poole-Frenkel effect and should only be observed at relatively high fields. Then the I-V characteristics of insulator films can be represented by

$$I = n_0 e \mu F \exp - \left(\phi - \frac{\beta_{P.F} F^{\frac{1}{2}}}{kT} \right) \dots (9)$$

where n_0 is the total density of electrons in the traps at

0° K , μ , the mobility of the carrier, k , the Boltzmann's Constant and T is the absolute temperature.

From equations (8) and (9) it is clear, that in simple terms, the initial form of the theories of the Schottky and Poole-Frenkel effects the coefficients of $F^{\frac{1}{2}}$ in the exponential differ by a factor 2 i.e. $\beta_{\text{P.F.}} = 2 \beta_{\text{S}}$. On this interpretation, current-voltage characteristics plotted as $\ln I$ versus $V^{\frac{1}{2}}$ should have slopes given by

$$m = \frac{\beta}{k T L^{\frac{1}{2}}} .$$

where β may be either $\beta_{\text{P.F.}}$ or β_{S} and L is the thickness of the film and is introduced to convert $V^{\frac{1}{2}}$ to $F^{\frac{1}{2}}$.

Since the coefficient β for either of these is given by essentially fundamental constants, it was originally thought that it should be possible to decide between the two effects from the numerical value of the coefficients. At this stage however, practical difficulties arise, since it has generally not been found possible to obtain satisfactory agreement with either theory. Simmons (1971) and Jonscher (1967, 1969) have quoted several examples from the literature where the experimental value of β did not agree with either of the theoretical values of β . So an attempt was made in this part of the project to find out the value of β in our devices (ZnTe - Ge heterojunctions) so that a definite idea of the electrical transport mechanism could be established. In order to proceed with this part it is quite relevant to discuss our experimental results in the

light of the various anomalies encountered in this field:

1. Ambiguous definition of dielectric constant ϵ :

According to Frenkel (1938) ϵ is the high frequency dielectric constant and has its value as the square of the refractive index. But in the later work, in order to bridge the gap between the experimental and theoretical values of β , several workers (for example Mead 1962, Hirose and Wada 1964) have digressed from this definition and have used abnormally high values of ϵ which sometimes seemed quite unrealistic. So, although the theoretical expressions for $\beta_{P.F}$ and β_S (as given earlier) depend only upon fundamental universal constants unanimity has not been reached as to which form of dielectric constant ϵ is to be used.

2. Different values of ϵ for ZnTe: No single generally accepted value of the dielectric constant(ϵ) of ZnTe has been found in the literature. Three different values, 7.28 (Marple 1964) , 9.67 (Segall et al 1967) and 10.1(Koch-Light Co. data)are widely used, and no single value could be chosen from among these three. In order to cope with these anomalous values, three set of calculations of our experimental results are done.

3. Anomalous expressions for β : The most widely used expressions for $\beta_{P.F}$ and β_S as put forward by Frenkel (1938) are

$$\beta_{P.F} = \left(\frac{e^3}{\pi \epsilon \epsilon_0} \right)^{1/2} \quad \beta_S = \left(\frac{e^3}{4\pi \epsilon \epsilon_0} \right)^{1/2}$$

Like several other research workers Boon (1971,

1972) is working to explain the difference between experimental and theoretical values of β by deriving modified expressions for β . In one of his papers (1972) he proposes the expression

$$\beta_{P.F.} = 2 \left(\frac{e^3}{\epsilon \epsilon_0} \right)^{\frac{1}{2}}$$

In another paper (1971) by discarding the classical model and making a quantum mechanical evaluation using the Virial theorem he derived a new expression

$$\beta_{P.F.} = \left(\frac{e^3}{4\pi \epsilon \epsilon_0} \right)^{\frac{1}{2}}$$

We have compared our experimental results of ZnTe - Ge with all these theoretical expressions.

4. Different expressions for current-voltage relationship:

Some authors (Padovani and Sumner 1965) improved the agreement between the experimental and theoretical values of β by adopting the rule of expressing the dependence on current as

$$I \propto \exp \left(\frac{e \beta E^{\frac{1}{2}}}{k(T + T_0)} \right)$$

where T_0 is a "suitable temperature". It is very difficult to justify this procedure on any physical grounds and to ascribe any significance to the parameter T_0 so this expression of I-V characteristics will not be employed in our future discussion.

(ii) Simmons (1967) has pointed out that in the case of absence of traps or even in the presence of traps and donor levels the expression for I-V characteristics is

$$I = I_0 \exp \left(\frac{\beta_{P.F.} F^{1/2}}{2kT} \right)$$

(iii) Mead (1962) has suggested that since traps abound in an insulator and since a trap having a Coulombic type barrier would experience the Poole-Frenkel effect at high fields, thereby increasing the probability of escape of an electron immobilised there in, the current density in thin film insulators containing shallow traps is given by

$$I = I_0 \exp \left(\frac{\beta_{P.F.} F^{1/2}}{kT} \right)$$

In view of all these alternatives it was considered advisable to calculate value of $\beta_{P.F.}$ and β_S from our experimental data of ZnTe -Ge heterojunctions using all the different algebraic expressions and all the different values of ϵ listed in (2). Then by observing which calculation gives the best fit it will be possible to draw conclusions about the mechanism of conduction in the ZnTe - Ge heterojunctions.

A table of calculated theoretical values of β is given on the next page.

TABLE: THEORETICAL VALUES OF β_F AND β_S .

All the values of β_F and β_S are expressed in units of $\text{ev } V^{-\frac{1}{2}} \text{ m}^{\frac{1}{2}}$ (ev, electron volt, V, volt, m, meter.)

EXPRESSION β	$\epsilon=7.28$	$\epsilon=9.67$	$\epsilon=10.1$
$\beta_F = \left(\frac{e^3}{\pi \epsilon \epsilon_0} \right)^{\frac{1}{2}}$	2.71×10^{-5}	2.43×10^{-5}	2.38×10^{-5}
$\beta_F = 2 \left(\frac{e^3}{\epsilon \epsilon_0} \right)^{\frac{1}{2}}$	9.93×10^{-5}	8.6×10^{-5}	8.43×10^{-5}
$\beta_F = \left(\frac{e^3}{4\pi \epsilon \epsilon_0} \right)^{\frac{1}{2}}$	1.40×10^{-5}	1.23×10^{-5}	1.18×10^{-5}

As $\beta_F = 2 \beta_S$ so the respective values of β_S for all these expressions are 2 times less than their corresponding values of β_F .

The comparison with the experimental values of β makes it clear that the expression $\beta = 2 \left(\frac{e^3}{\epsilon \epsilon_0} \right)^{1/2}$ does not come near to our results. The other expression $\beta = \left(\frac{e^3}{\pi \epsilon \epsilon_0} \right)^{1/2}$ gives much better agreement with the experimental results.

So in the following table only the comparison with the values of theoretical expression $\beta = \left(\frac{e^3}{\pi \epsilon \epsilon_0} \right)^{1/2}$ will be considered.

Another conclusion was also made that our experimental data did not fit with the expression for the current and voltage as

$$I = I_0 \exp \left(\beta F^{1/2} / 2kT \right)$$

but with

$$I = I_0 \exp \left(\beta F^{1/2} / kT \right)$$

The best fit with this expression (Mead 1962) is also consistent with our observations (Figs 39, 40, 41.) which indicate the presence of traps at low applied voltages to the ZnTe - Ge heterojunctions. So in the following table on the next page only the calculations are shown according to the formula:

$$I = I_0 \exp \left(\beta F^{1/2} / kT \right)$$

TABLE: EXPERIMENTAL VALUES OF β_F .

The notation of the columns is as follows:

T, thickness of the ZnTe films as measured.

S, experimental slope as measured from the plot $\ln I$ vs $V^{\frac{1}{2}}$.

β experimental value of β_F , from $\beta_F = SkTL^{\frac{1}{2}}$.

R(10.1) = Experimental value of $\beta_F \div$ Theoretical value of β_F for $\epsilon = 10.1$.

R(9.67) same as above but for $\epsilon = 9.67$.

R(7.28) same as above but for $\epsilon = 7.28$.

% Diff. Stands for the percentage difference between experimental and theoretical values of β_F for $\epsilon = 7.28$.

Units of β_F , as in previous table i.e. $\text{ev } V^{-\frac{1}{2}} \text{ m}^{\frac{1}{2}}$.

FOR EPITAXIAL ZnTe/Ge HETEROJUNCTIONS

<u>No.</u>	<u>T</u>	<u>S</u>	<u>β_F</u>	<u>R(10.1)</u>	<u>R(9.67)</u>	<u>R(7.28)</u>	<u>% Diff.</u>
1.	6500 Å	1.4	2.87	1.2	1.18	1.05	5.9
2.	8000 "	1.38	3.1	1.3	1.27	1.14	14.0
3.	7250 "	1.38	2.9	1.21	1.19	1.07	7.0
4.	4000 "	1.95	3.1	1.30	1.27	1.14	14.0
5.	4000 "	1.74	2.82	1.18	1.16	1.04	4.0
6.	5000 "	1.6	2.91	1.22	1.19	1.07	7.3
7.	4200 "	1.93	3.2	1.34	1.31	1.18	18.0

FOR POLYCRYSTALLINE ZnTe / Ge HETEROJUNCTIONS

1.	10,000 Å	3.91	9.9	4.15	4.08	3.65	
2.	9,000 "	4.0	9.75	4.1	4.02	3.59	

In view of the considerable range of values for ϵ for ZnTe in the literature, this agreement between the theoretical and experimental values of β is quite satisfactory and indicates that the experimental values are consistent with the Poole-Frenkel effect. This comparison is a good test of the applicability of the theories as the expression for β contains no unknown adjustable parameters.

The intercepts of the $\ln I$ versus $V^{1/2}$ plots with the current axis i.e. the experimental values of I_0 are not usefully analysable. Even the simplest expression for I_0 , that in equation

$$I = n_0 e \mu F \exp (- \phi / kT)$$

contains three unknowns n_0 , ϕ and μ . Moreover more than one type of centre, for example both donors and traps (Simmons 1971), leads to more complicated expression for I_0 containing still more unknown parameters. Thus without additional experimental information quantitative analysis of the experimental values of I_0 cannot be carried out.

The forward I-V characteristics of polycrystalline ZnTe / Ge specimens were also of the form $I = I_0 \exp (mV^{1/2})$ as shown in Fig. 42. In this case however, m was found to have experimental values which led to values which were far larger than those for the epitaxial films.

This small difference (~ 4 to 10%) between the experimental and theoretical values of β is quite understandable from the fact that only recently quite a number of papers have been published which have questioned

the fundamental assumptions and validity of Poole-Frenkel effect. It has been argued (Murgatroyd 1972, Jonscher 1967 ^{etal} Hall 1971, Connell/1972 and Hill 1971) that the interpretation of current voltage characteristics has not reached the point that they may be used unambiguously to identify particular macroscopic process which contribute to the conduction. For example Murgatroyd (1972) argued that commonly it is assumed or implied that the field dependence of the conductivity is entirely due to one effect i.e. due to the presence of high fields there occurs an increase of the rate of emission of trapped carriers from the localized centres. However, it is possible that other processes which influence the conductivity may be significantly perturbed in some way by high fields so that the observed conductivity is in fact determined by a combination of effects which may act independently or be inter-related. Jonscher (1967) even questioned the assumptions and treatment of impurities in the Coulombic potential. He questioned the justification of the assumption that if the bound carrier is capable of orbiting round the impurity and can be presumed to sample the potential over relatively large distances even still at high fields such as 10^5 V / cm the maximum potential occurs at a distance of $50 \text{ \AA}$ which is of the order of 10 interatomic distances. This shows that the Coulombic potential assumption is not justified in detail. Similarly Hall (1971) considers the the basis of Poole-Frenkel theory as essentially classical and stochastic. In his paper he takes account of the quantum

nature of the bound state occupied by the electron in the centre and assumes the existence of Wannier-like localised states. According to him the Poole-Frenkel expression for the thermally stimulated emission of electrons from donor-like centres is far from adequate.

So in view of all these short-comings in the basic assumptions and derivations of the Poole-Frenkel effect and doubtful available data for ZnTe, the small difference between the theoretical and experimental value of β seems quite plausible. It may be pointed out, that inspite of all these critical remarks the results quoted in this thesis are in better agreement with the theory than any other results quoted so far in the literature. For comparison sake some other results from the literature are given in the following table.

Comparison Table:

N; Name of author,

M: Material Used.

β_f : Experimental value of β_f .

C: Comparison with theoretical values of β_f . i.e. $\frac{\beta_{ex}}{\beta_{th}}$.

<u>No.</u>	<u>N</u>	<u>M</u>	<u>C</u>
1.	Stuart, 1967.	Silicon Oxide.	1.1 (10 %)
2.	Kirov. 1970	CdS	One order diff.
3.	Timson et al 1971	Boric Oxide	Do
4.	Present work 1972	ZnTe/Ge.	1.04 (4 %)

7.3. THE EFFECT OF APPLICATION OF HIGHER VOLTAGES

7.3.1. Negative Resistance And Switching

When the applied voltages to the specimens were increased to higher values say more than 15 volts then the behaviour of the epitaxial and polycrystalline films as far as negative resistance and switching is concerned, followed the general pattern outlined below:

In a small minority of the specimens (fig .44) current controlled negative resistance (CCNR) (Pamplin 1970) was observed which was similar to that observed by Chopra (1965) in the " formed " thin oxide films of Niobium, tantalum and titanium sandwiched between thin film electrodes. Beyond the negative resistance region the dynamic impedance of the device was almost zero and the current increased with virtually no change in voltage drop across the specimen.

The majority of the heterojunctions showed the phenomenon of switching. This behaviour is shown in fig. 45. The various branches of the observed I-V characteristics were traversed experimentally in the sequence indicated by the numbering. It was found that two conductivity states could be obtained. The specimens in their initial state gave rectifying characteristics shown as 1 to 3 . The curves marked 1 and 2 are the forward characteristic which was that obtained with the " p " type ZnTe biased positively . When a reverse bias voltage was applied that exceeded a critical value of few volts which varied from specimen to specimen,

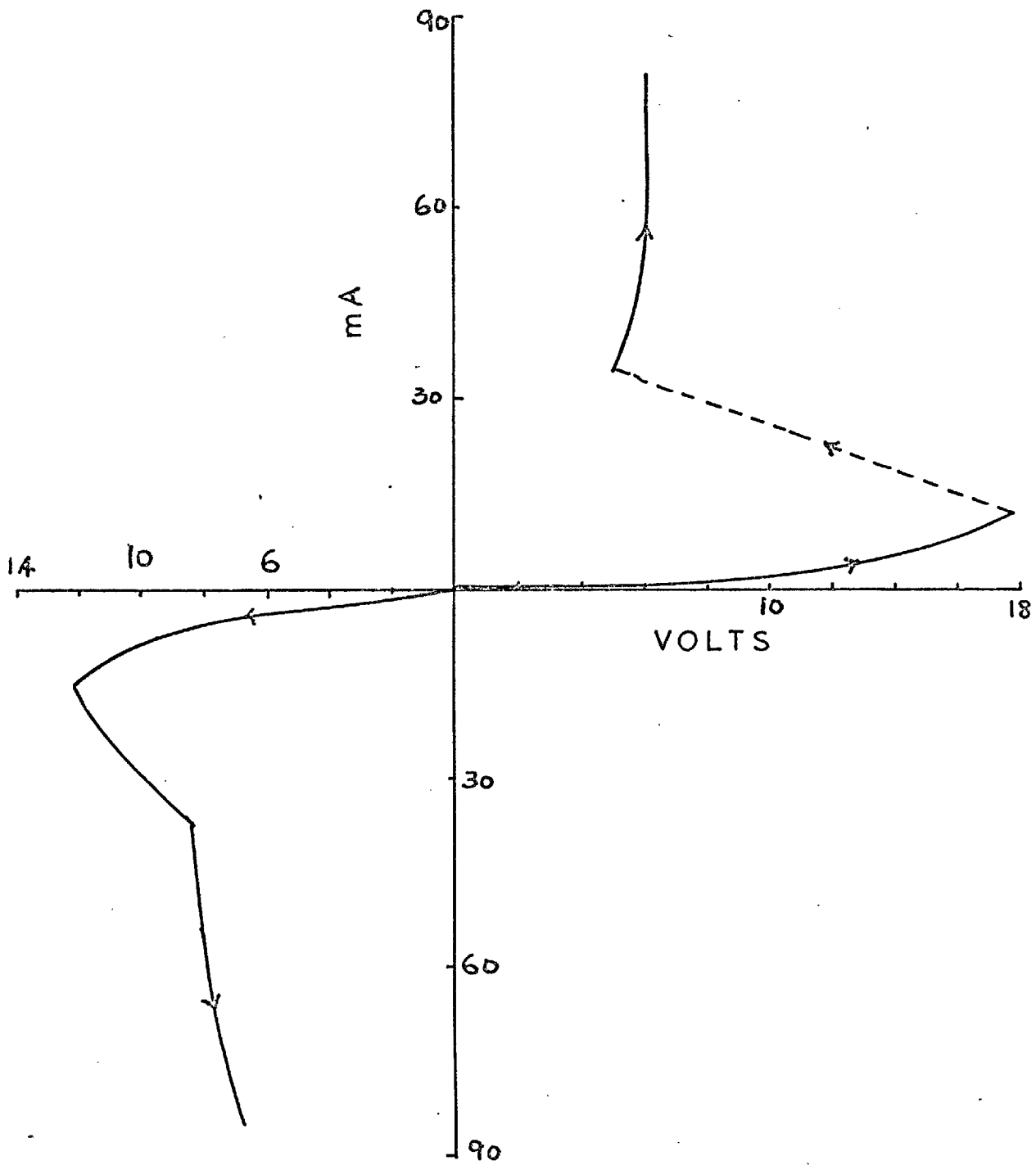


Fig. 44

Current-Voltage characteristics of an epitaxial ZnTe / Ge heterojunction showing "negative resistance".

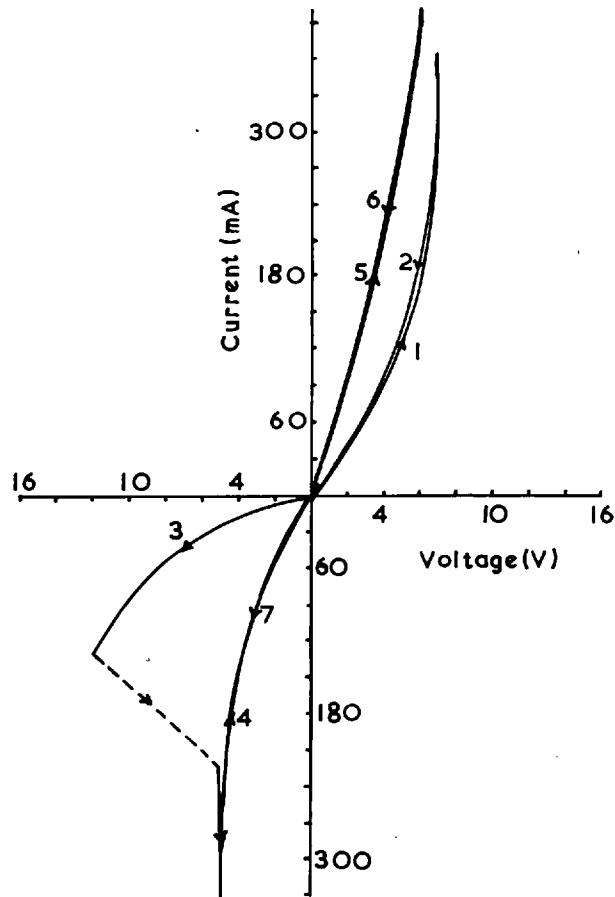


Fig. 45

Current-Voltage characteristics of a ZnTe-Ge heterojunction measured in consecutive order as numbered. At a critical reverse voltage the specimen switched permanently from the initial low conductivity characteristics 1,2,3 to high conductivity state of characteristics 5,6,4,7.

the specimens all switched permanently to low resistance characteristics of approximately ohmic form giving rise to the characteristics marked 5 and 6 and 4 and 7 . It has not been found possible to switch the specimens back to the high resistivity rectifying characteristics either by leaving the specimens without any voltage applied for periods upto several days nor by passing forward currents that were as large as possible without destructive heating of the films.

The observed switching is believed to be due to a change in the physical properties of the ZnTe film or heterojunction and not to gross structural or compositional changes in the specimens. The temperature was monitored by means of a thermocouple in contact with the gold film on the ZnTe placed near to the spring contact. It was observed that the temperature rises were small(5 to 10 degree C). Moreover they did not correlate with changes in the electrical properties. When at the end of the measurements the specimens were visually examined no changes in the films or gold contacts were seen. Moreover when the gold contacts were removed no changes in the ZnTe beneath could be seen by optical microscopy. The low conductivity and high conductivity states are also shown in fig. 46 which was taken with the help of a curve tracer. The state marked 1 is the low conductivity state while state 2 was obtained after applying a threshold reverse bias voltage which switched it from state 1 to the state 2.

In fact quite a number of times a number of

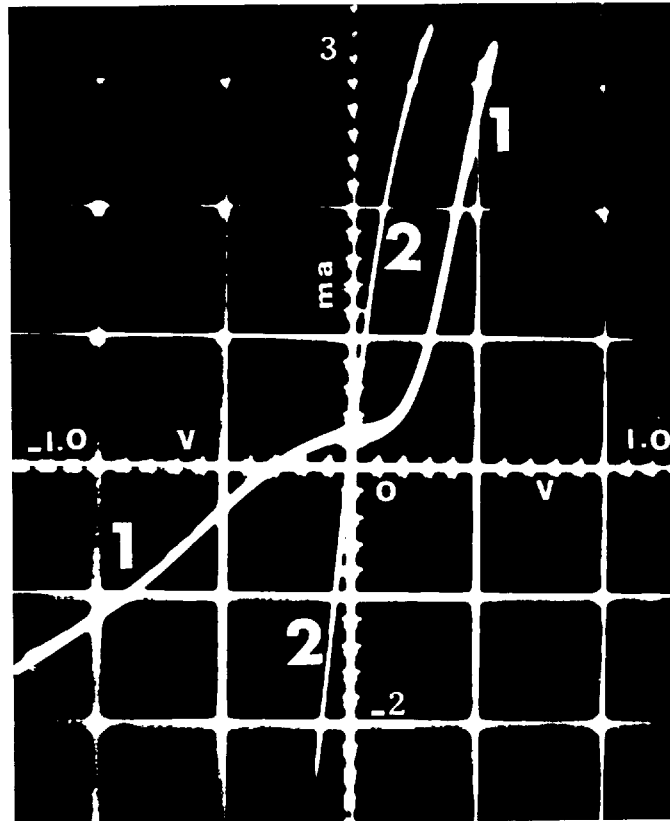


Fig. 46

Current-Voltage characteristics of an epitaxial pZnTe-nGe heterojunction as recorded by a curve tracer. The initial high resistivity "off" state 1 was switched permanently to the low resistivity "on" state 2 by applying a critical reverse voltage.

" metastable " " intermediate states " were observed between states 3 and 5 as shown in photograph (fig. 47). The fact that only a minority of the specimens (5 out of 20) showed intermediate conductivity states agrees with the observations of Hovel et al (1971) for the behaviour of his ZnSe / Ge heterojunctions. He has also pointed out that his number II type heterojunctions (which showed assymetrical I-V characteristics around the origin) showed less tendency to exhibit intermediate states as compared to type I ZnSe / Ge heterojunctions (for which the I-V characteristics were more or less symmetrical around the origin).

Like the Hovel's observations (1971) the forward biased high resistance state marked 1 and 2 in fig. 45 of ZnTe/ Ge is stable and switching did not occur out of this state and its memory was therefore infinite. The same was true for the reverse biased high resistance state at biases less than the threshold voltage. After switching had taken place the device remained in the low resistance state both at zero bias or with small applied voltage in either polarity.

A number of specimens, after switching from low to high conductivity states, were left from 2 to 6 days at zero bias. It was observed that at the end of the rest period most of the devices retraced their high conductivity state characteristics but two out of the 20 specimens showed a tendency to change impedences to slightly lower or slightly higher values. This odd behaviour was also observed by Hovel et al (1971) in some of his specimens of ZnSe / Ge.

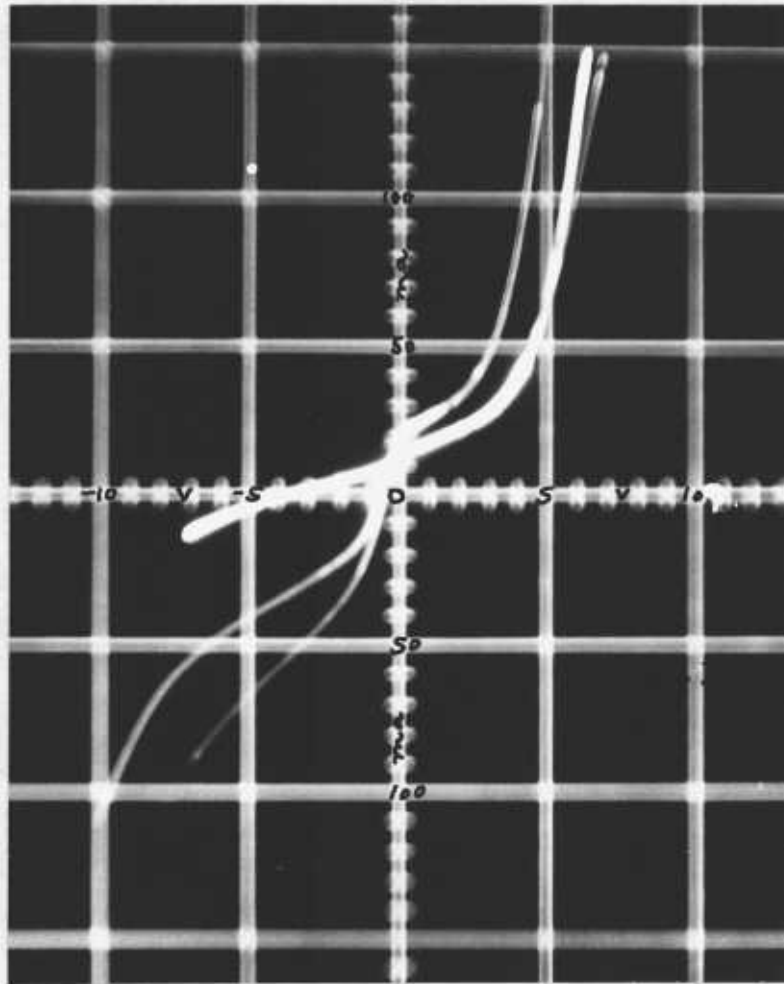


Fig. 47

Current-voltage characteristics of a ZnTe / Ge heterojunction showing the existence of " intermediate" or " metastable" states.

The low impedance state to which the heterojunctions switched was " non-volatile " that is the phenomenon reported here was an example of " memory switching". In other words the heterojunctions remained in the low impedance " on " state with no voltage applied. In " threshold switching " phenomenon, on the other hand, it is necessary to keep a voltage applied to pass a maintaining current through the device in order to prevent it reverting to the initial high impedance " off " state.

In the initial measurements as shown in fig. 45 switching was only observed with the reverse bias applied. No switching from the initial high impedance state to the low impedance state was observed in the forward direction. Moreover all attempts to switch back electrically by passing large forward currents in the low impedance state were unsuccessful although the currents were passed that were so large as to produce large temperature rises.

In order to test the conclusion that the conductivity behaviour observed in ZnTe / Ge heterojunctions belonged to ZnTe and not to the germanium some experiments were carried out to measure the I-V characteristics of ZnTe alone. The first method tried was to remove the Ge from some portion of the ZnTe by thinning from the substrate side. Although the thinning of germanium was successful, the area of the thinned portion of ZnTe was so small that good isolated gold-ZnTe contacts could not be made satisfactorily. So an alternative approach was used which tried to stop the current

passing through Ge, either by applying a -ve potential to the substrate or by introducing very high resistance on the Ge side, so that ^{little} current could pass through the heterojunction. For this kind of experiment two gold contacts instead of one on the ZnTe side were made. The circuits and corresponding I-V characteristics are shown in figs. 48 & 49. It is obvious from these circuits that our object of passing the current only through the ZnTe could not be achieved completely. Never the less the I-V characteristics obtained as shown in figs 48 and 49 gave some support for the view that these different states of conductivity belong to ZnTe and not to germanium.

In general switching is considered to be associated with " S-Shaped " or current controlled negative resistance characteristics (Pamplin 1970). These characteristics when as is conventional, I is plotted along the vertical axis and V along the horizontal axis , have the shape of the lower half of the letter "S" in the case of a forward characteristics or the upper part of the letter "S" for a reverse characteristic. That is current controlled negative resistance characteristic have two values of the current for a single value of the voltage over a high range of voltages. It can be seen that heterojunction switching was associated with "S-Shaped" I-V characteristics in the initial high impedance " off " state. This form of negative resistance was in general found in the ZnTe / Ge heterojunctions. As was noted in the experimental section the switching found here was of the " memory " or " non-volatile" type.

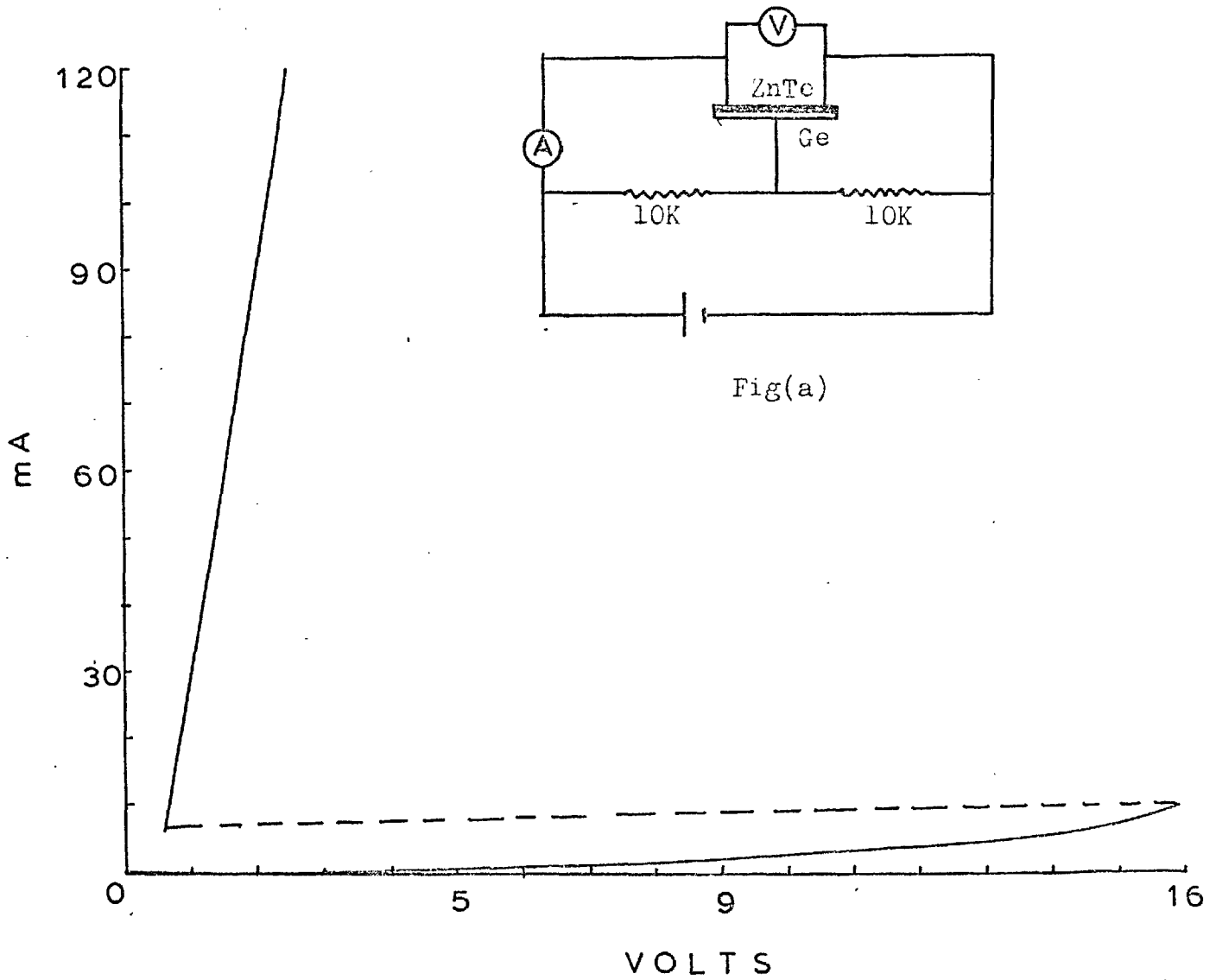


Fig. 48

Current-Voltage characteristics of an epitaxial ZnTe / Ge heterojunction. The circuit used for this measurement set is shown in fig (a).

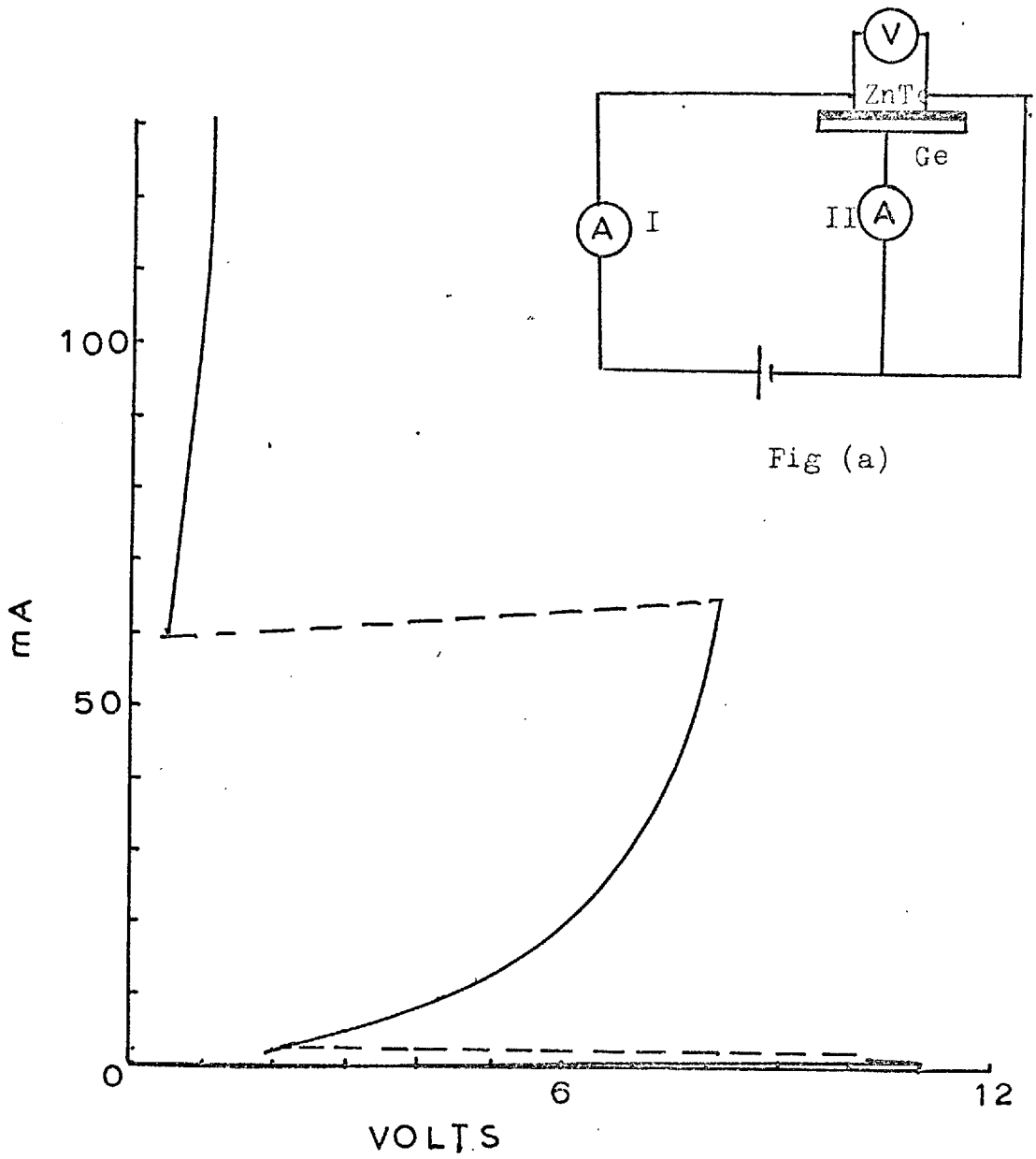


Fig. 49

Current-Voltage characteristics of an epitaxial ZnTe / Ge heterojunction. The circuit used for this measurement set is shown in fig(a).

The mechanism of switching in materials other than chalcogenide glasses is not well understood. It appears to be useful however to classify the sorts of mechanism that have been suggested as playing a role into those of a structural or chemical character and those of an electronic or thermal character. Structural or chemical mechanisms include such things as diffusion or injection into the material of atoms from the contact (Simmons 1971), and produce relatively permanent changes in behaviour. Effects of this type are often referred to as " forming " or breakdown/^{and} in some materials, including single crystals of ZnS with In contacts,^a are necessary preliminary to the appearance of switching phenomena. No such preliminary forming was found necessary in the present case. No gross structural changes could be seen in ZnTe layers after switching when the gold contact films were removed. Moreover, the heterojunctions did not spontaneously revert to their initial state. Electronic and thermal mechanisms that have been suggested to explain switching include trap filling by large densities of injected carriers which then eliminates trap-dominated conductivity and makes ohmic conductivity predominant.

Some mechanisms of the "S" type would appear to be consistent with the present observations. The fact that the initial forward current-voltage characteristic was of the Poole-Frenkel form suggests that the traps played a dominant role in the high impedance " off " state. The roughly ohmic nature of the low impedance " on " state

could arise from the injection of a sufficient number of charge carriers to fill the traps and still leave a number able to act as a gas of free charge carriers. But the traps on this view then remained filled " permanently " i. e. for upto a week at room temperature.

A number of other reports of switching in the II-VI compounds have appeared. The switching reported above is similar to that in heterojunctions of epitaxial ZnSe on Ge (Hovel et al 1971, Newbury et al 1972), of epitaxial ZnS on Si (Hovel 1970), of epitaxial ZnTe on InAs (Ota et al 1971) and also in sandwiches of Al-ZnTe-Al (Ota et al 1972), except that in the cases just listed the devices could be switched back electrically from the high conductivity "on" state to the high impedance "OFF" state. However Ota et al (1972) found that Ag-ZnTe-Ag and Au-ZnTe-Au sandwiches like our ZnTe / Ge heterojunctions could only be switched from the "off" state to the "on" state but not back again. All the examples mentioned thus far are cases of simple non-volatile or memory switching.

Two examples have also now been reported of switching behaviour in II-VI compounds which only appeared after a forming or breakdown process (Al-Al₂O₃-CdS-Al Srivastava and Bhattacharyya 1972). Even more remote from the type of switching observed in the present work is that reported in polycrystalline thin films sandwiches of Au-ZnS-Au (Sutherland 1971) . This is a form of memory switching associated with the "N-Shaped" or voltage

controlled negative resistance, of the type first found in thin films of SiO and other materials.

In his review (Simmons, 1971), stated that switching, negative resistance and non-volatile memory effects in thin films had been found in two classes of materials. These were firstly the semiconducting glasses and secondly most of the wide-band/^{gap} metal oxide insulators. It is now apparent that the II-VI compounds are a third group of materials showing switching effects in thin film and hetero-junction form.

The II-VI compounds also exhibit in a number of cases high frequency-generating domain type N-shaped negative resistance effects. CdTe (Ludwig 1967) and ZnSe (Ludwig et al 1967) exhibit Gunn effect oscillations and CdS and ZnO are of course two of the best materials for use in acousto-electric effect applications. Thus the II-VI compounds would appear to exhibit a wider range of negative resistance effects than any other class of materials. As they are also among the best luminescent and photoconducting materials the possibility of devices exploiting combinations of opto-electronic and negative resistance effects made of II-VI compounds would appear to exist.

7.4. SCANNING ELECTRON MICROSCOPE STUDIES

In order to begin the study of ZnTe / Ge heterojunctions with the Stereo Scan Electron Microscope some exploratory work was done in this project. Although no quantitative data were recorded in this work, the pictures confirmed that the specimens prepared in this project showed some interesting features and were quite suitable for further studies with the SEM.

The ZnTe / Ge specimens were lapped and were mounted in the SEM as shown in fig 50 so that they could be scanned over a face normal to the heterojunction. Some photographs were taken using the emissive, conductive and cathodoluminescence modes. Fig 51 shows a set of micrographs obtained from a single area of the section of one specimen. The striking features are the similarity of the three types of micrographs.

In the conductive mode the presence of several striations parallel to the heterojunction interface was notable. This interface is most clearly identified on the Y- modulation record as the locus of the points where the signal falls from the constant high value characteristic of the germanium. This contrast arises because the incident SEM electron beam scanning across the specimen surface creates large numbers of electrons / hole pairs within the specimen. In the region away from the junction, the electrons and holes recombine without contributing to the junction current, and so these regions are dark. In the field region of the junction

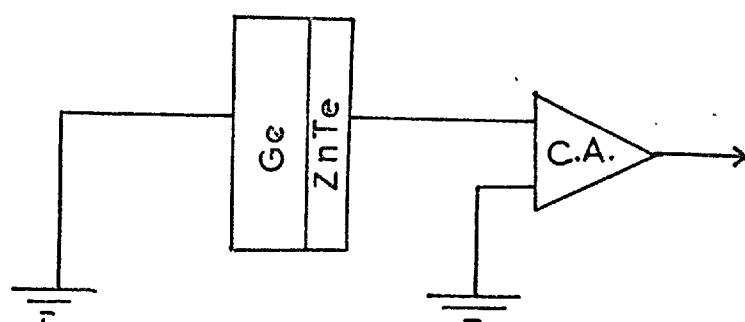


Fig. 50

The mounting arrangement of the specimen in SEM.



Fig. 51

← Ge | ZnTe →

SEM micrographs using:

(Top) Emissive mode. (Low mag. $\times 220$)

(Middle) Conductive mode. $\overline{0.4\mu}$

(Bottom) Cathodoluminescence mode. $\overline{0.4\mu}$

the electrons and holes contribute to the junction current and so this region is bright.

For cathodoluminescence mode, the light that is emitted from the specimen is collected and used as signal. This cathodoluminescence micrograph was produced by using the output from a 9665 B photo-multiplier as video signal. This photomultiplier was placed in the vacuum inside the specimen chamber adjacent to the specimen to maximise the pick up angle for light from the specimen falling on the photo-cathode.

CHAPTER VIII

CONCLUSIONS AND PROPOSALS FOR FUTURE WORK

This project was started with a two fold purpose. Firstly to grow reproducible and controllab-le epitaxial films of ZnTe on germanium with the minimum defect content and study their growth habits and structural properties. Secondly to study the electrical properties of ZnTe / Ge heterojunctions with a view to explore the possibilities of their use as electronic devices.

From the results of the part I of this thesis it is quite clear that the first objective was achieved to a satisfactory extent. With the study and adjustments of various growth parameters the epitaxial ranges of ZnTe on (111) and (100) oriented Ge substrates were explored. It was concluded that under certain conditions ZnTe films could be grown on Ge in epitaxial or polycrystalline forms according to the requirements. The next object of reducing the defect content in the films was also achieved as the films prepared for this project were free of three dimensional defects and the density of two dimensional defects was reduced to 10^{10} cm^{-2} which had not been achieved previously for the II-VI compounds. In order to make some useful electronic devices the defect density should be as small as possible so this branch is still open for further work. Most of the work for this project was done in high vacuum $\sim 10^{-6}$ torr and the various growth parameters were fully exploited in this range. So in order to make more perfect films, it is suggested that more films

should be grown in UHV range, 10^{-8} torr and below.

In the electrical measurement work the I-V characteristics of the heterojunctions were studied by manual and curve tracer methods and it was concluded that no difference was observed between the manually varied voltage curves and rapidly varying voltage (50 cycles / sec.) curves. So instead of using the time consuming manual method automatic measurement equipment similar to the curve tracer could usefully be built up. The behaviour of the heterojunctions under higher frequency biasing should also be investigated.

It was concluded that heterojunctions of epitaxial ZnTe films grown on "n" type (111) oriented Ge substrates behaved like diodes and showed a pronounced rectifying behaviour. As far as the mechanism of electronic transport is concerned it was established that these heterojunctions had characteristics of Poole-Frenkel effect form. Although the behaviour of the heterojunctions with polycrystalline films of ZnTe was of similar form to that of the epitaxial form of heterojunctions they had about two times greater slopes on $\ln I$ versus $V^{\frac{1}{2}}$ plots. This behaviour of polycrystalline ZnTe / Ge heterojunctions is not understood and it is suggested that more data should be collected for this type of heterojunction.

The behaviour of all the epitaxial ZnTe / Ge heterojunctions at high applied fields were of the same form and reproducible. The word " switching " cannot be applied in the usual way to this behaviour due to the non-reversal

of the states i.e. from high conductivity to low conductivity states as explained in section 7.3. Three methods were tested in efforts to switch the heterojunctions back to the initial low conductivity state, high forward currents, storage with no voltage applied and ultraviolet irradiation. Other methods could not be tested however due to the shortage of time. More heterojunctions could be made and left over for a longer time or stored at elevated temperatures for this purpose. However, the presence of only two conductivity states such as would arise due to electrical breakdown and thermal runaway can be ruled out by my observations as it was definitely observed that quite often ZnTe / Ge heterojunctions showed intermediate or metastable states between the two extremes of high and low conductivity states.

At the time of submission of this thesis it was suggested by Mr. M.I.Abdalla (private communication) that reversable switching is usually observed by applying a pulsed voltage instead of DC voltage. This was not the case in the work of Ota et al (1972) who applied pulsed voltages to ZnTe / glass heterojunctions with gold contacts and noted similar behaviour to that reported above for ZnTe / Ge heterojunctions i.e they found an irreversible switching to high conductivity states. However in order to give this suggestion of Mr.Abdalla a fair trial some more heterojunctions of ZnTe / Ge are being studied with pulsed applied voltages and it is hoped that some conclusion will be reached in a few weeks time.

Some specimens were studied on a trial basis with the help of Cambridge Scanning electron Microscope and as reported in the last section of this thesis the results were quite encouraging. It is suggested that after the present structural studies with the transmission electron microscope more emphasis should now be given to the studies with SEM.

APPENDIX I MOIRÉ PATTERNS

The moiré patterns are of value in relation to the resolution of crystal lattices, in that they represent, for the case of two overlapping perfect lattices, a pattern the periodicity of which is an enlarged version of the projected periodicities of the individual crystals. If the individual lattices have a spacing d (rotation moire patterns), and are rotated with respect to one another by a small angle α about the normal to the specimen plane, the spacing of the moire pattern is given by $\frac{d}{\alpha}$. We may refer to $\frac{1}{\alpha}$ as the moire magnification. Alternatively, the moire patterns have a spacing given by $\frac{d_1 d_2}{(d_2 - d_1)}$, where d_1 and d_2 are the spacings of the individual lattices, giving a moire magnification $d_1 / (d_2 - d_1)$ of the lattice of spacing d_2 .

Menter (1956) showed that the resolved image of a crystal lattice is formed in the electron microscope by interference in the image plane between the directly transmitted (zero order) beam and the first-order diffracted beam arising from the set of lattice planes resolved. A similar criterion applies to the formation of moire patterns except that the first-order diffracted beam from the single lattice is replaced by a beam which has been diffracted in opposite senses by each of the superposed lattices in succession (Dowell et al 1956, 57).

In fig AI (a) the large open and closed circles

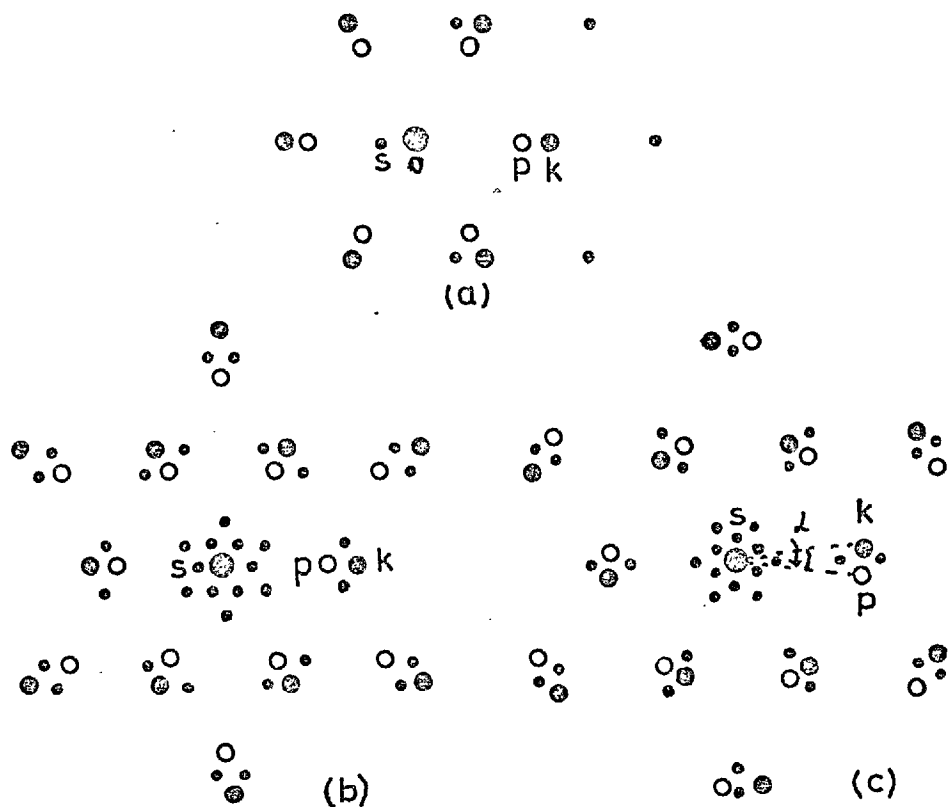


Fig. A I

The geometry of double diffraction. Large open and closed circles represent primary diffraction spots. (a) and (b) parallel case and (c) rotation case.

represent the primary diffraction spots from two superposed face-centred cubic crystals with their unit cell vectors parallel and $[111]$ parallel to the electron beam and normal to the plane of the paper. If the diffraction camera constant is R then $OP = R/d_1$ and $OK = R/d_2$ where d_1 and d_2 are the respective $(2\bar{2}0)$ spacings of the crystal. If the crystal 1 is uppermost then part of the $(2\bar{2}0)$ beam from this crystal passes undeviated through crystal 2 to form the spot P. If the third Laue condition is sufficiently relaxed, however, an appreciable part of this beam may be deflected again by the $(\bar{2}20)$ planes in crystal 2 to produce a double diffracted beam at S, where $PS = R/d_2$. Now

$$OS = PS - OP = R/d_2 - R/d_1 = \frac{R(d_1 - d_2)}{d_1 d_2}$$

i.e the position of the double diffraction spot S is that which would be expected from a grating of spacing $d_1 d_2 / (d_1 - d_2)$. It may also be shown in a similar way that for rotation patterns as illustrated in fig A I (c) the double diffraction spot is formed at a distance $OS = (R/d) 2 \sin \frac{1}{2} \alpha$, i.e at a position to be expected from a grating of spacing $\frac{1}{2}d \operatorname{cosec} \frac{1}{2} \alpha \sim d/\alpha$ when α is small. By repeated application of this construction to the remaining $(2\bar{2}0)$ reflections one obtains six such double diffraction spots around the zero-order beam.

It is easy to show that if two parallel line gratings are overlapped, the period of matching and mismatching (i.e the spacing of the moire pattern) is given by

$d_1 d_2 / (d_1 - d_2)$ as above, where d_1 and d_2 are the spacings of the two line gratings. Similarly, for the rotation case the moire pattern has a spacing of d/α . Thus the spacing associated with the double diffraction spot S is equal to the spacing of the moire pattern.

Suppose crystal 1 is rotated by a small angle θ with respect to crystal 2 for the case of parallel moire patterns with crystal 1 having the smaller lattice parameter. Since the double-diffraction spot S rotates through an angle ω about the central spot, the moire pattern will rotate through ω in the same sense, where

$$\frac{1}{a_2 \sin \omega} = \frac{1}{a_1 \sin(\omega + \theta)}$$

i.e.
$$\omega = \frac{a_1 \theta}{a_2 - a_1} \quad (\omega \text{ and } \theta \text{ small})$$

$$= M\theta,$$

where M is the moire magnification. Thus there is a large angular magnification of the rotation of the elementary lattice, indicating that the parallel moire patterns are very sensitive to lattice distortions, or misalignment of the two lattices. For the case of rotation moire patterns the main effect of small relative rotations is the change in spacing of the moire patterns, as given by

$$\frac{d}{\alpha} - \frac{d}{\alpha + \theta} = \frac{d\theta}{\alpha(\alpha + \theta)} = \frac{d}{\alpha} \left(\frac{\theta}{\alpha + \theta} \right)$$

Now consider fig A II. Suppose there is an edge dislocation in crystal 2, along the $[001]$ direction, for the

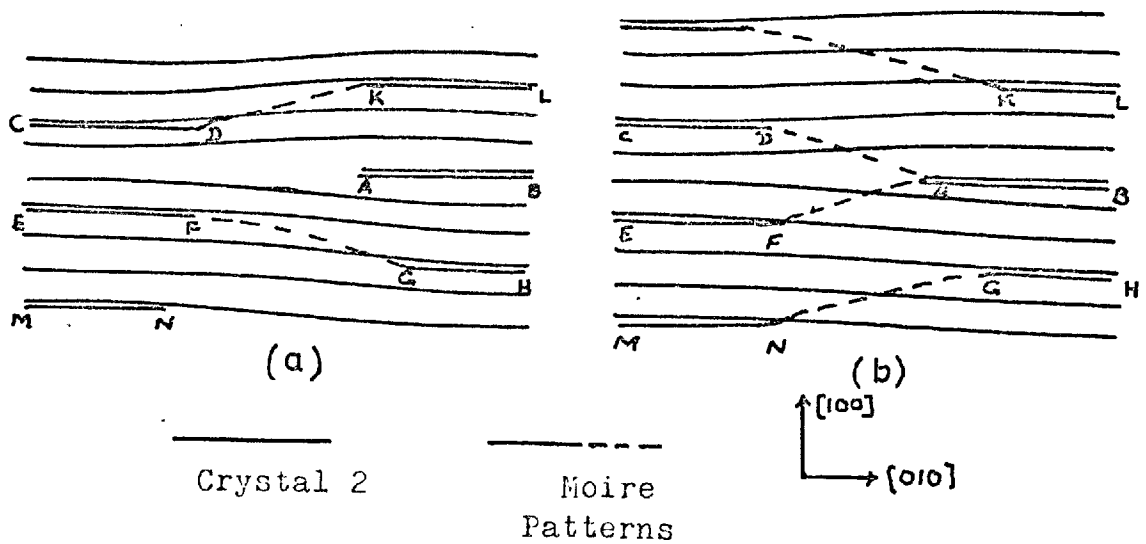


Fig. A II

The appearance^d of an edge dislocation on a parallel moiré pattern.

(a) Dislocation in the smaller lattice.

(b) Dislocation in larger lattice.

hypothetical case of a simple cubic structure and a Burgers vector of $[100]$. Consider first the case in which crystal 2 has the smaller lattice spacing. The (100) planes in crystal 2 are assumed, as a typical model, to be as shown in fig A II. For such a symmetrical case, the planes on the far-left-hand side are displaced by a half-spacing along the $[100]$ with respect to the planes on the far-right hand side. If crystal 1 is so placed that one of its (100) planes coincides with AB, and the spacings are such that, for example, every subsequent third (100) plane in crystal 2 coincides with a (100) plane in crystal 1, then the far left-hand side of the crystal 2 will coincide with crystal 1 along the planes CD, EF etc. The moire fringe pattern on the far left-hand side will therefore be displaced by half a fringe spacing with respect to that on the far-right hand side. It remains to be considered how the fringes on the two sides join up. Along EF, for example, the plane of crystal 2 starts to bend away at F, and from the result given previously it is expected that the fringes will bend through an angle enlarged by the ratio $a_1 / (a_1 - a_2)$. The integrated effect along the fringe causes EF to join with GH. Similarly, CD will join with KL. This leaves the fringe AB as an extra fringe on the right hand side.

For the case where the crystal 2 has the larger lattice spacing, the fringes on the two sides will join up in a different way. This is illustrated in Fig A II (b). Along EF, the moire fringe will bend in the opposite sense to the bend of EF at F and will eventually join up AB. Similarly CD, will

join with AB and MN will join with GH. The moire pattern will thus have an extra fringe on the left hand side, so that it will contain a dislocation of opposite sign to that in crystal 2.

More generally, it may be seen that an edge dislocation in one crystal, involving N extra half-planes will give rise to a dislocation in the moire pattern with N extra half-lines. If the dislocation is in the crystal of smaller spacing, the dislocation in the moire pattern has the same sign. If the dislocation is in the crystal of larger spacing, the dislocation in the moire pattern has the opposite sign.

The same arguments can be applied to rotation moire pattern. The details are given in Hirsch et al (1968) and Bassett et al (1958).

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