A Study of Defects in Epitaxial Films of ZnTe by Transmission Electron Microscopy

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The electron diffraction patterns of sphalerite structure ZnTe films evaporated in vacuum onto NaCl, BaF_2 and CaF_2 substrates contained numerous satellite spots. The diffraction patterns from (100) ZnTe films grown on cleavage faces of NaCl always contained satellite spots that arose from grains of wurtzite structure material with the (0001) plane parallel to the plane of the film and doubly positioned by a 30° rotation about the normal to the film. Other satellite spots occurred due to the presence of cubic microtwins and other types of included grains of wurtzite. Films grown under cleaner conditions had simpler structures.

The most prominent satellite spots in diffraction patterns from (111) films of ZnTe grown on NaCl, BaF_2 and CaF_2 were due to twinned sphalerite double positioning. Additional spots arose from microtwins.

Evidence of double diffraction was found in both the (100) and (111) diffraction patterns.

1. Introduction

The II-VI compounds are of great potential value for use in electro-optical devices such as lamps and lasers and for use in acousto-electric devices such as transducers. However the practical application of the II-VI compounds is prevented by the fact that they are not available as crystals of the purity and perfection required of semiconductors, and the fact that *p-n* junctions cannot generally be made in II-VI compounds. A method of production of semiconducting materials that has proved to be of considerable value in the cases of silicon and the III-V compounds, but which has not been extensively exploited for the II-VI compounds is epitaxial growth. Therefore a systematic study of the epitaxial growth of a number of II-VI compounds has been carried out as will be outlined below. ZnTe was made the subject of much of the work as it is one of the more interesting and less developed of these materials.

In an earlier paper [1] it was 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 many small included grains. Moreover, the films gave rise to electron diffraction spot patterns containing irrational satellite spots.

It was also reported at that time that 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 focused electron beam evaporation [2] epitaxial growth of ZnS could be obtained on NaCl over a very wide range of substrate temperatures [3, 4]. The use of focused electron beam evaporation was then found to result in epitaxial growth of CdS [5] and of ZnTe [6] on NaCl cleaved or polished faces over very wide ranges of substrate temperature. The best of the CdS and ZnS films produced diffraction patterns free of satellite spots. However films grown outside the optimum ranges of substrate temperature gave electron diffraction patterns containing satellite spots. It was found that these were due to doubly positioned grains of wurtzite in the sphalerite structure films [4]. It was then

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found however that electron beam evaporation produced less perfect films of ZnTe on CaF_2 than did hot metal evaporation. Moreover electron beam evaporation produced no epitaxial growth of ZnTe on BaF_2 at any substrate temperature [6].

In this paper are reported the results of analyses of the structures of the best ZnTe films, that is those electron beam evaporated on to NaCl and hot metal evaporated on to BaF_2 and CaF_2.

All the early studies of epitaxial films of II-VI compounds reported that analysis of the electron diffraction patterns showed both sphalerite structure (cubic phase) and wurtzite structure (hexagonal phase) material to have been present in the films. In none of this work (reviewed previously [7]) however, was the possibility of double diffraction considered. Pashley and Stowell [8, 9] have shown that double diffraction plays an important rôle in the diffraction patterns of epitaxial films of fcc metals. Their treatment will therefore be considered in relation to diffraction by epitaxial films of II-VI compounds.

2. The Sphalerite and Wurtzite Structure Factors

The sphalerite structure has an fcc space lattice with a basis of two atoms at each lattice point. An A atom occurs at 000 (the lattice point) and there is a B atom displaced by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, in terms of the fcc structure cell edges, from the lattice point. In the case of the diamond structure in which both types of site are occupied by the same type of atom, destructive interference between the diffracted beams from the two fcc sublattices (consisting of 000 and of $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ type sites) can be complete. This results in certain reflections having zero structure factor in addition to those having zero structure factor in the case of fcc structure materials. In sphalerite structure compounds, however, there is a difference in the atomic scattering factor of the atoms of the two fcc sublattices. Therefore destructive interference between the two sublattices cannot be complete and the only absent reflections are those that are also absent from the fcc reciprocal lattice. The amplitudes of the structure factors of the permitted reflections are not the same in the sphalerite and the fcc cases. However, due to the complications arising from the strong scattering of electrons, reliable intensity information is not available in electron diffraction work. The sphalerite and fcc reciprocal lattices may therefore be regarded as equivalent for present purposes.

The relationship of the wurtzite and the hcp structures is similar to that between the sphalerite and the fcc structures. That is, the wurtzite structure has a basis consisting of an A atom at each point of an hcp space lattice and a B atom displaced from the lattice point.

The scattering factors of the two sublattices again differ. Therefore there are no reflections that are absent from the wurtzite reciprocal lattice other than those that are absent from the hcp reciprocal lattice and the two reciprocal lattices are equivalent for the purposes of the present analysis. Moreover the II-VI compounds that have been measured all give c/a ratios for the hcp space lattice that are near the ideal value of 1.633. Values of c and a from Wyckoff [10] give, for ZnO $c/a = 1.603$, for ZnS $c/a = 1.636$, for CdS $c/a = 1.620$ and for CdSe $c/a = 1.632$. Values reported by Korneeva [11] for ZnSe yield $c/a = 1.658$; values determined by Spinulescu-Carnaru [12] for CdTe make $c/a = 1.637$ and values obtained by Spinulescu-Carnaru [13] for ZnTe give $c/a = 1.645$.

3. Satellite Spots in the Diffraction Patterns of the (100) and (111) Planes

Pashley and Stowell [8] showed that the reciprocal lattice points due to twins occurring on all the {111} planes of an fcc matrix either coincided with 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 undiffracted spot, $R = \lambda L / d_{pqr}$ is equal to that for an atomic plane spacing $d_{p'q'r'}$ of the fcc structure. A consequence of the equivalence of the fcc and the sphalerite reciprocal lattices is that the above conclusions also apply to the satellite spots due to twins on the {111} planes of a sphalerite matrix. These are generally known as microtwins.

Adding $\pm 1/3 \langle 111 \rangle$ to all of the {220} and {200} matrix spots in order to plot the twin spots near the (100) reciprocal lattice plans of the matrix produces the array shown in fig. 1. None of the twin spots are actually in the (100) reciprocal lattice plane since the $\langle 111 \rangle$ directions intersect the (100) plane obliquely.

Double diffraction in the twins and matrix may be treated by adding the matrix **g** vectors in

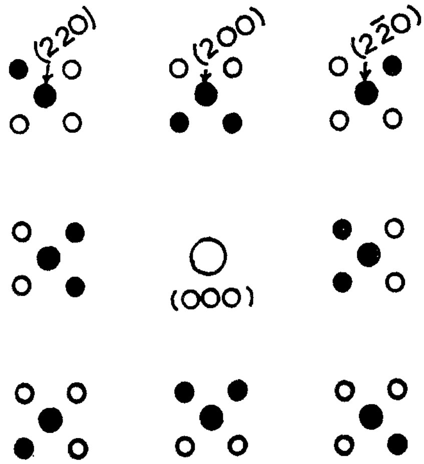


Figure 1 (100) reciprocal lattice plane of a twinned sphalerite-structure film (after Pashley and Stowell [8]). Sphalerite-structure film matrix spots (large solid circles) and satellite spots due to twins on all the {111} planes of the matrix (small solid spots) and to twin/matrix double diffraction (small open circles) in and near the (100) reciprocal lattice plane, are shown.

the (100) reciprocal lattice plane to each of the twin reflections. This results in the appearance of many additional spots shown in fig. 1 [8].

Pashley, Stowell and Law [9] showed that the reciprocal lattice points due to hcp material on each of the {111} planes of an fcc matrix occurred in one of three types of position: (i) coincident with a matrix reciprocal lattice point or (ii) displaced from a matrix point by vectors of $\pm$ 1/3 ⟨111⟩ or (iii) displaced from a matrix point by $\pm$ 1/6 ⟨111⟩. The permitted points of types (ii) and (iii) are those whose distance from the origin of the reciprocal lattice correspond to those for permitted reflections of the hcp structure. A consequence of the equivalence of the hcp and the wurtzite reciprocal lattices is that the positions of the wurtzite satellite spots too are determined by the rules just stated.

Proceeding in this way satellite spots due to the wurtzite structure regions occurring on each of the {111} planes of a sphalerite structure film with (100) orientation may be plotted. Double diffraction involving wurtzite grains and sphalerite matrix material then results in the array shown in fig. 2a [8].

The only satellite spots found in epitaxial films of ZnS [4], electron beam evaporated on to NaCl arose from a type of included grain not considered by Pashley *et al.* These grains were of doubly positioned wurtzite, that is, grains of wurtzite-structure material with (0001) planes parallel to the (100) plane of the sphalerite-structure matrix of the film and occurring in two orientations. These are related by a 30° rotation about the [0001] direction which is normal to the film.

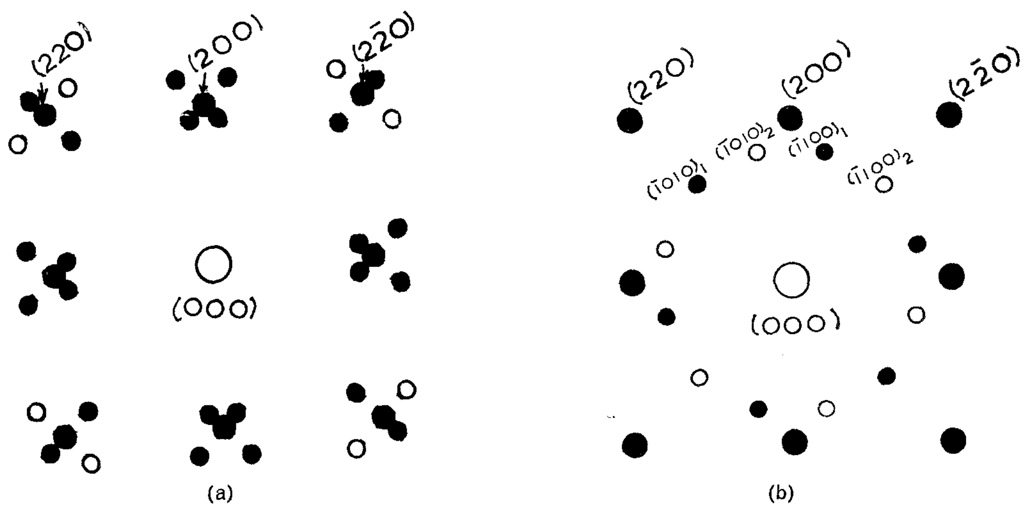


Figure 2 (100) reciprocal lattice planes of sphalerite structure films containing two types of wurtzite-structure included grains. Large solid circles are matrix spots. (a) Small solid circles are satellite spots due to wurtzite grains oriented with basal planes parallel to each of the {111} planes of the matrix, and small open circles are due to wurtzite/matrix double diffraction [8]. (b) Small circles are due to wurtzite grains with basal plane parallel to the (100) plane of the film and occurring in two positions related by a 30° rotation about the film normal (after Woodcock and Holt [4]). Small open circles arise from grains with the one position and small solid circles from grains of the other positioning.

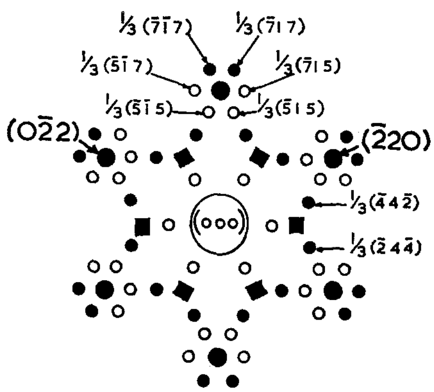


Figure 3 (111) reciprocal lattice plane of a twinned sphalerite-structure film. Large solid circles are {220} matrix spots and small solid circles are satellite spots due to twins on all the {111} planes of the matrix. Spots due to twin/matrix double diffraction (small open circles) in and near the sphalerite (111) reciprocal lattice plane, are also shown. The squares mark the positions of beams due to double positioning [14] i.e. twinning about [111], the normal to the film.

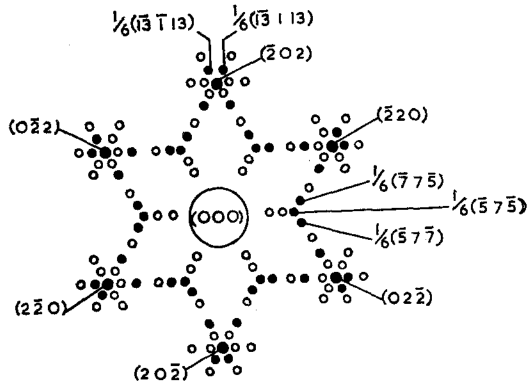


Figure 4 Sphalerite-structure matrix spots (large solid circles), wurtzite spots (small solid circles) and wurtzite/matrix double diffraction spots (small open circles) in and near the sphalerite (111) reciprocal lattice plane. This is the diffraction pattern due to a sphalerite structure film containing wurtzite structure included grains oriented with basal planes parallel to each of the {111} planes of the matrix.

Doubly positioned wurtzite grains give rise to the satellites plotted in fig. 2b.

In the same manner as that employed to treat (100) films, the positions of the satellite spots due to {111} microtwins can be plotted for (111) films of the sphalerite structure. The result is shown in fig. 3. 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 ⟨111⟩ direction) results in additional satellite spots [14] indicated by squares in fig. 3.

Plotting the satellite spots due to included grains of wurtzite-structure material with basal planes parallel to each of the {111} planes in (111) films with the sphalerite structure, produces the array shown in fig. 4. Again there is a six pointed star of satellite spots but it contains more spots than in the microtwin case of fig. 3. In fig. 4 there are *two* hexagons of satellite spots around each matrix {220} spot, one at $\pm 1/3$ ⟨111⟩ and the other at $\pm 1/6$ ⟨111⟩ from it.

4. Results

4.1. (100) ZnTe Films

The diffraction patterns obtained from the thicker epitaxial films of ZnTe grown on cleavage faces of NaCl and oriented with the electron beam parallel to [100] were as shown in fig. 5. Comparison with fig. 2 shows that the satellite spots in these diffraction patterns can be indexed in terms of doubly positioned wurtzite. A second interpretation of the observed satellites is possible [15, 16]. This attributes the satellite spots to sphalerite structure included grains with (211) planes parallel to the plane of the film and occurring in six different (twinned) azimuthal positionings. The two possibilities can be

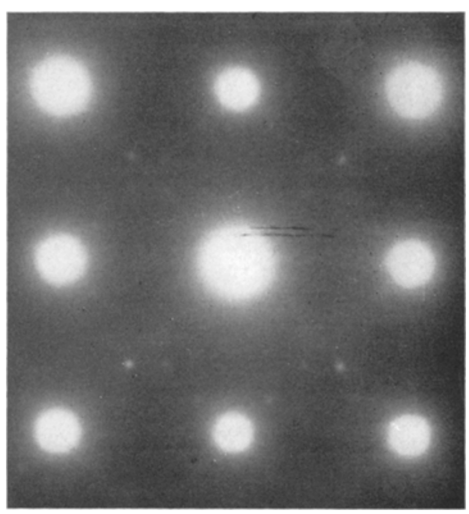
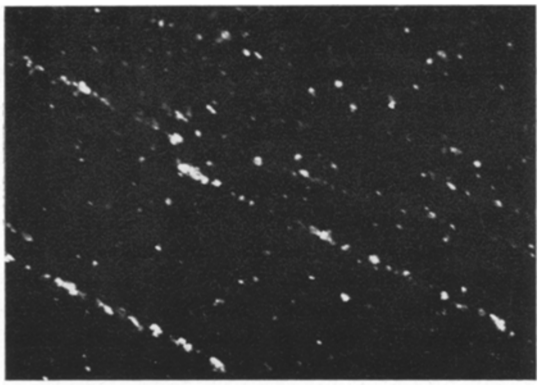
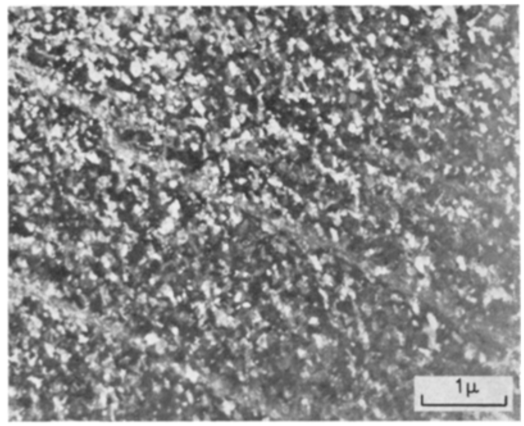


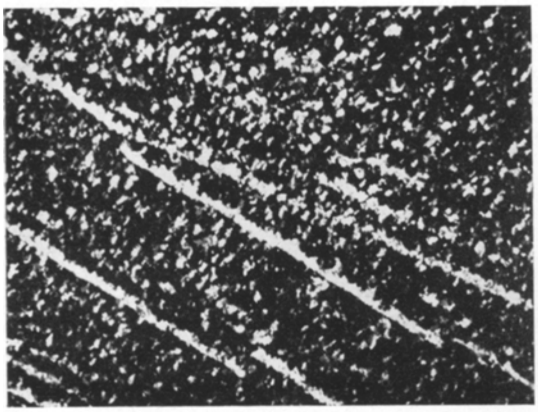
Figure 5 (100) selected area diffraction pattern of a film of ZnTe evaporated on to air cleaved NaCl held at 300° C.



(a)



(b)



(c)

Figure 6 Dark field electron micrographs of a film of ZnTe evaporated on to NaCl at 350° C. The beams used were, as indexed in fig. 2b: (a) $(\bar{1}010)_1$, (b) $(\bar{1}010)_2$ and (c) $(\bar{1}100)_1$.

distinguished by dark field electron microscopy. On the double positioning interpretation alternate beams around the ring of satellite spots of fig. 2b arise from the same grains, whereas on the multiple positioned (211) sphalerite interpretation they do not. Fig. 6 shows that alternate satellite beams in epitaxial films of ZnTe grown on NaCl did arise from the same grains confirming that doubly positioned (0001) wurtzite grains were present and were responsible for the observed satellite beams.

In many films, like that shown in fig. 6, the area covered by the doubly positioned wurtzite grains is approximately equal to the whole area of the film. The diffraction patterns from the films were however unambiguously those for (100) oriented sphalerite structure material as shown in fig. 5. Hence although the doubly positioned wurtzite grains occupy virtually the whole area, they occupy only a small part of the volume of the film. This must mean that they are thin "included grains" embedded in a thick sphalerite-structure matiix. The wurtzite structure grains probably nucleated at the substrate surface, often preferentially along cleavage steps as in fig. 6, but were overgrown by sphalerite-structure nuclei.

Tilting off the exact (100) orientation brings up additional satellite spots not in the (100) reciprocal lattice plane. In some films as shown in fig. 7, additional "spots" appeared displaced from the matrix {200} spots by $\pm 1/6$ $\langle 111 \rangle$. These satellites may arise from wurtzite-structure grains occurring with their (0001) basal planes parallel to the (111) planes of the sphalerite-structure (100) film matrix material. However, the elongated elliptical shape of these "spots" indicates that a major contribution arises from the intersection of the Ewald sphere with $\langle 111 \rangle$ streaks. On tilting to the (110) orientation the diffraction pattern of fig. 8 is obtained. It can be seen that there is strong streaking in the $[1\bar{1}\bar{1}]$ and $[\bar{1}1\bar{1}]$ directions. These are indicative of the presence of planar {111} defects. There are weak maxima at the positions displaced by $\pm 1/6$ $\langle 111 \rangle$ from the matrix spots, that is, displaced by 1/6 of the distance between matrix spots along the streaks. However the stronger maxima occur at the positions displaced by $\pm 1/3$ $\langle 111 \rangle$ from the matrix spots. Thus there is evidence for a small amount of wurtzite-structure material in the (0001)-parallel-to-{111} orientations, but the stronger satellites probably arise mainly from microtwins in the {111} orientations. This interpretation is supported by the observations on ZnTe films

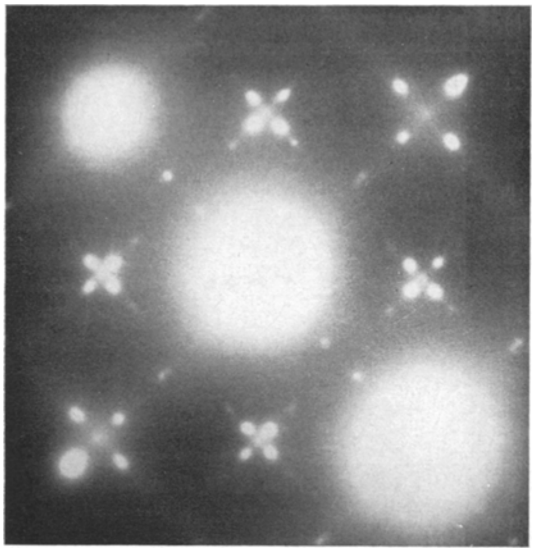


Figure 7 Selected area diffraction pattern tilted slightly off (100). The film of ZnTe was epitaxially grown on vacuum-cleaved NaCl in high vacuum at 350° C.

electron beam evaporated on to vacuum cleaved NaCl in ultra-high vacuum equipment previously described [17].

The ultra-high vacuum grown ZnTe (100) films had simpler, clearer (110) diffraction patterns as shown in fig. 9. The ⟨111⟩ streaks were still present as were the maxima at the positions 1/3 of the way between matrix spots. However all the ± 1/6 ⟨111⟩ maxima along the streaks were absent. That is the films grown in ultra-high vacuum were free of included grains of wurtzite formed on the {111} planes of the sphalerite-structure matrix. Observations of the

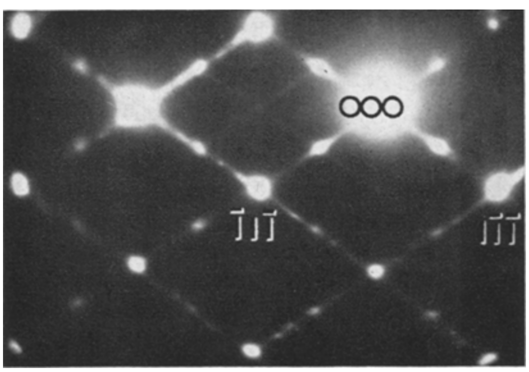


Figure 8 (110) selected area diffraction pattern of a ZnTe film grown on vacuum-cleaved (100) NaCl in high vacuum at 350° C. The film was tilted so that the electron beam was incident approximately parallel to the [110] direction.

(100) diffraction patterns of these films showed them to be identical with fig. 5 however. Therefore doubly positioned wurtzite included grains were present in these films and fig. 9 shows that microtwins occurred too.

4.2. (111) ZnTe Films

The diffraction patterns obtained from films of ZnTe grown epitaxially by electron beam evaporation on to faces of NaCl cut parallel to (111) and chemically polished as previously described [5], were, as shown in fig. 10a, similar to fig. 3 rather than fig. 4. The inner hexagon of spots occurring at distances of ± 1/6 ⟨111⟩ from the matrix {220} spots (including for example the spots indexed 1/6 ($\overline{13}\,\bar{1}\,13$) and 1/6 ($\bar{1}\bar{3}\,1\,13$) in fig. 4) and due to wurtzite included grains, was not observed. Nor were the more numerous satellite spots in the arms of the six pointed star in fig. 4, such as 1/6 ($\bar{7}\,7\,\bar{5}$) and 1/6 ($\bar{5}\,7\,\bar{5}$). Tilting failed to bring up these reflections. Thus the satellite spots in the diffraction patterns of ZnTe/(111)NaCl were due to sphalerite-structure twins. This conclusion was confirmed by observations of the (110) diffraction pattern of these films. As shown in fig. 10b intensity maxima occurred at the ± 1/3 ⟨111⟩ positions but not at the ± 1/6 ⟨111⟩ positions characteristic of (0001)-parallel-to-{111} wurtzite included grains.

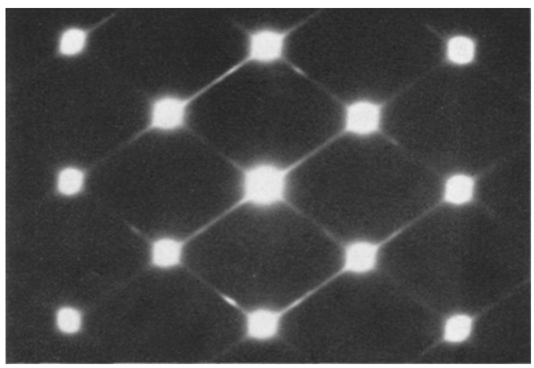
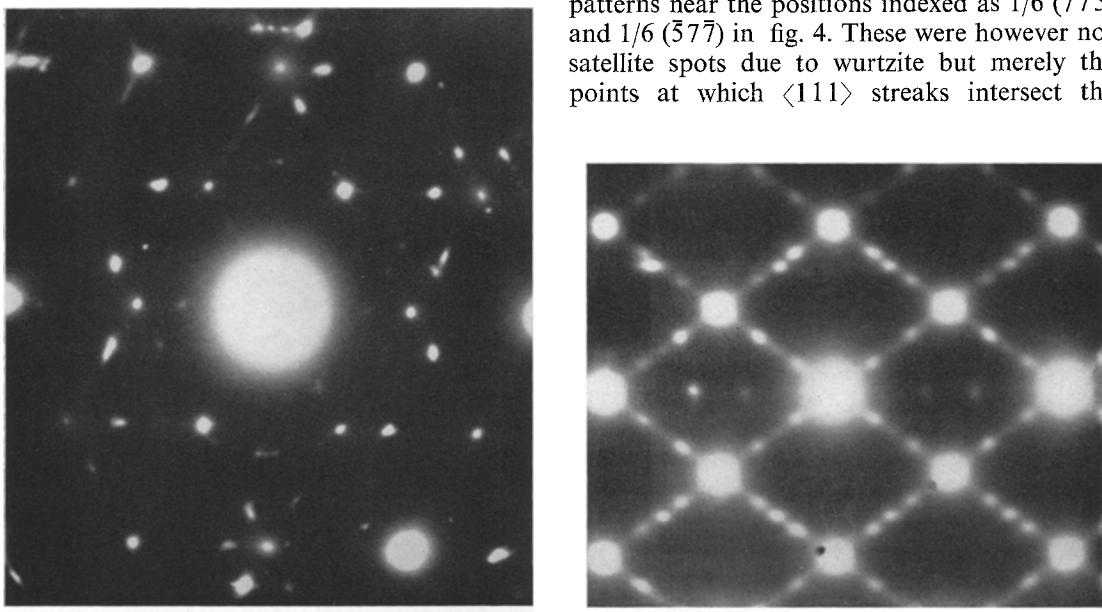


Figure 9 (110) diffraction pattern of a film of ZnTe grown on vacuum-cleaved (100) NaCl in ultra-high vacuum at 200° C.

The satellites indicated by squares in fig. 3 and due to double position twinning were always present in the ZnTe/(111)NaCl diffraction patterns. There are actually two spots at these positions one above the other. One is due to diffraction by {111} planes in the doubly positioned grains, the other is due to double diffraction successively by material in each of the twinned positions. Consequently in dark field imaging of beams in this position, it is possible to observe either domain contrast in which the whole area covered by material of one position appears bright, or outline contrast in which only the areas of overlap of material in the two positions appears bright. Which type of contrast occurs in any area depends upon which of the two beams is strongly excited locally [8]. Both types of contrast were observed and an example of domain contrast in a ZnTe/(1 1 1)NaCl film is shown in fig. 11. It can be seen that the film consisted of approximately equal areas of the two positions. These consisted of characteristic interlocking shapes reminiscent of a jigsaw puzzle in black and white domain contrast. This was the structure of most (1 1 1) ZnTe films grown on NaCl.

The diffraction patterns obtained from films of ZnTe grown epitaxially by evaporation from hot Ta tubes on to cleaved BaF_2 in high vacuum were similar to those just described. The satellite spots occurring in these patterns were those arising from microtwins and from doubly positioned sphalerite grains. The structure, shown in fig. 12, contained both microtwins marked M and large, isolated, irregular doubly-positioned grains marked D.

Films of ZnTe grown by hot-tantalum evaporation on to cleavage faces of CaF_2 also had diffraction patterns like fig. 3 rather than fig. 4. Spots sometimes appeared in the observed patterns near the positions indexed as 1/6 ($\bar{7}7\bar{5}$) and 1/6 ($\bar{5}7\bar{7}$) in fig. 4. These were however not satellite spots due to wurtzite but merely the points at which ⟨1 1 1⟩ streaks intersect the Ewald sphere as was shown by measurement on the patterns; this was confirmed by tilting.



(a) (b)

Figure 10 Diffraction patterns of a film of ZnTe grown on a chemically polished (1 1 1) face of NaCl at 350° C in high vacuum (a) (1 1 1) diffraction pattern, (b) (1 1 0) pattern from the tilted film.

The most prominent satellite spots in the diffraction patterns from these films were those due to double positioning. The double positioning structure as in the case of films grown on BaF_2 initially took the form of a few large, irregular, isolated grains of one (twinned) position in a matrix of the other position similar to those in fig. 12. Bombardment by the electron beam was then found to produce grain growth, resulting in an interlocking structure like that shown in fig. 11.

All these observations demonstrate that the satellite spots in diffraction patterns of films of ZnTe evaporated in vacuum on to (1 1 1) substrate surfaces were due to sphalerite structure twins.

5. Discussion

5.1. Included Grains

Two types of included grains in fcc films were considered by Pashley *et al* [8, 9]: twins on

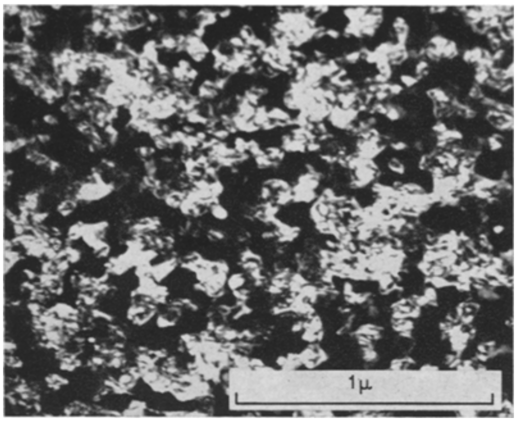


Figure 11 Dark field electron micrograph of the doubly positioned grain structure of a ZnTe/(111)NaCl 350° C film in domain contrast.

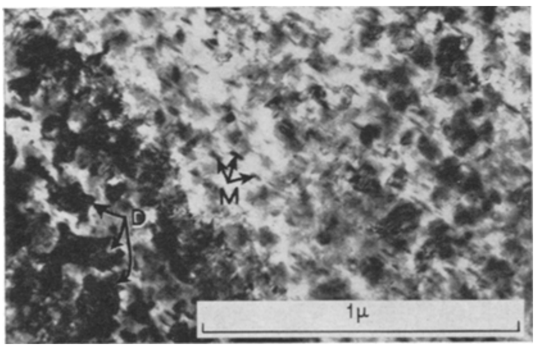


Figure 12 Bright field electron micrograph of an epitaxial film of ZnTe grown on BaF_2 at 450° C. D indicates a number of doubly positioned grains and M indicates several microtwins.

{111} planes and hcp grains with basal planes parallel to the {111} planes of the fcc matrix. However in epitaxial fcc metal films only twin spots were observed.

In the present work, satellite spots due to hexagonal (wurtzite) structure included grains were found to occur in the diffraction patterns of cubic (sphalerite) structure films, for example in figs. 5, 7 and 8. This difference is related to the fact that the II-VI compounds are polymorphic and have low stacking fault energies whereas the metals studied by Pashley *et al* occur only in the fcc form. Nevertheless, in epitaxial ZnTe films, twins were more important and less easy to eliminate than were included grains with the wurtzite structure. In the case of (111) films of epitaxial ZnTe twin (including double positioning) spots were either the only ones observed or were stronger than those due to wurtzite. In the case of (100) films improving the vacuum eliminated the wurtzite grains with (0001) plane parallel to the {111} matrix planes (but not the doubly-positioned wurtzite grains) leaving the microtwins (figs. 8, 9). This is in accordance with the fact that sphalerite is the equilibrium structure of bulk crystals of ZnTe.

Double positioning, that is the occurrence of grains in two different azimuthal orientations about the film normal was the most strongly marked and ubiquitous form of orientation relation between included grains and matrix in both (100) and (111) films. Doubly-positioned wurtzite in (100) films of sphalerite was not only prominent in the epitaxial ZnTe films reported here but was also the main type of included grain found in epitaxial (100) films of CdS [5] and the only type of included grain found in ZnS [4].

It has thus far proved impossible to grow ZnTe films free of included grains. ZnS however has been grown free of included grains. CdS has been grown free of both included grains giving rise to satellite spots and planar defects responsible for streaks in the diffraction patterns [5]. This behaviour is in line with the experience that the more ionic sphalerite structure materials are easier to grow [17] since the semi-empirically calculated charge on the ions, q, varies from 0.0 electrons for ZnTe to 1.0 for CdS and 1.1 for ZnS [18].

5.2. Double Diffraction

It is clear that double diffraction occurred in the ZnTe films. Many satellite spots appeared in positions that can only be explained by double diffraction. Examples of spots of this kind occur in figs. 10a, 12a and 13 at positions of the type indexed as 1/3 $(\bar{5}\bar{1}7)$ and 1/3 $(\bar{7}15)$ in fig. 3. Spots at these positions must arise through double diffraction, whatever the structure of the included grains as can be seen by comparing figs. 3 and 4. Additional examples of double diffraction spots appear as satellites of the $(2\bar{2}0)$ and $(\bar{2}20)$ matrix spots in fig. 7 as can be seen by comparing it with fig. 1.

Further evidence that double diffraction occurs was provided by the observation of outline contrast. The doubly-positioned grains were seen in (partial) outline because only along these sectors of the periphery did material in the two positions overlap along the direction of the electron beam. Hence only along these sectors could double diffraction first in material of the one position then in material of the other, twinned, orientation take place.

Thus double diffraction occurs and this must be taken into account in the interpretation of the diffraction patterns of epitaxial films of II-VI compounds. This was not done in the early work reported in the literature and reviewed previously [7].

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References

1. D. B. HOLT, *Brit. J. Appl. Phys.* **17** (1968) 1395.
2. B. A. UNVALA, *Le Vide* **104** (1963) 109.
3. B. A. UNVALA, J. M. WOODCOCK, and D. B. HOLT, *Brit. J. Appl. Phys.* **1** (1968) 11.
4. J. M. WOODCOCK and D. B. HOLT, *ibid* **2** (1969) 775.
5. D. M. WILCOX and D. B. HOLT, *J. Materials Sci.* **4** (1969) 672.
6. D. B. HOLT and R. PORTER, to be published.
7. D. B. HOLT, *J. Materials Sci.* **1** (1966) 280.
8. D. W. PASHLEY and M. J. STOWELL, *Phil. Mag.* **8** (1963) 1605.
9. D. W. PASHLEY, M. J. STOWELL, and T. J. LAW, *Phys. Stat. Sol.* **10** (1965) 153.
10. R. W. G. WYCKOFF, "Crystal Structures", Vol. 1 (Interscience, New York, 1960) Table III 1 (9).
11. L. V. KORNEEVA, *Sov. Phys. Cryst.* **6** (1961) 505.
12. L. SPINULESCU-CARNARU, *Phys. Stat. Sol.* **15** (1966) 761.
13. *Idem, ibid* **18** (1966) 769.
14. E. W. DICKSON and D. W. PASHLEY, *Phil. Mag.* **7** (1962) 1315.
15. P. S. AGGORWAL, and A. GOSWAMI, *Indian J. Pure Appl. Phys.* **1** (1963) 366.
16. D. B. HOLT and J. M. WOODCOCK, to be published.
17. M. CARDONA and G. HARBEKE, *J. Appl. Phys.* **34** (1963) 813.
18. R. J. CAVENEY, *Phil. Mag.* **17** (1968) 943.