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Epitaxial Growth of CdS on Ionic Substrates

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Transmission electron microscopy has been used to study the structure of films of CdS evaporated *in vacua* in the 10^{-6} torr range on to (100) cleavage faces and cut and polished (110) and (111) faces of NaCl, and also on to (111) cleavage faces of BaF_2. (111) substrate faces were found to produce wurtzite structure (hexagonal) films with great structural perfection over wider ranges of epitaxial growth temperature than (100) substrate faces. The (100) and (110) substrates produced sphalerite structure (cubic) films. Electron beam evaporation and generally clean growth conditions were found to produce good quality films at low substrate temperatures. The films were in general free of any included grains and the diffraction patterns free of satellite spots. $\langle 111 \rangle$ or $\langle 10\bar{1}0 \rangle$ streaking was present in the diffraction patterns, however, except in the case of films grown on BaF_2 above 170° C, and on NaCl (111) above 250° C. These films were also free of planar defects and only contained of the order of 10^{10} dislocations per cm^2.

1. Introduction

Recent papers have reported the variation with substrate temperature and with contamination, of the structure of vacuum evaporated films of ZnTe [1] and of ZnS [2, 3] deposited on to cleavage faces of ionic crystals. It was found in the case of (100) NaCl substrates that the minimum temperature for epitaxial growth was lowered and the structural perfection of the films greatly improved by eliminating contamination, and particularly by adopting electron beam evaporation [3].

It has been reported in the cases of CdTe, CdS [4] and CdSe [5] 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 not confirmed by the work of Holloway and Wilkes [6].

This paper presents the results of a study of the variation with substrate orientation, temperature and contamination of the structure of films of CdS, vacuum evaporated using an electron beam heater, on to ionic substrates.

2. The Structure of Epitaxial Films of II-VI Compounds

The II-VI compounds, and CdS in particular occur in two crystal structures, sphalerite (cubic) and wurtzite (hexagonal). In both cases a group of two atoms, one Cd and one S, is associated with each point of a space lattice. The lattice of the sphalerite structure is fcc and that of wurtzite is hcp. In all cases the c/a ratio for II-VI compounds with the wurtzite structure is very near the ideal value [7]. Since the atomic scattering factors for Cd and S are different, the structure factor for sphalerite allows all the same reflections as that for fcc structures and that for wurtzite allows all the same reflections as for hcp structures. An important consequence is that the analysis of the satellite spots due to microtwins and included grains of hexagonal material in fcc films due to Pashley and Stowell [8] and Pashley *et al* [9], applies also to satellite spots in the diffraction patterns from epitaxial films with the sphalerite structure.

Work on epitaxial films of other II-VI compounds has shown that the different types of defects that appear can be ranked in terms of

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their size and the ease with which they can be eliminated by improving the growth conditions. The largest and easiest to avoid are included grains. When these are absent there remain planar defects which can sometimes be eliminated by further refinements. This then leaves dislocations in the films [7, 12]. It will be shown below that this generalisation holds good for epitaxial films of CdS.

3. Experimental Methods

The vacuum system was a glass bell jar evacuated by backing and diffusion pumps through a liquid nitrogen trap. Evaporation was carried out by means of a focused electron beam furnace. Substrates were heated by a resistance furnace. The system was thus essentially similar to that used by Woodcock and Holt [3] which was found to give greatly improved ZnS films as compared with conventional systems employing hot metal evaporators. The rate of deposition was 10 Å/sec.

Substrates of NaCl and BaF_2 could be cleaved in the vacuum system. Other NaCl substrates had (110) or (111) faces which were polished mechanically and then finished by chemical polishing in a mixture of 38 % hydrochloric acid and water in a volume ratio of 7:3 [10]. In order to get epitaxial growth on the polished surfaces, careful, repeated rinsing in *anhydrous* ethyl alcohol was found to be essential. After this treatment the substrates were left to dry and then immediately used in the vacuum evaporator.

The CdS used was "electronic grade" powder obtained from Derby Luminescents Ltd; the NaCl and BaF_2 were obtained from the Harshaw Chemical Company.

After growth the films were floated off the NaCl substrates in water. Hot ammonium chloride solutions were used to loosen films from BaF_2 substrates and these too were floated off in water. The films were then examined in transmission in an AEI EM6G electron microscope.

4. Results

4.1. Epitaxial Temperature Ranges

It was found convenient to represent the results by means of the degree of orientation parameter, R, introduced by Ino *et al* [11]. This is given the value 0 for ring patterns, i.e. for randomly-oriented polycrystalline films, 100 for spot patterns from epitaxial films, and intermediate values for mixed ring and spot patterns. The value of the parameter then indicates the relative amount of oriented material in the film and makes it possible to present the results in a compact graphical form.

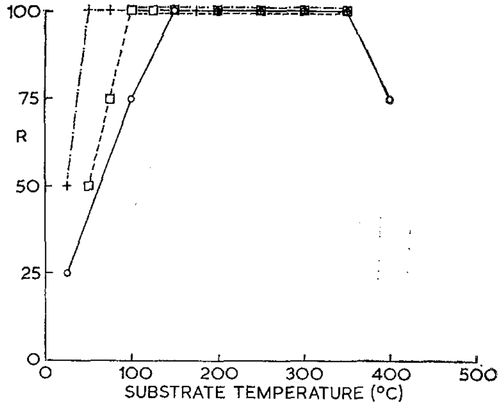
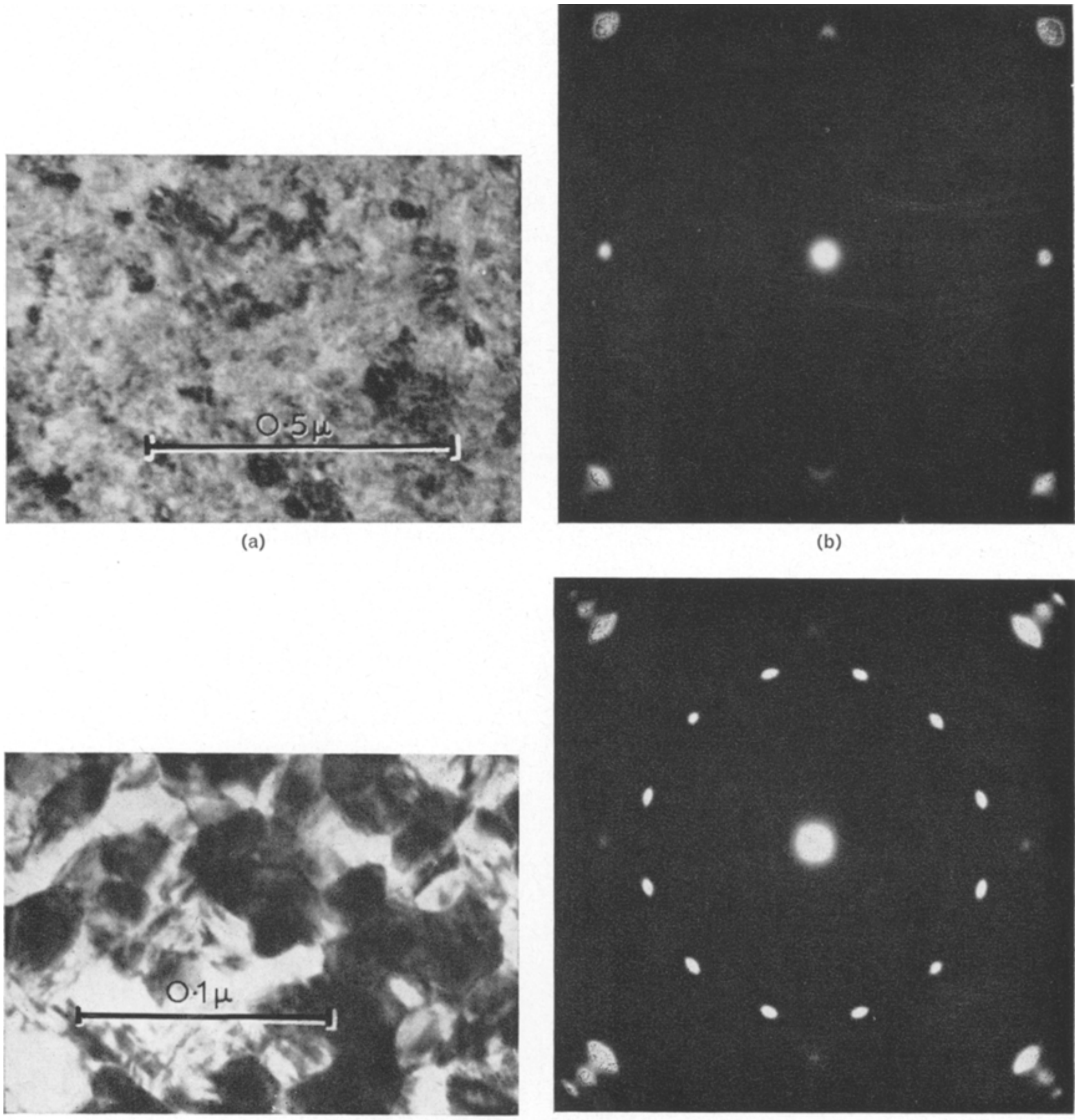


Figure 1 The degree of orientation, R, versus substrate temperature for films of CdS evaporated in vacuum (10^{-6} torr range) on to (100) and (110) surfaces of NaCl: ⊙ ——— air-cleaved (100) substrates; ☐— — — vacuum-cleaved (100) substrates; + —·—· chemically polished (110) substrates. The $R = 100$ films had the sphalerite structure and the same orientation as the substrate surface.

In the case of air-cleaved NaCl (100) substrates, reproducible epitaxial growth of films having the sphalerite structure was obtained for substrate temperatures from about 150 to 350° C and as fig. 1 shows, the effect of cleaving the substrate in vacuum was to lower the minimum temperature for epitaxy to 100° C.

It was found that the effect of increasing the deposition rate was to decrease the structural perfection of the films considerably. To illustrate this point fig. 2 compares 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 film had a diffraction pattern free of satellite spots (fig. 2b) and the micrograph (fig. 2a) shows only the fine-scale fringe and dot contrast, characteristic of planar defects in II-VI films [12, 28]. The rapidly deposited film, however, had a gross included grain structure, visible as large dark areas in fig. 2c. These grains gave rise to the extra satellite spots in fig. 2d (compare figs. 2b and 4a). Over most of the epitaxial ($R = 100$) temperature, range, films were obtained reproducibly that gave diffraction patterns free from satellite spots as shown in fig. 2b. These diffraction patterns could be indexed in terms of the cubic (sphalerite) structure. The absence of satellite spots means



(a) (b)

(c) (d)

Figure 2 Epitaxial films of CdS evaporated in vacuum on to air-cleaved NaCl at 150° C: (a) micrograph and (b) diffraction pattern of a film deposited at 10 Å/sec; (c) micrograph and (d) diffraction pattern of a film deposited at 100 Å/sec.

that these films were free of included grains. However, near the ends of the R-value plateaux, films were obtained that gave diffraction patterns containing satellite spots as shown in fig. 4a.

At the low temperature end of the R-value plateaux the satellite spots were due to doubly positioned wurtzite. The structure of the films is discussed in more detail in section 4.2. It is possible by dark field electron microscopy using satellite beams due to wurtzite structure material, as indicated in figs. 4a to c, to determine the percentage of the film area occupied by wurtzite structure included grains. The total percentage of the film area occupied by wurtzite structure material in the two positionings is plotted in fig. 3. It can be seen that films free of included grains of wurtzite structure material and giving rise to diffraction patterns free of satellite spots were obtained for substrate temperatures from 125 to 300° C.

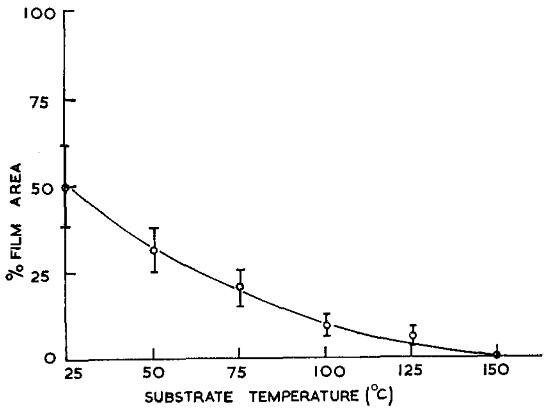
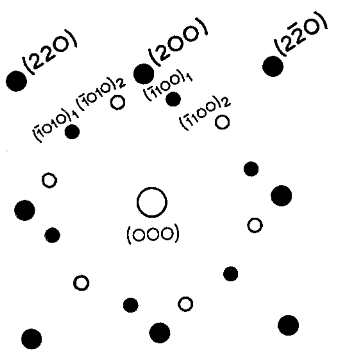


Figure 3 The percentage of the film area occupied by doubly positioned wurtzite structure grains (see fig. 4) for films of CdS evaporated in vacuum on to vacuum-cleaved (100) NaCl substrates.

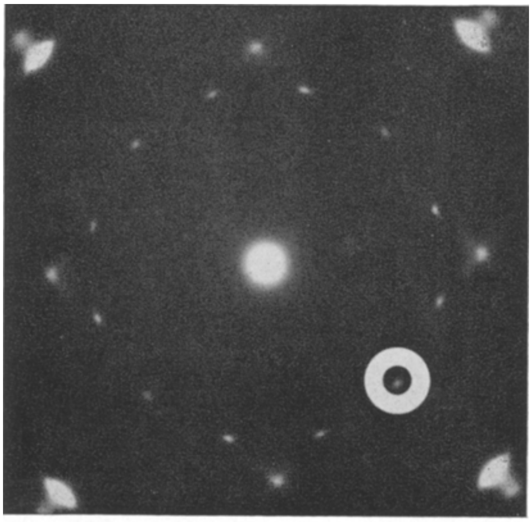
The range of epitaxial growth temperatures shown in fig. 1 for CdS evaporated on to (110) surfaces of NaCl (50 to 350° C) was wider than that for the equivalent case of air-cleaved (100) surfaces. Again films grown over most of the range of temperatures of the plateau for (110) substrates, produced diffraction patterns that contained no satellite spots. The diffraction patterns showed that the epitaxial films grown on substrates with this orientation had the sphalerite structure.

When chemically polished (111) surfaces of NaCl were used as substrates, as fig. 5 shows, epitaxial films with the wurtzite structure could be grown at substrate temperatures up to 400° C. Their diffraction patterns were free of satellite spots and the films contained no included grains, for substrate temperatures from 50 to 400° C.

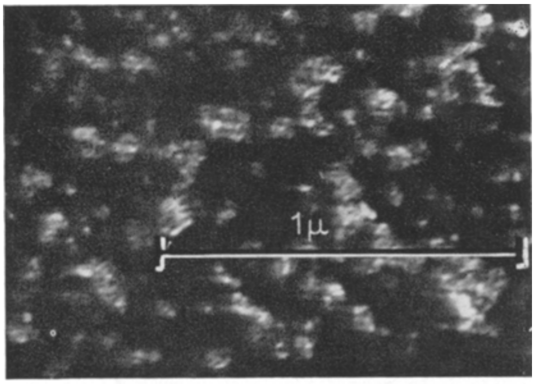
A still wider range of epitaxial growth temperatures was found when (111) vacuum-cleaved faces of BaF_2 were used as substrates. Epitaxy in fact occurred from room temperature to the highest temperature at which CdS would deposit as fig. 5 shows. The films had the wurt-



(a)



(b)



(c)

Figure 4 (a) Diagram showing satellite spots due to doubly positioned (00.1) wurtzite grains in a (100) film with the sphalerite structure. Small open and solid circles represent satellites from grains with the two positions rotated by 30° about the film normal; (b) diffraction pattern of CdS grown on vacuum cleaved NaCl at 75° C; (c) dark field electron micrograph taken with the beam encircled in (b).

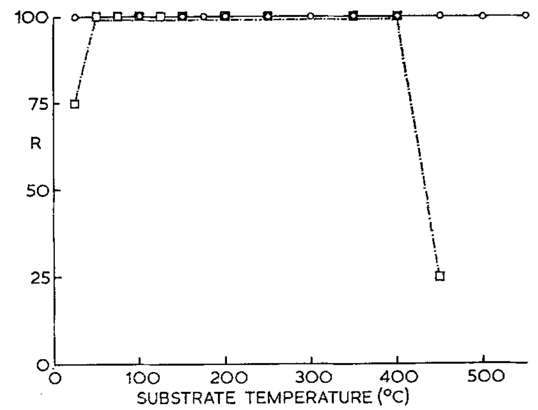


Figure 5 The degree of orientation, R, versus substrate temperature for films of CdS evaporated on to (111) substrate surfaces: ○ ——— vacuum-cleaved (111) BaF_2; □ – – – chemically-polished (111) NaCl. The $R = 100$ films all had the wurtzite structure and (0001) orientation.

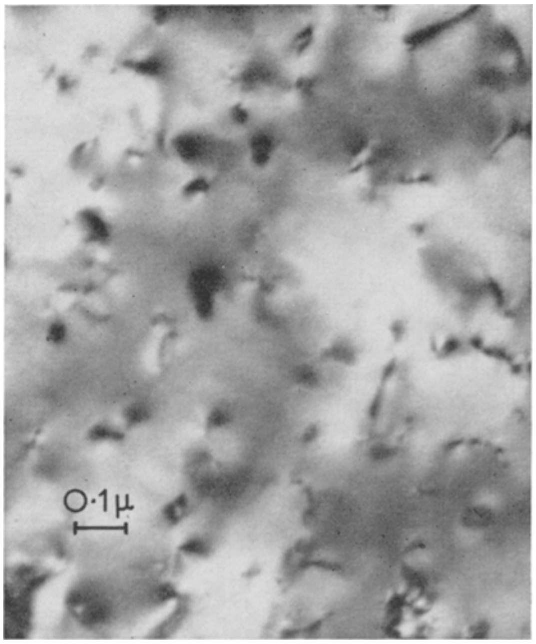


Figure 6 CdS film grown on vacuum-cleaved BaF_2 at 500° C.

zite structure and (0001) orientation. At no substrate temperature were films obtained that contained twins or sphalerite structure grains or that gave diffraction patterns containing satellite spots (fig. 6).

4.2. Included Grains in Epitaxial Films of CdS

As reported above, films grown at substrate temperatures in the ranges corresponding to the greater portion of the lengths of the plateaux of fig. 1 and to the whole of the plateaux of fig. 5 were free of included grains and gave rise to diffraction patterns that contained no satellite spots. The only exceptions were sphalerite structure films, grown on substrates at temperatures corresponding to points on the slopes at either end of the plateaux of fig. 1, which contained included grains of wurtzite that produced satellite diffraction spots. Wurtzite structure films grown on (111) substrates were epitaxial and free of all included grains except in the case of deposition on (111) NaCl at 450° C. These films were not epitaxial but contained many randomly oriented grains.

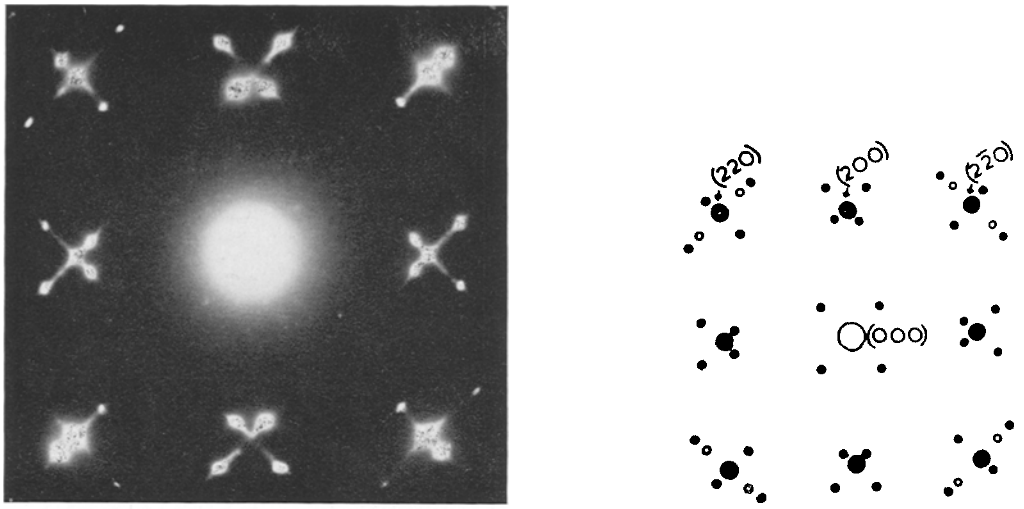
The satellites in diffraction patterns from films of CdS grown on (100) faces of NaCl at temperatures near the lower end of the R value plateau were those ascribable to included grains of wurtzite structure material growing with (00.1) basal planes parallel to the (111) planes of the cubic structure matrix as shown in fig. 4 [3].

The interpretation of the observed spots was checked by dark field imaging of the satellite beams. It was found that alternate beams revealed the same grains in bright contrast in the dark field micrographs, confirming that the included grains consisted of doubly positioned wurtzite in sphalerite structure films [12].

The satellites in diffraction patterns from films of CdS grown on (100) faces of NaCl at temperatures near the upper end of the R value plateau were displaced from the main, matrix spots in the $\langle 111 \rangle$ directions. Comparison of fig. 7a with the theoretical plot of the positions of the satellites displaced by $\pm \frac{1}{3} \langle 111 \rangle$ and $\pm \frac{1}{6} \langle 111 \rangle$ from the matrix spots [8, 9] in fig. 7b shows that the strongest of the satellites observed were due to single diffraction from included grains of wurtzite structure material oriented with basal planes parallel to the $\{111\}$ planes of the sphalerite structure material of the film. A few weak spots due to double diffraction can also be seen in fig. 7a. No spots due to microtwins were ever seen, however. The positions of the spots that would arise due to twinning in fcc metals were determined by Pashley and Stowell [8, 9] and the same analysis applies to materials with the sphalerite structure [7].

4.3. Replication of Substrate Surface Topography

Low magnification observations showed that surface topographical features such as steps on



(a) (b)

Figure 7 (a) Selected area diffraction pattern from a film of CdS evaporated on to vacuum-cleaved (100) NaCl at 350° C. (b) Diagram showing the (100) reciprocal lattice plane of sphalerite structure films containing wurtzite structure included grains. Large solid circles are matrix spots. 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. The satellites appearing in (a) correspond to the small solid circles in (b).

cleavage surfaces and etch-pit-like features on the polished surfaces, were replicated by the CdS films. This did not prevent epitaxial growth but in the case of the etch-pit-like features on polished substrate surfaces, included grains were found by dark field microscopy to be concentrated in the pits as shown in fig. 8. Thus it appeared that the substrate surface areas that were of an orientation other than the average one were preferred areas for the nucleation or growth of included grains.

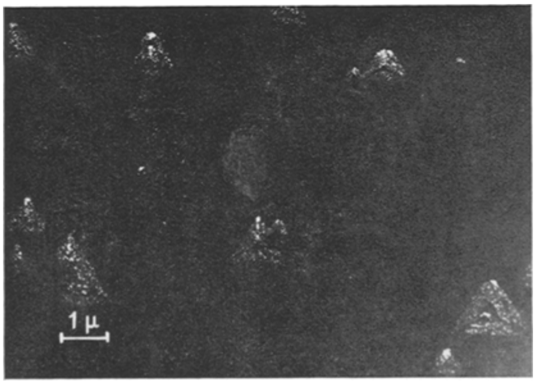
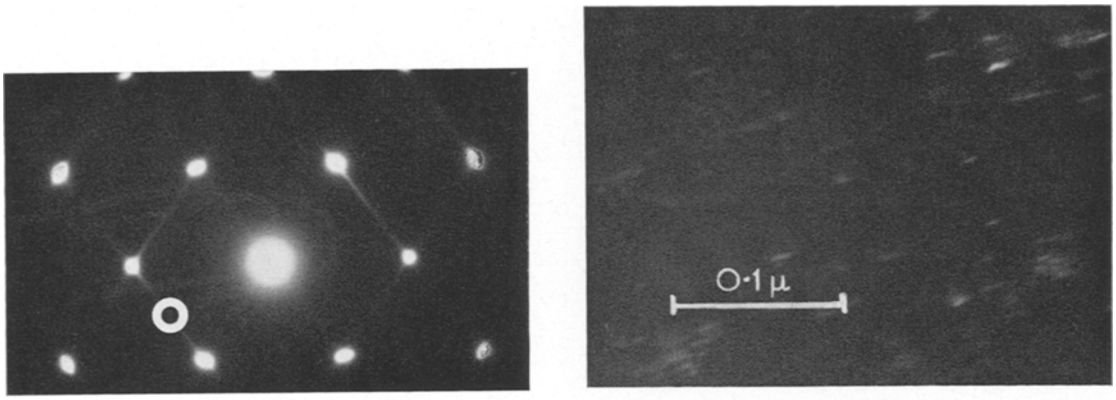


Figure 8 Etched features on polished (111) NaCl: dark field, showing included grains in etch-pits.

4.4. Streaks and Planar Defects

As in the case of ZnS [12] the satellite-spot-free diffraction patterns of sphalerite structure CdS in general contained continuous, uniform intensity streaks in the ⟨111⟩ directions. These were most readily observed in the (110) orientation as shown in fig. 9a. When electrons scattered into the ⟨111⟩ streaks were used to form a dark field image, a high density of planar defects on {111} planes were revealed as in fig. 9b.

In marked contrast to the case of ZnS on (100) NaCl, however it proved possible to eliminate the planar defects as well as the included grains from the best of the (0001) wurtzite CdS films grown on (111) substrates. The streaks were absent from the diffraction patterns of all CdS films grown on BaF_2 at substrate temperatures above 170° C and from all the films grown on (111) NaCl above 250° C. In the absence of the streaks and the planar defects responsible for them, the electron micrographs became free of the fine scale fringe and dot contrast [12] as comparison of fig. 6 with fig. 2a shows. The most obvious remaining defects when the planar ones had been eliminated were about 10^{10} to 10^{11} dislocations per cm^2. This density of defects is that usually found in epitaxial films of semiconducting materials evaporated on to ionic substrates. For example Catlin *et al* [13] found 10^{11} faults per cm^2 in Ge evaporated on to CaF_2



(a)

(b)

Figure 9 Film of CdS grown on (110) NaCl at 200° C: (a) diffraction pattern. Strong continuous streaks run in the ⟨111⟩ directions; (b) dark field electron micrograph taken with electrons scattered into the portion of a streak encircled in (a). A high density of defects can be seen on {111} planes.

in ultra high vacuum; Sloope and Tiller [14] reported 10^9 to 10^{10} dislocations per cm^2 in their best films of Ge evaporated on to CaF_2 and Matthews and Isebeck [15] found 10^{10} to 10^{11} dislocations per cm^2 in films of PbS evaporated on to NaCl. The number of dislocations in the CdS (0001) films was greatly reduced by annealing in vacuum.

5. Discussion

5.1. Epitaxial Ranges of Temperature

Comparison of figs. 1 and 5 shows that the width of the range of epitaxial growth temperature increased with decrease of contamination and with the change of the substrate orientation from (100) through (110) to (111). The beneficial effect of minimising contamination is found generally with II-VI compounds [3] and other semiconductor materials. It is however the opposite of the effect found in the case of gold, silver and copper evaporated in vacuum on to NaCl [11, 16] and in the case of iron deposited on to NaCl [17].

The best films grown in the present work were much more perfect than any CdS films previously reported. Epitaxial CdS films hitherto have always been found to be either two-phase [18-20] to contain included grains of orientations other than the predominant one [21] or profuse twinning [6], or else the films were not examined by techniques of high structure sensitivity [4, 22, 23] and so were of unknown structural perfection. In the present case not only were the films grown free of all included grains of a second phase, and free of microtwins in most cases, but films grown on BaF_2 above 170° C were free of planar defects as well. This improvement in structural perfection is probably mainly the result of the use of focused electron beam evaporation. This was found necessary in order to obtain films of ZnS free of included grains [3], and it has been found to produce greatly improved results in the cases of ZnTe on NaCl [24] and of ZnSe on Ge [25].

The observations of Weinstein, Wolff and Das [4] that the structure of epitaxial films of CdS could be changed by changing the substrate orientation was confirmed in the present work. Films grown on (111) substrates here had the wurtzite structure whereas those grown on (100) and (110) substrates had the cubic sphalerite structure. It may be an important practical advantage to be able to produce either structure at will. The thermodynamically stable wurtzite structure was obtained over a wider range of epitaxial growth temperatures and in a more perfect form than was the cubic structure. The fact that on BaF_2 substrates, CdS could be grown epitaxially down to room temperature may also be of practical importance. The thermal activation energy available at such low temperatures may be too low for significant diffusion or vacancy formation to occur. This suggests the possibility of growing *p-n* junctions by co-evaporating different dopants during the earlier and later stages of deposition.

Holloway and Wilkes [6] found that in the case of CdS vacuum evaporated on to InSb, cubic films were obtained regardless of substrate orientation. The reason for this difference from the orientation dependence found here, in the case of CdS vacuum evaporated on to NaCl, and by Weinstein *et al* [4], in the case of CdS deposited by HCl transport on to GaP, is not known, although Holloway and Wilkes suggest that contaminants may play the vital rôle.

It was suggested in an earlier paper [1] that the loss of orientation in the films at the highest substrate temperatures is due to the onset of substrate sublimation. There is now clear evidence that, at any rate, the cut off temperature above which films cannot be made to deposit is determined by substrate sublimation. The data for NaCl [26, 27] indicate that at 450° C the vapour pressure is about 4×10^{-6} torr, and it was found in the present work that for this vacuum pressure CdS films could not be made to deposit above 450° C. In the case of ZnS grown on NaCl it was also found that the temperature above which films could not be deposited, roughly equalled the sublimation temperature (at which the vapour pressure of NaCl equals the background pressure) over the range of pressures from 10^{-9} to about 5×10^{-5} torr [28]. Moreover in the cases of both Ge [29] and ZnTe [1] evaporated on to NaCl *in vacua* in the 10^{-5} torr range, the cut off was about 530° C, the sublimation temperature of NaCl.

5.2. Film Structure

The evidence concerning the growth conditions under which films were found to contain included grains, showed that the incorporation of wurtzite structure grains in sphalerite structure films was favoured by contamination and by excessively high or low substrate temperatures (figs. 1 and 3, 4 and 7). In the case of electron beam evaporated CdS it proved possible however, for all of the ionic substrates tried, to eliminate the included grains by adopting optimum substrate temperatures and substrate preparation techniques. On the basis of our experience of ZnS, ZnSe, ZnTe and CdS, and by comparison with the results of others as mentioned in section 1, it seems probable that the most important factor contributing to this success was the elimination of contamination by the use of focused electron beam evaporation. This interpretation is consistent with the fact that we did not observe any of the more complex and randomly oriented structures found by Aggarwal and Goswami [30] in films of CdS and ZnS evaporated, apparently under less clean conditions than those used here, on to (100), (110) and (111) faces of NaCl.

When the largest defects, the included grains, had been eliminated, planar defects dominated the appearance of the micrographs and diffraction patterns (fig. 9). It is not possible by means of observations like those of figs. 6 and 9, using diffraction contrast theory alone, to determine the nature of the planar defects observed. Any type of defect producing a relative displacement R of the crystal on opposite sides of the plane will produce stacking fault type fringes, and the areas of the defects were too small for detailed analysis. The most likely interpretations of the planar defects seen in many of the epitaxial CdS films are that they are either stacking faults or thin planar precipitates (Guinier-Preston zones).

Their elimination by growth on (111) substrates, at temperatures above 170° C for BaF_2 and 250° C for NaCl, results in films of high structural perfection (fig. 6). This perfection is comparable with that of some of the more highly developed semiconducting materials and is much greater than that of any previously reported films of II-VI compounds.

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