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Epitaxial growth and structure of CdS films evaporated onto Ge

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CdS evaporated in vacuum grew epitaxially at all substrate temperatures from 300 to 500°C on (100), (110) and (111) surfaces of germanium. On (100) substrates the CdS grew with the sphalerite structure in parallel orientation to the substrate. Films grown throughout the epitaxial range of temperature gave diffraction patterns that contained no satellite spots. They all contained ⟨111⟩ streaking, however. The films were therefore free of three-dimensional defects but contained a high density of {111} planar defects. On the (110) substrates the CdS grew with the sphalerite structure in parallel orientation for substrate temperatures below about 370°C and the diffraction patterns of these films were free of satellite spots but contained ⟨111⟩ streaks of low intensity. In the diffraction patterns of the films grown above about 370°C doubling of the spots appeared and a domain structure was observed in the micrographs. This was due to the occurrence of a domain-form phase transformation of the sphalerite structure. On the (111) substrates the CdS grew with the wurtzite structure in (0001) orientation. No satellite spots or streaks appeared in the diffraction patterns of these films. Moiré fringes were seen in the micrographs of both (100) and (111) substrate specimens.

1. Introduction

The epitaxial growth and structure of a number of II-VI compounds electron-beam evaporated in vacuum have been studied in this laboratory. Initially the films were deposited on ionic crystal substrates for ease of removal for transmission electron microscope study. More recently work has concentrated on the growth of II-VI compounds on semiconducting substrates, especially germanium. One of the compounds that was studied was CdS [1, 2]. It was found that CdS could be grown with a high degree of structural perfection as compared with the other II-VI compounds investigated namely ZnTe [3, 4] and ZnS [5, 6], over wide ranges of substrate temperatures on several ionic materials. Moreover it was shown that on NaCl, CdS grew with the cubic sphalerite structure on (100) and (110) substrate surfaces but with the hexagonal wurtzite structure on (111) substrate surfaces [1, 2]. Preliminary studies also showed that CdS could be epitaxially grown on (111) oriented surfaces of germanium by vacuum evaporation.

This paper presents the results of a study of the growth and structure of films of CdS evaporated onto (100), (110) and (111) surfaces of germanium in vacuum.

2. Experimental methods

The CdS was evaporated from an Unvala focused electron beam furnace [7] in an oil-pumped vacuum system at pressures in the low 10^{-5} Torr range. The substrates were held in a resistance-heated furnace above the evaporator. Two thermocouples were used to check the uniformity of the substrate temperature.

The substrates were 3 mm diameter discs. This size was chosen to fit the transmission electron microscope specimen holders. The discs were ultrasonically cut from slices and chemically polished in a solution of 30 cc of 40% hydrofluoric acid, 50 cc of 70% nitric acid and 30 cc of glacial acetic acid. It was used at about 60°C with gentle stirring.

To clean them, the substrates were heated up to 600°C in vacuum and immediately allowed to cool to the selected deposition temperature. This procedure had been found to give optimum results in previous work [2, 8]. It was observed that if the germanium was heated to above

600° C, pitting of the substrate surface occurred. The vapour pressure of germanium is many orders of magnitude too low at this temperature, however, for this effect to be due to thermal etching by sublimation, and surface diffusion was also thought to be an unlikely explanation. It was established that when the substrate-heater furnace assembly was cleaned between successive depositions by heating in vacuum to about 1000° C the effect disappeared. That is, under these conditions, no pitting of the substrates occurred even when the substrates were heated to 700° C before cooling to the deposition temperature. It appears that the pitting was due to chemical attack by material that deposited on the substrate heater assembly during the previous evaporation and then re-evaporated when the substrates were heated to 600° C or more. A likely possibility would appear to be a sulphur attack on germanium. Deposition was started and stopped by removing and replacing a shutter between the evaporator and the substrate. The films were grown to thicknesses of about 2000Å at a deposition rate of about 10Å $\sec^{-1}$.

The CdS was Optran powder obtained from BDH Ltd and the germanium was p-type in the (1 1 0) and (1 1 1) cases and n-type in the (1 0 0) case in the earlier work and p-type in the later work. The change in conductivity type in the (1 0 0) case did not alter the observed structures of the epitaxial CdS films.

After deposition of the CdS the substrates were thinned from the back by jet electropolishing [9] using a solution of 35 g of KOH and 3 g of NH_4Cl dissolved in 2000 cc of deionized water. The specimens were then examined by transmission in an AEI EM6G electron microscope.

The rate of evaporation that results when employing the Unvala focused electron beam evaporator is determined by the power supplied, i.e., the beam current times the accelerating voltage and by the focusing of the furnace. The power supplied was continuously monitored and could be made the same in all depositions. The focusing was adjusted visually to give the same apparent size of heated area. A preliminary series of experiments was carried out using an Edwards High Vacuum Quartz Crystal Monitor to measure the rates of evaporation in order to determine how great the variations of evaporation rate were with time, due to changing shape of the charge, in one evaporation and also how great were the variations from one evaporation to another. It was found that the rate of evaporation could be held constant to within 2 to 3% for up to 4 min during any one run, without readjusting the focusing. This considerably exceeded the evaporation times actually used to grow the films in this and in previous work in this laboratory. It was also found that when the same power input was used with visually optimized focusing on a number of separate runs, the rate of evaporation was the same to within about ± 4%.

3. Results

3.1. Epitaxial ranges of growth temperature

It is convenient to represent the structural information in the transmission electron diffraction patterns obtained from the films by means of the parameter R introduced by Ino *et al* [10]. This represents roughly the ratio of the relative intensities of the single-orientation, epitaxial spot diffraction pattern to the randomly-oriented polycrystalline ring diffraction pattern. It is given the value $R = 100$ for epitaxial films giving only the spot pattern, $R = 0$ for unoriented polycrystalline films and intermediate values for transitional film structures giving both ring and spot patterns.

The plot of R versus T for all substrates in Fig. 1 shows that the epitaxial range of growth temperatures was approximately 300 to 500° C. An epitaxial film was obtained at 550° C on one occasion. However, on a number of subsequent attempts no film deposited when CdS was evaporated on to (1 1 1) Ge substrates at 550 and 600° C. Instead the substrates were found to be etched. Thus the maximum temperature at which CdS could be made to deposit was about 550° C (± 5 or 10° C) and above this temperature pitting attack occurred. This observation confirms the evidence quoted earlier and interpreted as showing that, unless the substrate heater was adequately cleaned, a chemical attack of Ge occurred above about 600° C by a constituent of the CdS vapour which re-evaporated from the heater during predeposition heating to clean the substrates.

No decrease in the degree of orientation, R, occurred below this maximum-deposition temperature. Such a loss of epitaxy was previously observed to take place just below the maximum-deposition temperature in the case of the epitaxial growth of ZnTe on Ge (8].

The epitaxial ranges of growth temperature for CdS on (1 1 0) and (1 0 0) surfaces of germanium, as shown in Fig. 1, were the same as in the case of

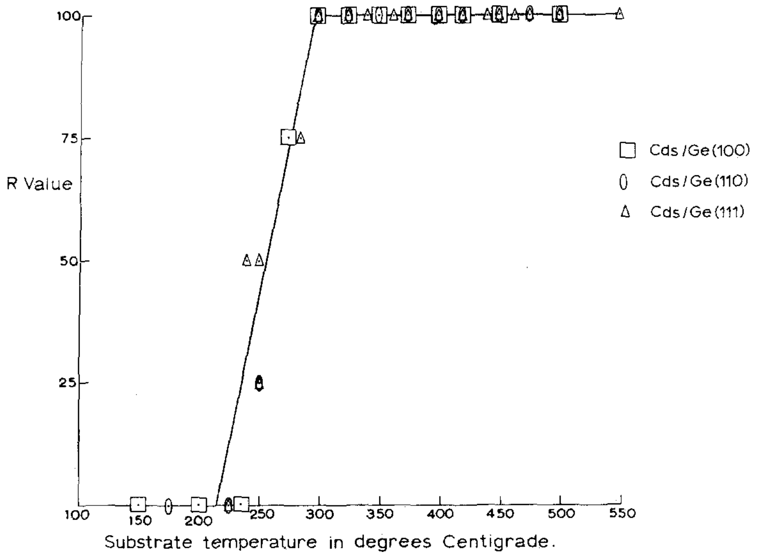

Figure 1 The degree of orientation parameter, R, versus substrate temperature for CdS films grown on Ge surfaces of three orientations. $R = 100$ indicates epitaxial growth.

(1 0 0) surfaces. Thus substrate orientation had no effect on the range of epitaxial growth temperatures although as will be shown below, the structures of the epitaxial films changed radically with substrate orientation.

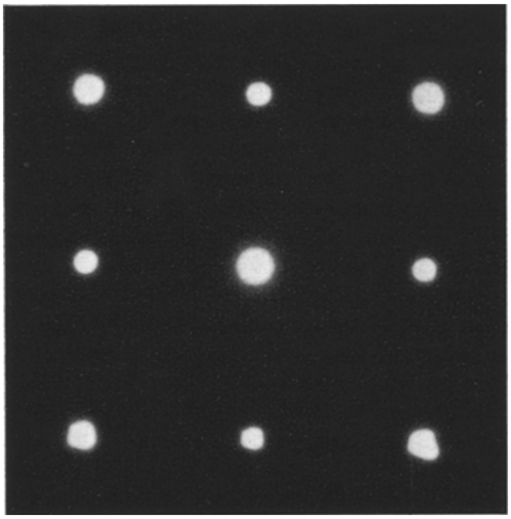

Figure 2 Transmission electron diffraction pattern of a film of CdS deposited on (1 0 0) Ge at 400° C. This pattern was recorded with the electron beam incident in the exact [1 0 0] direction.

3.2. Structure of the epitaxial films grown on (1 0 0) substrates

The epitaxial films of CdS grown on (1 0 0) germanium surfaces gave transmission electron diffraction patterns like that in Fig. 2. Indexing this and similar patterns showed that the films had the cubic sphalerite structure and were (1 0 0) oriented. By translating from thin regions consisting of CdS only to thick regions consisting mainly of Ge, it was confirmed that the diffraction spots of Ge coincided with the spots of the CdS diffraction patterns. Thus the CdS grew in parallel orientation on the germanium, that is with (1 0 0) CdS parallel to (1 0 0) Ge and [0 1 1] CdS parallel to [0 1 1] Ge.

No satellite spots were observed in the diffraction patterns of CdS films grown in this orientation for any temperature in the epitaxial growth range. Irrational or satellite diffraction spots arise from twins or included grains of material with the wurtzite structure [4, 11, 12]. The absence of these spots shows, therefore, that such three-dimensional defects were not present in any of the epitaxial films of CdS grown on (1 0 0) oriented germanium. However, the diffraction patterns of all the (1 0 0) epitaxial films were streaked in the $\langle 1 1 1 \rangle$ directions. This indicates the presence in the films of high densities of $\{1 1 1\}$ planar defects [2, 6]. The $\langle 1 1 1 \rangle$ streaks manifested themselves in the presence of satellite pseudospots in diffraction patterns reorded with the film tilted off the exact [1 0 0] beam direction as shown in Fig. 3a. That the groups of four intensity maxima consisted of pseudospots and not real satellite spots is shown by two facts.

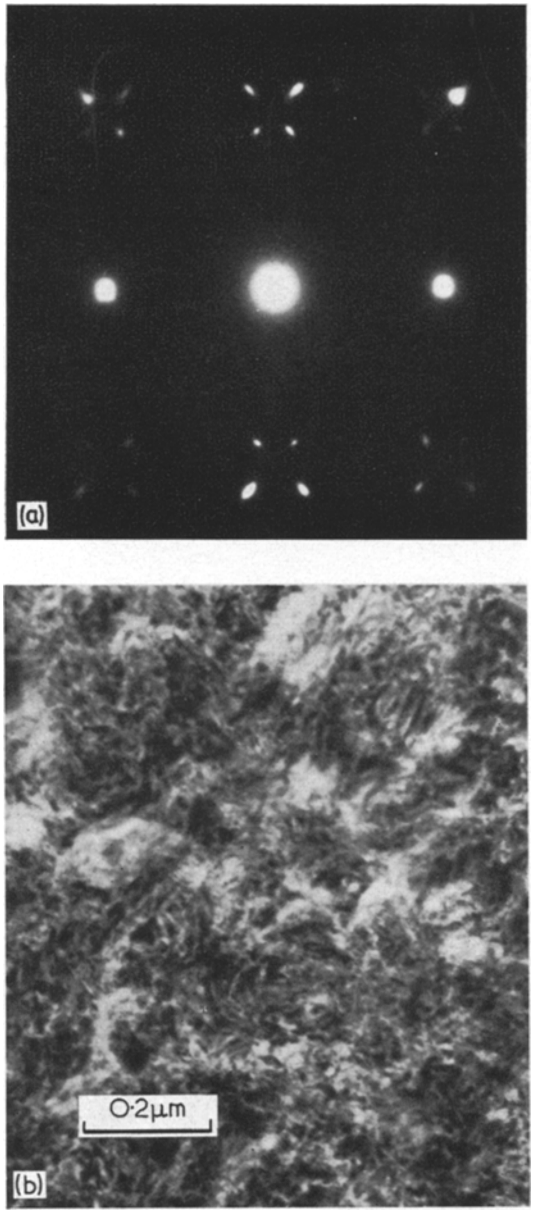

Figure 3 (a) Transmission electron diffraction pattern and (b) micrograph of a film of CdS deposited on (1 0 0) Ge at 420° C. The electron beam in this case was incident in a direction slightly off [1 0 0].

Firstly these spots are not circular but elliptical due to the fact that these beams correspond to positions where the sphere of reflection cuts through ⟨1 1 1⟩ streaks which are of circular cylindrical form. Secondly the distance of the pseudospots from the matrix spots (reciprocal lattice points) at the centres of the arrays was not constant as can be seen in Fig. 3a. The separations of the pseudospots 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 pseudospots have been previously observed and their interpretation investigated and explained in detail in work on ZnS [6] and CdS [2] films grown on (1 0 0) surfaces of NaCl. The interference of the beams corresponding to the satellite pseudospots gives rise to characteristic contrast effects. In the area covered by one {1 1 1} planar defect, which might be a stacking fault, one of the satellite pseudospot beams might be strongly excited. In such an area on the bright-field micrograph interference between the pseudospot beam and the direct, transmitted beam would give rise to a set of fringes. Examples of these fringes are shown in Fig. 3b. In the cases of ZnS [6] and CdS [2] films grown on (1 0 0) faces of NaCl these fringes were shown to occur with variable spacings corresponding to the variable positions of the pseudospots, 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 fine-scale fringe contrast was again the characteristic feature of the bright-field micrographs of the CdS films grown on (1 0 0) Ge in the present work.

3.3. Structure of the epitaxial films grown on (1 1 0) substrates

It is essential in reporting these results to divide the epitaxial growth range of substrate temperatures into two regions, that below and that above about 370° C. We consider first those films grown between 300 and about 370° C.

Indexing the transmission electron diffraction patterns of these epitaxial films, an example of which is given in Fig. 4a, showed that the structure was sphalerite in the (1 1 0) orientation. Investigation of both thin areas of the specimens consisting of CdS alone and thicker areas consisting of CdS and Ge showed that the films grew in parallel orientation. That is the epitaxial orientation relationship was (1 1 0) CdS parallel to (1 1 0) Ge and [0 0 1] CdS parallel to [0 0 1] Ge. The diffraction patterns of these films were all free of satellite spots but very faintly streaked in the ⟨1 1 1⟩ directions as in Fig. 4a. This means that the density of {1 1 1} planar defects in these

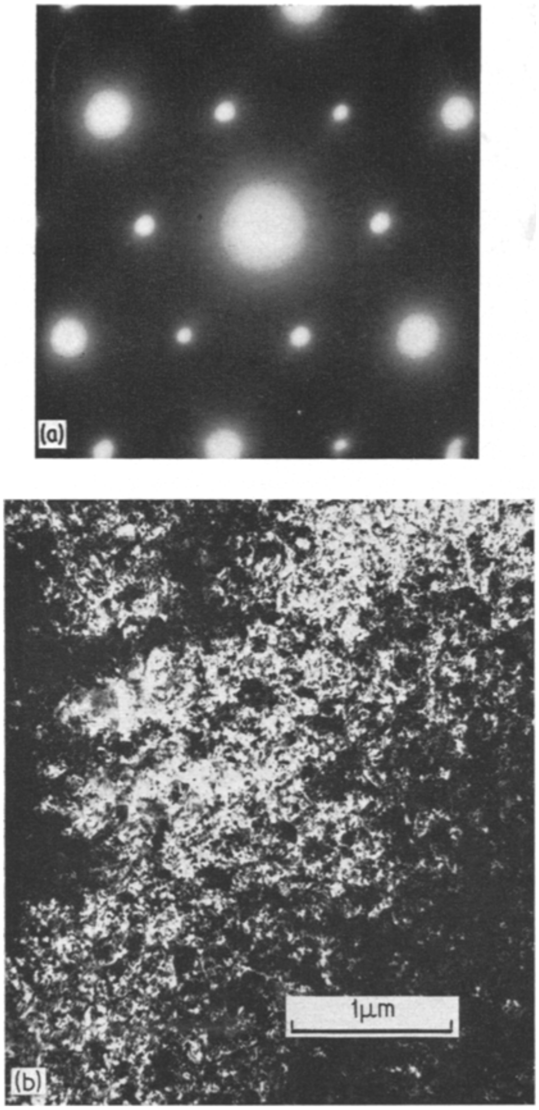

Figure 4 (a) Transmission electron diffraction pattern and (b) micrograph of a film of CdS deposited on a (1 1 0) surface of Ge at 300° C.

films while high was considerably less than in the epitaxial films grown on (1 0 0) oriented Ge substrates. The characteristic appearance of a bend extinction contour is shown in Fig. 4b.

The films grown on (1 1 0) surfaces of Ge substrates at temperatures from about 370 to 500° C were quite different from those just described. The form of the transmission electron diffraction patterns of these films was still basically that for the (1 1 0) plane of the reciprocal lattice of sphalerite but, as can be seen in the example in Fig. 5a, in general the spots were doubled. Tilting again established that this was due to the presence of ⟨1 1 1⟩ streaks normal to the two {1 1 1} planes that are inclined 35.3° to the [1 1 0] direction normal to the plane of the film as illustrated in Fig. 6. A domain structure consisting of interlocking, jig-saw-puzzle shaped areas was observed in the micrographs of these higher-

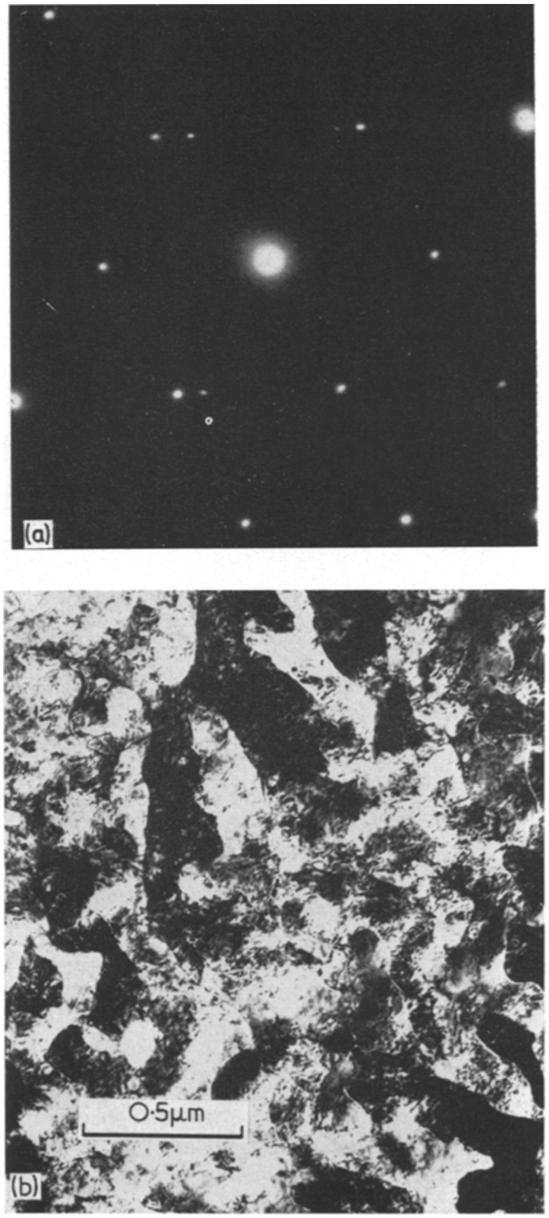

Figure 5 (a) Transmission electron diffraction pattern and (b) micrograph of a film of CdS deposited on a (1 1 0) surface of Ge at 420° C.

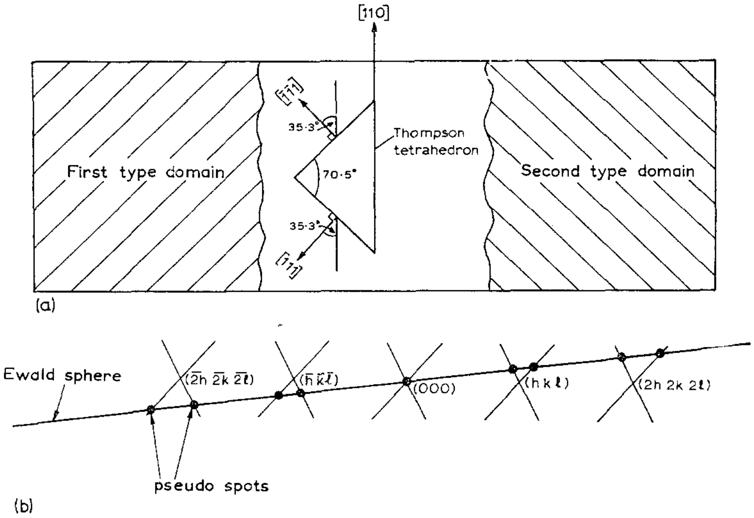

Figure 6 (a) The orientation of the two {1 1 1} planes which were found to be faulted in the two types of domains in the films of CdS grown on (1 1 0) surfaces of Ge at substrate temperatures above about 370° C. (b) A diagram of reciprocal space illustrating the way that the two ⟨1 1 1⟩ streaks normal to the {1 1 1} faulted planes shown in (a) give rise to the doubled spots when the (nearly planar) sphere of reflection is tilted slightly off the exact (1 1 0) orientation to cut the streaks at separate points.

temperature epitaxial (1 1 0) films. By dark-field transmission electron microscopy it was established that one type of domain was faulted on the one {1 1 1} plane and reflecting into the one pseudospot while the other type of domain was faulted on the other {1 1 1} plane and reflecting into the other pseudospot. This effect was of course responsible for the contrast in intensity between the two types of domain in micrographs like Fig. 5b. taken under conditions in which one pseudospot beam was more strongly excited than the other.

3.4. Structure of the epitaxial films grown on (1 1 1) substrates

By indexing the diffraction patterns like that of Fig. 7a of epitaxial films of CdS grown on (1 1 1) surfaces of germanium it was established that the films had the wurtzite structure in the (0 0 0 1) orientation. Having indexed the diffraction patterns of the CdS obtained from the thinnest areas of the specimens, it was possible to establish the epitaxial orientation relationship by comparison with the diffraction pattern for the germanium obtained from thicker areas of the specimens. This relation was found to be (0 0 0 1) CdS parallel to (1 1 1) Ge with [1 1 $\bar{2}$ 0] CdS parallel to [1 $\bar{1}$ 0] Ge as reported previously [2]. No satellite spots or streaks appeared in the diffraction patterns of films grown at any temperature in the epitaxial growth range.

Films grown at temperatures near the top end of the range contained large numbers of loops as shown in Fig. 7b.

3.5. Moiré fringe observations

Moiré fringes were the clearest and simplest form of contrast in the CdS on Ge heterojunctions. In the case of (1 1 1) heterojunctions the fringes occurred as sets of parallel lines over areas that were only 0.1 μm or less across as can be seen in Fig. 8b.

"Parallel" Moiré fringes are those that result from the interference of beams diffracted in two crystals one on top of the other, which are in parallel alignment but differ in lattice parameter. The spacing D_M of such parallel Moiré fringes is given by

$$D_M = \frac{d_1 d_2}{d_1 - d_2} \tag{1}$$

where d_1 and d_2 are the spacings of the planes giving rise to the Bragg reflections in the two crystals [13].

If the two crystals are rotated relative to one another through an angle θ, the Moiré fringes will be rotated through an angle ω, so that

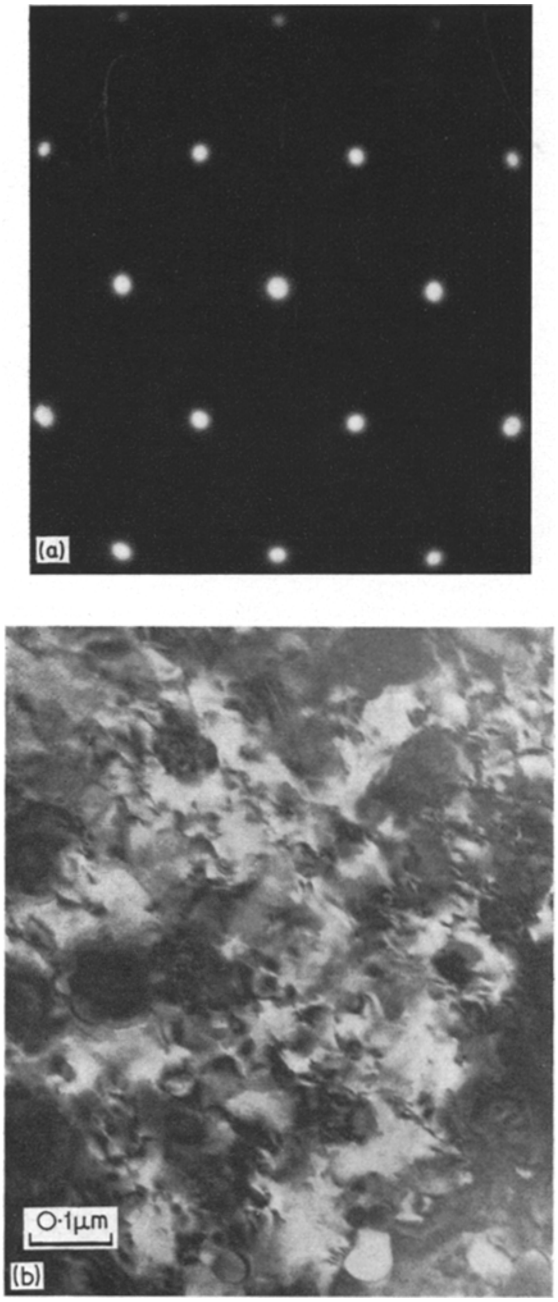

Figure 7 Epitaxial film of CdS grown on a (1 1 1) surface of Ge at 450°C. (a) Transmission electron diffraction pattern and (b) micrograph.

$$M\theta = \omega = \frac{d_1}{d_1 - d_2}\,\theta \qquad (2)$$

where M is known as the Moiré magnification. The spacing of such rotated parallel Moiré fringes becomes

$$D_{\mathrm{M}} = \frac{d_1\,d_2}{d_1 - d_2}\cos\omega\,. \qquad (3)$$

That is, the fringe spacing is reduced by a factor of cos ω.

The Moiré fringes in Fig. 8b arose through the interference of the $11\bar{2}0$ CdS and the $2\bar{2}0$ Ge reflections. For these reflections [14]

$$d_1 = 2.068\,\text{Å}$$

and

$$d_2 = 2.000\,\text{Å}\,.$$

The angle of rotation ω between the Moiré fringes in neighbouring areas of micrographs like that of Fig. 8b were measured and found to be from 23 to 28°. Substituting these values into Equation 3 gives values of $D_{\mathrm{M}} = 56$ to 53.5Å. While the "unrotated parallel Moiré fringe" spacing obtained by substituting into Equation 1 is $D_{\mathrm{M}} = 60.8$Å. The measured fringe spacings in Fig. 8b ranged from 53 to 59Å in good agreement with the theoretical values. Substituting the experimental values of the fringe rotations into Equation 2 gave the misalignment of the small areas of CdS on the Ge as 0.8 to 0.9°. This value is only slightly larger than the value of about 0.5° misorientation found between the areas of constant orientation in films of ZnTe on (1 1 1) Ge [8].

The dislocations appearing as extra half planes in the Moiré fringes, some of which are marked by circles in Fig. 8b, were counted. This gave a value for the dislocation density of about $2 \times 10^{11}\,\mathrm{cm}^{-2}$.

Only a few observations of the Moiré fringes in CdS on (1 0 0) Ge heterojunctions were recorded. However, these were similar to those in the (1 1 1) case as can be seen in Fig. 9. Again the areas of constant fringe direction were 0.1 µm or less across. The angles ω between fringes in neighbouring areas were measured as lying in the range from 16 to 22°. The Moiré fringes in this case arose from interference between the $\{2\bar{2}0\}$ beams reflected in the CdS and in the Ge. The calculated spacings for parallel Moiré fringes using Equation 1 and values for d_1 and d_2 from [14] was 70.9Å. For "parallel" Moirés with a rotation of ω from 16 to 22°, Equation 3 gave spacings of 68 to 66Å. The measured fringe spacings were 66 to 67Å, in good agreement with the calculated values.

4. Discussion

4.1. Epitaxial growth range of substrate temperatures

The minimum temperature for epitaxial growth

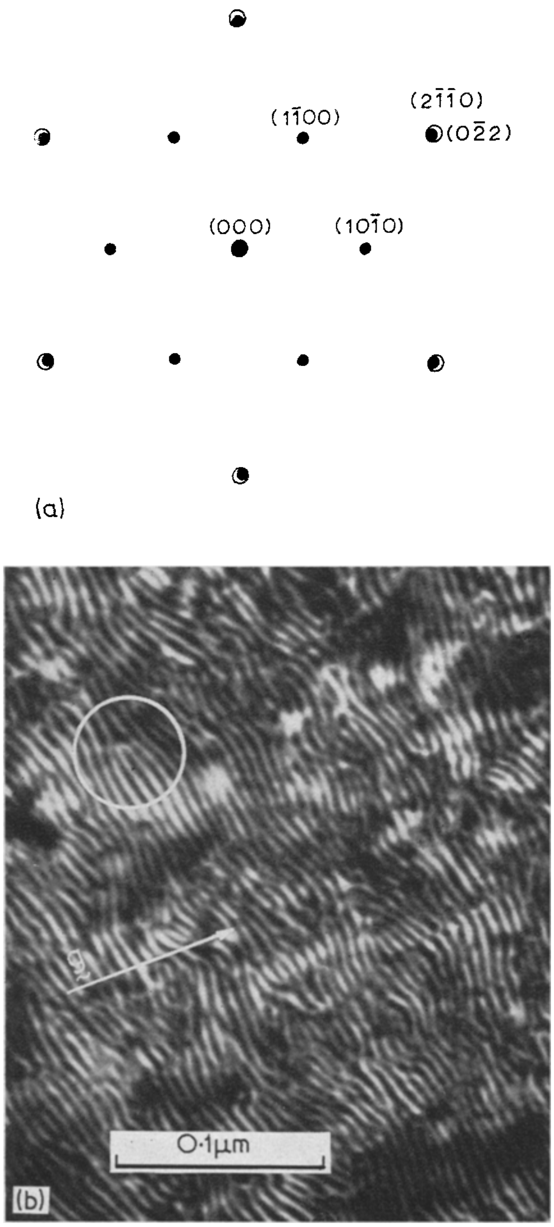

Figure 8 Moiré fringes in a heterojunction produced by epitaxial growth of CdS on a (1 1 1) surface of Ge. (a) Plot of the diffraction pattern of a CdS/(1 1 1) Ge heterojunction. Open circles are diffraction spots from Ge and solid circles are CdS diffraction spots. (b) Dark-field micrograph taken using the Ge 2$\bar{2}$0 and CdS 11$\bar{2}$0 spot. The circle marks the position of a dislocation.

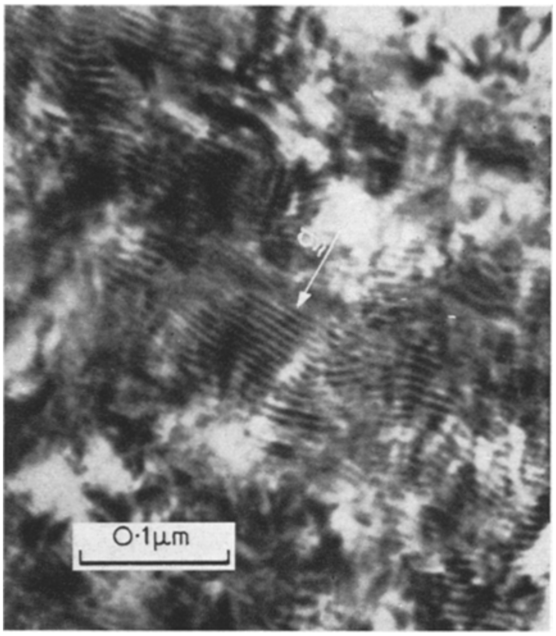

Figure 9 Moiré fringes in a CdS on (1 00) Ge heterojunction. The interference is between the 2$\bar{2}$0 CdS and Ge beams.

of CdS on Ge was 300° C for all the three singular low-index faces. This was also found to be the minimum temperature for the epitaxial growth of ZnTe on the (1 1 1) and (1 00) faces of Ge under similar conditions [8]. What determines the minimum epitaxial growth temperature is not at present known, but it is independent of whether the film structure is sphalerite or wurtzite.

The evidence quoted in Sections 2 and 3.1 indicated that the maximum substrate temperature at which CdS could be deposited on Ge by evaporation in vacuum (550 to 600° C) was determined by the onset of a chemical vapour-phase attack on germanium. In the case of ZnTe evaporated on to germanium it was also found that the maximum-deposition temperature was apparently limited by a chemical reaction between the ZnTe vapour and the Ge substrates. The maximum deposition temperature for CdS evaporated in vacuum on to Si substrates also appeared to be limited by vapour-phase chemical attack [15].

To attain results which may be related to basic thermodynamic properties of the materials concerned of course it is necessary to employ growth techniques that are sufficiently clean to ensure in so far as is possible that the observed behaviour is not dominated by the effects of uncontrolled contaminants [2, 16]. The observation of similar patterns of behaviour in several different but related cases as noted above, suggests that the growth techniques developed here are not entirely contaminant-dominated.

4.2. The role of substrate surface orientation in determining the structure of the epitaxial films

The fact that CdS can be grown with either the sphalerite or the wurtzite structure at will by altering the substrate surface orientation in the cases of both NaCl and Ge substrates may prove technologically useful, as the properties of the material with the two structures are significantly different. The ability to produce it in a variety of orientations too could be useful for example in acoustoelectric device applications.

The fact that the cubic phase (sphalerite) was obtained on the (1 0 0) and (1 1 0) substrate surfaces at low temperatures while the hexagonal phase (wurtzite) was obtained on the (1 1 1) substrate surface for both NaCl and Ge substrates suggested that this may be an example of a general pattern of behaviour.

This idea led to a review of the literature on the structures of epitaxial films of II-VI compounds [16]. Papers were found that reported the structures of films of CdS grown on eight different substrate materials in a total of seventeen different orientations. Information was also reviewed on epitaxial films of CdSe, CdTe, ZnS and ZnTe. The evidence in these reports as well as in all of our work [16] led to the generalization that II-VI compounds when grown at the low temperatures that are characteristic of epitaxial deposition by evaporation in vacuum, on (1 0 0) and (1 1 0) surfaces always had the cubic sphalerite structure. This can be understood in terms of the idea of symmetry matching. The symmetry of the (1 0 0) and (1 1 0) surfaces of cubic structure substrates cannot be matched by any planes in the hexagonal wurtzite structure. Hence if the wurtzite structure grows on (1 0 0) or (1 1 0) surfaces, there must be a large fraction of non-coincident lattice sites in the interface and the interface must be of relatively high energy. The number of non-coincidence sites can be reduced if the compounds grow with the cubic structure in parallel alignment with the substrate. In all cases recorded in the literature as well as in all the work carried out in this laboratory the cubic structure in parallel alignment was found to result from the epitaxial growth by vacuum evaporation on the (1 0 0) and (1 1 0) surfaces of ionic and covalent substrates [16].

In the case of (1 1 1) surfaces of substrate materials with cubic crystal structures, the II-VI compounds can deposit in either the (0 0 0 1) orientation of the hexagonal (wurtzite) structure or the (1 1 1) orientation of the cubic (sphalerite) structure and match the rotational symmetry of the substrate surface. The structure which was found in cases of this kind depended on a number of things. One influential factor was the polarity of the substrate surface in the case of semiconducting compound substrates, i.e., whether the substrate surface was of the A(1 1 1) type or the B($\bar{1}\bar{1}\bar{1}$) type [17-19]. In a number of cases the crystal structure with which the films deposited was found to vary with the growth temperature.

It is to be expected that the growth temperature will also help to determine which structure will grow on (1 0 0) and (1 1 0) oriented substrate surfaces. Symmetry matching considerations affect the interface energy as indicated above, but not the volume energy. The stable structure of CdS has been reported as cubic below 20° C and hexagonal above this temperature [20, 21]. However, it has also been found that the hexagonal or cubic phases can be obtained depending on the chemistry of the solution from which CdS was precipitated [22]. The evidence reported above showed that under the growth conditions used in this work, the films grew with the sphalerite structure on (1 1 0) surfaces of Ge at temperatures of about 370° C and less. Above that temperature the films grew with domain-form transformed structures. This is in broad agreement with the above mentioned evidence that CdS tends to take up the sphalerite structure at lower temperatures and the wurtzite structure at higher temperatures. It is also in agreement with the results of Igarashi who grew CdS by a vapour-phase technique at temperatures of 620 to 740° C on several crystallographic faces, including (1 1 0) and (1 0 0), of GaP, GaAs, InAs and CdTe and obtained films with the wurtzite structure in all cases [23].

Thus the orientation of the substrate surface can determine the structure of epitaxial films of CdS only if these are grown at temperatures below some critical value. The critical temperature under our growth conditions for (1 1 0) Ge surfaces was about 370° C.

4.3. The defect content of the films

The most perfect of the films were those grown on (1 1 1) oriented substrates in the epitaxial range of growth temperatures. This was shown both by the diffraction pattern and by the micrographic observations. The films grown on (1 1 1) substrates alone gave diffraction patterns that were free of both satellite spots and of streaks.

They were therefore free of three-dimensional defects such as twins and included grains of second-phase material. Their content of planar defects was below the density limit required to give visible streaks on the diffraction patterns. This interpretation was confirmed by micrographic observations like that of Fig. 7b which showed relatively low densities of defects that were therefore readily resolvable.

The films grown on (1 1 0) substrate surfaces at substrate temperatures below 370° C were less perfect. These films contained higher concentrations of planar defects giving rise to streaks in the diffraction patterns as shown in Fig. 4. The films grown on (1 0 0) surfaces were similar but had still higher densities of planar defects giving rise to more intense streaks which showed up as satellite pseudospots as shown in Fig. 3.

This observation is understandable as the lowest energy, thermodynamically stable form of CdS above some critical temperature near room temperature [20-21] is the wurtzite structure. This is the structure of the (0001) films which were found to be the most perfect. When grown on (1 0 0) and (1 1 0) surfaces the films had the less stable structure: sphalerite. In this case the films had a considerably higher defect content. When grown on (1 1 0) surfaces above 370° C indeed, the films although they had still had basically the sphalerite structure, were so heavily faulted on two particular {1 1 1} planes as to be partially transformed as shown in Figs. 5 and 6. A more complete analysis of the domain form of transformation in (1 1 0) sphalerite structure films will be given in a later paper [24].

The Moiré fringe observations show that the films consist of small areas 0.1 μm or less across which are misoriented by less than 1°. This is similar to the result of Moiré fringe observations made previously on ZnTe on Ge films. Presumably these small areas arise from separate nuclei that were initially slightly misoriented on the substrate. These small misorientations between nuclei that coalesce during growth may well be a major source for the 2×10^{11} dislocations per cm^2 that were observed. This defect density while it is high by the standards of well developed bulk semiconductors like Ge and Si is comparable with most reported values for other heteroepitaxial films [2, 8, 25-27]. To decrease this defect density will however continue to be one objective of the work in this laboratory. The electrical properties of films grown under the conditions used in this work are more likely to be dominated by their point defect than by their dislocation content. Large densities of point defects are likely to arise from small deviations from stoichiometric composition and by the entrainment of impurities.

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References

1. D. M. WILCOX and D. B. HOLT, *J. Mater. Sci.* **4** (1969) 672.
2. D. B. HOLT and D. M. WILCOX, *J. Crystal Growth* **9** (1971) 193.
3. D. B. HOLT, *Brit. J. Appl. Phys.* **17** (1968) 1395.
4. *Idem*, *J. Mater. Sci.* **4** (1969) 935.
5. J. M. WOODCOCK and D. B. HOLT, *Brit. J. Appl. Phys.* **2** (1969) 775.
6. D. B. HOLT and J. M. WOODCOCK, *J. Mater. Sci.* **5** (1970) 275.
7. B. A. UNVALA, *Le Vide* **104** (1963) 109.
8. A. R. MUFTI and D. B. HOLT, *J. Mater. Sci.* **7** (1972) 694.
9. G. BLANKENBURGS and M. J. WHEELER, *J. Inst. Metals* **92** (1963-64) 337.
10. S. INO, D. WATANABE, and S. OGAWA, *J. Phys. Soc. Japan* **19** (1964) 881.
11. D. W. PASHLEY and M. J. STOWELL, *Phil. Mag.* **8** (1963) 1605.
12. D. W. PASHLEY, M. J. STOWELL, and T. J. LAW, *Phys. Stat. Sol.* **10** (1965) 153.
13. G. A. BASSETT, J. W. MENTER, and D. W. PASHLEY, *Proc. Roy. Soc.* **A246** (1958) 345.
14. L. G. BERRY (Editor), 1970 Inorganic Index to the Powder Diffraction File (Joint Committee on Powder Diffraction Standards: Philadelphia).
15. J. B. STEYN, M.Sc. Dissertation, Imperial College, 1971.
16. D. B. HOLT and D. M. WILCOX, *Thin Solid Films* **10** (1972) 141.
17. M. WEINSTEIN, G. A. WOLFF, and B. N. DAS, *Appl. Phys. Letters* **6** (1965) 73.
18. M. WEINSTEIN and G. A. WOLFF in "Crystal Growth", Proc. Int. Conf. Crystal Growth, Boston (H. S. Peiser, Ed.) (Pergamon Press, Oxford, 1967) pp. 537-541.
19. H. HOLLOWAY and E. WILKES, *J. Appl. Phys.* **39** (1968) 5807-5809.
20. E. S. RITTNER and J. H. SHULMAN, *J. Phys. Chem.* **47** (1943) 537.
21. H. AHLBURG and R. CAINES, *ibid* **66** (1962) 185.
22. P. A. JACKSON, *J. Crystal Growth*, **3, 4** (1968) 395.
23. O. IGARASHI, *J. Appl. Phys.* **42** (1971) 4035-4043.
24. D. B. HOLT, M. I. ABDALLA and D. M. WILCOX, to be published.

25. J. W. MATTHEWS, *Phil. Mag.* 4 (1959) 1017-1029.
26. A. G. CULLIS and G. R. BOOKER, Proc. Seventh Int. Cong. Electron Microscopy, Grenoble (Soc. Franc. Micros. Electron, Paris, 1970) pp. 423, 424.
27. A. G. CULLIS and G. R. BOOKER, "Electron Microscopy and Analysis" (Inst. Phys., London, 1971) pp. 320-323.

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