JOURNAL OF MATERIALS SCIENCE 7 (1972) 694–700

Epitaxial growth and structure of ZnTe evaporated on to Ge in vacuum

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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 contain neither satellite spots nor streaks. 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.

1. Introduction

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 reduced and the structural perfection of the films can be improved by the systematic minimization of contamination from all sources in the system [1, 2].

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 [3] and CdS [2, 4] could readily be grown on Ge substrates in vacua in the 10^{-6} to 10^{-5} torr range but CdS could not be grown on Si substrates in vacua in this range [4].

The epitaxial growth and structure of ZnTe evaporated on to ionic substrates was previously investigated [5, 6] and ZnTe is a material with a number of possible important applications. In this paper the results of an investigation of the epitaxial ranges of substrate temperatures for the growth of ZnTe on Ge together with an initial analysis of the crystal structure of the films are reported.

2. Experimental methods

The films were prepared by evaporation from an Unvala focussed electron-beam heater in a vacuum in the 3 to 4 × 10^{-5} torr range in an oil diffusion pumped system similar to those described previously [2]. The substrates were held in a resistance heated furnace, resting on two thermocouples to check the constancy and consistency of the temperature readings.

The ZnTe was "Vactran" material obtained from BDH Ltd, and stated to be of "99.999 %" purity. The Ge was in the form of slices about 0.5 mm thick and 2 cm in diameter obtained from Metallurgie Hoboken. These were mechanically lapped using diamond polishes of, finally, 0.5 μm particle size. The slices were ultrasonically cleaned and mounted on glass slides using picene wax. 3 mm diameter discs were then ultrasonically cut, to fit into the transmission electron microscope specimen holder. The discs were cleaned by immersion in a succession of boiling carbon tetrachloride baths, and then washed in alcohol and deionized water. The discs were chemically polished in a solution consisting of 15 cc of glacial acetic acid, 25 cc of nitric acid of specific gravity 1.42, 15 cc of 40 % hydrofluoric acid plus one drop of bromine at about 60° C in a tilted, rotating PTFE beaker. The polishing time was about half a minute and was followed by repeated washing in deionized water and a final ultrasonic cleaning in deionized water. The discs were stored in deionized water until used as substrates for epitaxial growth.

The substrates were heated to 600°C in vacuum for thermal cleaning before the temperature was lowered to the chosen growth temperature.

After deposition of the film, the substrates had to be thinned from the other side for transmission electron microscopy. This was done by electropolishing using a horizontal jet of a solution containing 5.5 gms of KOH and 1.5 gm of NH_4Cl in a litre of deionized water. This is essentially the method of Blackenburgs and Wheeler [8].

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 by 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 and varied from 1000 to 3000 Å. Growth times were constant (one minute) so deposition rates also varied by a factor of three. The sticking coefficient of ZnTe on Ge fell rapidly above about 430°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. Results

3.1. Epitaxial ranges of growth temperatures

Films were deposited on germanium substrates with polished surfaces in both (111) and (100) orientations at a number of substrate temperatures ranging from 150 up to 500°C which was the highest temperature at which films could be made to deposit under the experimental conditions outlined above.

As in the cases 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* [7]. At low temperatures the films grow with a fine grained polycrystalline structure giving rise to ring diffraction patterns which are given the value $R = 0$. In the epitaxial temperature range films grow with a single orientation or a few simply related orientations (double positioning, twinning, etc.) and give rise to spot diffraction patterns which are given the value $R = 100$. Over a relatively narrow range of growth temperatures the film structures change from polycrystalline to epitaxial through a series of intermediate structures which are given values of R of 25, 50 or 75 on the basis of the relative intensities of the spot and ring patterns. Thus R gives an indication of the proportion of the volume of the film which has the epitaxial orientation [5, 7].

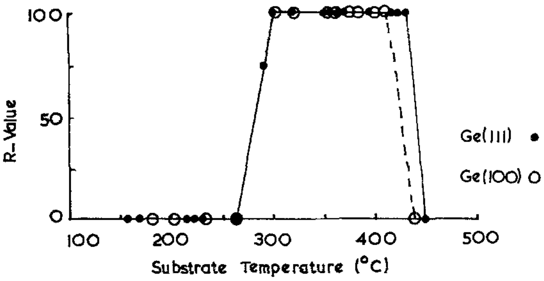


Figure 1 The degree of orientation against substrate temperature for ZnTe electron beam evaporated in high vacuum on to (111) oriented Ge discs ● and on to (100) oriented Ge surfaces ○. $R = 100$ indicates epitaxy.

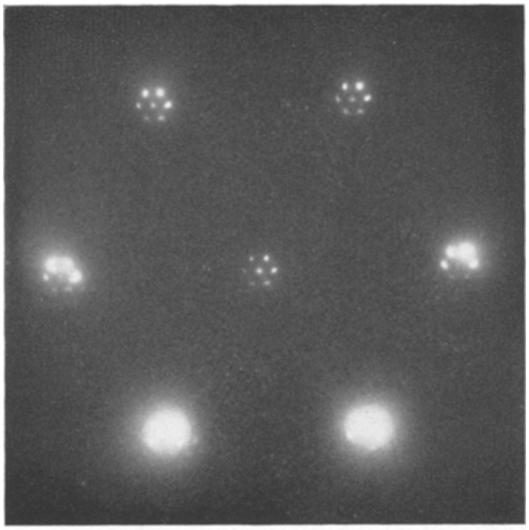
The results for (111) and (100) oriented Ge substrates were very similar. Fig. 1 for (111) substrates shows that the epitaxial growth range of substrate temperatures was 300 to about 430°C. The results for ZnTe on (100) oriented Ge substrates are also represented in fig. 1. Again the epitaxial range of growth temperatures was from 300 to about 430°C.

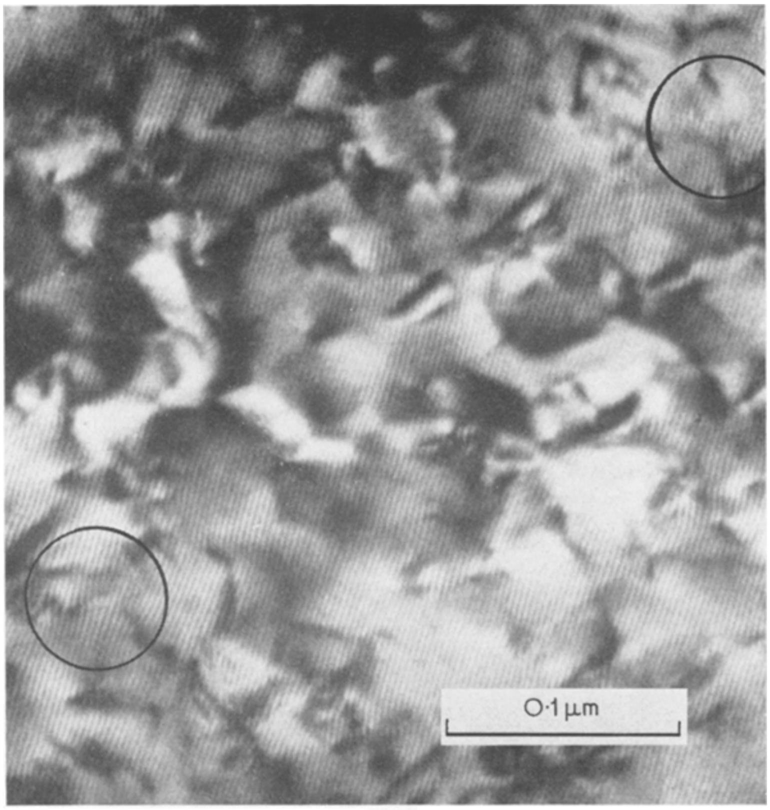
3.2. Crystal structure of the films

3.2.1. (111) films

Most films grown in the lower portion of the epitaxial plateau of fig. 1 from 300 to about 380°C gave diffraction patterns like that in fig. 2a. 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 as indicated in fig. 3a. Satellite spots due to {1 1 1} twins in the epitaxial ZnTe [6] would lie at much greater distances and in the <1 1 1> directions, not in the <1 1 0> directions, from the matrix spots as shown in fig. 3b. Thus the diffraction pattern of fig. 2a shows that the ZnTe films had the cubic sphalerite structure, and grew in parallel alignment on the Ge, that is with (1 1 1) ZnTe parallel to (1 1 1) Ge and $<1\bar{1}0>$ ZnTe parallel to $<1\bar{1}0>$ Ge. This interpretation is confirmed by the Moire fringe observations discussed below. These 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 the high densities that would produce streaks in the diffraction pattern.

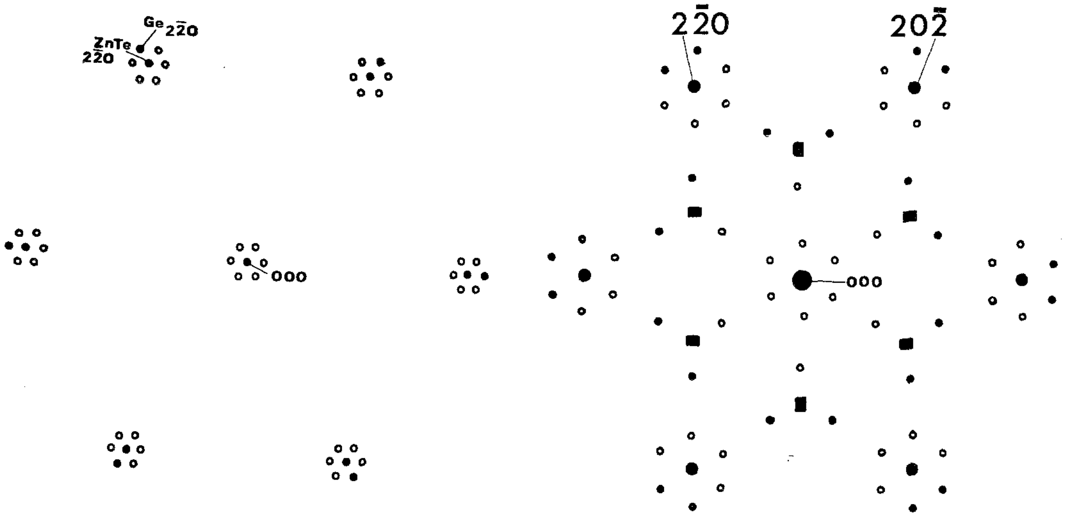
The indexing of the ring patterns obtained from ZnTe films grown on (1 1 1) Ge at temperatures below the epitaxial limit showed that


(a)



(b)

Figure 2 ZnTe film grown on (1 1 1) germanium at 370°C. (*a*) diffraction pattern. (*b*) micrograph.



(a) (b)

Figure 3 (*a*) Superposition of the (111) Ge and (111) ZnTe diffraction patterns. Central solid circles are ZnTe diffraction spots, outer solid circles are Ge diffraction spots and small 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 <110> 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.
(*b*) 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 ± 1/3 <111> which is 1/3 the distance to the centres of the triangles with 000 and two {220} spots as apices [6, 10, 11]. The satellite spots arising from (111) double positioning spots occur at the mid points of these triangles [10], at the points marked by solid squares.

in these polycrystalline films too, the structure was sphalerite.

Some films grown on (111) Ge, unlike the more perfect films grown in the lower range of epitaxial growth temperatures and described above (fig. 2), gave diffraction patterns containing satellite spots indicating the presence of {111} microtwins and (111) double positioning twins. It was found that annealing at an elevated temperature resulted in a sharper diffraction pattern of the form of fig. 3b in this case.

3.2.2. *(100) films*

The ZnTe films grown on (100) germanium at all temperatures in the epitaxial range gave diffraction patterns that were free of both satellite spots and streaks, as shown in fig. 4b. The films were therefore free of high densities of both three- and two-dimensional defects. The micrograph of fig. 4a shows only a low density of dislocations to be present in the films. The dark areas are due to incomplete removal of the Ge. Indexing of the diffraction patterns showed that the films had the sphalerite structure and grew in parallel orientation on the germanium. That is the epitaxial orientation relationship was (100) ZnTe parallel to (100) Ge and [0$\bar{1}$0] ZnTe parallel to [0$\bar{1}$0] Ge.

3.3. Moire fringes and stacking faults in (111) specimens

Interference between the 220 beams diffracted by germanium and by zinc telluride as shown in fig. 2a leads to the appearance of Moire fringes as shown in fig. 2b. These fringes are of the type called parallel Moires and are due to the overlapping of two crystals, the Ge and the ZnTe, of similar structure and in parallel alignment but differing in lattice parameter. For such Moire fringes, the spacing M is given by [12]

$$M = \frac{d_1\, d_2}{|d_2 - d_1|} \qquad (1)$$

Substituting for d_1 and d_2 the (220) spacings for ZnTe and for Ge obtained from

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

with $a = 5.6575$ for germanium [13] and $a = 6.1037$ for ZnTe [14], gives a value for the fringe spacing of 27.6 Å. The observed value in fig. 2b is 25 Å, in good agreement with the calculated value.

Here and there, at points such as those encircled in fig. 2b, localized bends and terminations of individual Moire fringes can be seen. These are a form of image of dislocations in the specimens [12]. Aside from this however the fringes are straight and parallel over large areas of the specimen. Over distances of up to 1 or 2 μm these fringes were found to be parallel to within 8°.

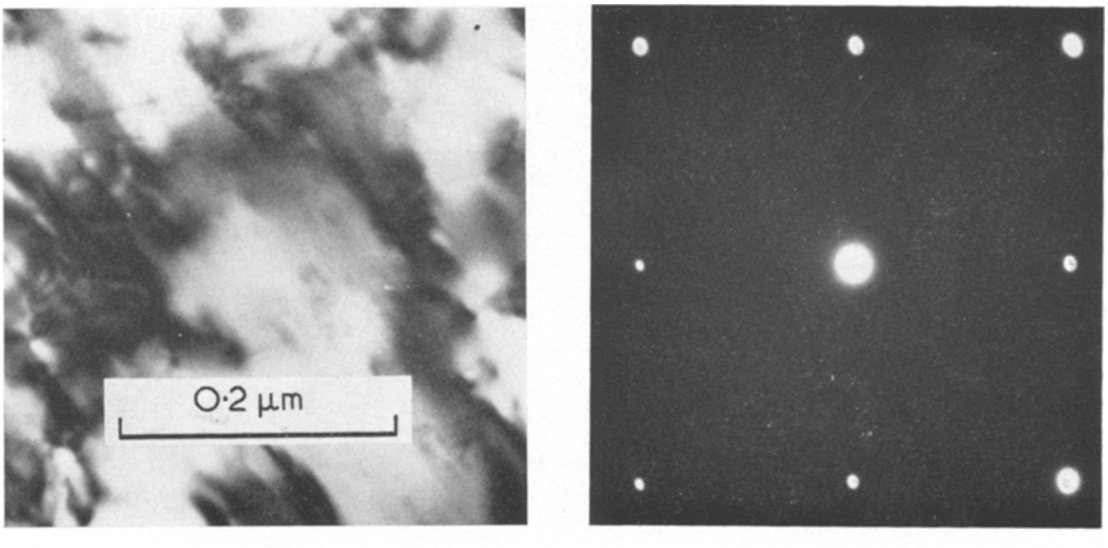
If two overlapping crystals that differ in lattice spacing are rotated through an angle θ from parallel alignment, the Moire fringes will be rotated through a much larger angle ω given [12] by

$$\omega = \frac{d_1}{|d_1 - d_2|}\,\theta \qquad (3)$$

Observation that the fringes in fig. 2b do not rotate through more than an angle ω of 8°, means on substituting the values of d_{220} for Ge and ZnTe from equation 2 into 3 that the lattice rotation angle θ cannot be more than about half a degree. That is, the parallel alignment of the ZnTe on (111) Ge is accurate to within this limit.

When the Moire fringes are out of contrast the most prominent features to be seen are bent stacking faults as shown in fig. 5. The density of the faults in films grown at temperatures near 350° C was found to be about 8×10^9 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 Matthews [15]. The projected widths of the faults are remarkably constant. In fig. 5 for example, the widths correspond to a film thickness of 1200 ± 100 Å. 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. Optical 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). Moreover in a number of these cases films were examined by scanning electron microscopy 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 focus on them.

In the ZnTe films, few of the stacking faults were observed to contain more than one bend, that is to contain more than one stair rod dislocation connecting stacking faults on intersecting planes. In the case of gold films grown on NaCl, however, more than half of all the stair



(a) (b)

Figure 4 Epitaxial film of ZnTe grown on (100) germanium at 380° C. (*a*) micrograph. (*b*) diffraction pattern.

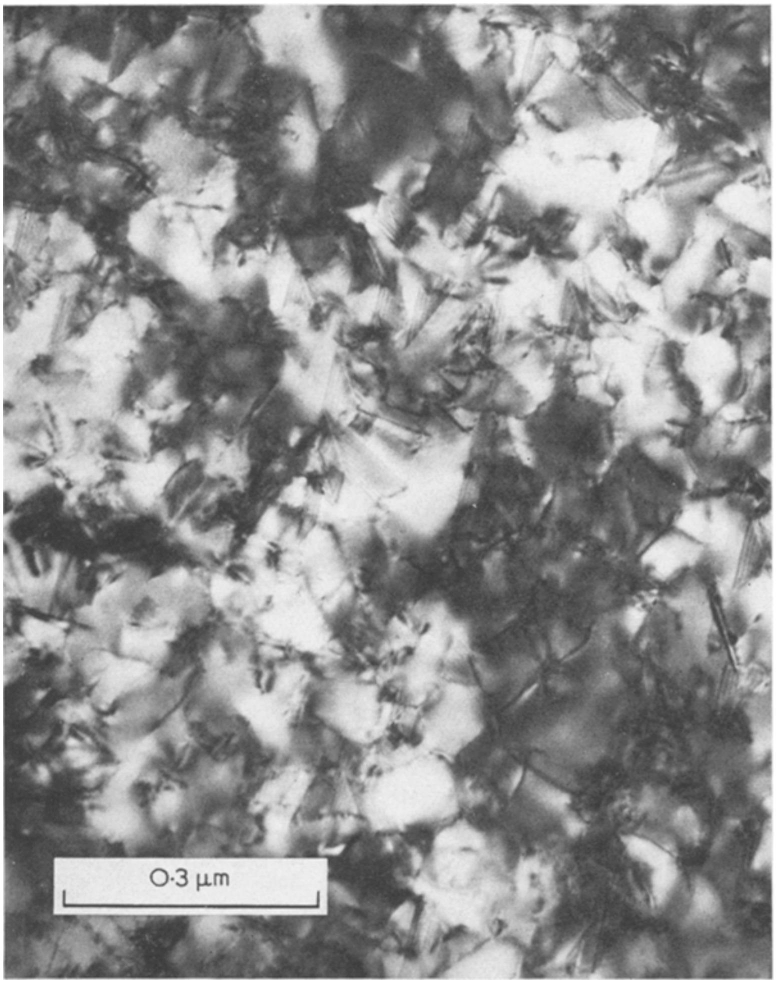


Figure 5 Transmission electron micrograph of a film of ZnTe grown on (1 1 1) Ge at 350° C.

rod dislocations occurred in stacking faults containing two or more bends [15].

4. Discussion

4.1. Epitaxial ranges of growth temperature

The ranges of substrate temperature over which ZnTe grew epitaxially on (1 0 0) and (1 1 1) 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 (1 1 1) surfaces of Ge [2]. The minimum epitaxial growth temperature would thus appear to be independent of the particular II–VI compound being deposited and of the orientation of the substrate surface.

The form of the *R* versus *T* curves of fig. 1 is similar to those obtained previously for ZnTe [5], ZnS [1] and CdS [9] evaporated in vacuum on to ionic crystal substrates. In all these cases, at the highest temperatures, the degree of orientation of the films falls just before the films cease to deposit. In the case of the ionic substrates this was due to the onset of the sublimation of the substrate. In the present case however, the temperature concerned is well below the sublimation temperature of germanium as is shown by vapour pressure data. A lower limit for this temperature is also known from the work done in establishing the temperature for thermally cleaning the substrates 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 germanium 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 germanium 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.

4.2. The crystal structure of the films

The growth of the 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 surfaces. 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 [2]. The degree of structural perfection of the films is relatively high. As compared with films of ZnTe grown on ionic crystal substrates [5, 6] 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 films grown in the (100) orientation at all temperatures in the epitaxial range. In fact as evidenced by both the relatively low density of stacking faults and the parallel alignment of the Moire fringes the best of these films of ZnTe on Ge were comparable in structural perfection with other heteroepitaxial films such as Au on NaCl [15] and the recently reported films of Ge grown on Si in ultrahigh vacuum [16, 17].

Acknowledgements

Thanks are due to Professor J. G. Ball for the provision of research facilities, to Mr B. H. Barter for assistance in the construction of the equipment and to Dr D. M. Wilcox for many helpful discussions.

One of us (A.R.M.) would also like to thank the Wali Mohammed Trust for financial support.

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Received 28 October and accepted 24 December 1971.