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The Epitaxy of Zinc Sulphide on Silicon

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The epitaxy of zinc sulphide films on silicon has been studied by means of X-ray and electron diffraction and by scanning electron microscopy. Results have shown that due to the nature of the stacking of atoms, planar defects will predominate in such a sphalerite structure material; this is similar to the results of Pashley and Stowell on face centred cubic metals. Such defects have been shown to be more prevalent on (111) and (110) orientations, compared with the (100) orientation which gave the best epitaxial single crystal films. These results agree with other work from this laboratory on the epitaxy of zinc selenide on germanium and silicon.

1. Introduction

In the past the overall technology and general usefulness of semiconductors have been directly related to the ease with which the materials concerned may be produced in single crystal form in a controlled and reproducible manner.

II-VI compounds form a group of semiconductor materials, which although having many potentially useful properties, have not been exploited to any great extent perhaps because of the difficulties involved in producing good quality single crystals.

For a variety of reasons most of the current semiconductor device technology is concerned with epitaxial single crystal films, thus it is no longer mandatory to produce bulk single crystals for useful devices. In addition, such films are perhaps more immediately compatible with other film deposit techniques used for interconnections and other components. In view of these considerations, and further that films may be considered more nearly as requiring control in two dimensions compared with three dimensions in bulk crystals, it seems more pertinent to study II-VI compounds in film form rather than bulk crystals.

Although a number of papers have been published concerning single crystal films of II-VI semiconducting compounds on ionic substrates (for example [1, 2] and those papers reviewed in connection with defects in such films [3], this work is of less immediate device interest. From this point of view there is rather more potential in those II-VI compound films which result in the formation of semiconductor heterojunctions, this work has been reviewed by J. T. Calow *et al* [4], although not with particular emphasis on II-VI compounds: there is of course interest in epitaxial films of such compounds on insulating substrates such as sapphire [5]. Some of these earlier studies (see [4]), have involved the interesting class of heterojunctions composed of II-VI materials on elemental group IV semiconductors – particularly ZnSe on Ge. More recent work has also examined this pair of materials [6, 7] and the II-VI compound with the largest energy gap – ZnS. ZnS has been grown on GaP [8], Si [9] and metals [10]. Two basic techniques have been used in this later work, firstly, vapour transport processes [6, 8, 10], and secondly vacuum evaporation [7, 9]. In most of this current work, however, a detailed examination of structure related to the quality of epitaxy has not been carried out, and in particular the question of large area epitaxy has not been investigated.

The work reported in this paper forms part of a study directed at the fabrication of semiconductor heterojunctions, for infra-red to visible image converters, between large energy gap II-VI compounds such as zinc sulphide or zinc selenide and other materials such as silicon or germanium. In particular in this instance, zinc sulphide on silicon is considered. The primary objective of this paper is to study the structure and the quality of epitaxy of such films in relation to growth conditions and morphology, and secondly to examine epitaxy on larger areas (tens of mm^2). A higher resolution examination of the films to study point defects will form the basis of a later paper.

2. Experimental

The films examined in this work were deposited by condensation of vapour sublimed from a zinc sulphide source (heated by electron bombardment) in an ion-pumped ultra-high vacuum system with ultimate pressure better than 7 nNm^{-2} (5×10^{-11} torr). For full details of sample fabrication, see [11]. The silicon substrates of (1 1 1), (1 1 0) and (1 0 0) orientations were of various resistivities and conductivity types with high quality polished surfaces. In general, substrates with low dislocation density were used. Zinc sulphide starting material was of the highest commercially available purity from various sources, and analysis by MS7 solid source mass spectrograph indicated the impurity content as about 100 ppm. A standard substrate cleaning procedure was used which resulted in a clean, flat surface with a minimum of work damage but having a small ($\sim$5 nm) thickness of oxide which was removed by sublimation in the UHV chamber (see [11]).

After the deposition process, the films were carefully mounted (without touching the surface) for examination by glancing angle electron diffraction. This was carried out using a high resolution diffraction stage in its position below the projector lens in an AEI EM6G electron microscope. Some additional transmission diffraction through thinned samples was carried out both in the normal sample position and in the high resolution stage. A further technique employed was glancing angle X-ray diffraction, using a specially modified goniometer, to hold the sample at glancing incidence to the beam; the diffracted beam was recorded using a Polaroid X-ray cassette, the geometry is then merely that of a forward transmission Laue camera. This enabled films thicker than about 0.4 μm to be examined. The films were also examined in the Cambridge Instruments Stereoscan scanning electron microscope, using both the reflected and emissive modes, at a beam voltage of 20 kV. In all these methods it was possible to examine the films non-destructively, thus enabling electrical and optical measurements to be made on the undisturbed surface.

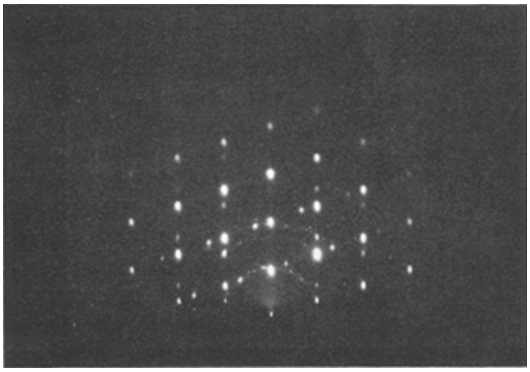

Figure 1 Glancing angle electron diffraction patterns from ZnS film evaporated onto (1 1 1) oriented silicon substrate, substrate temperature $\sim$ 275° C, 80 kV, [0 1 $\bar{1}$] azimuth.

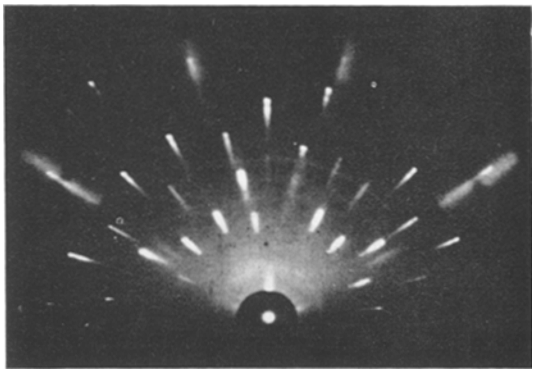

Figure 2 Glancing angle X-ray diffraction pattern from ZnS evaporated onto (1 1 1) oriented silicon substrate, substrate temperature $\sim$ 300° C, good mechanical polish.

3. Results

Films were grown on the three low index planes (1 1 1), (1 0 0) and (1 1 0) of silicon, the orientations were accurate to $\pm$ 1°. Initially it was not certain whether the films would be cubic or hexagonal in structure, consequently the (1 1 1) orientation was used. Fig. 1 shows a typical glancing angle electron diffraction pattern obtained from the better (1 1 1) films ([0 1 $\bar{1}$] azimuth). It is clear that, although a spot pattern is observed, many extra reflections occur. When films such as these are deposited at rather faster rates there is a tendency for the extra reflections lying along the diagonal directions to disappear. This only leaves extra reflections along the lines of spots perpendicular to the shadow edge. Glancing angle X-ray diffraction patterns from such films show diffuse spots (in fact streaks due to the geometry) superimposed on the sharper spots from the substrate (fig. 2).

When the best (100) films are examined by the X-ray diffraction technique the reflections from the layer are indistinguishable from those from the substrate and may only be detected for reflections which are forbidden for the substrate. Glancing angle electron diffraction patterns from these films show very faint extra reflections for films deposited at low rates, but otherwise good spot patterns. If the substrate temperature is dropped by only approximately 25° C these reflections become distinctly arced (fig. 3). The drop in temperature also has a marked effect on the appearance of the surface when examined by the Scanning Electron Microscope (SEM). At the higher temperature, fig. 4a, the surface appears randomly facetted, whereas at the lower temperature, fig. 4b, facetting disappears and only a random roughness is evident. If, on the other hand the substrate temperature is raised by approximately 25° C, though the diffraction patterns remain characteristic of single crystal films, the SEM shows that the surface takes on a definite crystallographic facet appearance (fig. 5). In addition, relatively sharp Coates Lines [12, 13] are observed. Some of these (100) samples have been thinned by jet etching, and though giving sharp spot patterns with no extra reflections when examined by selected area transmission electron diffraction, do in fact give extra reflections when using the high resolution diffraction stage (fig. 6).

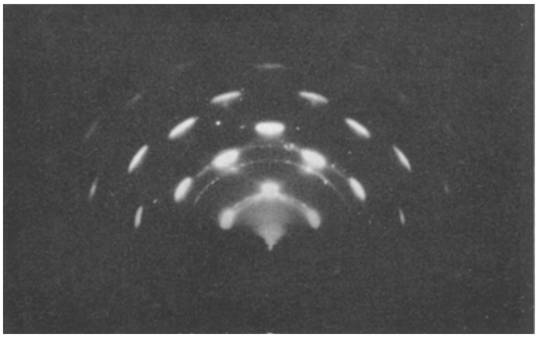

Figure 3 Glancing angle electron diffraction patterns from ZnS evaporated onto (100) oriented silicon substrates, substrate temperature ~275° C, [01$\bar{1}$] azimuth, 80 kV.

With (110) oriented substrates, electron diffraction produced good spot patterns at similar substrate temperatures, but as may be seen in fig. 7 a large number of additional spots occurred. Jet etched samples showed good transmission electron diffraction spot patterns with some interspot streaking.

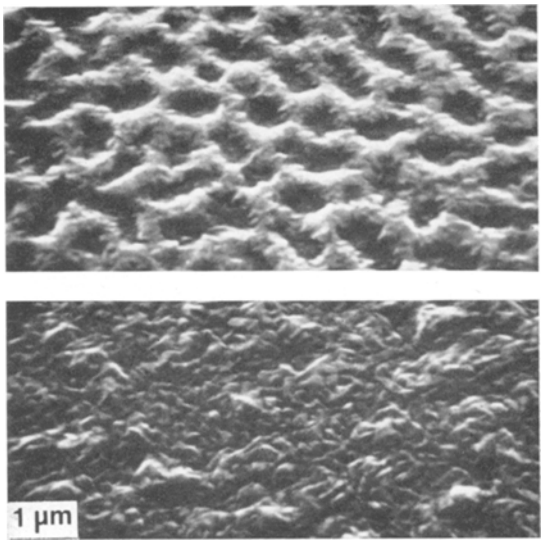

Figure 4 SEM photographs of the surface of a ZnS film evaporated onto (100) oriented silicon substrates, substrate temperature (a) 300° C, (b) ~275° C, emissive mode 45°.

The salient features of results obtained from approximately sixty samples are summarised in

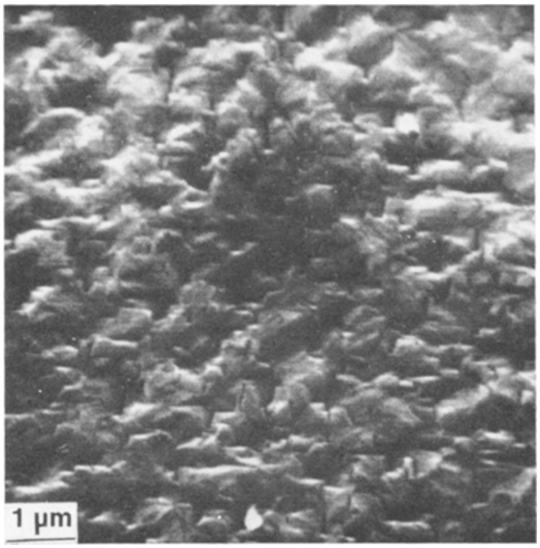

Figure 5 SEM photograph of the surface of a ZnS film evaporated onto (100) oriented silicon substrate, substrate temperature ~325° C, emissive mode 45°.

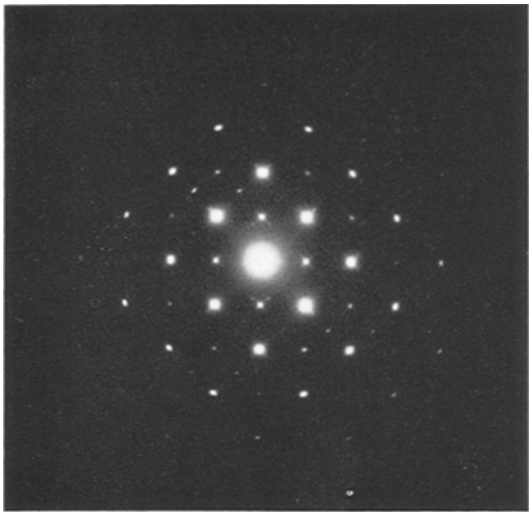

Figure 6 Transmission electron diffraction pattern from (100) sample, temperature $\sim$300° C, high resolution diffraction stage used, 80 kV.

the table. This includes samples ranging from those in which ordering began to occur, up to the best (100) epitaxial layers. All of the films were deposited using vapour arrival rates of from 10^{19} to 10^{20} molecules m^{-2} s^{-1}.

4. Discussion

4.1. Introduction

As a preliminary to a discussion of the above results, it seems worthwhile to note the crystallographic differences between the various forms of the fcc lattice involved in substrate and film. Certain of the possible fcc reflections for the diamond structure of the substrate are forbidden due to the fact that all atoms are the same. In principle the film can have either sphalerite (fcc) or wurtzite (hexagonal) structures, in practice all of the above results with one possible exception (see below) can be explained in terms of the sphalerite structure. Although the diamond and sphalerite structures are geometrically identical, reflections which are forbidden for the diamond structure are allowed in the sphalerite form because each atom has a dissimilar atom as nearest neighbour. Consequently for sphalerite all fcc reflections are allowed although the intensity distributions may vary substantially.

Defects which are primarily localised (point defects) do not alter allowed and forbidden reflections but they can broaden an individual

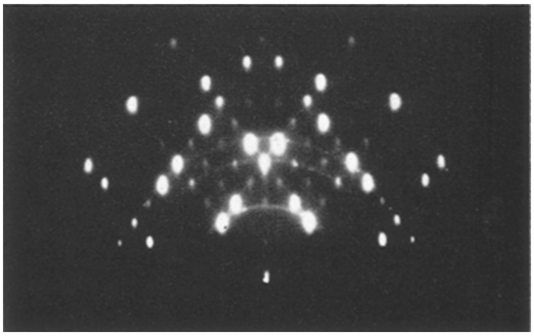

Figure 7 Glancing angle electron diffraction pattern from ZnS evaporated onto (110) oriented silicon substrates, substrate temperature $\sim$300° C, $[0\bar{1}0]$ azimuth, 80 kV.

Substrate orientation	*Substrate surface*	*Substrate temperature*	*Glancing angle electron diffraction*	*Glancing angle X-ray diffraction*	*Scanning electron microscope exam.*
(111)	Diamond polished, scratches	$\sim$200° C	Polycrystalline with 1 to 2 extra rings	Polycrystalline with ordering	Featureless
(111)	Diamond polished, scratches	See [9]	Slightly less polycrystalline	—	Featureless
(111)	Zirconia and alumina polished, featureless	$\sim$250 to 300° C	Single crystal patterns with extra spots	Single crystal patterns having diffuse spots	Observable roughness, weak coates lines
(100)	,,	$\sim$300° C	Single crystal patterns with weak satellite spots and streaks	Single crystal patterns sharp spots	Random facets, weak Coates Lines
(100)	,,	$\sim$300 to 325° C	Single crystal patterns		Crystallographic facets Coates Lines
(100)	,,	$\sim$275° C	Multi-crystal patterns having arced spots	—	Random roughness
(110)	,,	$\sim$300 to 325° C	Single crystal patterns with extra spots	—	Random facets, weak Coates Lines
(110)	,,	$\sim$275° C	Multi-crystal patterns having arced spots	—	Random roughness

reflection. However, more extended defects, eg grain boundaries and planar defects (such as stacking faults and twins), although not strictly altering allowed and forbidden reflections, may produce apparent forbidden reflections and other extra reflections.

In an investigation such as that described in this paper, which forms part of a larger study of properties other than structural, it was felt that although the occasional sample could be examined by destructive means, e.g. transmission electron microscopy, in general all techniques must be non-destructive. With films greater than about 5 μm in thickness this presents no real problem, for a reasonably complete study of almost all structural properties may be made by X-ray methods (except for the smallest point defects). When the film thicknesses are much less (0.2 to 1 μm), as in the present work, X-ray techniques are not completely adequate and glancing angle electron diffraction must be used. However, in much the same way that transmission electron microscopy does not really represent the sample (because of the small area examined), so glancing angle electron diffraction does not really represent the sample (because only the extreme surface layers are examined, approximately 5 atomic planes in good conditions [14]). In view of the surface sensitivity of glancing angle electron diffraction and particularly in view of the results obtained in this work, spot rather than streak patterns, indicating transmission through surface asperities, c.f. SEM photographs, it is important to use other complementary methods. Accordingly the glancing angle X-ray diffraction method described above was developed, it was necessary to use this because the more usual flat plate methods are not sensitive to films of this thickness. This method is a useful complement to the other glancing angle technique for it enables an investigation of structure with depth to be made and also shows the orientation of film relative to substrate. As there was some interest in the surface morphology in this work, not only from the growth viewpoint but also from the device side, films were examined in the SEM. In many respects this is more satisfactory than either optical microscopy (higher magnification and greater depth of focus) or replication (which can introduce artifacts) despite the somewhat lower resolution (10 to 20 nm) compared with replication ($\sim$2 nm). In addition the SEM can now provide crystallographic information [12, 13], this serves not only as a useful confirmation of the other techniques but also (due to the relatively large area examined, approximately 25 mm^2 per frame) as a criterion of large area epitaxy.

4.2. (111) Films

The initial deposits were polycrystalline and of sphalerite structure with one or two extra rings. Similar results have been published by Pashley *et al* [15, 16] in a study of gold films. In their work it was shown that the extra rings were due to twinning and subsequent double diffraction and not the presence of hexagonal phase material, the above results may be explained in the same way. These films were deposited on what one must conclude were rather poorly polished substrates, which resulted presumably in three-dimensional incoherent nucleation on the various surface features and subsequent growth of a polycrystalline film. It is of interest to note that although electron diffraction indicated that the film was polycrystalline, a certain amount of ordering was suggested by X-ray diffraction.

Films deposited on substrates with a good polish under identical conditions, gave in the best circumstances epitaxial single crystal films. It seems evident therefore, that the improvement in substrate surface reduced the amount of incoherent nucleation to such a stage that the film could give a good spot pattern, despite the diffuseness of the X-ray spots indicating a high density of defects, and despite the multiplicity of spots indicating a substantial amount of twinning. In fact similar diffraction patterns have been observed by Holloway [17] for films of III-V semiconductor compounds on Group IV semiconductors. Such results may be explained completely on the basis of the scheme put forward by Pashley and Stowell [16], in which it is shown that twinning in fcc lattices results in reciprocal lattice points described by reciprocal lattice vectors of the form

$$\mathbf{R} = \mathbf{r}_a \pm \tfrac{1}{3}(hkl) \qquad (1)$$

where $\mathbf{r}_a$ is an allowed reciprocal lattice vector for the matrix and (hkl) is the twin plane ((111) for the fcc lattice). It must be noted that not all of the twin spots suggested by equation 1 are in fact allowed, if (uvw) is an allowed reciprocal lattice point then a twin reciprocal lattice point must be: $(u \pm \frac{1}{3}h,\ v \pm \frac{1}{3}k,\ w \pm \frac{1}{3}l)$, but its distance from the origin must be equal to the reciprocal lattice vector of any allowed point, which puts a considerable theoretical limitation on possible twin points. In practice there are two means whereby further points may occur, firstly, by double diffraction and secondly, by the occurrence of multiple twinning. In double diffraction a beam diffracted by the matrix may be diffracted subsequently by a twinned portion of the crystal and vice versa. Multiple twinning is the result of the crystal twinning about a particular $\langle 111\rangle$ axis and then twinning again about either another or the same $\langle 111\rangle$ axis; multiple twinning has been considered in some detail by Holloway [17]. Some of the effects pertinent to this work are illustrated in fig. 8. The normal single crystal pattern for the $\langle 01\bar{1}\rangle$ azimuth of (111) oriented fcc samples is shown in fig. 8a, fig. 8b shows the extra twin spots occurring when a single (111) twin plane with axis parallel to the sample surface is introduced (assuming no double diffraction). In fig. 8c spots from all four possible {111} twin planes which are observable in this azimuth and the spots which would result from double diffraction in such circumstances are shown. Comparison of fig. 1 with fig. 8 shows that if the double diffraction points are omitted in fig. 8, almost all points are explained; however there are weak additional spots symmetrically placed at $\frac{1}{3}\langle 111\rangle$ positions about the (111) and higher order spots. As all spots due to single {111} twin planes have been included it must be concluded that these are due to multiple twinning, in particular in this instance, twofold twinning. Rotation of such samples about the surface normal to the $\langle 11\bar{2}\rangle$ azimuth, tends to confirm this, for very weak spots may be observed at the intersection of the diagonals of the rectangular arrays of the primary spots. These spots at approximate $\frac{1}{2}\langle 111\rangle$ positions cannot be explained on the basis of any of the (111) twin planes and subsequent double diffraction. There are three alternative explanations, either multiple twinning on (111) planes, stacking faults, or hexagonal structure material. Though the spot does occur at the correct position for a hexagonal reflection, this explanation must be ruled out, for other spots should then occur in $\langle 01\bar{1}\rangle$ and other azimuth directions, and these have not been observed. The effect of stacking faults (see next section and [17]) is to smear reciprocal lattice spots along $\langle 111\rangle$ directions, resulting in streaks; it is just conceivable that the extra spots observed are in fact a section of such a streak; as no streaking attributable to such faults has been seen in other azimuths this explanation is also ruled out. Thus the remaining alternative is of multiple twinning, which, having already been observed in other azimuths, seems to be the most likely explanation.

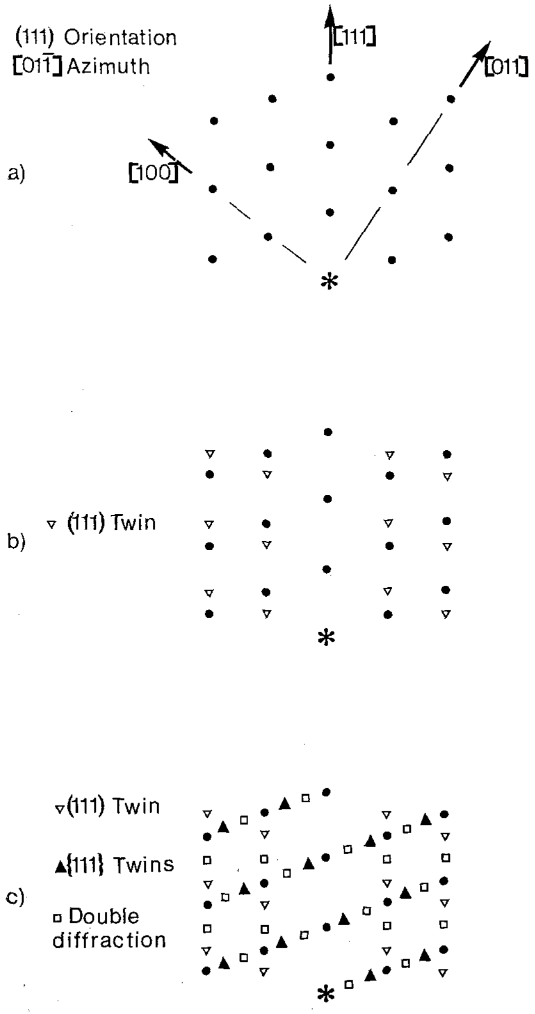

Figure 8 Reciprocal lattice sections for glancing angle electron diffraction from (111) oriented sample $[01\bar{1}]$ azimuth (a) twin free fcc crystal, (b) (111) twinning about an axis normal to sample surface, (c) all {111} twin spots observable in this azimuth and double diffraction.

Diffraction patterns obtained from films deposited at higher rates with $[01\bar{1}]$ azimuth agree identically with fig. 8b, thus it may be concluded that at the higher rate a single (111) twin occurred.

Together with the difference in structure for films having different deposit rates (more accurately growth rates) a difference in surface morphology has been found by SEM examination. As the growth rate increases, so the surface becomes more distinctly crystallographically facetted. SEM examination of the samples has

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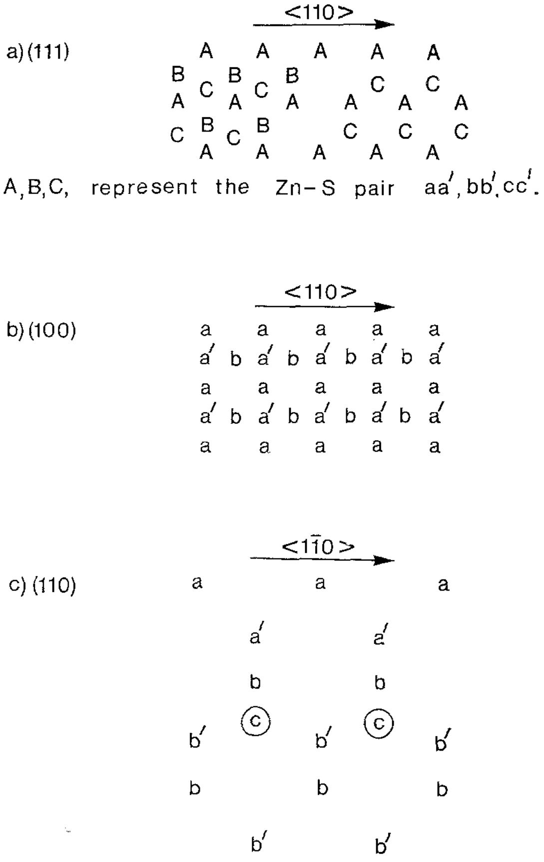
also shown particles of ZnS powder on the surfaces of samples but no inclusions in the film were observed, i.e. all the powder could be removed by light brushing; it is not entirely clear why no inclusions should occur. This is in agreement with weak and spotty ring patterns observed by electron diffraction. The rather diffuse Coates Lines, together with the broad X-ray spots observed, seem to suggest a consistent picture of an epitaxial single crystal with a relatively large density of defects, some of which are twins.

Although some few very preliminary examinations have been made of these films by transmission electron microscopy and diffraction, indicating plain (1 1 1) spot patterns, an examination of similar ZnS on silicon samples using these techniques has been reported [18] which has shown extra spots. In that study Wilkes examined samples prepared during the work of [9], and although he reaches the conclusion that the extra spots obtained are due to hexagonal material, there is an alternative explanation, namely twinning on $\{111\}$ planes and double diffraction, which in the light of the present work seems rather more likely. Pashley and Stowell [15] showed by a detailed dark field study of gold films that gave similar diffraction patterns, that the effects observed were due to twinning and double diffraction, similar work would be required to verify the alternative explanation proposed here. It seems possible that if the alternative explanation is true some of the line defects observed by transmission electron microscopy in [18] may in fact be micro twins which have to be very carefully distinguished from stacking faults. It should also be noted that some of the samples the author has been able to examine from the work of [9] have shown multiple twinning and stacking fault effects similar to those observed by Holloway [19].

It is of some interest to consider how these essentially planar defects can arise and in particular if there is any way of removing them. There seems little doubt that their main cause is double positioning associated with the well-known propensity for ZnS to form polytypes, which carries with it the implication of very small differences in energy for different atomic stacking sequences. The fcc sphalerite stacking sequence is $aa' - bb' - cc' - aa' - bb' \ldots$ and the hexagonal wurtzite is $aa' - cc' - aa' - cc' \ldots .$, where abc are one sort of atom and a' b' c' are the other sort, thus aa' etc. form a double layer of Zn and



A,B,C, represent the Zn–S pair aa', bb', cc'.

c atoms are double positioned.

Figure 9 Diagram illustrating atomic stacking sequences for (a) (1 1 1), (b) (1 0 0), (c) (1 1 0) orientations.

S atoms above one another, these are actually stacking sequences for $\langle 111 \rangle$ directions. Fig. 9a illustrates diagrammatically various of these stacking sequences, in the (1 1 1) orientation conventional fcc stacking is illustrated at the LHS of the figure and hexagonal on the RHS, the difference is merely the double positioning, i.e. the rotation of a [1 1 1] bond (the aa' pair = A) about 60°. If instead of continuing with hexagonal stacking the RHS reverts to fcc, a twin will result, equally by introducing another hexagonal stacked layer it can close the fault and revert to the same fcc stacking as the LHS leaving a micro twin, evidently defects between these extremes can occur as can the more methodical stacking involved in polytype formation. (See also [19-21]. In addition if one assumes that the A pair of atoms in the (1 1 1) orientaton represent substrate atoms, there is no *a priori* reason to suppose that the next double layer will go down preferentially as aa' or $a'a$. If this occurs over the substrate, similar faults in the stacking sequences to those above will occur where the growing layers from these areas meet. In any case therefore, when double positioning and twinning occur, a single layer (or more) of hexagonal stacking must occur and it can no longer be exactly correct to say that the film is cubic and does not contain any hexagonal material. It seems very likely from the above discussion that twinning must be a fairly frequent occurrence for ZnS with the (1 1 1) orientation.

4.3. (1 0 0) Films

Referring to fig. 9b, examination of the (1 0 0) stacking reveals that double positioning does not occur so that in this sense there is no ambiguity. If during the course of growth a (1 1 1) facet develops, twinning may occur (via double positioning); in addition there is, as in the (1 1 1) case, no *a priori* reason to prevent either a or a' atoms nucleating at different points on the substrate with consequent twinning, however, once nucleated, it is unlikely to change, for the structure would then require dissimilar atoms as nearest neighbours. On the above basis, at least qualitatively, one would expect rather less twinning for (1 0 0) films compared with (1 1 1) films.

Results obtained bear this out, if (1 1 1) twins are present no extra spots should be seen for the [0 1 0] azimuth which is in fact the case. However, for the $[0 3 \bar{1}]$ azimuth, any extra spots due to (1 1 1) twin planes should occur at the mid point of the line joining the central (1 1 1) spots to the lower spots in the adjacent row, if double diffraction occurs extra spots should occur at the mid point of the line to the upper spots in the adjacent row. In fact extremely weak spots are observed in these positions in the original plates. Moving to the $[0 1 \bar{1}]$ azimuth, weak spots at the $\frac{1}{3}\langle 1 1 1\rangle$ positions along the lines joining spots in adjacent rows show that (1 1 1) twins and double diffraction occur. In this azimuth as well, some slight streaking occurs along $\langle 1 1 1\rangle$ directions in some samples. Fig. 10 shows the appropriate reciprocal lattice sections for these cases and shows that, as in the (1 1 1) case, twins and double diffraction explain the extra reflections when they arise.

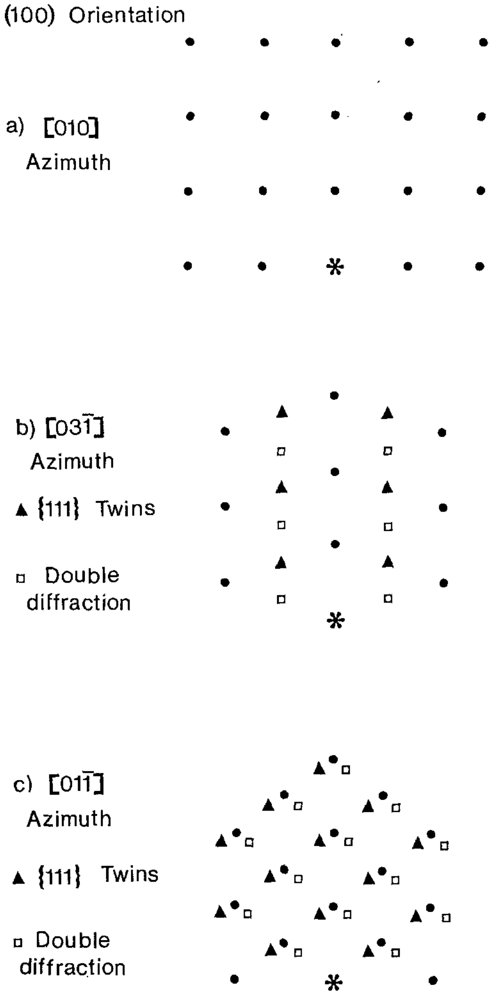


Figure 10 Reciprocal lattice sections for glancing angle electron diffraction from (1 0 0) oriented samples with twins and double diffraction. (a) [0 1 0] azimuth, (b) $[03\bar{1}]$ azimuth, (c) $[01\bar{1}]$ azimuth.

The reduction of the substrate temperature by about 25° C has a marked effect in introducing a considerable amount of polycrystalline arcing of spots as may be seen from fig. 3. In addition fig. 4 shows that there is a great difference in the appearance of the surface, which shows clearly that these surface features are related to the structure. In any case this may be seen in the rather better quality films deposited at slightly higher substrate temperatures which are much more distinctly facetted in crystallographic directions. That these films are of rather better crystal perfection than the best of the (1 1 1) oriented films is shown by the less diffuse Coates Lines, and the fact that the glancing angle X-ray spots are indistinguishable from the substrate spots, not in any way broadened and only identifiable because of those reflections which are allowed from the film and not from the substrate. In addition all twin spots etc. observed by glancing angle electron diffraction are very much weaker relative to those from the matrix in comparison with the (1 1 1) orientation.

One result has been obtained which tends to suggest that at least a small amount of hexagonal phase material has been detected. In the results discussed so far the question of hexagonal material occurring has not been countenanced because it would have necessitated introducing either additional reflections, which have not been observed, or finding another explanation for reflections which have been observed, so that a complete explanation has been possible in terms of the cubic structure. However, as the discussion of atomic stacking in the previous section has shown, whether it be by double positioning on a (1 1 1) surface, or by nucleation of different atoms on different parts of a substrate, at least one hexagonal stacked layer must occur during the formation of a growth twin. This implies that if a small enough volume is examined the effect of such hexagonal material may be observed. Selected area diffraction from a jet etched (1 0 0) sample merely shows a single crystal spot pattern and gives no indication of any extra spots, in fact for this orientation one would expect nothing because neither twin/double diffraction spots, nor hexagonal spots should occur in the (1 0 0) reciprocal lattice plane without moderate tilting or buckling of the sample. On moderate tilting no extra spots were observed. When the same sample was examined in the high resolution diffraction stage (although the areas examined are not necessarily the same), no deliberate tilting was required to produce the extra spots seen in fig. 6. Although in the original some faint spots are observable at positions corresponding to those expected for $\frac{1}{3}\langle 1\,1\,1\rangle$ twinning, all of the more obvious ones occur at positions attributable to hexagonal material, cf. Pashley and Stowell [15], the additional weak streaking observed seems likely to be due to stacking faults.

4.4. (1 1 0) Films

An examination of stacking in this orientation (fig. 9c) shows that double positioning can occur. In the figure this occurs by rotation of a *bb′* bond about its axis ($\langle 1\,1\,1\rangle$ direction) through 60°, so that the *c* atoms are no longer in the second layer of atoms but slightly above it. This in fact forms the Θ 250° 32′ tilt boundary or coherent orthotwin described by Holt [20], it should be recognised that this boundary, when it terminates, will result in another twin at 90° to the boundary with the line of intersection along $[1\,\bar{1}\,0]$ of the matrix. All of this suggests if anything that twinning and double diffraction will be even more predominant in (1 1 0) orientations than in (1 1 1). Glancing angle electron diffraction from such (1 1 0) films, see fig. 7, gives an exceedingly interesting confirmation of this result. Extra spots for this azimuth $[1\,\bar{1}\,0]$ are clearly distinguishable at all $\frac{1}{3}\langle 1\,1\,1\rangle$ positions, in addition the intensity distribution is such that the primary (1 1 1) twin spots are more intense than the double diffraction spots. There still remain extra spots in positions which are $\frac{1}{3}\langle 1\,1\,1\rangle$ related to the (1 1 1) twin spots and double diffraction spots themselves, so that any spot in the pattern has exactly the same distribution of diffraction spots about it as any other. The explanation of this is given in fig. 11 in terms of the occurrence of multiple twinning. Any hexagonal material contributing to the diffraction pattern should produce extra diffraction spots of which there are none.

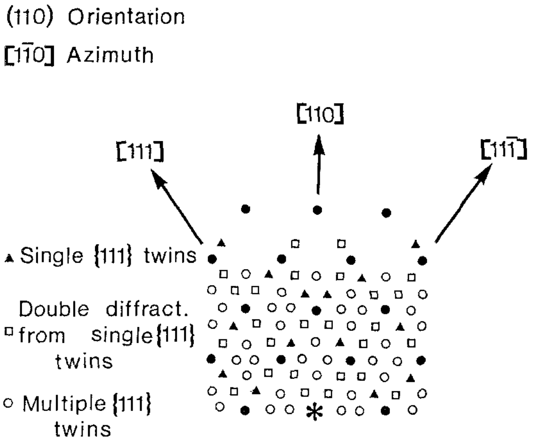


Figure 11 Reciprocal lattice section for glancing angle electron diffraction from (1 1 0) oriented samples including single twin spots, multiple twin spots and double diffraction, $[1\bar{1}0]$ azimuth.

For this orientation very marked interspot streaking was observed in selected area transmission electron diffraction which is indicative of the very marked stacking disorder.

4.5. Comparison of Results with Zinc Selenide deposited on Germanium and Silicon

Further (unpublished) work has been done in this laboratory using a similar deposition process to produce epitaxial films of ZnSe on (1 1 1) and (1 0 0) germanium and silicon in an ordinary oil diffusion pumped vacuum system at conventional pressures. Broadly speaking the results have confirmed those given above in some detail. The same {1 1 1} twins have been observed for ZnSe on (1 0 0) and (1 1 1) silicon as have been observed for high deposit rates of ZnS on silicon. Also the same {1 1 1} twins have been observed for ZnSe on (1 1 1) germanium. There is some indication that epitaxial films of ZnSe on (1 0 0) germanium are more perfect, having sharper Coates Lines, than ZnS on (1 0 0) silicon, although the surface is much less notably facetted and no transmission electron microscopy or diffraction has yet been done to verify this. Temperatures for epitaxy have been similar but the temperature for the rather less perfect (1 1 1) films is approximately 40° C lower than the (1 0 0) orientation. In addition, epitaxial films of ZnTe have been grown on top of ZnSe epitaxial films on (1 0 0) germanium and silicon.

5. Conclusion

Examination of the epitaxy of zinc sulphide films deposited on silicon has shown that for all three substrate orientations examined, large area single crystal films may be grown once a temperature of about 300° C has been reached. Above this temperature the evidence shows that the films tend to a greater perfection as the deposit rate increases (at least over the range investigated). As the films become more crystallographically perfect the surface topography tends to be a more and more pronounced facetting. Twinning and microtwins as well as stacking faults have been shown to occur and these defects account for almost all extra spots found on the diffraction patterns. The manner in which these defects arise has been discussed in terms of the stacking of individual atoms. It has been shown that this consideration of atomic stacking suggests that the (1 0 0) orientation should produce the most perfect films and this has been verified by the experimental results. Broad agreement with these results has been found for zinc selenide films deposited on silicon and germanium.

Although no specific examination of stoichiometry was undertaken, no features were observed that might be directly attributable to non-stoichiometry.

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