Defects in Epitaxial Layers of ZnS on Si

The vapour deposition of zinc sulphide layers on 111 silicon faces at 300 to 600° C has recently been described [1]. This letter reports the results of a study of these thin layers by transmission electron microscopy.

Small discs of silicon and of silicon with ZnS deposited on one face were individually thinned by chemical polishing: a jet of hydrofluoric acid was allowed to impinge on the silicon face of each disc until a thin transparent area appeared. The specimens were examined in an AEI 6G electron microscope at 100 kV accelerating voltage.

After deposition, the extreme thin areas showed far more frequent contours (fig. 1); these were presumably due to a shorter extinction distance in ZnS than the silicon. No moiré fringes were ever observed. However, the misfit between the ZnS and the Si on a (111) interface is $<1\%$ so that in the absence of faulting (e.g. twisting) in the deposition, the absence of moiré fringes is not too surprising.

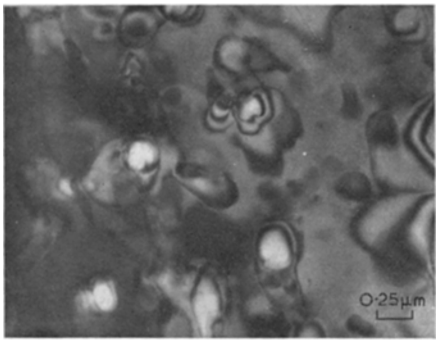
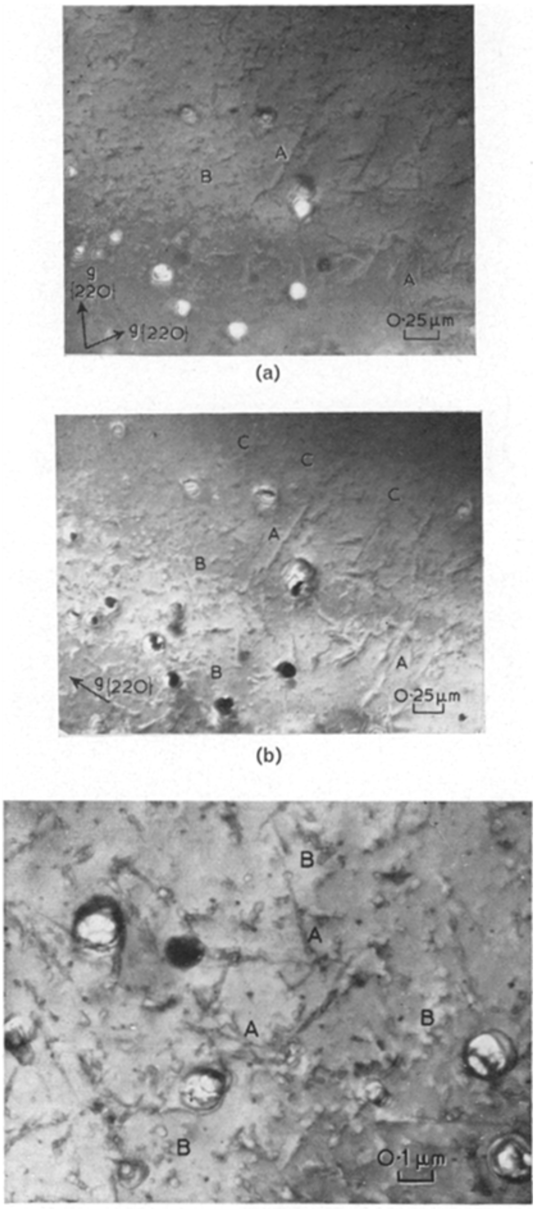


Figure 1 Thin area at the foil edge, showing additional contours.

In rather thicker regions of the foils many defects became visible (fig. 2). In a few specimens, where polishing was continued to perforation, occasional areas of ZnS could be seen overhanging the Si substrate. These were always very small but defects could be seen in such areas so that it was concluded that the defects are mainly in the ZnS layer. However, the presence of defects induced in the silicon by the deposition process cannot be ruled out.

Diffraction patterns from specimens varied depending on the thickness. In the thickest specimens a complete Kikuchi line pattern was visible (fig. 3). The symmetry of this indicated that all the specimens were within two degrees of the $\{111\}$ orientation. The only diffraction spots visible were the $\{220\}$ reflections common to Si and β-ZnS.



(a)

(b)

(c)

Figure 2 (a) Light field image of the defects in the deposited ZnS layer. (b) Dark field image ((220) reflection) similar to 2a. (c) Higher magnification picture of region similar to 2a.

In areas thin enough to show the defects in the ZnS layer, additional reflections were present,

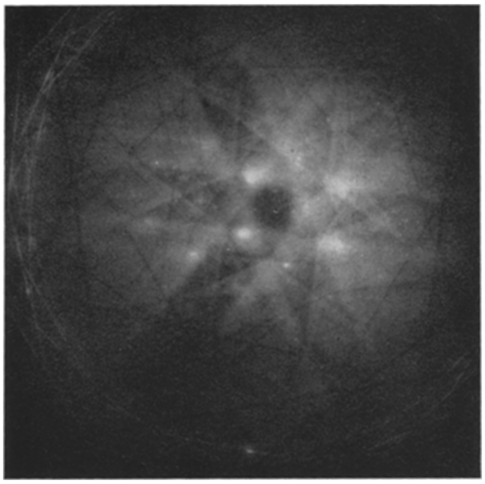
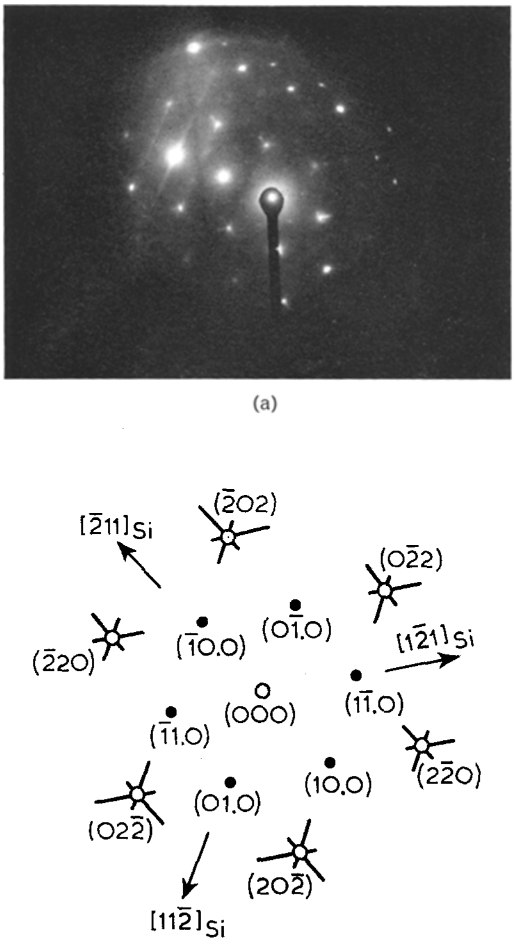


Figure 3 (1 1 1) Kikuchi line pattern from thick ZnS layer.



(a)

(b)

Figure 4 (a) Diffraction pattern from similar area to fig. 2. (b) Diagram interpreting 4a.

and also streaking of the Si $\{220\}$ spots in $<121>$ directions (fig. 4). The additional reflections were consistent with the $\{10.0\}$ of α-(hexagonal) ZnS. The orientation relation would then be

Si and β-ZnS $(111) // (0\ 0.1)$ α-ZnS
Si and β-ZnS $[2\bar{1}\bar{1}] // (10.0)$ α-ZnS

A relationship of this kind gives a satisfactory fit as can be seen in fig. 5. The reflections are much fainter than those of the Si/β-ZnS so that no suitable dark field micrographs were obtainable from them.

When the streaked Si/β-ZnS reflections were used for dark field micrography (fig. 2b) the defects remained visible; assuming that most of the defects are in the deposited ZnS layer this implies that the layer is predominantly β-ZnS. This confirms the X-ray diffraction evidence [1] which revealed only β-ZnS (X-ray results were only feasible from rather thicker layers than these which are ~ 1000 Å). Any hexagonal zinc sulphide present is therefore in the form of a thin interfacial layer or as "pockets" or precipitates.

The streaked $\{220\}$ reflections may be interpreted as being due either to stress fields or to thin layers. As no stress fields were visible, the latter explanation is preferred. The streaks then imply thin plates in the layers, lying in $\{112\}$ planes and about two or three atom layers thick.

Defects visible in the micrographs (fig. 2) will now be discussed in the light of the diffraction evidence.

(*i*) *Defects of Type A* These are visible as long straight lines lying on the traces of the $\{112\}$ planes. They are the only defects which can explain the streaking on the diffraction patterns. They could then be plates on $\{112\}$ planes visible edge-on as lines. Stacking faults common in β-ZnS [2] could give rise to this effect.

(*ii*) *Defects of Type B* These range from black dots to visible dislocation loops apparently in the plane of the foil.

The α- and β-ZnS structures are simply related. The β consists of an fcc structure of sulphur-atoms with a Zn-atom in the centre of each tetrahedron of sulphur-atoms. The α consists of similar tetrahedron stacked so that the sulphur-atoms lie on a cph system. A single layer of either structure in a matrix of the other constitutes a stacking fault. It seems unlikely that a complete layer of either structure will form initially. Probably nuclei of both types form and the β-form grows preferentially to overgrow the

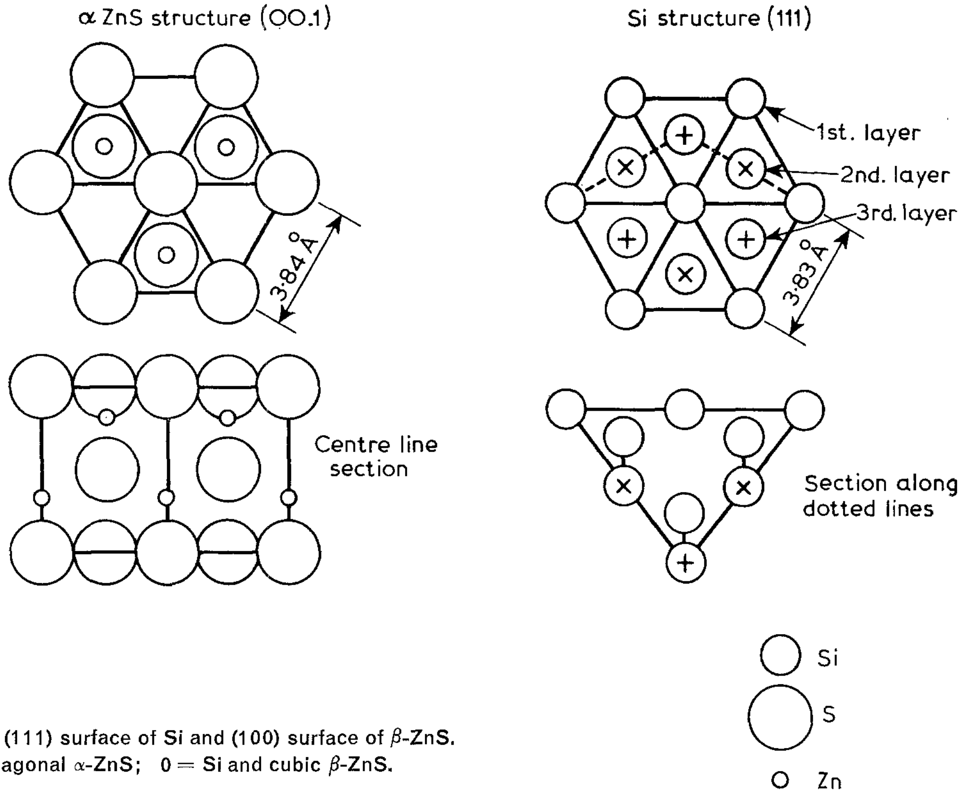


Figure 5 (111) surface of Si and (100) surface of β-ZnS. o = hexagonal α-ZnS; 0 = Si and cubic β-ZnS.

α, leaving the α-nuclei as flat discs. Such discs would have the appearance of defects of type B and give rise to the extra reflections noted on the diffraction pattern.

(*iii*) *Defects of Type C* These are dislocations showing dot contrast. In view of the method of preparation they are probably screw dislocations growing in the deposited layer and ending on the interface. There are many more of them than there were in the original silicon, so they cannot be extensions of dislocations present in the substrate.

References

1. P. JONES, C. N. W. LITTING, D. E. MASON and V. A. WILLIAMS, *Brit. J. Appl. Phys.* **1** (2) (1968) 283.
2. H. JAGODINSKI, *Acta. Cryst.* **2** (1949) 298.

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Book Reviews

Solid-State Chemistry

N. B. Hannay

Paperback, pp xi + 225 (Prentice-Hall, 1967) £2

In an age when the veracity of the aphorism "Of the making of many books there is no end . . ." is persistently demonstrated, it is refreshing to review one which has not only been written for the right reasons, but has, also, much else to commend it. As Dr Hannay himself emphasises, there is at present feverish research activity in the general field of solid-state chemistry, yet many of the teaching programmes in Departments of Chemistry in British and American Universities still tend to ignore this well-defined branch of the subject. It is an encouraging sign that this book is the first in a series devoted to fundamental topics in physical chemistry. Many zealous materials scientists, and their more immediate progenitors,