JOURNAL OF MATERIALS SCIENCE 5 (1970) 1054-1060

The Growth and Properties of Epitaxial Layers of Zinc Sulphide on Germanium

P. J. DEASLEY
English Electric Valve Company, Chelmsford

S. J. T. OWEN
University of Nottingham, Electronic and Electrical Engineering Department

P. W. WEBB
University of Birmingham, Electronic and Electrical Engineering Department

Vacuum deposition of epitaxial films of zinc sulphide onto (111) 0.1Ω cm p type germanium substrates is described. The films contain stacking faults similar to those observed in epitaxial thin films of other substances and possess similar electrical characteristics to bulk crystals. Activation studies show that a.c. electroluminescence may be obtained by an embedding process. The zinc sulphide/germanium heterojunctions fabricated by the methods described are not efficient radiation detectors.

1. Introduction

Zinc sulphide is a well known luminescent material, but it has been little studied in epitaxial thin film form, most of the work having been performed on single crystals or embedded powders. However, recent studies of evaporated films of this compound onto rock salt [1] and silicon [2] have been reported.

This paper describes the growth and properties of epitaxial thin films of ZnS deposited on p-type 0.1Ω cm germanium substrates. Heterojunction systems of this type are being studied because of their possible use in infrared to visible wavelength converters with a response extending to 1.5 μm [3]. The results of some luminescent activation studies of the films are described and the relevant electrical and optical properties of the heterojunction have been investigated briefly to see whether this pair of materials could be used in a wavelength converter.

2. Film Growth

Epitaxial films were fabricated by vacuum evaporation of 4N pure ZnS powder. An oil diffusion pump system, incorporating a liquid nitrogen trap, was used. The apparatus was fitted with viton rubber O rings enabling the work chamber and trap to be baked to 180° C. The ultimate pressure achieved was 10^{-8} torr.

The evaporation source, shown in fig. 1, consisted of two concentric close-fitting high purity quartz tubes housed in a tantalum box. The outer tube carried two spiral tungsten heaters and the inner sealed tube carried a charge of ZnS, above which was inserted a quartz wool plug to prevent spitting. The substrate holder was located accurately over the end of the inner quartz tube and housed a shutter to shield the substrate during source outgassing. The temperatures of all three zones were held constant by Eurotherm controllers.

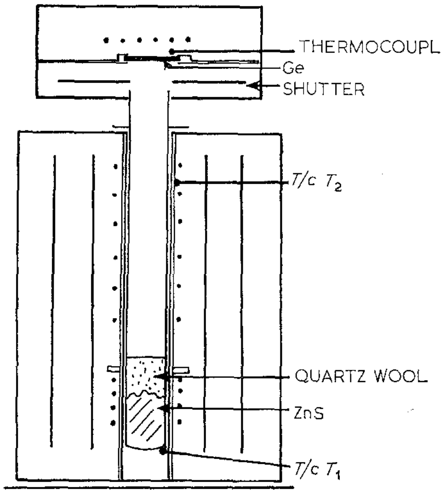


Figure 1 Evaporation source.

The germanium substrates were prepared by electropolishing using a 0.1 % solution of sodium hydroxide. A circular area of 8 mm diameter was prepared by passing a current of one amp for 3 min. The substrate was then washed in deionised water and allowed to dry in a dust-free environment before loading into the vacuum system.

Although studies on Ge surfaces had shown that higher outgassing temperatures should be used [4], the temperature was restricted to 450°C in this work to avoid gross chemical attack of the substrate by zinc sulphide, which always contaminated the vacuum chamber. The growth cycle adopted was as follows. An inner quartz tube and substrate holder, freshly cleaned in aqua-regia, were loaded with ZnS and a Ge substrate respectively and inserted into the vacuum system which was pumped down to about 10^{-5} torr. The work chamber and nitrogen trap were then baked to 180° C for 3 h. Immediately after this bake, the source and tube were outgassed to 750° C and the substrate to 450° C. Heat was maintained until the system pumped down to 10^{-6} torr, when liquid nitrogen was added to the trap. After about 6 h further pumping, a pressure of 5×10^{-8} torr was achieved. The source and tube were slowly heated to 600° C and then, together with the substrate, up to the growth temperature. After a suitable interval the shutter was opened and deposition commenced. Typical running pressures were of the order of 10^{-6} torr, but could be lowered by extending the duration of the system bake-out. An overnight bake yielded running pressures of about 10^{-7} torr.

3. Structure Analysis

A combined reflection-transmission Laue X-ray diffraction technique as described in an earlier paper [3] was used, the germanium being removed with the sodium hydroxide electropolishing solution. The X-ray photographs were characterised by the method of Ino *et al* [5] which utilises a parameter R corresponding to the degree of ordering of the material, 100 being equivalent to a single crystal (spots only) and zero being equivalent to polycrystal (rings only). Other techniques used were chemical etching followed by study under a Vickers polarising microscope and X-ray powder pattern methods. These give information regarding the crystal structure, polarity and defect nature of the films. A few films were also examined in an electron diffraction camera.

4. Electrical Methods

Electrical characteristics were investigated using indium contacts prepared by vacuum evaporation, a grid geometry being used for optical work. Activated deposits were prepared by evaporation of ZnS:Mn phosphor powders prepared by the method of Antcliffe [6] and also ZnS:Cu, Cl by the embedding technique, due to Vecht [7].

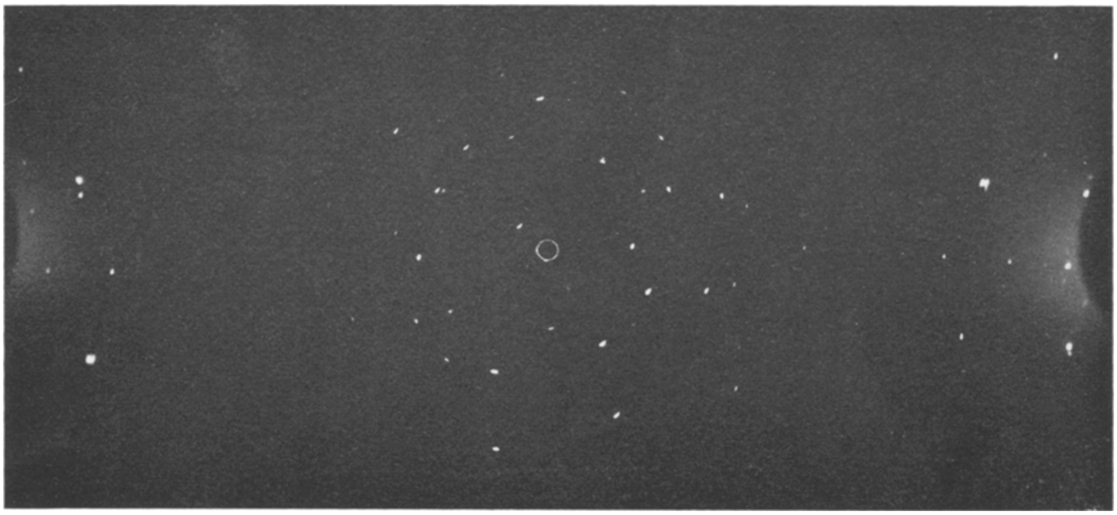
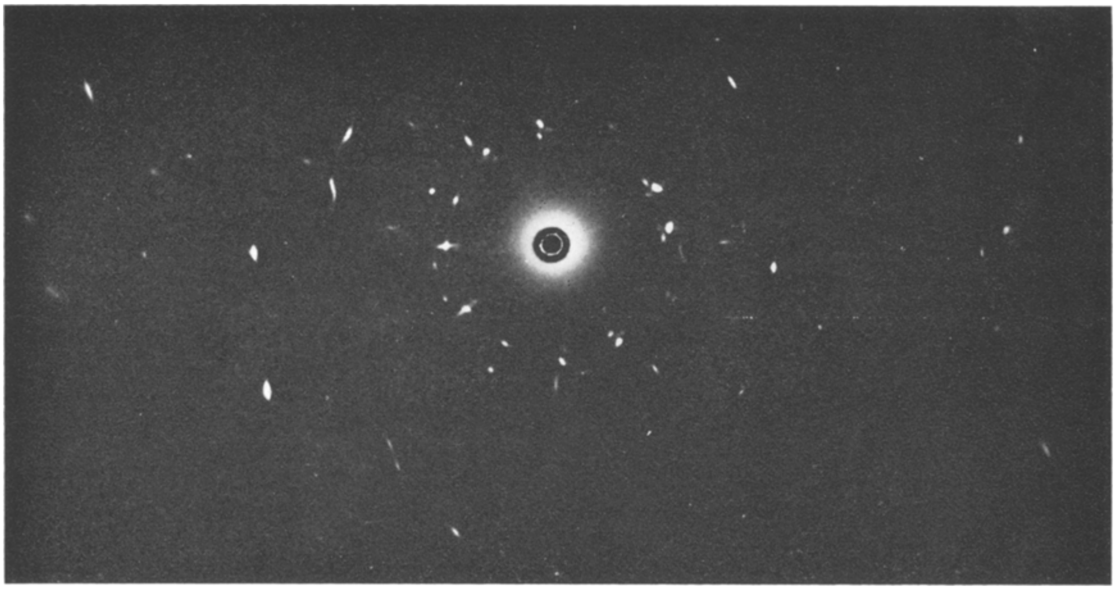


Figure 2 X-ray diffraction photographs.
2a Single crystal non-adheront deposit for (100) orientation, substrate temperature 550° C.



2b Ordered adherent deposit for (100) orientation, substrate temperature 500° C.

2c Single crystal adherent (111) deposit, substrate temperature 450° C.

5. Results

5.1. Epitaxial Growth

Typical X-ray diffraction photographs are shown in fig. 2, the inner pattern corresponding to transmission, the two outer patterns to back reflection. For the (100) orientation single crystal adherent deposits were not reliably obtained. At sufficiently high substrate temperatures the single crystal films tended to be non-adherent, fig. 2a. On lowering the substrate temperature the deposits became less ordered and more adherent, fig. 2b.

For (111) deposits, epitaxy can be readily achieved over a range of source and substrate temperatures, as shown in figs. 2c and 3. The optimum conditions correspond to a substrate temperature of 450° C and source and tube temperatures of 930° C giving a growth rate of 1.5 μm/h.

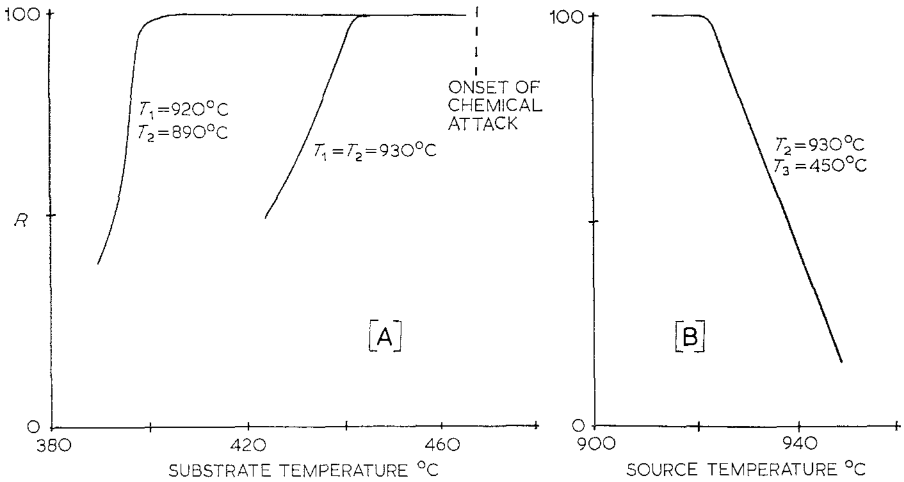


Figure 3 The effect of growth parameters for deposition onto (111) substrates.
3a The effect of substrate temperature. 3b The effect of source temperature.

5.2. Structure of Deposits

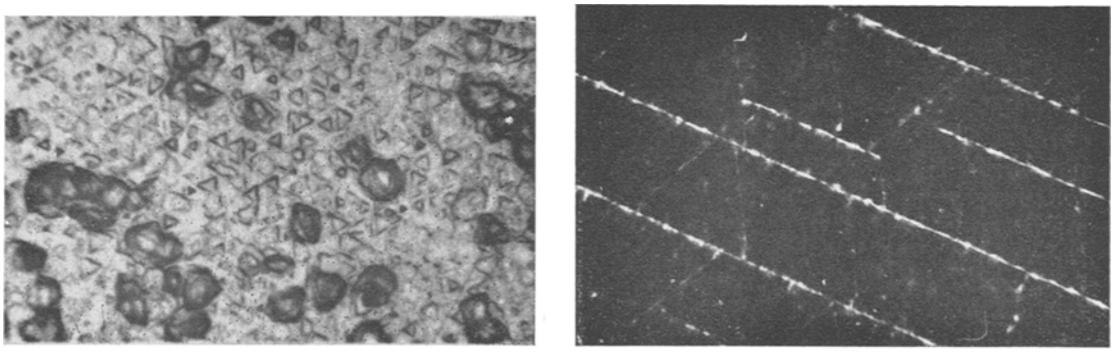
Optical microscopy showed that the deposits were isotropic which for (1 1 1) orientated layers is equivalent to either the cubic or basal plane hexagonal crystal modifications. As ZnS assumes both crystallographic modes, X-ray powder patterns were used to distinguish between them. By this technique the deposits were found to be cubic; no evidence of any hexagonal phase material was found.

The layers exhibited two distinct surface features which never occurred simultaneously. These were discrete triangles, fig. 4a, or more usually networks of 60 degree lines, fig. 4b.

Quite often patches of less ordered material were also seen. The form of the surface features was dependent on growth conditions. Higher substrate temperatures reduced the area of the polycrystalline inclusion while lower pressures tended to break up the network of 60 degree lines into discrete portions, fig. 5.

All the deposits were markedly affected by chemical etching. Fig. 6a shows a layer after etching with chromic acid, fig. 6b after etching with orthophosphoric acid. In the latter case conical etch pits may be seen.

Results using electron diffraction could only be obtained with difficulty due to charging of the sample. They indicated that some twinning had occurred and although the deposits were crystallographically "good" Kikuchi lines were not observed.



(a) (b)

Figure 4 Surface features of ZnS layers.
4a Triangular features (× 500). 4b 60 degree line networks (× 500).

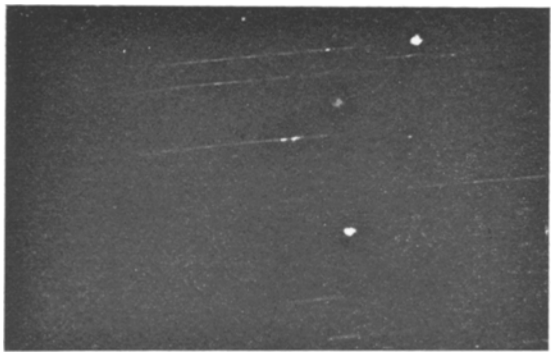


Figure 5 Line network showing the effect of lower pressure (grown at 10^{-7} torr instead of 10^{-6} torr) (× 500).

5.3. Electrical, Photoelectric and Electroluminescent Properties

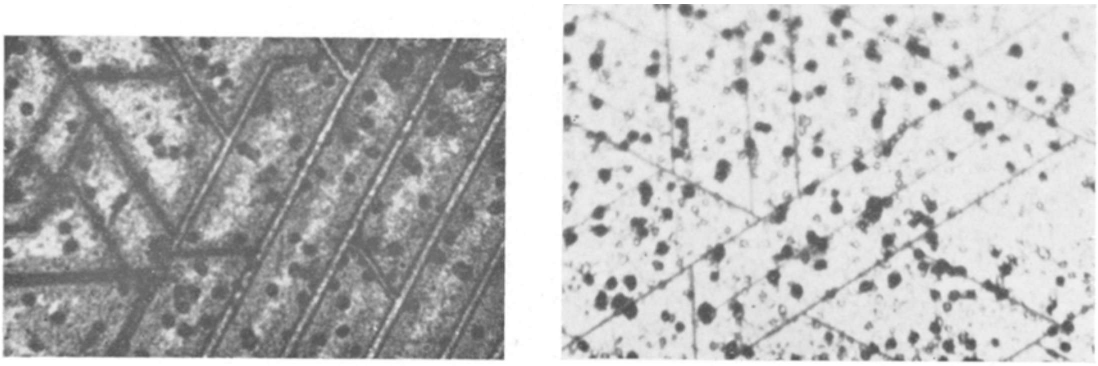
Using indium contacts similar electrical characteristics to those observed with bulk zinc sulphide crystals were obtained [8, 9]. For small applied voltages the electrical characteristic of the heterojunction was completely dominated by the high resistivity ZnS.

When devices were subjected to large reverse biases, however (i.e. with the germanium negative) the current obeyed a law where $\log I \propto V^{\frac{1}{2}}$. This law was consistent with the thermionic emission of electrons from the germanium valence band into the zinc sulphide conduction band. A small additional reverse bias photocurrent could be produced at room temperatures when radiation was directed at the heterojunction through the zinc sulphide and it was possible to measure the main features of its spectral response. Using the thermal emission law it was possible to calculate the effective magnitude of the conduction band discontinuity at the heterojunction, typical values lie in the range 0.24 eV → 0.34 eV. A value for the same discontinuity could be found from the photocurrent response assuming a simple symmetrical spherical band structure. The photocurrent showed a rapid fall starting in the range 1 → 1.1 μm which agreed with the reverse bias measurements. Neither of these results was regarded as very accurate, the latter because the devices had a poor photocurrent sensitivity (approximately $10^{-6} \rightarrow 10^{-7}$ electrons /photon), but they did yield similar results.

The a.c. electroluminescence of the activated layers was monitored with a RCA type 5819 photomultiplier. Luminescence was never observed with ZnS:Mn films even in the presence of excess zinc [6] which apparently is necessary for this process. To confirm the presence of manganese in the host lattice, electron spin resonance was used. For ZnS:Cu,Cl films electroluminescence was readily observed and the effects reported by Vecht were verified. The luminance was in the order of 10^{-10} lamberts.

6. Discussion

It can be seen from fig. 3a that the production of epitaxial layers was limited by the chemical attack of the germanium substrate which was particularly intense at high temperatures. This prevented reliable growth onto (100) substrates where the epitaxy temperature was high. It seems probable that epitaxy would occur on this plane, if lower pressures were available [1].



(a) (b)

Figure 6 Layers after chemical etching.
6a Chromic acid etch (× 120). 6b Orthophosphoric acid etch (× 500).

The triangular defects were similar to those found in autoepitaxial deposits of silicon [10, 11] germanium and gallium arsenide [13]. These were attributed to the existence of three inclined stacking faults forming a tetrahedron whose apex coincided with the substrate-deposit interface. The equilateral nature of the triangles confirmed the existence of a true (1 1 1) epitaxial deposit. In silicon, complex structures, due to the interaction of the triangular defects, commonly occur [14]. The networks of 60° lines correspond to such interactions, the rarer isolated triangular features being displayed on deposits where better nucleation of the film had occurred.

Chemical etching produced conical etch pits indicative of a sulphur face [15, 16]. This pointed to a Zn-Ge bond. However, similar polarity with ZnS films on quartz was explained by a zinc-oxygen bond [17]. Such a system was possible in this work as chemical attack of the substrate prevented thorough outgassing.

It was interesting to observe the lack of electroluminescence for the ZnS:Mn films, although Mn^{2+} ions were present. A noticeable feature of these films was the absence of increased conductivity when grown in the presence of excess zinc, a well known donor for ZnS [18]. It was, therefore, probable that excess zinc was not entering the lattice and so, according to Antcliffe [6], electroluminescence was not to be expected.

Although electroluminescent ZnS:Cu,Cl single crystal films may be easily obtained by the methods described, the heterojunction formed between germanium and zinc sulphide was unsuitable for use in a practical wavelength converter. There are two main reasons for this.

Firstly, in the present case the quantum efficiency is much too small, although one might hope to improve this considerably by a different fabrication method. This low efficiency is presumably due to interface states and an unsuitable effective mass ratio. Efficient electron transport has been reported across heterojunctions where the lattice mismatch is just as great as ZnS/Ge (4.6%) and where the carriers move in the direction of decreasing effective mass. An example of the former is the CdS/Si heterojunction transistor [19] where oxide passivation of the silicon before deposition of cadmium sulphide makes interface recombination very small.

Secondly, the potential profile at the heterojunction shows an effective conduction band discontinuity of 0.24 → 0.34 eV which corresponds to a long wavelength cut-off of approximately 1.1 μm. This is too short a value for the image converters which are currently being proposed and corresponds to an electron transition from the germanium valence band to an energy corresponding to the bottom of the zinc sulphide conduction band.

The critical energy discontinuity from which the wavelength cut-off is calculated may be determined from the conduction band discontinuity. Assuming that the emitted electrons go via the germanium conduction band, then only direct transitions are important in this case. An electron arriving at an energy corresponding to the conduction band edge of the ZnS must, therefore, have been excited through an energy of $0.8 + 2\ (0.3 - 0.14)$ eV. 0.8 eV being the band to band energy of germanium at $k = 0$, 0.14 eV the energy difference between the conduction band minimum and the minimum at $k = 0$ and 0.3 eV an average value of the conduction band discontinuity, taken from the thermionic emission experiments. The argument assumes a simple spherical band structure at $k = 0$ in the germanium. The calculation yields a cut-off wavelength of 1.1 μm. If it is assumed, incorrectly, that the energy gate which gives rise to the cut-off is 0.67 eV + 0.3 eV (i.e. Eg added to the band discontinuity) then the wavelength cut-off is 1.28 μm.

The agreement of the measured cut-off wavelength and the former value suggest that this simple mechanism of operation is correct. One might expect the theoretical value of wavelength cut-off to be shorter than the measured value due to field lowering of the barrier at the interface, the accuracy of the results in this paper however make such a correction irrelevant.

There are other associated problems, the most important being the thermalisation of excited carriers; again the effect of this process will be exaggerated by the presence of a conduction band discontinuity at the heterojunction.

7. Conclusions

It has been demonstrated that epitaxial films of zinc sulphide on germanium can be grown by vacuum evaporation. The vacuum process was complicated by chemical attack of the substrate by the zinc sulphide when thermal cleaning of the former was attempted. This possibly affected the polarity of the zinc sulphide films and the efficiency of the heterojunction as a photodetector.

The films were shown to be similar in terms of defect structure, to the films of the group IV elements and III-V compounds. The electrical characteristics were similar to those of other single crystals of zinc sulphide.

AC electroluminescence was displayed in films activated by similar techniques to those used for bulk crystals, and there seemed no reason why dc electroluminescence should not be displayed also. The luminescent films described here could be used at the output of a wavelength converter, but their heterojunction with germanium was too restricted in wavelength and too inefficient to be of practical importance.

Acknowledgements

P.J.D. would like to acknowledge the support of the Science Research Council and the laboratory facilities provided by the Electronic and Electrical Engineering Department, University of Nottingham and P.W.W the facilities of the Electronic and Electrical Engineering Department, University of Birmingham in the completion of this investigation.

References

1. B. A. UNVALA, J. M. WOODCOCK, D.B., *Brit. J. Appl. Phys.* series 2, **1** (1968) 11.
2. P. L. JONES, C. N. W. LITTING, D. E. MASON, and V. A. WILLIAMS, *ibid* **1** (1968) 283.
3. J. T. CALOW, S. J. T. OWEN, and P. W. WEBB, *Phys. Stat. Sol.* **28** (1968) 295.
4. A. J. ROSENBERG, P. H. ROBINSON, and H. C. GATOS, *J. Appl. Phys.* **29** (1958) 771.
5. S. INO, D. WATANABE, and S. OGAWA, *J. Phys. Soc. Japan* **19** (1964) 881.
6. G. A. ANTCLIFFE, *Brit. J. Appl. Phys.* **16** (1965) 1467.
7. A. VECHT, *Phys. Thin Films* **3** (1966) 165.
8. G. F. ALFREY and I. COOKE, *Proc. Phys. Soc.* **B70** (1957) 1096.
9. W. RUPPEL, *Helv. Phys. Acta* **31** (1958) 311.
10. G. R. BOOKER, R. STICKLER, *J. Appl. Phys.* **33** (1962) 3281.
11. R. H. FINCH, H. J. QUEISSER, G. THOMAS, and J. WASHBURN, *ibid* **34** (1963) 406.
12. T. B. LIGHT, "Metallurgy of Semiconductor Materials" (AIME Metall. Soc. Conf. Interscience, New York 1968) p. 137.
13. H. HOLLOWAY, K. WOLLMAN, and A. S. JOSEPH, *Phil. Mag.* **11** (1965) 263.
14. S. MENDELSON, "Single Crystal Films" (Ed. H. Sato, Pergamon, Oxford 1963) p. 251.
15. A. VECHT, W. GRINDLE, and R. MEARS, *J. Appl. Phys.* **36** (1965) 2935.
16. A. VECHT, W. GRINDLE, and R. MEARS, *ibid* **37** (1966) 3321.
17. W. J. MERTZ, *Sol. St. Physics in Electronics and Telecomm.* **2** (1960) 811.
18. H. BABA, *J. Electrochem. Soc.* **110** (1963) 79.
19. S. BROJDO, T. RILEY, and G. T. WRIGHT, *Brit. J. Appl. Phys.* **16** (1965) 133.

Received 12 June and accepted 18 September 1970.