Properties of $PbS_{1-x}Se_x$ epilayers deposited onto PbS substrates by hot-wall epitaxy

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Properties of $PbS_{1-x}Se_x$ epilayers deposited onto PbS substrates by hot-wall epitaxy (HWE) have been investigated. By compensating with a secondary selenium vapour source, both n- and p-type epilayers with carrier concentrations up to 10^{18} cm^{-3} have been obtained. Alloy compositions were determined using an X-ray method and found to be dependent upon the selenium furnace temperatures used during growth. Diodes were fabricated from wafers consisting of n-type substrates and p-type $PbS_{1-x}Se_x$ epilayers of various compositions. Typical R_0A products are 5 Ω cm^2 for $x = 0.70$. Microprobe analysis indicated that the junctions are abrupt. Diode properties were found to be strongly dependent upon the qualities of the substrates used for epitaxy deposition.

1. Introduction

Fabrication of hetero-structure lead-salt opto-electronic devices requires thin epitaxial layers. Present methods of epilayer preparation are liquid phase epitaxy (LPE), vapour phase epitaxy (VPE), vacuum evaporation and sputtering. Hot-wall epitaxy (HWE) is a comparatively new technique which differs from the previous methods in its near-thermodynamic equilibrium growth conditions. HWE has been used to grow epilayers of PbS [1, 2], PbTe [3], PbSe [4] and the pseudobinary compound PbSnTe [5, 6]. A similar method has been recently used in growing $PbS_{1-x}Se_x$ epilayers [7]. The introduction of an independent chalcogen vapour source [8] enabled the reproducible preparation of lead-salt epilayers with controlled stoichiometry and hence defined carrier types and concentrations. This eliminated aftergrowth annealing processes for obtaining low carrier concentration materials. It also avoided the possible lead or chalcogen precipitation when epilayers were cooled from their growth temperatures. This communication represents results of our recent efforts in growing $PbS_{1-x}Se_x$/PbS hetero-junctions by HWE.

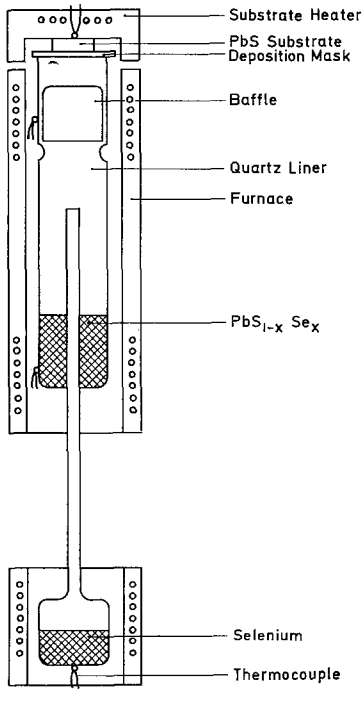

Figure 1 Schematic diagram of the HWE epilayer deposition system.

2. Epilayer growth

Fig. 1 shows a schematic diagram of the HWE system used during the present work. Although similar HWE systems have been described elsewhere [1-7], there are some modifications which will be explained in this section. A quartz growth tube, 1 cm diameter, was placed inside a 3-zone furnace made of a stainless steel cylinder around which insulated tantalum wires were

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wound for ohmic heating. Owing to the larger heat capacity, the present design ensures more stable temperature profiles than previous versions. The temperatures of various zones of the furnace were kept to within $\pm$ 0.1°C by the standard controlling technique with alumel-chromel thermocouples as temperature sensing elements. The substrates were mounted beneath a stainless steel heater block also heated by insulated tantalum wires. The substrate holder was built in such a way that it could be moved between several furnaces for growing epilayers of various materials. Hetero-structures can thus be grown successively without opening the vacuum system to atmospheric pressure. The substrate was lowered down to the growth tube only when the temperatures of the furnace had reached set values, and was again moved away from the growth tube when epilayers with desired thickness had been grown. The complete system is built inside an oil-free ultra-high vacuum system which was maintained at $\leqslant 1 \times 10^{-8}$ Torr during deposition.

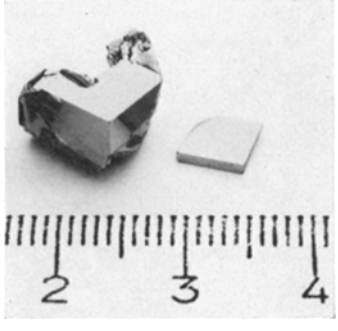

Figure 2 PbS crystal and a cleaved wafer to be used as substrate for epilayer deposition.

The PbS substrate crystals for the epitaxy were vapour phase grown [9] at 820°C in sealed quartz ampoules from metal-rich powder. After 1 week's growth, the ampoule was removed from the growth furnace and annealed in the same ampoule at 500°C for a further week before water quenching. Typical electron concentrations obtained are 3×10^{18} cm^{-3} together with 77 K Hall mobilities around 10 000 cm^2 $V^{-1}sec^{-1}$. Fig. 2 shows a typical PbS crystal and a cleaved slice which was used as substrate. As source material, small $PbS_{1-x}Se_x$ crystals, grown in the sealed quartz ampoule from the vapour phase, were crushed into coarse grains and about 8 g were loaded into the source zone of the furnace. 0.5 g 5·N grade selenium pellets were used in the second furnace. The typical temperature used for the substrate was 300°C, with 500 and 550°C for the $PbS_{1-x}Se_x$ source and baffle zone respectively. Temperatures for the selenium source varied between 100 and 145°C, depending upon desired epilayer carrier types and concentrations. With the above temperatures, sublimed molecules from $PbS_{1-x}Se_x$ and the selenium source distributed themselves inside the growth tube. Owing to the maintained temperature gradient, there was a net flow of molecules towards the substrate, resulting in a deposition of an epilayer onto the substrate.

3. Epilayer properties

The epilayers have mirror-like shiny surfaces if grown with the selenium compensation source [8, 10] and the thickness of the epilayers is very homogeneous. This can be seen in Fig. 3a which shows a micrograph of the cross-sectional view of a cleaved 16 μm thick $PbS_{0.28}Se_{0.72}$ epilayer on PbS substrate. Some cleavage steps are seen across the cleavage plane. Although junctions are vaguely visible under a microscope, the etching solution used previously [11] for diffused junctions, was found to delineate junctions successfully. Fig. 3b shows the same junction after etching. Etch pit densities were measured with a solution similar to that used in [12]. For a $PbS_{0.28}Se_{0.72}$ epilayer deposited onto PbS substrate, a typical density was found to be 10^6 cm^{-2} in the layers.

McLane and Sleger [7] reported an increase in x values of the epilayers compared to those of the starting source material composition in their work on $PbS_{1-x}Se_x$ epilayer preparation by co-evaporation with an independent selenium source. To study this effect, x values of $PbS_{1-x}Se_x$ epilayers grown under various conditions were measured. This was accomplished by first determining the lattice constants of the $PbS_{1-x}Se_x$ epilayer by employing the standard X-ray Bragg diffraction method. Knowing the lattice constants, x values were determined using Vegard's law which states that lattice constants of a binary alloy system are linearly dependent upon the alloy compositions. Fig. 4 shows a recording trace from the Bragg diffractometer. A $K\alpha$ monochromatic X-ray source from a filtered Co target was used. The diffraction peaks due to the (600) lattice planes of the $PbS_{1-x}Se_x$ epilayer and also the PbS substrate

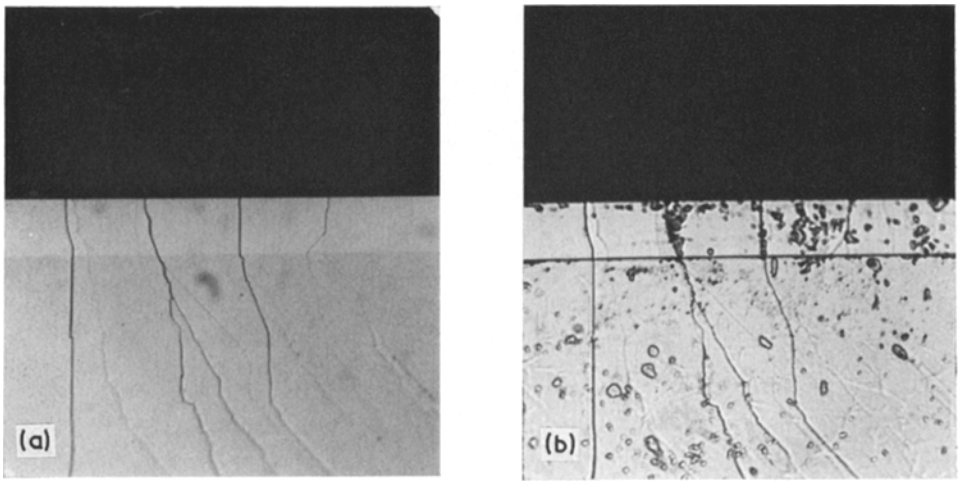

Figure 3 (a) Cross-sectional view of $PbS_{1-x}Se_x$ epilayer grown on PbS substrate. (b) Same junction after etching for junction delineation.

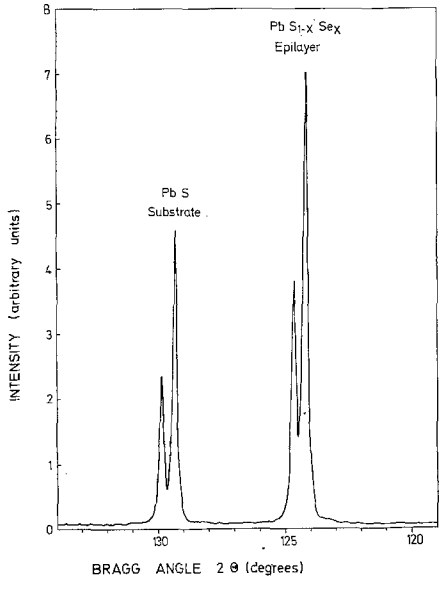

Figure 4 Recording trace of Bragg diffractometer for alloy composition determination.

are shown in Fig. 4. The $K\alpha_1$, $K\alpha_2$ doublets of the Co target are well resolved, indicating high crystalline perfection of the epilayer and the substrate. It is advantageous to have the diffraction peaks from the substrate as an internal standard. Since there are some cases in which deviation from Vegard's law were observed [13, 14], it was important to test the validity of this law in the $PbS_{1-x}Se_x$ pseudobinary case. For this purpose the lattice constants of vapour grown $PbS_{1-x}Se_x$ crystals of known compositions $x = 0.0$, 0.385, 0.6 and 1.0 were measured and are shown in Fig. 5. It is obvious from the plot that the dependence of lattice constants on alloy composition is indeed linear. There is also the question as to whether any variation of lattice constants exists due to deviation from stoichiometry [15]. This was studied for PbSe by measuring the lattice constants of epilayers, both lead-rich and

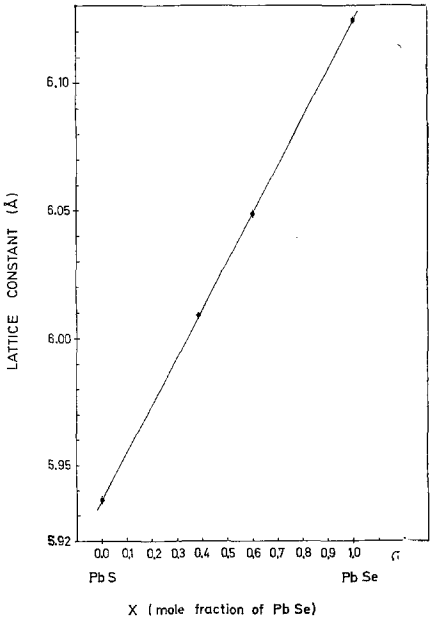

Figure 5 Lattice constants as a function of alloy compositions of pseudobinary $PbS_{1-x}Se_x$ system.

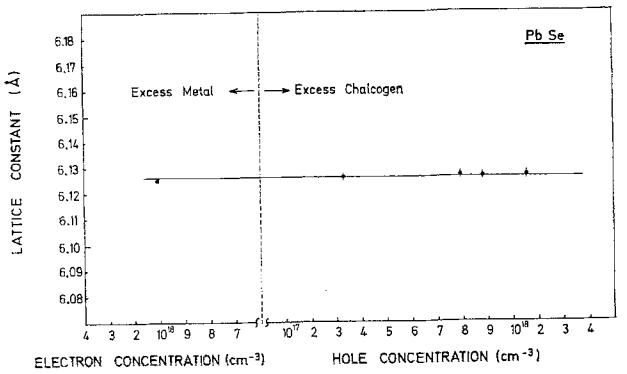

Figure 6 Lattice constants of PbSe as a function of deviation from stoichiometry. Free carrier concentrations were used as an indication of the degree of non-stoichiometry.

selenium-rich, with varying degrees of non-stoichiometry. For this investigation PbSe epilayers were grown onto NaCl substrates and the measured carrier concentrations were used as a measure of the degree of deviation from stoichiometry. Fig. 6 shows the result of these measurements. The lattice constant was found to be independent of carrier concentrations up to 1.53×10^{18} holes/cm^3, and is 6.126 ± 0.001 Å, which agrees with the accepted value for PbSe [16]. In the carrier concentration range of interest, therefore, lattice constants are not dependent on the deviation from stoichiometry as expected.

Several series of $PbS_{1-x}Se_x$ epilayers have been grown using starting source material compositions of 0.0, 0.385 and 0.6. For each series grown, only the temperature of the selenium source was varied systematically, giving a series of epilayers with varying degrees of non-stoichiometry. With a metal-saturated source material, epilayers can be prepared either metal-rich or chalcogen-rich depending upon the selenium source temperature employed. The compositions for the three series of epilayers have been measured and plotted in Fig. 7. The carrier types were determined by thermal probe and the n-type conduction was represented by dots, the p-type by circles. For each series, the composition is plotted as a function of increasing selenium source temperature. As can be seen, there are some shifts of composition of the epilayer as expected. In the case of series (a), values of x increased from 0.65 to 0.81 when the selenium temperature was raised from 130 to 145°C. Because of this effect, the desired $PbS_{1-x}Se_x$ epilayer carrier concentrations and alloy compositions can be obtained by carefully choosing the appropriate starting material composition and selenium source temperature.

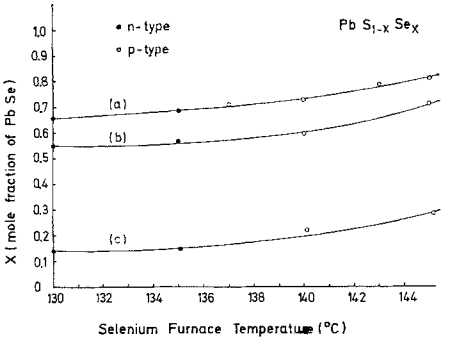

Figure 7 Dependence of epilayer alloy compositions on selenium source temperatures. Three series were grown from $PbS_{1-x}Se_x$ source materials of different compositions (a) $x = 0.6$ (b) $x = 0.385$ (c) $x = 0.0$.

As can be seen from Fig. 4, the width of the Bragg defraction peak of the epilayer is as narrow as that from the binary substrate. This indicates the good homogeneity of the epilayer. In addition, the composition homogeneity along the direction normal to the junction plane was studied by microprobe analysis. An electron beam was directed perpendicularly to the surface of a cleaved cross-section, and characteristic X-ray emissions from both S and Se atoms were collected by a detector. By comparing the ratio of Se and S X-ray counts with that from samples of known x values, the composition could thus be determined. Fig. 8 is a plot of x values obtained by this method. For higher resolution, each datum point was obtained by moving the electron beam parallel to the junction at various distances from the junction plane. For the particular sample shown, the x value for the epilayer was measured as 0.70 which is in good agreement with the value obtained by the Bragg diffraction method.

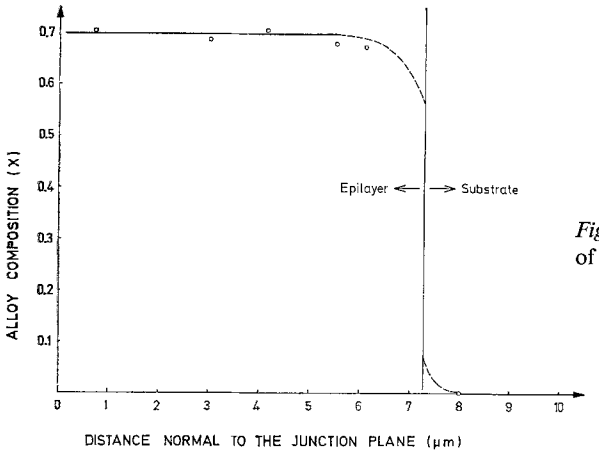

Figure 8 Alloy composition of HWE epilayer as a function of depth.

The metallurgical boundary drawn in the figure was determined from the contrast of the secondary electron emission in a scanning electron microscope. Owing to the 1 μm resolution limit of the microprobe, the composition profile close to the boundary cannot be determined. For Hall measurements, $PbS_{1-x}Se_x$ epilayers were also deposited onto cleaved NaCl substrates. Typical Hall mobilities were measured to be around 10 000 $cm^2\ V^{-1}\ sec^{-1}$ at 77 K. Carrier types and concentrations depend strongly on the selenium temperatures used during growth as reported earlier [4].

4. $PbS_{1-x}Se_x$/PbS hetero-junction diodes

Diodes have been fabricated from wafers consisting of p-type HWE $PbS_{1-x}Se_x$ epilayers deposited onto cleaved n-type PbS substrates. The back of the wafer was first lapped and polished down to a thickness of 600 μm before gold was vacuum evaporated onto both sides for ohmic contacts. The plated wafer was then cleaved into chips of 1 mm^2 and mounted onto transistor headers with silver epoxy. Fig. 9 shows the 77 K *I-V* characteristic of a diode made with a p-$PbS_{0.28}Se_{0.72}$ epilayer. Zero bias resistance was 3 kΩ and the R_0A product 5Ω cm^2. The junction properties depend strongly on the quality of the substrates. The correlation between substrate quality and junction properties has been investigated in detail. A series of p-type epilayers were deposited onto various n-type PbS substrates under the same conditions. Better diodes were reproducibly obtained from more perfect substrate crystals. The parameter used to characterize the substrate quality was the halfwidth, $W_{1/2}$, of the X-ray Bragg diffraction

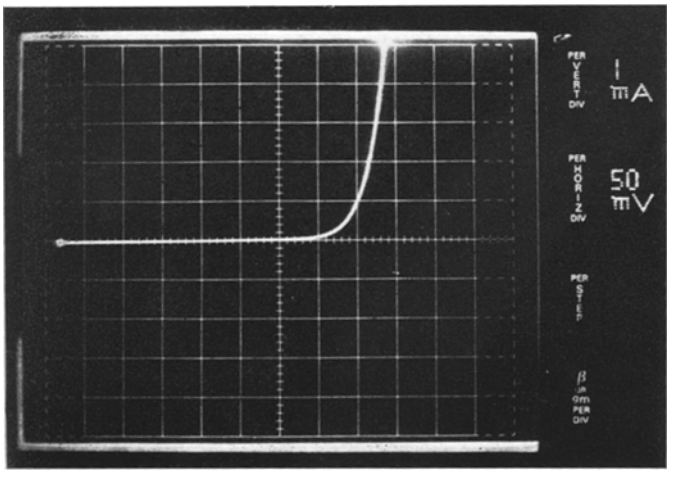

Figure 9 I-V curve of a typical p-$PbS_{0.28}Se_{0.72}$/n-PbS hetero-junction diode at 77 K; $R_0 = 3\ k\Omega$, $A = 1.5 \times 10^{-3}\ cm^{-2}$.

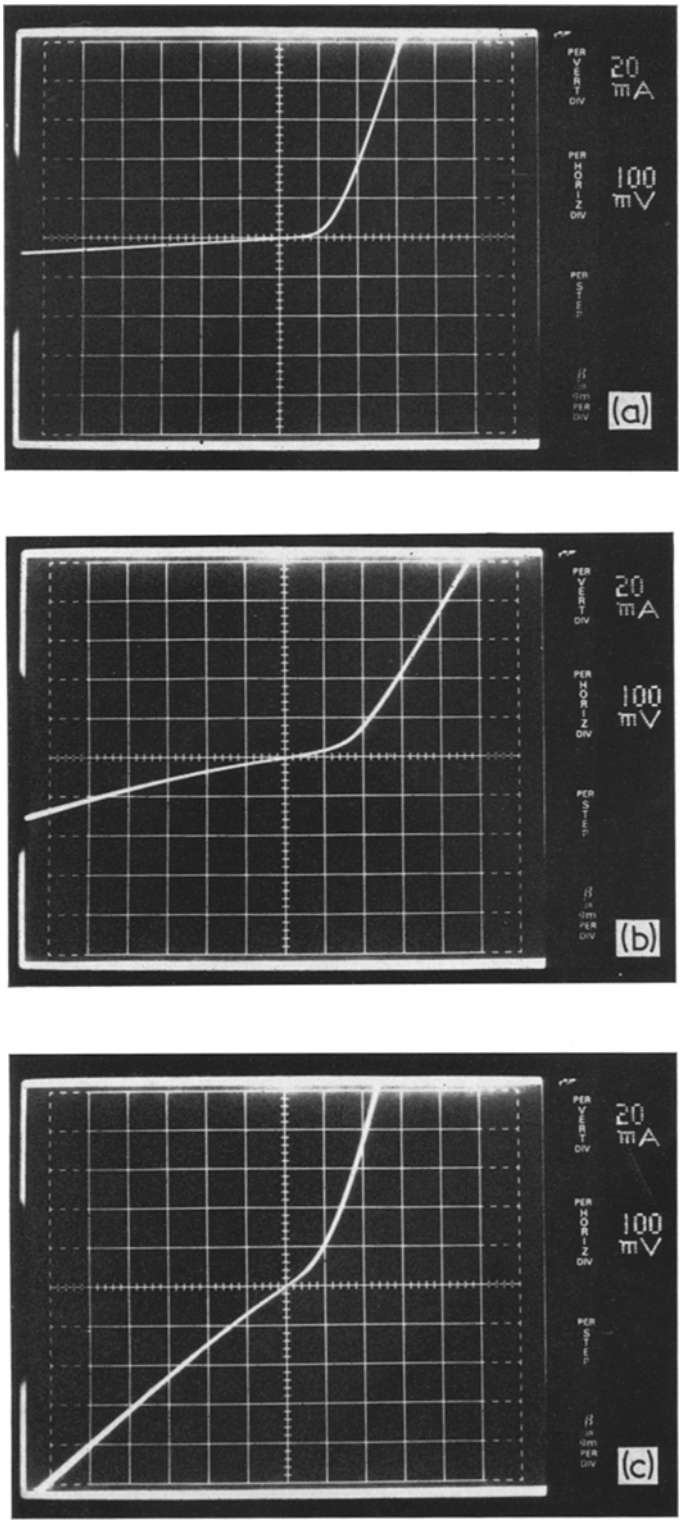

Figure 10 The dependence on substrate quality, halfwidth of X-ray diffraction peak, of HWE heterojunction diodes. (a) $W_{1/2} = 0.126°$, (b) $W_{1/2} = 0.157°$, (c) $W_{1/2} = 0.166°$.

peak from the (600) lattice planes of the crystals. Fig. 10 shows *I-V* curves of diodes made from substrates of varying halfwidth. Each curve is typical for 6 diodes measured. As the halfwidth, $W_{1/2}$, of the substrates increases from 0.126° to 0.166°, the reverse current becomes larger. Detailed conduction mechanisms are not known at this stage, but there seems to be evidence that the leakage current is due to crystal defects associated with lead inclusions present in the substrate crystals.

5. Conclusions

Properties of $PbS_{1-x}Se_x$ epilayers deposited on PbS substrates using the hot-wall epitaxy method have been presented. The use of a separate Se source enabled us to grow layers with high perfection and homogeneity and with defined n- and p-type carrier concentrations. X-ray Bragg diffraction was found to be a convenient tool to determine the composition of the layers with high accuracy, which is dependent on the composition of the source material and the temperature of the compensating Se-reservoir. Any desired composition and carrier concentration may be obtained by choosing the appropriate source material and Se-reservoir temperature.

The *I-V* characteristics of the hetero pn-junctions are strongly dependent on the quality of the substrate crystals.

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References

1. P. HUDOCK, *Trans. Met. Soc. AIME* **239** (1967) 338.
2. M. PAIC, V. PAIC, K. DUH and J. N. ZEMEL, *Thin Solid Films* **12** (1972) 419.
3. A. LOPEZ-OTERO and L. D. HAAS, *ibid* **23** (1974) 1.
4. K. DUH and H. PREIER, *ibid* **27** (1975) 247.
5. R. F. BIS, J. R. DIXON and J. R. LOWNEY, *J. Vac. Sci. Tech.* **9** (1972) 226.
6. I. KASAI, J. HORNUNG and J. BAARS, paper presented at the 16th Electronic Materials Conference, Boston, September (1974).
7. G. F. MCLANE and K. J. SLEGER, paper presented at the 16th Electronic Materials Conference, Boston, September (1974).
8. K. DUH, A. LOPEZ and J. N. ZEMEL, paper presented at the American Physical Society Meeting, San Diego, March (1973).
9. H. PREIER, R. HERKERT and H. PFEIFFER, *J. Crystal Growth* **22** (1974) 153.
10. M. PAIC and V. PAIC, *J. Mater. Sci.* **7** (1972) 1260.
11. H. PREIER and H. PFEIFFER, *J. Electrochem. Soc.* **121** (1974) 595.
12. B. B. HOUSTON and M. K. NORR, *J. Appl. Phys.* **31** (1960) 615.
13. R. F. BIS and J. R. DIXON, *J. Appl. Phys.* **40** (1969) 1918.
14. J. W. WAGNER and J. C. WOOLLEY, *Mater. Res. Bull.* **2** (1967) 1055.
15. R. F. BREBRICK, *J. Phys. Chem. Solids* **24** (1963) 27.
16. H. E. SWANSON, N. T. GILFRICH and J. M. UGRINIC, NBS Circular, No. 539, Vol. 5 (1963).

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