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PbS–Si heterojunctions: growth and structural properties

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The PbS–Si (1 1 1) heterostructures were fabricated by various chemical methods. It has been observed that uniform single and multilayer PbS films, which are mostly polycrystalline, could be prepared. Strongly oriented films have also been deposited by the Davis and Norr method. Substrate preparation prior to the deposition of the films, is found to have a more pronounced effect on the first layer, rather than on the subsequent layers. Orientation of these films is observed to change with the thickness and etchants used in this study. As film thickness increases, size defects and strain defects decrease for these heterostructures. An anisotropy is noted in domain size and strain in these films.

1. Introduction

Inspite of the large lattice mismatch (~ 9%) and thermal mismatch between lead sulphide and silicon, PbS–Si heterojunctions (HJs) have been reported in recent years to be successful for infra-red (IR) detection [1, 2], IR photography [3, 4] infra-red charge couple device (IRCCD) imagers [5, 6] and gas detection [7, 8]. Lead sulphide films, deposited on to single crystal silicon substrates either by vacuum techniques [9, 10] or by chemical solution growth methods, are generally polycrystalline; but, using chemical solution growth methods such as that of Davis and Norr [11], well-oriented PbS films on single crystal silicon substrates can also be obtained, as reported by several investigators [12–16].

Furthermore, it is interesting to note that by adopting the Davis and Norr method (DN method), Rahnamai *et al.* [8, 15] obtained strongly oriented PbS films along ⟨1 0 0⟩ with other weak reflections present, while Elabd and co-workers [12–14] observed strong (2 2 0) and (3 1 1) reflections without any measurable (2 0 0) reflection when (1 1 1)-Si is used as the substrate. A strongly oriented PbS structure along ⟨1 0 0⟩ was observed also by Elabd *et al.* [14] only when (1 0 0)-Si was used as the substrate. Chemical deposition generally yields films with a thickness less than a fraction of a micrometer in a single deposition. As pointed out by Jhabvala and Barrett [2], multilayer-PbS films silicon are necessary for fabricating devices with a very high infra-red sensitivity, as well as high resistance. Thus it would be of interest to investigate whether the preferred orientations of the crystallites, if any, observed in the first layer of PbS (on silicon) would be maintained in subsequent depositions in multilayered structures.

Preparation of the substrates (i.e. cleaning and etching) prior to film deposition generally have an effect on the structure of heterojunctions and, consequently, on their electronic and opto-electronic behaviour [17, 18]. In view of this a study of these aspects in PbS–Si devices, was undertaken. The present paper discusses the effects along with the growth and structure of the PbS films on (1 1 1)-Si obtained by chemical methods. The structure of PbS films deposited by other chemical techniques such as spray-pyrolysis [19] dip–dry [20], and the ammonium hydroxide [21] methods are also reported for the first time.

2. Experimental techniques

2.1. Film growth

Single crystal silicon wafers of (1 1 1) orientation and n-type conductivity having 3 to 6 Ωcm resistivity were used as substrates in the present study. Prior to deposition of the PbS films, the substrates were thoroughly cleaned to remove organic and inorganic contaminants from their surfaces, using the procedure suggested by Kern and Poutinen [22]. Two different etchants, dilute HF (1 : 10) and CP-4 solution, were used to remove the silicon oxide layer. The substrates were then washed in ultrapure running water until the flourine contamination was removed, and they were then transferred immediately into a freshly prepared deposition bath.

Lead sulphide films were prepared by various chemical methods, e.g. the sodium hydroxide, ammonium hydroxide, spray and dip-dry methods. PbS films were deposited on to the polished surfaces of the substrates. While thicker films can be prepared conveniently at room temperature using the method described by Davis and Norr [11], the other methods required either an elevation of the solution temperature, or a large number of repeated depositons. Using the method of Davis and Norr, thicker films were obtained whether altering the timings used, or by repeated deposition from freshly prepared solutions. The most successful devices have been reported to be made by the method of Davis and Norr, therefore, in the present work a more detailed study of film growth, the effects of film thickness and etchants used, on the crystallite orientation and microstructure for these PbS–Si (1 1 1) heterojunctions prepared by this method, has been undertaken.

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TABLE I Diffraction data of PbS–Si (1 1 1) heterostructures prepared by various chemical methods

hkl	I/I_0* Pbs powder	I/I_0 PbS–Si (1 1 1) heterostructure (single layer)			
		Davis and Norr method	Acharya and Bose method	Spray method	Dip–dry method
1 1 1	84	26.5	87	74	56
2 0 0	100	100	100	100	100
2 2 0	57	19.9	46	63	31
3 1 1	35	13	39	39	19
2 2 2	16	6.6	17	25	16
4 0 0	10	6.6	12	10	8

*Diffraction data from the ASTM file.

2.2. Film thickness and surface topography

The average film thickness was determined by the gravimetric method using an assumed PbS film density of 7.596 g cm^{-3}. The thickness was also measured by an optical interferometric method and the measured values agree within ± 5%. The spatial uniformity of a film deposited on to a glass substrate treated at the same time as silicon substrate, in the same solution bath, was investigated by scanning the film surface with a focused light spot from a microdensitometer (Enraf Nonius Delft, Model-II) along the length of the film. The distance between successive scans along the breadth of the film was maintained at ± 5 mm.

The surface topography of these heterostructures was studied using a scanning electron microscope (Philips PSEM : 500). Thin gold films were deposited on to the surfaces of these films by the sputtering technique, to reduce charging effects and to obtain better quality images. In this study, films deposited as single layers as well as multilayers were used. A cross-section of a multilayer-film on (1 1 1)-Si substrate has also been examined.

The PbS–Si (1 1 1) heterostructures were characterized by X-ray diffraction techniques. These experiments were performed using a Philips 1140/90 diffractometer fitted with a balanced Ni-filter and a Cu$K\alpha$ radiation source.

3. Results

A study of the diffraction patterns of these heterostructures prepared by the methods mentioned above, shows that these patterns are of polycrystalline PbS film, superimposed on the pattern of (1 1 1) single crystal silicon only, indicating the absence of any other crystalline materials, such as oxides of silicon or lead, in major concentrations (> 1%) (Table I). However, trace impurities may be present. An examination of the intensities of various diffraction lines from films prepared by different methods (Table I), and those from powder PbS, indicates that except for the film prepared by the Davis and Norr method, all others show more or less random orientation of the crystallites. From the widths of the diffraction lines, it was noted that the crystallite sizes in the films obtained by other methods are smaller compared to those obtained from the Davis and Norr method.

The diffraction patterns of PbS–Si (1 1 1) structures prepared by the Davis and Norr method, are shown in detail in Table II. The table shows the plane indices, the normalized intensities of a number of lines for films of different thicknesses and different etchants used, and a corresponding powder pattern of lead sulphide along with a pattern of a PbS film on a glass substrate. It may be noted from this table that as the thickness increases, the preferred orientation of PbS crystallites changes from (1 1 1) to (2 0 0) and then to (2 2 0) planes, when the substrates were etched with CP-4 solution. For films deposited on silicon substrates etched with dilute HF, it is observed that when the film thickness increases up to 1.0 μm, the PbS film shows a strong preferred orientation along ⟨1 0 0⟩. However, for a film thickness fo 1.14 μm, a strong (1 1 1) growth has been observed.

For films grown on glass substrates, it was observed that the (2 0 0) line was the strongest, with the (1 1 1), (2 2 0) and (3 1 1) lines having moderate intensities. This indicates that the films grown on amorphous

TABLE II Diffraction data of PbS–Si (1 1 1) heterostructrues for different film thicknesses (using the Davis and Norr Method)

hkl	(I/I_0)* PbS powder	(I/I_0) of PbS–Si (1 1 1) heterostructures											PbS film on glass substrate, 450 nm
		CP-4 etched (1 1 1) Si surface					Dilute HF etched (1 1 1) Si surface						
		115 nm film	165 nm film	200 nm film	350 nm film	Elabd† and Steckl	350 nm film	420 nm film	500 nm film	720 nm film	114 nm film	Rahnamai *et al.*‡	
1 1 1	84	100	94	30	49	21.05	61	26.5	19	2	100	5.6	22
2 0 0	100	56	100	60	72	undetermined	100	100	100	100	1.5	100	100
2 2 0	57	24	59	100	100	100	38	19.9	23	2		4.7	30
3 1 1	35	12	27	28	42	97.9	19	13	15	3		11.2	23
2 2 2	16					–	9	6.6	4	1		–	10
4 0 0	10					26.32	7	6.6	6	6		7.5	6

*ASTM diffraction data file

†H. Elabd and A. J. Steckl [12].

‡H. Rahnamai, H. J. Gray and J. N. Zemel [15].

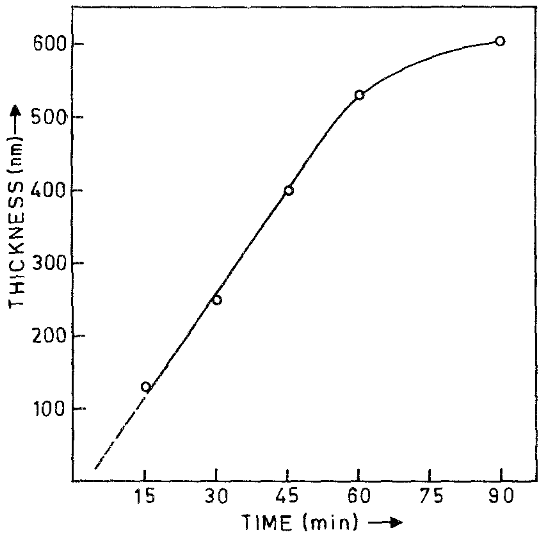

Figure 1 Growth rate of PbS films deposited on glass substrates at room temperature (~ 28° C).

substrates also exhibit a preferred orientation to a certain extent.

4. Discussion

The PbS–Si (1 1 1) heterostructures could be prepared by various chemical methods. As shown in Fig. 1, the growth rate of PbS films (Davis and Norr method) is linear up to approximately 60 min, and then becomes slower due to depletion of available ions from the solution, attaining a saturation limit. Hence, to obtain thicker films, multilayer depositions must be carried out using freshly prepared solution baths. As is evident from Fig. 2, these films are deposited quite uniformly. However, the quality of the films depends on conditions such as the cleanliness and surface nature of the substrate. The scanning electron micrographs in Fig. 3, show that the crystallites in the films deposited by the Davis and Norr method were more uniform and evenly distributed, compared to those of films deposited by other methods. The size of the crystallites of the films grown on silicon were smaller than those of the films on glass substrates. The crystallites size increases with thickness. It may be seen clearly from the micrographs of the sectional melt, shown in Fig. 4 that the orientation of the crystallites in different layers is not always the same, i.e. growth is not columnar. This is in contrary to the studies of Rahanamai *et al.* [15]. The interlayer region, shown distinctly in the photograph, may however, contain oxygen and other impurities, as reported by Elabd and Steckl [12, 13] from Auger analysis of their PbS–Si heterostructures. The presence of such impurities may lead to interface states, which in turn affect the subsequent electrical and photoelectric properties of these devices.

Elabd and Steckl [12, 13] have estimated the size of the coherently diffracting domains (D) in PbS films, using the Scherrer equation, attributing the entire line broadening to the size effect only, ignoring any strain inside the domains. Although broadening of X-ray line profiles is also due to strain, it is not possible to separate these effects by an integral breadth method, because of the absence of higher order reflections. Therefore, in the present study, D has been determined by the Scherrer equation [23], attributing the entire line broadening to the particle size.

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where θ is the Bragg angle, β the integral width of the pure diffraction profile, λ the wavelength of radiation used, and K is the shape factor which takes the value of unity.

If the entire broadening is attributed to strain only,

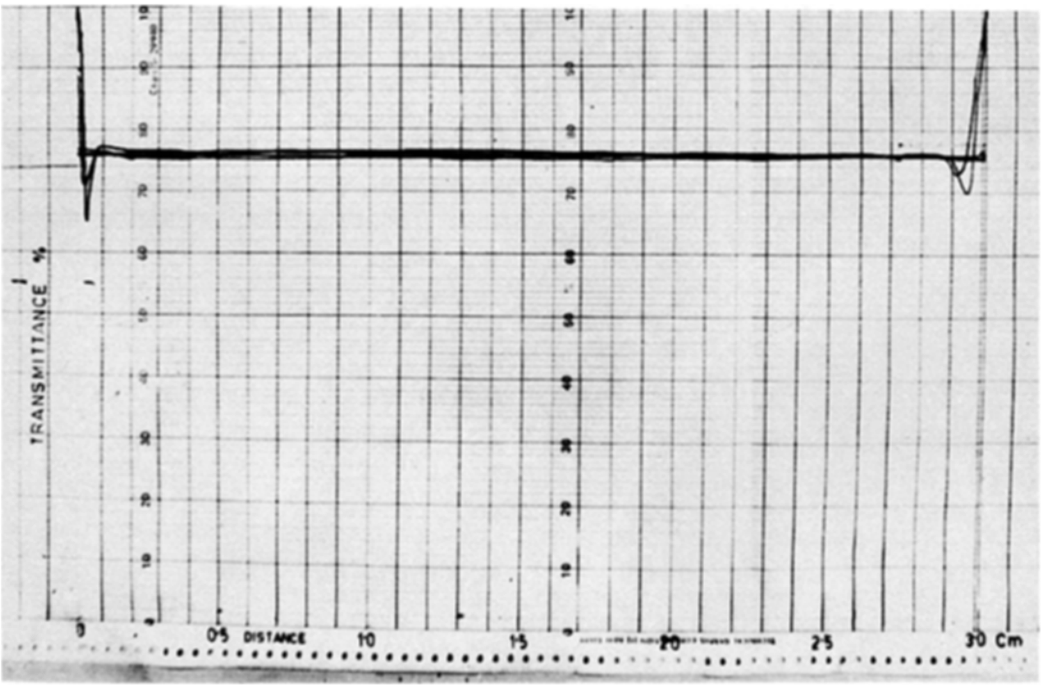

Figure 2 Spatial uniformity of a typical PbS film on glass substrate, obtained as the transmittance of a focused light spot, scanned across the length of the film.

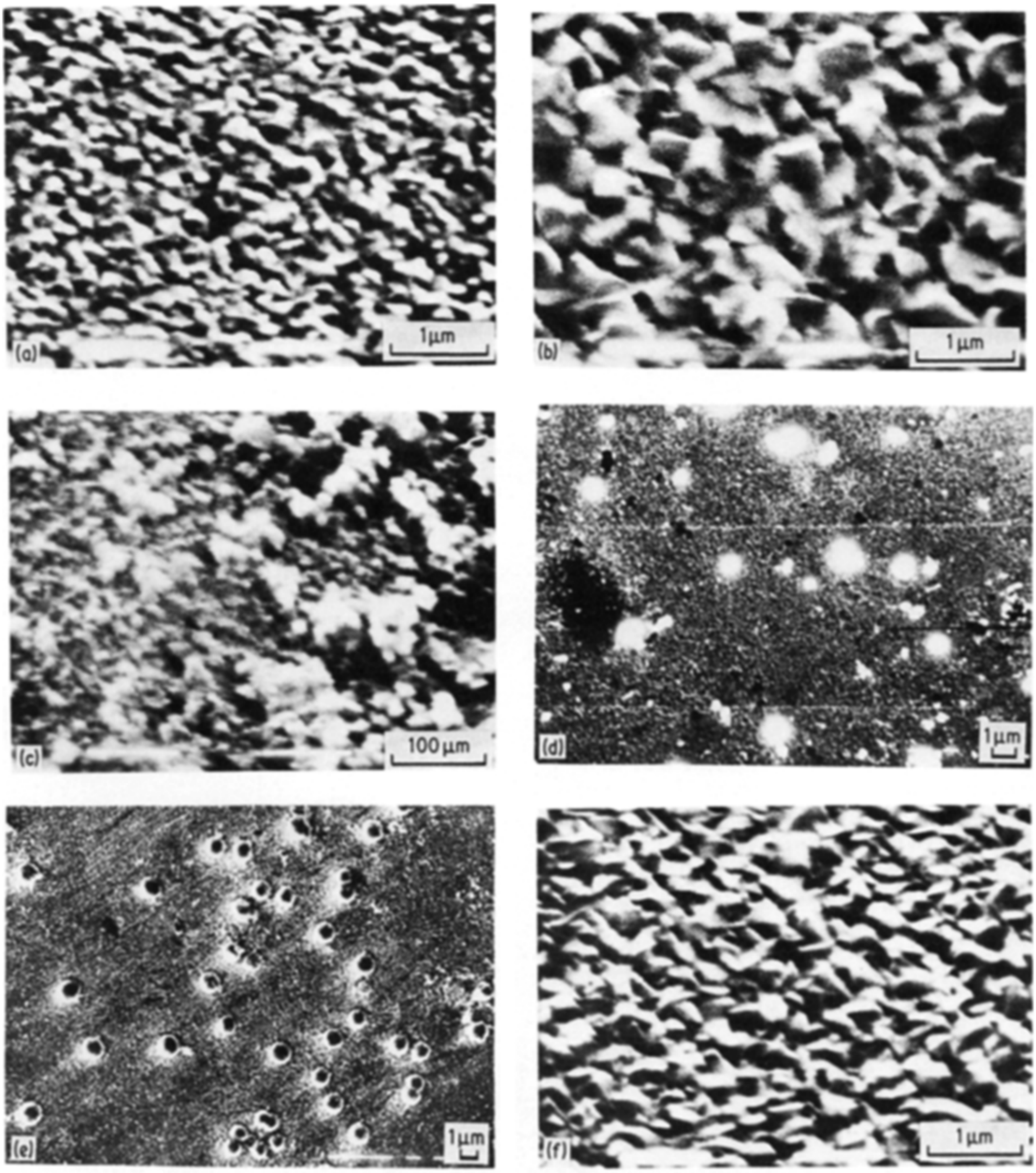

Figure 3 Scanning electron micrographs of the surfaces of PbS films deposited by various chemical methods on (1 1 1)-silicon substrates and a glass substrate. Davis and Norr method: (a) 300 nm film; (b) 850 nm film. (c) Acharya and Bose method. (d) Spray method. (e) Dip–dry method. (f) PbS film on glass substrate (Davis and Norr method).

the strain, is determined by

$$\sigma = \frac{\beta}{2\tan\theta} \qquad (2)$$

where σ is the maximum probability of strain. The pure diffraction broadening is determined by the equation

$$\sigma = (B - b) \qquad (3)$$

where B is the integral width of a reflection from the PbS film, and b is that of an annealed PbS powder. Using Equations 1 to 3, crystallite size and strain for several films on (1 1 1) silicon have been calculated and are given in Table III. It is evident from this table that there is an anisotropy in domain size and strain. As the film thickness increases, size and strain defects decrease. It must be noted that these results are obtained by considering that the integral widths are only due to *either* crystallite size *or* strain.

Changes in the orientation of crystallites of the PbS films with etchants used, may be because while dilute

TABLE III Crystallite size and lattice strain for different PbS films on (1 1 1) silicon substrates

Film thickness (nm)	Etchant used	Particle size (nm)		Strain ($\times 10^{-3}$)	
		⟨1 1 1⟩	⟨1 0 0⟩	⟨1 1 1⟩	⟨1 0 0⟩
200	CP-4	23.8	52.3	14.40	5.70
350	CP-4	35	63	9.00	4.50
1140	Dilute HF	173	235	1.97	1.18

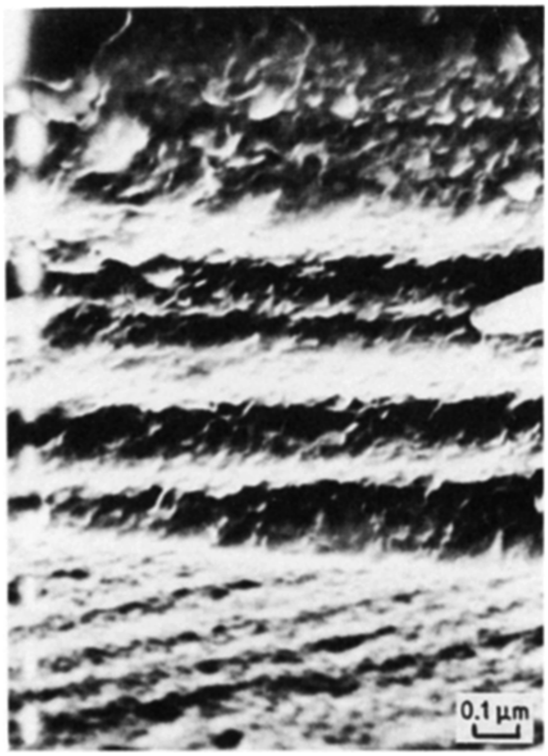

Figure 4 PbS–Si (1 1 1) heterostructure cross-section.

HF removes only the silicon oxide layer from the surface, CP-4 solution exposes twins and etch pits on the silicon substrate in addition to the removal of the oxide layer. The changes in the orientations of the multilayer depositions are most likely due to the fact that after each deposition of the film, some precipitate particles from the solution stick to the surface even after washing the film with a jet of distilled water, and their effect is reflected in the growth of the subsequent layers. From the present study, it seems that after the first layer of deposition, the substrate orientation has no effect on the orientations of subsequent layers.

Electrical characteristics and photoelectric properties of these heterojunctions will be reported in a subsequent paper elsewhere.

5. Conclusions

Although polycrystalline PbS films can be deposited on to silicon substrates by various chemical methods, strong orientation effects are observed only in films prepared by the method described by Davis and Norr. The orientation of the crystallites in single-layer PbS films on (1 1 1) silicon substrate is sensitive to the substrate preparation technqiues. However, subsequent multilayers are little affected by these techniques. The preferred orientations of the crystallites in subsequent layers are not necessarily the same as those present in previous layers.

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References

1. H. SIGMUND and K. BERCHTOLD, *Phys. Status Solidi* (*a*) **20** (1967) 255.
2. M. J. JHABVALA and J. R. BARRETT, *IEEE Trans. Electron Dev.* **Ed-29** (1982) 1900.
3. N. I. BOKHAREVA, L. G. PARITSKII and S. M. RYVIKIN. *Sov Phys. Semicond.* **5** (1971) 849.
4. W. E. PINSON, *J. Appl. Photogr. Engng.* **5** (1979) 18.
5. E. S. KOHN and M. L. SCHULTZ, Tech. Report No. AFCRL-TR-74-0375, RCA Laboratories, Princeton, New Jersey, USA (1974).
6. A. J. STECKL, M. MOTAMEDI, S. P. SHUE, H. ELABD and K. Y. TAM, Proceedings of the CCD '78 Conference, San Diego, California, USA (1978) p. 239.
7. J. N. ZEMEL, *Anal. Chem.* **47** (1975) 265A.
8. H. RAHNAMAI, PhD thesis, University of Pennsylvania, Pittsburgh, USA (1976).
9. R. N. LEE, P. K. SCHARNHORST and R. B. SCHOOLAR, NOL-Technical Report, No. TR-73- 213, Naval Ordanance Laboratory, Maryland, USA (1974).
10. L. G. BAKUEVA, T. I. ZUBKOVA and V. I. IL'IN, *Sov. Phys. Semicond.* **13** (1979) 199.
11. J. L. DAVIS and M. K. NORR, *J. Appl. Phys.* **37** (1966) 1670.
12. H. ELABD and A. J. STECKL, *ibid.* **51** (1980) 726.
13. *Idem*, *J. Electron. Mater.* **9** (1980) 525.
14. H. ELABD, A. J. STECKL and W. VIDINSKI, *Solar Cells* **1** (1980) 199.
15. H. RAHNAMAI, H. J. GRAY and J. N. ZEMEL, *Thin Solid Films* **69** (1980) 347.
16. Y. S. SARMA, H. N. ACHARYA and N. K. MISRA, paper presented at the Indo-U.S.Workshop on "Preparation and characterization of Materials", Indian Institute of Sciences, Bangalore, India (1981) unpublished.
17. A. G. MILNES and D. L. FENCHT, "Heterojunctions and Metal–Semiconductor Junctions" (Academic Press, New York, 1972) Ch. 9.
18. B. L. SHARMA and R. K. PUROHIT, "Semiconductor Heterojunctions" (Pergamon, New York, 1974) Chs. 3 and 4.
19. R. C. TYAGI, S. K. AGARWAL and V. C. SETHI, *Ind. J. Pure Appl. Phys.* **15** (1977) 670.
20. T. K. CHAUDHURY, H. N. ACHARYA and B. B. NAYAK, *Thin Solid Films* **83** (1981) L 169.
21. H. N. ACHARYA and H. N. BOSE, *Phys. Status Solidi* (*a*) **6** (1971) 43.
22. W. KERN and D. A. POUTINEN, *RCA Rev.* **31** (1970) 187.
23. P-H. KLUG and E. L. ALEXANDER, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials" (Wiley, New York, 1974) Ch. 9.

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