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Investigation of surface activity and photoinduced diffusion of metals in solution deposited amorphous films of As_2S_3

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Surface activity of solution deposited (SD) amorphous films of As_2S_3 has been investigated. Silver and copper are readily deposited on such films from appropriate aqueous ionic solutions. The metals diffuse into the films upon irradiation with energetic photons. Structure and properties of SD films have been investigated using electron microscopy, optical spectroscopy and differential scanning calorimetry. The amorphous films tend to crystallize upon metal diffusion. The stability of amorphous films, the deposition of metals on their active surfaces and the photoinduced diffusion may all be attributed to the presence or production of charged defects in amorphous chalcogenide films.

1. Introduction

It is well established that certain chalcogenide glasses, both in bulk and thin film forms are richly photoactive. When illuminated with photons of energy greater than the band gap, these glasses undergo various optical [1, 3–7], structural [1–4], and electrochemical transformations [8, 9] such as shift of the absorption edge [1], changes in optical constants [2, 5], film thickness [2, 11, 13–15], microhardness [12], rate of chemical dissolution [9, 10], diffusion of metals [16, 17] into the glass etc. These characteristic features of non-crystalline phases have been investigated extensively in arsenic-based chalcogenide glasses. Until recently, most of the studies were made with glasses prepared in the bulk form by melt quenching and with thin films obtained from thermal evaporation or sputtering.

Chern and Lauks [18] have recently developed a new method of depositing amorphous thin films of various silver- and germanium-based chalcogenide glasses from their respective solutions. Solutions are prepared by dissolving the chalcogenide powders in low molecular weight amines and thin films are cast by fairly rapid evaporation of the solvent from the solution. The resulting thin films are then baked at higher temperatures in order to remove the excess amines and are found to be essentially amorphous. It has been reported [18] that their physical properties are in some ways different from those prepared from other conventional methods. For example, it has been found [18] that the amorphous films obtained from the solution route possess active surfaces. When such films are dipped in ionic salt solutions such as $AgNO_3$ [17] or $CuSO_4$, corresponding metals (silver or copper) are rapidly deposited on their surfaces. Furthermore, when the films deposited with metals are exposed to electromagnetic radiation of energy greater than the band gap of the chalcogenide of the film, an inward migration of the deposited metals occurs. Such photo-

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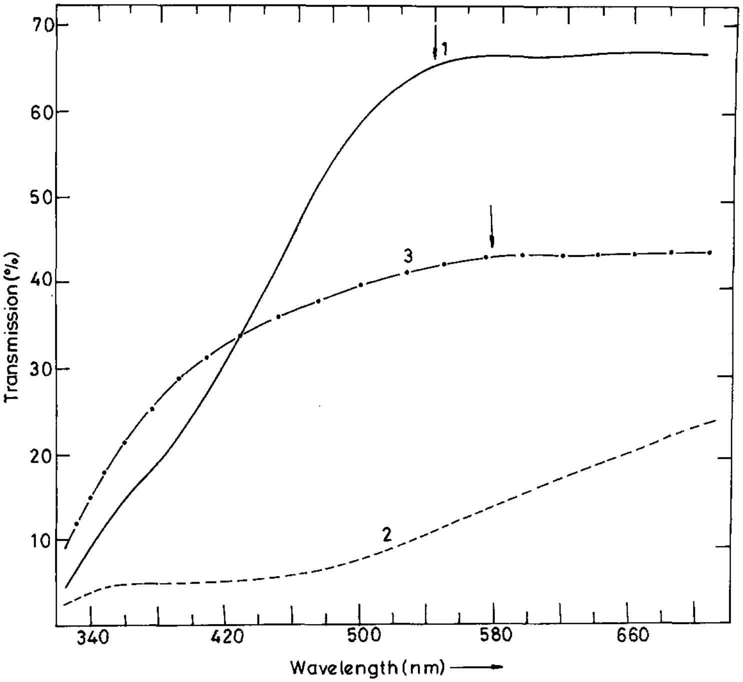

Figure 1 Transmission (%) as a function of wavelength spectra for (1) virgin, (2) silver deposited, (3) silver photodiffused films of As_2S_3. (Arrows indicate the absorption edge.)

induced diffusion of metals has enormous application potential [19], and hence the importance of this technique. However, the nature of metal deposition and its photoinduced diffusion into the film have not been clearly understood. We feel that combination of structural, thermal and spectroscopic investigations may help in understanding the origin of both surface activation and photoinduced migration of metals. In this communication we report some of our preliminary investigations of SD films by using electron microscopy, differential scanning calorimetry (DSC) and ultraviolet visible spectroscopy.

2. Experimental details

Thin films of As_2S_3 were prepared from the solution as follows. About 0.3 mg high purity (99.999%) powder (Koch-Light Company, UK) was dissolved in 10 ml, ethylene diamine. The solution was centrifuged and filtered. The films were obtained by dipping thoroughly cleaned microscope glass slides and by evaporating the excess amines by baking around 110° C. The thickness of the resulting films could be varied by varying the concentration of the chalcogenide in solution. The thickness of the films for structural studies was less than 100 nm and those for metal deposition and diffusion were of the order of 250 nm. The metal deposition (silver and copper) was carried out by dipping the films in 0.025 N $AgNO_3$ solution for approximately 5 sec and in 1.0 N $CuSO_4$ solution for about 30 sec. A Xenon lamp source at an intensity of $\sim 10\,mW\,cm^{-2}$ was used for the irradiation of the films. Excess undiffused silver on the surface was removed by treating with a stripping solution prepared from 74.5 g KI, 1.5 g I_2 and 50 ml distilled water. Excess copper was similarly removed by treating with 50% HNO_3. Optical transmission spectra were recorded on a Pye-Unicam SP 800 double beam spectrophotometer. Structural studies were made on films which were lifted on to 400 mesh copper grids and introduced into the specimen holder of a Phillips EM301 electron microscope. Sample heating by electron beam and the electron beam-induced structural changes were reduced by employing low beam conditions (current densities were maintained at $\sim 1\,\mu A\,cm^{-2}$). Differential scanning calorimetry on films (baked for about 1 h at 110° C to remove the excess amine) was carried out on a Perkin-Elmer DSC2, in the temperature range 293 to 473 K at a heating rate of $20\,K\,min^{-1}$.

3. Results and discussion

The optical transmission spectrum of solution deposited (SD) thin As_2S_3 film is shown in Fig. 1 (also in Fig. 2). It may be noted that the percentage transmission drops rapidly below

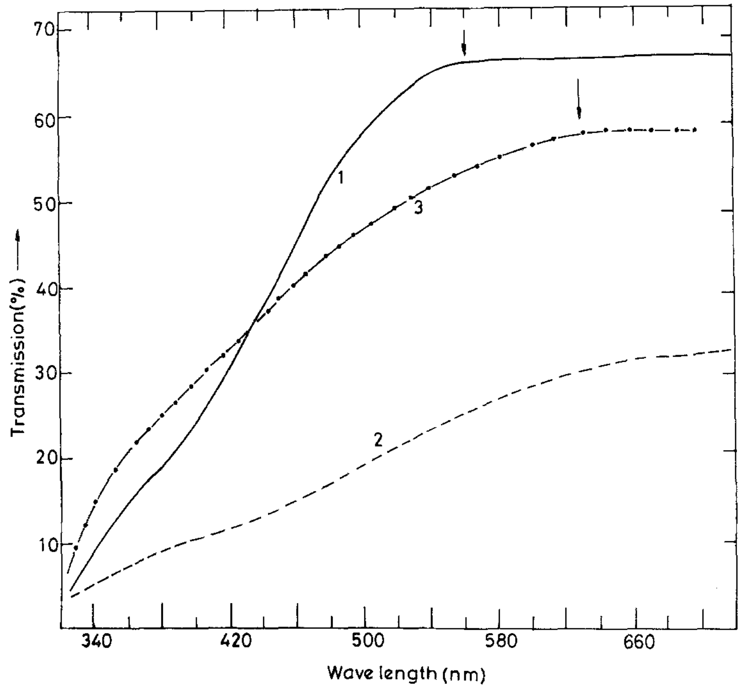

Figure 2 Transmission (%) as a function of wavelength spectra for (1) virgin, (2) copper deposited, (3) copper photodiffused films of As_2S_3. (Arrows indicate the absorption edge.)

540 nm. The absorption edge from the spectrum agrees well with the reported value of the band gap for the bulk As_2S_3 (2.3 eV). The radiation from xenon lamp source contains enough intensity of frequencies above this band gap energy. The transmission spectra of the films with the surface metal films and after irradiation (and removal of excess metal) are also presented in Figs. 1 and 2. The electron micrograph of the virgin As_2S_3 film is shown in Fig. 3 along with its diffraction pattern (inset). Electron micrographs and diffraction patterns (inset) of films after metal deposition (silver and copper) and irradiation (and removal of excess surface metal) are presented in Figs. 4 and 5, respectively.

From Fig. 3, it may be noted that the SD films of As_2S_3 are truly amorphous. The films appear to be continguous islands in bright field. Films with diffused metals also possess similar appearance in the regions where metal ions have diffused. Pale regions in the micrographs of Figs. 4 and 5 are amorphous as revealed by their diffraction patterns. However, the diffraction patterns of the dark metal-rich regions shown in the insets contain spotted and sharp rings indicating the crystalline nature of these regions. It may be noted from Figs. 1 and 2 that the absorption intensities are considerably increased after photodiffusion and result in a broad and diffuse absorption edge in the optical spectra.

DSC scans of virgin SD-As_2S_3 films are shown in Fig. 6 for two successive runs up to 473 K. The thermogram of the metal coated film material before photodiffusing the metal is shown in

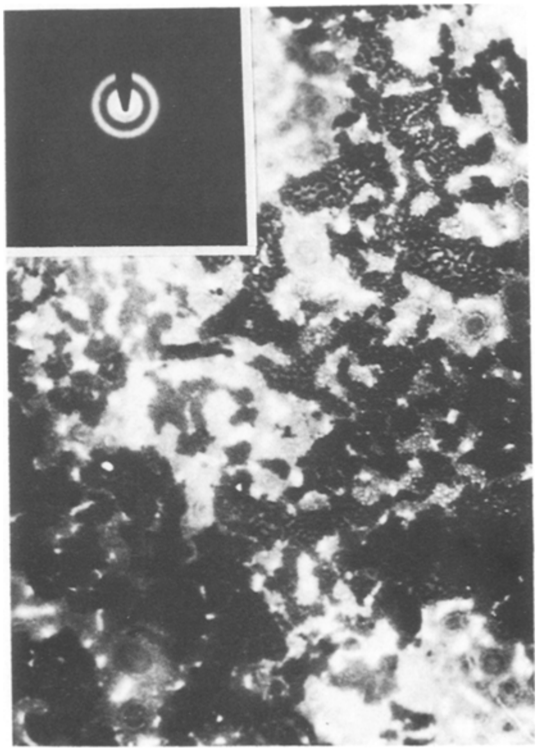

Figure 3 Electron micrograph of the virgin As_2S_3 film along with its diffraction pattern (inset).

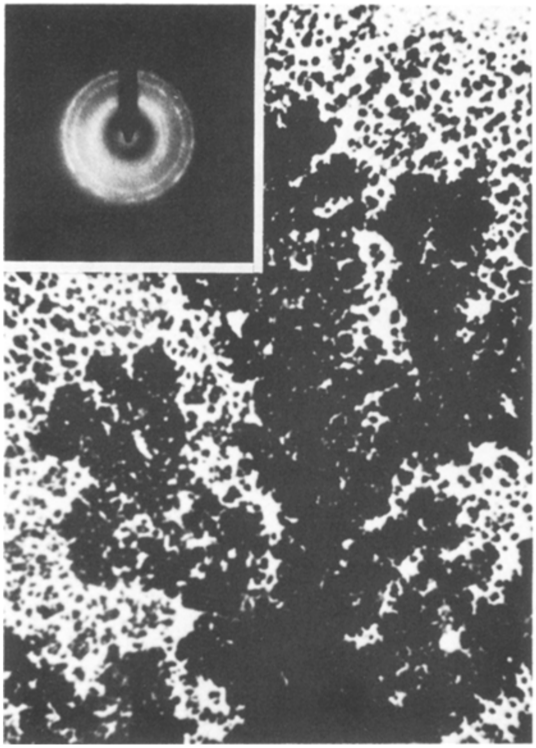

Figure 4 Electron micrograph of the As_2S_3 film after photodiffusion of silver along with its diffraction pattern (inset).

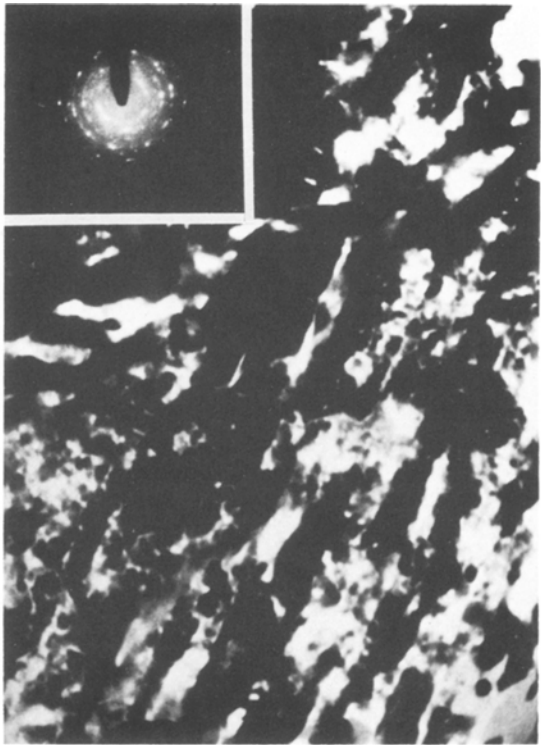

Figure 5 Electron micrograph of the As_2S_3 film after photodiffusion of copper along with its diffraction pattern (inset).

Fig. 7, against for two successive runs. The DSC scans of the virgin films strongly suggest that they contain substantial amounts of bound amine molecules which are eliminated upon heating and therefore give rise to the broad endotherm in the region of 370 K which is absent in the repeat scans of the same material. The repeat scan suggests that the small increase in the endothermic amplitude in DSC scan around 410 K is probably due to a glass transition-like behaviour of the SD films. The composition of the film is unlikely to be very different from the stoichiometric As_2S_3. Therefore, such a thermal event which occurs at much lower temperature than in melt-quenched bulk As_2S_3 glasses ($T_g \simeq 460\,K$) may be a characteristic temperature of such solution deposited amorphous films.

The first DSC scan (Fig. 8) of the SD films with silver deposited on them, also exhibits an endotherm in the region of 370 K which again corresponds to the loss of bound amine molecules. But following the endotherm is a highly energetic exotherm which could be due to the crystallization of the sample. We would like to imply from the behaviour of the thermograms that the metal containing films have a pronounced tendency for crystallization. This tendency is perhaps activated and assisted by irradiation with band gap photons, since irradiation results in bond breaking, ultimately resulting in the formation of charged defects. Such an observation is supported by diffraction patterns in Figs. 4 and 5 (inset).

We therefore feel that the charged defects play an important role in stabilizing SD amorphous films in the deposition of metals upon their surfaces and in the photoactivated diffusion of such deposited films. When a concentrated amine solution of chalcogenide is evaporated, an agglomeration of the solute, As_2S_3 units, begins to occur resulting in the formation of fine As_2S_3 particles presumably of sizes smaller than conventional colloidal particles. We have not, however, confirmed the formation of such colloidal particles using optical experiments. It is possible that such extremely fine particles are stabilized by a sheath of amine molecules and the bonding at the

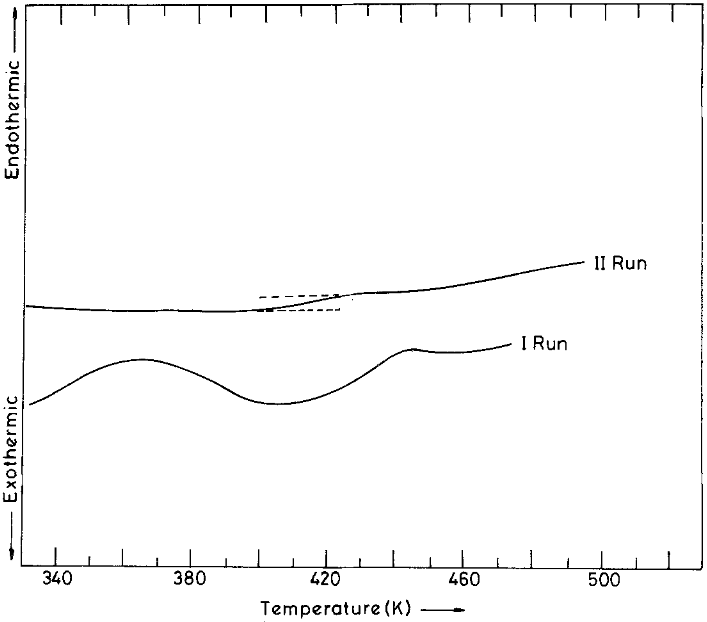

Figure 6 DSC scans of virgin As_2S_3 films.

interface between the chalcogenide particles and the amines may be Coulombic. However, it may also be noted that while nitrogen atoms in the amine molecules possess lone pairs, the sulphur atoms on the As_2S_3 clusters possess dangling bonds. Hence the overlap of the lone pair orbital of nitrogen with the half filled p-orbital of the sulphur can give rise to weak but effective bonding between the amine and the As_2S_3 cluster. A stabilization of the cluster that ensues from such an interaction is weaker than that from either a fully ionic or a fully covalent bond and therefore the amine is easily removed during baking around 370 K. After the removal of the amines during baking, the cluster surfaces are left with dangling bonds which may rearrange and give rise to overcoordinated and undercoordinated charged defect centres of the type $S_3^{\oplus}$ and $S_1^{\ominus}$. It is these charged defects, which effectively bind the silver (or copper) ions deposited on the film surface.

When SD films with silver deposited on them

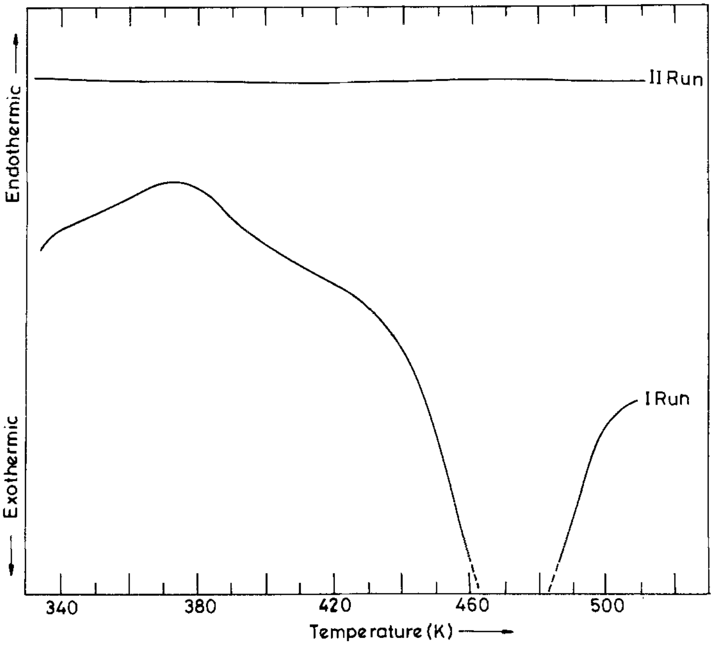

Figure 7 DSC scans of metal coated (silver) film before photodiffusion.

are irradiated with photons of energy greater than the band gap energy, a further concentration of defects is created in the interior of the As_2S_3 clusters. As a consequence, the surface silver atoms are exposed to a free energy gradient driving the Ag^+ ions to the interior of the clusters. Silver ions diffuse into regions of high sulphide ion ($S_1^\ominus$ defect) concentration. Such a diffusion of Ag^+ ions necessitates the concentration of $S_3^\oplus$ centres to decrease, which is easily achieved by appropriate snapping of the over-coordinated bonds of sulphur. This might imply reformation of even homoatomic $>$As–As$<$ bonds. Furthermore, it is extremely likely that the first layer of deposited silver is present only as Ag^+ ions. But, further layers are present only as silver atoms. Also, such continued deposition of silver is likely, due to direct photodecomposition of silver salt in solution, catalysed by an initial layer of silver atoms. This latter process has little to do with the defects in the films, because these layers of silver atoms are well separated from the chalcogenide film. The fact that copper is deposited to a very limited extent by dipping the SD films in copper sulphate solution is also consistent, because it is well known that copper sulphate does not undergo such photodecomposition in solution.

The regions of SD films into which silver ions diffuse extensively undergo structural rearrangements relatively easily because of the predominance of ionic (non-directional) bonding between $S_1^\ominus$ centres and Ag^+ ions. Crystallization occurs in such regions forming Ag_2S. Analysis of the diffraction pattern in Fig. 3 suggests that the *d* values corresponding to the various sufficiently well-defined rings indeed correspond very closely to the *d* values reported for Ag_2S. The observed and reported *d* values for Ag_2S are given in Table I. The corresponding *d* values for Cu_2S obtained from SD films diffused with copper are given in Table II. It may be noted that the analysis of the behaviour of SD films diffused with copper is very similar to that of the films diffused with silver. Indeed, there is a shift in the absorption edge towards long wavelengths which may also be attributed to the formation of Ag_2S (or Cu_2S) (Figs. 1 and 2).

TABLE I *d* spacings for Ag_2S in silver-diffused SD films

Calculated (nm)	Reported (nm)
0.269	0.267
0.235	0.238
0.152	0.151
0.132	0.132

TABLE II *d* spacings for Cu_2S in copper-diffused SD films

Calculated (nm)	Reported (nm)
0.334	0.331
0.304	0.305
0.253	0.254
0.226	0.222
0.214	0.214

Both the diffusion of metal ions and resultant crystallization should be considerably influenced by the sizes of the ions. The radii of copper and silver (Cu^+ and Ag^+) are 0.098 and 0.113 nm, respectively. They both appear to diffuse readily. In fact a ready photoinduced reaction of copper and silver has been observed with evaporated chalcogenide films [20]. That it has not been possible to photodiffuse gold (ionic radius of $Au^+ = 0.137$ nm) in a similarly fascile manner, strongly suggests that the sizes of the diffusing ions *vis à vis* the nature of the chalcogenide network is an important factor.

It is interesting to note in this context that a similar deposition of either silver or copper does not occur in SD films of pure chalcogens (e.g. selenium). This seems to be quite in agreement with a charged defect model. Because, in the case of pure chalcogens, charged defects tend to remain spatially in close proximity and the Coulombic field of such intimate valence pair upon the silver ion is very low. Hence silver (or copper) deposition does not seem to take place on pure chalcogen films. It is for similar reasons that such intimate valence pairs of defects produced upon photo-irradiation do not generate a sufficiently strong Coulombic field gradient for the migration of any deposited ions on the surface. We may also note that the lower structural free volume in pure chalcogens as compared to arsenic chalcogenides may also prevent ready inward diffusion of metal ions.

Acknowledgements

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References

1. J. P. deNEUFVILLE, "Optical Properties of Solids – Recent Developments" (North-Holland, Amsterdam, 1975) p. 439.
2. I. SHIMIZU and H. FRITZSHE, *J. Appl. Phys.* **47** (1976) 2969.
3. K. TANAKA and Y. OHTSUKA, *Thin Solid Films* **48** (1978) 17.
4. *Idem, J. Appl. Phys.* **49** (1978) 6132.
5. J. P. deNEUFVILLE, S. C. MOSS and S. R. OVSHINSKY, *J. Non-Cryst. Solids* **13** (1974) 191.
6. K. TANAKA, *Appl. Phys. Lett.* **26** (1975) 243.
7. S. RAJAGOPALAN, BHANWAR SINGH, P. K. BHAT, D. K. PANDYA and K. L. CHOPRA, *J. Appl. Phys.* **50** (1977) 489.
8. Y. UTSUGI and S. ZEMBUTSU, *Appl. Phys. Lett.* **27** (1975) 508.
9. M. S. CHANG and T. W. HON, *Opt. Commun.* **24** (1978) 220.
10. M. S. CHANG and J. T. CHEN, *Appl. Phys. Lett.* **33** (1978) 892.
11. M. KASAI, H. NAKATSUI and Y. HAZIMOTO, *J. Appl. Phys.* **45** (1974) 3209.
12. B. T. KOLOMIETS, S. S. LANTRATOVA, V. M. LYUBIN, V. P. PUKH and M. A. TAGIRDZHANOV, *Sov. Phys. Solid State* **18** (1976) 686.
13. K. L. CHOPRA, K. SOLOMON HARSHAVARDHAN, S. RAJAGOPALAN and L. K. MALHOTRA, *Solid State Commun.* **40** (1981) 387.
14. *Idem, Appl. Phys. Lett.* **40** (1982) 428.
15. K. SOLOMON HARSHAVARDHAN, S. RAJAGOPALAN, L. K. MALHOTRA and K. L. CHOPRA, *J. Appl. Phys.* **54** (1983) 1048.
16. A. MATUSUDA and M. KIKUCHI, *J. Jpn. Soc. Appl. Phys.* **42** (1973) 239.
17. H. MIZUNO, K. TANAKA and M. KIKUCHI, *Solid State Commun.* **12** (1973) 999.
18. G. C. CHERN and I. LAUKS, *J. Appl. Phys.* **53** (1982) 6979.
19. A. YOSIKAWA, O. OCHI, H. NAGAI and Y. MIZUSHIMA, *Appl. Phys. Lett.* **29** (1976) 677.
20. L. A. FREEMAN, R. F. SHAW and A. D. YOFEE, *Thin Solid Films* **3** (1969) 367.

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