JOURNAL OF MATERIALS SCIENCE **40** (2005) 455–459

Characterization of thermally evaporated $AgGaTe_2$ films grown on KCl substrates

R. KUMAR
Department of Physics, DAV College, Amritsar, India

R. K. BEDI*
Material Science Laboratory, Department of Physics, Guru Nanak Dev University, Amritsar 143005, India
E-mail: rkbedi@rediffmail.com

Silver gallium telluride ($AgGaTe_2$) films have been grown by thermal evaporation technique onto the KCl substrates kept at different temperatures (483–563 K) in a vacuum of 1.3×10^{-3}Pa. The experimental conditions were optimised to obtain better crystallinity of the films. The films so prepared have been studied for their structural, optical and electrical properties. Observations reveal that the crystallinity of the films increases with increase in substrate temperature. Average crystallite size of 0.2–0.5 μm has been observed in case of films deposited at 563 K. Analysis of optical spectra of the films in the range 300–1100 nm show an allowed direct transition near the fundamental absorption edge (E_{g1}) in addition to a transition originating from crystal field split levels (E_{g2}). It has been observed that the carrier concentration and Hall mobility of films increases with increase in substrate temperature.

1. Introduction

$AgGaTe_2$ belongs to I-III-VI_2 family of semiconducting materials that crystallize in space group $1\bar{4}2d$ with the tetragonal chalcopyrite lattice [1]. These are ternary analogues of the $A^{II}B^{VI}$ compounds with cubic zincblende structure. The c/a ratio is not exactly equal to two because of the different attractive forces between each kind of metal atom and the chalcogen atoms in the chalcopyrite structure. Due to the tetragonal distortion (2-c/a) this class of materials shows a great deal of applications in non-linear optics (NLO) and photovoltaic (PV) energy conversion [2–4]. $AgGaTe_2$ is a direct band gap semiconductor with an energy gap of 1.32 eV at 300 K and crystallizes in chalcopyrite structure [5]. Because of its high absorption coefficient and energy band gap value lying close to solar spectrum, this material may be considered as a potential candidate for the fabrication of thin film solar cells. The growth and characterization of $AgGaTe_2$ thin films have been reported by Patel *et al*. [6, 7]. Konstantinova *et al*. [8] have studied the optical properties of $AgGaTe_2$ single crystals. Investigations on electrical properties of Cu_{1-x} Ag_xGaTe_2 films were made by Kuhn *et al*. [9]. Julien *et al*. [10] have studied the optical and electrical properties of ternary compounds in the Ag-Ga-Te system. Birefringence, indices of refraction, infrared transmission and temperature dependence of the band gap of $AgGaTe_2$ have been discussed by Ohmer *et al*. [11]. The dielectric properties of $AgGaTe_2$ have been studied by Xue *et al*. [12]. Investigation of the optical properties of $AgGaTe_2$ films obtained by laser deposition has been discussed by Bodnar *et al*. [13].

In this communication, we report the synthesis of $AgGaTe_2$, the structural, optical and electrical properties of thermally evaporated films obtained thereof onto the KCl single crystal substrates kept at different temperatures.

2. Experimental

2.1. Preparation of $AgGaTe_2$ compound

The silver gallium telluride was synthesized from high purity (99.999%) silver, gallium and tellurium obtained from Nuclear fuel complex (NFC), Hyderabad (India). Silver, gallium and tellurium were taken in stoichiometric proportions in evacuated quartz ampoule at a pressure of 1.3×10^{-3} Pa at 1300 K in horizontal furnace for 48 h and then broken after cooling (1/2 deg./min) in ice-cold water. The product so obtained was powdered and was again sealed in quartz ampoule for retreatment for 24 h to ensure the homogeneity of the product. The ampoule was again quenched in ice-cooled water and the material was powdered to 150-mesh size. Homogeneity of the alloy is confirmed by the X-ray diffraction pattern.

2.2. Preparation of $AgGaTe_2$ films

Before carrying out the deposition, the vacuum chamber was baked at 500 K for one hour to degas the vacuum

*Author to whom all correspondence should be addressed.

chamber. Films were obtained on to the freshly cleaved KCl single crystal substrates by thermal evaporation of the pellets of $AgGaTe_2$ from molybdenum boat kept at 1500 K in vacuum of 1.3×10^{-3} Pa. Radiant heater was used to heat the substrate in the temperature range 450–600 K. The substrate temperatures were controlled by PID temperature controllers using K-type thermocouple obtained from Omega Eng. (USA). The order of the vacuum was maintained using liquid nitrogen trap during evaporation. The thickness of the films was monitored during evaporation using digital thickness monitor (DTM-101) and was kept around 1.7μm and deposition conditions were maintained almost the same for all the films. In order to study the effect of substrate temperature on the properties of films, they were grown under identical conditions by keeping the source temperature (1500 K), residual pressure (1.3×10^{-3} Pa) during deposition, source to substrate distance (15 cm) and rate of deposition (100 Å/sec) constant. The deposition rate was kept constant by allowing the same amount of current to pass through the boat, and every time all the material in the boat was completely evaporated in order to ensure the stoichiometry of films. The compositional analysis of films has been carried out using X-ray fluorescence (XRF) and weight percentages of silver, gallium and tellurium have been found comparable with those of stoichiometric powder. The films so obtained were annealed at 500 K and kept in vacuum to prevent direct contact from the atmosphere.

2.3. Measurements

To study the surface topography and influence of different substrate temperatures on the growth of films, a series of scanning electron micrographs of the films were taken using Jeol JSM-6100 (Japan) scanning electron microscope. The XRD scans of films were taken using Cu K_α (wave length = 1.5405 Å) radiation in the 2θ range 5–60° by Philips diffractometer.

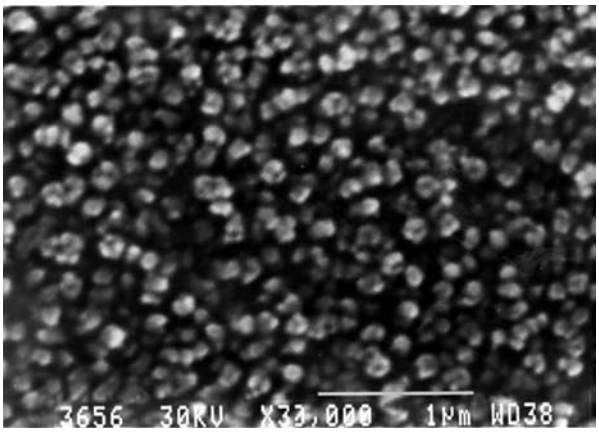
The optical band gap studies have been carried out by taking transmittance spectra of films in the photoenergy range 1.4–2.4 eV from UV-1601PC (Shimadzu, Japan) Spectrophotometer.

The electrical resistivity, Hall mobility and carrier concentration of the $AgGaTe_2$ films were determined in vacuum of the order of 10^{-2} Pa using Vander Pauw's [14] four probe technique in the temperature range 193–413 K. Silver contacts were used to connect electrical leads to the films and were verified to be ohmic from the symmetric straight line of current-voltage (I-V) characteristics passing through origin.

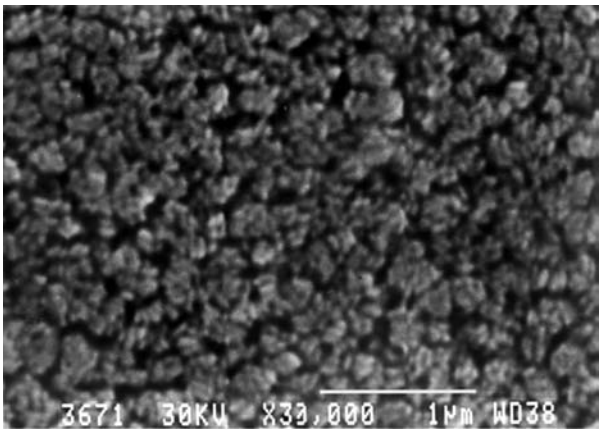
3. Results and discussion

3.1. Structural characterization

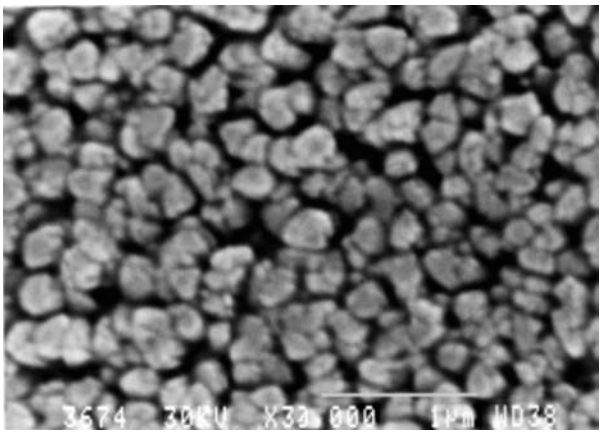
Fig. 1a, b and c show the scanning electron micrographs of $AgGaTe_2$ films deposited onto KCl substrate kept at different temperatures. The surface topography in these micrographs illustrates the distribution, shape and size of crystallites. An appreciable increase in crystallite size with substrate temperature has been noticed (Table I). The average crystallites size of



(a)



(b)



(c)

Figure 1 Scanning electron micrographs of $AgGaTe_2$ film deposited at: (a) 483 K, (b) 523 K and (c) 563 K respectively.

0.2–0.5 μm has been obtained for the films deposited at 563 K.

The X-ray diffractogram obtained for $AgGaTe_2$ film deposited at 563 K (Fig. 2) shows the presence of many well sharp and resolved lines, which confirm its crystalline behaviour. The d-values are calculated for θ values corresponding to different peak positions using Bragg's equation $2d \sin\theta = n\lambda$ taking $n = 1$. These d values are in good agreement with those found in literature [11] thus confirming the formation of $AgGaTe_2$ film on the substrate. The films appear to have a high degree of crystallographic texture in the [112]

TABLE I Experimental data of average crystallite size, activation energy and optical band gap of $AgGaTe_2$ films deposited on KCl substrate kept at different temperatures

Substrate temperature (K)	Crystallite size (μm)	Activation energy (eV)	Optical band gap energy (eV)	
			E_{g1}	E_{g2}
483	0.22	0.048	1.29	1.84
523	0.32	0.043	1.31	1.87
563	0.50	0.035	1.32	1.90

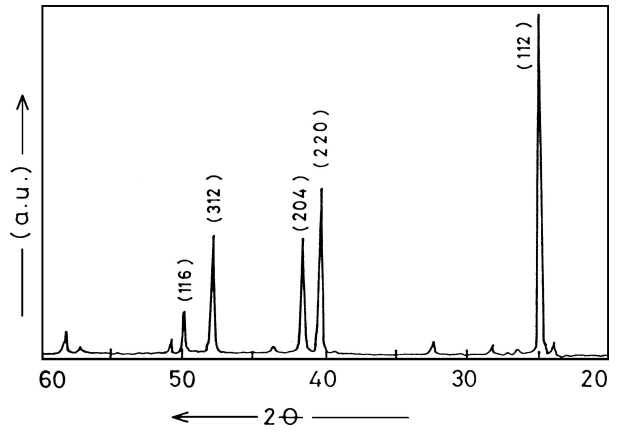


Figure 2 X-ray diffraction pattern of $AgGaTe_2$ film deposited at 563 K.

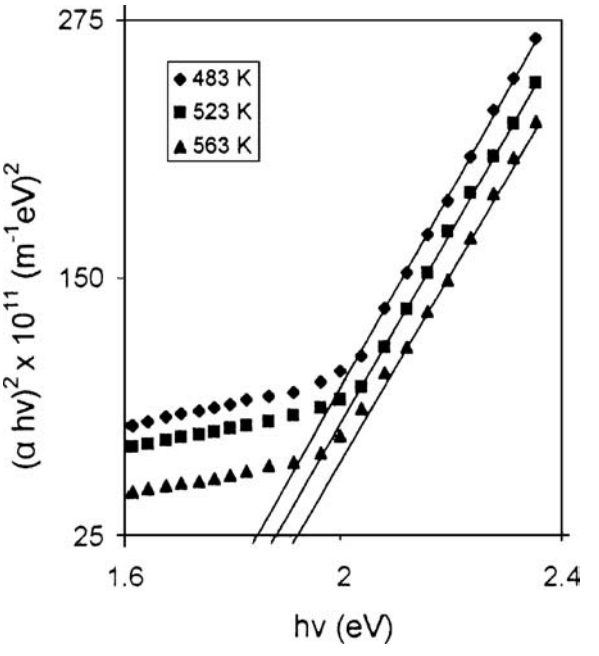
direction. Also, the diffraction lines are comparatively sharp for the films deposited at higher substrate temperature thus indicating a higher degree of crystallinity [15].

3.2. Optical properties

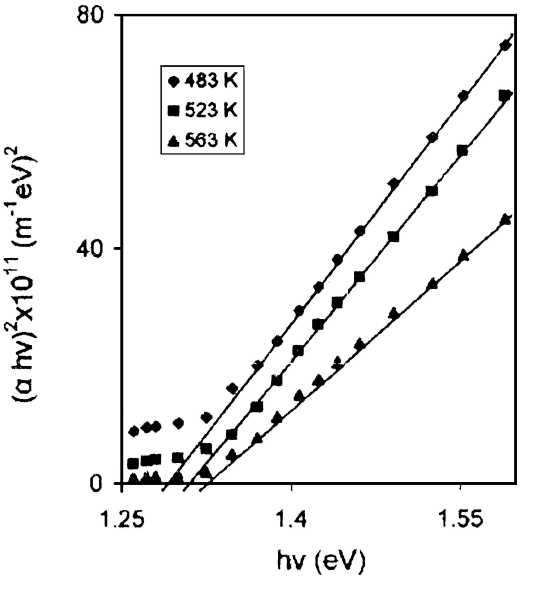
The optical spectra of films recorded at room temperature in the wavelength range from 300 to 1100 nm show two absorption humps. The first hump occurs in the photon energy range $1.2 > h\nu > 1.6$ eV and has been examined in terms of allowed direct transition from the top of the valance band to the conduction band minimum at the centre of the Brillouin zone using equation of Bardeen *et al.* [16], which states that

$$\alpha h\nu = A(h\nu - E_{gl})^{1/2}$$

where A is the constant and ν is the frequency of the incident light. Fig. 3a shows the spectral variation of square of absorption coefficient (α) for films deposited onto KCl substrate of 1 mm thickness kept at different temperatures. The extrapolation of the linear portion to $\alpha h\nu = 0$, gives the value of the optical band gap (E_{g1}) under direct allowed transitions for $AgGaTe_2$ films and found to lie in the range 1.29–1.32 eV (Table I). The second hump has been observed in the energy range $1.6 > h\nu > 2.4$ eV with the energy gap E_{g2} lies in the range 1.84–1.90 eV (Fig. 3b) which is due to the transition from the crystal-field split valance band that results from the interaction between the valance electrons and the non-cubic crystal field of chalcopyrite



(a)



(b)

Figure 3 Spectral variation of α for $AgGaTe_2$ films deposited at different temperatures in the photon energy range: (a) 1.2–1.6 eV and (b) 1.6–2.4 eV.

to the conduction band minimum. Also, an increase in band gap energy with the substrate temperature has been noticed which may be attributed to the fact that films deposited at higher substrate temperatures, exhibit larger grain size and show more ordered structure which give comparatively less contribution to the absorption [17].

3.3. Electrical properties

The Arrhenius plots of temperature dependence of electrical conductivity for the $AgGaTe_2$ films deposited on glass substrates kept at different temperatures, is shown in Fig. 4. It has been observed that the electrical conductivity increases with increase in temperature, within the

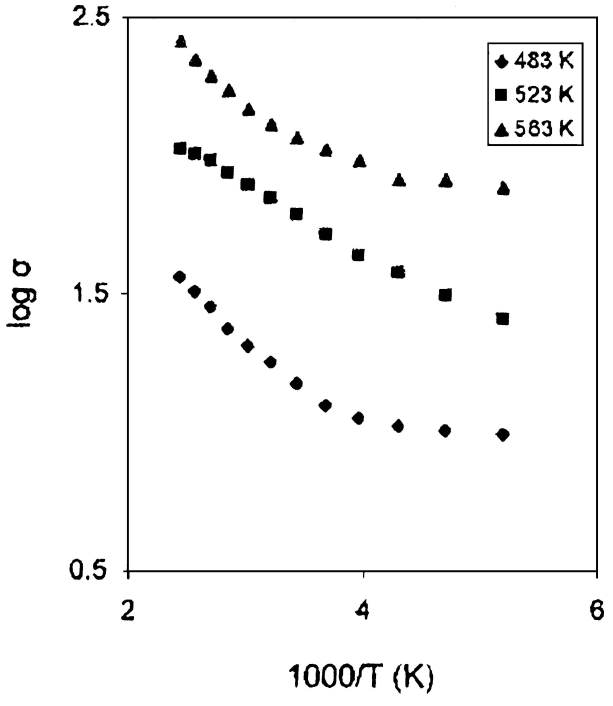


Figure 4 Inverse absolute temperature dependence of log of conductivity of $AgGaTe_2$ films deposited at different temperatures.

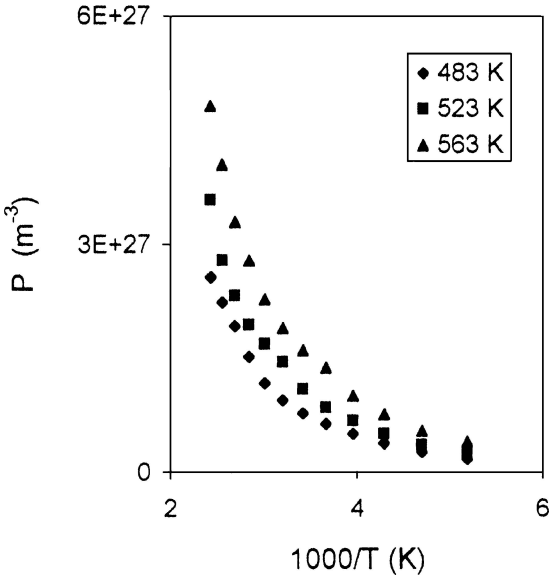


Figure 5 Variation of carrier concentration with inverse absolute temperature for $AgGaTe_2$ films deposited at different temperatures.

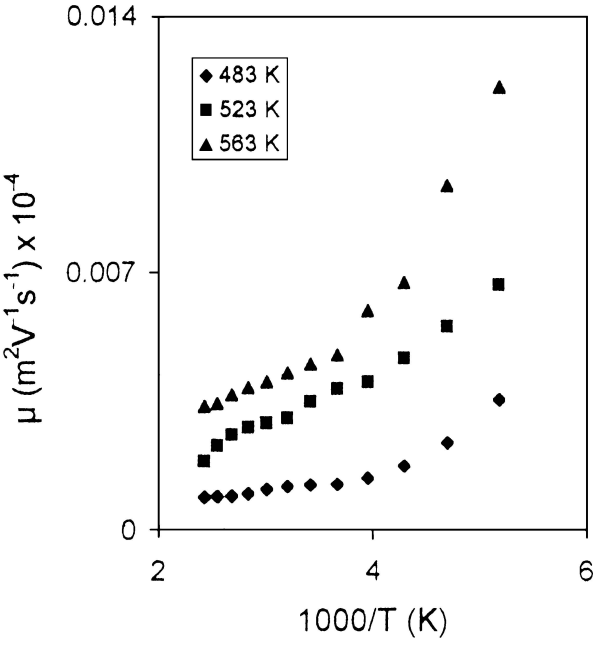


Figure 6 Variation of carrier mobility with inverse absolute temperature for $AgGaTe_2$ films deposited at different temperatures.

experimental temperature range investigated and can be represented by equation

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where E_a is the thermal activation energy. In addition, the electrical conductivity increases with increase in the substrate temperature, which can be explained using Petritz's barrier model [18]. Observations reveal that the electrical conductivity of $AgGaTe_2$ films grown on KCl substrate increases by factor of about 10^1 as compared to the thermally evaporated films deposited on glass [19]. The activation energies obtained from the slopes of these plots have been found to decreases with the increase in substrate temperature and are listed in Table I.

The Hall effect studies indicates that $AgGaTe_2$ films are p-type, thus holes as dominant charge carriers. The Hall coefficient (R_H) has been determined using the relation [20],

$$R_H = V_H d \times 10^2 / IH \mathrm{m^3 C^{-1}}$$

where I is the current in Ampere, H is in Tesla, thickness d is in m and V_H in volts. The Hall coefficient (R_H) appears to lie in the range 1.3×10^{-9}–3.6×10^{-8} $\mathrm{m^3 C^{-1}}$. The observations reveal that the films deposited at 483 K show comparatively higher R_H value than those deposited at 563 K. The temperature dependence of charge carrier concentration (p) for $AgGaTe_2$ films with inverse absolute temperature (Fig. 5) indicates that the carrier concentration increases with increase in temperature. The films show comparatively high carrier concentration when deposited at higher substrate temperature.

The variation of carrier mobility with inverse absolute temperature has been shown in Fig. 6. The mobility values lie in the range 8.9×10^{-8}–1.2×10^{-6} $\mathrm{m^2 V^{-1} s^{-1}}$, which are comparatively large compared to those reported for $AgGaTe_2$ films prepared by thermal evaporation [19]. Investigations reveal that the carrier mobility increases with increase in substrate temperature, which may be attributed to the fact that increase in substrate temperature increases the grain size and thereby reducing the interpotential barrier and causes an increase in overall mobility. Similar results have been observed for II-VI [21], III-V [22, 23] and I-III-VI_2 [15] films.

4. Conclusions

The $AgGaTe_2$ films are crystalline in nature and average crystallites size of 0.2–0.5 μm is observed in films

deposited at 563 K. The optical band gap energy of films lies in the range 1.29–1.90 eV. The substrate temperature (T_s) appears to influence the properties of the films. The electrical conductivity, carrier concentration and optical band gap of the films increase with increase in substrate temperature.

Acknowledgements

The authors wish to thank Council of Scientific and Industrial Research (CSIR), New Delhi for providing financial assistance for this project. Thanks are also due to Sh. M. L. Sharma, RSIC, Punjab University, Chandigarh for providing SEM facility.

References

1. H. V. CAMPE, *J. Phys. Chem. Solids* **44** (1983) 1019.
2. J. L. SHAY and J. H. WERNICK, "Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications" (Pergamon, Oxford, 1975).
3. D. S. CHEMLA, P. J. KUPCEK, D. S. ROBERTSON and R. C. SMITH, *Opt. Commun.* **3** (1971) 29.
4. G. D. BOYD, H. M. KASPOER and J. H. MCFEE, *IEEE J. Quantum Electron.* **7** (1971) 563.
5. V. P. ZHUZE, V. M. SERGEEVA and SHTRUM, *Zh. Tekh. Fiz.* **28** (1958) 2093.
6. S. M. PATEL and M. C. PATIL, *Mater. Lett.* **7** (1989) 338.
7. B. H. PATET, P. G. PATEL and S. S. PATEL, *Semicond. Dev., Proc. SPIE* **2733** (1995) 412.
8. N. N. KONSTANTONOVA and YU. V. RUD, *Soviet Phys. -Semicond.* **23** (1989) 1101.
9. B. KUHN, FRIEMELT, K. FESS and E. BUCHER, *Phys. Stat. Sol.* (a) **160** (1997) 151.
10. C. JULIEN, I. IVANOV, A. KHELFA, F. ALPANI and M. GUITTARD, *J. Mater. Sci.* **31** (1996) 3315.
11. M. C. OHMER, J. T. GOLDSTEIN, D. E. ZELMON, A. W. SAXLER, S. M. HEGDE, J. D. WOLF, P. G. SCHUNEMANN and T. M. POLLAK, *J. Appl. Phys.* **86** (1999) 94.
12. D. XUE, K. BETZLER and H. HESSE, *Phys. Rev.* B **62** (2000) 13546.
13. I. V. BODNAR, V. F. GREMENOK, I. A. VIKTOROV and O. N. OBRAZTSOVA, *J. Appl. Spectrosc.* **64** (1997) 809.
14. L. J. VANDER PAUW, *Philips Res Rep.* **1** (1950) 1.
15. AMARJIT SINGH and R. K. BEDI, *Thin Solid Films* **398** (2001) 427.
16. J. BARDEEN, F. J. BLAITT and L. H. HALL, "Photoconductivity Conf." (Wiley, New York, 1956).
17. AMAN MAHAJAN and R. K. BEDI, *J. Appl. Phys.* **89** (2001) 7866.
18. R. L. PETRITZ, *Phys. Rev.* **104** (1956) 1508.
19. R. KUMAR, A. SINGH, A. MAHAJAN, R. K. BEDI and T. SINGH, *Indian J. Mater. Sci. Engng.* **7** (2000) 411.
20. A. GOSWAMI and S. M. OJHA, *Thin Solid Films* **16** (1973) 187.
21. I. S. ATHWAL and R. K. BEDI, *J. Appl. Phys.* **64** (1998) 6345.
22. TAMINDER SINGH and R. K. BEDI, *Thin Solid Films* **298** (1997) 1421.
23. S. KAUR and R. K. BEDI, *Mater. Res. Bull. (USA)* **25** (1990) 1421.

Received 24 April 2003
and accepted 23 January 2004