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Effect of He^+ irradiation on the optical properties of vacuum evaporated silver indium selenide thin films

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ABSTRACT

We prepared polycrystalline silver indium selenide thin films by vacuum evaporation on glass substrate at a high temperature using the stoichiometric powder. The samples were subjected to the irradiation of 1.26 M eV He^+ ion. The effect of irradiation on the optical properties has been investigated for different fluencies of He^+. The thin films were characterized by X-ray diffraction and UV–vis–NIR spectroscopy. It is observed that the band gap of silver indium selenide thin films decreases gradually from 1.17 to 0.82 eV with ion fluency.

1. Introduction

$AgInSe_2$ is a member of the I–III–VI_2 group of semiconductors. In recent years, the ternary chalcopyrite semiconductors have been receiving considerable attention because of their adaptability, as an absorber component, in thin film solar cells. The I–III–VI_2 compounds are the ternary analogues of II–VI compounds. $AgInSe_2$ is a ternary analogue of CdSe, which has been used for a number of electronic devices. $AgInSe_2$ is a semiconductor with energy gap of 1.20 eV [1]. They crystallise in the chalcopyrite structure, which is closely related to zinc blend structure. Ternary chalcopyrite compounds have photovoltaic potential for solar cells since their optical band gap lies between 0.8 and 2.0 eV and they can be grown either n or p type [2].

The commonly used methods for preparing these thin films are flash evaporation [2,3], pulsed laser deposition [4], rf magnetron sputtering [5], thermal evaporation [6,7], electrodeposition [8] and solution growth technique [9]. Santhosh Kumar and Pradeep [10] reported co-evaporation technique for the preparation of silver indium selenide thin films. In the present work we employ bulk thermal evaporation technique in high vacuum.

Ion irradiation is a very effective technique to induce structural and micro-structural modifications in materials and have been used to tailor the properties of various materials including metals, semiconductors, insulators and polymers. High electronic energy released by the ion beams in a very short interval of time produces significant excitation of the lattice, causing changes in the structural, electrical, and optical behaviour of the materials. Since the presence of defects and irradiation-induced disorder significantly affect the optical properties, optical absorption spectrometry is an ideal technique for investigating the effect of irradiation in semiconductor thin films. The objective of the present work is to investigate the effect of irradiation on the optical properties of silver indium selenide. However there is no published work available on optical properties of He^+ irradiated $AgInSe_2$ thin films.

2. Experimental

Bulk silver indium selenide was prepared by fusing the stoichiometric composition of individual elements in a quartz ampoule. The quartz ampoule was evacuated to 10^{-5} mbar and sealed. This is then fired to a temperature of 1273 K by increasing the temperature in steps of 200 K. The ampoule is kept at the temperature for 48 h and cooled slowly to room temperature. The ampoule is carefully cut and the silver indium selenide is powdered. This powder was evaporated from molybdenum

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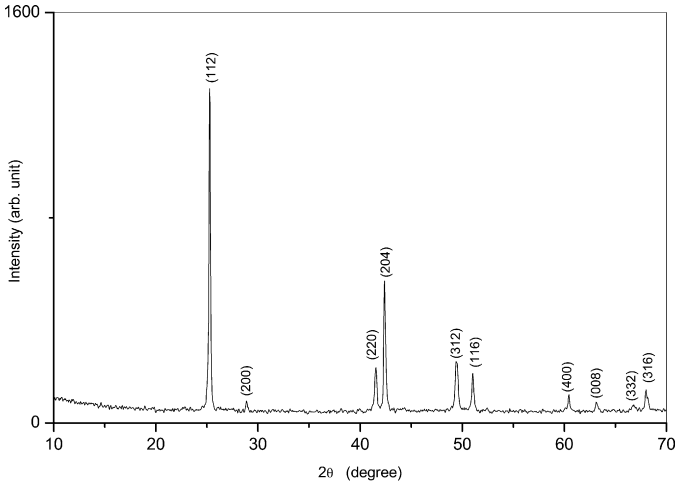

Fig. 1. XRD pattern of $AgInSe_2$ powder sample.

boat in a vacuum of 10^{-5} mbar. The glass substrates were mounted on a substrate holder with a heating arrangement and temperature was measured with the help of a fine wire chromel–alumel thermocouple. The temperature of the substrate was maintained at 523 ± 5 K throughout the deposition [10]. XRD spectra were recorded using Regaku D-Max C XRD unit. Optical absorption was recorded by Hitachi 3410 UV–vis–NIR spectrophotometer. He^+ irradiation was carried out at 3.0 MV tandom pelletron accelerator, at ion beam laboratory, Institute of Physics, Bhubaneswar, India. 1.26 MeV ion beam was used for the irradiation. The irradiation was done at ion fluencies of 1×10^{14}, 5×10^{14} and 1×10^{15} ions/cm^2. The range of ions was calculated using TRIM (transport of ions in matter) code [11]. Tolansky's multiple beam interferometric method [12] was used to measure the thickness of thin films. The thickness of the films used for the present studies is approximately 600 nm.

3. Results and discussion

3.1. Structural studies

Silver indium selenide belongs to the chalcopyrite group of compounds with a space group $I\bar{4}_{2d}$-$D_{2d}{}^{12}$. Fig. 1 shows the XRD pattern of silver indium selenide powder sample. The powder sample shows the prominent (1 1 2) peak of chalcopyrite phase. There are other peaks of lower intensity, which are in good agreement with JCPDS 75-0118. Silver indium selenide thin films were prepared using the powder sample by resistive heating in vacuum using a molybdenum boat. Fig. 2 shows the XRD pattern of pristine and irradiated silver indium selenide thin films prepared by vacuum evaporation. It is evident from the figure that the films prepared at 523 K using the powdered silver indium selenide shows a mixed phase with the prominent (1 1 2) peak of chalcopyrite phase. The peak at $2\theta = 21.50^\circ$, 43.95° and 38.30° are the $AgIn_5Se_8$ phase. The volume fraction of $AgIn_5Se_8$ (C_B) is determined using the following relationship [13]:

$$C_B = \frac{1}{1 + R_B I_A / R_A I_B} \quad (1)$$

where I_A and I_B are intensities of $AgInse_2$ (1 1 2) and $AgIn_5Se_8$ (1 1 0) peaks respectively, R_A and R_B are constants. The value of C_B is 0.28 approximately. Fig. 3 shows the EDAX spectrum of the sample, which gives an atomic ratio of 12.22:25.76:62.02 for Ag, In and Se

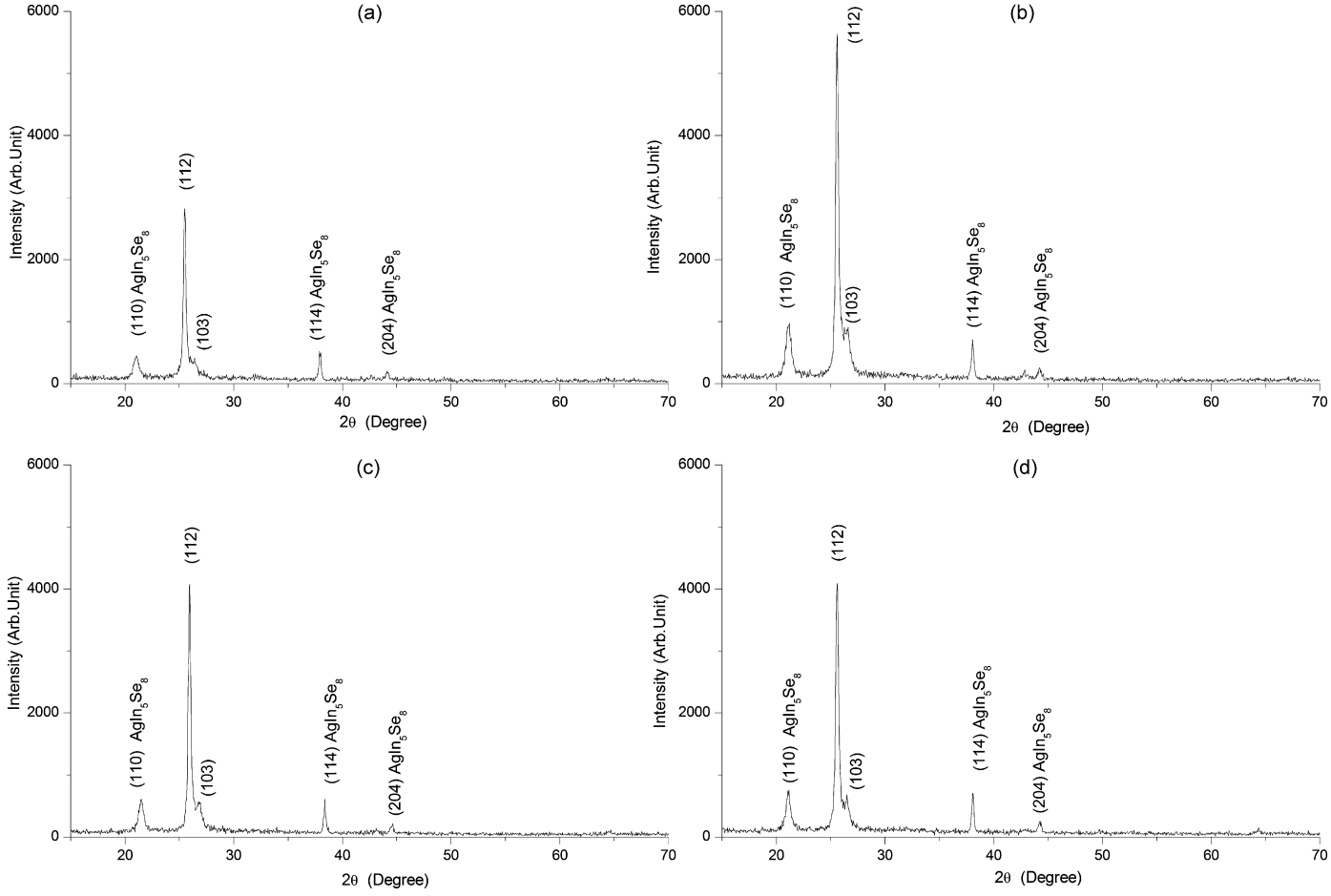

Fig. 2. XRD pattern of silver indium selenide thin films prepared by direct evaporation of the powder (a) unirradiated, (b) at a fluency of 1×10^{14} ions/cm^2, (c) at a fluency of 5×10^{14} ions/cm^2 and (d) at a fluency of 1×10^{15} ions/cm^2.

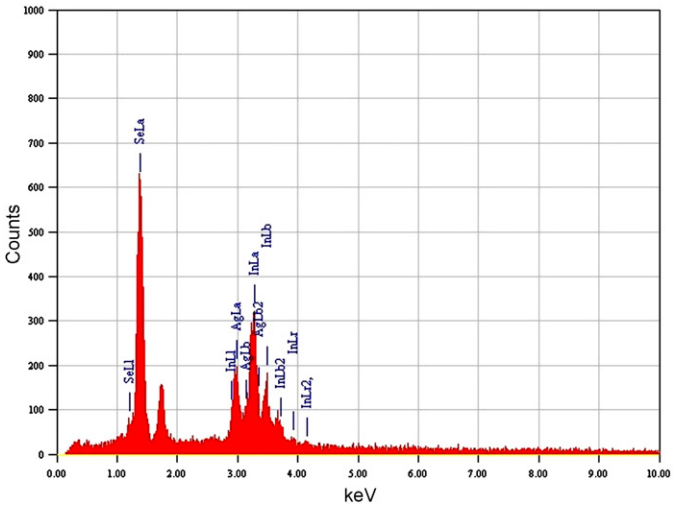

Fig. 3. EDAX spectrum of $AgInSe_2$ films.

respectively. This shows that the samples are Ag deficient and there by confirm the presence of $AgIn_5Se_8$ phase formation in the sample.

It is found that the intensities of XRD peak increase with a fluency of 1×10^{14} ions/cm^2 and it deceases with higher fluencies. The ion irradiation and energy depositions process can be explained on the basis of thermal spike model [14]. According to this model, deposited energy produces secondary electrons along the path of the ion track. The secondary electrons those have higher energy move away from the ion track by leaving a row of positively charged ions. The electrons with lower energy transfer their energy and come in equilibrium within 10^{-12} s. This energy is transferred to the atomic lattice by electron–phonon coupling that can induce a local temperature rise along the track. The local rise in temperature in a very short span of time induces crystallization in the material. Since, the total amount of energy deposited into the lattice increases with ion fluency, hence the degree of crystallinity also enhances resulting in the increase of XRD peak intensities [15]. It is however, interesting to observe that, at the fluencies of 5×10^{14} and 1×10^{15} ions/cm^2 intensities of all XRD peaks reduce. This indicates a decrease in crystallinity that could originate from either the ion beam generated defects and dislocations [16,17], or the grain splitting effect [18] at high fluency; which dominates over the thermal spike induced crystallization process.

3.2. Optical Studies

The optical studies were carried out on the silver indium selenide thin films prepared by evaporation of the powder $AgInSe_2$. Optical transmission spectra of the as prepared as well as the He^+ irradiated samples were recorded from 500 to 2500 nm. Fig. 4 shows the variation of optical transmission of proton irradiated silver indium selenide thin films with the as prepared sample of thickness 600 nm. The absorption coefficient and refractive index were calculated from the spectra using the theory of Swanepoel [19]. The variation of absorption coefficient with wavelength at different irradiation fluencies is shown in Fig. 5. The optical band gap energies were calculated using the equation:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where E_g is the band gap, α is the absorption coefficient, ν is the frequency, A is a constant and n can have values 1/2, 3/2, 2 and 3 depending up on the mode of inter band transition i.e. direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively. $n = 1/2$ offer the best fit for the optical

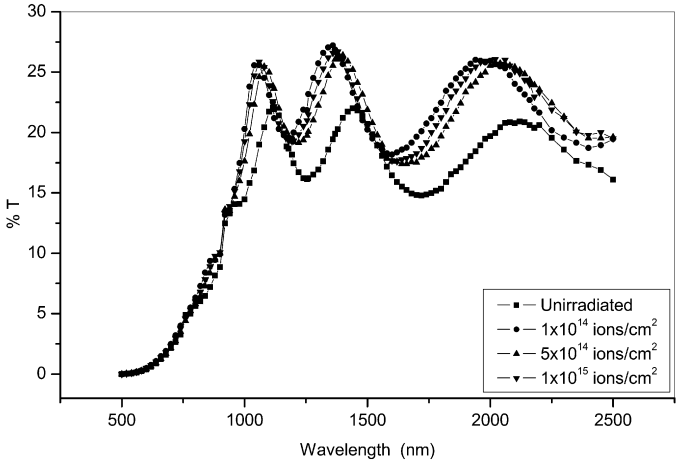

Fig. 4. Transmission spectra of silver indium selenide thin films different He^+ irradiation.

absorption data of silver indium selenide thin films. In order to evaluate the optical band gap, $(\alpha h\nu)^2$ versus $h\nu$ plot is made, which is shown in Fig. 6. It is observed that the band gap of silver indium selenide thin films decreases gradually with He^+ fluencies. The as deposited sample has a band gap of 1.17 eV, which decreased to 0.82 eV at a fluency of 1×10^{15} ions/cm^2.

The refractive indices of the films at different irradiation dose were determined by the envelope method developed by Swanepoel

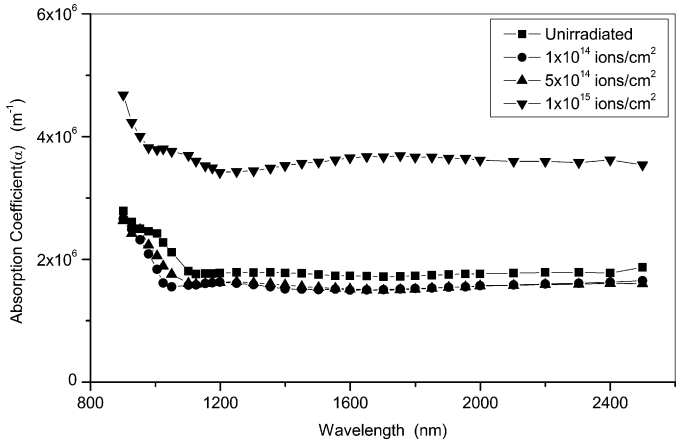

Fig. 5. Absorption coefficient of silver indium selenide thin films with He^+ irradiation.

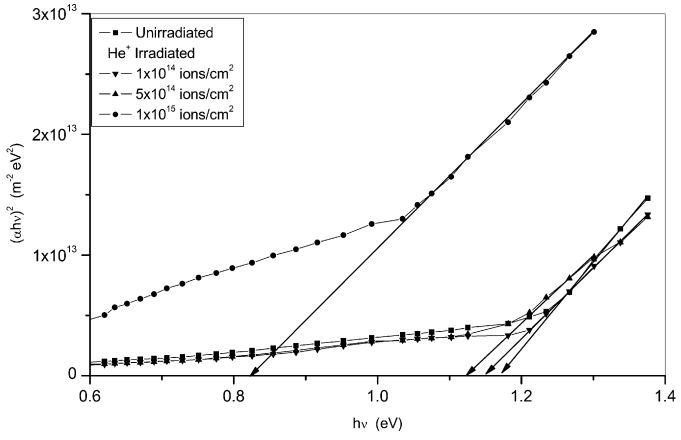

Fig. 6. $(\alpha h\nu)2$ versus $h\nu$ plot of silver indium selenide thin films with He^+ irradiation.

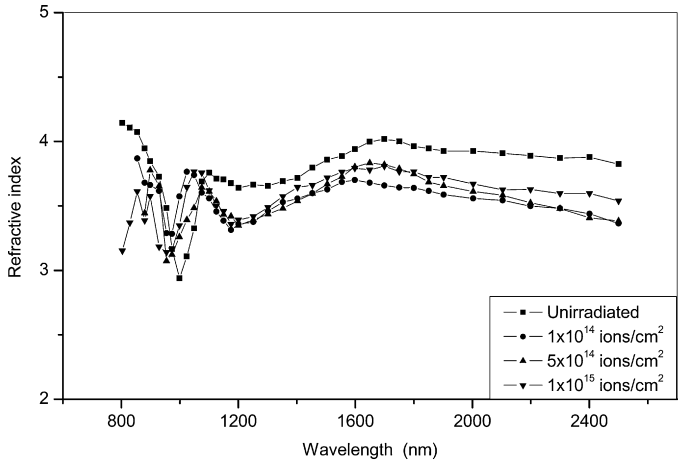

Fig. 7. Refractive index of silver indium selenide thin films with He^+ irradiation.

[19]. The envelope method permits the refractive index calculation of the films that exhibit at least two interference fringes in their week absorption and transparent spectral region by constructing envelope curves of transmittance spectra. The envelopes are the two curves designated as T_M and T_m, which connect the peaks and valley of the interference pattern in the transparent region respectively. Both envelopes merge together at the beginning of the strong absorption region where the interference fringes can no longer be observed. According to this theory the refractive index, n, is given by the equation:

$$n = \left(N + \sqrt{N^2 - n_0^2 n_s^2}\right)^{1/2} \quad (3)$$

where

$$N = \frac{n_0^2 - n_s^2}{2} + 2n_0 n_s \frac{T_M - T_m}{T_M T_m} \quad (4)$$

where n_0 is the refractive index of the surrounding medium (air) which is 1 and n_s is the refractive index of the glass substrate, which is taken as 1.51. The variation of refractive indices of silver indium selenide thin films with wavelength at different proton dose is shown in Fig. 7. The refractive indices of all irradiated samples decreased slightly in comparison to the pristine sample in the entire spectral region under study. The film thickness d also can be calculated from the formula given by Swanepoel [19]:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (5)$$

where n_1 and n_2 are refractive indices of two adjacent transmittance maxima or minima of the interference fringes located at λ_1 and λ_2 respectively. Choosing $\lambda_1 = 1059$ nm and $\lambda_2 = 1355$ nm and corresponding $n_1 = 3.75$ and $n_2 = 3.3.70$ for two adjacent maxima in the transparent region, yields a thickness value of 610 nm. This value is very close to value obtained earlier.

Another parameter, which is significantly affected by irradiation-induced disorder, is the sharpness of the band edge. To understand the effect of irradiation on the crystallinity of the films, the Urbach relation [20] was used to compute the width of band tail states. The width of band tail can be estimated by the relation:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_e}\right) \quad (6)$$

Table 1
Band gap and band tail variation of He^+ irradiated silver indium selenide thin films.

Sample	Band gap (eV)	Band tail (eV)
Unirradiated	1.17	0.166
1×10^{14} ions/cm^2	1.15	0.176
5×10^{14} ions/cm^2	1.12	0.187
1×10^{15} ions/cm^2	0.82	0.247

where α_0 is a constant and E_e the band tail width. The reciprocal of the slope of $\ln(\alpha)$ versus $h\nu$ plot give the width of band tail. The extend of band tail is found to increase gradually with proton dose. The calculated values of band gap and band tail are given in Table 1 with He^+ fluencies.

The band gap energy of the films was found to decrease with He^+ fluencies. The extend of band tail is found to increase with dose. The increase in band tail indicates the creation of defects during irradiation. Irradiation with ions produces point defects such as vacancies, interstitials and antisite defects. Defect clusters such as He bubbles, dislocation loops, etc. can also be expected to form during irradiation [21]. The defects produce band tailing. The observed reduction in band gap arises due to this band tailing. This kind of reduction in band gap is observed in evaporated silver indium selenide films after H^+ irradiation as well [22].

4. Conclusions

Silver Indium Selenide thin films were prepared by vacuum evaporation of powder sample prepared by fusing the stoichiometric composition of individual elements. The XRD studies indicate that the as prepared films are multiphase in nature. It contains peaks of $AgIn_5Se_8$ phase. The He^+ irradiation is found to affect the optical properties of the films. The optical band gap energy is found to decrease with He^+ irradiation fluency.

References

[1] B. Tell, J.T. Shay, H.M. Kasper, J. Appl. Phys. 43 (1972) 2469–2471.
[2] C.M. Joseph, C.S. Menon, Semicond. Sci. Technol. 11 (1996) 1668–1671.
[3] P. Paul Ramesh, S. Uthanna, B. Srinivasalu Naidu, P. Jayarama Reddy, Vacuum 47 (1996) 211–213.
[4] H. Mustafa, D. Hunter, A.K. Pradhan, U.N. Roy, Y. Cui, A. Burger, Thin Solid Films 515 (2007) 7001–7004.
[5] R.D. Weir, P.E. Jessop, B.K. Garside, Can. J. Phys. 65 (1987) 1033–1036.
[6] A. El-Korashy, M.A. Abdel-Rahim, H. El-Zahed, Thin Solid Films 338 (1999) 207–212.
[7] Yoshinori Ema, Nobuyoshi Harakawa, Jpn. J. Appl. Phys. 34 (1995) 3260–3265.
[8] D. Raviendra, J.K. Sharma, Phys. Status Solidi (a) 88 (1985) 365–368.
[9] R.P. Sharma, Indian J. Pure Appl. Phys. 33 (1995) 711–713.
[10] M.C. Santhosh Kumar, B. Pradeep, Vacuum 72 (2004) 369–378.
[11] J.P. Biersack, L.G. Haggmark, Nucl. Instrum. Methods 174 (1980) 257–269.
[12] K.L. Chopra, Thin Film Phenomena, McGraw-Hill, New York, 1969, pp102.
[13] B.D. Cullity, Elements of X-ray Diffraction, Addison-Wesley Publishing Company, Massachusetts, 1956, pp 388-393.
[14] M. Toulemonde, C. Dufour, Phys. Rev. B 42 (1992) 14362–14369.
[15] R. SivaKumar, C. Sanjeeviraja, M. Jayachandran, R. GopalaKrishnan, S.N. Sarangi, D. Paramanik, T. Som, J. Appl. Phys. 101 (034913) (2007) 5.
[16] Y.S. Chaudhary, S.A. Khan, R. Shrivastav, V.R. Satsangi, S. Prakash, D.K. Avasthi, S. Dass, Nucl. Instrum. Methods B 225 (2004) 291–296.
[17] Y.S. Chaudhary, S.A. Khan, R. Shrivastav, V.R. Satsangi, S. Prakash, U.K. Tiwari, D.K. Avasthi, N. Goswami, S. Dass, Thin Solid Films 492 (2005) 332–336.
[18] A. Berthelot, S. Hemon, F. Gourbilleau, C. Dufour, B. Domenges, E. Paumier, Philos. Mag. A 80 (2000) 2567–2590.
[19] R. Swanepoel, J. Phys. E: Sci. Instrum. 16 (1983) 1214–1222.
[20] F. Urbatch, Phys. Rev. 92 (1953) 1324–1326.
[21] K.L. Narayanan, K.P. Vijayakumar, K.G.M. Nair, N.S. Thampi, Physica B 240 (1997) 8–12.
[22] M.C. Santhosh Kumar, B. Pradeep, Appl. Surf. Sci. 255 (2009) 8324–8327.