Effect of Thermal Annealing on the Physical Properties of $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ Thin Films Deposited by Close Spaced Sublimation Technique

Muhammad Arslan^{1)†}, Riaz Muhammad¹⁾, Arshad Mahmood²⁾ and Rashad Rasheed²⁾

1) Department of Applied Physics, Federal Urdu University of Arts, Sciences and Technology, Islamabad, Pakistan

2) National Institute of Lasers and Optronics, Nilore, Islamabad, Pakistan

[Manuscript received 22 April 2013, in revised form 16 July 2013]

© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg

Thin films of $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20$) were grown on glass substrates by closed space sublimation technique. The deposited films were annealed at 200 °C and 400 °C in air for 1 h. The annealed samples have been investigated through Rutherford backscattering spectroscopy (RBS), X-ray diffraction (XRD), spectroscopic ellipsometer, spectrophotometer and Raman spectroscopy. Through RBS, the composition of the films was calculated and compared with the initial concentration. Structural characterization including crystal structure, crystal orientation, lattice parameter, grain size, strain and dislocation density were carried out using XRD data. From XRD spectra it was revealed that the as-deposited and annealed films were polycrystalline in nature with zinc-blende structure. However, the crystallinity and the grain size were improved with the increase of annealing temperature. According to Raman spectroscopy, it was observed that as deposited and annealed samples have the same characteristic vibrational modes of ZnSe at low and high frequency optical phonon modes while another mode was observed for 400 °C annealed samples at 745 cm^{-1} . Spectroscopic ellipsometer has been used to found annealing effect on the optical properties of ZnSe. The band gap energy has been determined using transmission spectra. It was found that the band gap energy of the film increased with the increase of annealing temperature.

KEY WORDS: Closed space sublimation; Annealing effect; Structural; Transmission; Band gap; Spectroscopic ellipsometer; Raman spectroscopy

1. Introduction

Zinc Selenide (ZnSe) is a promising direct band gap semiconducting material, for the development of solid state devices. ZnSe can be prepared in both n- and p-type forms^[1]. It has unique physical properties, such as wide optical energy band gap (~ 2.7 eV)^[2], high refractive index, low optical absorption in the visible and infrared spectral region. ZnSe films have several potential applications in electro-optics devices^[3–5]. Several methods have been used to prepare films of ZnSe ^[6–12]. Since most electronic devices are produced in the form of thin films, the film preparation and characterization plays a vital

role in the applications of semiconductor technology. Although the ZnSe thin films have been extensively studied, preparation of copper doped zinc selenide and its characteristics have not been reported with greater concentrations of copper. In the present work, we attempted to study physical properties of copper doped zinc selenide thin films using ZnSe and copper as precursors. Furthermore, effect of annealing has been discussed in detail for all the deposited films. For annealing treatment, different methods have been adopted, such as for ZnSe films thermal annealing and laser annealing^[13] have been used. Also different Parameters such as temperature, annealing time, atmosphere and pressure could be varied. For instance Ashraf *et al.*^[14] reported that the crystalline quality of the films was found to increase with the increase of the annealing temperature. Optical studies revealed that the energy band-gap and refractive index increases with the increase of the annealing temperature. Bacaksiz *et*

† Corresponding author. Tel.: +92 51 2831146 or +92 345 5341788; E-mail address: shani_788@yahoo.com (Muhammad Arslan)

al.^[15] showed that the annealing temperature of 200–400 °C did not affect the predominant (111) orientation but affected the degree of preferred orientation of ZnSe thin film deposited at the substrate of –73 °C and 275 °C. Optical band gap decreases with annealing temperature. Kumaresan *et al.*^[16] prepared ZnSe thin films by photochemical deposition, from an aqueous solution and then annealed at 300 and 400 °C.

In this work, $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20$) thin films were deposited on the glass substrates by closed space sublimation and annealed at temperatures of 200 °C and 400 °C in air for 1 h. Comprehensive studies on the structural and optical properties have been investigated and complete comparison of all the physical parameters for as-deposited and annealed films have been discussed. According to my knowledge the effects of thermal annealing on the structural, optical and vibrational properties of the films have been investigated and discussed for the first time with greater concentrations of copper.

2. Experimental

$\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ thin films were deposited on glass substrates by closed space sublimation technique at room temperature. A high vacuum coating unit (Edwards E-19/A) supported by a diffusion pump, has been used. Pressure inside the chamber was $\sim 2.6665 \times 10^{-3}$ Pa throughout the deposition processes. High quality ZnSe and Cu, with ~ 99.999 purity, fine powder were taken in proper molar concentration and mixed for two hours to obtain a homogenous mixture with different concentrations of copper.

In the 2 g samples the concentration of Cu (x) is increased to $x = 0.05, 0.10, 0.15, 0.20$. Homogenous mixture of $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ for various concentrations of Cu was heated by a halogen lamp (1000 W) connected to the main power through temperature controller with K-type thermocouple (Chromel & Alumel, 270 to 1350 °C). The evaporated powder was deposited on the rotating clean glass substrates at room temperature. The deposition time of all the samples is 5–7 min. The samples of all compositions were prepared under similar conditions. After deposition, the films were annealed at temperatures of 200 °C and 400 °C to observe the effect of the annealing temperature on the physical properties. In all cases the temperature rate was about 5 °C/min.

RBS measurement was carried out on the 5 MV tandem accelerator (5UDH-2, NEC) using a 2.023 MeV He^+ collimated beam. The structural properties were analyzed by PANalytical 3040/60 X, Pert PRO X ray diffraction unit with $\text{CuK}\alpha$ (15.4 nm) radiation. The study of vibrational modes was carried out by using Raman Spectroscopy at 442 nm He-Cd laser source (MST-4000A). The Raman spectrum was taken in the range from 200 cm^{-1} to 1200 cm^{-1} . The transmission spectra of the prepared films were taken

by Hitachi U-4001 spectrophotometer for the determination of band gap energy of the films. The optical constants (refractive index n and k) were determined by spectroscopic ellipsometer (J.A. Woolam M-200VI) Co. Inc. consisting of QTH lamp as the light source and a dual grating scanning monochromator (370–1670 nm) was employed at room temperature in air to measure the optical constants. All the spectra were taken at an angle of incidence of 70°.

3. Results and Discussion

3.1 Rutherford backscattering results

RBS spectrum of as-deposited and annealed $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ ($x = 0, 0.05$) films along with simulated spectrum are shown in Fig. 1(a) and Fig. 1(b). The collected RBS spectra were fitted by the code Rump^[17] to find the relative concentrations of various elements in the film. The atomic percentage of the deposited films is calculated and the composition of the sample was compared with the initial percentage. The composition was found to be nearly stoichiometric and the percentage of copper content is accurate along with Si and O elements from the substrate. It is observed that the films annealed at 200 °C have small quantity of oxygen due to annealing in air atmosphere but as the annealing temperature is increased to 400 °C, the oxygen content is reduced. The deposited films were uniform and well adherent with the substrate. Film thickness for as-deposited and the annealed samples was also estimated by simulated spectra and is given in Table 1. It was observed

Fig. 1 Rutherford backscattering spectra of as-deposited and annealed (200 °C and 400 °C) $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ films: (a) $x = 0$, (b) $x = 0.05$

Table 1 Band gap of the $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ films calculated by transmission spectra and film thickness calculated by Rutherford backscattering

Cu concentration	Film nature	Band Gap (eV)	Film thickness by RBS (nm)
$x=0.00$	As-deposited	2.63	240
	Annealed 200 °C	2.65	230
	Annealed 400 °C	2.82	220
$x=0.05$	As-deposited	2.57	290
	Annealed 200 °C	2.59	300
	Annealed 400 °C	2.67	300
$x=0.10$	As-deposited	2.50	210
	Annealed 200 °C	2.50	215
	Annealed 400 °C	2.54	255
$x=0.15$	As-deposited	2.37	180
	Annealed 200 °C	2.50	215
	Annealed 400 °C	2.54	255
$x=0.20$	As-deposited	2.26	195
	Annealed 200 °C	2.27	200
	Annealed 400 °C	2.35	210

Fig. 2 XRD patterns of as-deposited and annealed (200 °C and 400 °C) $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ thin films: (a) $x=0$, (b) $x=0.10$, (c) $x=0.15$, (d) $x=0.20$

that the film thickness increases with the increase in annealing temperature. Thickness of the films determined by RBS technique, quartz crystal and Spectroscopic ellipsometry were in good agreement.

3.2 Structural characterization

To investigate the crystal structure and phase, $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ thin films were characterized by X-ray diffractometer of wavelength CuK_α ($\lambda=0.15405$ nm) radiation. The range for the angle 2θ is from 20° to 60° . The X-ray diffraction patterns of as-deposited

and annealed (200 °C and 400 °C) $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ films ($x=0, 0.10, 0.15, 0.20$) are shown in Fig. 2. The preferential orientation of the crystal planes in all the films is (111) and the crystal structure is cubic (zinc blende). It is observed that the annealing temperature of 200 °C and 400 °C did not affect the predominant (111) crystallographic texture however, the intensity of (111) peaks increases with the annealing temperature. This increase of the peak intensity is due to the improvement of clusters, relocation of atoms and elimination of defects formed during the film deposition. When the annealing temperature was

increased to 400 °C, broadening of the peak decreases and a considerable improvement in crystallinity indicated by a more intense and sharper (111) peak was observed, suggesting larger crystallite sizes. The presence of other peaks in the figure confirms the polycrystalline nature of these films. The peaks due to (220) and (311) reflections became weak at higher annealing temperatures because of the improvement in crystallinity of the films. The reflection peak appeared adjacent to (111) peak after annealing at 400 °C for $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ ($x=0.10$) is not elemental peak and can be attributed to the experimental noise. Furthermore, as the concentration of Cu approaches to $x=0.15$, another peak corresponding (102) direction appears and which increases as x increase to 0.20, the peak at (102) direction is not associated with the ZnSe and may be assigned to unbound Cu contents. Intensity of (102) peak also decreases with annealing temperature confirming the diffusion of unbound Cu into the ZnSe.

The decrease in the lattice constant in the annealed samples is directly correlated with the crystallinity and improved crystallite size of the annealed films, because of the increase in the grain size of the annealed films as compared with the as-deposited films, there is a decrease in the lattice parameter in the as-deposited ZnSe lattice. The inter-planar distances (d) are determined by using Bragg's relation and the grain size is determined by Sherrer formula^[18].

$$t = 0.9\lambda/\beta \cos \theta \quad (1)$$

where λ is the wavelength of the incident X-rays (0.15406 nm) and β is the full width half maxima (FWHM). It is observed that the grain size decreases when the films are annealed at 200 °C temperature due to the increase in oxygen content, However, as the annealing temperature is increased to 400 °C, there is a simultaneous decrease in the oxygen content and this leads to a significant increase in the grain size as compared to 200 °C annealed films. Therefore, a variation in the grain size is observed due to decrease in the oxygen ion content with 400 °C annealing temperature, which indicates the improvement in crystallinity of the films. Strain (ε) and dislocation density (δ) was also measured by XRD parameters. The strain and dislocation density developed in the $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ film were calculated from the following equations^[14,19].

$$\varepsilon = \beta \cos \theta \quad (2)$$

$$\delta = \frac{15\varepsilon}{aD} \quad (3)$$

where a is the lattice parameter and D is the grain size. The strain varies with the annealing effect as shown in Fig. 3(a). It can be seen that strain and the dislocation density decreases with increasing anneal-

Fig. 3 Variations of strain ε (a) and dislocation density δ (b) of as-deposited and annealed (200 °C and 400 °C) $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ thin films with Cu concentration

ing temperature. The decreasing trends of strain and dislocation density with annealing temperature are due to the enhancement of crystallization. The smaller values of the strain and dislocation density exhibits good crystalline quality of $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ films annealed at higher temperature. The variation of the dislocation density with the annealing temperature is shown in Fig. 3(b). We can conclude that the strain and dislocation density of $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ film strongly depend on the annealing temperature, moreover, it is observed that 400 °C annealed films have better crystallinity than at lower temperatures. Structural parameters for the (111) peak such as diffraction angle, lattice spacing, grain size, strain and dislocation density are summarized in Table 2.

3.3 Raman spectroscopy

Raman spectra of the as-deposited and the annealed $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ thin films for $x=0, 0.10, 0.15, 0.20$ are shown in Fig. 4. Samples were focused by illuminating ordinary flash light through objective lens (100X/0.70, $f=200$). After focusing in image mode, the sample was shined by intense helium cadmium (He-Cd) laser source, wavelength 442 nm/80.0 mW for Raman. The signals were collected and detected in a scan mode by the same objective lens and air

Table 2 Structural parameters for (111) peak of as-deposited and annealed (200 and 400 °C) Zn_{1-x}Cu_xSe thin films

Cu concentration	Film nature	Peak position (deg.)	d-spacing (nm)	Grain size (nm)	Lattice constants (nm)	Strain (10 ⁻⁴ lin ⁻² .m ⁻⁴)	Dislocation density (10 ¹⁴ lin.m ⁻²)
<i>x</i> =0.00	As-deposited	27.26	0.327	53.30	0.566	6.6741	3.405
	Annealed 200 °C	27.23	0.316	32.20	0.570	6.7024	3.554
	Annealed 400 °C	27.25	0.316	41.64	0.547	4.9529	1.941
<i>x</i> =0.05	As-deposited	27.26	0.327	53.30	0.566	6.6741	3.405
	Annealed 200 °C	27.22	0.318	51.35	0.551	6.2509	3.068
	Annealed 400 °C	27.25	0.316	52.12	0.547	4.5543	1.641
<i>x</i> =0.10	As-deposited	27.28	0.327	59.50	0.566	5.8431	2.610
	Annealed 200 °C	27.27	0.316	51.35	0.547	5.7838	2.646
	Annealed 400 °C	27.22	0.316	60.28	0.547	4.1474	1.361
<i>x</i> =0.15	As-deposited	27.35	0.326	41.50	0.565	8.3860	5.386
	Annealed 200 °C	27.33	0.315	42.01	0.546	7.4705	4.423
	Annealed 400 °C	27.20	0.316	60.20	0.547	5.8441	2.702
<i>x</i> =0.20	As-deposited	27.38	0.326	34.69	0.565	10.013	7.679
	Annealed 200 °C	27.14	0.317	34.66	0.549	8.3219	5.459
	Annealed 400 °C	27.25	0.316	51.35	0.547	6.6746	3.525

cooled (−50 °C) charged couple device (CCD) detector. All compositions have two low frequency principal longitudinal optical (LO) phonon modes located at 489 cm⁻¹ to 504 cm⁻¹ and two high frequency modes with Raman shift at 244 cm⁻¹ to 258 cm⁻¹. These modes are shifted to higher and lower frequency with annealing temperature. These observed phonon modes are attributed to the cubic phase of ZnSe and thus confirm the ZnSe thin film with cubic structure. Both the as deposited and the annealed samples have the same vibrational modes however another mode was observed for 400 °C annealed samples at 750 cm⁻¹. This observed mode is associated to ZnSe^[20]. In addition, the peak intensity of Raman Spectra's increases and become sharper with annealing which is due to improvement in the crystalline structure with the grain growth. The annealing also causes the tensile stress and strain to develop in the ZnSe film as indicated by the Raman shift to lower wave number. However the increased intensity and sharpness of the Raman peak can be associated with the better crystallinity and also has been observed in our XRD results. It is also observed that the peak position of LO mode, has a shift from 250.4–251.1 cm⁻¹, with the increase of annealing temperature up to 400°C which in fact shows that the effect of compressive stresses decreases and change to tensile. Similar results for thin film stresses and strain have been reported with annealing for ZnO thin films on fused silica^[21].

3.4 Transmission studies

Transmission of the films at various annealing temperatures as a function of wavelength is shown in Fig. 5. The transmittance spectra were measured in the range of wavelength from 300 nm to 800 nm. The sharp fall of transmittance spectra at the lower wavelength confirms that the deposited films are crystalline. It can be observed that the transmittance

increases with the increase of the annealing temperature which may be related to the increase in the grain size of the films that was confirmed by XRD measurements. The films annealed at 400 °C show greater transmittance as shown in Fig. 5(b) and interference pattern at higher wavelengths with a sharp fall at the band edge which shows the uniformity and good crystallinity of the films. Further, the band edge shifts towards the higher wavelength side with increasing the Cu content, indicating a decrease in band gap energy. The variation in absorption edge is due to the improvement in structural order and removal of compressive stresses. The shift may be attributed to structural changes in the films such as increase in the grain size as confirmed by the XRD results. The value of the absorption co-efficient α (nm⁻¹) has been calculated using the relation^[22].

$$\alpha = \frac{-\ln T}{t} \quad (4)$$

The band gap was determined using the α vs $h\nu$ relation^[23].

$$(\alpha h\nu)^2 = A(E_g - h\nu) \quad (5)$$

where ν is the frequency, A is a constant but is different for different transitions, E_g is the band gap energy of the material and h is Planck's constant. A plots of $(\alpha h\nu)^2$ versus $(h\nu)$ for as-deposited and 400 °C annealed films are shown in Fig. 6. As ZnSe is a direct semiconductor^[24] so the values of the band gap energy can be determined by extrapolating the linear portion of curves to $(\alpha h\nu)^2 = 0$. Results show that the band gap energy of the films increases with the increasing of the annealing temperature. It was found to be 2.63 eV for as-deposited ZnSe ($x=0$) films and shows 0.07 eV blue shift from the normal bulk value (2.70 eV). The band gap of the 200 °C and 400 °C annealed ZnSe ($x=0$) thin films were found to be 2.65 eV and 2.82 eV,

Fig. 4 Raman spectra of as-deposited and annealed (200 °C and 400 °C) $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ thin films: (a) $x=0$, (b) $x=0.10$ (c) $x=0.15$, (d) $x=0.20$

Fig. 5 Transmission spectra of $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ ($x=0, 0.10, 0.15, 0.20$) thin films: (a) as-deposited and 200 °C annealed, (b) 400 °C annealed

which show 0.05 eV blue shift for 200 °C annealed and 0.12 eV red shift for 400 °C annealed film from the normal bulk value. The increase in the band gap from 2.63 eV to 2.65 eV and 2.82 eV shows that annealing the film causes strong red shifts of 0.02 eV and 0.19 eV in the optical spectra to that of characteristic bulk ZnSe. The variation of the band gap energy with the annealing temperature is found to be almost linear as shown in the inset of Fig. 6(a). The calculated values of the band gap are in good agreement with that of the films deposited by vacuum evaporation (2.60–2.67 eV)^[14].

3.5 Ellipsometry analysis

Spectroscopic ellipsometry analysis has been used to find the optical constants such as refractive in-

dex and extinction coefficient of as-deposited and annealed $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ thin films. Psi (ψ) and delta (Δ) spectra were measured at the incidence angle 70 °. To determine the optical constants (n and k), a theoretical model “effective medium approximation” was used to fit the experimental data.

The refractive index and extinction coefficient of $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ films are shown in Fig. 7. These figures indicate that the refractive index and extinction coefficient have an inverse relation with the wavelength. It is also clear that these optical constants decrease with increasing temperature but the refractive index increases with heat treatment which is reported by Rusu *et al.*^[7]. Our results indicate that the refractive index increases with the increase of the annealing temperature that may due to the improvement in the crystalline structure, increase of the grain size and

Fig. 6 Band gap energy of as-deposited and 400 °C annealed $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ films, determined from transmission spectra (inset in Fig. 6(a) showing the variation of band gap energy of as-deposited and annealed (200 °C and 400 °C) $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ films with Cu concentration)

Fig. 7 Variations of the refractive index (n) and extinction coefficient (k) of $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ films with wavelength: (a) $x=0$, (b) $x=0.10$, (c) $x=0.20$

Fig. 8 Variations of therefractive index (a) and extinction coefficient (b) of as-deposited and annealed (200 °C and 400 °C) $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ films with Cu concentration at $\lambda=550$ nm

reduction of the dislocation density. The variations in n and k values with the increase of the temperature in the films confirm the solid solution formation between Cu and ZnSe binary compounds. The decrease in the optical constants is attributed to the mixing of a highly conductive metal Cu with a wide band gap semiconductor ZnSe. For k , the curvature of graph shifts towards the higher wavelength. This is may be due to the increase in transmittance with annealing effect. The decrease in extinction coefficient indicates that the films become transparent with the increase of the annealing temperature. This is due to the fact that as annealing temperature increases the band gap

energy of the films increases. Variations of n and k at $\lambda=550$ nm are shown in Fig. 8.

4. Conclusion

Closed spaced sublimation technique was employed to deposit highly (111) oriented polycrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ thin films for the first time with greater concentrations of copper. The effect of post deposition thermal annealing on structural, optical and vibrational properties of $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$ thin films was investigated using diagnostic tools RBS, XRD, Raman spectroscopy, spectrophotometer and

spectroscopic ellipsometry. By increasing the annealing temperature of films from 200 °C to 400 °C the physical properties have improved significantly which shows that the annealing effect is very prominent in the properties of thin films. XRD data predict the improvement of the crystallinity and increase in the grain size with the increase of the annealing temperature. Raman spectra show that both the as deposited and the annealed samples have the same vibrational modes however another mode was observed for 400 °C annealed samples at $\sim 750\text{ cm}^{-1}$, the peak intensity of Raman Spectra's increases and become sharper with annealing which is due to improvement in the crystalline structure with the grain growth. Spectrophotometer data reveal that the optical transmittance increases slightly and the band gap increases with increasing annealing temperature. Spectroscopic ellipsometry analysis reveals that the optical constants *i.e.* (n & k) decreases with the increase in the annealing temperature. Moreover thickness decreases with increasing temperature which is also confirmed by spectroscopic ellipsometry and Rutherford backscattering spectroscopy.

REFERENCES

- [1] L.T. Chu and S.C. Shirley. Thin Film II-VI Photo-voltaics. Solid-State Electron. **38** (1995) 533.
- [2] C. Mehta, G.S.S. Saini, J.M. Abbas and S.K. Tripathi, Appl. Surf. Sci. **256** (2009) 608.
- [3] S. Venkatachalam, D. Mangalaraj, S.K. Narayandass, K. Kim and J.Yi. Vacuum **81** (2007) 928.
- [4] M.J. Tafreshi, K. Balakrishna and R. Dhansekaran, J. Mater. Sci. **32** (1997) 3517.
- [5] P. Juza, H. Zajicek, H. Sitter, M. Helm, W. Faschinger and K. Lischka, Appl. Phys. Lett. **61** (1992) 3133.
- [6] C.W. Huang, H.M. Weng, Y.L. Jiang and H.Y. Ueng, Vacuum **83** (2009) 313.
- [7] G.I. Rusu, M. Diciu, C. Pirghie and E.M. Popa, Appl. Surf. Sci. **253** (2007) 9500.
- [8] A. Rumberg, C. Sommerhalter, M. Toplak, A.J. Waldau and M.C.L. Steiner, Thin Solid Films **172** (2000) 361.
- [9] C. Wang, X.F. Qian, W.X. Zhang, X.M. Zhang, Y. Xie and Y.T. Qian, Mater. Res. Bull. **34**(10/11) (1999) 1637.
- [10] A. Rizzo, M.A. Tagliente, L. Caneve and S. Scaglione, Thin Solid Films **368** (2000) 8.
- [11] C. D. Lee, B.K. Kim, J.W. Kim, H.L. Park, C.H. Chung, S.K. Chang, J.I. Lee and S.K. Noh, J. Cryst. Growth **138** (1994) 136.
- [12] P. Pramanik and S. Biswas, Electrochem. Soc. (1986) 350.
- [13] M. Orita, T. Narushima and H. Yanagita, Jpn. J. Appl. Phys. **46** (2007) L976.
- [14] M. Ashraf, S.M.J. Akhtar, A.F. Khan, Z. Ali and A. Qayyum, J. Alloys Compd. **509** (2011) 2414.
- [15] E. Bacaksiz, S. Aksu, I. Polat, S. Y?lmaz and M. Altunbas, J. Alloys Compd. **487** (2009) 280.
- [16] R. Kumaresan, M. Ichimura and E. Arai, Thin Solid Films **414** (2002) 25.
- [17] L.R. Doolittle, Nucl. Instrum. Methods B. **9** (1985) 344.
- [18] P.K. Kalita, B.K. Sarma and H.L. Das, Bull. Mater. Sci. **23** (2000) 313.
- [19] J. Sharma and S.K. Tripathi, Physica B **406** (2011) 1757.
- [20] D. Nesheva, M.J. Scepanovic, S.A. Skrabic, Z. Levi, I. Bineva and Z.V. Popovic, Acta Phys. Polon. A **116** (2009) 75.
- [21] A. Mahmood, N. Ahmed, Q. Raza, T.M. Khan, M.M. Hassan, M. Mahmood and N. Mahmood, J. Phys. Scr. **82** (2010) 065801.
- [22] T.H. Yeh and A.E. Blakesee, Electrochem. Soc. **110** (1963) 1018.
- [23] J.J. Pankove, Optical Properties in Semiconductors, Prentice-Hall, Englewood Cliffs, NJ, 1971.
- [24] R. Venugopal, R.P. Vijayalakshmi, D.R. Reddy and B.K. Reddy, Mater. Res. Bull. **30** (1995) 1431.