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Investigations on structural, optical and electrical parameters of spray deposited ZnSe thin films with different substrate temperature

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Abstract. ZnSe thin films have been deposited on high cleaned glass substrate by spray pyrolysis technique within the glass substrate temperature range (400 °C to 450 °C). The structural properties of ZnSe thin films have been investigated by (XRD) X-ray diffraction techniques. The X-ray diffraction spectra showed that ZnSe thin films are polycrystalline and have a cubic (zinc blende) structure. The most preferential orientation is along the (111) direction for all spray deposited ZnSe films together with orientations in the (220) and (311) planes also being abundant. The film thickness was determined by an interferometric method. The lattice parameter, grain size, microstrain and dislocation densities were calculated and correlated with the substrate temperature (T_S). The optical properties of ZnSe thin films have been investigated by UV/VIS spectrometer and the direct band gap values were found to be in the region of 2.65 eV to 2.70 eV. The electrical properties of ZnSe thin films have been investigated using the Van der Pauw method and the high quality ZnSe thin films were observed to develop at 430 °C with a resistivity of $56,4 \times 10^5$ ohm cm, a conductivity of 1.77×10^{-7} $(\Omega\ \mathrm{cm})^{-1}$ and a hall mobility of 0.53 $\mathrm{cm}^2/\mathrm{Vsec}$.

PACS. 52.77.Fv High-pressure, high-current plasmas (plasma spray, arc welding, etc.) – 68.55.Jk Structure and morphology; thickness; crystalline orientation and texture – 78.66.Db Elemental semiconductors and insulators – 07.78.+s Electron, positron, and ion microscopes; electron diffractometers

1 Introduction

Binary semiconductors are considered to be important technological materials because of their potential applications in optoelectronic devices, solar cells, IR detectors and lasers [1,2]. Binary compounds of group IIB and group VIA elements, commonly referred to as II-VI compounds, have technologically important applications. Among these compounds, only CdTe and ZnSe can be prepared in both n- and p-type forms [3]. The synthesis of II-VI semiconductors has recently been the focus of much attention for various optoelectronic applications, especially in blue light-emitting diodes and laser diodes [4–6]. It is known that the photoelectronic and other properties of the II-VI class of compound thin films are highly structure sensitive, which in turn can heavily influence the device performance [7]. The structure parameters; the crystallinity, the crystal phase, the lattice constant, the average stress and strain, the grain size orientation etc, are strongly dependent on the deposition parameters [8]. Thin films of ZnSe have attracted considerable interest over the years owing to their wide range of applications in various optoelectronic devices, ultrasonic transducers, photodetectors and in solar cells. It has a direct band gap (2.68 eV) and is transparent over a wide range of the visible spectrum. More progress has been achieved in fabrication of blue-green light emitting diodes, dielectric mirrors, filters and other optically sensitive devices [9,10]. ZnSe thin films have usually been grown by molecular beam epitaxy and chemical vapor deposition [11,12]. On the other hand, several reports on the electrodeposition from aqueous solutions [13,14] as well as from molten salts have been published. Although many investigations on ZnSe thin films have been done so far, [15,16] limited study has been undertaken on the spray pyrolysis ZnSe thin films, but in these studies little attention is given to their structural characterization and their correlation to other properties. The spraying pyrolysis technique is a simple, economical and viable technique which produces films of good quality for device applications.

Keeping all of these aspects in view, an experimental study on the structural characterization of spray deposited ZnSe thin films has been undertaken. We present a detailed study on spray deposited ZnSe thin films at different substrate temperatures and a correction between substrate temperatures and different structural parameters has been highlighted in this paper.

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2 Experimental studies

ZnSe thin films were deposited on highly clean glass substrates (about 1 cm^2 of geometric area) at different temperatures within the substrate temperature range (400 °C to 450 °C) by using spray pyrolysis technique. ZnSe thin films were spray deposited from an aqueous solution containing 0.05 moles/lt $ZnCl_2$ and 0.05 moles/lt SeO_2. 100 mlt spraying solution was prepared at the same ratio (Zn:Se=1:1) , the spray flow rate was adjusted to about 0.3 mlt per minute and the distance between the nozzle (head of the sprayed source) and the substrate was kept at 20 cm in all cases. The film thickness was determined by an interferometric method (using multiple-beam Fizeau fringe method at reflection of monochromatic light, $\lambda = 550$ nm [17] and for samples ranging from 0.9 to 1.4 μm. The films were characterized by using a Philips model X-ray diffractometer with CuK_α radiation ($\lambda = 1.5405$ Å. The XRD patterns of all thin films were taken from 10° to 70° (2θ). Absorption coefficient measurements were made with a UV/VIS double-beam Jasco 3200 model spectrophotometer. A correction for substrate absorption was made by placing an identical uncoated glass substrate in the reference beam. The Van der Pauw method was used to measure the resistivity, conductivity and hall mobility. Details on the experimental studies are given in previous study [18].

3 Results and discussions

The various structural parameters for spray deposited ZnSe thin films deposited at different substrate temperature (T_S) are calculated using relevant formulae and are systematically represented in Table 1.

3.1 X-ray studies

The XRD patterns of sprayed ZnSe thin films prepared at different substrate temperatures are shown in Figure 1. The diffractograms indicating the presence of all the prominent peaks of ZnSe are arising from (111), (220) and (311) reflections from the ZnSe thin films which are polycrystalline, having f.c.c cubic zinc blende structure. It is also observed that the XRD patterns of all ZnSe thin films show a preferred orientation along the (111) plane. The (111) direction is the close-packing direction of the zinc blende structure. As the substrate temperature increases the peak intensities increase up to 430 °C, indicating the formation of more crystallites with well-defined orientation (111). Beyond 430 °C, partial decomposition may be taking place, giving rise to a decrease in intensity.

The lattice constant 'a' for the cubic phase structure is determined by the relation

$$a^2 = \frac{\lambda^2(h^2 + k^2 + l^2)}{4\sin^2\theta} \quad (1)$$

where θ is the diffraction spectra (Bragg's angle), λ is the wavelength of the X-ray. Lattice parameters for ZnSe thin films spray deposited at different T_S (°C) are calculated using the relevant formula and systematically represented in Table 1. The variation of the lattice constant with substrate temperature is shown in Figure 2. The lattice constant 'a' first decreases, reaches a minimum value around 430 °C and then appears to increase with substrate temperature as shown in Figure 2. The change in lattice constant for the spray deposited thin film over the bulk clearly suggests that the film grains are strained which may be due to the nature and concentration of the native imperfections changing. The variation of the substrate temperature is associated with the changes in grain size and boundary. The grain size tends to reach its minimum value around 430 °C.

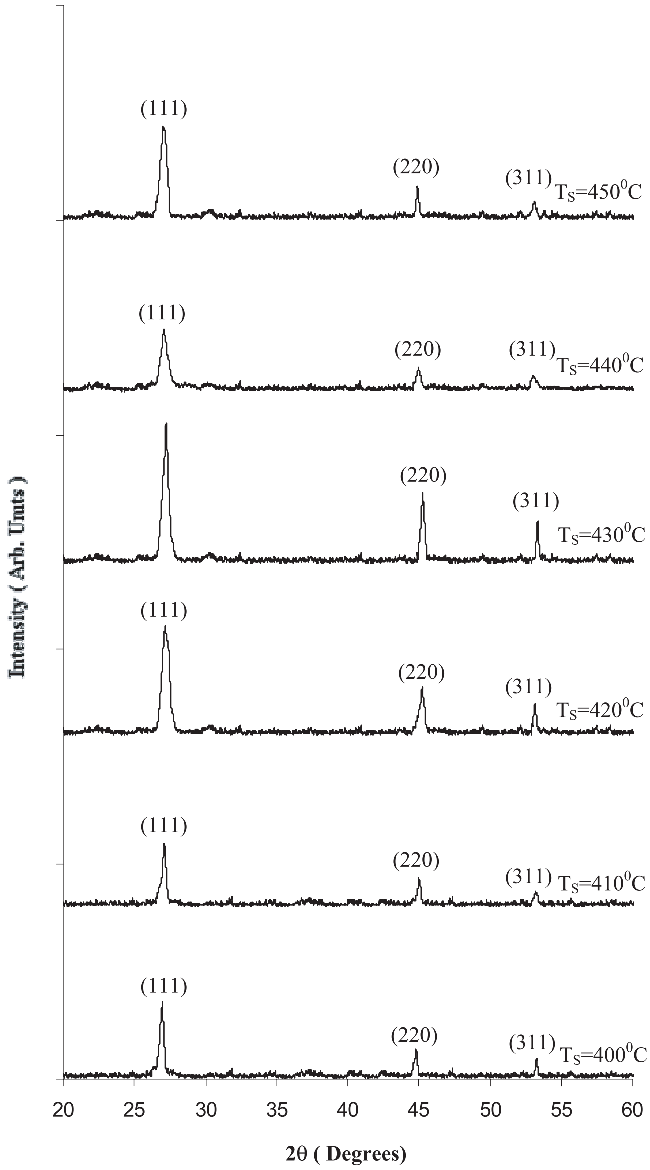

Fig. 1. XRD traces for representative ZnSe films having the same ratio (Zn:Se=1:1) and deposited within substrate temperature range (400 °C–450 °C).

Table 1. Structural parameters of spray deposited ZnSe thin films within substrate temperature range (400 °C–450 °C).

Substrate Temp. (°C)	2θ (Degrees)	(hkl)	Lattice const. (Å)	d(Å) Grain size	ε (10^{-3}) Microstrain	$\rho(10^{11})\text{cm}^{-2}$ Dislocation density
400	26.98	(111)	5.7190	59	6.56	6.4
	44.82	(220)	5.7146	–	–	–
	53.28	(311)	5.6974	–	–	–
410	27.12	(111)	5.6900	63	6.07	6.87
	45.02	(220)	5.6904	–	–	–
	53.22	(311)	5.7703	–	–	–
420	27.18	(111)	5.6777	53	7.29	5.79
	45.22	(220)	5.6666	–	–	–
	53.16	(311)	5.7093	–	–	–
430	27.24	(111)	5.6654	50	7.77	5.47
	45.28	(220)	5.6595	–	–	–
	53.36	(311)	5.6895	–	–	–
440	27.06	(111)	5.7024	57	6.80	6.2
	44.98	(220)	5.6953	–	–	–
	53.08	(311)	5.7173	–	–	–
450	27.02	(111)	5.7173	61	6.32	6.62
	44.92	(220)	5.7025	–	–	–
	53.14	(311)	5.7133	–	–	–

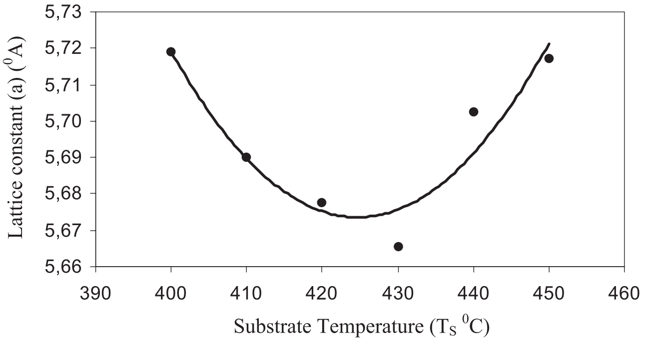

Fig. 2. Variation of the lattice constant (a) with substrate temperature T_S (°C).

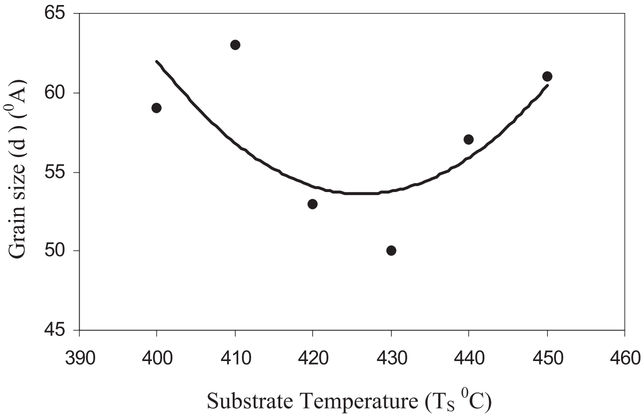

Fig. 3. Variation of the grain size (d) with substrate temperature T_S (°C).

3.2 Grain size studies

It is observed that the XRD patterns of all ZnSe thin films show a most preferred orientation along (111) plane. The grain size of the ZnSe thin films were estimated for the (111) plane by using the Scherrer formula [19].

$$d = \frac{\lambda}{D\cos\theta} \tag{2}$$

where d is the grain size, λ is the X-ray wavelength used, D is the angular line width of the half-maximum intensity and θ is the Bragg angle.

The variation of the grain sizes with substrate temperature is shown in Table 1. The grain size 'd' firstly shows a decreasing tendency, reaching a minimum value around 430 °C and then shows an increasing tendency with substrate temperature from 430 °C to 450 °C as seen in Figure 3. The density of the film is therefore expected to change in accordance with the change of lattice constant and grain size [20,21]. The change in lattice constant for the deposited thin film over the bulk clearly suggests that the film grains are strained which again may be due to the nature and concentration of the native imperfections changing [7]. The grain size of the deposited ZnSe thin films is small and within the range 50 Å to 63 Å. The change of grain size with T_S is prominent.

3.3 Microstrain studies

Misfit stresses occur in crystalline films due to the geometric mismatch at interphase boundaries between crystalline lattices of films and substrate. Therefore, a stress is also developed in the film due to the lattice misfit [22,23]. However, the stress has two components: thermal stress arising from the difference of expansion coefficient of the film and

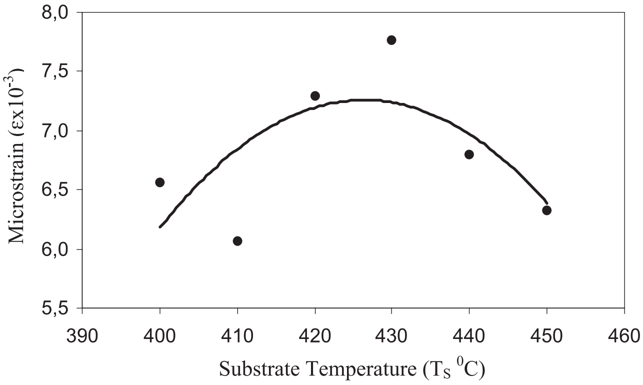

Fig. 4. Variation of the microstrain (ε) with substrate temperature T_S (°C).

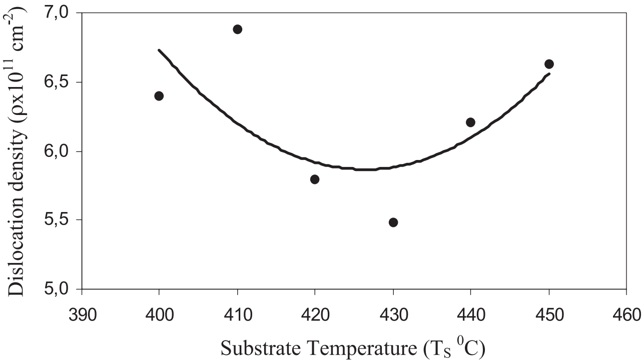

Fig. 5. Variation of the dislocation density (ρ) with substrate temperature T_S (°C).

substrate and internal stress due to the accumulating effect of the crystallographic flaws that are built into the film during deposition [24]. The average stresses of the deposited films are found to be compressional in nature. The compressive stress is due to the grain boundary effect, which is predominant in polycrystalline film [25,26]. Compressive stress is also likely to be due to the native defects arising from the lattice misfit. Native imperfections probably migrate parallel to the film substrate with their surface mobility modified by the substrate temperatures. The origin of the strain is also related to the lattice misfit which in turn depends upon the deposition conditions. The microstrain (ε) developed in the sprayed ZnSe thin films were calculated from the equation (3) and given in Table 1. The variation of microstrain with substrate temperature is given by Figure 4.

$$\varepsilon = \frac{D\cos\theta}{4} \tag{3}$$

where D is the full width at half maximum of the (111) peak.

Figure 4 shows that the variation of the microstrain (ε) with T_S in ZnSe thin films. It is observed from Figure 4 that the microstrain (ε) exhibits a slow increasing trend up to about 430 °C and afterwards ε decreases with higher substrate temperatures. This type of change in microstrain may be due to the predominant recrystallization process in the polycrystalline thin films and due to the movement of interstitial Zn atoms from inside the crystallites to its grain boundary which dissipate and lead to a reduction in the concentration of lattice imperfections as explained in previous studies [27,28].

3.4 Dislocation density studies

Dislocations are an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with respect another part. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections, i.e. thermodynamic considerations are insufficient to account for their existence in the observed densities. In fact, the growth mechanism involving dislocation is a matter of importance. In this study, the dislocation density is determined from Williamson's and Smallman's method using the following relation for cubic ZnSe thin films [29] and the variation of the dislocation density with substrate temperature is shown in Table 1.

$$\rho = {}^{15\varepsilon}/_{aD}. \tag{4}$$

Figure 5 shows the variation of the dislocation density (ρ) with T_S in ZnSe thin films. It is observed that dislocation density (ρ) exhibits a slow decreasing trend up to about 430 °C and afterwards increases with higher values of T_S. As seen from Table 1 and related figures, lattice constants, grain sizes and dislocation densities tend to decrease but microstrain increases with increase of substrate temperature from 400 °C to 430 °C. These parameters indicate the formation of high quality ZnSe thin films deposited on the well cleaned glass substrate by spraying pyrolysis method at 430 °C substrate temperature.

In order to the examine the microstructure characteristics of the sprayed ZnSe thin films, the degrees of preferred orientation are correlated with T_S which is showed in Figure 6. The degree of preferred orientation in ZnSe thin films can be obtained by the ratio of the peak intensity of (111) to that of (220) reflection on the same scale. As seen from Figure 6 the degree of preferred orientation of the crystallites decreases with lattice constant, grain size and dislocation density when the microstrain is increased. The degree of preferred orientation ($I_{(111)}/I_{(220)}$) decreases, reaching a minimum value around 430 °C and then shows an increasing tendency with substrate temperature as shown in Figure 6. This may be attributed to enhance the reduction mechanism of imperfections originating from lattice misfit in the films. A review of dependence of the above structural parameters on the substrate temperature indicates that the degree of preferred orientation, along with the other microstructural features, are more effective than the crystal size for low thickness films. This type of correlation is suggested recently by other work [30,31].

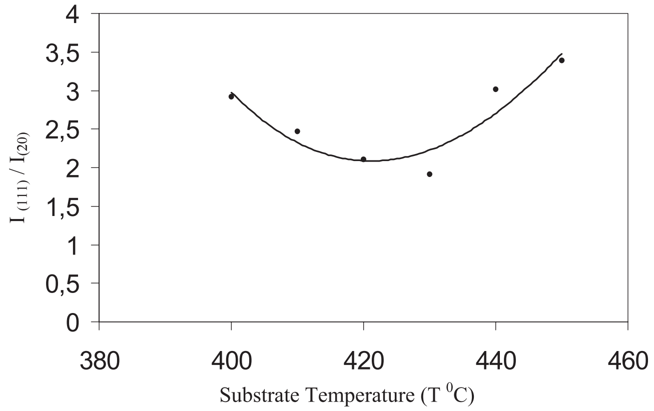

Fig. 6. Variation of the degree of preferred orientation with substrate temperature T_S (°C).

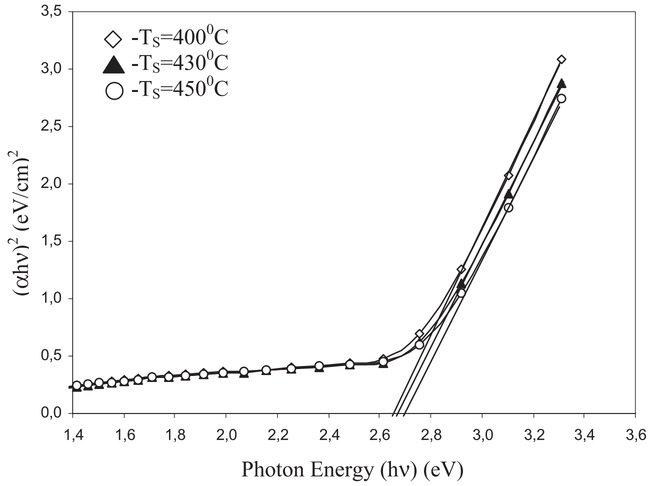

Fig. 7. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for ZnSe thin films spray deposited at 400 °C, 430 °C and 450 °C substrate temperatures.

3.5 Optical studies

Optical absorption studies of the sprayed Znse thin films on the glass substrate at different substrate temperature have been carried out in the wavelength range of 300 nm to 900 nm employing a UV/VIS spectrophotometer (Jasco 7800 model). The absorption coefficient as a function of photon energy was calculated and plotted for allowed direct transitions (neglecting exciton effects) by using the expression [32,33].

$$\alpha = \frac{A}{h\nu}(h\nu - E_g)^{1/2} \tag{5}$$

where $h\nu$ is the photon energy, E_g denotes the optical energy bandgap, and A the characteristic parameter (independent of photon energy) for respective transitions. Figure 7 shows that the dependences of $(\alpha h\nu)^2$ as a function of photon energy hν indicates the direct nature of band-to-band transitions for the studied samples. The values of the optical bandgap, E_g have been determined by extrapolating the linear portions of respective curves to $(\alpha h\nu)^2 \to 0$. For the studied three different samples which were deposited at different substrate temperature ranges (400, 430, 450 °C), these bandgap values are in a good agreement with the values of E_g obtained for bulk ZnSe crystals [34–36]. It is seen from Figure 7 that the bandgap energy increased from 2.64 eV to 2.70 eV as the deposition temperature was increased from 400 °C to 450 °C.

3.6 Studies on electrical parameters

The electrical properties of the sprayed ZnSe thin films with the same ratio (Zn:Se=1:1) at different substrate temperature, resistivity, conductivity and hall mobility values have been investigated by using the Van der Pauw method. To apply this method, four indium square ohmic contacts were prepared on the ZnSe thin films by the evaporation method. For the hall mobility measurements, thin films were placed in a magnetic field of 500 mT perpendicular to the film plane. The details of the experimental set up and measurement techniques are given in a previous study [18].

The various electrical parameters (resistivity, conductivity and hall mobility) for spray deposited ZnSe thin films deposited at different substrate temperature (T_S) are represented in Table 2. The resistivity, conductivity and hall mobility curves against the substrate temperature of Znse thin films are shown in Figure 8a, b and c, respectively. As seen from Figure 8a, b and c, while the resistivity has a minimum value at 430 °C, the conductivity and hall mobility of ZnSe thin films have maximum values at the same substrate temperature. As the substrate temperature is increased, the resistivity decreases and reaches its minimum value of 56.4×10^5 ohm cm at 430 °C. On the other hand, as the substrate temperature is increased the conductivity and hall mobility increase and reach maximum values of 1.77×10^{-7}(ohm cm)$^{-1}$ and 0.53 cm^2/Vm, respectively, at 430 °C. These results indicate that a relatively good ZnSe thin film, prepared by using spray pyrolysis method, can be grown on a glass substrate at 430 °C and the resistivity, conductivity and Hall mobility of the ZnSe thin films are strongly dependent on the substrate temperature. Also, the crystallinity of the samples are dependent on the substrate temperature. This means that all properties of the ZnSe thin films are dependent on the substrate temperature which closely affects the structure of the films. It is also suggested that the observed changes in resistivity, conductivity and Hall mobility may be a consequence of the variation of the substrate temperature which is associated with the changes in grain size and boundary.

The main effect of oxygen absorption is to cause a decrease in the Hall Mobility and an increase in the resistivity of thin films. It is known that oxygen molecules are first physically adsorbed onto the ZnSe thin film surface and the transition from physical to chemical adsorption then takes place by the capture of conduction band electrons. Therefore, chemisorption effects on the mobility are attributed to the chemisorption of oxygen at the

Table 2. Electrical measurement results of the ZnSe thin films grown by using spray deposited technique on glass substrate at different substrate temperature.

Substrate Temp (°C)	Resistivity (10^5) (Ω cm)	Conductivity (10^{-7}) (Ω cm)$^{-1}$	Hall mobility (cm^2/V m)
400	86.5	1.16	0.31
410	72.3	1.38	0.37
420	63.2	1.58	0.42
430	56.4	1.77	0.53
440	62.8	1.60	0.46
450	66.1	1.51	0.41

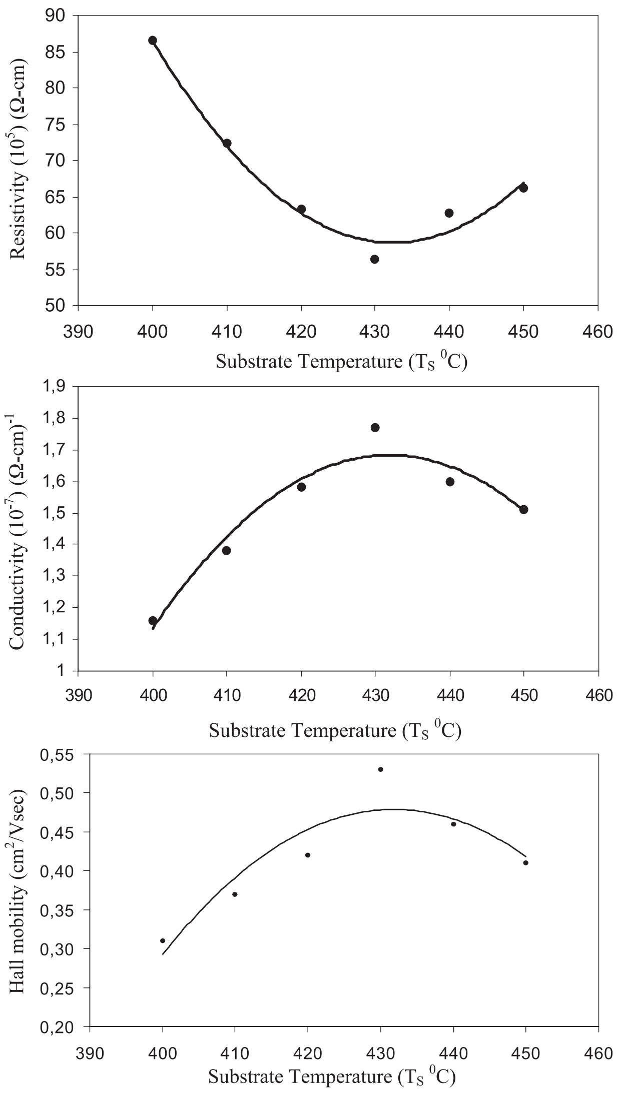

Fig. 8. Variation of (a) resistivity, (b) conductivity and (c) hall mobility within substrate temperature range (400 °C–450 °C) of spray deposited ZnSe thin films.

grain boundaries which alter the barrier height and barrier width. However, because of the small grain boundary area compared to the film surface the change in the electron density should be attributed to the chemisorption of oxygen at the film surface. Under photoexcitation, the adsorbed oxygen at the film surface and at the grain boundaries acts as additional recombination centres.

4 Conclusions

All of the ZnSe thin films prepared by spray depositing on to a high cleaned glass substrate within the substrate temperature range (400 °C–450 °C) are polycrystalline with f.c.c zincblende type structure. Each film shows a preferred orientation along the (111) plane in addition to two other prominent planes, (200) and (311). The variation of lattice constant, grain size, microstrain and dislocation density of ZnSe thin films with substrate temperature has been determined. It is observed that the lattice constant, grain size and dislocation density tend to decrease but the microstrain increases with increasing substrate temperature from 400 °C to 430 °C. A direct optical bandgap of 2.65–2.70 eV was found for the investigated films. The resistivity of ZnSe thin film has a minimum value at 430 °C and the conductivity and hall mobility have maximum values at the same substrate temperature. These results indicate that there is a strong relation between the structural, optical and electrical properties and substrate temperature of the spray deposited ZnSe thin films and also indicate that good ZnSe thin films can be deposited on to a high cleaned glass substrate at around 430 °C by using spray pyrolysis technique.

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