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Estimation the Density of Localized State Glassy $Se_{100-x}Zn_x$ Thin Films by Using Space Charge Limited Conduction Measurement

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ABSTRACT

The dc conductivity in vacuum evaporated amorphous thin films of the glassy alloys $Se_{100-x}Zn_x$ ($2 \leq x \leq 20$) are measured in the temperature range (308 - 388 K). The dc conductivity (σ_{dc}) is increases with increased of Zn concentration in the glassy alloys. The activation energy (ΔE) decreases with increase of Zn content. The conduction is explained on the basis of localized state in the mobility gap. To study the effect of electric field, a Current-Voltage characteristic has been measured at various fixed temperatures. The Current-Voltage data are fitted into the theory of space charge limited conduction in case of uniform distribution of traps in mobility gap at high electric fields ($E \sim 10^4$ V/cm) of these materials. The density of localized state (g_0) are estimated by fitting in theory of space charge limited conduction (SCLC) at the temperature range of (352 - 372 K) in the glassy $Se_{100-x}Zn_x$. The density of localized state (g_0) near the Fermi level are increases with increase of Zn concentration in the ($Se_{100-x}Zn_x$) thin films and explain on the basis of increase of the Zn-Se bond.

Keywords: Density of Localized State; DC Conductivity; Activation Energy (ΔE); SEM; Thin Films

1. Introduction

Chalcogenide glasses belongs to a special group of amorphous semiconductors, which include one, two and more chalcogenide elements S, Se, Te from the VI group of the periodic table. From the technical point of view's Se based glassy alloy is most useful because of their potential applications. Se based is important due to its recent use as photoreceptors in TV Videocon pick-up tubes [1], conventional xerographic machine and digital X-ray imaging [2,3]. The chalcogenide glassy semiconductors are strongly used amorphous semiconductors point of application in optics, electronics and optoelectronics like as holography, infrared lenses, ionic sensors, ultra fast optical sensors. To overcome difficulties, confirm additives are used and mostly Se-Te, Se-Ge, Se-Sb, Se-ln and Se-Zn is the great interest important properties such as greater hardness, higher sensitivity, higher conductivity and smaller aging effects as compared to pure a-Se. Recently, we are focusing on the glass composition of Se-Zn system and the materials are found to be suggestive for their electrically, optically, dielectrically and kinetically parameters by other workers [4,5]. It can be easily observed at high fields in the glassy alloy because of high resistivity and the amorphous semiconductors are most convenient for high field conduction studies. On the other hand we can say high field effects are most readily observed in these materials because of their low conductivity (Joule heating is negotiable small at moderate temperatures) and are prepared by various groups working in this field [6,7]. Here, we are measured the temperature dependent dc conductivity and the density of localized state near the Fermi level by using the space charge limited conduction (SCLC) measurements for the glassy system Se-Zn. The method of the space charge limited conduction (SCLC) is an important because it depends upon the composition in the glassy $Se_{100-x}Zn_x$. All the stable glasses have good photosensitive properties and it can be N-type or P-type amorphous semiconductors. In low field conduction, the mobility and free carrier concentration are considered to be constant with field. However, the application of high field to free carrier system may affect both the mobility and the number of charge carriers.

2. Experimental

Glassy alloys of $Se_{100-x}Zn_x$ (x = 2, 5, 10, 20) are prepared by melt quenching technique with high purities (99.999%)

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materials which are weighed according to their atomic percentage and are sealed in quartz ampoules (of length 7 cm and internal diameter ~8 mm) with a vacuum ~10^{-5} Torr. The ampoules containing the constituent materials are heated to 850˚C and held at the temperature for 11 and half hours. The temperature of the furnace is raised gradually at a rate of 4˚C - 5˚C/min due to obtained homogenous glassy alloys. All the ampoules are constantly rocked while heating by rotating a ceramic rod to which the ampoules are connected in the furnace. The ampoules are removed from the furnace after rocking for about 11 hours and are cooled rapidly in ice-water to obtain the amorphous nature. The quenched samples $Se_{100-x}Zn_x$ are removed by breaking the quartz ampoules. The thin films of $Se_{100-x}Zn_x$ glassy alloy are prepared by vacuum evaporation technique using a standard thermal evaporation unit and keeping clean glass substrates. The predeposited indiums of different electrode gaps are use as a substrate for depositing thin film in the planar geometry. These films are prepared in a vacuum ~10^{-3} Torr. The thin film is kept in the deposition chamber and in the dark at least 24 hours before mounting it in the sample holder. The deposition parameters are kept almost the same for all the samples so that a result could be come systematically for various glassy samples. The measurement of dc conductivity and I-V characteristics are carried out in a specially design sample holder where a vacuum of ~10^{-3} Torr could be maintained. It is sufficient for annealing at room temperature so that a Meta stable state thermodynamic equilibrium may be attained in the sample suggested by Abkowitz [8]. The thickness of the films is about ~500 nm. Vacuum evaporated indium electrodes below the deposited films are used for the electrical contact. The co-planar structure (of length ~2.5 cm and electrode gap d = 0.8 mm) is used for the present measurements. A vacuum of ~10^{-3} Torr is maintained though the entire temperature ranges (308 K to 388 K). Before measuring the dc conductivity (σ_{dc}), the thin films are first annealed at 308 K for one and half hour in a vacuum and a power supply (ST4073) 1.5 volts were used as a constant dc source for the measurement of dc conductivity. A dc high voltage source of (0 - 400 V) Model EHT-11 was used across the sample with different electrode gap and the resulting current was measured by a digital Pico-Ammeter, Model DPA-111. The temperatures are measured by mounting a copper-constant thermocouple near to the sample. It is preferred to taking I - V characteristics, annealing of thin films of all glassy near to their glass transition temperature T_g which ranged from 345 - 368 K was carried out for one and half hour in the sample holder.Wayne Kerr LCR meter (4300) was used for measurement of capacitance of the bulk samples at lower frequency (100 Hz) and at room temperature, which also is helpful to determine the density of localized states.

3. Characterizations

3.1. Powder X-Ray Diffraction Analysis

X-ray diffraction patterns of all samples are recorded at room temperature by using (A Panalytical (PW 3710) X-ray powder diffractometer with Cu Kα radiation (λ = 1.5405 Å). All the samples were scanned in angular range of 5˚ - 70˚ with scan speed of 0.01˚/s under the similar conditions. From XRD pattern it was clear that all the four samples $Se_{98}Zn_2$, $Se_{95}Zn_5$, $Se_{90}Zn_{10}$ and $Se_{80}Zn_{20}$ are belongs to similar structure of polycrystalline in nature as shown in **Figure 1(a)**. The clear sharp peak are indicates the Selenium peaks in this XRD patterns. Therefore, the peaks are increases with increases the Zn concentration in the glassy alloy. The crystallize size is calculated using Scherer's formula ($D = k\lambda/\beta\cos\theta$) of all the specimens and found to be increases with increasing the Zn concentration in the glassy system $Se_{100-x}Zn_x$ and the values of crystallized size are given in the **Table 1**.

3.2. Scanning Electron Microscope

Figure 1(b) Shows the Scanning electron micrographs of all the samples and confirms the polycrystalline nature of the synthesized materials. The numbers of nanocrysts are increases with increase of Zn concentration in the complete system. It is clear from SEM micrograph at highest 20% Zn content that the nanocrysts are easy to see multi structures with the thickness in the glassy alloys ($Se_{100-x}Zn_x$). The thickness of synthesis nanocrysts are found in the range of (174 - 217 nm) in the system. The morphology of SEM micrograph is agreement with the powder XRD result because the numbers of clear sharp peaks are increases with increase of Zn concentration in the glassy system.

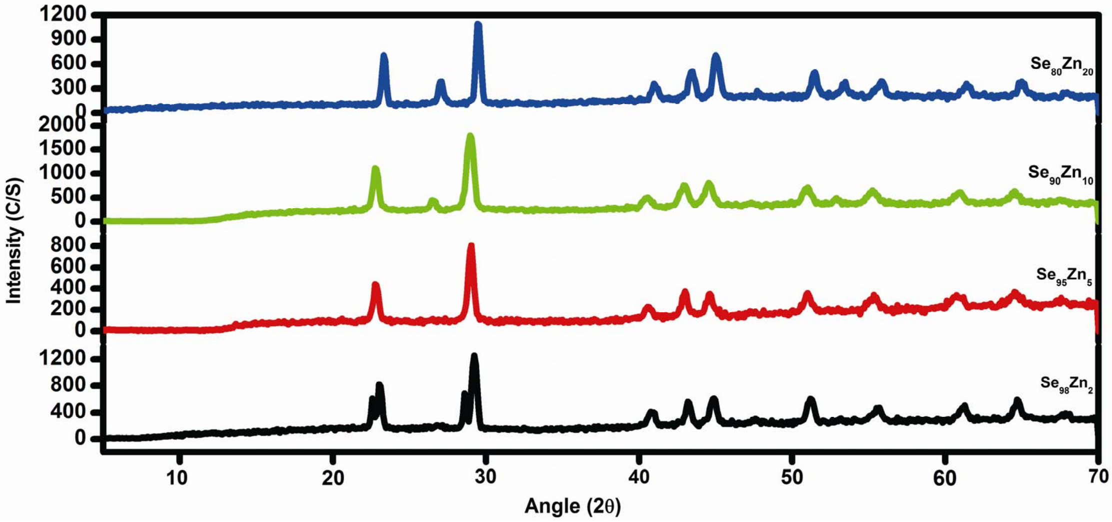
4. Results and Discussion

4.1. Temperature Dependence of (dc) Conductivity

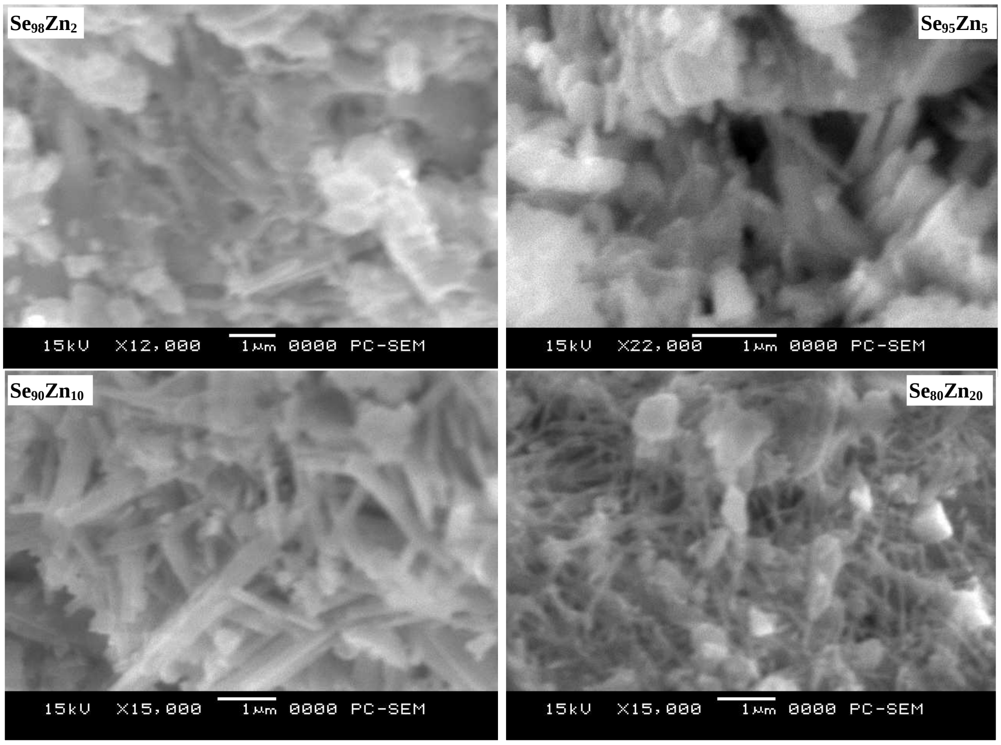
The temperature dependence of dc conductivity (σ_{dc}) in thin films for various binary sample of $Se_{100-x}Zn_x$ (x = 2,

Table 1. Electrical parameters in $Se_{100-x}Zn_x$ alloys at 368 K.

Glassy Alloy	σ_{dc} ($\Omega^{-1}\cdot cm^{-1}$)	ΔE (eV)	σ_0 ($\Omega^{-1}\cdot cm^{-1}$)	Crystallize Size (L) nm
$Se_{98}Zn_2$	3.56×10^{-10}	0.73	5.19×10^{-4}	111.64
$Se_{95}Zn_5$	4.16×10^{-10}	0.70	3.83×10^{9}	222.36
$Se_{90}Zn_{10}$	13.47×10^{-10}	0.69	1.35×10^{12}	222.98
$Se_{20}Zn_{20}$	19.06×10^{-10}	0.42	5.43×10^{5}	223.52



(a)



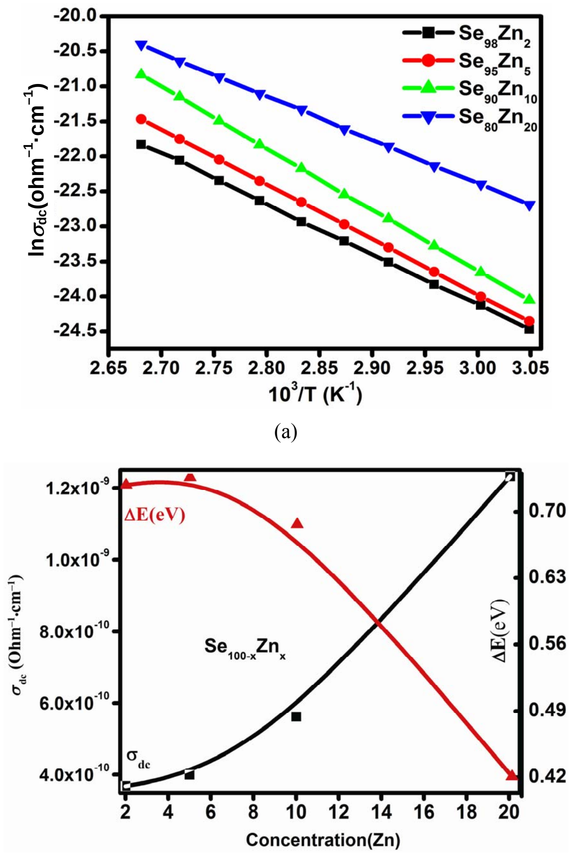
(b)

Figure 1. (a) XRD diagrams for all the samples of $Se_{100-x}Zn_x$; (b) SEM micrograph for all the samples of $Se_{100-x}Zn_x$ glassy alloys.

5, 10, 20) are measured**.** From the **Figure 2(a)** the dc conductivity (σ_{dc}) is decreases exponentially in the temperature range (308 - 388 K). The dc conductivity (σ_{dc}) is increases with increases the Zn content as shown in the **Figure 2(b)**. The activation energy (ΔE) is decreases with increases the Zn concentration as given in the **Figure 2(b)**. These result clearly shows the electrical conduction is through thermally activated process with single activation energy in these glasses [9,10]. The conductivity σ_{dc} is represented by well known relation in case of the disorder materials [11].

$$\sigma_{dc} = \sigma_0 \exp\left[-\frac{\Delta E}{kT}\right] \tag{1}$$

where (ΔE) is the activation energy for the dc conduction mechanism and "k" is the Boltzmann constant, "σ_0" is



(a)

(b)

Figure 2. (a) The plots of lnσ_{dc} vs. in the temperature range (368 - 393) for $Se_{100-x}Zn_x$; (b) DC conductivity, Activation energy vs. Zn concentration for $Se_{100-x}Zn_x$.

the pre-exponentional factor. The activation energy (ΔE) and pre-exponentional factor (σ_0) calculated from the slope of $10^3/T$ vs. lnσ_{dc} for each glassy sample by using the Equation (1) and the values are given in the **Table 1**.

The plots of $10^3/T$ vs. lnσ_{dc} for all the samples yield straight lines, which indicate thermally activated process for dc conduction mechanism. The value of activation energy (ΔE) and pre-exponentional (σ_0) is giving the information about through thermally assisted tunneling of charge careers movement in the band tails of localized states. The alone activation energy doesn't provide information as weather taken to conduction takes place in the extended states above the mobility space or by hopping conduction in the localized states. Therefore, Mott [12] has been suggested that for all conduction in localized states σ_0 should be about 10^4 [11] which are two or three orders smaller than for conduction in the extended states. The values of pre-exponential factor (σ_0) for low sulfur concentration (x < 2) the conduction mechanism is dominant through the localized states whereas for sample with high sulfur (S) concentration (x = 2, 5 and 10) the values of σ_0 (10^5 - 10^9 - 10^{12} $\Omega^{-1}\cdot cm^{-1}$) indicate that the conduction is through the extended states [13].

4.2. High Field Conduction Studies

Figure 3(a) shows the Current-Voltage (I - V) characteristics of all samples of $Se_{100-x}Zn_x$ at the electrode gap (d = 0.8 mm) at room temperatures. The (I - V) characteristics are studies between the temperatures range (352 - 372 K) in thin films of $Se_{100-x}Zn_x$ ($2 \le x \le 20$). It is observed an ohmic behaviour in the low field ($\le 10^3$ V/cm) and a non-ohmic behaviour are observed due to predominant of charge injection from the electrode gap to the samples at high field at (~10^4 V/cm) in the glassy alloys. The **Figure 3(b)** Shows the plots of V vs. ln(I/V) at different fixed temperature in the range (353 - 372 K) for the glassy $S_{98}Zn_2$. The similar results are obtained for other samples (the result not shown here). The plots of V vs. ln(I/V) are gives to the straight lines and have different values of slopes (S) at different temperatures. Furthermore, the values of these slopes (S) are plotted as a function of temperature in **Figure 4(a)**. However, the slope of each sample is decreases with increases the temperatures as given in **Figure 4(b)** and the **Table 2**.

According to the theory of SCLC, in the case of uniform distribution the density of localized states (g_0), the relation between current-voltage is given by the following Equation (2) [14].

$$I = KV \exp\left(SV\right) \tag{2}$$

where K is a constant and S is given by

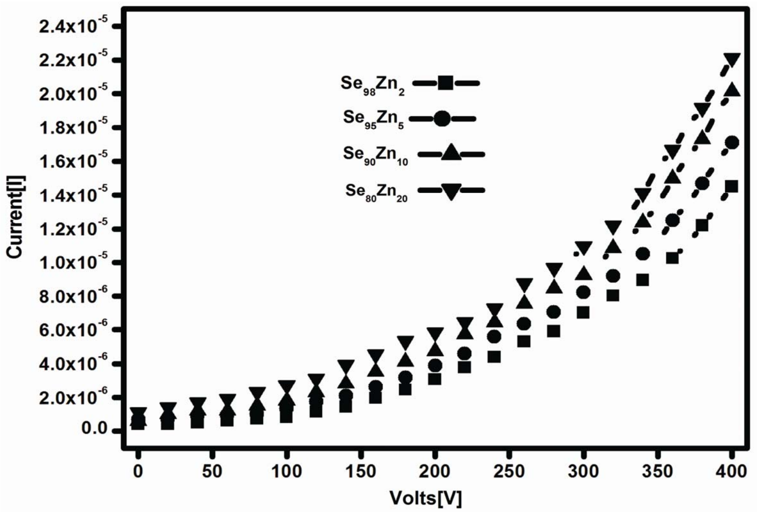
$$S = \frac{2\varepsilon_r \varepsilon_0}{q g_0 \left(E_F\right) kTd^2} \tag{3}$$

Here, ε_r is the relative dielectric constant, (d) electrode spacing gap, ε_0 is the permeability of free space and k is the Boltzmann constant. It should be noted that the Equation (2) is not an exact solution of the SCLC equation. But it is good approximation for one carrier space charge limited current under the condition of uniform distribution of traps.

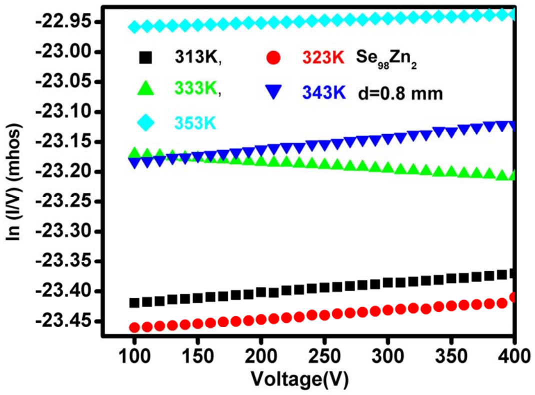
The study of charge carrier of these glasses is known to behaving like as p-type materials [15]. In the mea-

Table 2. Estimated values of density of localize state in $Se_{100-x}Zn_x$ glassy alloys at the temperatures range (352 - 372 K).

Glassy Alloy	Slope of S vs. 10^3/T curve	ε_r (100 Hz)	g_0 ($eV^{-1}\cdot cm^{-3}$)
$Se_{98}Zn_2$	1.42×10^{-6}	74.22	2.14×10^{13}
$Se_{95}Zn_5$	8.54×10^{-6}	20.35	9.46×10^{13}
$Se_{90}Zn_{10}$	1.20×10^{-6}	10.0	3.21×10^{14}
$Se_{20}Zn_{20}$	5.90×10^{-7}	9.0	5.70×10^{14}



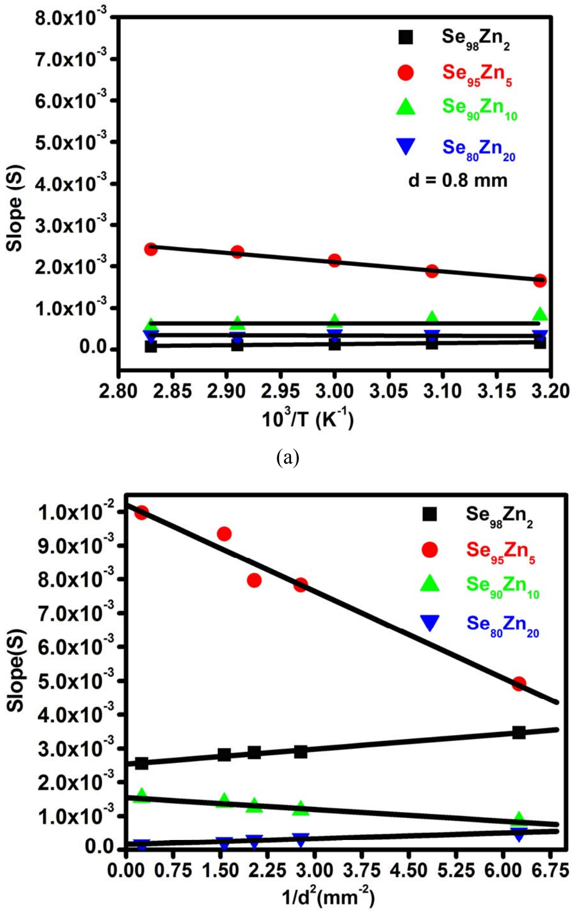
(a)



(b)

Figure 3. (a) Current (I) vs. voltage (V) with electrode gap (d = 0.8 mm) at room temperature 208 K for the glassy $Se_{100-x}Zn_x$ and (b) The plots of V vs. ln (I/V) at different fixed temperature with electrode gap (d = 0.8 mm) in the range (353 - 372 K) for the glassy $S_{98}Zn_2$.

surement, it is observed a very limited range of energy near the Fermi level. It's give the assumption of a uniform distribution strongly justified [16]. The results are observed in the presence of SCLC for each sample. It is mentioned here the nearly linear plots of V vs. ln(I/V) as well as decrease of slope (S) with increases the temperatures in terms of Space charge limited conduction (SCLC). However, in the field dependent conductivity the plot of V vs. ln(I/V) is independent from the electrode gap spacing (d) for Pool-Frenkel effect. But on the other hand in case of SCLC mechanism, the similar plot gives the different curve at different values of gap spacing (d). The Pool-Frenkel effect is tried and found invalid for $Se_{100-x}Zn_x$. The values of slopes (S) in the case of Se-Zn are plotted against the $1/d^2$ as shown in the **Figure 4(a)**. This is confirm the validity of Equation (3) in these samples and exclude the possibility of high-field conduction due to Pool-Frenkel effect. Hence, the present measurement confirm the presence of SCLC in these samples. It is also clear from the **Figure 4(b)** g_0 cannot be obtained from the slope of S vs. $10^3/T$ curve only of the value of ε_r is known. Here ε_r is to be measured at room temperature with the frequency 100 Hz, the calculated value of g_0 is plotted in **Figure 5** and given in **Table 2**. It is also clear that the density of localized state $g_0 = 2.14 \times 10^{13}\ eV^{-1}\cdot cm^{-3}$ for pure a-Se is satisfied with other workers [15,17]. The density of localized state g_0 increases with increase concentration of Zn in the glassy $Se_{100-x}Zn_x$.This types of variation can be described in terms of charged impurity in the structure of Zn-Se bonds. The introduction of Zn decreases the Se ring concentration and Se-Zn mixed ring and polymeric chains of Zn-Se is increases. One is vacant orbital in the hybridization used to form a donating bond with the lone pair of Se and consequently the bond breaking the between Se-Se has been taken. These types of reaction are expected to occur in the glass prepa-



(a)

(b)

Figure 4. (a) Slope (S) vs. 10^3/T (K^{-1}) curves at different temperature with electrode gap (d = 0.8 mm) and (b) Slope vs. 1/d^2 (mm^{-2}) for the glassy Se$_{100-x}$Zn$_x$.

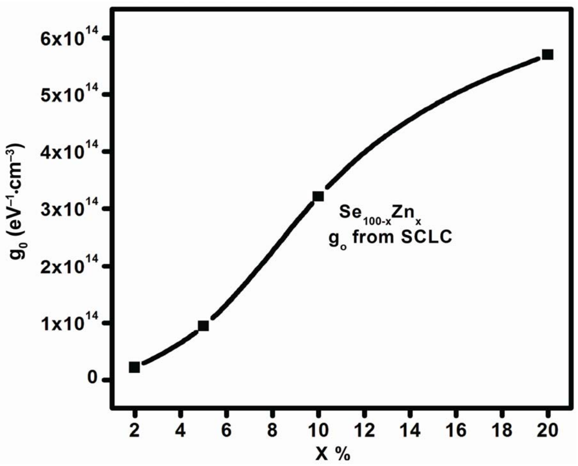


Figure 5. The plot density of localized states g$_0$ vs. Zn concentration for different electrode gaps in Se$_{100-x}$Zn$_x$.

ration process. Furthermore, increases Zn content, the bonding in Zn-Se is rise up indicate the large number of defect state including with mobility gap which decrease the activation energy in the glassy system. The Zn-Se bond concentration increases during the bond stuck between in the chalcogenide atoms and have been seen in selenium base glassy alloy like Bi, Pb, In and Al etc. On the other hand bond stuck is decreases in such types of Se-Se Samples with other workers [15,16,18].

5. Conclusions

On the basis of XRD and SEM micrograph picture the crystallinity is increases, crystallize size and increases the numbers of nanocryst with increases of Zn concentration in Se-Zn glassy system.

The temperature dependent dc conductivity (σ_{dc}) is increases and the activation energy (ΔE) decrease with increases of Zn content because of defect states are increases in the mobility gap. An ohmic behaviours is observed at low fields and non-homic behavior is observed at high fields (~10^4 V/cm). The density of localized states g$_0$ near the Fermi-level is estimated by fitting the data into the theory of space charge limited conduction (SCLC), assuming uniform distribution of localized states. The density of localized states g$_0$ near the Fermi-level is increases with increase the concentration of Zn in Se-Zn system on temperature range (352 - 372 K. These above results are explained upon Se-Zn bonding in the glassy S$_{100-x}$Zn$_x$.

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