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Effect of Composition on Electrical and Optical Properties of Thin Films of Amorphous Ga_xSe_{100-x} Nanorods

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Abstract We report the electrical and optical studies of thin films of a-Ga_xSe_{100-x} nanorods ($x = 3, 6, 9$ and 12). Thin films of a-Ga_xSe_{100-x} nanorods have been synthesized thermal evaporation technique. DC electrical conductivity of deposited thin films of a-Ga_xSe_{100-x} nanorods is measured as a function of temperature range from 298 to 383 K. An exponential increase in the dc conductivity is observed with the increase in temperature, suggesting thereby a semiconducting behavior. The estimated value of activation energy decreases on incorporation of dopant (Ga) content in the Se system. The calculated value of pre-exponential factor (σ_0) is of the order of $10^1 \ \Omega^{-1} \ cm^{-1}$, which suggests that the conduction takes place in the band tails of localized states. It is suggested that the conduction is due to thermally assisted tunneling of the carriers in the localized states near the band edges. On the basis of the optical absorption measurements, an indirect optical band gap is observed in this system, and the value of optical band gap decreases on increasing Ga concentration.

Keywords a-Ga_xSe_{100-x} nanorods · XRD pattern · SEM images · TEM image · dc conductivity · Activation energy · Absorption coefficient · Optical band gap

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Introduction

The search of new materials to use in device technology is a never ending process. Discovery and study of new materials, whose properties can be tailored made constitute the core of development of solid state technology. In the last several decades, a remarkable increase in the application of amorphous materials has been made possible by constant innovations in the technology of their preparation. It is well understood that the mode of bonding of the elements in the structural network of amorphous materials is not strictly defined as in long-range ordered systems (crystals), so that the transport processes in these glassy materials are largely dependent on the nature and degree of short-range order [1]. Therefore, the relationship between the structure and properties of glasses and conditions of their preparation is of special significance. The consequence of structural–technological modifications [2], i.e., the possibility of adjusting the physico–chemical parameters on the basis of specially selected compositions and technological procedures of their preparation opens up new possibilities in the area of practical application of glassy materials.

Gallium selenide film is a III–VI layered semiconductor having a hexagonal close-packed structure. The primitive layer consists of four atomic planes in the sequence Se–Ga–Ga–Se. The bonding between primitive layers is due to Vander Waals force, while the interlayer bonds have a strong ionocovalent character. Therefore, the inter primitive layer bonding is much weaker than the intra primitive layer bonding. So, it is considered that the bonding property of GaSe film would strongly influence the growth of layered compound film. Due to outstanding nonlinear optical and electronic properties, it has been widely investigated during the last few years. Results on harmonic generation [3–5], parametric oscillations, [6], or frequency mixing [7, 8] in the near and middle IR, as well as effects related to excitonic optical nonlinearties giving rise to optical bistability [9, 10], are available in the literature. It has also potential applications for frequency doubling and fast optical gating [11] and behaves as an X-ray detector [12]. Electronic and optoelectronic properties of GaSe, GaS, and InSe materials indicate the possibilities of realizing phototrigger devices [13] photodiodes and photoresistors [14], and solar cells [15].

The synthesis of one-dimensional nanostructures in form of nanobelts, nanorods, and nanowires has stimulated intense research activity due to their novel physical properties and their potential applications in nanotechnology [16–20].

Recently, nanostructures of chalcogenides have been produced by several workers [21–28] using different methods; therefore, this has become an interesting topic of research. It is expected that once these chalcogenides are produced as nanoscale, they will show a dramatic change in their optical and electronic properties due to reduction in size. However, studies on nano-chalcogenides are still at the beginning, and accordingly, overall features have not been discovered.

Understanding the electrical and optical processes in chalcogenide compounds such as GaSe at nanoscale is of interest both from fundamental and technological point of view. In recent years, owing to their very interesting physical properties, this particular material has raised considerable deal of research interest followed by technological applications in the field of micro/optoelectronics. Significant research efforts have been focused to the study of the electrical and optical properties of this compound in thin film formation. Since the optimization of device performance requires a well-established knowledge of the electrical and optical properties of GaSe thin films, in this paper, we report the results on electrical and optical measurements of amorphous thin films of GaSe nanorods prepared by vacuum evaporation technique.

Experimental

Glassy alloys of Ga_xSe_{100-x} ($x = 3, 6, 9$ and 12) are prepared by conventional melt-quenching technique. High-purity (5 N) elements Ga and Se, in the appropriate weight proportion, are vacuum sealed (10^{-6} Torr) in quartz ampoules and heated up to 950°C in a furnace at a heating rate of 2–3°C/min. The ampoules are frequently rocked at the highest temperature for 10–12 h to make the melt homogeneous. Throughout the entire heating process, ampoules are rotated in clockwise and anticlockwise directions with the help of motor to ensure homogeneity of the composition within the samples. Once this process is over, the melt is rapidly quenched in ice water to make it amorphous. The bulk glassy alloys were characterized by X-ray diffraction technique and found to be amorphous in nature as no prominent peak was observed in the XRD spectrum.

For electrical measurements, well-degassed corning glass plates having pre-deposited indium electrodes (two thick indium electrode) are used as a substrate for depositing amorphous films in the planer geometry. All films are deposited by thermal evaporation technique keeping substrate at room temperature and at a base pressure of about 10^{-6} Torr. The thickness of the amorphous films is measured by quartz crystal thickness monitor (Edward model FTM 7), and it is ≈ 4000 A^0. The films are kept in deposition chamber in the dark for 24 h before mounting them in the sample holder. This is done to allow sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the samples as suggested by Abkowitz [29] for chalcogenide glasses. The deposition parameters are kept almost the same for all the samples so that a comparison of results could be made for various glassy samples. The prepared thin films are then mounted in a specially designed metallic sample holder, where a vacuum of about 10^{-3} Torr is maintained throughout the measurements. A dc voltage (1.5 V) is applied across the sample, and the resulting current is measured by a digital electrometer (Keithley, Model-617). The temperature is measured by mounting a calibrated copper-constantan thermocouple near to the sample.

For optical measurements, we have used thin films of glassy alloy of Ga_xSe_{100-x} with $x = 3, 6, 9$, and 12 of 3000Å thickness deposited onto ultrasonically cleaned glass substrates at room temperature on a base pressure of 10^{-6} Torr. A JASCO-V-500-UV/VIS/NIR computerized spectrophotometer is employed for measuring optical absorption. The morphology and microstructure of thin films of glassy alloy of Ga_xSe_{100-x} have been observed by scanning electron microscopy and transmission electron microscopy.
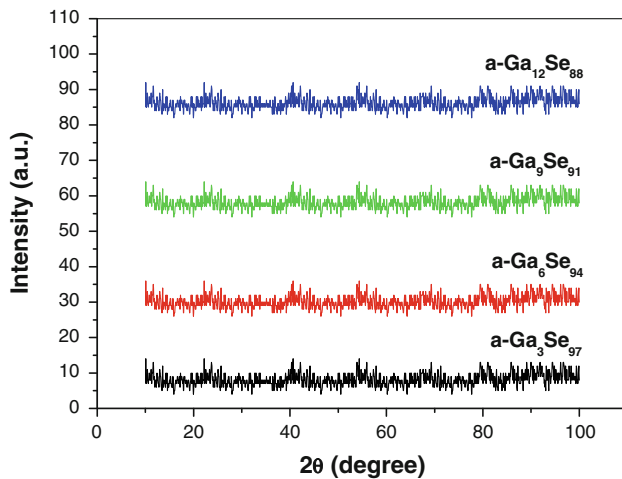
Fig. 1 XRD pattern of a-Ga$_x$Se$_{100-x}$

Results and Discussion

Electrical Transport Properties

Figure 1 shows the X-ray diffraction pattern of a- Ga$_x$Se$_{100-x}$ glassy alloys. There is no any significant peak observed for the present system. Overall, all of these alloys show amorphous nature. From SEM images of a-Ga$_x$Se$_{100-x}$, it is observed that the thin films for all the compositions of Ga ($x = 3, 6, 9$ & 12) contain high yield of nanorods, and their diameter is of the order of several hundred nanometers. Here, the scanning electron microscopy images of a-Ga$_{12}$Se$_{88}$ film are presented in Fig. 2a, b. TEM image of these nanorods is presented in Fig. 3. It is clear from the image that the diameter of the nanorods varies from 140 to 180 nm, and the length is of several hundreds of nanometers.

Figure 4 presents the temperature dependence of the dc conductivity of thin films of a- Ga$_x$Se$_{100-x}$ nanorods ($x = 3, 6, 9$ and 12) in the temperature range 298–383 K. It

is evident from this figure that the dc conductivity (σ_{dc}) increases exponentially with increasing temperature from 298 to 383 K for all samples, indicating that conduction in these glassy alloys is through an activated process that also shows the semiconducting behavior of these alloys. The variation of dc conductivity with different composition of Ga$_x$Se$_{100-x}$ ($x = 3, 6, 9$ and 12) nanorods is presented in Table 1.
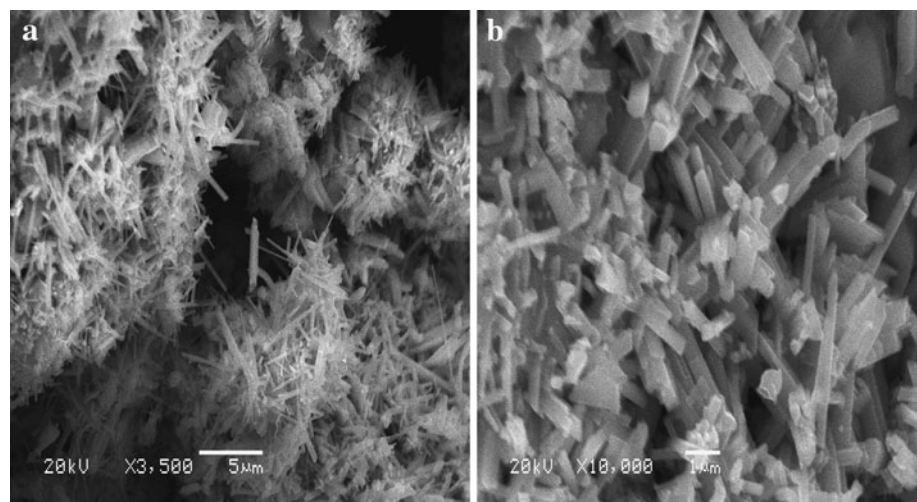
DC conductivity can be expressed by the relation,

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E / KT) \quad (1)$$

where, σ_0 and ΔE represent the pre-exponential factor and activation energy, respectively, and K is Boltzmann constant.

On the basis of best fitting of our data with thermally activated type of conduction, the values of activation energy and pre-exponential factor are calculated, and these values are given in Table 1. On the basis of the calculated values of activation energy and pre-exponential factor, it is suggested that the conduction is due to thermally assisted tunneling of charge carriers in the localized states in band tails. The activation energy alone does not provide any indication about the conduction mechanism whether it takes place in the extended states above the mobility edge or by hopping in the localized states. This is due to the fact that both these conduction mechanisms can occur simultaneously. The activation energy in the former case represents the energy difference between mobility edge and Fermi level, ($E_c - E_f$) or ($E_f - E_v$). An overall decreasing trend is observed for dc conductivity of this system when compared to the initial value. This decrease in conductivity could be caused by the increase in the defect states associated with the impurity atoms [30]. In order to obtain a clear distinction between two conduction mechanisms, Mott and Davis [31] have suggested that the pre-exponential factor for conduction in the localized states should be two to three orders lower than the conduction in the

Fig. 2 a, b SEM images of a-Ga$_{12}$Se$_{88}$ nanorods
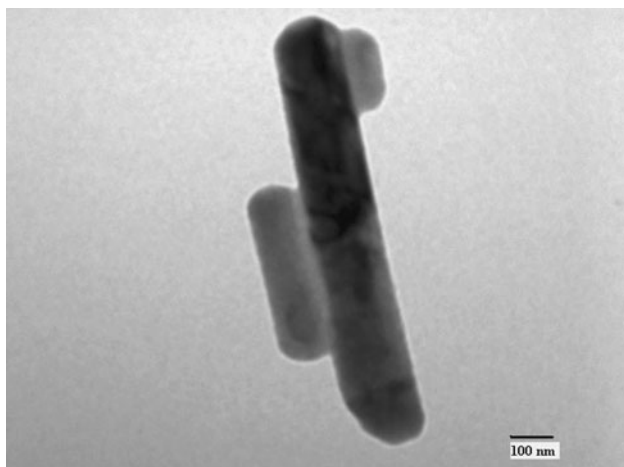
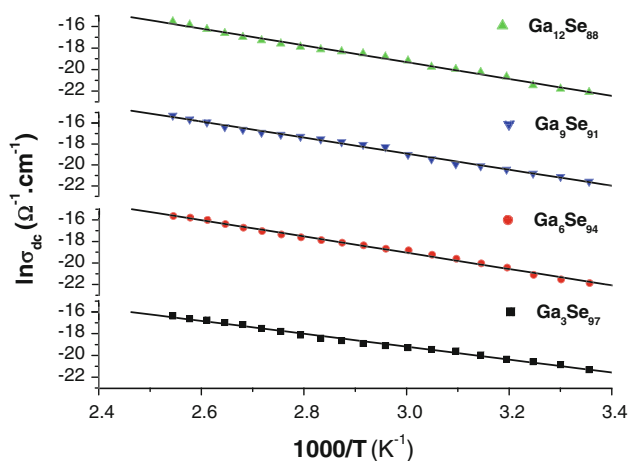**Fig. 3** TEM image of a-$Ga_{12}Se_{88}$ nanorods

Fig. 4 Temperature dependence of dc conductivity in the temperature range (298–383 K) at various concentration of Ga of thin films of a-Ga_xSe_{100-x} nanorods

extended states and should become still lower for the conduction in the localized states near the Fermi level. Thus, in our present system, the value of pre-exponential factor (σ_0) is of the order of $10^1\ \Omega^{-1}\ cm^{-1}$. On the basis of this value of σ_0, it is suggested that the conduction is taking place in the band tails of localized states. A significant change in σ_0 is observed when Ga contents are incorporated in the Se. These are explained using the shift of Fermi

level on adding Se impurity. Therefore, the decrease in the value of σ_0 may be due to the change in Fermi level on adding Ga in the Se (Table 1).

Optical Properties

The values of the absorption coefficient (α) are calculated using the relation,

$$\alpha = \text{Absorbance/Film Thickness} \tag{2}$$

It has been observed that the value of absorption coefficient (α) increases with the increase in photon energy for the thin films of Ga_xSe_{100-x} nanorods. The order of the calculated values of the absorption coefficient for Ga_xSe_{100-x} nanorods is in the range $\sim 10^4\ cm^{-1}$, which is consistent with the result of other workers [32, 33].

The present system of Ga_xSe_{100-x} nanorods obeys the rule of indirect transition and the relation between the optical gap, optical absorption coefficient α and the energy $h\nu$ of the incident photon is given by [32, 33],

$$(\alpha h\nu)^{1/2} \propto (h\nu - Eg) \tag{3}$$

The calculated values of absorption coefficient (α) are given in Table 1. Figure 5 shows the variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for the thin films of a-Ga_xSe_{100-x} nanorods. The value of indirect optical band gap (E_g) is calculated by taking the intercept on the X-axis. The calculated values of E_g are given in Table 1. It is clear from this table that the value of optical band gap (E_g) decreases with increasing Ga concentration in this system. Since the optical absorption also depends on short-range order in the amorphous states and defects associated with it, the decrease in optical band gap may be explained on the basis of "density of state model" proposed by Mott and Davis [34]. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds are produced as the result of an insufficient number of atoms deposited in the amorphous film [35]. The unsaturated bonds are responsible for the formation of some of the defects in the films, producing localized states in the amorphous

Table 1 Electrical and optical parameters in Ga_xSe_{100-x} nanorods at $T = 298$ K

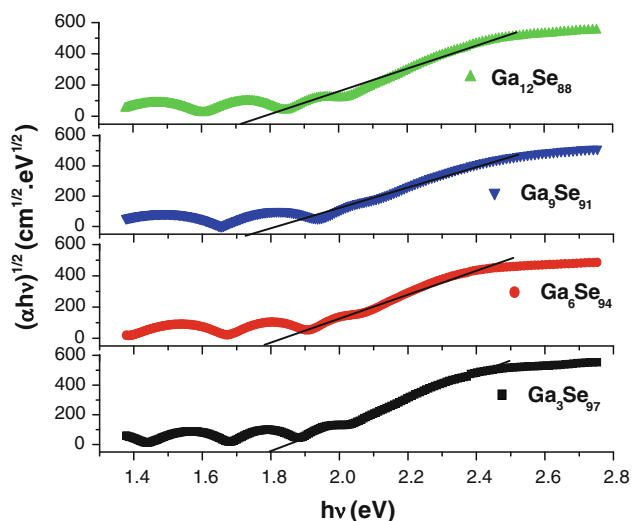| Sample	σ_{dc} ($\Omega^{-1}\ cm^{-1}$)	σ_0 ($\Omega^{-1}\ cm^{-1}$)	ΔE_c (eV)	α (cm^{-1}) (10^4)	E_g (eV)
Ga_3Se_{97}	5.48×10^{-10}	20.25	0.51	0.51	1.80
Ga_6Se_{94}	3.21×10^{-10}	37.90	0.65	0.46	1.78
Ga_9Se_{91}	2.51×10^{-10}	56.04	0.66	0.44	1.74
$Ga_{12}Se_{88}$	4.24×10^{-10}	59.62	0.68	0.52	1.72

Fig. 5 $(\alpha h\nu)^{1/2}$ against photon energy $(h\nu)$ of thin films of a-Ga_xSe_{100-x} nanorods

solids. The presence of high concentration of localized states in the band structure is responsible for the decrease in optical band gap on increasing the dopant concentration in these amorphous films of Ga_xSe_{100-x} nanorods. This decrease in optical band gap may also be due to the shift in Fermi level whose position is determined by the distribution of electrons over the localized states [36].

The decrease of the optical gap with Ga content can be correlated with the character of the chemical order of chalcogenide amorphous semiconductors. According to the model described by Kastner [37], the dominant contribution for states near the valence band edge in materials having chalcogen atoms as major constituents, comes from chalcogen atoms, especially from their lone-pair p-orbital. The lone-pair electrons in these atoms adjacent to electropositive atoms will have higher energies than those close to electronegative atoms. Therefore, the addition of electropositive elements to the alloy may raise the energy of some lone-pair states sufficiently to broaden further the band inside the forbidden gap. The electronegativities of Ga and Se are 1.52 and 2.14. According to these values, it is noticed that Ga is less electronegative than Se, so the substitution of Ga for Se may raise the energy of some lone-pair states and hence broaden the valence band. This will give rise to additional absorption over a wider range of energy leading to band tailing and hence shrinking of the band gap. The optical gap decreases from 1.80 to 1.72 eV for $x = 3$ to $x = 12\%$ of Ga content as shown in Table 1. The addition of Ga in the glass structure causes deeper band tails extended in the gap and thereby, leading to a decrease in the value of optical band gap.

Conclusion

Thin Films of a-Ga_xSe_{100-x} nanorods have been synthesized by thermal evaporation technique. The dc conductivity and optical absorption in these nanorods have been studied. From the temperature dependence of dc conductivity, the activation energy and pre-exponential factor are calculated. The estimated value of activation energy decreases on increasing Ga content in the Se system. On the basis of pre-exponential factor (σ_0), it is suggested that the conduction is due to thermally assisted tunneling of the carriers in the localized states near the band edges. The pre-exponential factor (σ_0) increases with increasing dopant (Ga) concentration. The increase in the value of σ_0 may be due to the change in Fermi level on adding Ga in the Se. From optical measurement, we conclude that optical band gap is indirect in nature and it decreases on increasing Ga concentration. This may be due to the decrease in the grain size, the increase in the disorderedness of these systems. This may also be due to the increase in the density of defect states, which results in the increase in band tails.

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