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Effect of proton irradiation on electrical properties of a-As_2S_3

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ABSTRACT

This paper reports the effect of proton irradiation on the electrical properties of a-As_2S_3 in the temperature range of 323–418 K and frequency range 0.1–100 kHz. The variation of transport property is studied with proton irradiation dose (1×10^{13} ions/cm^2 and 1×10^{15} ions/cm^2). It has been observed that proton irradiation changes the dc conductivity (σ_{dc}), dc activation energy (ΔE_{dc}) and ac conductivity ($\sigma_{ac}(\omega)$). The σ_{dc} and σ_{ac} (ω) increases with dose of proton irradiation. The value of frequency exponent (s) decreases with the temperature and irradiation dose. These results are explained in terms of change in density of defect states in these glasses.

1. Introduction

Chalcogenide glassy semiconductors continue to attract the attention of scientists, because they possess very attractive properties and offer new applications in engineering. Chalcogenide glasses are transparent in the VIS and IR spectral ranges [1–3], with relatively high refractive index ($2\leq n\leq3.7$) and low optical losses. The low characteristic vibrational frequencies of chalcogenide bonds allow them to transmit far out, into the infrared [4]. These glasses show a variety of photo-stimulated phenomena when exposed to light or other radiations [5,6]. When these glasses are irradiated with high energy particles or light, bond breaking and bond rearrangement can take place, which results in the change in local structure of the glassy materials. These include subtle effects such as shifts in the absorption edge (photobleaching and photodarkening), and more substantial atomic and molecular reconfiguration such as photoinduced refractive index changes and photodoping effects [7]. In general, these phenomena are associated with the changes in the optical constants [8] and absorption edge shift [9], allowing the use of these materials in the fabrication of a large number of optical devices. Since change in the structure can have an influence on photogeneration, charge carriers transport, charge carrier trapping and other important fundamental properties. Therefore the knowledge of electrical properties of such materials is needed for further improvement of their characteristics in device applications.

Amorphous arsenic sulphide is one of the stable stoichiometric and technically important chalcogenide glasses. Arsenic sulphide glasses are largely studied materials, mainly due to their unique light induced effects [8,9]. Changes in physical properties of a-As_2S_3 induced by high power radiations (electrons, x-ray, gamma ray etc.) have been reported [10,11]. The interaction of ion beam with a solid is a non-equilibrium process. An energetic ion loses its energy during its passage through material mainly by electronic energy loss (inelastic collision) and nuclear energy loss (elastic scattering). The nature of modification depends upon the electrical, thermal and structural properties of the target material, mass of projectile ion and irradiation parameter [12]. Impedance spectroscopy is a powerful technique for the study of ion transport processes [13]. Measurements of ac conductivity of amorphous chalcogenide semiconductors have been extensively used to understand the conduction process in these materials [14].

In the present work, we have irradiated the binary chalcogenide glass, a-As_2S_3, with 3 MeV proton beam at different doses, and studied the ion induced electrical effects in this material. These results have been explained on the basis of the structural changes occurring in the material due to irradiation.

2. Experimental

The chalcogenide glasses were prepared by melt quenching technique as described earlier [15]. The amorphous nature of glasses

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has been verified using x-ray diffraction (XRD). No peaks in the XRD pattern confirm that the prepared material was amorphous in nature. The pellets were prepared by compressing the finely grounded powder of a-As_2S_3 to maximum compactness to form circular pellets having approximately the same dimensions (diameter = 0.677 cm, thickness ~0.08–0.10 cm). While making compressed pellets, the powder is compressed to maximum compactness so that there were no voids in the sample. All pellets were annealed at 420 K for 24 hours in order to minimize the effect of grain boundaries. These pellets were irradiated with 3 MeV proton beam using Cyclotron facility at the Physics Department, Panjab University, Chandigarh, India. The beam current density was of the order of 20 nA/cm^2 and samples were irradiated at a fluence of 1×10^{13} ions/cm^2 and 1×10^{15} ions/cm^2. The beam was focused using a circular collimator so that an area of ~0.36 cm^2 on the pellet received a uniform ion dose. All irradiations were performed in vacuum (~10^{-6} Torr) at a room temperature. The radiated pellets are again annealed at 420 K for 6 hours, so that the effects of radiation on the temporary defects are stabilized inside the material and we could study only the permanent changes in the material. Pellets were coated on both sides with aquadag (a commonly used conducting emulsion) for ohmic contacts [15]. The ohmic contacts were confirmed through linear I–V characteristics. A General Radio Bridge (Model 1615-A, USA) was used for the measurements of frequency dependent ac conductivity. The bridge consists of an audio oscillator (Model 1311), a tuned amplifier (model 1232-A) and a null detector, which permits balance to a resolution of one part in a million. All electrical measurements were made over a wide range of temperature (323–418 K) and frequency (0.1–100 kHz).

3. Results

3.1. DC Conductivity

The value of dc conductivity has been obtained from I–V characteristics at different temperatures. Fig. 1 shows the temperature dependence of the dc conductivity (σ_{dc}) in a-As_2S_3 of virgin and irradiated pellets. It is clear from the figure that ln σ_{dc} versus 1000/T curves are straight lines in the measured temperature range (323–418 K). This indicates that the conduction in these glasses is through an activated process having single activation energy in the measured temperature range. σ_{dc} can, therefore, be expressed by the relation

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

where σ_0 is the pre-exponential factor and ΔE_{dc} is the dc activation energy.

The values of ΔE_{dc} are calculated using the slopes of the curves of Fig. 1 and are listed in Table 1, which also contains the values of σ_{dc} at 331 K. σ_{dc} increases with proton irradiation and ΔE_{dc} decreases. The value of σ_0 is also calculated and inserted in Table 1. A value of σ_0 in the range 10^3–10^4 Ω^{-1}cm^{-1} in chalcogenide glasses indicates that the conduction is mostly in extended states. A smaller value of σ_0 indicates a wide range of localized states and conduction by hopping [16,17]. The values of pre-exponential factor of the investigated samples indicate the dominance of hopping between localized states in the band tails.

3.2. AC Conductivity

The ac conductivity ($\sigma_{ac}(\omega)$) for all the amorphous semiconductors increases with frequency according to the following equation [17,18]

$$\sigma_{ac}(\omega) = \sigma_{tot}(\omega) - \sigma_{dc} = A\omega^s \quad (2)$$

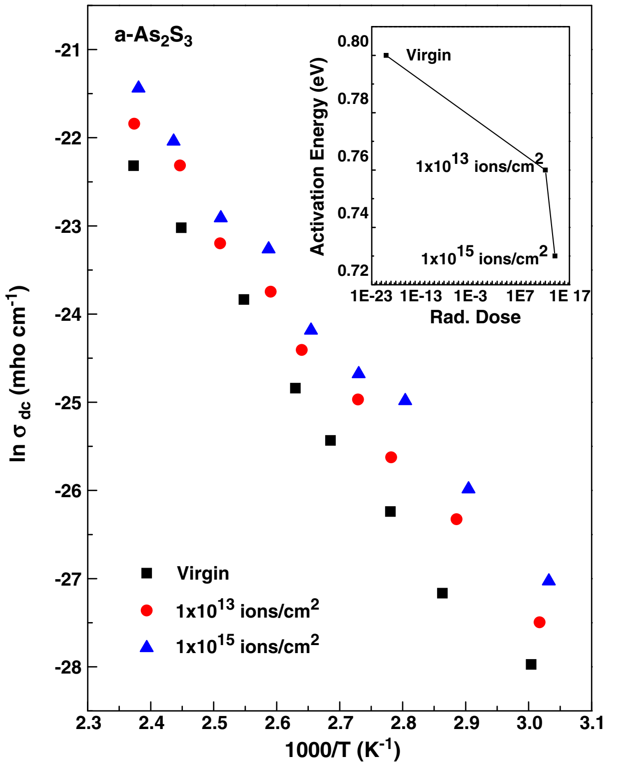

Fig. 1. Temperature dependence of dc conductivity (σ_{dc})for bulk a-As_2S_3 and bombarded with 3 MeV proton beam at a dose of 1×10^{13} ions/cm^2 and 1×10^{15} ions/cm^2. Inset: shows the variation of activation energy (ΔE_{dc}) with radiation dose.

where σ_{dc} is the dc part of the total conductivity $\sigma_{tot}(\omega)$, 's' is frequency exponent, A is the constant and ω ($=2\pi f$) is the angular frequency. Fig. 2 shows the frequency dependence of measured conductivity at different temperature for virgin a-As_2S_3. It is clear from the figure that $\sigma_{ac}(\omega)$ increases linearly with frequency. The same behavior of the frequency dependence of $\sigma_{ac}(\omega)$ was obtained for the irradiated sample at different doses (1×10^{13} ions/cm^2 and 1×10^{15} ions/cm^2). Values of the frequency exponent 's' were obtained from the slopes of these lines in the figure. The temperature dependence of 's' is shown in the inset figure. This figure shows a decrease in the exponent 's' with an increase in temperature through the measured temperature range.

Fig. 3 shows the frequency dependence of measured conductivity for virgin a-As_2S_3 and irradiated samples at 368 K. It is clear from the figure that $\sigma_{ac}(\omega)$ increases with the proton irradiation. Also $\sigma_{ac}(\omega)$ increases linearly with frequency for all the samples. The value of 's' decreases with the irradiation. This signifies that dispersion with frequency is reduced on irradiation.

Fig. 4(a) and (b) show the temperature dependence of measured ac conductivity at 5 kHz and 100 kHz for virgin and irradiated a-As_2S_3 respectively. From the figure, it is clear that the conductivity increases with temperature and irradiation dose.

Table 1
The value of radiation dose, dc conductivity (σ_{dc}), pre-exponential factor (σ_0), dc activation energy (ΔE_{dc}) and frequency exponent (s).

Dose (ions/cm^2)	σ_{dc} (Ω^{-1} cm^{-1}) (at 331 K)	σ_0 (Ω^{-1} cm^{-1})	ΔE_{dc} (eV)	$\sigma_{ac}(\omega)$ (Ω^{-1} cm^{-1}) (at 331 K)	s (368 K)
Virgin	7.097×10^{-13}	0.813	0.80	3.694×10^{-10}	0.797
1×10^{13}	1.145×10^{-12}	0.437	0.76	4.512×10^{-10}	0.734
1×10^{15}	1.826×10^{-12}	0.179	0.73	4.987×10^{-10}	0.726

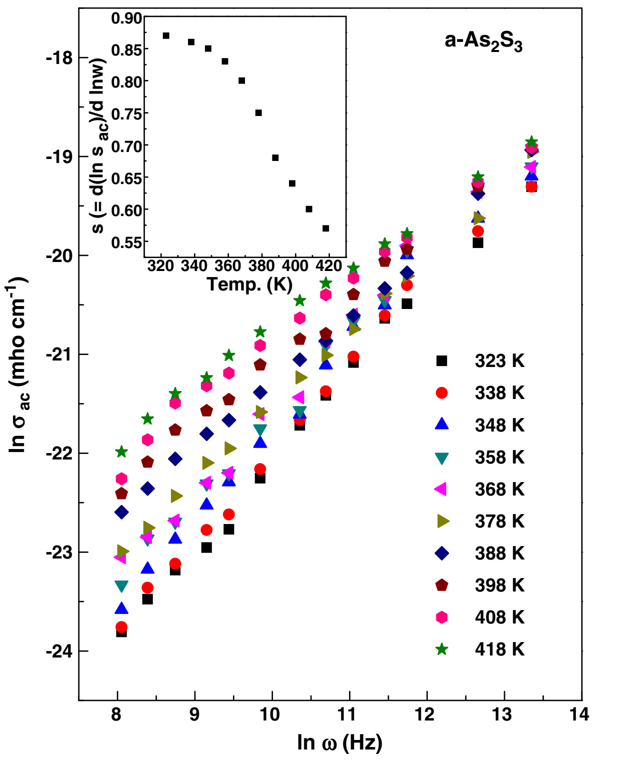

Fig. 2. Temperature dependence of ac conductivity for bulk a-As_2S_3 at different frequencies. Inset: shows variation of 's' with temperature.

4. Discussions

The smaller ac activation energy and increase in $\sigma_{ac}(\omega)$ with increased frequency for the investigated samples confirm that the

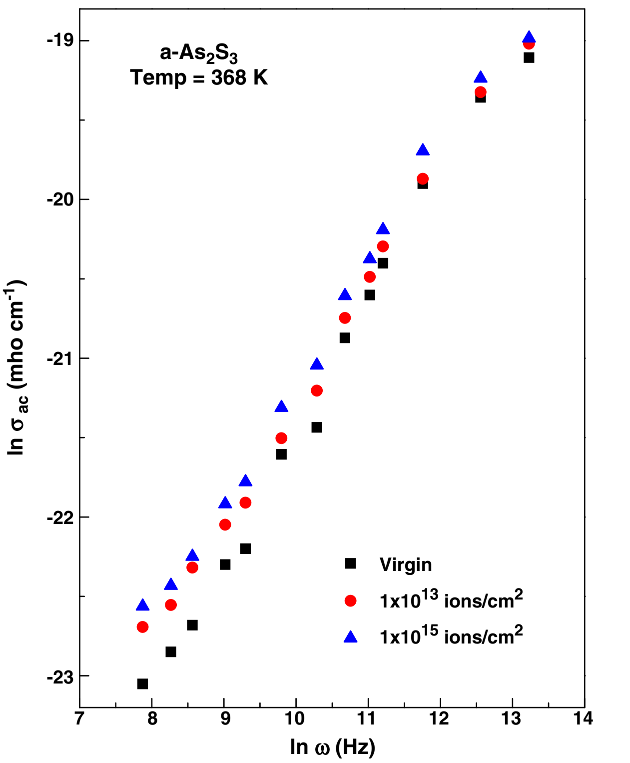

Fig. 3. Frequency dependence of ac conductivity for bulk a-As_2S_3 and irradiated samples at 368 K.

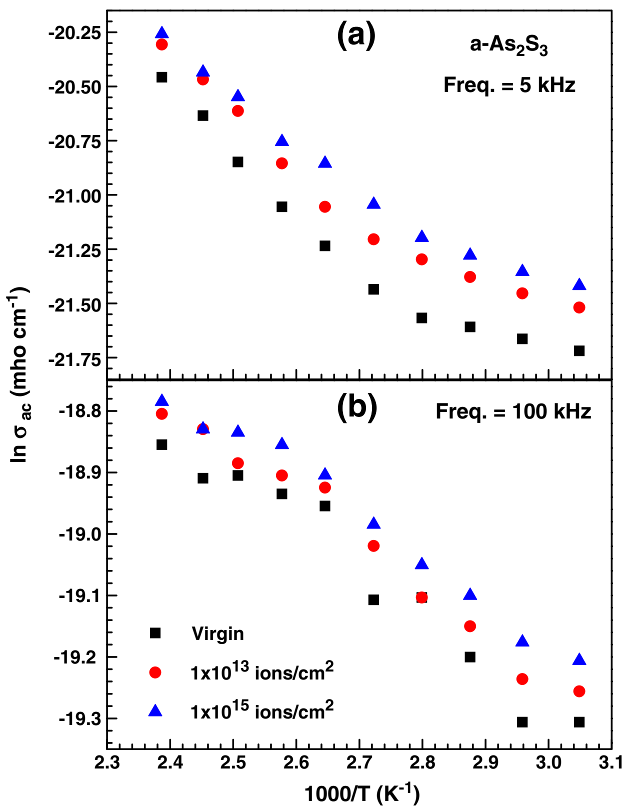

Fig. 4. Temperature dependence of ac conductivity for bulk a-As_2S_3 and irradiated samples at different frequencies (a) 5 kHz and (b) 100 kHz.

model of correlated barrier hopping (CBH model) can be used for the interpretation of the results [19,20]. According to the CBH model, ac conductivity is given by [19,20]

$$\sigma_{ac}(\omega) = \frac{n\pi^2 NN_p \epsilon' \omega R_\omega^6}{24} \tag{3}$$

where n is the number of polarons involved in the hopping process, NN_p is proportional to the square of the concentration of states and ϵ' is the dielectric constant. R_ω is the hopping distance for conduction $(\omega\tau = 1)$ and is given as

$$R_\omega = \frac{4ne^2}{\epsilon'[W_m - kT\ln(1/\omega\tau_0)]} \tag{4}$$

where W_m is the maximum barrier height and τ_0 is the characteristic relaxation time for the material.

It is evident from the Fig. 4 that $\sigma_{ac}(\omega)$ is very sensitive to temperature in the higher temperature regime at lower frequencies. The low temperature ac conduction can be explained by considering bipolaron hopping between D^+ and D^- centers, whereas the higher temperature behavior is due to thermally activated single polaron hopping. At higher temperatures, a number of thermally generated D^0 centers are produced with a temperature dependent concentration

$$N_0 = N_T \exp\left(-U_{eff}/2kT\right) \tag{5}$$

where N_T is the concentration of D^+ or D^- centers at $T = 0$ K. The defect concentration factor NN_p in Eq. (3) is replaced by

$$NN_p = N_T^2/2 \qquad (bipolaron\ hopping)$$

$$NN_p = N_T^2/2\ \exp\left(-U_{eff}/2kT\right) \qquad (single\ polaron\ hopping)$$

Thus for single polaron hopping this factor is thermally activated and hence $\sigma_{ac}(\omega)$ is also activated.

According to the CBH model [20]

$$B = W_m - W_1 + W_2 \tag{6}$$

where B (~$2\Delta E_{dc}$) is optical band gap, W_m is the maximum band width. The behavior with angular frequency ω is given by the expression

$$\sigma_{ac}(\omega) = A\omega^s \tag{7}$$

Here [21],

$$s = \frac{d(\ln\sigma_{ac})}{d\ln\omega} = 1 - 6kT/W \tag{8}$$

while $W = W_m$ for bipolaron hopping and $W = W_1$ or W_2 for single polaron hopping. The behavior of 's' $(= 1 - 6kT/W)$ (Eq. (8)) can be seen in Fig. 2. This indicates that the value of 's' decreases with the increase in temperature. During irradiation two competitive processes take place. The process of radiation damage increases the amount of dangling bonds and the process of defect annihilation reduces them. Chalcogenide materials consist of lone pair orbital forming the valance band [22], whereas conduction band is formed by the antibonding orbital. The irradiations with higher energies excite electrons from the bonding states to antibonding states (free electrons). The vacancies created in these states are immediately filled by the outer electrons with Auger transitions that in turn induce more holes in the bonding state. This kind of bond making and breaking process would eventually lead to an effective change in structural order at a nanoscale [8,22]. Thus, the increase in conductivity is attributed to the proton induced defects [22,23], which generates defect localized states at around the Fermi level. The large number of states and available carriers take part in the hopping process and the low values of σ_0 suggest the effective hopping through the localized gap and tail states. Accordingly, the decrease in ΔE_{dc} is associated with the increased tailing of band edges and production of localized defect states near the Fermi level. Tripathi *et al.* [8] has reported that with proton irradiation there is decrease in the optical band gap (B) and increased tailing of band edges. The increase in ac conductivity with irradiation again suggests the increase in the density of localized states in the band tails. This can be explained by considering the increase in the density of neutral defect states (D^0) as explained by Shimakawa *et al.* [21].

5. Conclusions

Electrical conductivity measurements have been taken for virgin and irradiated a-As_2S_3 sample. Frequency-dependent $\sigma_{ac}(\omega)$ measurements at different temperatures show that the value of $\sigma_{ac}(\omega)$ increases with the increase in dose of radiation. The value of 's' decreases at all doses of irradiation. The analysis of the results of the conductivity suggests that the proton irradiation process induces a wide distribution of localized states in the band gap. Accordingly, the decrease in ΔE_{dc} is associated with the increased tailing of band edges and production of localized defect states near the Fermi level. The ac conductivity of the sample is found to be proportional to 's' and the temperature dependence of both the ac conductivity and the frequency exponent 's' are reasonably well interpreted in the context of the CBH model.

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