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EFFECT OF PHOTO AND THERMAL DISSOLUTION OF SILVER ON THE ELECTRICAL PROPERTIES OF a-As_2S_3

N. Goyal, A. Zolanvari, S. K. Tripathi

Department of Physics, Center of Advanced Study in Physics, Panjab University, Chandigarh, 160014, India

The paper reports the effect of dissolution of silver in arsenic sulphide. The conductivity of As_2S_3 decreases with doping. The a.c conductivity is proportional to ω^s for undoped as well as doped samples. The value of frequency exponent "s" increases with doping. A new structural model along with Correlated Barrier Hopping model has been used to explain these results.

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1. Introduction

The photo - dissolution of Ag into chalcogenide glasses is a promising phenomenon for ultrahigh resolution photolithographic process and for fabrication of optical components [1,2,3]. The investigations have shown the possibility to use Ag photo doped chalcogenide glasses (Ge-Te, As-Ge-Te) for temperature and voltage sensors [4,5]. The results of the measurements indicate that the conductivity of chalcogenide glasses decreases with photo/thermal dissolution of Ag into these glasses. The conductivity of glasses for given voltage/temperature, parameters increases tremendously after dissolution of Ag.

Structural studies using Raman spectra have indicated that the silver photo-doped films of $As_{30}S_{70}$ are homogeneous and have a structure similar to that of bulk glass $Ag_{30}As_{22}S_{48}$ [6, 7].

However, it has been observed that (by alloying Ag with As_2S_3 (bulk doping) the conductivity of As_2S_3 increases [8,9] and the large increase in the conductivity has been explained on the basis of the increase in the number of charged dangling bands. We report here measurements of electrical properties of As_2S_3 before and after dissolution of Ag into it. They show how the electrical properties of As_2S_3 change after the dissolution of silver. The interesting results (different than bulk doping of Ag) have been explained on the basis of the structural changes occurring in the material as a consequence of dissolution of Ag. A new model has been proposed. The modified Correlated Barrier Hopping model (CBH model) [10-12] has been used to explain the effect of doping.

2. Experimental

The samples in the form of pellets (diameter: 0.687 cm; thickness: 1 ÷ 2 mm) were prepared by compressing the finely ground powder of a-As_2S_3 to maximum compaction at 10^7 Pa, using a hydraulic press. All pellets were annealed at 398 K for 24 hours in order to minimize the effect of grain boundaries. X-ray diffraction pattern of the material and pellets confirmed the amorphous nature of the samples. The undoped sample was an amorphous As_2S_3 pellet, coated with aquadag on both faces for obtaining electrical contacts. The dissolution of silver into As_2S_3 was carried out separately on pellets by coating their faces with a thick layer of conducting silver paste and thereafter subjecting them to two different treatments i.e. (i) *optical*, and (ii) *thermal*. In first case, both faces of silver-coated pellets were exposed to intense UV radiations for two hours on each face. In the second case, the silver coated pellet was given a heat treatment by transferring it immediately into oven at different temperatures (below T_g) varying between 363 K to 393 K for 24 hours.

A General Radio Bridge (model 1620-A) was used for measurements of frequency dependence a.c conductance and capacitance of the samples over a frequency range of 1 kHz to 100

kHz in the temperature range 273 - 373 K. A three terminal sample holder was used for these measurements.

3. Results

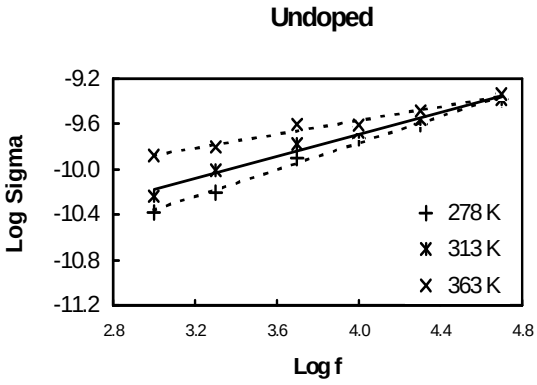

Fig. 1. Conductivity vs. frequency for different temperatures of undoped arsenic sulphide.

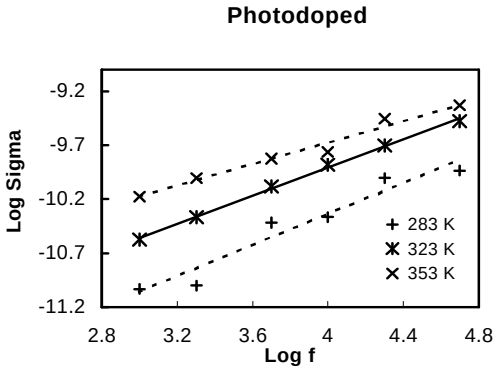

Fig. 2. Conductivity vs. frequency for different temperatures of photo - doped arsenic sulphide.

Figs. 1,2 show the frequency dependence of the measured conductivity for undoped, photo-doped and thermal-doped samples.

The following law is valid:

$$\sigma_{ac} = A\,\omega^{s} \tag{3.1}$$

The figures show that the slope of the decreases with increasing temperature for all samples. This clearly indicates that the value of “s” decreases with increasing temperature.

Fig. 3 shows the temperature dependence of frequency exponent “s” for all the samples. Figure indicates that the value of “s” decreases with increasing temperature, but increases with doping at same temperature.

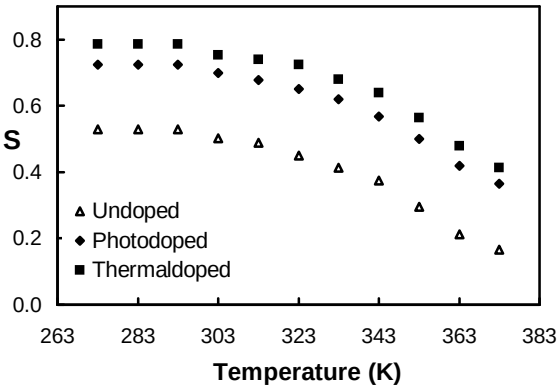

Fig. 3. Frequency exponent "s" temperature vs. for undoped, photo doped & thermal - doped samples.

However it has been observed that in case of thermal doping, if the doping temperature is increased, the value of “s” also increases (Fig. 4).

Fig. 5(a, b, c and d) shows the frequency dependence of dielectric constant k at the four different temperatures for undoped, photo-doped, and thermal-doped As_2S_3.

Figures clearly indicate that at lower temperatures, the dielectric constant is same for photo-doped and undoped As_2S_3 whereas it is higher for thermal-doped As_2S_3.

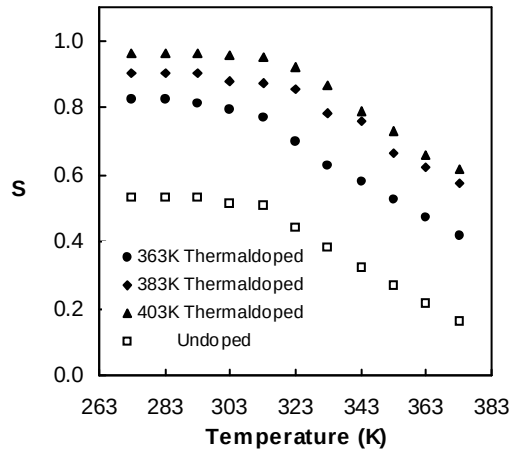

Fig. 4. Frequency exponent "s" vs. temperature for thermal - doped Ag-As_2S_3 (doping temperature being different).

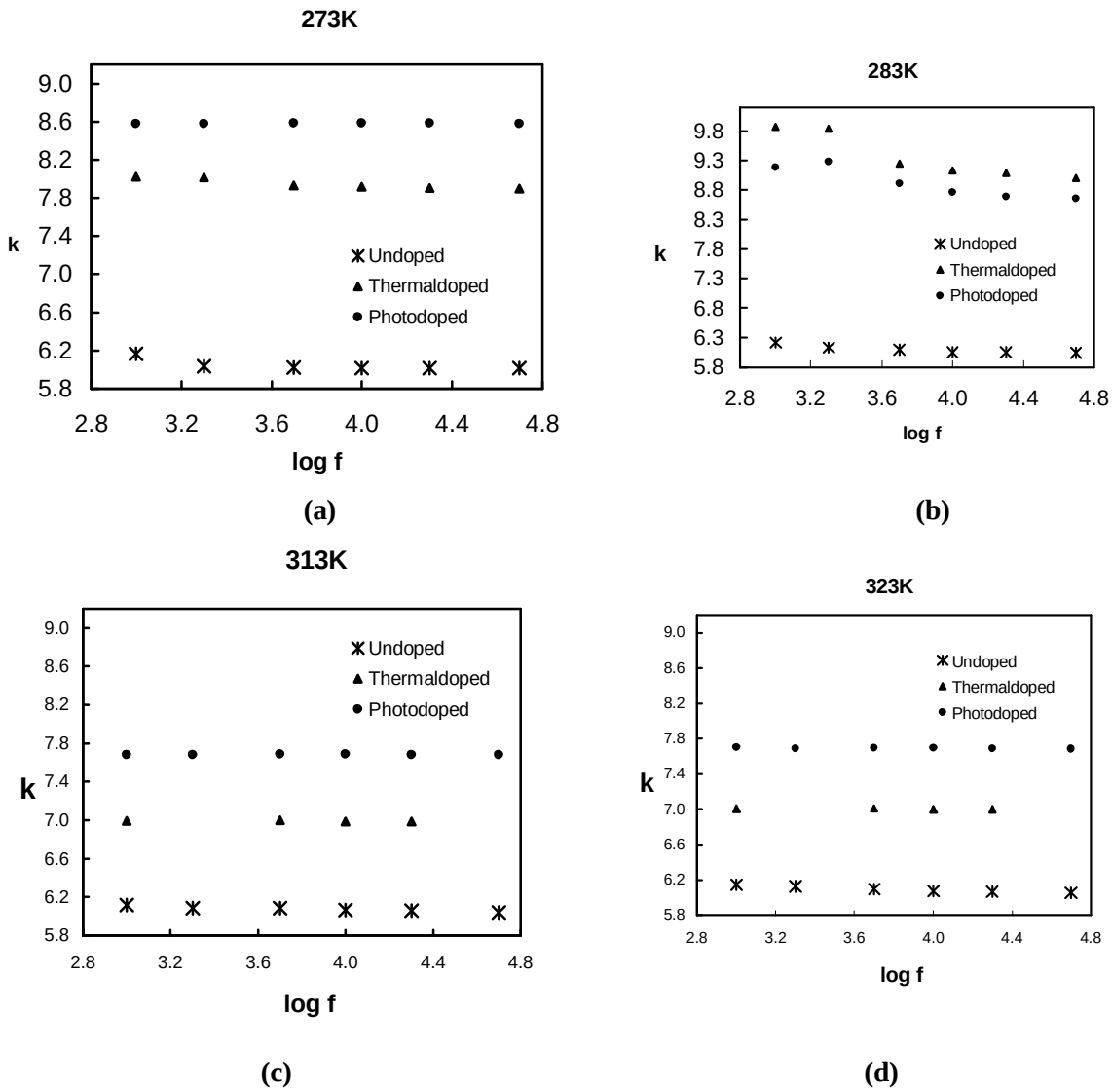

Fig. 5. Dielectric constant vs. log of frequency for undoped, photo doped and thermal doped Ag – Ad_2S_3 samples at (a) 273K, (b) 283K, (c) 313K and (d) 323K.

However, at higher temperatures the value of the dielectric constant, k, is maximum for photo-doped As_2S_3, whereas the value of k for undoped As_2S_3 does not vary much with temperature.

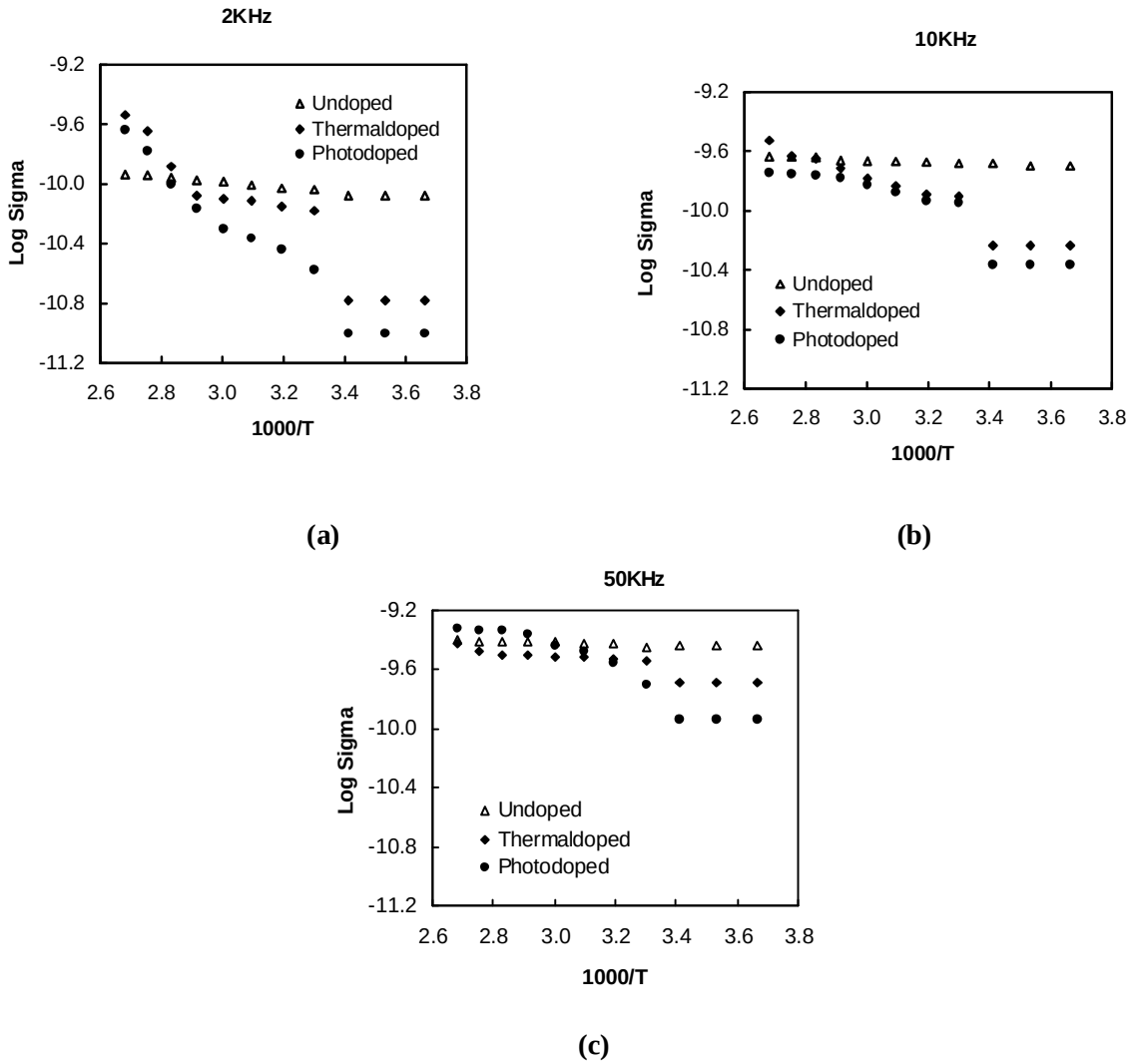

Fig. 6. Arrhenius plot for conductivity for undoped, photo doped and thermal doped samples at (a) 2 kHz, (b) 10 kHz and (c) 50 kHz.

Fig. 6(a, b & c) shows the temperature dependence of all samples of As_2S_3 at 2 kHz, 10 kHz and 50 kHz. Figures indicate that for undoped sample conductivity does not change much with temperature. However, in the case of Ag-doped samples, the conductivity shows a sharp jump in the conductivity at around 283K. It is also clear from figures that the conductivity of As_2S_3 decreases on doping, particularly in the lower temperature range. The figures show that the fall in conductivity, because of doping is maximum for photo-doped As_2S_3 at lower temperatures.

Fig. 7(a, b) shows the temperature dependence of dielectric constant k at two different frequencies (2 kHz & 50 kHz). The figures indicate that at lower temperatures the value of k for undoped and photo-doped samples is nearly constant, whereas it is slightly more for thermal-doped sample. However, at about 283K, the value of k suddenly increases for thermal - doped sample and at about 293 K there is a jump in the value of k for photo-doped sample. This jump in the value of k is higher for photo-doped samples than for thermal-doped samples.

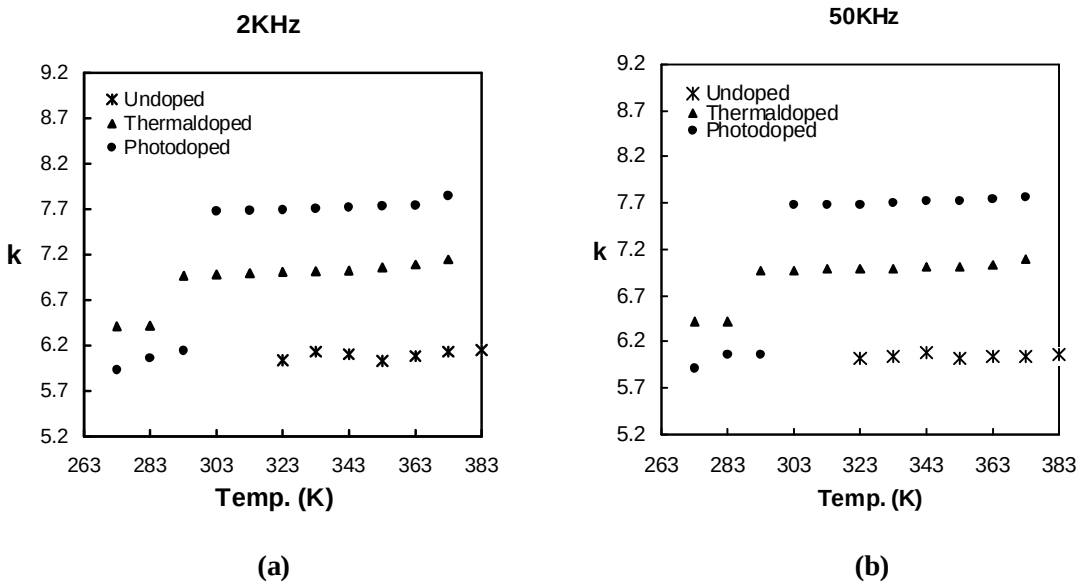

Fig. 7. Dielectric constant vs. temperature for undoped, photo doped and thermal - doped samples at (a) 2 kHz and (b) 50 kHz.

4. Discussion

The above results can be easily explained using a modified Correlated Barrier Hopping Model (CBH). It has been established that the dissolution of silver into chalcogenide involves the migration of Ag^+ ions and electrons. We have large number of D^+, D^- and unsaturated D^0 defect sites in chalcogenides [11, 12].

A new equilibrium is expected after the migration of Ag^+ and electrons, i.e.

$$D^- + Ag^+ \rightarrow [(D^-)(Ag^+)]^0 = [(As_2S_3)\text{-}(Ag^+)]^0 \tag{4.1}$$

and

$$D^0 + e^- \rightarrow D^- \tag{4.2}$$

These reactions suggest that, on doping, the concentration of D^0 centres decreases.

According to Correlated Barrier Hopping model [10]:

$$\sigma_{ac} = \frac{n}{24}\pi^2 N N_P \varepsilon' \omega R_\omega^6 \tag{4.3}$$

Where **n** is the number of polarones involved in the hopping process R_ω is the hopping distance for the condition $\omega\tau = 1$ and is given by [10, 11]:

$$R_\omega = \frac{4ne^2}{\varepsilon'\{\omega + kT\ln(\omega\tau_\circ)\}} \tag{4.4}$$

The value of frequency exponent s is calculated from equations (4.3) and (4.4) and is equal to:

$$S = \frac{d(\ln\sigma_{ac})}{d(\ln\omega)} = 1 - \frac{6kT}{W - kT\ln\left(\frac{1}{\omega\tau_\circ}\right)} \tag{4.5}$$

NN_P is given by [11]:

$$\mathbf{NN_P = N_T^{\,2}} \qquad \text{(for bipolaron hopping)} \tag{4.6}$$

Where $\mathbf{N_T}$ is the number of density of states.

$$\mathbf{NN_P = N_T^{\,2} \exp\left(\frac{-U_{eff}}{2kT}\right)} \qquad \text{(For single polaron hopping)} \tag{4.7}$$

Total conductivity is the combined mechanism of these hopping processes.

These processes are bipolaron hopping between D^+ and D^- centres, single polaron hopping between D^0 and D^- centres, and D^0 and D^+ centres. Also W is equal to W_M, which is slightly less than band-gap for bipolaron hopping, whereas, it is equal to W_1 and W_2 for two types of single-polaron hopping, which are substantially less than W_M for bipolaron hopping. The smaller values of W_1 and W_2 for single polaron hopping means, that value of R_W is much more for single polaron hopping as compared to bipolaron hopping as per equation (5), which in turn means that the contribution of each D^0 centre to conductivity is much more than D^+ or D^- centre (equation 4.3). Therefore, the diminishing in D^0 centres causes a decrease in the value of conductivity at lower temperatures as has been observed in Fig. 6a,b,c.

The neutral dipolar states $[D^-Ag^+]^0$ are expected to interact with each other, thereby forming long dipolar chains. These dipolar chains do not contribute to conductivity at lower temperatures. Fig. 6 shows that at lower temperature the dielectric constant is almost the same for pure As_2S_3, and optically doped Ag-As_2S_3, thereby indicating that the dipolar states Ag^+-D^- do not contribute to dielectric constant. However, a higher value of dielectric constant at lower temperatures for thermal-doped Ag-As_2S_3 indicates that some of these dipolar states [Ag^+-D^-] may be non-interacting (not being part of long dipolar chains) and, thereby, contributing to dielectric constant. However, at higher temperatures, the dielectric constant is higher than in undoped As_2S_3 for both thermal-doped Ag-As_2S_3 and optically doped Ag-As_2S_3. This indicates that at higher temperatures these dipolar chains break down and start contributing to increased capacitance/dielectric constant.

A jump in the value of conductivity and dielectric constant for doped As_2S_3 at higher temperatures as per Figs. 6 and 7 can be also attributed to breakage of dipolar chains. A jump in the dielectric constant of optically doped Ag-As_2S_3, which has been observed at higher temperature than that of thermal-doped Ag-As_2S_3 is also indicative of the fact that interaction of dipolar states is stronger for optically doped Ag-As_2S_3 and, therefore, requires higher energy for breaking-down the dipolar chains.

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