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# Characterization of Al photodoped amorphous $Ge_{0.1}As_{0.3}Se_{0.6}$

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Thermally evaporated amorphous $Ge_{0.1}As_{0.3}Se_{0.6}$ thin films were deposited on glass substrates afterwards an aluminum film of 100 nm thickness was deposited on top of the amorphous film. Optical absorption spectra of $Ge_{0.1}As_{0.3}Se_{0.6}$ and Al-$Ge_{0.1}As_{0.3}Se_{0.6}$ films were investigated at room temperature for as-deposited and light irradiated samples. Changes in optical parameters due to deposition of the Al thin layer as well as the effect of light irradiation time were explored. Absorption coefficient decreased after deposition of Al layer and then starts to increase with exposure time to light. In the photodiffusion process, two stages of metal diffusion could be distinguished. Optical energy gap generally decrease with deposition of Al thin layer and time exposure. A theoretical approach combining both photodiffusion kinetics and glass network approach was utilized to explain the photodiffusion process.

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## 1. Introduction

Photoinduced solid-state chemical reaction between various metals (e.g., Ag, Cu, Al or Zn) and chalcogenide glasses (also known as photodoping, photodissolution or photodiffusion) has been widely studied [1-5]. The mechanism for this phenomenon is still a subject of active investigations.

Photodiffusion is a process by which one can fabricate metal rich chalcogenide films with homogenous impurity profile without clustering of the constituting phases [6]. The incorporation of appreciable amounts of a metal in the chalcogenide material alters the composition and hence the structure and the physicochemical properties of the material. The photodiffusion process, kinetics, diffusion mechanism, diffusion profiles have been well characterized and exploited in optoelectronics (diffraction gratings, photonic band gap structures and nanolithography) [7]. The mechanism for this phenomenon is still a subject of active investigations. Understanding the kinetics of the photodissolution process and finding new suitable host glass-matrices are crucial points for these technological applications. In the present paper, detailed investigations of the photoinduced diffusion of Al in $Ge_{0.1}As_{0.3}Se_{0.6}$ glassy film are reported. Also, a theoretical approach combining both photodiffusion kinetics and glass network approach is utilized to explain the photodiffusion process.

## 2. Materials and methods

Amorphous $Ge_{0.1}As_{0.3}Se_{0.6}$ composition was prepared by melt quenching technique from Se, As and Ge of 5N purity. Appropriate amounts of elements were placed in a clean dry silica ampoule and then sealed under a vacuum of $10^{-4}$ torr. Ampoule was then heated in steps up to a temperature of $900^0$C and kept at this temperature for 20 h. The ampoule was then quenched in ice-water mixture to obtain the amorphous material. The prepared ingots were confirmed to be homogeneous and completely amorphous using X-ray diffraction. Thin films of $Ge_{0.1}As_{0.3}Se_{0.6}$ were thermally deposited on glass substrates kept at room temperature using an Edwards E-306 thermal evaporator under a pressure in the order of $10^{-5}$ torr. Film growth rate and film thickness were monitored during growth using a quartz crystal thickness monitor. The growth rate was about 10Å/S and film thickness was about 1000Å. Thin layer of Al, 100 Å, was deposited on top of the amorphous films. Amorphous nature of the grown films was confirmed using X-ray diffractometer, type Shimadzu XD-D series. Films were confirmed to have the desired composition using an EDX unit attached to Joel SEM. Photodoping was performed using a halogen lamp through an IR cut filter to irradiate samples from the Al deposited side. The intensity was estimated to be approximately $10mW/cm^2$. The temperature of the glasses was kept at 25±2 °C during the irradiation process. Diffusion of Al into the chalcogenide film (homogeneity of the photodoped thin films) were clearly confirmed by the electron dispersive X-ray (EDX) at different points of the film. Optical measurements were carried out at room temperature in the spectral range from 200nm-1100nm using UV/VIS Shimadzu 160A spectrophotometer.

## 3. $Ge_{0.1}As_{0.3}Se_{0.6}$ network and photodoping process

Photodiffusion of metals into chalcogenide glasses is driven by the formation of charged defects in the chalcogenide glass. Charged defects are formed by exposure to light and results in the creation of an electrical potential within the metal-chalcogenide film interface. Exposure to light is critical for metal photodiffusion, where light is absorbed at or near the interface between the doped and pure chalcogenide layers [9,10]. In this process, electrons are trapped by metal ions [11,12], while holes move further into the chalcogenide film and are trapped there. The electric field formed by the negatively charged chalcogen atoms and positively charged metal ions can be sufficient for the metal ions to overcome the energy barrier at the interface. Therefore the penetration of the metal into the chalcogenide during photodoping is due to the difference in electrochemical potentials and the process was considered to be similar to that occurring in a galvanic cell, where the more electropositive metal is dissolved into the electrolyte [13]. Kluge [14] considered the process of photodiffusion of metals in chalcogenides as an intercalation reaction. This can be realized in chalcogenide glasses mainly because they possess relatively rigid covalent bonds mixed with soft van der Waals interconnections. This type of structure ensures formation of voids and channels where the diffusing ions can migrate and can be hosted. The reaction can be efficient when the reversible transport of ions and electrons can be achieved, accompanied by formation of bonds with the host matrix, according to the reaction:

$$C_2^0 + e\text{-} + M^+ \rightarrow C_1^- M^+ \qquad (1)$$

This reaction describes the transition of an initially twofold covalently bonded chalcogenide atom $(C_2^0)$ into a $C_1^-$ charged unit possessing only a single covalent bond and an excess electron that establishes an ionic bond with positive metal ion $(M^+)$. Equation (1) shows the importance of the potential in forming the new $C_1^- M^+$ bonds of the intercalation product. The possible number of these bond-units is fairly high as the chalcogenide glasses are capable of forming a number of single $C_1^-$ centers under the influence of light illumination. Once metal is introduced into the chalcogenide glass, its further migration into the chalcogenide glass continues. The photodiffusion kinetics depends on a number of factors such as light intensity [15], light wavelength [16], temperature [17], pressure [18], external electric field [19], composition of the hosting glass [20], and the atmosphere in which the diffusion process is performed [21]. Referring to figure (1) suggested by Elliott [22], photodiffusion (PD) reaction starts in a small amount, region (I) known as the 'induction' period. This is followed by what is known as an acceleration region (II) may be observed where PD increases linearly with time. Another region known as deceleration region (III) marked by a parabolic behavior may also be observed. Eventually the reaction stops (IV) when the metallic layer is totally photodissolved or has penetrated the entire thickness of the chalcogenide film. In the Current work diffusion front propagates through the chalcogenide film following the behavior shown in figure (2). Comparing the obtained curve with that in Fig. 1, two stages of diffusion process can be distinguished. The first stage appears at the beginning of the diffusion process, in which the rate of change of the photodoped thickness is more rapid than the second stage. Transition between the two stages may be related to the exhausting of the metal layer source. This type of two-stage behavior was also reported by other authors [23-24]. Another approach that may help in clarifying the photodiffusion process is the study of coordination number change and the consequent change of the glass network type during and after photodiffusion process. The concept of continuous random network (CRN) introduced by Zachariasen [25], assumes that the structure of an amorphous solid can be viewed as a network of bonds between atoms that are topologically disordered. For a chalcogenide compounds of the type Ge-As-Se, where Ge stands for any atom that is fourfold bonded, As any atom that is threefold bonded and Se any atom that is twofold bonded. When twofold-coordinated Se atoms dominate, the network is flexible, and does not resist external strain, so the elastic modulus are zero in this model and remain quite small when the neglected forces are included[26], as external strains can be accommodated without changing covalent bond lengths and bond angles in the network. As the chemical composition is changed and the concentration of As and Ge atoms increases, at some point the network becomes rigid. This means that bond lengths and/or bond angles must be changed, at a considerable cost in energy, when the network is deformed. This situation is described as rigidity percolation. Composition of the type $Ge_x\ As_y\ Se_{1\text{-}x\text{-}y}$ mainly consists of atoms with coordination 4, 3 and 2 respectively, and forms a large random covalent network that contains no dangling bonds. For a total number of atoms is N, there are $n_r$ atoms with coordination r where:

$$N = \sum_{r=2}^{4} n_r$$

The mean coordination can be defined as:

$$\langle r \rangle = \frac{\sum_{r=2}^{4} r n_r}{\sum_{r=2}^{4} n_r} = 2 + 2x + y$$

The mean coordination number, $\langle r \rangle$, (where $2 \le \langle r \rangle \le 4$), gives a partial but very important description of the type of network. It can be the determining parameter in describing many experimental results that relate to structure, vibrations, hardness, the glass–transition temperature, etc. [27–29]. Applying the above formula to the composition under investigation with the ratios of Ge, As and Se are 0.1, 0.3 and 0.6 respectively, the mean coordination number is 2.5. The value of $\langle r \rangle$ = 2.4 is known as rigidity percolation threshold, RPT. Above $\langle r \rangle$

= 2.4 the network is predominantly composed of rigid regions while below this value it has mainly floppy regions. This means that $Ge_{0.1}As_{0.3}Se_{0.6}$ will have a rigid network structure. When Al atoms are incorporated into the glass network via photodoping process, the mean coordination number of the composition will increase, as the coordination number of Al is 4. A change in the type of glass network towards a more rigid network occurs as a result of Al addition. This type of structure ensures formation of voids and channels where the diffusing ions can migrate and can be hosted.

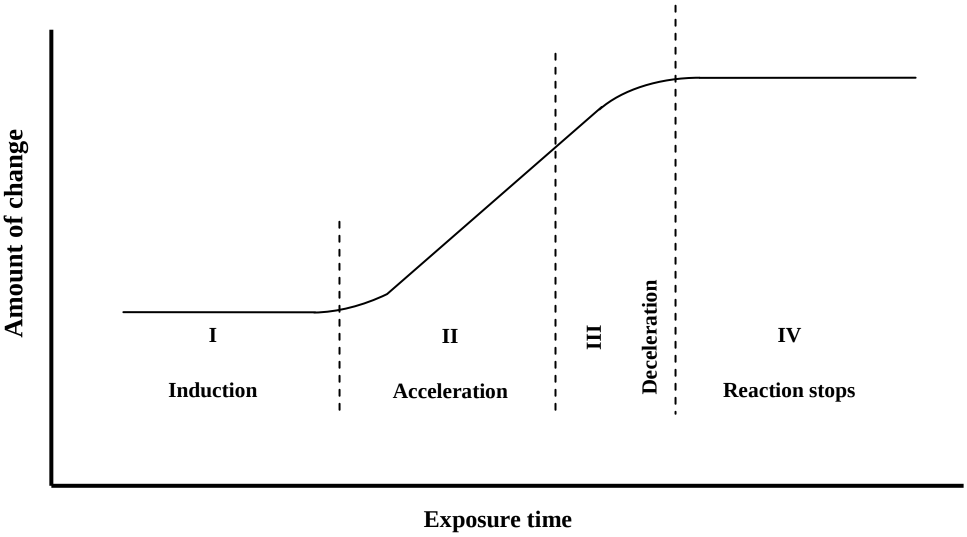

*Fig. 1. Schematic illustration showing the various stages encountered in the photo-dissolution of metals in chalcogenide glasses*

## 4. Results and discussions

Diffusion of Al layer into $Ge_{0.1}As_{0.3}Se_{0.6}$ film was monitored by measuring optical absorption with exposure time. Fig. 3 shows variation of absorption coefficient with photon energy for pure and Al-photodoped samples. The absorption coefficient generally increases with photon energy for all samples. Deposition of Al layer onto the chalcogenide film causes a decrease in absorption coefficient while the same pattern of change with photon energy is preserved. Exposure to light resulted in increasing absorption coefficient due to the photodiffusion of Al into the chalcogenide layer. This also leads to a decrease in optical energy gap. However, with increasing exposure time for more than two hours, absorption coefficient decreases and then goes to saturation or steady state where nearly no change occurs with increasing exposure time, Fig. 2. This indicates that Al layer is now totally dissolved into the chalcogenide layer. Fig. 4, shows the variation of $(\alpha h\nu)^{1/2}$ with photon energy, hν. Optical energy gap was determined by extrapolating the nearly linear part of the plot and taking the intersection with energy axis to be the optical energy gap value. Variation of optical energy gap with exposure time is shown in Fig. 5. A decrease in optical energy gap is observed with addition of Al layer. This may be due to the incorporation of Al atoms into the chalcogenide matrix. Diffusion of Al into the chalcogenide film may lead to the increase the randomness and field fluctuations into the matrix. This consequently results in increasing density of localized states into the gap which will in turn increases transition probabilities between valence and conduction bands and hence narrowing of the gap. The obtained experimental results are confirmed by the theoretical results discussed above. The obtained results are consistent with that of references [30-32].

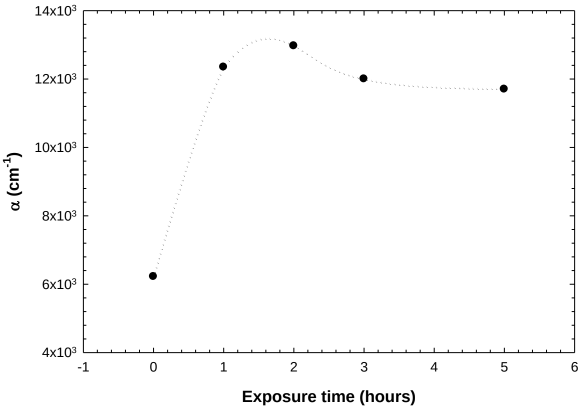

*Fig. 2. Change of absorption coefficient with exposure time*

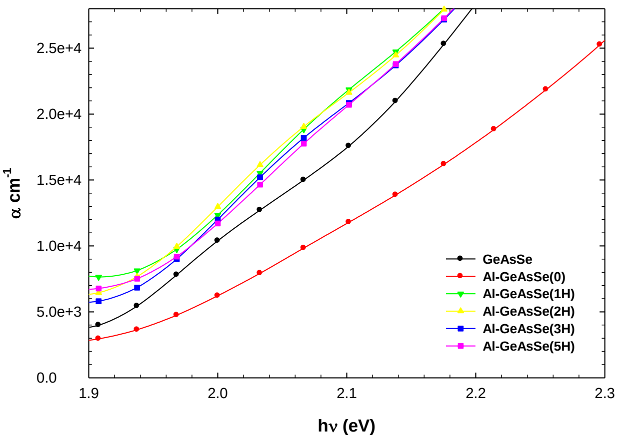

*Fig. 3. Absorption Coefficient Vs. incident photon energy for pure and Al-photodoped $Ge_{0.1}As_{0.3}Se_{0.6}$*

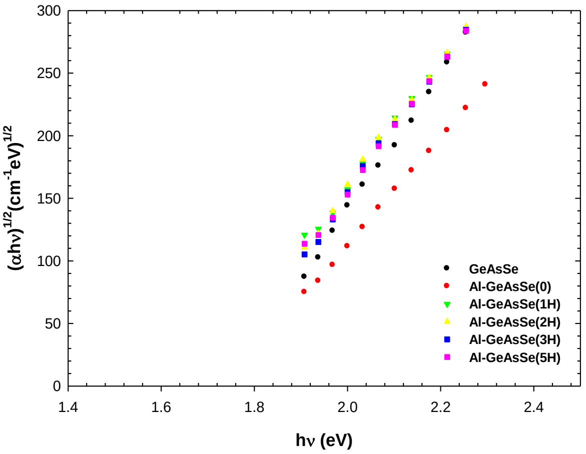

*Fig. 4. Variation of $(\alpha h\nu)^{1/2}$ with photon energy pure and Al-photodoped $Ge_{0.1}As_{0.3}Se_{0.6}$*

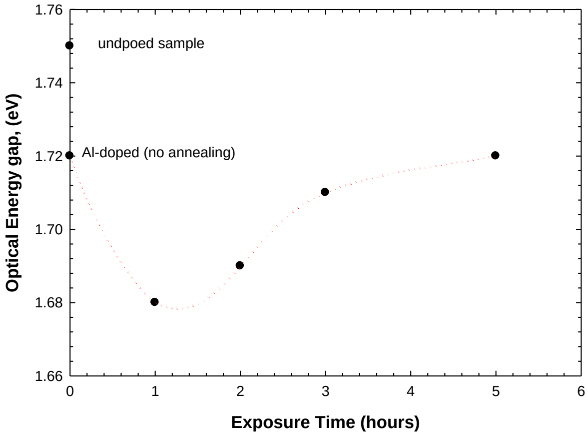

*Fig. 5. Variation of Optical energy gap with exposure time*

## 5. Conclusions

Addition of Al metal to chalcogenide amorphous thin films by photodoping method is possible although it occurs in a slaw manner. Incorporation of Al into the chalcogenide glass network using photodoping technique leads to increasing the mean coordination number and a consequent change of the type of glass network towards a more rigid network. The photodoping process in the current work was observed to occur in two stages. Also, the addition of Al leads to a decrease in the optical energy gap to a certain limit and then a increase is observed which goes to steady state with time. This may be related to photodiffusion of metal atoms until the metal layer is totally exhausted.

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