# Effects of electric fields on the silver photodoping of As<sub>2</sub>Se<sub>3</sub> films

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The effects of different electric fields (4.2, 8.3, 12.5, 16.7 and  $20.8 \text{ V cm}^{-1}$ ) on the sheet resistance,  $R_s$ , and optical band gap,  $E_{obg}$ , of As<sub>2</sub>Se<sub>3</sub> samples (1 × 10<sup>5</sup> nm) that were photodoped by Ag (5 × 10<sup>3</sup> nm) have been studied. The  $R_s$  and  $E_{obg}$  of samples subjected to an electric field of 12.5 V cm<sup>-1</sup> decrease linearly to a distance of 5 mm from both electrodes, and then saturate at larger distances. This result suggests that there is a critical value of the electric field which affects photodoping. The dependence of  $R_s$  and  $E_{obg}$  on the distance from the electrodes shows similar profiles for these electrodes.

### 1. Introduction

The Ag photodoping phenomenon in chalcogenide glass is widely known. After the publication of the photoanalysis of silver, which was epitaxied on chalcogenide, by Kostyshin et al. [1], there have been many experiments on the mechanism of Ag photodoping on chalcogenides and about the electrical, structural and optical properties of Ag-photodoped chalcogenides. The fact that the depth of Ag doping induced by light in chalcogenides is as deep as 20 µm was reported by Shimizu et al. [2]. Kokado et al. [3] reported that the photodoping of Ag, unlike thermal doping, has directionality which is dependent on the direction of the light. Also, Yamaguchi et al. [4] stated that the diffusion of Ag photodoped on Ag<sub>2</sub>Se<sub>3</sub> is a two-stage process: diffusion in a direction parallel to the light is followed by diffusion due to density gradient. In these experiments, since Ag is ionized in photodoping on Ag<sub>2</sub>Se<sub>3</sub>, and a Coulomb attractive field is induced in the incident direction of the light, Ag is doped. Although many experimental results have been obtained, the understanding of the photodoping mechanism is still incomplete and many more experimental investigations are necessary.

In this paper, during the process of photodoping Ag to  $Ag_2Se_3$  film, the effects of the electric field, which is perpendicular to the field induced by light in the chalcogenide glass on photodoping, on Ag have been examined using measurement of the sheet resistance and the optical band gap.

## 2. Experimental procedure

Reagents used in this work are As with a purity of 99.999%, Se with a purity of 99.999%, and Ag with a

purity of 99.99%. First, As and Se are mixed in the correct composition, placed on the quartz tube, and the tube is evacuated. Then, it is melted at 990 °C in an electric furnace and cooled quickly to get a substrate. The sample was made using the following procedures: first, two Au electrodes on a slide glass were made by vacuum evaporation using Au with a purity of 99.99% as shown in Fig. 1. After making a  $1 \times 10^5$  nm As<sub>2</sub>Se<sub>3</sub>



Figure 1 Schematic diagram of the sample to be photodoped with Ag while the field is applied to an  $As_2Se_3$  film.  $\Box$ ,  $\alpha$ -As\_2Se\_3 (10<sup>5</sup> nm);  $\boxtimes$  Ag layer (5 × 10<sup>3</sup> nm);  $\bigotimes$  Au electrode.

film on the epitaxial Au electrodes, Ag with a thickness of  $5 \times 10^3$  nm was evaporated on the As<sub>2</sub>Se<sub>3</sub> film for the purpose of photodoping.

The photodoping and the electric fields were provided by applying voltages of 5, 10, 15, 20 and 25 V to each electrode and simultaneously irradiating the sample with light  $(0.8 \text{ mW cm}^{-2})$  from a mercury discharge tube (300 W). In this process, the resistance of the Ag film increases as photodoping proceeds [5]; thus, when the resistance becomes  $> 30 \text{ M}\Omega$ , the photodoping stops. Au was evaporated on to a photodoped sample to make planar type electrodes for the purpose of measuring the sheet resistance, and was then divided by scratching with a razor blade at intervals of 1 mm from electrodes, as shown in Fig. 2. The sheet resistance  $(R_s)$  of each sample was derived from the I-V characteristic which was obtained using a d.c. power supply (HP 6002A) and an electrometer (Keithley 602). The light absorption curve was obtained from the light absorption spectrum via a dual beam spectrometer (HP 8430).

### 3. Results and discussion

For samples that were treated with applied voltages of 5 and 10 V, the change of the sheet resistance between the two electrodes was almost constant ( $R_s = 2.5 \times 10^9 \,\Omega \,\mathrm{cm}^{-2}$ ). However, for samples subjected to 20 and 25V, the As<sub>2</sub>Se<sub>3</sub> film at the electrode site was destroyed, as shown in Fig. 3. The sample with a 15V applied voltage showed a sheet resistance profile where the resistance decreased linearly to a point 5 mm from both electrodes and had a constant value beyond that point as shown in Fig. 4.

Although there may be other explanations of the photodoping process of Ag on  $As_2Se_3$ , Kokado explains it in the following manner [3]. Light irradiates the  $As_2Se_3$  to be photodoped with Ag. The irradiated light creates photocarriers (electron-hole pairs) in the  $As_2Se_3$ ; then Ag captures the hole and ionizes to make Ag<sup>+</sup>. The ionized Ag from this process is diffused into the  $As_2Se_3$  by the Coulomb interaction from the anion in the  $As_2Se_3$ . This Ag diffusion is considered to be photodoping, because the electric field is induced by light; it is sometimes called a photo-induced field [6]. Thus, applied electric fields below 10 V do not affect the photo-induced field which is present under photo-doping, and this explanation was easily ascertained by comparison with samples which were not subjected to



Figure 2 Schematic diagram of the sample divided by grooves 1 mm apart made from one electrode to the other to measure the sheet resistance and the absorption curves.  $\boxtimes$ , Au electrode;  $\Box$ , cleaved As<sub>2</sub>Se<sub>3</sub> (Ag photodoped).

a voltage during photodoping. The destruction of the  $As_2Se_3$  film for applied voltages above 20 V is considered to be a destruction of the insulation induced by an excessive transfer of Ag ions due to the new effect of an applied voltage beyond the range of the photo field. The clear changes of the sheet resistances of the photodoped samples for applied voltages under 15 V are due to the effect of smooth migration of the Ag ion to the anode while simultaneously maintaining the Coulomb interaction between the Ag ion and the anion. The sudden movement of the Ag ion and the anion seems to cause the film to destruct. The clear



Figure 3 A photograph of the destruction of the sample near the two electrodes when the applied voltage is 20 V.



Figure 4 Variation of the sheet resistance with respect to the distance from the electrodes when Ag is photodoped with an applied voltage of 15 V.



Figure 5 Variation in absorption with respect to the separated parts in the sample. Applied voltage of 15V. (The arrow shows the direction of increasing distance from the electrodes in increments of 1 mm. The curves with distance greater than 5 mm are not shown as they overlap with the curve at 5 mm.)

variation of the sheet resistance at 15 V is due to the effects of moving the Ag ions smoothly to the cathode and synchronously maintaining the Coulomb interaction between the Ag ions and the negative ions.

The absorption curves for the samples with applied voltages under 10 V in the photodoping process show similar behaviour when the distance from the electrodes is varied (1.35 eV < optical band gap) $(E_{obg}) < 1.37$  eV). However, when the applied voltage is 15V, the curves move until the distance is over 6 mm, and the curves overlap as shown in Fig. 5. The values of  $E_{obg}$  calculated from these results are shown in Fig. 6. It can be seen that  $E_{obg}$  decreases linearly with distance until a distance of 5 mm, and then  $E_{obg}$  is constant beyond that point. This result is similar to that for the sheet resistance. As with the optical band gap, activation energy and resistivity decrease as the quantity of Ag doped in As<sub>2</sub>Se<sub>3</sub> gets larger [7, 8]; this means that the photodoped Ag continues to ionize tc  $Ag^+$  and to transfer to the cathode.

#### 4. Summary and conclusions

From the experimental results, when Ag is photodoped in  $As_2Se_3$ ,  $Ag^+$  moves and is affected by the applied field. However, there is a threshold value for the applied voltage to affect the movement of an Ag ion, which was  $15V (12.5V \text{ cm}^{-1})$  for our experiments. When the applied voltage was 15V, the sheet resistance and the optical band gap showed linear



*Figure 6* The variation of the optical band gap with respect to the distance from the electrodes when Ag is photodoped with an applied voltage of 15 V.

characteristics with respect to the distance from the electrodes; however, the sheet resistance and the optical band gap saturated beyond this distance, which is a peculiar effect needing more study. Finally, if the composition of Ag in the samples is measured with respect to the distance from the electrodes, the relation between the photo-induced field and the applied voltage can be analysed quantitatively. Furthermore, this can be helpful in clarifying the photodoping effect (especially photo-induced fields) of Ag in chalcogenide glass.

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