# The Optical and Electrical Properties of Metal Photo-doped Chalcogenide Glasses

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The optical and electrical properties of the metal photo-doped chalcogenide glasses were studied. The optical absorption of the chalcogenide glasses (*e.g.*, the As–S, As–S–Te, and As–S–Se systems) was increased by the photo-doping of such metals as Ag and Cu in the region of their absorption edges. The electrical conductivity of the glasses also increased with the photo-doping of the metals. The effective band gap obtained from the results of the temperature dependency of the electrical conductivity decreased with the increase in the amount of metal which was photo-doped in the glasses. The results obtained in this study suggest that the metals photo-doped in the chalcogenide glasses behaved as structural modifiers of the glasses, and that the state of density in the gap was increased by the metal photo-doping.

When a binary layer of metal and chalcogenide glass is exposed to light, the metal diffuses into the glass layer. We gave the term "photo-doping"[1] to the phenomenon by analogy with the doping of foreign materials into a crystalline semiconductor. As a result of the metal photo-doping, some drastic changes take place in the optical, electrical, and chemical properties of the chalcogenide glasses. We have succeeded in using the metal-chalcogenide system as a recording process of the optical image.[2] For example, the difference in optical absorption between the metal-doped and undoped areas of the chalcogenide glass layer is sufficiently large to be recorded directly on the system by image-by-image exposure. We obtained a fine relief pattern from the image-by-image exposed layer by taking out the undoped metal with an acid and by etching the undoped chalcogenide glass area with an alkaline solution. This technique is useful in making an optical mask in microfabrication technology. It should be noted that the metal-chalcogenide glass system is suitable for holographic recording.

This paper will report the results on the optical absorption and electrical conductivity of various chalcogenide glasses in which metal is doped by illumination. Judging from the results of our studies undertaken from the standpoint of the band theory, the photo-doped metals in the glass act as structure modifiers of the chalcogenide glass.

## Experimental

The materials were prepared by fusing a mixture of appropriate quantities of elements in an evacuated fused quartz tube at 650 °C for 8 hr with occasional agitation. Four compositions of the glasses, $(As_2S_3)_1I_x$, were prepared with $x=$ 0.55, 1.0, 1.5, and 2.0 by heating a mixture of $As_2S_3$ and iodine in an Ar gas atmosphere.

The binary layer of chalcogenide glass and metal was prepared on a substratum (slide glass) by the successive vacuum evaporation ($1\times10^{-5}$ Torr) of the chalcogenide glass and metal (Ag or Cu).

The absorption spectra of the films were measured with a spectrophotometer, Shimadzu MPS-50L. A multi-beam interferometer, Mizojiri Model II, was used to measure the thickness of the layers.

The electrical-conductivity measurements were taken with surface-type cells having Au electrodes 1 mm apart from each other and with a micro-ammeter Takeda Riken TRA-1 (DC apparatus).

## Results and Dsicussion

The absorption spectrum of the binary layer represented the sum of the optical absorptions of the metal and chalcogenide glass layers. An area which had been illuminated showed an increase in transmittance in the visible and infra-red regions. This implies that the metal layer was doped into the chalcogenide glass by exposure to light. A typical example of the spectral change in the layer, showing the photo-induced reaction caused between metal and chalcogenide glass, is shown in Fig. 1. The photo-induced reaction took place at the interface of the layers when the incident photons had sufficient energy to excite the electrons of the chalcogenide glass. The tail of the absorption spectrum of the metal photo-doped glass was shifted to a longer wavelength than that of the undoped chalcogenide glass. The disappearance of the metal on the glass was confirmed by observing the decrease in the optical absorption of metal in the infrared region. To

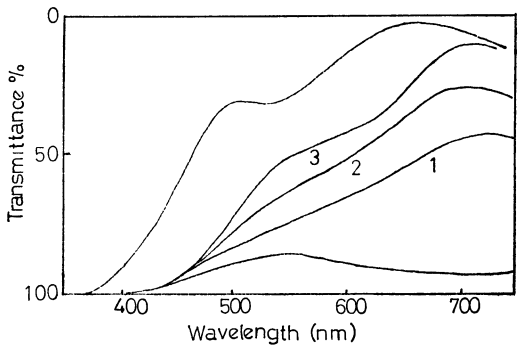


Fig. 1. Spectral transmission as affected by exposure to the light from a mercury lamp ($5\times10^{-3}$W/cm$^2$) for the indicated time $t$(sec). The top curve shows the transmission of the chalcogenide glass ($As_{16}S_{80}Te_4$) alone and the bottom curve that of the glass plus a 309 Å Ag layer before irradiation. Curve 1: $t$=60, 2: $t$=120, 3: $t$=300

1) I. Shimizu, H. Sakuma, H. Kokado, and E. Inoue, This Bulletin, **44**, 1173 (1971).

2) H. Sakuma, I. Shimizu, H. Kokado, and E. Inoue, Proceeding of the 3rd conference on solid state devices, Tokyo, 1971, p. 76.

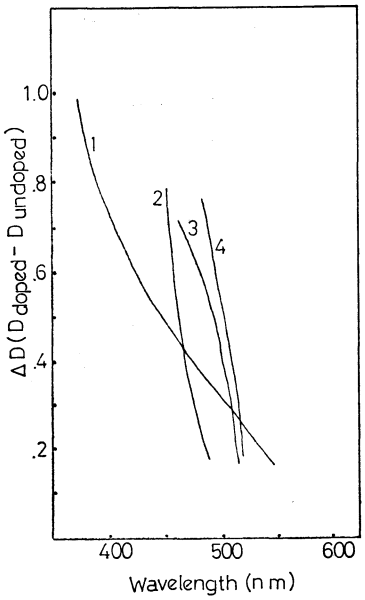


Fig. 2. Difference spectra of Ag(200 Å) photo-doped chalcogenide glasses (As-S system).
Curve 1: $As_{14.8}S_{85.2}$, 2: $As_{43.5}S_{56.5}$, 3: $As_{40}S_{60}$, 4: $As_{21.3}S_{78.7}$
$\Delta D$ shows the difference of the optical absorption of the glasses in which Ag of 200 Å in thickness have been photo-doped and the undoped ones.

show the change in the optical absorption of the chalcogenide glass layer caused by the photo-doping of the metal, the difference spectrum was made by plotting the difference in the optical absorption between doped and undoped glasses against the wavelength. Since chalcogenide glass layers (0.5 $\mu$m) thicker than the metal layer (200 Å) were used in these measurements, the change in the thickness of the chalcogenide glass layers resulting from the metal photo-doping was negligible. The difference spectral curves of As–S systems in which Ag 200 Å in thickness was photo-doped are shown in Fig. 2. The optical absorption

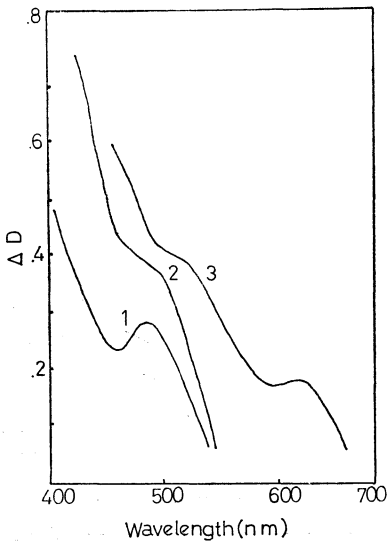


Fig. 3. Difference spectra of the Ag photo-doped chalcogenide glasses (As-S-Te system).
Ag of 100 Å (curve 1) and 200 Å (curve 2) photo-doped in $As_{16}S_{80}Te_4$. Curve 3: Ag (200 Å) photo-doped in $As_{30}S_{50}Te_{20}$

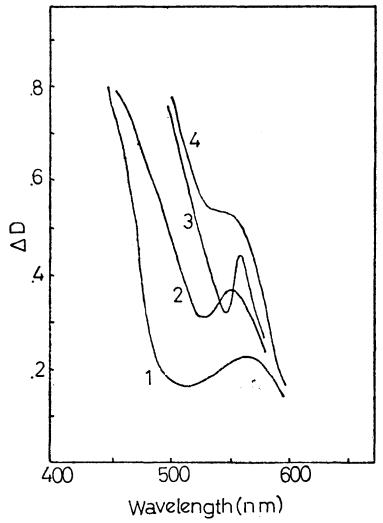


Fig. 4. Difference spectra of Ag (200 Å) photo-doped glasses (As–S–Se) system).
Curve 1: $As_{17.7}S_{70.8}Se_{11.5}$, 2: $As_{30}S_{50}Se_{20}$, 3: $As_{18}S_{40}Se_{42}$, 4: $As_{19}S_{27}Se_{54}$

was increased by metal photo-doping in each glass. Increases in the optical absorption were observed near the absorption tails of the glasses. Since no detectable change in the electron-beam diffraction pattern could be observed in the Ag photo-doped glass layer, it can be assumed that no devitrification was brought about by the Ag photo-doping. The increase in the optical absorption resulting from Ag photo-doping was also observed in other systems, such as As–S–Te and As–S–Se. The difference spectral curves are shown in Figs. 3 and 4. The increase in the optical absorption was in proportion to the amount of Ag which was photo-doped (see Curves 1 and 2 in Fig. 3). In the As–S–Se system, a discrete absorption band (maximum at 565 nm) was observed in the difference spectra, in addition to the increase in the optical absorption which was observed in the absorption tails of the host glasses.

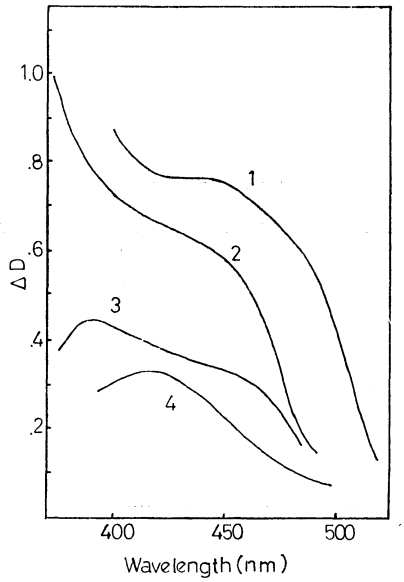


Fig. 5. Difference spectra of Ag (200 Å) photo-doped glasses ($(As_2S_3)_1I_x$).
Curve 1: $x$=0, 2: $x$=0.51, 3: $x$=1.0, 4: $x$=1.98.

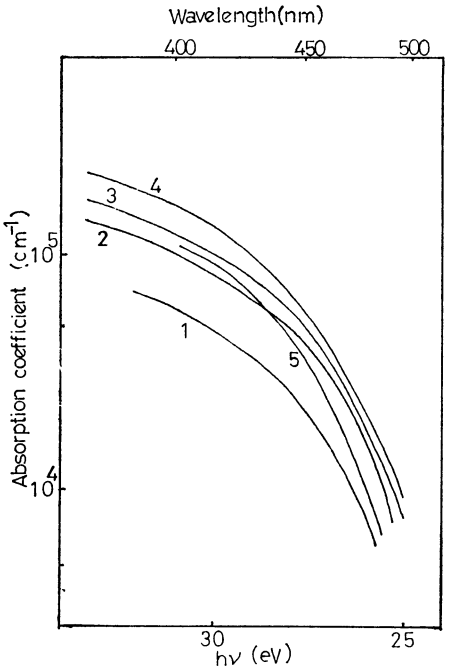


Fig. 6. Absorption spectra of the chalcogenide glasses ($(As_2S_3)_1I_x$).
Curve 1: $x=0$, 2: $x=0.51$, 3: $x=1.0$, 4: $x=1.98$.

The height of the band increased with an increase in the Se content in the glass. In this case, some localized level caused by the interaction between Ag and Se was assumed to be formed in the band gap by Ag photo-doping.

In the glass containing a halogen such as iodine, a charactristic effect on the optical absorption was observed when Ag was doped by illumination. Figure 5, for example, shows the difference spectral curves of the $(As_2S_3)_1I_x$ glass, in which Ag (200 Å in thickness) was photo-doped. A conspicuous increase in the optical absorption was found in the Ag-doped $As_2S_3$ ($x=0$). On the other hand, the increase in the optical iodine absorption was inhibited by the addition of to the glass. In this case, the tails of the optical absorption of the glasses ($(As_2S_3)_1I_x$) themselves extended to longer wavelengths than those of $As_2S_3$, as is shown in Fig. 6. From these results, it can be supposed that the photo-doped Ag in the glass is captured by iodine, forming a strong bond such as AgI.

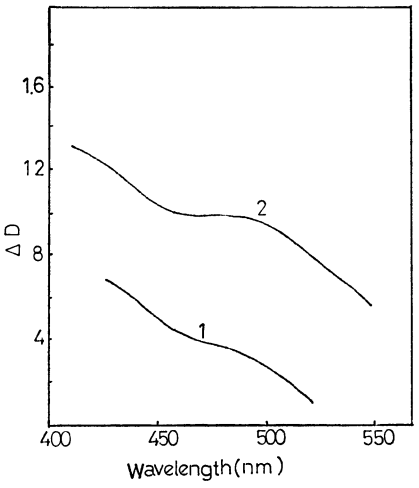


Fig. 7. Difference spectra of the Ag (200 Å) (curve 1) and the Cu (200 Å) (curve 2) photo-doped glass ($(As_2S_3)_1I_{1.98}$)

Figure 7 presents the difference spectral curves of $(As_2S_3)_1I_x$, in which the same amount of Cu as Ag was photo-doped. The increase in the optical absorption caused by the photo-doping of Cu was larger than that of Ag. In the case of Cu photo-doping, the range where the increase in the optical absorption was observed was extended to a longer wavelength than in the case of Ag.

The temperature dependence of the electrical conductivity of chalcogenide glass is generally written as:

$$\sigma = \sigma_0 \exp(\Delta E/kT) \quad (1)$$

where $\sigma$ and $\sigma_0$ are the conductivities and whose $\Delta E$, $k$, and $T$ denote the activation energy, the Boltzmann factor, and the temperature in an absolute value (K) respectively. This relation tells us that there exists a gap between valence and conduction bands such as in the intrinsic crystalline semiconductors. Since thin film was used for photo-doping in our experiment, the electrical conductivity was measured by means of a surface type cell with Au electrodes 1 mm apart from each other. The current measured with the cell while applying DC voltage (IV) increased with an increase in the magnitude of Ag which had been photo-doped, as is shown in Fig. 8. Besides, the current while applying DC voltage (10 V) against the reciprocal of the absolute temperature was shown as a straight line in the chalcogenide glass ($As_{16}S_{80}Te_4$), in which a corresponding amount of Ag had been photo-doped (see Fig. 9). The $\Delta E$ values obtained from the slope of the lines are shown in Table 1. These results imply that the conductivity was increased by the Ag photo-doping, and that, at the same time, "the electrical band gap" ($2\Delta E$) was decreased. These results coincided qualitatively with those of studies of the effect of Ag as a foreign material on the electrical conductivity of chalcogenide glass.[3] In that experiment, the chal-

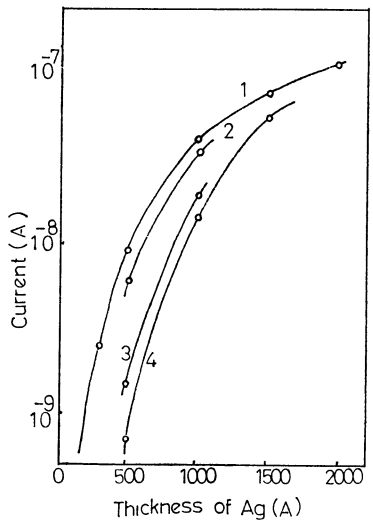


Fig. 8. Current of the Ag photo-doped glasses *vs.* the thickness of the Ag layer which has been doped in the glasses.
Curve 1: $As_{16}S_{80}Te_4$, 2: $As_{40}Se_{60}$, 3: $As_{24}S_{70}Te_6$, 4: $As_{40}S_{60}$

3) R. Andreichin, *J. Non-Crystalline Solids*, **4**, 73 (1970).

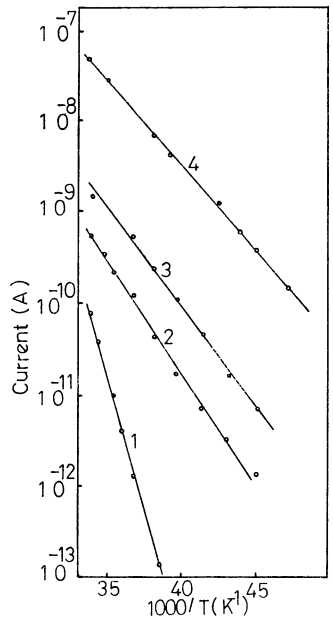


Fig. 9. Current of the Ag photo-doped glass ($As_{16}S_{80}Te_4$) *vs.* reciprocal temperature.
Curve 1: non-doped one, 2: Ag (300 Å), 3: Ag (500 Å), 4: Ag (2000 Å) photo-doped one.

TABLE 1. "ELECTRICAL BAND GAP ($2\Delta E$)" OF THE Ag PHOTO-DOPED CHALCOGENIDE GLASSES

| Composition | Photo-doped Ag (Å) | Band gap (eV) |
|---|---|---|
| $As_{16}S_{80}Te_4$ | 0 | 2.32 |
| | 300 | 0.98 |
| | 500 | 0.88 |
| | 2000 | 0.75 |
| $As_{40}Se_{60}$ | 0 | 1.88 |
| | 500 | 0.72 |
| | 1000 | 0.68 |

cogenide glass containing Ag was prepared by fusing the chalcogenide glass and Ag.

Figure 10 shows the curve obtained by plotting the current against ($1/T$) for the $As_{16}S_{80}Te_4$ layer, in which Cu of a thickness of 500 Å had been photo-doped. The effective gap obtained from the slope was 0.48 eV.

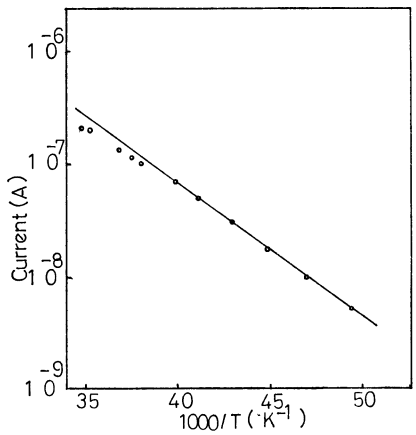


Fig. 10. Current *vs.* reciprocal temperature for the Cu (500 Å) photo-doped glass ($As_{16}S_{80}Te_4$).

This value was smaller than that of the same glass in which Ag of a thickness of 2000 Å had been photo-doped. This result coincided with the results of the effect of the photo-doped Cu on the optical absorption of the chalcogenide glass presented above. This means that Cu is a more effective modifier of the electrical structure of chalcogenide glass than is Ag.

From the theoretical ponit of view, the electrical structure of chalcogenide glass, with which the optical absorption and electrical conductivity mechanism can be elucidated sufficiently, is not clear. It is assumed by Mott[4] that the band structure of the semiconductor is retained, but with some alteration, especially since the curves of the density of the states from tails fall well inside the forbidden gap. Also Fritzsche, Cohen, and Ovshinsky[5] proposed the FCO band model modifying Mott's model to elucidate the optical and electrical properties of chalcogenide glasses.

From the standpoint of the band theory, the role of the metal which was doped into chalcogenide glass by illumination was considered to be a modifier in the band structure of the glass.

As was suggested by the band theory for the crystalline semiconductor, the absorption coefficient ($\alpha$) in an indirect transition can be written as:

$$\alpha = \text{const}\frac{|M|^2}{h\nu}(h\nu - E_0)^2 \qquad (2)$$

where $M$ is the matrix element of the electrical transition and whose $h\nu$ and $E_0$ denote the energy of the absorbed photon and the band gap respectively. If $M$ is constant, plotting $(\alpha h\nu)^{1/2}$ against $h\nu$ should result in a straight line. Typical curves showing $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the Ag photo-doped chalcogenide glasses are shown in Fig. 11. When the binary layer is used,

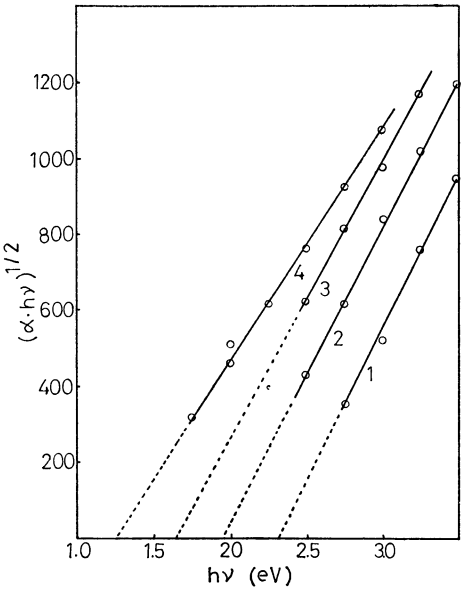


Fig. 11. $(\alpha h\nu)^{1/2}$ *vs.* $h\nu$ for the Ag photo-doped glass ($As_{16}S_{80}Te_4$).
Curve 1: non-doped one, 2: Ag (100 Å), 3: Ag (300 Å), 4: Ag (500A) photo-doped one.

4) N. F. Mott, *Advan. Phys.*, **16**, 49 (1967).
5) M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, *Phys. Rev. Lett.*, **22**, 1065 (1969).

TABLE 2. "OPTICAL GAP ($E_0$)" OF THE Ag PHOTO-DOPED CHALCOGENIDE GLASSES

| Composition | Photo-doped Ag (Å) | Optical gap (eV) |
|---|---|---|
| $As_{16}S_{80}Te_4$ | 0 | 2.30 |
| | 100 | 1.95 |
| | 300 | 1.65 |
| | 500 | 1.25 |
| $As_{43.5}S_{56.5}$ | 0 | 2.14 |
| | 200 | 1.14 |
| $As_{14.8}S_{85.2}$ | 0 | 2.24 |
| | 200 | 1.50 |
| | 400 | 1.25 |

the photo-induced doping is caused at its interface and the distribution of the photo-doped metal in the glass is not uniform. To improve the uniformity, therefore, the thin layer of the chalcogenide glass (600 Å) was used in this measurement. Except for their tails, the plots all show straight lines. The extrapolation of the linear portions of Fig. 11 intersect with the abscissa at the energy $E_0$; they are shown in Table 2. This value ($E_0$) is a convenient fiducial mark for locating the structureless absorption curve; one refers to it as the optical gap. The value for $E_0$ decreased with the increase in the amount of Ag which was photo-doped in the glass. This shows a tendency similar to the effect of photo-doped metal on the value for $2\Delta E$. However, the value for $E_0$ does not correspond quantitatively to that for $2\Delta E$ in each sample.

These results also support the idea that the photo-doped metals behave as structure modifiers in covalent noncrystalline semiconductors such as chalcogenide glasses. And resulting from the photo-doping of the metal, the state-density in the band gap increased. It may be supposed that the increases in the optical absorption and the electrical conductivity of the metal photo-doped chalcogenide glass are caused by the increase in the state-density in the gap.