4-5 INVITED: The Photo-Doping of Metal into Chalcogenide Glasses

Eiichi INOUE, Hiroshi KOKADO and Isamu SHIMIZU
Imaging Science and Engineering Laboratory, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo, Japan

When a double layer of metal and chalcogenide glass is exposed to light, the metal is doped into the glass layer. As a result of this " photo-doping ", some drastic changes take place in the optical, electrical and chemical properties of the chalcogenide glasses [1) ~ 7)]. These property changes are expected to be usefull for the imaging systems [8), 9)].

In this paper, the basic properties of the photo-doping are presented to study the process mechanism. Through the experiments, the double layers of Ag - As_2S_x ($2.6 \leqq x \leqq 18$) coated on the deck glass were used as a model photosensor.

The absorption spectra of the As_2S_x thin layers showed the blue shift as the sulphur content increased at the range, $x = 2.6 \sim 14.9$. The similar change of the action spectra was observed for the photo-doping of Ag into As_2S_x glasses, corresponding to the absorption spectral shift of the glasses. This means that the photo-doping of Ag proceed by the light absorption of the glasses.

Based on the photo-doping characteristics (optical density of Ag layer - exposure time curve) of Ag - $As_2S_{11.5}$ photosensor, under the constant irradiation at 9.2 mW/cm^2, High pressure Hg lamp, the doping process was classified into two or three stages. The initial stage was very rapid process and proceeded linearly with the irradiation time. The second stage was a slow process and was observed only when a thick Ag layer was adopted to the chalcogenide glasses.

The photo-doping rate at the initial stage changed linearly with the light intensity at the range, 0.1 ~ 100 mW/cm^2. The activation energy of the photo-doping of Ag into $As_2S_{9.6}$ glass was 0.033 eV at the temperature $-196 \sim 20$ °C. From these results, the initial stage process seemed to be the photochemical solid state change between Ag layer and the glass, including an electronic process.

The initial photo-doping rate changed with the sulphur content of the glasses at the range, $x = 2.6 \sim 18$, showing the maximum rate at $x = 6 \sim 12$. The photo-doping rate would be related with the change of the structure and the bonding state of the glass.

The photo-solubility of Ag was measured for the different chalcogenide glasses. The maximum thickness of the photo-doped Ag layer into the glass (600 Å) was determined as follows ; $As_2S_{2.6}$: 200 Å, $2As_2S_3 \cdot As_2Te_3$: 300 Å, $As_2S_{11.5}$: 400 Å, $As_{16}S_{80}Te_4$: more than 400 Å.

By the EMX measurement for the photosensor of Ag (1500 Å) - $As_{16}S_{80}Te_4$ (2 mm), it was confirmed that the doped Ag went through the glass to about 20 micron depth from the surface and its density was almost kept uniform over the doped region. The diffusion of Ag into the bulk from the surface seemed to be carried out by the hammer action with the light, because the light did not reach into the bulk zone. This was a quite different character from the thermal diffusion of Ag in the chalcogenide glasses.

The density and the doping depth of Ag in the glasses were changed with the light intensity and the irradiation time. These problems will be presented in detail. The diffusion of Ag to the lateral direction in the glasses was measured under the irradiation during and after the doping. It was confirmed to be less than 1 micron.

References ;

1) M.T.Kostyshin, E.V.Mikhailovskaya and P.F.Romanenko ; Soviet Phys. Solid State. 8, 451 (1966)

2) I.Shimizu, H. Sakuma, H.Kokado and E. Inoue ; Bull. Chem. Soc. Japan 44, 1173 (1971)

3) H.Sakuma, I.Shimizu, H.Kokado and E. Inoue ; ibid, 44, 1449 (1971)

4) H.Sakuma, I.Shimizu, H.Kokado and E. Inoue ; ibid, 44, 1723 (1971)

5) H.Sakuma, I. Shimizu, H. Kokado and E. Inoue ; The proceedings of the 3rd Conference on Solid State Devices, Tokyo 1971, Supplement to OYO BUTURI 41, (1971)

6) I. Shimizu, H. Sakuma, H.Kokado and E.Inoue ; Bull. Chem. Soc. Japan 46, 1291 (1973)

7) I.Shimizu, H.Kokado and E.Inoue ; Chemistry Letters (Chem. Soc. Japan) pp 15 (1973)

8) J.Malinowski ; Photo. Sci. Eng. 15, 175 (1971)

9) I.Shimizu, H.Sakuma, H.Kokado and E.Inoue ; Photo. Sci. Eng. 16, 291 (1972)