## A New Method for Producing Low-electrical-resistivity Patterns in Insulating Chalcogenide Glasses

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In a previous communication, 1) we have reported light-stimulated metal diffusion (named "Photo-doping") in some chalcogenide glasses. This reaction is observed even under room light, but not in the dark. The thermal diffusion of metals into chalcogenide glasses such as As<sub>2</sub>Se<sub>3</sub> has been reported thus far with respect to electrode problems, 2) but no such rapid photo-reaction between metal and chalcogenide glass had ever been reported until our previous paper, 1) in which the chemical aspect of this phenomenon was discussed. This phenomenon is thought to be related to the disordered structures of chalcogenide glasses. 3) The detailed mechanisms are now under investigation.

In this paper, we will report on marked changes in the electrical properties of metal photo-doped chalcogenide glasses. Thin metal layers (Ag, Cu, etc.) were deposited in vacuo onto the surfaces of the evapolated films (or bulks) of chalcogenide glasses composed of As, S, and Te elements (such as  $As_{24}S_{70}Te_6$  (atomic %)). As is illustrated in Fig. 1, the optical transmission of the film ( $As_{24}S_{70}Te_6$ ) decreased to a low level upon metal (Cu) deposition (Curve (1)—Curve (2)). The (1) and (2) curves of Fig. 1 are the transmission spectra

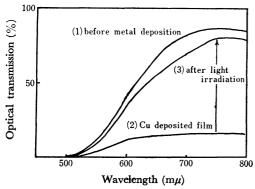


Fig. 1. Optical transmission spectra of Cu doped chalcogenide film

of the film before and after metal deposition respectively. Photo-doping was performed by light irradiation from a 250 W high-pressure Hg lamp.¹) The progress of photo-doping was followed by the change in the optical transmission of the metal-chalcogenide glass double layer as a result of metal diffusion (Curve (2)→Curve (3)). A detectable change in the transmission was observed within a few seconds. In all the cases measured, the transmission spectra of the metal-doped films

(Curve (3)) were nearly equal to those of the chalcogenide layers (Curve (1)) except for slight shifts of the thresholds to longer wavelengths.

Gold electrodes, which undergo no photo-reaction with chalcogenide glasses, were deposited onto metal-doped film surfaces and the electrical conductivity of these surface-type cells was measured (Fig. 2 (a)). The changes in the conductivity of the Ag-doped and the Cu-doped chalcogenide glass films are shown in Fig. 2 (b) and compared with those in the undoped film. The conductivity change depended on the quantity of doped metal and was over the order of magnitude of 106 in the case of Ag doping. These high electrical conductivities may originate from the formation of new compositions with doped-metal elements.

It should be noticed that the metal-doped areas which show high electrical conductivity can be formed at desired positions of the chalcogenide glass film by imagewise exposure and by the removal of unnecessary metal. (It may also be possible to utilize the undoped metal as low resistivity patterns.) A resolution of 1000 lines/mm was obtained from a preliminary examination by holographic means. If necessary, undoped chalcogenide areas can be dissolved by alkaline solutions and insoluble metal-doped areas thus left on the substrate.

This method for producing low resistivity patterns can possibly be used for a photo-imaging system and may also find applications in optical memories.<sup>4)</sup>

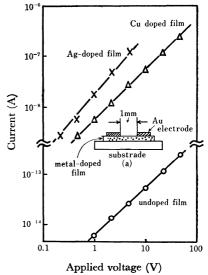


Fig. 2 (b). I-V characteristics of metal-doped chalcogenide

<sup>1)</sup> I. Shimizu, H. Sakuma, H. Kokado, and E. Inoue, This Bulletin, 44, 1173 (1971).

<sup>2)</sup> L. A. Freeman, R. F. Shaw, and A. D. Yoffe, *Thin Solid Films*, 3, 367 (1969).

<sup>3)</sup> B. T. Koloniets, Phys. Status Solidi, 7. 359, 713 (1964).

<sup>4)</sup> H. Sakuma, J. Shimizu, H. Kokado, and E. Inoue, This Bulletin, 44, (1971), in press.