The Photo-doping of Metals into Solids for New-type Imaging Systems

Isamu SHIMIZU, Hiraku SAKUMA, Hiroshi KOKADO, and Eiichi INOUE

Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received February 23, 1971)

New imaging systems are presented by using photosensitive thin films of chalcogenides-metal or metal halogenides-metal systems. Photosensitive thin films of PbI_2-Ag have been used for recording the hologram by Tubbs,[1] and the photoreaction was described as follows:

$$PbI_2 \xrightarrow{h\nu} (PbI_2)^*$$
$$(PbI_2)^* + 2Ag \longrightarrow Pb + 2AgI \quad (1)$$

Kostyshin *et al.*[2] mentioned, without giving any details, that Ag could be reacted with As_2S_3 by light.

The photosensitive double layers were prepared by the successive vacuum (10^{-5} Torr) evaporation of viterous chalcogenides (ex., As_2S_3, $As_2Se_3As_2Te_3$, *etc.*) and metal (Ag, Cu, Cd, *etc.*) on glass supports. When the (As_2S_3-Ag) sample was irradiated with light at room temperature, a metal (Ag) was diffused into the chalcogenide layer (As_2S_3). The photoinduced reaction may be presented as follows:

$$As_2S_3 + Ag \xrightarrow{h\nu} As_2S_3(Ag) \quad (2)$$

The name "photo-doping" is given to the reaction. The light absorption in the visible region due to the Ag layer was diminished by the irradiation. On the other hand, the absorption edge of the Ag-doped As_2S_3 layer (As_2S_3 (Ag)) was shifted to a longer wavelength. The absorption spectra of As_2S_3 and As_2S_3 (Ag) are shown in Fig. 1. The reaction (2) occurred upon irradiation with light from a He–Ne laser (6328Å). As the light absorption was not admitted at 6328Å on the As_2S_3 layer, the photoreaction seemed to be induced by the excitation of Ag with light as follows:

$$Ag \xrightarrow{h\nu} Ag^*$$
$$Ag^* + As_2S_3 \longrightarrow As_2S_3(Ag) \quad (3)$$

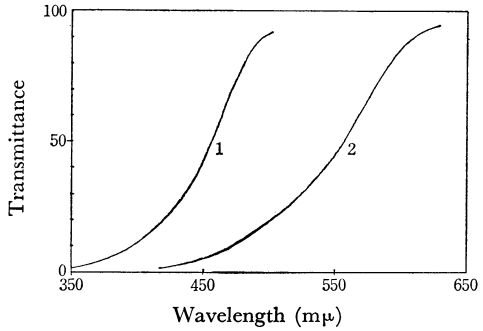

Fig. 1. Absorption spectra of As_2S_3 and As_2S_3(Ag).
1. As_2S_3
2. As_2S_3(Ag)
} thickness 1250 Å

After the image-wise exposure, the fixed image was obtained by dissolving out the unchanged Ag layer by using a mixture of sulfuric acid and potassium dichromate. As As_2S_3 was easily soluble in an alkali solution, while As_2S_3 (Ag) was not, an As_2S_3 (Ag) image which well resists etching with acids, including that of a HF solution, was obtained by dissolving the As_2S_3 part.

The photo-doping efficiency greatly depended on the host materials. A layer of Ag more than 0.1 μ thick was doped in the $As_2Se_3As_2Te_3$ layer (1 μ thick) within a few seconds by irradiation with a 250W-Hg lamp. The "photo-doping" process has a number of advantages, such as a high resolution, a wide range of sensitivity in the visible region, and a higher sensitivity than photopolymers; it is thus of considerable interest in the recording of images and photomicrofabrication.

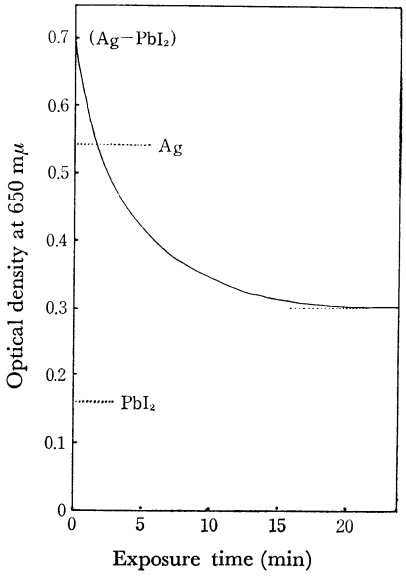

Fig. 2. Density change of PbI_2-Ag system under illumination of a Hg lamp.
thickness of PbI_2: 0.2 μ
light intensity (high pressure Hg lamp): 3.5×10^{-2} W/cm^2

Concerning the PbI_2-Ag system, the Ag layer was diffused into the PbI_2 layer by irradiation with light, and it educed Pb upon continuous irradiation. The relation between the irradiation time and the density change in the PbI_2-Ag system is shown in Fig. 2. The photoinduced reaction of PbI_2-Ag may be represented as follows:

$$(PbI_2)^* + 2Ag \longrightarrow PbI_2(2Ag)$$
$$PbI_2(2Ag) \longrightarrow Pb + 2AgI \quad (4)$$

The first step of this reaction is similar to the photo-doping of the As_2S_3-Ag system. The difference in electrical resistivity between PbI_2 and PbI_2 (Ag) was enough to make electrophotographic images. The electrical properties were also drastically changed by the photo-doping of metals in viterous semiconductive chalcogenides; this is of interest for the making of electronic devices.

1) M. R. Tubbs, *J. Photogr. Sci.*, **17**, 162 (1969).
2) M. T. Kostyshin, E. V. Mikhailovskaya, and P. F. Romanenko, *Soviet Phys. Solid State*, **8**, 451 (1966).