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Pressure Dependence of Ag Photodoping in Amorphous As-S Films

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The photodoping process in Ag/As₂₅S₇₅ layers subjected to hydrostatic compression up to 100 kbar has been studied. With an increase in pressure, the response becomes faster and then quenched above a threshold pressure, which is 70–80 kbar when light is incident upon the Ag surface. The characteristic suggests that migration of Ag ions between As-S molecular clusters and/or accumulation of electronic carriers in the Ag-doped region is responsible for the photodoping.

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The photographic phenomenon observed in the bilayer structure consisting of amorphous As₂S₃ and metallic Ag was discovered by Kostyshin *et al.* in 1966.¹ Since then, considerable work has been carried out for applications to image recording and ultrahigh-resolution photolithography.² The process was termed “photodoping,” “photodissociation,” or “photoenhanced diffusion,” and has been found in a wide class of amorphous chalcogenide semiconductors contacted with metals and alloys such as Ag, Cu, and Ag₂S. Despite the universality and the technological importance of this phenomenon, the understanding of its mechanism remains unresolved.

Photodoping is considered as resulting from photoinduced migration of metallic ions in chalcogenide glasses.¹ Different from the thermal diffusion process, however, it has been shown that the depth profile of the metal concentration in the photodoped region is nearly constant.¹ We assume therefore that the actual process under light illumination proceeds in a trilayer structure consisting of metal-photodoped region-undoped chalcogenide glass. One of the essential problems here is the composition and microscopic structure of the doped region. This problem cannot be answered easily, since the phenomenon is observed in various metal/chalcogenide systems. Nonetheless, extensive work by Owen and co-workers^{1,3} has demonstrated that a homogeneous glassy phase of compositions around AgAsS₂ is produced when Ag is photodoped into As_xS_{100-x} films with $x \simeq 30$. Recent studies give microscopic structural models for the Ag-doped glass.⁴ In contrast, it is known that the Ag(Cu)-chalcogenide glassy alloy is a good ionic conductor,⁵⁻⁷ a fact which implies that ionic conduction is involved in the photodoping process. However, the details are not known. Novel insight is required to elucidate the migrational motion of the Ag⁺ ions. Another problem is where the actinic radiation is absorbed. To solve this problem, much work has been done on studying the spectral dependence and the so-called lateral photodoping phenomenon.¹ The result, although it is ambiguous, suggests that photoinduced electronic excitation in and around the doped region is responsible for the photodoping.

We take a new approach to this phenomenon. Although it is known that the photodoping process is suppressed at low temperature,^{1,7} which lends support to the ionic-migration model, no studies have been conducted to examine the photodoping at high pressure. We have measured the change in the photodoping efficiency as a function of hydrostatic pressure up to 100 kbar. The photodoping efficiency increases and then decreases with increasing pressure. This result is discussed in relation to structural and electronic changes in chalcogenide glasses induced by compression.

The photodoping process in vacuum-evaporated bilayer films consisting of 250-Å-thick Ag and 1.5-μm-thick As₂₅S₇₅ has been examined.⁸ The bilayer film, which was peeled off from substrates, was pressurized in a gasketed diamond-anvil cell, with pressure calibration using the ruby photoluminescence.⁹ In addition, the pressure dependences of the optical transmittance and volume compression in As₂₅S₇₅ films and in Ag-doped films, which had a composition nearly equal to AgAsS₂ throughout the thickness,¹⁰ were measured using microscope optics.¹¹

Upon light excitation, the optical transmittance of the bilayer film increases in response to a decrease in the Ag-layer thickness, and the photodoping efficiency can be evaluated through the changing rate of the transmittance.¹² The results obtained using light beams of photon energies 2.0 and 2.3 eV are plotted in Fig. 1 as a function of applied pressure. The transmittance change, typically from 10% to 70%, was monitored using weak monochromatic light of photon energies 1–2 eV, which were selected to be lower than the optical-absorption edge (Fig. 3) in the pressurized chalcogenide films. Under the present experimental conditions, the transmittance change was governed by the Ag-layer reduction, and the so-called photodarkening phenomena can be neglected.^{13,14} In Fig. 1, the accuracies in the vertical and horizontal directions are approximately $\pm 30\%$ and ± 3 kbar; the vertical accuracy is mostly due to the intensity variation of the excitation illumination, the result of stringent optical alignment.^{9,11}

We see in Fig. 1 that the overall feature is, with in-

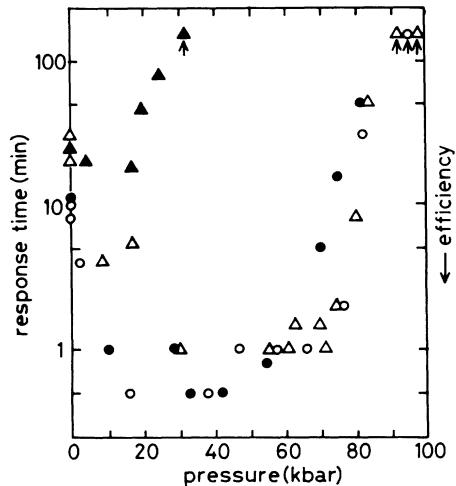


FIG. 1. The response time of the photodoping in Ag/As₂₅S₇₅ films under hydrostatic pressure induced by light illumination with photon energies and intensities of 2.0 eV and 100 mW/cm² (circles) and 2.3 eV and 1 mW/cm² (triangles) incident upon the As-S (solid symbols) and the Ag surfaces (open symbols). The response time, which is proportional to the inverse of the efficiency, is defined as the exposure time needed to effect half of the total transmittance increase resulting from Ag photodoping. Arrows indicate data points off the vertical scale.

creasing pressure, an increase in the efficiency followed by a drastic decrease. However, the characteristic depends on which surface is irradiated and the photon energy of excitation. Illumination on the As-S surface shows a marked dependence on the photon energy, while no remarkable photon-energy dependence exists if light impinges upon the Ag film.

The most interesting behavior in Fig. 1 may be the threshold at 70–80 kbar, which is independent of the photon energy, observed when the Ag film is illuminated. This can be interpreted in two ways, and the final decision remains.

The first is a structural interpretation. It is known that As_xS_{100-x} glass with $x \leq 40$ is composed mainly of As-S bonds with some S-S bonds.^{3,4,15} Although the medium-range structural order of chalcogenide glasses is a subject of controversy and it is known to depend on preparation procedures,^{14,16-18} we may assume that these atoms form molecular clusters held together with weak van der Waals forces. The intermolecular distance (the distance between the center of gravity of the clusters) can be evaluated from the position of the first peak of x-ray- or neutron-diffraction patterns. It is inferred to be about 5 Å in As_xS_{100-x} with $x \leq 40$ at 1 atm.¹⁶ When subjected to pressure, the weaker intermolecular bonds are compressed preferentially, and thus a dramatic contraction in macroscopic dimension appears as shown in Fig. 2.¹⁹ The compression behavior suggests the distance to be 4.5 Å at 80 kbar. Taking the molecular structure of As-S glasses into account,^{15,16} we can estimate the

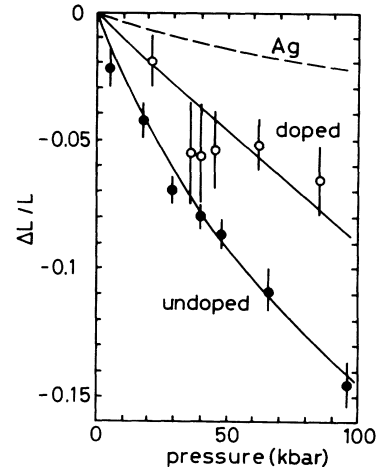


FIG. 2. The pressure-length relations for As₂₅S₇₅ films and As-doped As-S films having an approximate composition AgAsS₂. Solid lines show best fits using the Murnaghan equation, which gives a bulk moduli of 122 kbar for the undoped films and 345 kbar for the doped film, under the assumption of isotropic compression. The characteristic for Ag is cited as a reference [from *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill, New York, 1972)].

free separation length between the clusters to be about 4 Å at 80 kbar. In contrast, it is argued that in the photodoped region an Ag ion is inserted into the low-dimensional clusters, forming threefold to fourfold coordination to S atoms.^{3,4} The linear length of S-Ag-S can be calculated as 4.8 Å using the Pauling atomic radii, and hence the actual separation between the coupled S atoms may be around 4 Å depending upon the bond angle. We can assume therefore that above 70–80 kbar Ag ions cannot be inserted or intercalated between the As-S amorphous clusters because of the geometrical hindrance. This structural interpretation is consistent with the experimental results demonstrating the decrease in Ag ionic conductivity in As₂Se₃ and other glasses under pressure.²⁰ In light of this model, the threshold pressure may be regarded as a percolation threshold, the existence of which is implied by Kluge.²¹

An electronic model is conceivable. The photodoping characteristics at 1 atm have been examined in a variety of metal/chalcogenide systems, and it is known empirically that the Ag-doped region has a smaller band-gap energy than the undoped region, without any exceptions.¹ Figure 3 shows the pressure dependence of the band-gap energies in the doped (AgAsS₂) and undoped (As₂₅S₇₅) films. The undoped glass exhibits a dramatic decrease in the band-gap energy, which is mostly due to the broadening of the valence band.²² The broadening is ascribed to an enhanced overlap of wave functions of lone-pair electrons in chalcogen atoms as a consequence of the reduced intermolecular distance. In Ag-chalcogenide glass, however, the pressure effects on the energy gap (and the linear dimension shown in Fig. 2) are

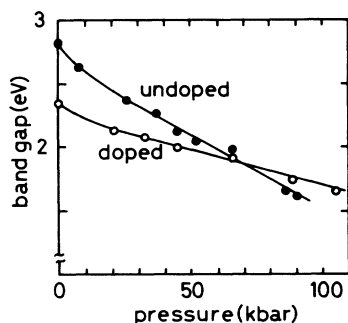


FIG. 3. The pressure dependence of the optical band-gap energies in the two films shown in Fig. 2. The band-gap energy is defined as the photon energy where the optical-absorption coefficient is 10^4 cm^{-1} .

smaller, probably because Ag ions are inserted between the molecular clusters.

We see in Fig. 3 that the band gap in the doped region is smaller than that in the undoped region below 70 kbar, where efficient photodoping is observed, but above that pressure the band-gap relation is reversed. This band-gap reversal may be a cause of the photodoping quenching above 70–80 kbar.

The implications of the relationship between the band-gap energy and the photodoping efficiency are speculative at present, since electronic properties in the doped region are not known in detail.⁶ If the energy gap of the doped region is smaller than that of the undoped region as in the low-pressure region, the electrons and/or holes photogenerated in (and around) the doped region can be (diffused and) accumulated in the doped region. The accumulation increases the electronic conductivity in the doped region, and also the ionic conductivity sustained by Ag^+ ions, since the Ag-chalcogenide material is a so-called mixed ionic-electronic conductor, in which electronic and ionic conductivities are cooperatively coupled.^{5,23,24} In this respect, the doped region may be regarded as a “photoenhanced ionic conductor.” This enhanced ionic conductivity, or diffusivity, may be a necessary element of the photodoping phenomenon. When such a band-gap condition is not fulfilled, the ionic conductivity seems to be low, and the photodoping process may be suppressed, as is seen experimentally at pressures higher than 70–80 kbar.

In order to reveal which mechanism is preferred, Cu/ $\text{As}_{25}\text{S}_{75}$ films have been examined. The Cu^+ ion has a smaller dimension than the Ag^+ ion, and thus the threshold would shift to a higher pressure, if the structural model were justified. However, at room temperature, 500-Å-thick Cu films diffused thermally into the chalcogenide films within 30 min after deposition and the photodoping could not be probed. Other systems suitable to obtain further insight may be $\text{Ag}(\text{Cu})/\text{Ge-S}(\text{Se})$, but we have no detailed experimental data for the composition of the doped materials at present.

Other features noted in Fig. 1 are (i) the faster response with pressure for 0–20 kbar and (ii) the response suppression at high pressure when illumination is provided from the As-S side. These observations can be accounted for by assuming photoelectronic excitation in (and around) the doped region.¹ When 2.0- and 2.3-eV excitations, which at 1 atm are slightly smaller than the optical band-gap energy in $\text{As}_{25}\text{S}_{75}$,¹⁸ are used for irradiation, the absorption in the doped region increases first with pressure, because the compression induces redshifts of the optical-absorption edge (Fig. 3). Hence, the response becomes faster in the low-pressure region. In contrast, at high pressures the absorption coefficient in $\text{As}_{25}\text{S}_{75}$ becomes greater than 10^4 cm^{-1} (Fig. 3), and thus the excitation provided through the chalcogenide film cannot reach the reaction region. Furthermore, the carriers excited near the illuminated surface cannot traverse the chalcogenide film, since the diffusion length is less than 500 Å.¹⁸ A quantitative analysis based on this notion can explain the photodoping suppressions above 20 kbar for 2.3-eV light and above 70 kbar for 2.0-eV light.²⁵ In short, these experimental findings lend support to the idea that light absorption in (and around) the doped region is responsible for the photodoping phenomenon.^{1,12,24}

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¹³The actual response time depended upon the light intensity (1–100 mW/cm²), the excitation photon energy (1.7–3.4 eV), the precise sample thickness, and so forth, varying from 1 s to more than 1 day. It was confirmed that the light-intensity and photon-energy dependences at 1 atm were consistent with previous results [see, for instance, D. Goldschmidt and P. S. Rudman, *J. Non-Cryst. Solids* **22**, 229 (1976)]. It was also confirmed that no photodoping was induced with probe light and with pressure without excitation.

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