Photoluminescence and Electrical Conductivity of As$_2$S$_3$\textit{(Au)} and As$_2$S$_5$\textit{(Au)} Glasses

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Received May 31, 2003; in final form, July 22, 2003

Abstract—The 77-K photoluminescence spectra of (As$_2$S$_3$)$_{100-x}$Au$_x$ and (As$_2$S$_5$)$_{100-x}$Au$_x$ ($0 \leq x \leq 0.04$) semiconducting glasses are measured for the first time. At low doping levels, the spectra of the (As$_2$S$_3$)$_{100-x}$Au$_x$ glasses are split into two components, one of which arises from the Au dopant. The temperature-dependent conductivity of the glasses shows two breaks at low Au concentrations and anomalous behavior in the range 300–360 K. Qualitative analysis of the conductivity data suggests that most of the impurity atoms have saturated valence bonds and form solid solutions with host atoms, changing the band gap of the material. A small fraction of the impurity atoms, those having unsaturated valence bonds, produce an electrically active level responsible for impurity conduction.

INTRODUCTION

Most semiconductor devices take advantage of doped crystals with tailored properties. This has generated considerable research interest in the behavior of impurities in semiconducting chalcogenide glasses (SCGs). Early studies [1, 2] showed, however, that most impurities introduced into the melt in the course of glass preparation had little or no effect on the physical properties of SCGs, being optically and electrically inactive, i.e., producing no localized states in the band gap of the material. As shown in a number of studies, reviewed by Kolomiets [3], the electrical conductivity of SCGs is far lower than that of their crystalline counterparts, is independent of impurity concentration, and shows no break related to the transition from intrinsic to impurity conduction.

The reason for the negligible electrical activity of impurities in glasses is that, in disordered systems, all of the valence electrons of impurity atoms can be used for bond formation. Accordingly, impurities in glasses exhibit neither donor nor acceptor properties. This behavior of impurities in SCGs has long been regarded as a distinctive feature of such glasses. There is, however, substantial evidence that impurities may influence the physical properties of SCGs. Some impurities, e.g., Cu and Ag, were shown to have a significant effect on the electrical conductivity and other properties of glassy arsenic and germanium chalcogenides [4–7]. Unfortunately, the Cu and Ag concentrations in those studies were so high that it was difficult to ascertain whether the observed increase in conductivity was due to the formation of impurity states or a reduction in band gap $E_g$ upon the formation of a new compound.

The observation of photoluminescence (PL) in SCGs and their crystalline analogs [8] has stimulated the study of the effect of various impurities on their PL properties. It has been found that doping typically produces no additional emission bands in broad ranges of temperatures and photon energies. The radiative recombination in SCGs at $T = E_g/2$ is due to native defects with a negative correlation energy ($\sim U$). At the same time, (GeS$_3$)$_{100-x}$Bi$_x$ glasses were shown to have an additional emission band (centered at 0.81 eV), in contrast to (As$_2$S$_3$)$_{100-x}$Bi$_x$ glasses [9]. An additional PL band was also observed in the spectra of amorphous (GeS$_3$)$_{100-x}$Bi$_x$ powders [10]. Those studies were concerned with the effect of Bi impurity on the PL of glasses with a tetrahedral and chain-layer structures [9, 10]. Note that the well-known crystalline analogs of SCGs are GeS$_2$ and As$_2$S$_3$. The effects of most impurities on the properties of SCGs are still poorly understood.

In this paper, we report the PL properties and conductivity of (As$_2$S$_3$)$_{100-x}$Au$_x$ and (As$_2$S$_5$)$_{100-x}$Au$_x$ semiconducting glasses at low Au concentrations ($0 < x \leq 0.04$).

EXPERIMENTAL

Nominally undoped and Au-doped glasses were prepared by melting appropriate mixtures of As, S, and Au (V-5 grade) in evacuated silica tubes, followed by vibration stirring of the melt. To avoid any explosion hazard, the process was run in two steps. First, the tubes

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were heated in a tubular furnace to 800–850 K at a rate of 0.1–0.2 K/s and held there for 15–20 h. Next, the temperature was raised to the melting point of Au at 0.05–0.1 K/s and then maintained constant for 20–25 h, followed by quenching in ice-cold salt water.

To ascertain whether the materials were in the glassy state, we used x-ray diffraction (diffuse scattering with no diffraction peaks) and microstructural analysis of polished and fractured surfaces under a Neophot optical microscope (no microinclusions or inhomogeneities).

Steady-state PL was excited by the radiation from a DKSL 1000-W xenon lamp. PL and excitation spectra were measured at 77 K. To rule out the effect of reabsorption, the PL was recorded in a backscattering geometry. The signal was detected by silicon and germanium photodiodes. Luminescence excitation spectra were taken at the peak-emission wavelength. The luminescence spectra were recorded under excitation at a photon energy corresponding to the maximum in the excitation spectrum. Given that the glasses studied were subject to PL fatigue, the spectra were measured after a quasi-steady state had been reached, and the fatigue effect during the measurements could be neglected.

In conductivity measurements, we used pressure contacts. Plane-parallel samples 0.85–2 mm in thickness were clamped between two soft graphite wafers 10 mm in diameter, pressed into copper blocks. The total resistance of the assembly was 0.2 Ω. Leakage currents were negligible.

EXPERIMENTAL RESULTS

The PL spectra of the nominally undoped glasses showed a single, broad band centered at $\frac{\hbar}{2}$, arising from native defects with a negative correlation energy. The excitation spectra showed a single maximum, corresponding to the absorption coefficient in the exponential portion of the intrinsic edge, $\alpha \approx 10^2 \text{ cm}^{-1}$.

The PL and excitation spectra of the undoped and doped glasses are displayed in Figs. 1 and 2. Increasing the Au content of the stoichiometric glass shifts the PL band at $\frac{\hbar}{2}$ to lower photon energies. Even small amounts of Au in $(\text{As}_2\text{S}_3)_{100-x}\text{Au}_x$ glasses result in an additional emission band. At $x = 0.01$, the spectrum is split into two components at $\hbar_1 = 1.26 \text{ eV}$ and $\hbar_2 = 0.95 \text{ eV}$, with a full width at half maximum (FWHM) of about 0.1 eV. The excitation spectra of the $E_{\text{PL1}}$ and $E_{\text{PL2}}$ emissions show bands at $E_{\text{ex1}} = 2.4 \text{ eV}$ and $E_{\text{ex2}} = 2.1 \text{ eV}$, respectively. With increasing Au content, the main bands in the PL and excitation spectra shift to lower photon energies, while the components at $\hbar_2$ and $E_{\text{ex2}}$ undergo no significant changes. The PL and excitation spectra of the glasses with $x > 0.04$ show a single broad band.

Figures 3 and 4 display the Arrhenius plots of conductivity for the glasses studied. The conductivity of $\text{As}_2\text{S}_3$ and $\text{As}_2\text{S}_5$ exhibits Arrhenius behavior,

$$\kappa = \kappa_0 e^{[-E_a/(kT)]},$$

with a roughly constant activation energy. The plots for the glasses containing gold ($x \geq 10^{-5}$) show a change in slope, indicating a change in activation energy. Increasing the Au content to $x = 0.01$ increases the conductivity of the glasses by two orders of magnitude and reduces the activation energy for conduction by 0.3 eV. More-