STRUCTURAL ORDERING OF EVAPORATED AMORPHOUS CHALCOGENIDE ALLOY FILMS: ROLE OF THERMAL ANNEALING

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Thermal annealing of evaporated GeSe₂ films doped with traces of ¹¹⁹Sn is studied using Mössbauer spectroscopy. Films deposited at room temperature display a substantial non-tetrahedral Sn-fraction which thermally anneals irreversibly with an activation enthalpy ranging from 70 to 150 meV in the temperature range 20°C < T_A < 400°C.

INTRODUCTION

The molecular structure of vapor deposited amorphous thin-films is both of basic and technological interest. The network structure of such films deposited onto substrates held at a temperature (T_s) much below T_g, can in general be expected to deviate from those of corresponding bulk glasses. Specifically broken bonds and partially polymerized fragments must proliferate in such films largely because of the limited surface mobility of vapor deposited species. Metastable local configurations can be expected to be frozen in such films particularly at T_s<<T_g, and furthermore these configurations to thermally relax systematically as T_s approaches T_g. In particular, when T_s = T_g, one may expect the molecular structure of the vapor deposited film to closely resemble that of the bulk glasses. Experimentally, one could also perform post-deposition thermal annealing of amorphous films and characterize the various frozen configurations by their activation energies and enthalpies.

To examine the underlying problem in detail, we have focussed on the Ge_xSe_1-x binary. Our understanding of the molecular structure of Ge_xSe_1-x bulk glasses has advanced significantly during the past five years. Much of
this advancement has emerged on account of progress both in theory\textsuperscript{1,2} and experiments. Experimentally a concerted effort has been made to explain results of diffraction\textsuperscript{3}, Raman\textsuperscript{4,5} scattering and Mossbauer spectroscopy\textsuperscript{6,7} experiments in a coherent fashion.

Our approach is to study Sn-doped GeSe\textsubscript{2} amorphous thin-films prepared by vapor deposition and to examine these films in optical absorption edge (OAE), Raman scattering and Mossbauer spectroscopy experiments. There is clear evidence that the principal defect in the stoichiometric binary chalcogenide glass-GeSe\textsubscript{2}, are like-atom bonds\textsuperscript{8}. These bonds are signature of network or fragmentation. On general grounds one could expect the concentration of such bonds to sharply increase in vapor deposited films. In this work we report on Mossbauer spectroscopy which provides striking evidence of increased concentration of like-atom bonds in evaporated GeSe\textsubscript{2} films. Thermal annealing of these films leads to an irreversible structural and chemical ordering as the network polymerizes qualitatively. Our experiments show that the structural ordering process in thin-films is characterized by an activation enthalpy $\Delta H^\alpha$ which varies between 74(5)meV at low $T$ ($20^\circ C<T<300^\circ C$) to 150(15)meV at high $T$ ($300^\circ C<T<400^\circ C$). Raman scattering and optical absorption edge studies on these films are currently in progress and will be reported in due course.

EXPERIMENTAL CONSIDERATIONS

Melt-quenched glasses of the composition Ge\textsubscript{0.98}Sn\textsubscript{0.02}Se\textsubscript{2} were first prepared starting with the pure elements including enriched $^{119}$Sn metal as described previously\textsuperscript{9}. Glass chips were loaded in a Radak furnace incorporated in a bell jar evacuated to a base pressure of ca. $10^{-7}$torr. Amorphous thin-films were evaporated at a temperature of about 400\degree C when an evaporation rate of 10A/sec was realized. Al foils at room temperature were used as a substrate for the films. Film thicknesses used were in a range of 5-10\textmu.

$^{119}$Sn Mossbauer spectra of the films were recorded at 4.2K using a set up described previously\textsuperscript{9}. Figure 1(a-d) displays the spectra of the films in the virgin state (a) and the annealed state (b,c and d) at indicated annealing temperatures ($T_A$). At a given $T_A$ films were annealed for a period of 24 hours. The films were annealed in helium gas using a system described elsewhere\textsuperscript{10}. Kinetic experiments, as a function of annealing time, were also performed at a given $T_A$, and results of these experiments will be discussed elsewhere.
Figure 1: $^{119}$Sn Mossbauer spectra of evaporated Ca$_{0.98}$Sn$_{0.02}$Se$_2$ amorphous films in the (a) virgin and (b, c, and d) annealed state. The annealing temperature and the site intensity ratio $I_B/I$ is indicated appropriately.
Figure 2: Semilog plot of the ratio \( C/C_i \) versus \( 1/T_A \) exhibiting thermally activated behavior. \( C_i \) represents the initial concentration of B-sites in the spectra while \( T_A \) the annealing temperature.

Spectra of the films are characterized by two sites (A, B) which have previously been identified by their nuclear hyperfine structure. Briefly, the A site represents Sn replacing Ge in tetrahedral Ge(Se\(_{1/2}\))\(_4\) units. The B site is characterized by a doublet which is ascribed to a Sn atom replacing a Ge site in an ethane-like unit. The present results show that the site intensity ratio \( I_B/(I_A+I_B) = I_B/I \) steadily declines as a function of thermal annealing temperature \( T_A \) starting from an initial value of 0.49(1) in a virgin film to a value of 0.21(1) in a film annealed at \( T_A = 375^\circ C \) for 24 hours.

Figure 2 displays a semilog plot of the ratio \( C(T_A)/C_i \) as a function of \( 1/T_A \). \( C_i \) represents the initial concentration of B sites, i.e. \( I_B/I \) in the virgin film, while \( C(T_A) \) represents the B site concentration prevailing in a film after thermal annealing at \( T=T_A \). We note that ratio \( C/C_i \) is thermally activated with two activation enthalpy difference: one of \( \Delta H_A^{\pm} = 74(5) \) meV at
low $T_A$ (25°C $<$ $T_A$ $<$ 300°C) and another $\Delta H_A^{\text{M}}$=150(15)meV at high $T_A$ (300°C $<$ $T_A$ $<$ 400°C). In Figure 2, the open and filled circles correspond to independent evaporation runs. Although $C_4$ for the two preparations are not the same, the thermal annealing behavior of the two samples is remarkably similar.

**DISCUSSION**

The present Mossbauer results clearly demonstrate that the concentration of the chemically disordered sites ($I_B/I$=0.5) in vapor deposited amorphous GeSe$_2$ films is qualitatively larger than the value observed in the corresponding bulk glass$^9$ ($I_B/I$=0.16(1)). These sites are signature of Ge-Ge bonds. In Raman scattering, the 180cm$^{-1}$ feature represents a vibrational mode of ethane-like units (signature of Ge-Ge bonds) and its scattering strength in amorphous GeSe$_2$ films is qualitatively enhanced$^{11}$ over what is found in GeSe$_2$ bulk glass. Optical absorption edge studies of Connell$^{12}$ also reveal a broadening of the Tauc edge in evaporated films in relation to the bulk glass which presumably arises due to an increased concentration of like-atom bonds in the films. Thermal annealing of such films leads to a sharpening of the edge with an activation enthalpy difference of $\Delta H_A^{\text{R}}$=0.61eV. We note that this value of $\Delta H_A^{\text{R}}$ is at least a factor of 4 larger than the activation enthalpy difference $\Delta H_A^{\text{M}}$ deduced from the present Mossbauer measurements.

Tracer diffusion in ternary Se-Ge-As glasses have been studied by Eichorn and Frischat$^{13}$ who have reported observing activation enthalpies $\Delta H_A^{\text{a}}$ of 0.71(2)ev in these chalcogenide glasses.

In our view the small activation enthalpy difference $\Delta H_A^{\text{M}}$ presently reported are suggestive of a correlated motion of a large group of atoms in which the restoration of chemical order is achieved by the following chemical reaction

$$\text{(Ge-Sn)} + \text{(Se-Se)} \rightarrow \text{(Ge-Se)} + \text{(Sn-Se)}$$

(1)

Since the Pauling electronegativities of Sn and Ge are very similar, we presume that the $\Delta H_A^{\text{M}}$ characterizing reaction (1) is the same as the one for reaction (2)

$$\text{Ge - Ge} + \text{(Se-Se)} \rightarrow 2\text{(Ge-Se)}$$

(2)

The like-atom bonds are thought to dress characteristic clusters$^6$ and as those clusters rotate reaction 1 or 2 is realized, polymerizing one cluster (Se-rich cluster) at the expense of the other (Ge-rich cluster).

An analogy$^{14}$ can be drawn between the above process and semiconductor surfaces reconstruction such as Si(111). Theoretical estimates$^{15}$ of the
chemical ordering of amorphous GeSe$_2$ films as probed by the present Mossbauer experiments involves single atom (like Se) translation diffusion$^{12}$ although such a physical process in chalcogenide glasses is certainly conceivable and probably occurs in the tracer-diffusion experiments. However such a translation diffusion process may not necessarily involve restoration of chemical order.

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REFERENCES:

14. J.C. Phillips (private communication).