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

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Thermal annealing of evaporated $GeSe_2$ films doped with traces of ^{119}Sn is studied using Mossbauer 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 $T_S \ll T_g$, and furthermore these configurations to thermally relax systematically as T_S approaches T_g. In particular, when $T_S \approx T_g$, 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[1,2] and experiments. Experimentally a concerted effort has been made to explain results of diffraction[3], Raman[4,5] scattering and Mossbauer spectroscopy[6,7] experiments in a coherent fashion.

Our approach is to study Sn-doped $GeSe_2$ 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-$GeSe_2$, are like-atom bonds[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 $GeSe_2$ 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 ΔH_a^M which varies between 74(5)meV at low T (20°C<T<300°C) to 150(15)meV at high T (300°C<T<400°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 $Ge_{0.98}Sn_{0.02}Se_2$ were first prepared starting with the pure elements including enriched ^{119}Sn metal as described previously[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°C when an evaporation rate of 10Å/sec was realized. Al foils at room temperature were used as a substrate for the films. Film thicknesses used were in a range of 5-10μ.

^{119}Sn Mossbauer spectra of the films were recorded at 4.2K using a set up described previously[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[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.

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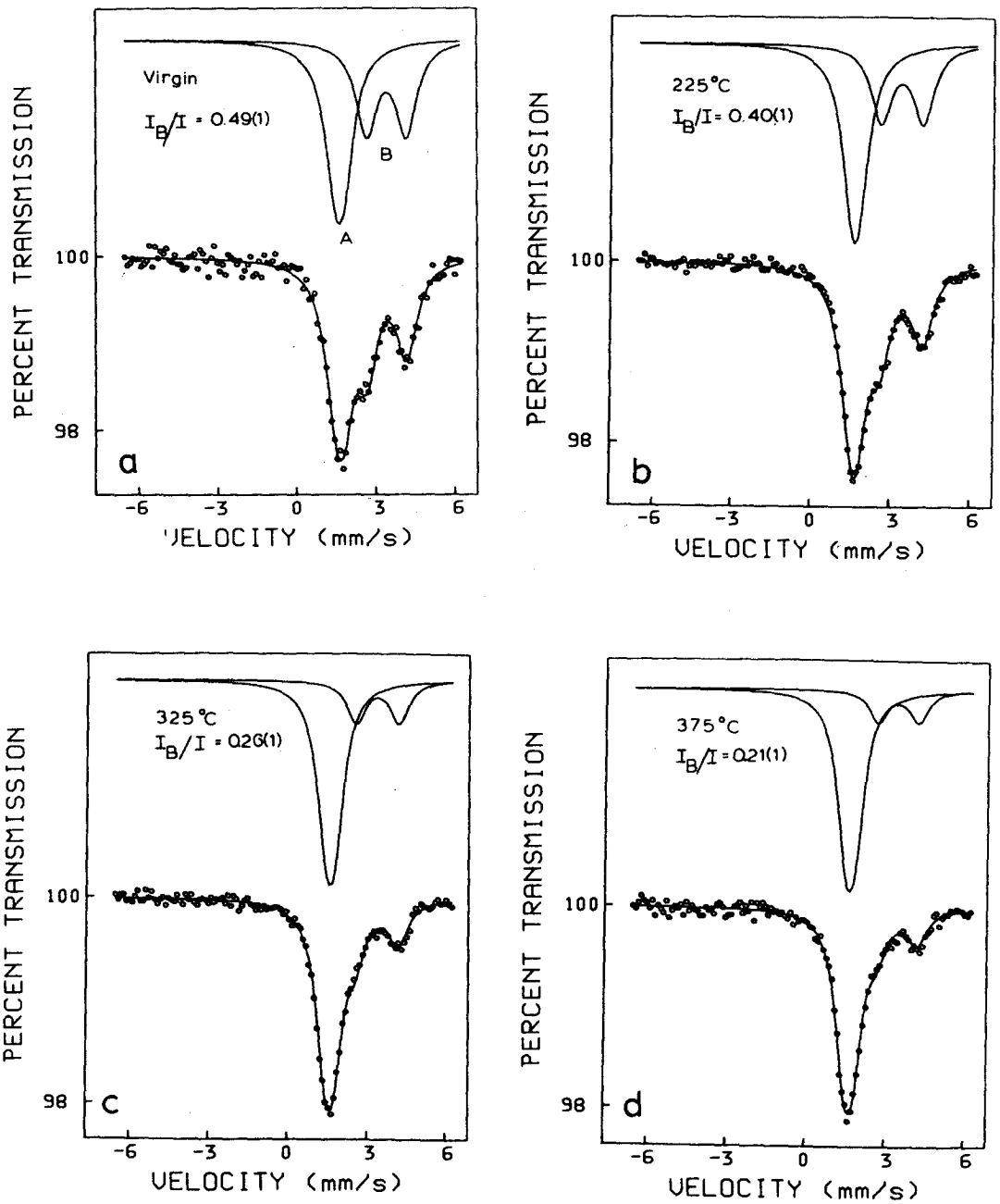

Figure 1: ^{119}Sn Mossbauer spectra of evaporated $Ge_{0.98}Sn_{0.02}Se_2$ amorphous films in the (a) virgin and (b, c, and d) annealed state. The annealing temperature and the site intensity ratio I_B/I is indicated appropriately.

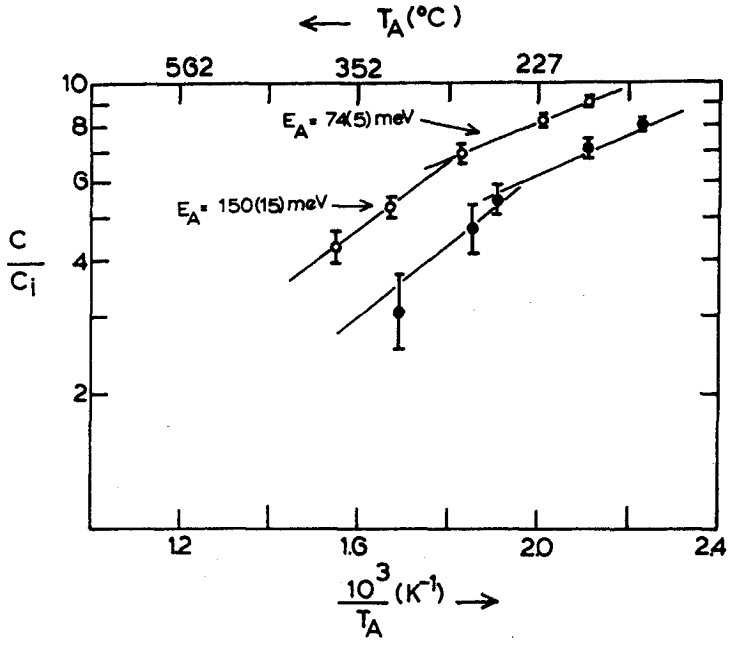

Figure 2: Semilog plot of the ratio C/C_i versus $1/T_A$ exhibiting thermally activated behavior. C_i represents the initial concentration of B-sites in the spectra while T_A the annealing temperature.

Spectra of the films are characterized by two sites (A,B) which have previously[9] 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°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 ΔH_A^M=74(5)meV at

low T_A ($25°C<T_A<300°C$) and another ΔH_A^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_i 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 ΔH_A^O=0.61eV. We note that this value of ΔH_A^O is at least a factor of 4 larger than the activation enthalpy difference ΔH_A^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 ΔH_a^d of 0.71(2)eV in these chalcogenide glasses.

In our view the small activation enthalpy difference ΔH_a^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

$$(Ge\text{-}Sn) + (Se\text{-}Se) \rightarrow (Ge\text{-}Se) + (Sn\text{-}Se) \qquad (1)$$

Since the Pauling electronegativities of Sn and Ge are very similar, we presume that the ΔH_a^M characterizing reaction (1) is the same as the one for reaction (2)

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

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:

1. J.C. Phillips, J. Non Cryst. Solids, 34, 153 (1979).
2. M.F. Thorpe, J. Non Cryst. Solids, 57, 355 (1979).
3. P.H. Fuoss, P. Ensenberger, W.K. Warburton and A. Bienenstock, Phys. Rev. Lett. 46, 1537 (1981).
4. K. Murase, T. Fukunaga, K. Yakushiji, T. Yoshimi and I. Yunoki, Jour. Non Cryst. Solids 59 and 60, 883 (1983); Also see K. Murase and T. Fukunaga in Materials Research Society Symposium proceedings 61, 101 (1986).
5. J.E. Griffiths, G.P. Espinosa, J.C. Phillips and J.P. Remeika, Phys. Rev. B 28, 4444 (1983); Also see P.M. Bridenbaugh, G.P. Expinosa, J.E. Griffiths, J.C. Phillips and J.P. Remeika, Phys. Rev. B20, 4140 (1979).
6. P. Boolchand in Physical Properties of Amorphous Materials, Ed. by David Adler, Brian B. Schwartz and Martin C. Steele (Plenum Publishing Corporation, 1985) p.221.
7. W.J. Bresser, P. Boolchand, P. Suranyi and J.P. deNeufville, Phys. Rev. Letters 46, 1689 (1981); Also see W. Bresser, P. Boolchand and P. Suranyi, Phys. Rev. Letters 56, 2493 (1986).
8. P. Boolchand in Materials Research Society Symposia Proceedings 61, 57 (1986) Ed. Frank L. Galeener, David L. Griscom, Marwin J. Weber, Publ. Materials Research Society, Pittsburg.
9. P. Boolchand, J. Grothaus, W.J. Bresser and P. Suranyi, Phys. Rev. B 25, 2975 (1982).
10. P. Boolchand, B.B. Triplett, S.S. Hanna and J.P. deNeufville, Mossbauer Effect Methodology 9, 53 (1974) Plenum Press New York.
11. R.J. Nemanich, G.A.N. Connell, T.M. Hayes and R.A. Street, Phys. Rev. B 18, 6900 (1978).
12. G.A.N. Connell, Phys. Rev. B 24, 4560 (1981).
13. V. Eichorn and G.H. Frischat, J. Non Cryst. Solids 30, 211 (1978).
14. J.C. Phillips (private communication).
15. J.E. Northrup and M.L. Cohen, Phys. Rev. Lett. 49, 1349 (1982).