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Pressure-enhanced interdiffusion in amorphous Si/Ge multilayers

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We have investigated the effect of hydrostatic pressure on interdiffusion in multilayers composed of alternating layers of amorphous Si (2.7 nm) and Ge (3.1 nm). Samples were annealed at 420 °C at pressures between 0 and 2.8 GPa in an externally heated diamond anvil cell. Interdiffusion was measured by monitoring the decay with annealing time of the intensity of the first-order x-ray reflection resulting from the effects of composition modulation. The decay curves for all pressures could be made to coincide by scaling the annealing times. This made it possible to separate the effects of pressure on the interdiffusivity from those of composition and structural relaxation. The interdiffusivity increased with applied pressure, with an activation volume of $-5.0 \text{ cm}^3/\text{mole}$, or -0.42 times the atomic volume of crystalline Si. © 1996 American Institute of Physics. [S0003-6951(96)01109-9]

The rates of atomic transport processes, such as diffusion, decrease with increasing pressure in most materials.¹ However, in some materials with an open (covalent) network structure, such as GeO_2 (Ref. 2) and some silicate melts,^{3,4} the fluidity has been observed to increase with pressure. Pressure enhancement has also been demonstrated for the growth rate of quartz⁵ into amorphous silica and for solid phase epitaxial growth (SPEG) of Si and Ge into their amorphous phases.⁶ Because the tetrahedral bonding in these and other open-structured materials implies a low coordination number and a correspondingly low atomic density, the bond-angle distortions required for atomic migration are expected to cause a reduction in the local volume during motion. Thus, pressure should enhance the atomic mobility in such systems. This experiment was designed to investigate the effects of pressure on the interdiffusion of amorphous Si and Ge: to test whether pressure enhancement is indeed observed, and to compare its activation volume to that of other atomic transport processes.

The effect of pressure on diffusion may be characterized by an “activation volume”, ΔV^* . The Arrhenius form of the diffusivity is

$$D = g\lambda^2\nu \exp(-\Delta G^*/kT), \quad (1)$$

where g is a geometric factor, λ a jump distance, ν an attempt frequency, ΔG^* the Gibbs free energy of activation, and kT has the usual meaning. The activation volume, ΔV^* , is related to the Gibbs free energy by

$$\Delta V^* = \frac{\partial \Delta G^*}{\partial P} \Big|_T. \quad (2)$$

Because the pressure dependence of the prefactors in Eq. (1) can be shown to be negligible,⁷ combining Eqs. (1) and (2) leads to the relation

$$\Delta V^* \approx -kT \frac{\partial \ln D}{\partial P} \Big|_T. \quad (3)$$

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ΔV^* can be either negative or positive, depending on whether D increases or decreases with pressure, respectively. For systems in which the concentration of point defects remains in equilibrium as P and T are varied, ΔV^* is composed of two components

$$\Delta V^* = \Delta V_f^0 + \Delta V_m, \quad (4)$$

where ΔV_f^0 , the formation volume, is the volume change in the system upon formation of one defect in its standard state. ΔV_m , the migration volume, is the additional volume change when the defect reaches the saddle point in its migration path. The former term characterizes the pressure dependence of the equilibrium point defect concentration, while the latter term characterizes the pressure dependence of the defect mobility.

If the defects have a sufficiently long time to reach thermodynamic equilibrium at each pressure studied, both the formation and migration volumes contribute to the measured pressure dependence. However, if the time scale is too short for the defects to equilibrate, the change in the diffusivity with pressure is dominated by the corresponding change in the defect mobility. If the number of defects remains constant in a series of experiments, the measured activation volume is equal to the volume of migration. Amorphous semiconductors contain a substantial concentration of point defects, such as dangling bonds or vacancies,⁸ some of which are thought to govern atomic transport processes such as SPEG⁶ and viscosity.⁹ The interdiffusivity in these systems is sufficiently small^{10,11} to preclude equilibration of point defects before the onset of crystallization; at most, a slow decay in the excess defect concentration is observed (structural relaxation).^{8,12} Furthermore, model studies of atomic configurations which govern diffusion, flow or crystallization indicate that the structural changes required to “activate” an existing dangling bond into a mobile defect (e.g., the breaking of an additional bond nearby) result in a negligible change of the remaining bond angles, and therefore of the local volume.^{13,14} The activation volume measured in the present experiment, therefore, should primarily reflect the volume of migration.

The multilayer sample was prepared using Ar^+ ion-beam sputtering from alternating elemental targets and consisted of

120 bilayers of alternating pure amorphous silicon and amorphous germanium. From the positions of the first seven x-ray reflections, the bilayer repeat length was found to be 5.8 nm.⁷ The spatially averaged composition of the film was determined by Rutherford backscattering spectrometry and was found to be 47 at.% Si, 52 at.% Ge, and 1 at.% Ar, which corresponds to Si and Ge layer thicknesses of 2.7 and 3.1 nm, respectively. The film was deposited onto small pieces of 20 μm thick polished (100) Si (Virginia Semiconductor) on a water-cooled substrate holder. Deposition stresses, which resulted in a noticeable curvature in the 20 μm thick Si pieces, were relieved by annealing in an overpressure of He at 350 °C for 3 h. These conditions have been shown to be sufficient to relieve the stress⁹ and do not cause noticeable interdiffusion. The samples were then broken up into very small pieces suitable for use in a diamond anvil cell (DAC). The typical sample size was $\sim 150 \mu\text{m} \times 150 \mu\text{m}$. X-ray scans were taken of the DAC-sized samples using Mo $K\alpha$ radiation in a fixed-anode x-ray system (48 kV, 18 mA). After initial x-ray scans, the samples were separately annealed at 420 °C, along with several small pieces of Sm-doped YAG crystal, in a Merrill-Bassett style DAC.¹⁵ The annealing chamber consisted of a 380 μm hole in an Inconel foil that had been preindented by the diamonds. The top and bottom of the chamber were the opposing diamond culets. The pressure inside the DAC, both before and during the anneals, was determined by observing the positions of the fluorescence lines of the Sm:YAG spectrum, whose shift with pressure has been well calibrated.¹⁶ The uncertainties in the measured pressures were approximately ± 0.2 GPa. The pressure medium was liquid argon, which is both inert and hydrostatic at high temperature. Each sample was annealed at a different pressure. It was then removed from the DAC, examined by x-ray diffraction, and returned to the DAC for further annealing at that same pressure. Sample curvature that arose during high pressure annealing was removed by flattening the samples in a specially designed x-ray sample mount.⁷ The control (~ 0 GPa) sample was annealed in Ar gas at atmospheric pressure inside the DAC. Further experimental details are described elsewhere.⁷

The diffusivity during each anneal was determined by measuring the drop in the integrated intensity of the first x-ray reflection resulting from the composition modulation. In the kinematic scattering regime, the integrated intensity of each x-ray reflection is proportional to the square of the corresponding Fourier coefficient in the expansion of the composition profile.¹⁷ The average interdiffusivity is then

$$\tilde{D} = -\frac{\lambda^2}{8\pi^2} \frac{d \ln(I)}{dt}, \quad (5)$$

where λ is the multilayer repeat length, I is the integrated intensity of the first peak, and t is the annealing time. The intensity decay curves for the four samples studied in this experiment are shown in Fig. 1. Comparing the decay curves at different pressures, we see that increased pressure causes significantly enhanced rates of interdiffusion. Thus, the activation volume for interdiffusion is a negative quantity. However, we cannot directly determine ΔV^* from Eq. (3) because \tilde{D} is not constant over an experimental series at a single temperature and pressure. Indeed, previous studies of inter-

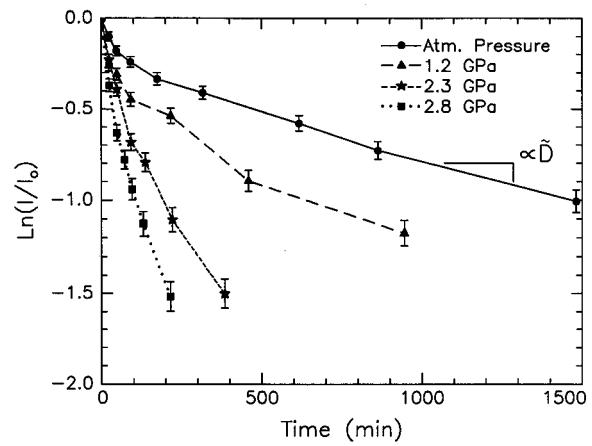


FIG. 1. Intensity of the first-order x-ray reflection from the composition modulation in amorphous Si/Ge multilayers vs annealing time for four samples annealed at 420 °C and at pressures ranging from atmospheric pressure (~ 0 GPa) to 2.8 GPa. The instantaneous slope of each curve is proportional to the interdiffusivity.

diffusion in *a*-Si/*a*-Ge multilayers, at ambient pressure, have shown that the interdiffusivity is dependent on concentration and time.^{10,11}

In order to isolate the effect of pressure for a meaningful determination of ΔV^* , we use a method¹⁸ analogous to Wu's¹⁹ for isolating the effect of temperature for the determination of ΔH^* . We introduce a normalized time variable

$$s = \gamma(P) \cdot t, \quad (6)$$

where $\gamma(P)$ is a scaling factor that depends only on pressure. We then attempt to scale the time axis of each intensity decay curve in Fig. 1 by a factor $\gamma(P)$ to make that curve overlay the atmospheric pressure curve. If the experimental decay curves taken at different pressures can be scaled successfully, the pressure dependence in the interdiffusivity can be factored out:

$$\tilde{D}(c, t, P) = \gamma(P) \cdot f(c, \gamma t), \quad (7)$$

where $\gamma(P)$ can be identified as a pressure enhancement factor, with $f(c, \gamma t)$ an unspecified function containing all of the

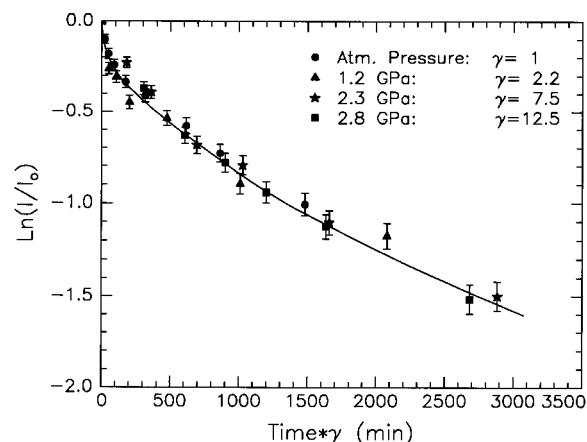


FIG. 2. Pressure-scaling analysis applied to decay curves in Fig. 1. The time axis of each curve has been multiplied by a pressure-dependent scaling factor γ , chosen to make it overlay the atmospheric pressure decay curve.

concentration and time dependence. Combining Eqs. (3) and (7), we see that the activation volume becomes

$$\Delta V^* = -kT \left. \frac{\partial \ln(\gamma)}{\partial P} \right|_T . \quad (8)$$

We applied this pressure-scaling technique to the decay curves shown in Fig. 1. The resulting overlay curves are shown in Fig. 2. The smooth line in the figure is a guide to the eye that shows that a single curve can be drawn through most of the points. Plotting γ as a function of pressure in Fig. 3, we see that the best-fit line to these points gives an activation volume of $-5.0 \pm 0.3 \text{ cm}^3/\text{mole}$, or $-0.42 \pm 0.03 \Omega_{\text{Si}}$, where the atomic volume of Si at standard temperature and pressure (Ω_{Si}) is $12.0 \text{ cm}^3/\text{mole}$.

These experimental results providing convincing support for the hypothesis, discussed in the introduction, that atomic transport in network materials requires fluctuations with large bond-angle distortions and an associated decrease in volume. A comparison with pressure enhancement of SPEG in amorphous Si and Ge allows us to be more specific. The

activation volumes measured in the SPEG experiments ($-0.28 \Omega_{\text{Si}}$ and $-0.46 \Omega_{\text{Ge}}$, respectively) bracket the one found in this experiment.⁶ The most plausible mechanism for SPEG is based on the migration of a dangling bond along a ledge in the crystal-amorphous interface.^{6,13} Investigation of the physical interface model used to develop the mechanism clearly shows the large bond-angle distortions and the volume decrease associated with the motion of the dangling bond. The similarity of the activation volumes suggests that dangling bond motion may also play an important role in atomic diffusion.

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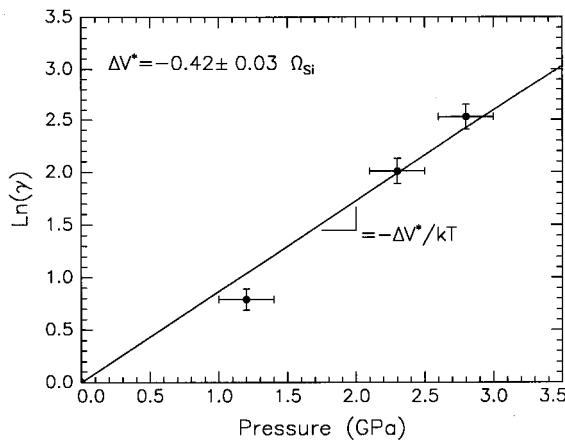


FIG. 3. Natural logarithm of the scaling factor $\gamma(P)$, as a function of pressure. The straight line fit to the data is constrained to pass through the origin (0 GPa) because the high-pressure decay curves were scaled to the atmospheric pressure (~ 0 GPa) decay curve.

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