Structural relaxation and order in ion-implanted Si and Ge

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Raman scattering measurements are reported as a function of annealing temperature on heavily damaged, ion-implanted Ge and Si. Changes in the opticlike, TO Raman bandwidth of amorphous Ge are found to correlate with the estimated heat of structural relaxation obtained from the data of Donovan *et al.* This result is consistent with a bond-strain model, demonstrating that structural relaxation is primarily associated with short-range bond-angle ordering. The results also allow an estimate of the temperature dependence of the width of the bond-angle distribution to be obtained with annealing. The Raman spectra of ion-implanted Si indicate greater order in the amorphous state than similarly prepared amorphous Ge. Estimates of the corresponding heat of structural relaxation of amorphous Si suggest that this should be observable.

INTRODUCTION

The degree of short-range or intermediate-range order in amorphous solids is known to depend on the conditions of formation.[1] Ion implantation of crystalline semiconductors is one often utilized means of forming amorphous semiconducting systems. Little is known in detail, however, about the local order and physical properties of amorphous solids formed in this manner relative to that of thin film or bulk noncrystalline materials. Of considerable interest are the microscopic aspects of the collisional induced disorder, as well as the role of structural relaxation and recrystallization. Special interest also concerns the influence of annealing on the degree of order within the amorphous state. This includes the relation of the as-implanted amorphous state to its modification by normal or self-annealing effects, as well as to other amorphous materials. Of special interest are whether basic differences occur in the properties of ion-implanted and thin-film-prepared amorphous materials due to the dependence of the latter on film growth and micromorphology. The absence of such growth effects in ion-implanted amorphous semiconductors, such as *a*-Si and *a*-Ge, imply that intrinsic effects associated with network order may be essentially separable from extrinsic phenomena. The latter are associated with internal surfaces of volume defects, such as voids, that may be microscopic in size.[2]

Detailed studies of thin-film amorphous (*a*-) Ge and Si,[3] as well as their alloys with H,[4] have demonstrated that network short-range structural order is a function of the conditions of formation or of subsequent annealing. The strongest evidence for an intrinsic change in structure is provided by Raman scattering studies of the vibrational states. Theoretical models,[5,6] as well as inelastic-neutron-scattering measurements,[7] have supported the view that changes in the bond-angle distribution width modify the phonon density of states. As a first approximation, these studies indicate that the width of the high-frequency TO Raman band is proportional to the width of the bond-angle distribution. These studies also suggest that a relatively anneal-stable, maximally ordered state exists prior to crystallization. With the exception[8] of Raman studies on laser-quenched *a*-Si, the role of variable order in the amorphous state has been primarily explored in vapor-deposited films. Recent studies of ion-implanted amorphous Ge have suggested that annealing may lead to structural relaxation of the amorphous network.[9] Differential-scanning-calorimetry (DSC) measurements of Donovan *et al.* exhibited an extended precrystallization tail in ion-implanted *a*-Ge that decreases with annealing temperature. Similar measurements on *a*-Si did not exhibit this behavior, however.

The primary contribution to the energy released in modifying or crystallizing amorphous semiconductors such as *a*-Ge and *a*-Si may be approximately related to the square of the width of the bond-angle distribution function characterizing the amorphous network. As such, the macroscopic heat evolved in calorimetric studies should be correlated with the vibrational states of the system. To determine if this relationship exists as well as to explore the extent to which annealing modifies ion-implanted *a*-Si, we have studied the Raman spectra of samples prepared under the same conditions as those of earlier DSC studies.[9] The results indicate that structural relaxation occurs in both *a*-Ge and *a*-Si, but that the relative initial order in low-temperature, high-energy ion-implanted *a*-Si is greater than that of *a*-Ge. A comparison of the estimated structural relaxation energy released in calorimetric studies and changes in Raman-line widths confirms that the dominant change in structural order is associated with bond-angle distribution narrowing.

EXPERIMENT

The conditions utilized to form a uniform, high-damage ion implantation are shown in Table I. The

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TABLE I. Ar-implantation conditions for amorphous Ge and Si samples.

	Energy (MeV)	Dose (10^{14}/cm^2)
Ge(100)	0.36	0.46
	0.80	0.75
	1.50	1.0
	2.50	1.2
Si(100)	0.50	2.0
	0.80	2.5
	1.40	3.0
	2.10	4.0

TABLE II. Measured heat of structural relaxation obtained from Ref. 9 for a-Ge samples.

Temperature (°C)	H_{SR} (kJ/mol)
27	8.0
167	6.89
267	3.67
367	1.45

chosen doses lead to a thick amorphous layer in which the Ar concentration is nearly uniform and whose thickness is in excess of the optical penetration depth for Raman measurements. The implanted Ar concentration of ~ 0.01 at. % is relatively small, being significantly below values of 2–5 at. % observed in thin-film, rf-diode-sputtered (RFS) a-Ge and a-Si deposited at room temperature. To maximize structural disorder, single-crystal, Syton polished substrates of Ge and Si were pressure-clamped to a liquid-nitrogen-cooled platform under conditions identical to those utilized for DSC studies.[9] The use of a low-temperature contact reduces the effect of self-annealing during ion implantation due to sample heating. Raman scattering measurements at 5145 Å excitation wavelength were performed on a Spex third monochromator system at 300 K. Both VH and HH polarization measurements were performed (V is vertical and H is horizontal).

In order to compare the Raman spectra to the results of calorimetric measurements, a more detailed analysis of the tail of the DSC data was required. As Raman scattering measurements in a-Ge have shown that an anneal-stable state occurs prior to crystallization, we have normalized the areas of the major crystallization peaks of different annealed, ion-implanted spectra of Donovan *et al.*[9] Thus for $T > 400\,°\mathrm{C}$, the same heat of crystallization, H_{ac}, was assigned to all annealing stages to obtain from the DSC data the normalized heat released per unit mass in the structural relaxation process. The total DSC heat $H_t = H_{ac} + H_{SR}$, where H_{SR} is the structural relaxation contribution. From the results of Donovan *et al.*, the error associated with H_{SR} values shown in Table II, due to baseline and other factors, is estimated to be $\sim 18\%$.

RESULTS AND DISCUSSION

Raman scattering measurements of a-Ge exhibit substantial changes upon annealing as indicated in Figs. 1 and 2. As in previous annealing studies of sputtered a-Ge, the width of the high-frequency TO band decreases, while its intensity relative to the TA band increases as the annealing temperature T_a increases.[10,11] These changes indicate a decrease in the width of the bond-angle distribution function $P(\theta)$ as the amorphous state orders, without crystallization. These changes are observed for both VH and HH components as Fig. 2 illustrates. The results of Fig. 2(a) indicate a variation of the TO half-width with T_a similar to that of very-thin-film, rf-sputtered a-Ge.[10]

As a first approximation the width of the TO band, Δ_{TO}, is proportional to $\Delta\theta$, the width of $P(\theta)$.[6,12] If structural relaxation involving $P(\theta)$ occurs, then a bond-strain model has $H_{SR} \sim (\Delta\theta)^2$. This implies that $(H_{SR})^{1/2}$ is proportional to Δ_{TO}. Figure 3 is consistent within experimental error with this theoretical prediction. In the comparison of $(H_{SR})^{1/2}$ to Δ_{TO}, the latter full width at half maximum was estimated by smoothly extrapolating to lower frequency the smooth portion of the TO band below its peak. This extrapolation procedure is required, given that changes in the form of the low-frequency portion of the TO band occur due to overlap with the LA band. An alternative approach utilizing the high-frequency portion of the TO band is more difficult here, given the weak signal levels and the greater difficulty of distinguishing width changes quantitatively.

The results of Fig. 3 indicate a near-linear correlation, within the experimental uncertainties, between changes in the heat evolved due to structural relaxation and

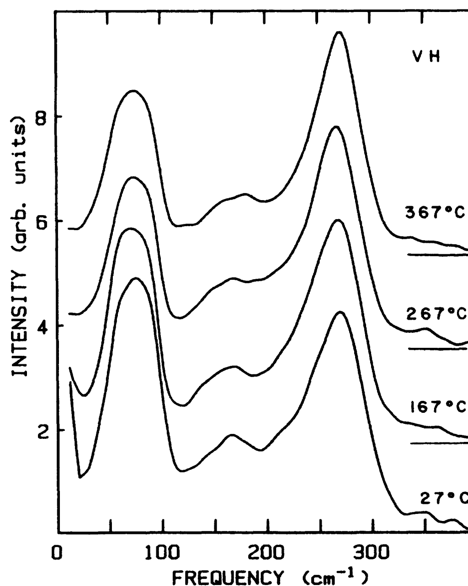

FIG. 1. Room-temperature VH Raman spectra for different annealing temperatures of ion-implanted a-Ge.

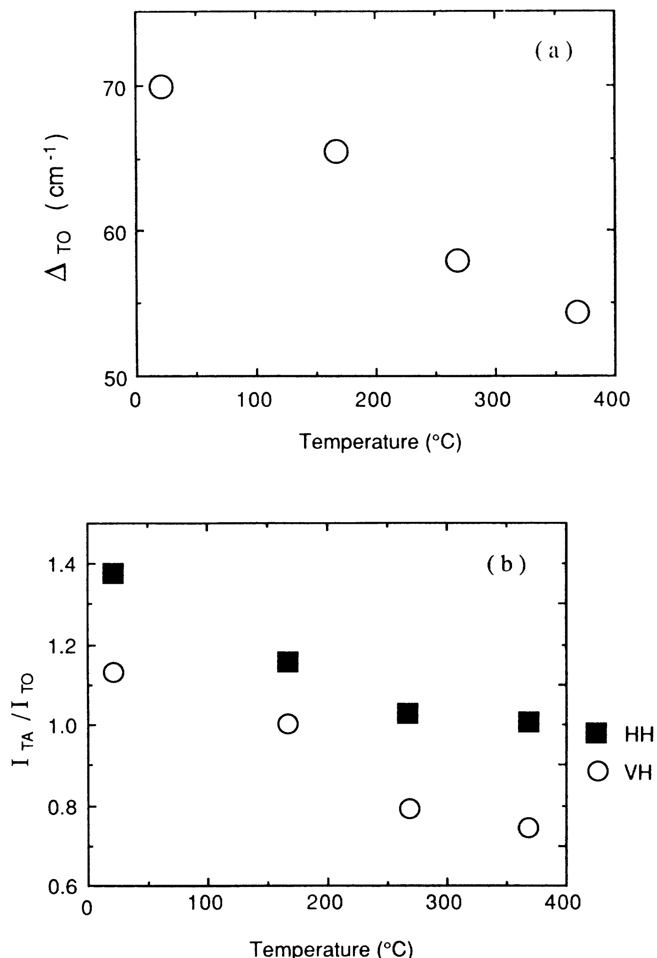

FIG. 2. (a) Variation of the width (FWHM) of the TO Raman band of ion-implanted a-Ge with annealing temperature. (b) Ratio of TA to TO intensities at 300 K of ion-implanted a-Ge as a function of annealing temperature; circles denote the VH component, squares the HH component.

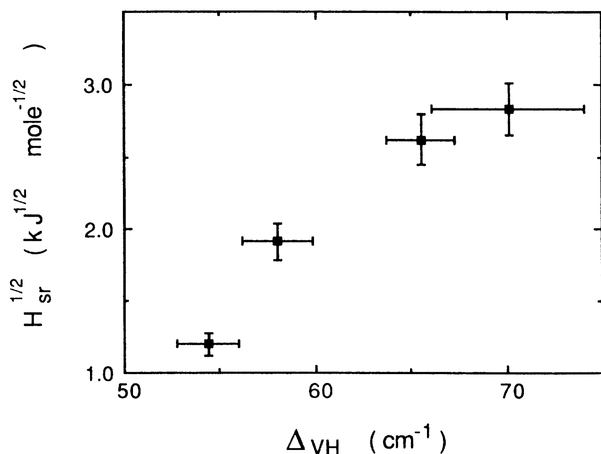

FIG. 3. Comparison of heat of structural relaxation and TO Raman bandwidth.

changes in the Raman width parameter. The results of Fig. 3 thus indicate consistency with a simple bond-strain model in which the energy stored in the distorted tetrahedral bonds varies as $(\Delta\theta)^2$. Were one to extrapolate this linear fit to $H_{SR}=0$, then a width approximately a factor of 2 greater than the TO band of c-Ge is obtained. This result is consistent with a phase transformation between amorphous and crystalline states, rather than a uniform transition, as might arise in microcrystalline models of the former.

The heat associated with structural relaxation is related to microscopic changes in the kinetic and potential energy with annealing. The kinetic-energy term is associated with changes in the vibrational density of states. For a fixed form of a dominant pairwise interaction, the potential-energy term is related to variations in the radial distribution function.[13] For a-Ge inelastic-neutron studies indicate some changes in the densities of states; however, the average vibrational energy does not change substantially.[7] This indicates that the heat released prior to crystallization is essentially due to structural ordering. Density measurements of ion-implanted a-Si indicate a density 2% below crystalline Si, but no variation was observed between the as-implanted to 500 °C annealed state.[14] This result and the small changes in the area of the a-Ge first coordination peak in the radial distribution function[2] (RDF) implies that structural relaxation is predominantly associated with bond-angle effects on the second RDF peak region.

The variation of H_{SR} with T_a may be fitted to the form

$$H_{SR}(T_a)=A+B\exp(-E_{ac}/kT_a)\ , \tag{1}$$

where A and B are constants and E_{ac} an activation energy. This yields an activation energy from room temperature to 327 °C of $\sim 0.16\pm 0.01$ eV for both a-Si and a-Ge. This value is also obtained from the present Raman spectra and agrees with Raman data obtained on rf-sputtered and evaporated a-Ge films.[11] This is reasonable, given the similar temperature dependence of Δ_{TO} with T_a for ion-implanted and rf-sputtered a-Ge.[10] These results indicate that the process of short-range structural ordering is primarily a function of network order rather than film density, microstructure, or strain states that are growth related.

It is useful to note that the temperature variation of the Raman and DSC data (see Fig. 2) exhibit a more rapid variation of these parameters above $\sim$200 °C. Studies of a-Ge properties associated with extrinsic film effects such as density-, porosity-, and surface-related dangling bonds have also been shown to have a qualitatively similar behavior to that of Fig. 2.[15] This may suggest that changes in film microstructure, such as void density, require rearrangements of the surrounding network. This is logically reasonable, given the connection between the interface of these defective regions and their constraint by the surrounding network.

The simple bond-strain model implies that

$$H_{SR}(ij)=C(\Delta\theta_i^2-\Delta\theta_j^2) \tag{2}$$

and

$$H_{ac}=C(\Delta\theta^2)_{min} , \tag{3}$$

where C is a constant and i and j refer to the initial and final states in the annealing process; $\Delta\theta_{min}$ is the minimum value of $\Delta\theta$ for the $a \rightarrow c$ transition. If state j corresponds to a minimum in $\Delta\theta$, as it does here, then

$$H_{SR}/H_{ac}=\left[\frac{\Delta\theta_i}{\Delta\theta_j}\right]^2-1 . \tag{4}$$

It is then possible to estimate $\Delta\theta_i$ (T_a) from H_{ac} and H_{SR}. The values of $\Delta\theta$ entering Eq. (4) are, in general, rms values. Previous estimates of the bond-angle distribution width have assumed a Gaussian (*G*) form for $P(\theta)$ so that the width $\Delta\theta_G=\Delta\theta_{rms}$. Recent evaluation[16] of a set of theoretical models based on structural relaxation of structures derived from Polk-Boudreux models[17] indicate, however, non-Gaussian behavior. While it is possible to fit $P(\theta)$ to a Gaussian for lower deviations from the mean, to obtain $\Delta\theta_G$ these values are less than the $\Delta\theta_{rms}$, especially at larger bond-angle distortions. Figure 4 indicates the values of $\Delta\theta(T_a)$ obtained for $\Delta\theta_{min}=9.2°$ and 10.0°. The former is the estimated rms value obtained from RDF and Raman studies and would be appropriate if the distributions are Gaussian. The latter value was, in contrast, obtained from the relation between the Gaussian and rms widths from a set of theoretical models in which $P(\theta)$ was non-Gaussian.[16] This procedure yields the initial state of disorder of the ion-implanted *a*-Ge annealed to 300 K as having an estimated bond-angle distribution width of 12°–13°. The 12° Gaussian distribution value is in excellent agreement with previous estimates based on the experimental and theoretical *VH* Raman component.[1] Other estimates of the range of $\Delta\theta$ of 7.7°–10.5° are lower than these values.[6] In addition, the ratio of these maximum and minimum values of order predict from Eq. (4) a significantly larger ratio of H_{SR}/H_{ac} than observed experimentally. We believe that the experimental results and more detailed Raman modeling support a larger $\Delta\theta_{min}$ as well as a smaller fractional variation due to increased disorder.

Annealing studies of ion-implanted *a*-Si also indicate changes in the Raman spectral form with T_a as shown in Fig. 5. Given the results in *a*-Ge relating $(H_{SR})^{1/2}$ to Δ_{TO}, this strongly implies that similar structural relaxation processes occur in *a*-Si. The relative, mass-normalized width of the TO band in implanted *a*-Si annealed to $T_a=27\,°C$ is narrower, however, than that of *a*-Ge. This implies that the degree of disorder in ion-implanted *a*-Si is less than that of *a*-Ge. As the thermal conductivity of *c*-Si is greater than that of *c*-Ge at the implantation temperature, the absence of an observed heat of relaxation cannot be due to self-annealing effects. Similarly, the lighter mass of the Si atom and the larger Ar dose implies that greater atomic displacements are expected in the ion-implantation process relative to Ge. This suggests that the greater order in implanted *a*-Si is a consequence of either larger atomic rearrangements after collision-cascade processes or larger annealing effects between 77 and 300 K. Greater structural order in *a*-Si relative to *a*-Ge may be a consequence of the increased strength of the covalent bond, as well as the greater strength in noncentral bond-angle interactions of Si that drive atomic rearrangements after ion damage. Alternatively, these interactions could account for enhanced low-temperature annealing effects in *a*-Si. Differentiating between low-temperature ordering or annealing effects requires *in situ* Raman studies that are not generally feasi-

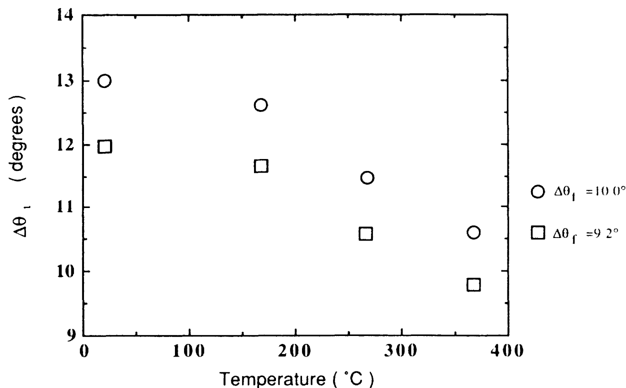

FIG. 4. Estimate of the rms bond-angle variation of ion-implanted *a*-Ge with T_a based on Eq. (4).

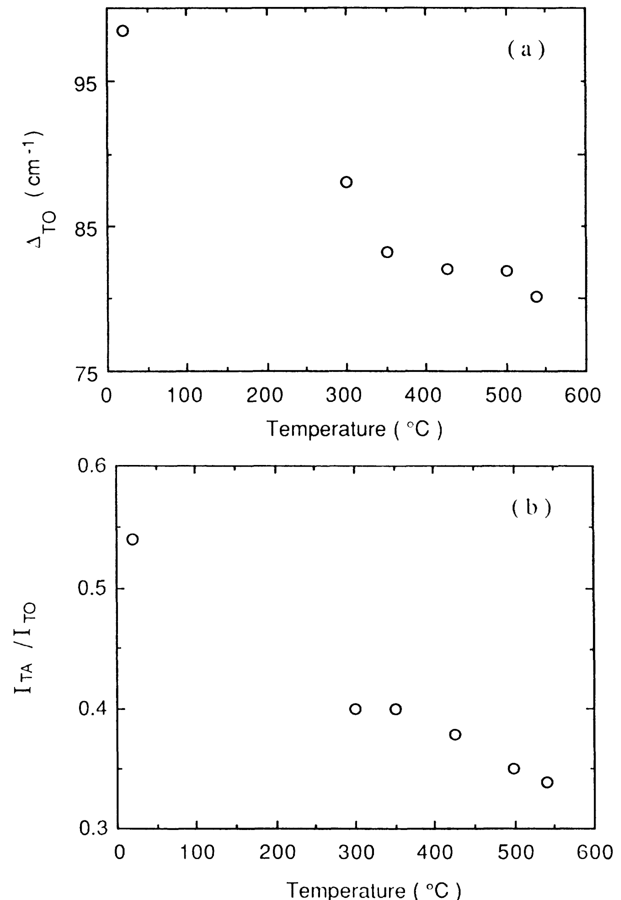

FIG. 5. (a) Variation with annealing temperature of the *VH* Raman TO bandwidth and (b) TA to TO intensity for ion-implanted *a*-Si.

ble for ion-implantation processes.

While H_{SR} has not been observed in *a*-Si, a theoretical estimate of its values may be obtained from the *VH* Raman spectra. Detailed Raman spectra of rf-sputtered and CVD *a*-Si materials have been utilized along with theoretical calculations of the *VH* component to estimate the relation between Δ_{TO} and $\Delta\theta$. These results and Eq. (4) yield theoretical values of H_{SR}. For the 27 °C annealed state of *a*-Si, $H_{SR}/H_t \simeq 0.24$. This value is substantially less than the ratio of 0.41 of *a*-Ge at 27 °C and is consistent with the relatively narrower TO width in *a*-Si. The contribution of H_{SR} should, however, be observable experimentally. The ~65% larger temperature interval for the relaxation process of *a*-Si and its higher-temperature range imply that such measurements are more difficult than in *a*-Ge. Estimates of H_{SR} for more highly disordered, rf-sputtered *a*-Si yield H_{SR}/H_t values comparable to that of *a*-Ge. This material may thus be more amenable to confirming the presence of a heat of relaxation in *a*-Si.

The Raman spectral widths in *a*-Ge imply the existence of a high degree of disorder in the as-implanted material that is comparable to that obtained in low-pressure rf-diode-sputtered films deposited near room temperature.[12] In the latter films ~2 at. % Ar is incorporated, while here the Ar concentration is <0.01 at. %. While it might be thought that more highly disordered states of *a*-Ge require impurities for their stability, the degree of disorder of ion-implanted samples indicate this is not necessary. Raman scattering studies performed *in situ* on dc-sputtered *a*-Ge deposited at 90 K indicate further that changes in bond-angle order occur upon annealing to 300 K.[18] As such, the observed structural order of ion-implanted samples annealed to 300 K is logically greater than that of the as-prepared lower-temperature state. This is also consistent with the observation of monotonic changes in structural order upon annealing above 300 K. Similar low-temperature annealing effects are also expected for *a*-Si. The present results in *a*-Ge and *a*-Si also suggest that structural ordering of ion-implanted III-V compounds should occur with a corresponding heat of relaxation.

ACKNOWLEDGMENTS

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