Calorimetric Evidence for Structural Relaxation in Amorphous Silicon

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Differential scanning calorimetry of amorphous silicon (*a*-Si) prepared by ion implantation shows a one-time low-temperature heat release, equal to one-third of the heat of crystallization. This heat release is direct evidence for structural relaxation of *a*-Si. It is in agreement with predictions made on the basis of Raman spectrometry.

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The structure of amorphous silicon (*a*-Si) has been the subject of study for many years and the emerging picture is that of a covalently bonded continuous random network.[1] On the average, the angles between bonds diverge 7°–12° from the ideal tetrahedral angle in a perfect crystal, yet there is only short-range order due to a large freedom in rotation around the axes parallel to the bonds.[1,2] It is generally assumed that the bond lengths are only slightly distorted. The strain energy associated with tetrahedral bond angle distortions is thought to constitute the main portion of the excess enthalpy of *a*-Si relative to crystalline Si (*c*-Si).[3] Ball and stick models[1,2] as well as computer simulations[4–6] indicate that changes in network topology coincide with changes in average bond angle distortion ($\Delta\theta$), and consequently with changes in the excess free energy of *a*-Si. A decrease in $\Delta\theta$ upon annealing is known as structural relaxation.

Experimental indications that structural relaxation does indeed occur in *a*-Si came from Raman spectroscopy.[7–9] In these measurements the phonon density of states is probed, and changes in the phonon spectrum after thermal annealing treatments can be related to changes in $\Delta\theta$. These changes consist essentially of a decrease in the width and a shift in the position of the first-order transverse-optic-like (TO) peak. The width is thought to be approximately linearly dependent on $\Delta\theta$.[3] Although there is little doubt that this interpretation of Raman spectra is qualitatively correct,[3,9–14] there is no general agreement on the quantitative relation between Raman spectra and bond angle distributions. In addition, the force constant in Si which relates bond bending to strain energy is not exactly known.[3] Estimates of the minimum and maximum obtainable strain energy were originally 12 and 40 kJ/mol.[7] Although these are values for the strain energy at 0 K, they may be used to estimate the heat of relaxation $\Delta H_{\mathrm{relax}}$. It follows that $\Delta H_{\mathrm{relax}}$ may be as high as 28 kJ/mol. More recent estimates for $\Delta H_{\mathrm{relax}}$ are 9 kJ/mol[3] and 4 kJ/mol.[14]

A calorimetric study of crystallization in *a*-Si and *a*-Ge showed that both materials release a considerable amount of heat upon crystallization.[15] However, a heat release prior to crystallization which could be attributed to structural relaxation occurred only in *a*-Ge and not in *a*-Si. Thus, a controversy arose. Computer modeling experience and Raman scattering experiments indicate a possible continuous spectrum of average bond angle distortions. On the other hand, the corresponding variable strain energy in *a*-Si has been denied by calorimetric experiments. It must be noted, however, that the latter experiments[15] were undertaken with the aim to study crystallization and no attempt was made to prove or disprove the existence of a variable strain energy in *a*-Si. For the case of *a*-Ge, the observed low-temperature heat release has indeed been related to a decrease in the TO peak width of the Raman spectrum.[13] In view of the similarity between *a*-Si and *a*-Ge it is therefore expected that *a*-Si does also exhibit a variable strain energy. In addition, the infrared optical properties of *a*-Si and *a*-Ge behave similarly upon low-temperature annealing. The changes in optical constants have been tentatively related to a decrease in $\Delta\theta$ upon annealing,[11] which is another indication that *a*-Si should exhibit a heat release qualitatively similar to that of *a*-Ge.

In an attempt to resolve this controversy we have undertaken a series of precision differential scanning calorimetric (DSC) measurements of the heat of relaxation in ion-implanted *a*-Si layers. The first results of these studies indicate that structural relaxation in *a*-Si is indeed accompanied by a measurable heat release, as is reported in this Letter.

Circular disks of 7.5 mm diam were cut out of a 200-μm-thick, double-sided polished, high-resistivity float-zone Si wafer. After cutting, these disks were annealed under flowing dry N_2 to remove crystal damage which may have formed. Subsequently, layers of *a*-Si were formed by multiple ion implantation of 0.5-, 1-, and 2-MeV ^{28}Si or ^{40}Ar ions into both the fronts and backsides of the Si disks. The total dose was 5×10^{15} atoms/cm^2 for the Si implants and 2×10^{15} atoms/cm^2 for the Ar implants. During implantation the disks were cooled us-

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ing liquid nitrogen and the ion beam was scanned electrostatically over the samples. This resulted in an amorphized surface layer of 2.2 ± 0.1 μm as determined by Rutherford backscattering spectrometry (RBS) and channeling of 1-MeV H^+ ions. A second type of samples consisted of ≈ 20-μm-thick Si sheets which were implanted (on one side only) to give *a*-Si layers of either 2.2 or 1.45 μm (1.45-μm layers were formed using only 0.5- and 1-MeV beams). Implantations and RBS analyses were performed using the new ion-beam facility of the FOM-Institute for Atomic and Molecular Physics.[16] Ion implantation rather than vacuum evaporation was used because the latter method is known to result in *a*-Si layers which contain voids, and upon exposure to air, may take up impurities such as water vapor.[17] This can only be prevented by raising the substrate temperature during evaporation and/or by a thermal anneal before exposure to air. However, these procedures obviously result in *a*-Si films which are already partially relaxed. Self-implantation, on the other hand, yields well defined layers of pure *a*-Si without any voids or impurities, and is thus ideally suited for the preparation of high-quality material. Moreover, ion implantation with MeV beams makes it possible to form *a*-Si layers of several microns thickness, whereas evaporated *a*-Si is often found to peel off the substrate when films become thicker than ≈ 0.5 μm.

Precision differential scanning calorimetry (DSC) measurements were performed using a Perkin Elmer 7 series DSC. A DSC consists essentially of two identical furnaces. It measures the extra power that has to be fed to one furnace, in comparison to the reference furnace, in order to keep both furnaces at the same temperature, while the temperature is scanned over the range of interest. The main problem with DSC is to obtain a reliable power base line which can be compared with the actual measurement. Small changes in the DSC, as are produced by removing and immediately replacing a sample, result in relatively large base-line differences. Even when the DSC is not touched between two identical measurements there is a difference due to a different thermal history. This difference, however, is to a large extent reproducible. Measurements were performed using two sets of samples in the following way: First an ion-implanted sample was loaded in the left DSC furnace and a *c*-Si reference sample in the other one. Then one run was made consisting of an isothermal scan at the starting temperature (313 K) followed by a scan over the entire temperature range and a second isothermal scan at the final temperature. After cooling down, an identical run was made using exactly the same sequence. Subtraction of the signal of the second run from that of the first run gives the heat release in the left DSC furnace plus the signal due to unbalance caused by thermal history effects in the DSC. Then the reference sample was loaded in the left DSC furnace and a second implanted sample was inserted in the right furnace. The same sequence of measurements was performed with this second sample. Because the sample is in the other furnace, subtraction gives a negative signal when the sample releases heat. This signal is superimposed on the same thermal history signal as was found on the first sample. Subtraction of the second difference signal from the first yields the sum of the heat release in both samples, while the signals due to thermal history effects are canceled.

The above procedure can be viewed as a method to average the signals from different samples in such a way that the influence of unbalance in the DSC is minimized. For scans over a temperature range from 300 to 1000 K at a scan rate of 40 K/min, it gives base lines with total deviation less then 0.15 mW over the entire temperature range. Most of this deviation is due to unbalance at temperatures above 800 K. Although the improvement over single-difference curves is small, it is important when accurate base lines over a wide temperature range extending to high temperatures are necessary. The influence of base-line drifts was further minimized by stacking two or three samples at a time in the DSC heads. Samples from Si disks were placed directly in the DSC heads, whereas samples made from thin Si sheets rested on *c*-Si disks and made no contact with any material but Si.

Figure 1 shows three DSC difference curves. Curve *a* was taken on *c*-Si reference samples and serves to give an indication of base-line stability. Curves *b* and *c* were taken at 40 K/min on implanted samples containing in total ≈ 25 μmol *a*-Si, where curve *b* was taken on samples that were preheated to 813 K and curve *c* on as-implanted samples. Preheating was done in the DSC by raising the temperature at a constant rate of 80 K/min to 813 K immediately followed by quenching. Both curves show a peak near 950 K, which is recognized as crystalli-

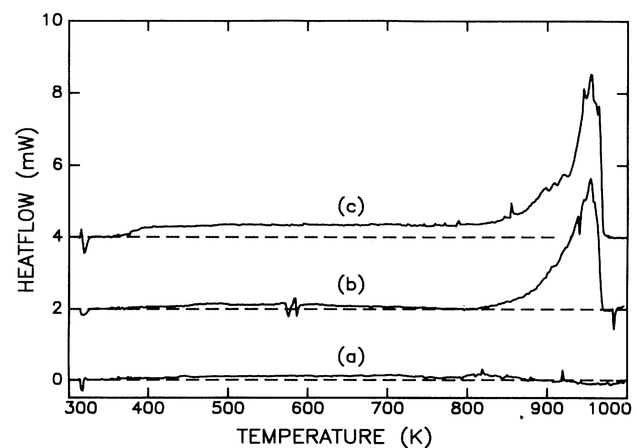

FIG. 1. Differential scanning calorimetry difference traces for (*a*) *c*-Si, (*b*) *a*-Si which has been preannealed to 813 K, and (*c*) as-implanted *a*-Si. Scan rate, 40 K/min. Curves *b* and *c* have been shifted over 2 and 4 mW, respectively, for clarity.

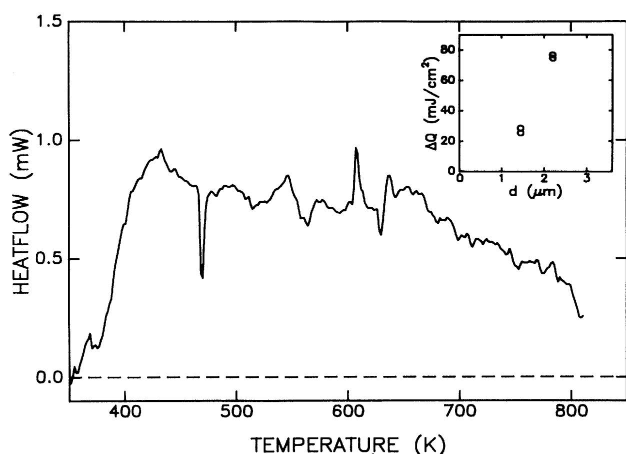

FIG. 2. Differential scanning calorimetry difference trace for as-implanted a-Si. Scan rate, 80 K/min. Inset: Integrated heat release, normalized to surface area, for a-Si layers of different thickness.

zation. Integrating the area under these peaks gives values for the heat of crystallization of a-Si equal to 12.8 kJ/mol (curve c) and 10.5 kJ/mol (curve b). This is in reasonable agreement with the value of 11.9 kJ/mol reported by Donovan *et al.*[15] The exponential shape of the curve corresponds to thermally activated regrowth at the c-Si/a-Si interface.[15,18] In addition to this peak, curve c for the as-implanted sample shows a low-temperature heat release which is absent for curve b of the preannealed sample. This signal begins around 400 K and remains constant at a level of ≈ 0.4 mW until ≈ 900 K. Since the uncertainty in the area under curve c in Fig. 1 is still considerable, DSC traces were taken at 80 K/min and in a narrower temperature range. This made it possible to determine more precisely the amount of heat released. An example of such a trace is shown in Fig. 2. The integrated power under the curve amounts to 186 mJ. Combined with the amount of a-Si in the DSC (49.1 μmol) this gives a heat release of 3.6 kJ/mol.

Analysis of the crystallized sample by RBS and channeling showed that no detectable chemical changes have occurred on the Si samples. Channeling analysis of samples that were preannealed to 813 K showed that the a-Si/c-Si interface had not moved beyond 50 nm from its original position. This limits the contribution of crystallization to the low-temperature heat release to less than 20 mJ. It was found that the low-temperature heat release scales with the thickness of the a-Si layer (see inset in Fig. 2). This is a clear indication that the heat is released by the bulk of the a-Si rather than by the interface with the substrate. A second possible cause for the heat release may be a relaxation of mechanical stresses in both the a-Si film and the substrate. These stresses are caused by the small density difference between a-Si and c-Si. The energy due to these stresses can be estimated by $U_{\text{stress}} = V_{\text{mole}} B (\Delta V/V)^2/2$, where V_{mole} is the molar volume of Si (12 cm^3), B is the bulk modulus of Si (0.988×10^{11} N/m^2), and $\Delta V/V$ is the volume change upon amorphization (taken to be 1%). This results in 60 J/mol. It is noted, however, that this energy is supposed to be released mainly upon crystallization, because only then the density difference vanishes completely. One final possibility to be considered is the heat release due to removal of dangling bonds (DB) from the material. Spitzer, Hubler, and Kennedy[19] have used electron paramagnetic resonance to determine the DB density in ion-implanted a-Si before and after thermal annealing. They found a decrease in the DB density from 2×10^{19} to 1×10^{19} cm^{-3}. In order to explain the observed heat release by removal of DB only, each removed DB should yield an energy of more than 1 keV, which is clearly not the case.

The combined effect of macroscopic stress, low-temperature crystallization, and DB removal is estimated to amount to 0.4 kJ/mol at maximum. Thus, the only remaining plausible origin for at least 80% of the observed low-temperature heat release is structural relaxation in the a-Si. Calorimetry results are summarized in Table I. From these data it is concluded that the high-temperature heat release is 11.7 ± 1.0 kJ/mol and that the low-temperature heat release is 3.7 ± 0.2 kJ/mol.

Raman spectra of a-Si support the conclusion that the

TABLE I. Measured values for the heat of relaxation (low T) and crystallization (high T) in a-Si (Si^+ implanted, except set 2=Ar^+ implanted; ellipses indicate not measured).

Sample	Amount in DSC (μmol)	Heat release (mJ) low T	Heat release (mJ) high T	ΔH_{relax} (kJ/mol)	ΔH_{cryst} (kJ/mol)
Set 1	27.5	···	352	···	12.8
Set 2	74.4	266	···	3.6	···
Set 3	49.1	186	···	3.8	···
Set 4	24.2	···	254	···	10.5
Set 5	43.4	164	521	3.8	12.0
Set 6	41.6	145	470	3.5	11.3
Average				3.7 ± 0.2	11.7 ± 1.0

observed low-temperature heat release is caused by structural relaxation of a-Si. In order to check whether the (Si implanted) a-Si samples used for this work show the same behavior as found previously,[7-9,13,14] some samples (set 3) were subjected to analysis by Raman spectroscopy. Indeed, the half-width $\Gamma/2$ of the TO peak was found to decrease from 43 cm^{-1} for the as-implanted to 34 cm^{-1} for the relaxed sample. Moreover, Raman spectra indicate that relaxation saturates at a temperature-dependent level.[7,8] This implies that the accessible relaxation level decreases continuously upon temperature ramping which gives rise to heat release over the entire temperature range. This is indeed the nature of the heat release that is observed in Fig. 1, curve c.

From the values shown in Table I, it can be seen that the strain energy stored in the a-Si network varies between 15.4 kJ/mol for as-implanted to 11.7 kJ/mol for well annealed a-Si. The value for ΔH_{relax} is probably an underestimate, for the following reasons: Firstly, it is possible that the a-Si did not relax completely during the first DSC scan to 813 K. If that is indeed the case, relaxation will continue during the second run so that the difference curve gives an underestimate for ΔH_{relax}. Secondly, the values for ΔH_{relax} in Table I were determined up to 813 K. Comparison of curves b and c in Fig. 1 shows that relaxation probably continues during the beginning of crystallization. Thus, part of the heat which is attributed to crystallization may also be due to relaxation.

In conclusion, we have undertaken a series of precision differential scanning calorimetric measurements on pure a-Si. In addition to a heat release due to crystallization, a one-time low-temperature heat release of 3.7 kJ/mol is found. This heat release is attributed to structural relaxation in a-Si which lowers the strain energy, stored mainly in distorted bonds in the amorphous network, from 15.4 to 11.7 kJ/mol. These findings are in good qualitative agreement with predictions based on Raman experiments.[3]

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