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Low temperature relaxation in amorphous silicon made by ion implantation

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Abstract

A 3 μm thick surface layer of small crystalline Si discs has been made amorphous by ion implantation at liquid nitrogen temperature. Upon heating the samples to room temperature for the first time, an irreversible heat release is observed, which is attributed to low-temperature structural relaxation of the amorphous Si. The time constant at –50°C is about 3–4 times longer than those at 200°C and 500°C. The instantaneous heat release during the heating phase is larger than above room temperature, but not as large as would be expected if the heat release were proportional to the number of states at the Fermi level that is removed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Pure amorphous silicon (a-Si) made by ion implantation releases a considerable amount of heat when it is heated for the first time from room temperature (RT) up to its crystallization temperature [1]. About 1/3 of this heat is released over a wide temperature range and it is associated with structural relaxation. Structural relaxation has been explained as point defect annihilation. It is accompanied by changes in other properties as well, including the width of the TO-like peak in the Raman spectrum.

In situ Raman measurements of a-Si made at liquid nitrogen temperature [2] showed that this width is much larger than in room-temperature stabilized a-Si. The TO-like band peak width increases roughly linearly as the temperature is decreased to 77 K, which would imply that the heat released upon relaxation is roughly linear with the temperature range over which the relaxation took place. This is similar to the behaviour between RT and 600°C, where a flat heat release was observed. It is quite different from the behaviour of the equilibrium electronic density of states (DOS) at the Fermi level, which has been found from conductivity measurements to decrease sharply between 77

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K and RT [3]. The heat release has also been linked to point defect annihilation in the a-Si, and if the heat release per degree temperature increase scales linearly with the decrease in the DOS over the same temperature range, than the heat release should be much larger below RT than above.

Calorimetry at subambient temperatures requires that either the DSC is done in situ, or that the a-Si samples are removed from the vacuum chamber, transported to the calorimeter, and loaded in the DSC samples pans without heating up appreciably. I used the second approach and will discuss some consequences of this choice in the following sections.

2. Sample preparation: ion implantation and loading

Circular discs of 7.6 mm diameter were cut out of 100 μm thick undoped float-zone c-Si wafers and mounted in a vacuum chamber. The (polished) backside of the discs was clamped, with a small dot of silverpaste, to the front surface of a c-Si wafer that had been heat sunk on a Cu block by means of vacuum grease and clamps. The Cu block was brought down to 77 K by filling it with liquid nitrogen and the discs were implanted with Si ions of 0.5, 1, 2, 3, and 4 MeV. The ion doses were 5×10^{15} ions/cm^2 for the first three implantations and 5.25×10^{15} and 5.42×10^{15} ions/cm^2, respectively, for the 3 and 4 MeV treatments. The heat load was maintained at less than 1 W/cm^2 during most of the implantation and further reduced during the last 10% of the ion dose to avoid structural relaxation by beam-heating of the small samples. This implantation treatment is expected to amorphize a 3 μm thick surface layer of the c-Si samples.

After the implantation, the sample holder was removed from the vacuum chamber but without removing the liquid nitrogen from the Cu reservoir. Small screwdrivers and tweezers with cooled tips were used to remove the clamps holding the small discs whereupon the samples fell and were caught in a styrofoam container filled with liquid nitrogen. This container was covered and brought to the calorimetry room. Before and during the ion implantation, the DSC had been cooled down and allowed to equilibrate by repeating a few times the scans and isotherms to be applied to the a-Si samples, but with dummy samples. The discs were then loaded in one of the sample pans and the actual data collected.

3. Low temperature calorimetry

Calorimetry was done with a computer controlled Perkin-Elmer DSC-7 instrument equipped with a liquid-nitrogen reservoir and continuously purged with dry, high-purity He gas. Each measurement consisted of an isotherm at −150°C, which was started after the DSC instrument had reached a stable temperature reading at that value, a scan from −150 to −50°C at a scan rate of 40 K/min, and an isotherm of 20 min at −50°C, immediately following the scan. After the first sequence of isotherm/scan/isotherm, the DSC was brought down to −150°C and the procedure was repeated. The power difference required to keep both sample pans at the same temperature was recorded and the difference between the first sequence and the second yields the heat release by non-reversible phenomena in the sample pans during the first sequence.

Normal DSC procedure would require that the sample pans are dry and clean before and during the measurements which means that the sample pans are heated up to room temperature, loaded, and cooled down again. By loading cold samples into cold sample pans, inevitably some condensation occurs and in the present case, small particles of silver paste may also end up in the sample pans. The highest temperature of the measurement runs is −50°C, so that any ice particles present during the first sequence, are still present during the second one. Neither ice nor silver paste by itself would give a non-reversible signal, however sudden discontinuities may occur if during the first or second run the samples "settle" in the pans leading to a sudden change in thermal contact between sample pans and samples.

Following the low-temperature DSC, the instruments and the samples were allowed to warm up to room temperature, the samples were thoroughly cleaned and dried, and a similar measurement was done with the same samples, but now between +50°C and +200°C. This latter

measurement provides a link between the current, low-temperature DSC measurements and earlier, scan and isotherms at higher temperatures.

4. Results and discussion

Fig. 1 shows the isotherms at −50°C and +200°C measured immediately after the low-and high-temperature scans, respectively. The isotherm baseline measured with non-implanted c-Si discs in both sample pans is shown for comparison. The insert shows the temperature scan from −200°C to −50°C which exhibits a large discontinuity attributed to settling. The smooth line through the isotherms are single exponential fits to the data between 60 and 1000 s. Table 1 shows the results of the fits as well as other related data. Equally good fits can be obtained with bimolecular or streched exponential functions but a single exponential was used here to allow comparison with the single-exponential decay times determined earlier at high temperatures as reported in Ref. [1].

The low-temperature isotherm decays much (3–4 times) slower than the high-temperature isotherm. This is remarkable, since it was found earlier that the isothermal decay time remains fairly constant at higher temperatures (see Table 1). The instantaneous heat release during the temperature scans just before the start of the isotherm is similar for both measurements, but somewhat higher (12.3 W/mol) at −50°C than at +200°C (8.8 W/mol). These values scale reasonably well with the change in TO-band width as determined by Raman spectroscopy. Had the heat release scaled with changes in the DOS, than the heat release at −50°C would have to be at least 4 times as large as that at 200°C and that is clearly not the case.

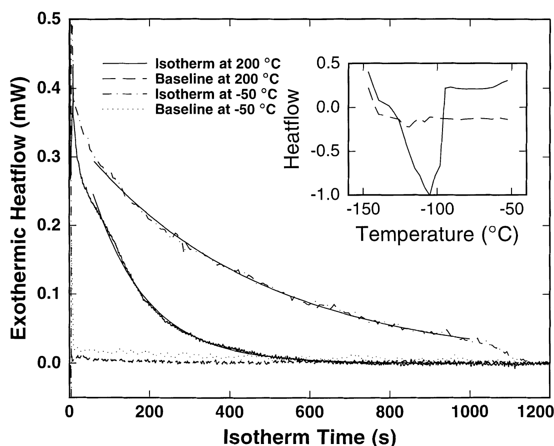

Fig. 1. Heat release from amorphous silicon held at −50°C (dash-dotted line) and at +200°C (solid wiggly line). The isotherms were measured immediately after heating at 40 K/min from −150°C and +50°C, respectively. The dotted and dashed line depict the baseline as measured on c-Si reference samples. Inset: Heat release during the heating phase. Solid line: Signal from a-Si; dashed line: baseline signal from c-Si.

Does the absence of a giant heat release below ambient, such as would be expected based on the conductivity measurements, imply that the heat release is not due to defect annihilation? I do not think so. I suggest that the energy stored per defect is not the same for the defects that are removed at low temperature and those that are removed at high temperature. Rather, it is not clear that the entire defect structure associated with a state in the gap is removed at the same time as the gap-state. Gap states can be passivated either by impurities such as hydrogen or by small local rearrangements that do not involve the type of atomic mobility required for extensive defect repair and long (nm) range diffusion. Such rearrangements would turn a defect with a gap state into another defect but one without a gap state. The energy stored in strained bonds surrounding the defect would only be recovered at higher temperature once the defect is fully removed.

As a final remark, the DSC data presented here are not entirely satisfactory because of the settling discontinuities and because only a few samples were investigated. It remains of interest to repeat the measurements a few times and to try to measure isotherms at even lower temperatures (−100°C should be achievable).

5. Conclusions

In conclusion, the heat release induced by structural relaxation of amorphous silicon has been measured at subambient temperatures. The magnitude of the heat release between −150°C and

Table 1
Summary of DSC, Raman, and conductivity data on a-Si at low and high temperature

Calorimetry	Ref. [1]			This work	
Temperature (°C)	200	350	500	−50	200
Decay time (s)	113	107	115	443	136
Instantaneous (W/mol)	8.8	7.5	5.6	12.3	8.8
Raman	Ref. [1]			Ref. [2]	
TO half-width (cm^{-1})	41.0	38.0	34.1	45	39.2
Conductivity	Ref. [3]			Ref. [3]	
DOS at E_F (cm^{-3} eV^{-1})	1.0×10^{20}	7.3×10^{19}	4.4×10^{19}	2.1×10^{20}	1.0×10^{20}

−50°C is slightly, but not substantially higher than that during high-temperature annealing. I tentatively conclude that the heat release scales with the Raman to-like band width and not with the electronic density of states at the Fermi level as measured by conductivity measurements. The time constant is much larger than above room temperature, which represents a departure from the constant behaviour from +150°C to +500°C.

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