



# Radiation damage in silicon studied in situ by nanocalorimetry

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## Abstract

In situ observations of thermal processes involving nJ energies are impractical, if not impossible, with conventional differential scanning calorimetry (DSC), but the nanometric scale of recently developed nanocalorimetry systems should make such observations possible. Nanocalorimetry is based on membrane calorimeters made using nanofabrication technologies. Here we present initial results of an in situ investigation of damage dynamics in amorphous silicon (a-Si). A thin film of a-Si was deposited on the calorimeter membrane and implanted with low-energy Si ions. One-time heat releases were measured for doses ranging from  $10^{12}$  to  $10^{14}$  ion  $\text{cm}^{-2}$ . Subsequent calorimetry scans showed no difference with the baselines, indicating that the damage remaining is stable over the temperature of operation. The measurements were taken immediately after ion implantation in the same environment and were repeated. For doses of  $10^{12}$  ion  $\text{cm}^{-2}$  and less, the signal intensity was below the sensitivity limit. A saturation of the total heat released was observed. This saturation was correlated with previous DSC measurements and attributed to the relaxation of ion beam implanted a-Si.

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## 1. Introduction

One of the techniques used to study structural processes in crystals is calorimetry. Differential scanning calorimetry (DSC) measures temperature-activated processes during a temperature scan usually starting at room conditions. An adiabatic system is difficult to build and precision is affected by ex situ measuring conditions. We present a new in situ method to explore heat processes during the

structural transformation that damage undergoes during annealing. Nanocalorimetry allows to measure heat exchanges of the order of the nJ/K in systems of nanometric scale and has been used to study many phenomena, including melting point depression [1,2]. The  $\text{SiN}_x$  membrane-based system, operated at very fast heating rate, offers almost adiabatic measuring conditions. The temperature can be controlled during implantation and maintained for the calorimetry scan.

Amorphous silicon (a-Si) has been extensively studied in the past decades, both experimentally and theoretically. The usual picture of a-Si is that of a random network structure for which the local

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structure is similar to the crystalline form, with the bond angle distortions varying between  $7^\circ$  and  $12^\circ$  [3] from the tetrahedral structure. In a-Si prepared by self-implantation, an excess of free energy is released upon relaxation, accompanied by a decrease in average bond angle distortion. Once a-Si is relaxed, it can be brought back to the unrelaxed state by additional ion implantation [3]. Here, we measure by nanocalorimetry the heat released by damage in a-Si after ion implantation for different doses. We have observed a saturation of this released heat versus dose and correlated these results with previous ex situ DSC experiments [3,4].

The aim of this article is to show our ability to measure in situ the heat exchanges during thermal annealing in ion-implanted a-Si, to discuss its sensitivity and to present the preliminary results we have thus obtained. The technique will first be introduced, followed by damage relaxation measurement results and discussion.

## 2. Nanocalorimetry experiment

A nanocalorimeter consists of a thin free  $\text{Si}_3\text{N}_x$  membrane (typically 150 nm thick and several mm in height and width) supported by a Si frame. A metallic heater strip made of Pt (25 nm thick) is deposited on one side of the membrane. By inducing a current through such a metallic heater, it will serve to heat the membrane and will provide a way to calculate its temperature. For this purpose the heater resistivity is calibrated against the temperature prior to the experiments. Very fast heating, up to  $10^6$  K/s can be achieved by this method, making the radiative and conductive losses negligible, since the losses are roughly time-proportional. The system is thus operated in nearly adiabatic conditions. Fast heating-rates also transform small amounts of energy into measurable power. This set up has been tested in extenso with melting point depression experiments of In and Sn. In our experiments, a thin layer of a-Si is deposited on the membrane of two calorimeters, on the opposite side of the metallic strip (Fig. 1). One calorimeter is used as is and it serves as a reference sensor. The other is implanted

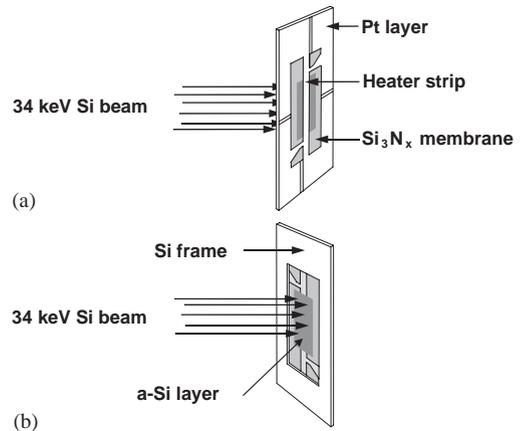


Fig. 1. Calorimeter view from: (a) the front side and (b) the back side. The 150 nm layer of a-Si is deposited on the backside of the calorimeter, as opposed to the Pt layer, which is on the front side. The implantation is carried out from the backside. The a-Si layer is not in contact with the Si frame, to prevent heat losses by conduction.

in order to induce damage. During the experiment, a current pulse passes through the heaters of the sample and reference simultaneously. The voltage and current across the heaters are measured and used for power and temperature calculations. From this, we can deduce the heat as a function of temperature necessary for damage relaxation. The measurements are done in situ, immediately after the implantation, offering the possibility of a high reproducibility rate with environment and temperature control during implantation and measurement.

In these experiments a 150 nm a-Si film has been deposited by plasma-sputtering on the membrane of the sample and reference calorimeters. These are then heated to  $500^\circ\text{C}$  in a vacuum chamber in order to carry out the calibration, that is, a four-point resistance measurement as a function of temperature while the system cools off. After a set of baseline measurements has been acquired, the sample is irradiated with a 34 keV Si-beam. The baselines give the intrinsic difference in heat capacity between the sample and the reference calorimeters versus temperature. Different implantation doses ranging from  $10^{12}$  to  $10^{14}$  ions  $\text{cm}^{-2}$  have been carried out. At 34 keV, the Si ions, which have a projected range of 56 nm according to SRIM-2000 [6], are completely stopped within

the a-Si layer and none penetrate the membrane or Pt layer at the back. This can be verified by observing the resistance during implantation. At higher energies, the ions induce damage in the metallic strip, changing its resistance and thus the calibration, leading to erroneous temperature measurements. The sensitivity in this experiment is of the order of 0.2 mW (10 nJ/K at 22 000 K/s). Better precision can be achieved by using a baseline subtraction system and a second amplification stage.

Fig. 2 shows a typical measurement of the voltage across each calorimeter, the current passing through and the differential voltage between both, which has been multiplied by a factor of 5. For the differential voltage, the dash-dotted line represents the baseline and solid line represents the experiment, which diverges slightly from the first beginning at 8 ms, due to the relaxation process in a-Si. The signal coming from relaxation is a one-time heat release, which means that the deviation from baseline is seen only on the first scan after implantation. The slope in the baseline results from the differences in the voltages shown due to dissimilar calorimeter properties. The current and voltage curves are used to calculate the resistance, which is converted to

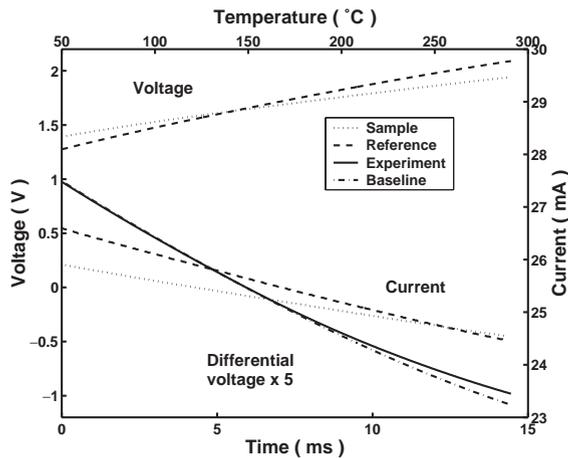


Fig. 2. Voltages and currents on sample and reference sensors and differential voltage across the two as a function of time or temperature. The temperature scale is calculated using the current and voltage curves along with the calibration. It is almost linear with time for short current pulses.

temperature using the calibration carried out before the experiment. The current pulse in this experiment has a duration of 15 ms. The temperature increases almost linearly with time.

### 3. Heat flow results

Fig. 3 shows heat flow curves for different implantation doses. We find no signal at  $10^{12}$  ions  $\text{cm}^{-2}$  or less. The heat released increases monotonically with the dose from  $10^{13}$  to  $2 \times 10^{14}$  ions  $\text{cm}^{-2}$  although not linearly, as we shall see in the next figure. Each curve results from the first calorimetry scan after implantation, where we believe all damage relaxes and moves into a state stable over the temperature range of the experiment. The second and subsequent curves contain no signal and are identical to the baselines. We therefore assume that a nanocalorimetry scan brings the system to its original state and that calorimeters can be used more than once.

The heat flow calculation from these signals is described by Allen et al. [5]. This includes baseline subtraction to account for the fact that calorimeters are not identical. The shape of the curves, the fact that they decrease in negative heat flows, determines that heat is generated by the irradiated

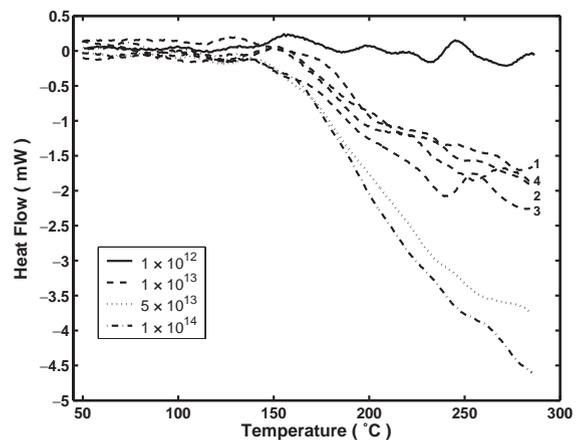


Fig. 3. Heat flow as a function of temperature for different implantation doses. The dashed lines all refer to the dose of  $10^{13}$  ions  $\text{cm}^{-2}$ . These were taken in the order shown by the numbers on the right.

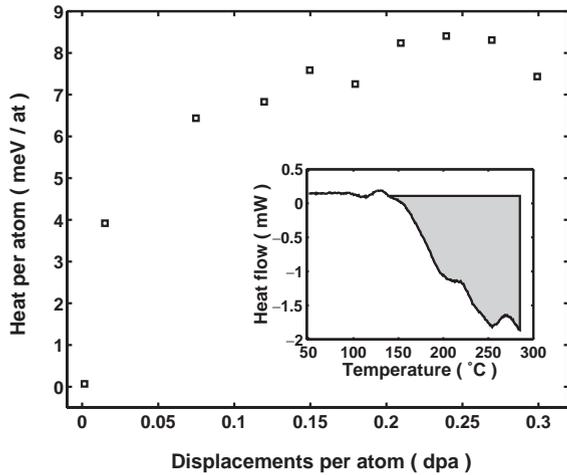


Fig. 4. Total heat liberated per lattice atom between the surface and a depth of 75 nm during experiment between 140°C and 285°C as a function of atomic displacement. Each data point corresponds to the integrated heat flow as shown in the inset. A possible offset has been removed, chosen to minimize the integration in the 50–140°C region.

system. It can be seen that damage relaxation liberates energy over a large temperature region, which starts at about 140°C. The dashed curves all correspond to the same dose (repeated) of  $10^{13}$  and demonstrate the reproducibility of the results. Fig. 4 shows the total heat produced during annealing after implantation between 50°C and 285°C. Each dot corresponds to a numerical integration of the area over the calorimetric curves in Fig. 3. These were performed with boundaries at 140°C and 285°C, and with an offset removed. We see a saturation of this energy release versus displacement so that it is not a linear function. As the implantation dose increases, a-Si returns to its unrelaxed state. After a certain dose, the process reaches saturation. This phenomenon was observed by DSC measurements between 0.01 and 1 dpa and by Raman spectroscopy under similar conditions [3,4]. Our in situ results correlate fairly well with these experiments, both qualitatively and quantitatively.

#### 4. Conclusion

This work demonstrates the use nanocalorimetry as an in situ tool to study and understand damage relaxation and dynamics. Here, we have studied these processes in implanted a-Si. We have measured the heat released by relaxation during annealing between 140°C and 285°C for doses ranging between  $10^{12}$  and  $2 \times 10^{14}$  ions  $\text{cm}^{-2}$ . The results are well reproducible. We have found that the heat released does not vary linearly with implanted dose but saturates over  $5 \times 10^{13}$  ions  $\text{cm}^{-2}$ . This saturation is interpreted as an indication of unrelaxation of the a-Si.

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