# THERMAL EVOLUTION OF DEUTERIUM IN 4H-SIC

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## ABSTRACT

4H-SiC samples were implanted at room temperature with 30 keV $D^+$ ions at a dose of $5x10^{16}$ $D^+/cm^2$. Nuclear reaction analysis (NRA) and secondary ion mass spectroscopy (SIMS) measurements were performed to study the deuterium profiles after subsequent annealing at 1000-1250°C for 10min.Also, analytical techniques: RBS/C and thermal desorption spectroscopy (TDS) were carried out to characterize the evolution of implantation induced defects upon annealing. According to the NRA measurements, no deuterium release was found in the sample annealed at 1000°C. However, increasing the temperature to 1150°C led to a 40% decrease of deuterium content. Similar results about the evolution of D profiles upon annealing have also been obtained by SIMS measurements. In addition, SIMS measurements show that the maximum of the deuterium concentration shifts to the surface. Deuterium desorption at annealing temperatures higher than 1000°C was further confirmed by TDS experiments. Results from RBS/C indicated that during the desorption of deuterium, the implantation induced damage was annealed. These results are discussed.

## INTRODUCTION

Silicon carbide is a wide-band gap semiconductor material and its excellent physical and electrical properties make it a good candidate to operate under extreme conditions. SiC devices can work at temperatures, frequencies and power higher than for Si and GaAs. The control of the p and / n-type doping is still a problem to obtain good SiC-based devices. One of the problems is related to interaction of hydrogen impurity with electrically-active centers. Hydrogen is also used in a Smart-Cut© process to create SiC on insulator (SiCOI) films. Whereas hydrogen behaviour in silicon is relatively well understood, investigations of hydrogen in SiC are still in the beginning [1-4]. Hence it is of interest to understand the effects of deuterium implantation induced defects during annealing.
Several groups investigated retention and release of implanted deuterium in SiC [5,6]. It was shown that in the temperature range from RT to 500°C deuterium is effectively trapped in the sample even at implanted doses as high as $5x10^{17}$ $D^+/cm^2$. No deuterium release was observed at temperature below 800°C. In this study we report investigation of the deuterium behaviour after high-temperature (>800°C) annealing.

## EXPERIMENTAL

The 4H-SiC samples (phosphorus-doped) produced by CREE Inc. were implanted at IRI in Delft, the Netherlands. They were implanted with deuterium ions at 30 keV and with a dose of $5x10^{16}$ $D.cm^{-2}$. Then, they were annealed in a Rapid Thermal Annealing furnace in a nitrogen ambient in a temperature range from 1000°C to 1250°C during 10 minutes. Both NRA and

RBS/C were performed by using the 3.5 MeV van de Graaf implanter (CERI Orleans). In these measurements 1.2 MeV $^3He^+$ beam is used to detect the deuterium by detecting protons and alphas from nuclear reaction $D(^3He,p)^4He$ for NRA and backscattered $^3He$ for RBS/C. In Thermal Desorption spectroscopy (TDS) deuterium effusion was monitored by a quadrupole mass spectrometer at masses 3 and 4 in order to study the release as HD and $D_2$ molecules. Temperature ramp rates of 1 and 3 K/s were used. Calibration of gas release was performed by admitting a known amount of gas into the experimental chamber. SIMS measurements were performed at the INSA, Villeurbanne.

## RESULTS

### NRA profiles

Figure 1 gives the NRA spectrum obtained for the as-implanted sample. The fitting results according to SIMNRA code are also presented in this figure. In this fitting a multi layer model was used. Each layer consisted on silicon carbide with a small amount of deuterium $(SiC)_{1-x}D_x$. By fitting processes we could compare simulated and experimental curves until we got the right profile according with the experimental charge. Figure 2 presents the evolution of the deuterium profiles versus annealing temperatures. The as-implanted sample provides a peak centered at 390 nm with a maximum concentration of $1.7x10^{21}$ at.cm$^{-3}$. No significant change is observed after a 1000°C annealing step, the peak shape and the maximum concentration remain unchanged. However, an annealing at 1150°C results in a decrease of deuterium concentration and a shift of 20 nm in the peak.

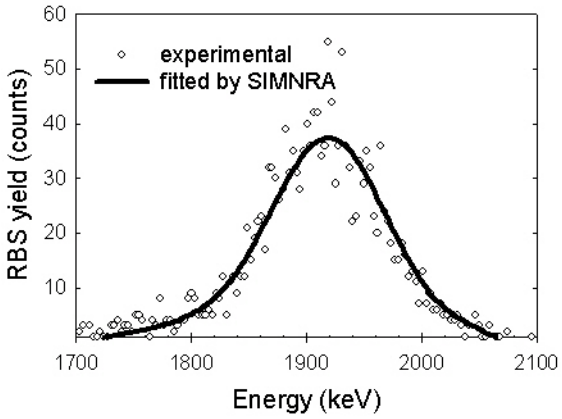


**Figure 1 :** Comparison of deuterium profiles in an as-implanted sample obtained by experimental NRA measurements and a simulated curve (SIMNRA) using a multi-layer model.

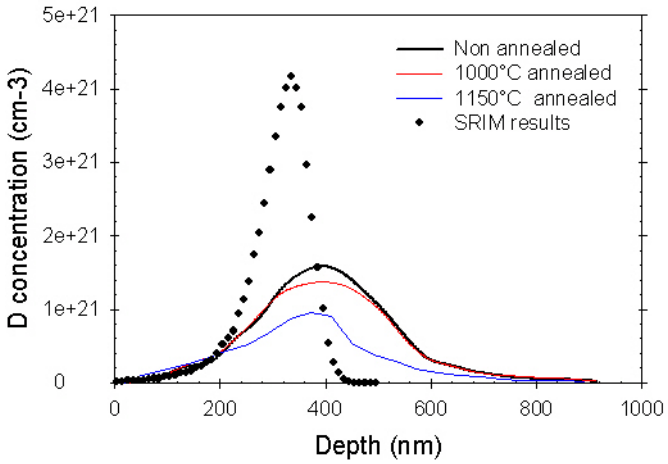


**Figure 2 :** Deuterium profiles performed by NRA measurements for samples annealed up to 1150°C under flow of nitrogen gas. Also included are SRIM2000 predictions.

## SIMS profiles

Figure 3 shows the deuterium profiles in implanted samples before and after annealing at temperature up to 1250°C. For the as-implanted sample the maximum deuterium concentration is measured to be about $3x10^{21}$ at.cm$^{-3}$, which corresponds to 3.1 % of SiC atomic density. This value is slightly lower than expected from SRIM simulations. After the first annealing step at 1000°C, shape of the peak changes slightly. Deuterium seems to have diffused to the surface but has not reached it yet. The temperature seems to be high enough to induce diffusion of deuterium but the process is still very slow. At 1150°C the peak decreases curtly and the distribution of deuterium extends from the peak region to the surface. For the last step at 1250°C just a small amount of deuterium is still present in the sample and most of it is trapped in the region of the damage peak. This temperature induces a very fast deuterium desorption process. Difference between deuterium profiles obtained by SIMS and NRA are discussed below.

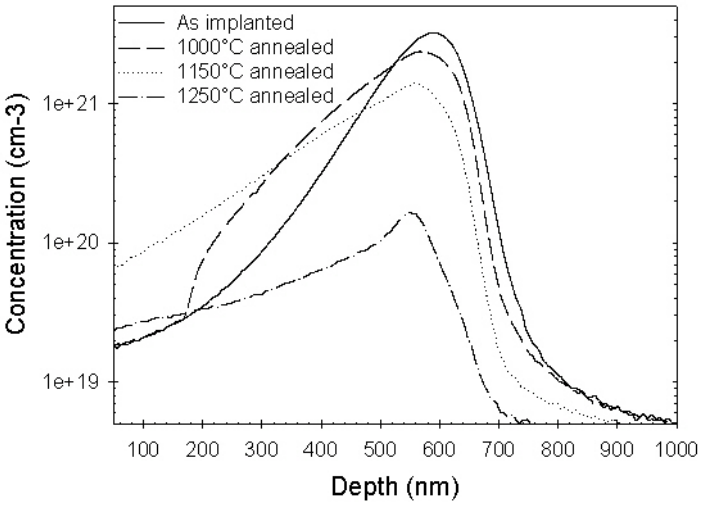


**Figure 3 :** Deuterium profiles obtained by SIMS measurements versus annealing temperature.

## TDS

Thermal desorption spectroscopy gives reliable information on the amount of gas in different traps and the activation energies for release from these traps. TDS spectrum is presented in figure 4. We can see a very weak peak at low temperatures about 800 K (see an inset). Strong deuterium release is observed at 1400-1600 K. No deuterium is still present in the sample after this ramp annealing. In the assumption of the first order desorption an activation energy of 4.2 eV corresponds to the deuterium release at these temperatures (see Shiryaev et al[7]).
Comparison of the TDS results with that obtained by both NRA and SIMS measurements (table 1) shows that significant deuterium release from SiC is observed at temperatures above 1000°C. It should be noted that heating at a slow ramp rate ( 1 K / s) induces gas release at higher temperatures, than in the case of isochronal annealing.

## Channeling

We use RBS/C to follow the evolution of defects as a function of thermal annealing. From the data , we should be able to determine in which configuration the desorption of D occurs. As an example to illustrate the evolution of RBS/C spectra in the thermal annealing processes, a sequence of spectra is shown in figure 5 for the 4H-SiC sample implanted at room temperature to a dose of $5x10^{16}$ $D.cm^{-2}$ and subsequently annealed at several temperatures. The random and virgin spectra, taken from an unimplanted area, are also included. The RBS yield decreases with the increase of the annealing temperature until 1150°C, indicating the recovery process of the crystalline quality in the region between the surface and the projected range. Small peak is observed at the energy of 450 keV in the spectra of the annealed samples. This peak is probably related to the oxidation of the SiC surface. After the 1250°C annealing step the RBS yield is strongly increased (not shown), probably due to severe surface oxidation.

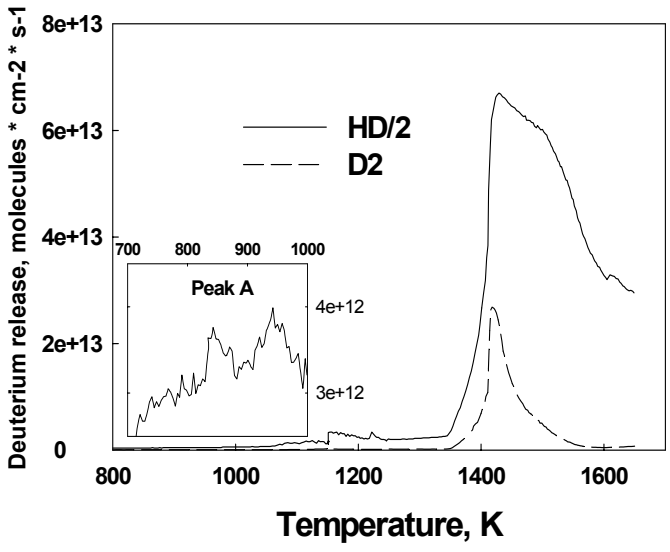


**Figure 4 :** Deuterium thermal desorption from SiC samples. Temperature ramp of 1 K/s.

**Table 1 :** Deuterium retained in the sample versus annealing temperature during 10 min. from three different techniques.

| | SIMS (%) | NRA protons (%) | NRA $^4$He (%) |
|---|---|---|---|
| **Non annealed** | 100 ± 3.2 | 100 ± 6.1 | 100 ± 6.9 |
| **1000°C annealed** | 97 ± 3.1 | 96 ± 5.9 | 95.4 ± 6.7 |
| **1150°C annealed** | 64.8 ± 3.1 | 60.6 ± 3 | 58.2 ± 3.8 |
| **1250°C annealed** | 7.8 ± 3.1 | 2 ± 0.5 | - |

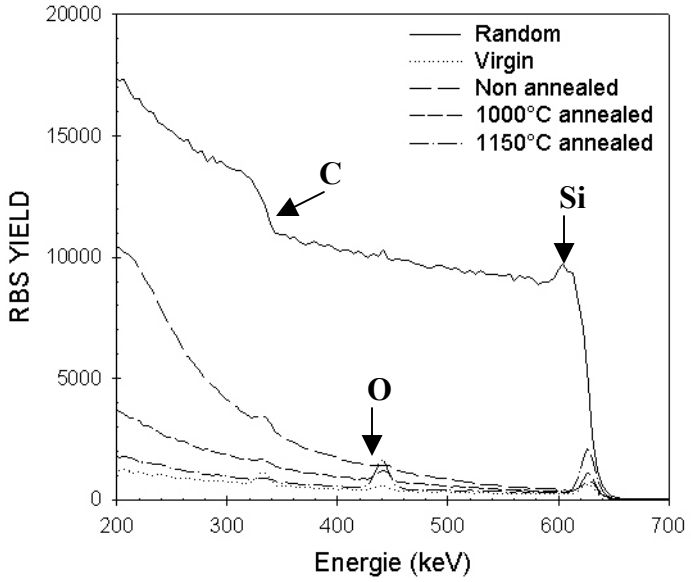


**Figure 5 :** Evolution of RBS/C spectra in the thermal annealing processes implanted at RT and subsequently annealed at several temperatures.

## DISCUSSION

As reported in table 2, there are some differences between the deuterium profiles obtained by different techniques (NRA and SIMS). The projected range *Rp* are similar for NRA and SRIM calculations but are different from SIMS results. However, the peak shapes are similar for SRIM and SIMS whereas NRA gives different distribution. SRIM calculations are not very reliable for light ions and can have an error in the order of 10-20 %. Several attempts to understand the difference in between the results of different techniques were made (e.g. correction for the lower density of ion-implanted layer). However, more work is needed to found a real explanation of the mentioned discrepancy.

Isochronal annealing experiments were performed to investigate implantation-induced defects and their interaction. A significant reduction of the damage was observed in the annealed samples. This result rules out full amorphization, whereas partial one could be present. This observation is corroborated by work of Bohn et al [8]. These authors found that no recovery of fully amorphized SiC occurs until annealing at very high temperatures.

Grisolia et al [9] reported that annealing of heavily hydrogen implanted SiC leads to the formation of one specific type of defects, namely platelets. These defects are 2D precipitates of hydrogen atoms in a stable configuration.

**Table 2 :** Comparison of the projected range and of the maximum concentration deduced from the three different methods.

| | SRIM | SIMS | NRA |
|---|---|---|---|
| **Rp** | 340 nm | 560 nm | 390 nm |
| **Maximum concentration** | $1.8 \times 10^{22}$ $cm^{-3}$ | $3.2 \times 10^{21} cm^{-3}$ | $7 \times 10^{21}$ $cm^{-3}$ |

SIMS profiles showed that some deuterium are still trapped at the *Rp* even after 1250°C annealing. This residue may correspond to deuterium trapped in these platelets. The activation energy of platelet growth is 3.4(0.5) eV. This activation energy is characteristic of the exchange of H atoms from one defect to another. Deuterium thermal desorption gives a value of the deuterium release (4.2 eV). These two energies are very close and might lead to the conclusion that the two phenomena are linked.

## CONCLUSION

We investigated the thermal desorption of deuterium from SiC by three methods. Qualitatively the thermal evolution of the deuterium concentration is roughly the same for the three methods. The study clearly demonstrates that deuterium outdiffusion from SiC occurs at about 1000°C. Even after annealing at 1250°C some amount of deuterium is still present in the samples. It is possible that this fraction resides in the deuterium platelets.

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