

# Positron and thermal desorption studies on He ion implanted nuclear graphite

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**Abstract.** The positron beam Doppler Broadening (DB) and Thermal Helium Desorption Spectroscopy (THDS) techniques are applied to study the behavior of radiation induced point defects in IG-110 nuclear graphite. The defects are introduced by irradiation at room temperature with 200keV He<sup>+</sup> at doses ranging from 10<sup>15</sup> to 10<sup>17</sup> He/cm<sup>2</sup>. In the thermal desorption spectroscopy, the release of He<sup>+</sup> is observed between 500K and 800K. With increasing He<sup>+</sup> implantation dose, the fraction of He<sup>+</sup> desorbed decreases from 27% to 3%. In the DB-curves showing the *S* parameter values versus positron implantation depth, the derived vacancy type defect distribution are in accordance with those obtained by SRIM calculations. Subsequent annealing of the implanted samples in steps of 100K for 5 minutes up to 1200K shows a distinct decrease of the *S* parameter value to its reference value between 500K and 700K. This temperature interval corresponds to the literature values for single vacancy migration energy of 1-2eV.

## 1. Introduction

In the High Temperature Gas-cooled Reactor (HTGR), which is one of the most promising advanced nuclear energy systems due to its inherent safety and economic competitiveness [1,2] nuclear graphite is applied as the moderator, reflector and as structure material because of its excellent performance and mechanical stability. Given the hostile (neutron) radiation conditions, for the safe operation of such a reactor it is therefore important to understand the behavior of radiation induced point defects in this material. To mimic the effects of neutron irradiation IG-110 nuclear graphite is implanted with 200keV He<sup>+</sup> ions. The displacement damage after implantation and annealing treatment is studied by the positron beam Doppler Broadening (DB) technique. In addition, Thermal Helium Desorption Spectroscopy (THDS) is applied to study the thermal behavior of the implanted helium.

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## 2. Experimental

IG-110 nuclear graphite produced by Toyo Tanso Co. Ltd. was used in this work. Three specimens ( $20 \times 20 \times 2$  mm<sup>3</sup>, density 1.76 g/cm<sup>3</sup>) have been implanted with 200keV He<sup>+</sup> ions at the Institute of Semiconductors, Chinese Academy of Science. The doses were  $10^{15}$ ,  $10^{16}$  and  $10^{17}$  He/cm<sup>2</sup>, respectively at a flux of several  $\mu\text{A}/\text{cm}^2$ . The temperature during implantation was about 350K. From the implanted samples smaller pieces for THDS are cut, with masses and dimensions shown in table 1.

**Table 1.** Masses and dimensions of the THDS samples for different He doses.

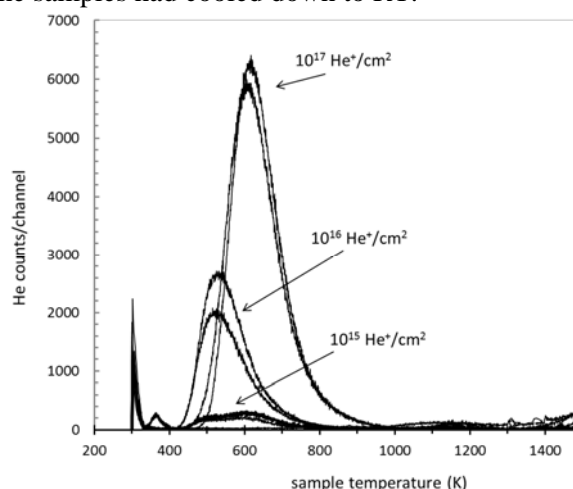
Sample NO.	1	2	3	4	5	6	7
dose (He/cm <sup>2</sup> )	0	$10^{15}$	$10^{15}$	$10^{16}$	$10^{16}$	$10^{17}$	$10^{17}$
length (mm)	1.45	1.51	1.50	1.44	1.62	1.65	1.48
width (mm)	1.92	1.91	2.01	1.73	1.73	2.20	2.18
thickness (mm)	1.95	1.99	1.92	1.44	1.76	1.98	1.99
mass (mg)	9.55	10.09	10.33	7.74	9.07	12.38	11.41

In the THDS experiments a tuned quadrupole mass spectrometer is used for the detection of the He atoms that are released into the desorption vacuum chamber from the linearly heated sample. The temperature of the sample is measured with a WRe25%-WRe3% thermocouple. The heating rate (controlled by a PID feedback loop) from RT up to 1500K is set at 0.33 K/s. The level of background signal (at a base pressure of  $10^{-8}$  torr) is reduced by overnight baking-out of the desorption vacuum chamber at 375K. Calibration of the quadrupole is performed by admission of a known amount of He gas and measuring the spectrometer response.

The Positron Annihilation Doppler Broadening (PADB) experiments on the three implanted and one *in situ* annealed sample ( $10 \times 10 \times 2$  mm<sup>3</sup>) are performed at the Delft Variable Energy Positron beam (VEP) [3]. By selecting positron implantation energies between 0.1 and 25keV the maximum obtained positron mean implantation depth is 4 $\mu\text{m}$ . This is well beyond the 1  $\mu\text{m}$  range of the displacement damage distribution (with a 200nm wide maximum at 800nm depth) predicted by SRIM [4]. The measured *S*-parameters are calculated as the ratio of the counts registered in a fixed momentum window, with  $|p_{\parallel}| < 3.5 \times 10^{-3} m_0 c$ , to the total number of counts in the 511keV photo peak. Here  $p_{\parallel}$  is the momentum of the electrons in the direction of gamma emission. The sample implanted with a dose of  $10^{17}$  He/cm<sup>2</sup> has been selected for the PADB annealing study. The annealing was carried out *in situ* of the positron beam for 5 minutes at temperatures from 300K to 1200K in steps of 100K. The PADB experiments were started after the samples had cooled down to RT.

## 3. Results and Discussion

The desorption spectra of figure 1 show that for the implanted samples the majority of He release occurs in the temperature interval between 400 and 900K. The sharp spike at 310K in all spectra is an artefact caused by switching on the heater filament. In the temperature interval between 1000K and 1300K, an increase in the He counts in both implanted and reference samples is observed. Since in non-graphite samples, this is not reproduced, the origin of this increase may be due to the release of other gases (O, N) adsorbed tightly onto the graphite surface causing an increased background. With these observations in mind the total amount of He



**Figure 1.** Helium desorption spectra obtained for IG-110 nuclear graphite implanted with 200keV He<sup>+</sup> ions to the doses indicated.

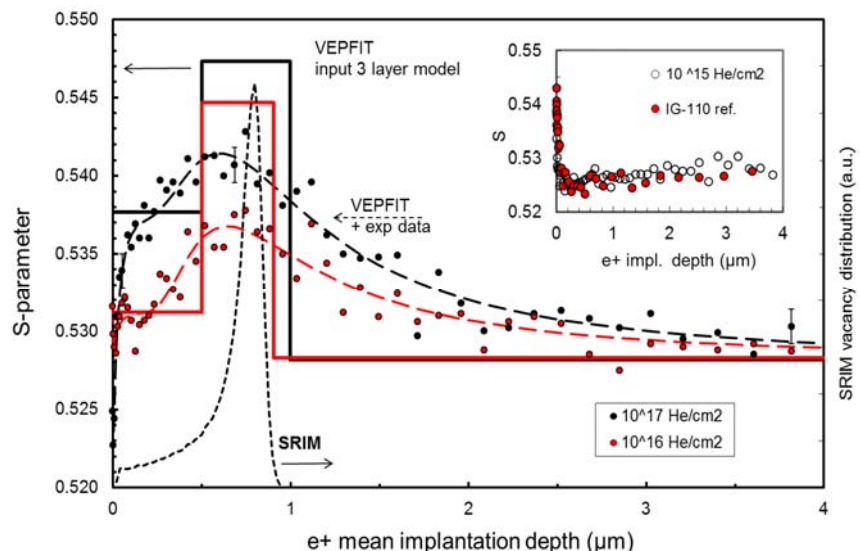
desorbed is determined in the temperature range from 400K to 1000K only. For each implantation dose two samples have been desorbed, the results of which are reproducible. A closer inspection of the spectra shows that for the sample implanted with  $10^{15}$  He/cm<sup>2</sup> two peaks around 500K and 600K are found. For the samples implanted with  $10^{16}$  and  $10^{17}$  He/cm<sup>2</sup> a single broad peak with maxima at 520K and 600K are observed, respectively. Clearly, the release of He is from the traps in the He implantation zone and apparently two types of He traps may be formed or the traps may have different He occupation number. This is in line with hydrogen desorption experiments [5] from which it was concluded that the implantation conditions have an effect on the position of the hydrogen release peaks. The amount of He desorbed (between 400 and 100K) as a function of implantation dose is presented in table 2. It can be seen that the relative amount of desorbed He decreases from 27% to 3% with increasing He<sup>+</sup> implantation dose. This trend is comparable with observed re-emission of He during the implantation of 40 keV He at 300K [6] where complete retention of the implanted He is found at low fluences only. Moreover, the re-emission rate was found to be dependent on the type of graphite and implantation temperature

**Table 2.** Calculated fraction (%) of He<sup>+</sup> desorbed from IG-110.

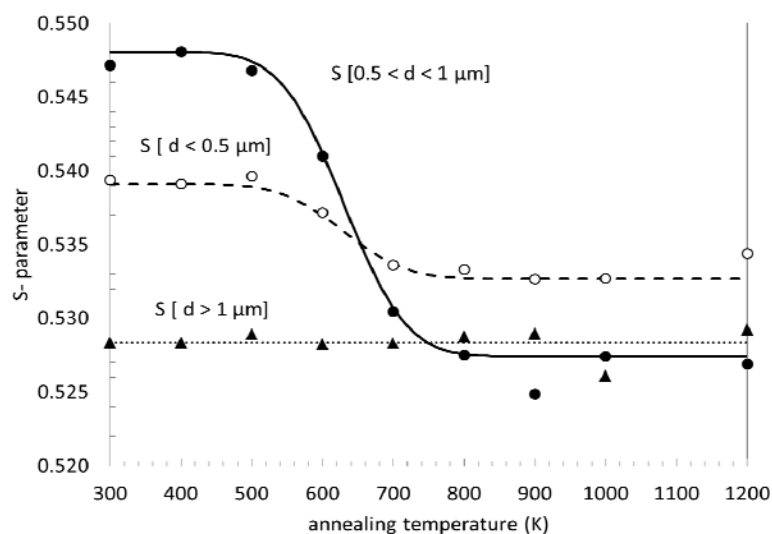
Sample NO.	1	2	3	4	5	6	7
dose (He/cm <sup>2</sup> )	0	$10^{15}$	$10^{15}$	$10^{16}$	$10^{16}$	$10^{17}$	$10^{17}$
Desorbed He <sup>+</sup> (%)	-	27	24	16	17	3	4

The results of the Positron Annihilation Doppler Broadening experiments are presented in figure 2. The data in the inset shows that in comparison to the reference sample, the implantation at the low dose of  $10^{15}$  He/cm<sup>2</sup> has little effect on the *S* values. For the higher doses the formation of open volume defects is clearly visible by the higher values of *S* which, in the implantation region, increases with He dose. The data has been analysed with VEPFIT [7] using a layered structure model. It is clear that three layers are sufficient to obtain a good fit which is represented by the full lines. The corresponding *S* parameters and their depth ranges are indicated by the dashed lines. For the higher He doses the model thus adequately describes the distribution of vacancies as calculated by SRIM. This model is further used for the analysis of the results obtained after *in situ* annealing of the sample implanted with the highest He dose. The annealing was carried out for 5 minutes at temperatures between 300K and 1200K in steps of 100K. The resulting fitted values of *S* for the three layers are plotted in figure 3. The lines through the data for the *S* parameters in the two near surface layers are obtained by fitting a cumulative normal distribution. The line through the *S* values beyond 1μm represents the average value. From the normal distributions the temperature at which the *S* parameter has decreased to a value halfway between that of the defect and the bulk is found to be 630K with a

**Figure 2.** The *S*-parameter as a function of the positron mean implantation depth for the high dose samples. The dashed lines through the data are obtained with VEPFIT using a 3 layer structure. The fitted *S* parameters and layer boundaries are indicated by the profiles together with the distribution of the damage events calculated by SRIM. The inset shows the *S* for the reference and low dose sample.



FWHM of approximately 160K. These values correspond well with the maximum temperature and the width of the He desorption peak measured at the sample with the same (high) dose. SRIM calculations show that the He distribution coincides with the peak in the damage profile. We thus conclude that the annealing of the defects is accompanied by the release of He. Recalling that positrons are preferentially trapped at vacancy type defects, the decrease in  $S$  between 500 and 700K can be explained by a decrease in the defect concentration. Migration energies for interstitial and vacancy motion are discussed in the paper by Telling [8]. The quoted value of 1.75eV for single vacancy migration corresponds to peak temperature between 500 and 600K for heating rates comparable to that applied in this work. The migration energy for interstitials (of the order of tens of meV) is too low to survive the irradiation temperature. It is noteworthy that the  $S$  value nearest the surface does not recover to the reference value. Since in this region the initial defect concentration after implantation is lower compared to the deeper layer, clustering of vacancies to larger, more stable defects is unlikely. Surface erosion caused during the implantation, which may account for the decrease in desorbed He needs further investigation.



**Figure 3.** Fitted  $S$  values as a function of the annealing temperature for the depth ranges indicated. The lines represent a cumulative normal distribution or average value.

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#### 4. Conclusion

Thermal desorption and positron annihilation techniques have been applied to study the thermal behaviour of He and implantation defects in IG-110 nuclear graphite. From the observed two desorption temperatures in the THDS spectra two types of He<sup>+</sup> traps are believed to exist which are associated with (single) vacancies which are annealed out between 500 and 700K.

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