Migration behaviour of Europium implanted into single crystalline 6H-SiC

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Highlights

• Eu ions were implanted into 6H-SiC at 600 °C.

• Annealing studies were performed at temperatures ranging from 1000 to 1400 °C.

• The migration of Eu together with annealing of radiation damage were performed.

• The migration of Eu was explained in terms of trapping and de-trapping by radiation damage.

Abstract

Migration behaviour of Europium (Eu) implanted into 6H-SiC was investigated using Rutherford backscattering spectroscopy (RBS), RBS in a channelling mode (RBS-C) and scanning electron microscopy (SEM). Eu ions of 360 keV were implanted into 6H-SiC at 600 °C to a fluence of 1×10^{16} cm^{-2}. The implanted samples were sequentially annealed at temperatures ranging from 1000 to1400 $^{\circ}$C, in steps of 100 °C for 5 hours. RBS-C showed that implantation of Eu into 6H-SiC at 600 °C retained crystallinity with some radiation damage. Annealing of radiation damage retained after implantation already took place after annealing at 1000 °C. This annealing of radiation damage progressed with increasing annealing temperature up to 1400 °C. A shift of Eu towards the surface took place after annealing at 1000 °C. This shift became more pronounced and was accompanied by loss of Eu from the surface at annealing temperatures > 1000 °C. This shift was accompanied by

broadening of Eu peak /Fickian diffusion after annealing at temperatures > 1100 °C. The migration of Eu occurring concurrently with the annealing of radiation damage was explained by trapping and de-trapping of Eu by radiation damage.

1. Introduction

The containment of fission products (FPs) is critical in the design of the nuclear reactors [1]. In Generation IV nuclear reactors, fuel kernels (UO_2) are coated by four successive layers [2]. These layers are graphite buffer, inner pyrocarbon (PyC), silicon carbide (SiC) and an outer pyrocarbon. The main function of the low density PyC layer, (the buffer layer) is to attenuate fission recoils and to provide voids for gaseous FPs and carbon monoxides that are produced. The inner PyC retains gaseous FPs. The SiC layer retains solid fission products or acts as barrier to solids fission products and provides adequate structural stability during fuel compact fabrication. The outer high-density PyC protects SiC layer mechanically. This coated particle is known as tri-isotropic (TRISO) particle.

TRISO particles retain most of the FPs well with the exception of silver (Ag), strontium (Sr) and Europium (Eu) during operation [2, 3]. Generation IV Reactor program includes high temperature reactors (HTR's), operating at temperatures well above 1000 °C to enhance their efficiency, especially in view of process heat applications for hydrogen generation [4]. Extensive investigations have been performed in the migration behaviour of Ag in SiC in the temperatures below and above 1000 ^{o}C [5]. Very little has been reported on the migration behaviour of Eu in SiC [1, 6]. Europium is a highly reactive metal which react with Si to form a stable silicide and with carbon to form a stable carbide. Consequently, one would expect that at high temperatures (like those used in this study) and at the concentration levels used in this study (i.e. a maximum 2 atomic percent) that Eu would dissolve in the SiC. Eu is toxic to lungs and mucous membrane if inhaled, it is corrosive and an irritant to skin [7]. In the reported studies of the migration behaviour of Eu in SiC, the influence of radiation damage has not been investigated. In the nuclear reactor environment, SiC is continuously exposed to irradiation, hence the influence of radiation damage in the migration of Eu in SiC is crucial.

In this study we report, on the investigation of influence of radiation damage in the migration behaviour of Eu implanted into 6H-SiC to a fluence of 1×10^{16} cm^{-2}. The radiation damage retained after implantation played a major role in the migration behaviour of implanted Eu.

2. Experimental method

Single crystalline 6H-SiC wafers from Valley design Corporation were used in this study. Implantation was performed with 360 KeV Eu ions at 600 ℃ to a fluence of 1×10^{16} cm^{-2}. To avoid channelling, implantation was done at an angle of 7° relative to normal incidence. The implanted wafers were isochronal annealed in vacuum using a computer controlled *Webb 77* graphite furnace at temperatures ranging from 1000 to 1400 °C, in steps of 100 °C for 5 hours. Eu distribution before and after annealing was monitored by Rutherford backscattering spectroscopy(RBS) at room temperature by the production of a collimated beam of He$^+$ particles with energy 1.4 MeV at a scattering angle of 165°. The same set-up was also used to investigate radiation damage in the single crystalline samples by Rutherford backscattering spectroscopy in a channelling mode spectroscopy (RBS-C). The backscattered energy in channels were converted into depth (in nm) using the energy loss data and the density of pristine SiC i.e. 3.21 gcm^{-3}. Samples surfaces before and after annealing were investigated by field emission scanning electron microscopy (FEG-SEM) employing a Zeiss Ultra 55 instrument fitted with the usual SEM detectors and an in-lens detector.

3. Results

RBS spectra (both Random and aligned) of Eu implanted 6H-SiC at 600 °C are shown in Fig. 1. The un-implanted 6H-SiC (virgin) spectrum is included for comparison. Arrows in Fig. 1 indicate the surface energy positions in channels of the elements. Implantation at 600 °C resulted in the appearance of the broad peak around channel 230. This peak indicates the amount of radiation damage retained after implantation. The radiation damage peak in Fig. 1 does not overlap the random spectrum, indicting the absence of amorphous material. The lack of amorphization is due to the availability of thermal energy to the displaced atoms that increase the probability of recombination. Similar results have been reported for other implanted FPs surrogates at the same implantation temperature [8-14].

The measured Eu depth profile (from RBS), the TRIM simulated Eu depth profile and displacement per atom(*dpa*) are shown in Fig.2. The projected range of measured Eu depth

profile is in reasonable agreement with TRIM simulation, while the as-implanted profile is broader than the simulated due to TRIM approximations. The major dpa are closer to the surface as compare to the implanted Eu profile.
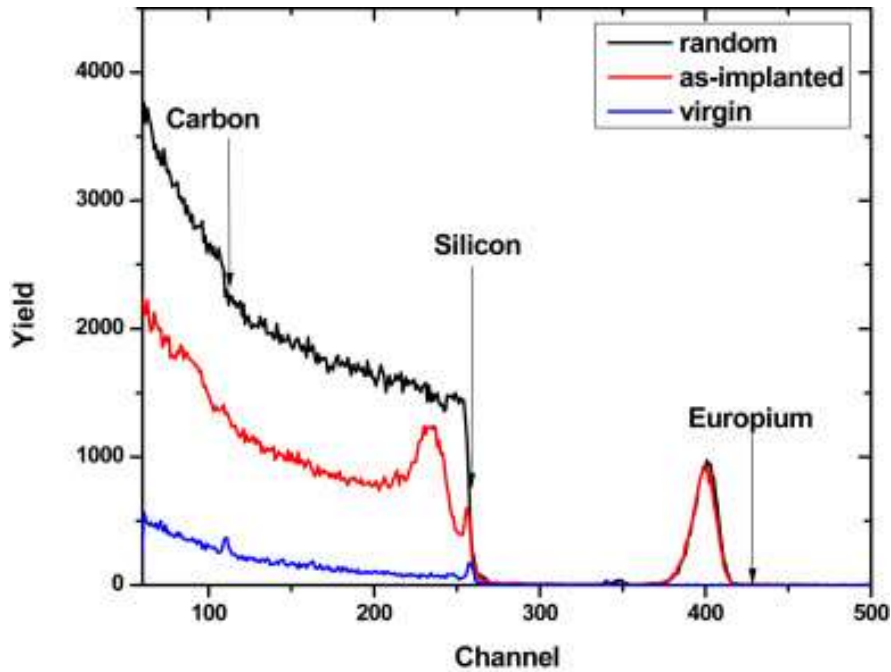

Fig. 1: *RBS spectra of 6H-SiC implanted with 270 KeV Eu ions (both Random and aligned) at 600 ºC and the virgin spectra is included.*
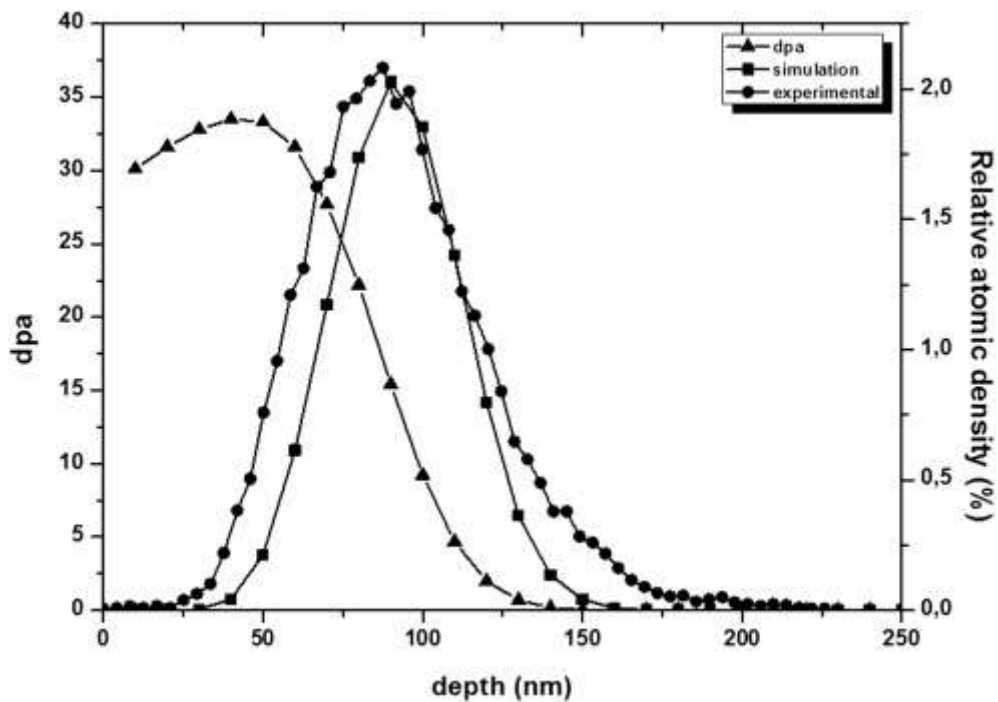

Fig. 2: *The as-implanted Eu(360 keV) depth profile(from RBS),TRIM simulated Eu depth profile and displacement per atom(dpa).*

The aligned silicon depth profiles of the implanted 6H-SiC after isochronal annealing at 1000, 1100, 1200, 1300 and 1400 °C are shown in Fig. 3 (the random, virgin and as implanted spectra are included for comparison). Annealing at 1000 ℃ caused some reduction in the radiation damage peak, indicating some annealing of radiation damage at this temperature. This reduction of radiation damage was more pronounced at 1100 ℃, indicating further annealing. The radiation damage peak was further reduced after annealing at 1200 ℃ indicating a continued annealing of radiation damage. The peak completely disappeared after annealing at 1300 and 1400 ℃. Even though the reduction of radiation damage within the lattice is significant after annealing at 1400 ℃, it is still high compared to the un-implanted (virgin) sample, indicating that the total annealing of radiation damage was not achieved at these temperatures.
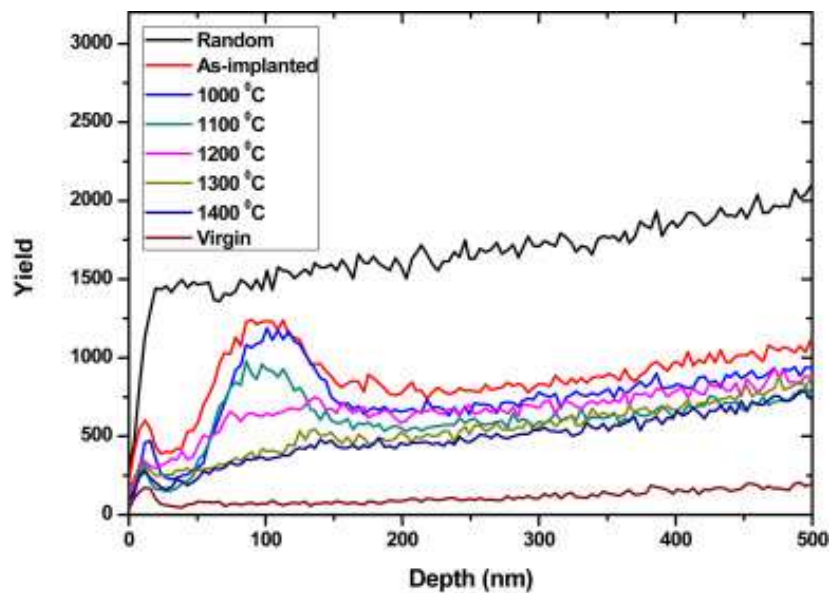

Fig. 3: *Si depth profile of Eu implanted into SiC by 270 KeV Eu ions and annealed at various temperatures.*

The migration of Eu implanted into 6H-SiC was investigated simultaneously with the annealing of radiation damage. The Eu depth profiles obtained from RBS after isochronal annealing are shown in Fig. 4 (the as-implanted profile is included for comparison). Comparing the radiation damage results in Fig.3 with the Eu depth profiles, the as-implanted is initially embedded in radiation damage region. Annealing at 1000 ℃ resulted to a shift of Eu peak towards the surface, indicating the migration of Eu towards the surface is already taking place (see Fig.5. (c)). This migration towards the surface became more significant with increasing annealing temperature.
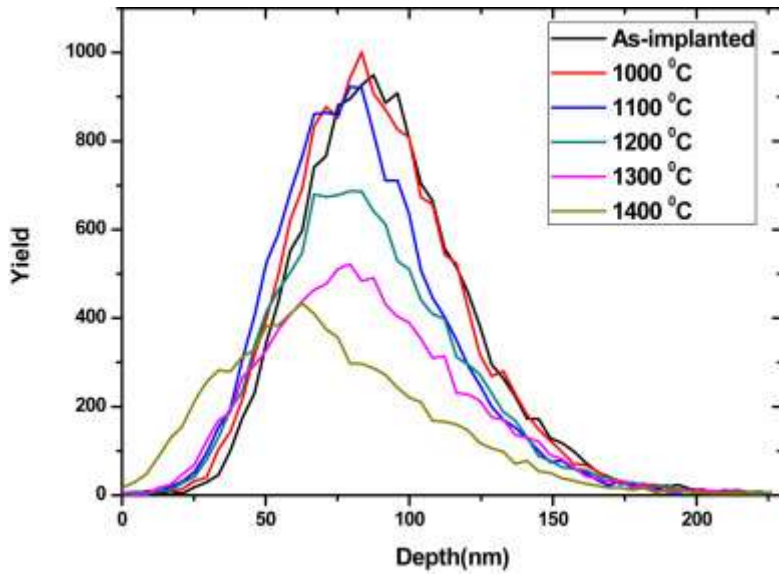
Fig. 4: Eu *depth profiles of Eu implanted into 6H-SiC at 600 °C after isochronal annealing at various temperatures for 5 hours.*
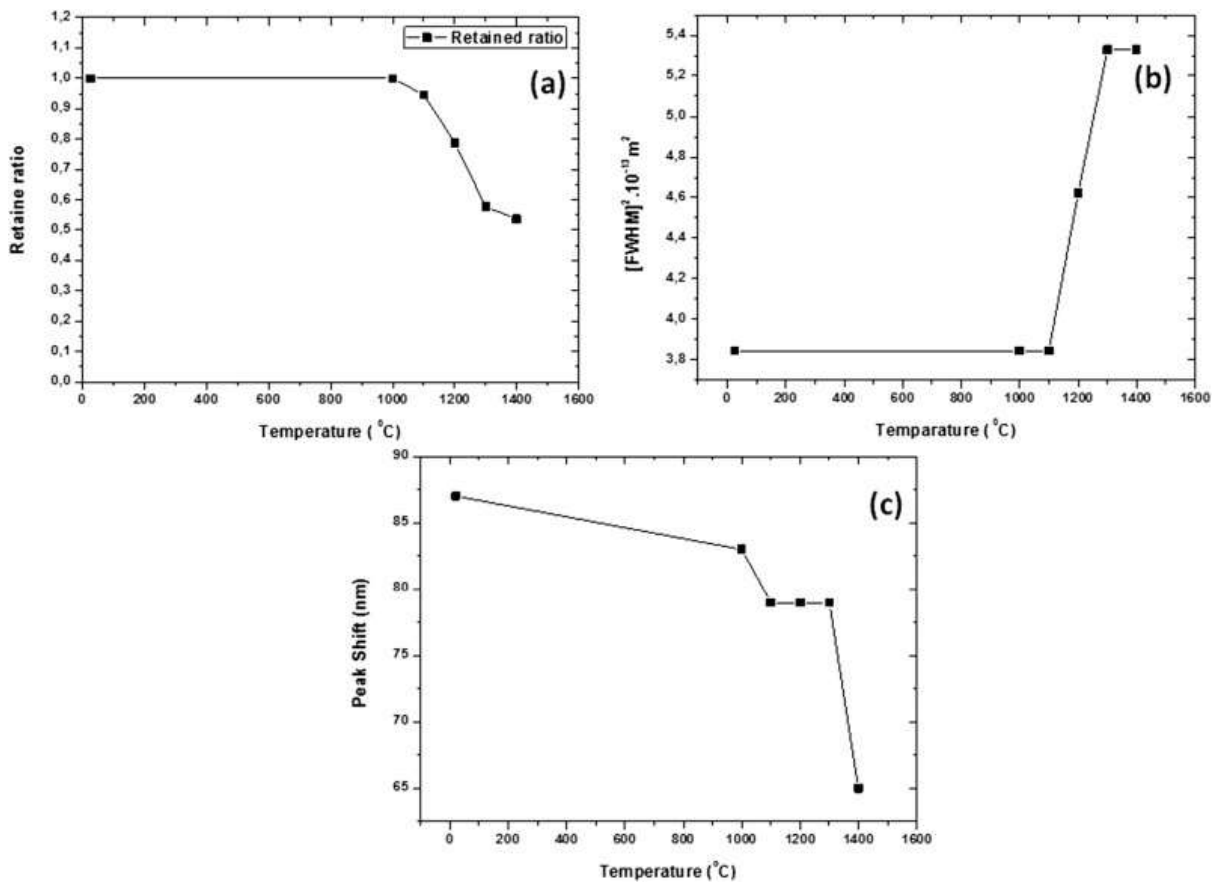

Fig. 5: (a) *Retained ratio of Eu implanted into 6H-SiC at 600 °C after isochronal annealing at different temperatures for 5 hours (b) Full width at half maximum plotted as a function of temperature for 270 KeV of Eu ions in 6H-SiC implanted at 600 °C after isochronal annealing at different temperatures for 5 hours and (c) Peak shift of the Eu profile of as-implanted and annealed at 1000 to 1400 °C in steps of 100 °C.*

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The retained ratios were calculated as the ratio of the area of Eu counts after annealing to that of as-implanted and the results are illustrated in-Fig. 5 (a). The retained ratio reveals that the migration of Eu towards the surface was accompanied by a subsequent loss from the surface at annealing temperatures above 1000 °C. About 10% of Eu is lost after annealing at 1100 °C and about 50% was lost after annealing at 1300 and 1400 °C.

The diffusion of implanted Eu was investigated by comparing the full width at half maximum (FWHM) of the Eu depth profiles of the as-implanted and the annealed samples. The FWHMs square is plotted as a function of temperature in Fig. 5 (b). The FWHM obtained after annealing at 1000 to 1100 ºC, showed no broadening indicating no detectable Fickian diffusion after annealing at these temperatures, however the Eu peak shifted towards the surface as observed in Fig. 5 (c). The broadening of the FWHM was observed after annealing at 1200 and 1300 °C indicating the beginning of Fickian diffusion at these temperatures. Annealing at 1400 °C showed no broadening of the FWHM. No further Eu peak shift (as compare to 1100 °C) was observed at 1200 and 1300 °C, indicating that the Eu loss was purely due to Fickian diffusion, while a further shift was observed at 1400 °C

The shift of Eu peak towards the surface combined with annealing of radiation damage, may be due to trapping and de-trapping of Eu implants. On the as-implanted samples Eu is trapped by radiation damage retained after implantation. As these radiation damage are annealed, de-trapping of Eu occurs which allows the Eu to shift towards the surface. This process progresses with increasing temperature until the temperature where diffusion take place.

The surface topography of the as-implanted compared with annealed samples are shown in Fig. 6. The as-implanted samples were fairly smooth. No major changes were observed after annealing up to 1200 °C. These results indicate that the shift towards the surface after annealing up until 1100 °C, is not caused by changes in the samples' surface which confirms the trapping and de-trapping of implants theory suggested earlier. Also the SEM images show the deterioration on the surface after annealing at 1300 and 1400 ºC. This is due to thermal etching of the material during annealing [15]. However, this thermal etching took place at lower temperatures than the one at which it occurred (1500 ºC) [15]. The peak broadening is not observed after annealing at 1400 ºC but the shift and loss of Eu is considerably high. This can be explained by the severe surface changes of the sample after annealing at this temperature. Also more Eu might have been etched away during thermal etching of the material at these high annealing temperatures.
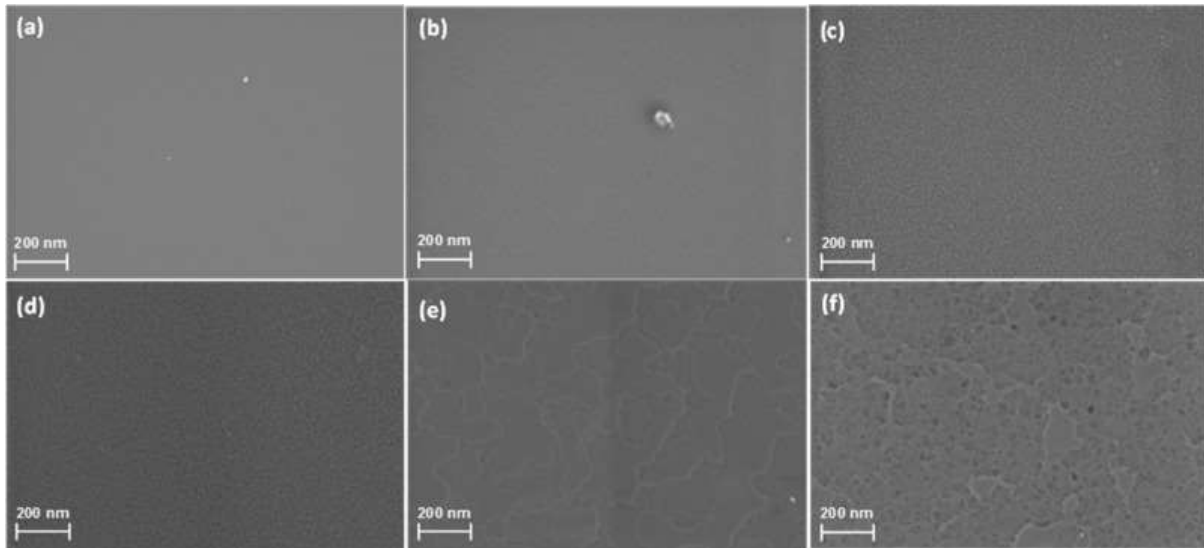
Fig 6: *SEM images of Eu ions implanted into 6H–SiC at 600 °C: (a) as-implanted, subsequently annealed at (b) 1000, (c) 1100, (d) 1200, (e)1300 and (f) 1400 °C.*

4. Summary

This study focused on the migration behaviour of Eu implanted into 6H-SiC at 600 ℃. Implantation temperature retained crystallinity of 6H-SiC with some defects. This was expected as the implantation temperature was above the critical temperature of SiC amorphization. Annealing of radiation damage retained after implantation already took place after annealing at 1000 °C. This annealing of radiation damage progressed with increasing annealing temperature up to 1400 °C. The shift of Eu towards the surface was already taking place after annealing at 1000 °C and became more pronounced with increasing temperature (where it was accompanied by Eu loss from the surface). Fickian's diffusion of Eu was only observed after annealing at 1200 °C and continued up until 1300 °C. No Fick's diffusion was observed after annealing at 1400 °C. The shift of Eu profiles after annealing from 1000 to 1200 °C was explained using trapping and de-trapping of the implanted ions by defects. A further shift of Eu at 1400 °C was due to thermal etching of the surface.

Acknowledgements

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