Iodine assisted retention of implanted silver in 6H-SiC at high temperatures

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Abstract

The effect of high temperature thermal annealing on the retainment and diffusion behaviour of iodine (I) and silver (Ag) both individually and co-implanted into 6H-SiC has been investigated using RBS, RBS-C and heavy ion ERDA (Elastic Recoil Detection Analysis). Iodine and silver ions at 360 keV were both individually and co-implanted into 6H-SiC at room temperature to fluences of the order of 1×10^{16} cm\textsuperscript{-2}. RBS analyses of the as-implanted samples indicated that implantation of Ag and of I and co-implantation of $^{131}$I and $^{109}$Ag at room temperature resulted in complete amorphization of 6H-SiC from the surface to a depth of about 290 nm for the co-implanted samples. Annealing at 1500 °C for 30 hours (also with samples annealed at 1700 °C for 5 hours) caused diffusion accompanied by some loss of both species at the surface with some iodine remaining in the iodine implanted samples. In the Ag implanted samples, the RBS spectra showed that all the Ag disappeared. SEM images showed different recrystallization behaviour for all three sets of samples, with larger faceted crystals appearing in the SiC samples containing iodine. Heavy Ion ERDA analyses showed that both $^{109}$Ag and $^{131}$I remained in the co-implanted SiC samples after annealing at 1500 °C for 30 hours. Therefore, iodine assisted in the retainment of silver in SiC even at high temperature.

Keywords: RBS; ERDA; SEM; implantation; co-implantation, diffusion

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1. Introduction

The safety of modern nuclear reactors depends on the retainment of all the radioactive fission products that may leak during its operation. This is normally achieved by coating the fuel kernel with chemical vapour deposited layers of pyrolytic carbon and silicon carbide (SiC) [1]. These layers act as diffusion barriers for the fission products produced in the UO$_2$ kernels during reactor operation. The most important diffusion barrier layer is polycrystalline SiC [1, 2]. Hence, the diffusion of the important fission products in SiC has been investigated extensively over the past two decades. Early studies [3, 4] already pointed out that the silver isotope $^{110m}$Ag seems to diffuse more easily through polycrystalline SiC layer than the other major fission products during reactor operating conditions. This finding has been confirmed by several other studies – see reviews [5, 6, 7]. Other studies have shown that silver does not diffuse in crystalline SiC [4, 8 - 15]. Silver diffusion in CVD-SiC is now well understood. It is mainly due to grain boundary diffusion [10, 16-17]. However the influence of grain boundary structure on diffusion is still unclear [16-17].

In all the above mentioned studies, the migration of silver in SiC was investigated without considering the effect of other fission products. In a nuclear reactor environment silver coexists with other fission products. These other fission products might positively or negatively influence the migration of silver. Up to date, only the influence of Pd and Cs on silver(Ag) migration have been investigated experimentally and theoretically respectively [18] [19]. This study focuses on the effects of thermal annealing on iodine and silver co-implanted and individually implanted into 6H-SiC at room temperature.

2. Experimental Method

The starting material was hexagonal 6H-SiC from *Intrinsic Semiconductors*®. $^{109}$Ag$^+$ and $^{131}$I$^+$ of 360 keV were implanted into 6H-SiC to a fluence of $1\times10^{16}$ cm$^{-2}$ at room temperature respectively. During implantation, the flux was kept below $10^{13}$ cm$^{-2}$s$^{-1}$ to avoid the target reaching too high a temperature. Channelling during implantation was reduced by tilting the sample by an angle of 7º relative to normal incidence. Annealing was done under vacuum using a computer controlled *Webb 77* graphite furnace. For this study, two annealing temperatures were used, i.e. 1500 °C and 1700 °C. The annealing times were 30 h for the 1500 °C annealing and 5 h for the 1700 °C annealed samples.
The as-implanted and annealed samples were initially analysed by Rutherford Backscattering Spectroscopy (RBS) and Rutherford Backscattering Spectroscopy in a channelling mode (RBS-C) at the University of Pretoria using 1.6 MeV He\(^+\). The experimental details are found in [9].

The microstructure of the SiC surfaces was investigated by a field emission gun scanning electron microscopy (FEG-SEM) employing a Zeiss Ultra 55 instrument fitted with the usual SEM detectors and an in-lens detector. In this study we employed an accelerating voltage of 2 kV. With this low primary voltage, it is possible to detect the decomposed carbon layer on the surfaces of our samples by the clarity of the images.

Finally the as-implanted and the annealed samples were analysed by Heavy Ion Elastic Recoil Detection Analysis (ERDA) at iThemba LABS Gauteng. The ERDA technique detects recoil ions knocked off the surface region of a target sample by a projectile beam coming in at 20° grazing incidence angle to the sample surface. The detector system employed is a Time of Flight – Energy (ToF-E) spectrometer. It consists of two carbon foil based timing detectors, 0.60 m apart, and a silicon PIPS® detector for measuring the ToF-E of the recoil ions in coincidence [20]. This coincidence measurement leads to separation of recoil particles according to their atomic mass. It is then possible to extract elemental energy spectra from the 2D ToF vs Energy plots and thence calculate depth profiles using an energy-depth conversion algorithm [21].

3. Results and Discussions

The RBS and RBS-C spectra of the as-implanted sample are shown in Fig. 1, compared with theoretical simulation by the SIMNRA code [22]. The surface positions of the elements are indicated by arrows. Co-implanting \(^{131}\)I and \(^{109}\)Ag at room temperature completely amorphised 6H-SiC from the surface up to about 290 nm. This is indicated by the aligned spectrum overlapping the random spectrum from the Si surface as shown in Fig. 1. Similar results were observed when silver and iodine were implanted individually into 6H-SiC at room temperature [9, 23]. The dip beyond the Si surface edge indicates the position of the implants in the SiC matrix. The Gaussian peak between channel 400 and 500 is due to the implanted ion species. It is evident that RBS is not unambiguous in trying to distinguish between the implanted silver and iodine. The failure of RBS to separate these implants is due
to its poor mass resolution for heavy ions and the problem of mass-depth ambiguity.
Simulation using the Stopping and Range of Ions in Matter (SRIM) code predicted projected ranges of 97.1 nm and 107.3 nm for iodine and silver respectively [24]. The slightly larger projected range of the silver combined with its lower fluence resulted in the combined I and Ag profile to be skewed towards smaller channel numbers (i.e. deeper in the sample.) The RBS spectrum of the implants was not converted into depth profiles with the method described in [9] because the implants’ energy spectra could not be separated.

The results of the co-implanted samples after annealing at 1500°C for 30 hours are shown in Fig. 2. The as-implanted results are included for comparison. Thinning of the amorphous region from the back towards the surface due to epitaxial growth from the bulk and due to thermal etching of SiC from the surface was observed. Most of the implants were lost due to diffusion out of the surface during annealing at this temperature as can be seen in Fig. 2. Since RBS cannot distinguish between the implanted ions, one could not predict whether the remaining impurity atoms were Ag or I or both.

To ascertain whether the remaining fission product was I or Ag, extra sets of samples were prepared: 6H-SiC implanted with only 360 keV silver at room temperature and another set of 6H-SiC samples implanted with only 360 keV iodine at room temperature. Both sets of samples were annealed at 1500 °C for 30 hours. The results are shown in Figs. 3 and 4. For the silver implanted sample, no silver signal was detected after annealing. For the iodine implanted sample, while most of the initially implanted iodine was lost, some was still retained. The iodine profile was significantly broadened which indicated Fickian diffusion. However, as will be seen below from the SEM results, the surfaces of these samples developed severe topography, which will result in broadening of the iodine RBS profile. Similar results for the silver and iodine implanted SiC were also obtained for the samples annealed at 1700 °C for 5 h. From the results, one can conclude that silver diffuses faster than iodine in and out of the amorphised 6H-SiC. These are interesting results but not conclusive enough as far as the co-implantation is concerned. This is because in the co-implantation samples there might be some interaction between the implants or implants and SiC causing the migration and loss to be completely different.

The RBS carbon peak was higher (i.e. more carbon was detected) for the silver implanted samples after annealing at 1500 °C for 30 hours than for the iodine implanted samples. A
similar result was found for the two sets of samples annealed at 1700 °C for 5h. This increase in the carbon peak is due to the decomposition of SiC at this annealing temperature causing Si to evaporate and leaving C on the surface [2]. Similar decomposition of SiC have been reported in [9] at annealing temperatures above 1500 °C for silver implanted at 350 °C and 600 °C. Comparing these results, it is quite clear that the initially amorphised SiC decomposes at lower annealing temperatures. A similar extent of decomposition was not observed for both the iodine implanted, and the iodine co-implanted with silver 6H-SiC after annealing at 1500 °C for 30 h.

After implantation at room temperature, the SEM images of all three sets samples were similarly featureless and smooth because the ion bombardment caused amorphization of the 6H-SiC in the implanted region in line with our previous RBS studies [1, 7 – 10, 23]. After annealing at 1500 °C and at 1700 °C, the morphologies of these three sets of samples are different. The Ag-implanted SiC surface is relatively smooth with small crystals visible - see Fig. 5 (a). A comparison with RBS/channeling showed that this recrystallization started at growth points within the amorphous layer and not necessarily at the amorphous/crystalline interface. The surface is covered by a carbon layer due to the decomposition of the SiC, as discussed above. The surface of the I-implanted SiC (Fig. 5(b)) is significantly more rough than the Ag-implanted surface, with large crystals visible and cavities. This recrystallization forming crystals occurs according to a step-flow mechanism [25]. The cavities result from crystal surfaces with higher surface energies growing proportionally faster than surfaces with lower surface energies via surface diffusion, according to Wulf's law [26], thereby lowering the total energy of the system. A cross-sectional SEM image of a fractured sample (Fig. 5(c)) shows that the large crystals extend to the interface between the bombardment-induced altered layer and the 6H-SiC substrate. Small cavities are visible at this interface. The origin of these cavities has been discussed elsewhere [7].

The surface of a co-implanted and annealed sample (Fig. 5(d)) is also very rough with crystals and cavities. The crystals are smaller than in the case of the I-implanted SiC. The crystals have facetted planes due to the competing processes of thermal etching, step bunching and crystal growth at this high temperature. The surfaces are again covered by a carbon layer, which is thinner than the one on the annealed Ag⁺ implanted SiC but thicker than in the case of the I-implanted SiC. In the latter case, the decomposed carbon layer has less wrinkles than in the other two cases.
From the above, one can concluded that the implanted iodine perhaps reacts with the SiC to form some compound which is stable against decomposition at high temperatures and it also promotes recrystallization of the bombardment-induced amorphous SiC. These conclusions are supported by our SEM investigations of samples annealed at lower temperatures.

To get more insight into the co-implanted results, heavy ion ERDA analyses were performed using a 26 MeV Cu\(^{7+}\) incident beam. Results from the as-implanted sample are depicted in Fig. 6, where the depth profile shows the variation in relative atomic concentration with depth. This technique can separate the co-implanted silver and iodine relatively well making it more effective in the study of the migration of the co-implanted ion species during thermal annealing. The atomic % of SiC and C are overlapping indicating equal amount of Si and C as expected in SiC. From the areas under the ERDA profiles it follows that more iodine was implanted than silver. The silver profile was slightly deeper inside the SiC than the iodine profile in line with its lower mass resulting in a deeper projected range for the Ag ions.

The ERDA results of the co-implanted silver and iodine SiC after annealing are depicted in Figure 6. A significant reduction in atomic concentration of both implants after annealing at 1500 °C as compared to the as-implanted SiC is observed. This is due to the diffusion of silver and iodine in the SiC towards the surface where they evaporated and sublimated into the vacuum. The diffusion of the implants in the amorphised 6H-SiC is also indicated by the broadening of silver and iodine profiles respectively as compared to the as-implanted profiles.

The fact that Ag still exists in the co-implanted SiC samples after annealing at 1500 °C while no silver is detected in the only Ag implanted and annealed SiC, indicates that the implanted iodine has a synergistic effect in the SiC. In line with our SEM results, the ERDA and RBS results suggest that the iodine perhaps reacts with the SiC to form some stable (at high temperatures) compound and/or that the recrystallized structure of the annealed SiC impeded the outdiffusion of Ag from the SiC. These are very important results for nuclear reactors where different fission products co-exist. These results indicate that the diffusion behaviour
of single elemental fission products in SiC can differ significantly to the case when other fission products are present.

4. Conclusions

Co-implantation of 360 keV iodine and silver ions into 6H-SiC at room temperature completely amorphised the 6H-SiC matrix from the surface to a depth of about 290 nm. Annealing the co-implanted 6H-SiC at 1500 °C for 30h caused some epitaxial growth of the amorphous 6H-SiC from the bulk. RBS analyses of the diffusion of singly implanted I and singly implanted Ag are accompanied by loss from the surface was observed after annealing. In the case of the silver implanted SiC, RBS showed that no (within the RBS detection limit) Ag existed in the sample after annealing at 1500 °C for 30h (and naturally for implanted samples after a 1700 °C for 5h annealing).

The SEM investigations indicate room temperature implantation of Ag and of I in 6H-SiC caused the implanted region to become amorphized. Vacuum annealing at 1500 °C for 30h and at 1700 °C for 5h caused recrystallization of these amorphized layers. In the case of the Ag implanted samples only small faceted crystals are observed while for the iodine and for the co-implanted samples, large crystals and cavities on the surface appear. Iodine, therefore, aids the recrystallization of the amorphised SiC layer.

Heavy ion ERDA results indicated that even though both implants were lost during annealing at an annealing temperature of 1500 °C for 30h, some of the iodine and silver were still retained in contrast to single Ag implanted SiC annealed under similar conditions. In the case of iodine there was partial retainment of the iodine after annealing at 1500 °C and at 1700 °C. Comparing these results it is evident that iodine somehow played a role in the retainment of silver during annealing of the co-implanted 6H-SiC matrix at 1500 °C for 30 hours.

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6. REFERENCES


7. Figure s

Fig.1. Aligned and random spectra of silver and Iodine co-implanted into 6H-SiC at room temperature as compared with SIMNRA simulation. The surface positions are indicated by the arrows.

Fig.2. Aligned and random spectra of silver and iodine co-implanted into 6H-SiC at room temperature compared with the aligned and random spectra of the sample annealed at 1500°C.
Fig. 3: The random spectrum of silver implanted at room temperature compared to the after annealing spectrum of the same sample annealed at 1500 °C for 30h.

Fig. 4: The random spectrum of Iodine implanted at room temperature compared to the after annealing spectrum of the same sample annealed at 1500 °C for 30h.
Fig. 5. In-lens SEM images of the different implanted SiC surfaces after vacuum annealing at 1700 °C for 5 h. (a) 360 keV Ag\(^+\) implanted to a fluence of \(2 \times 10^{16}\) cm\(^{-2}\). (b) 360 keV I\(^+\) implanted to a fluence of \(2 \times 10^{16}\) cm\(^{-2}\). (c) A cross-section SEM image of the SiC wafer implanted with 360 keV I\(^+\) implanted to a fluence of \(2 \times 10^{16}\) cm\(^{-2}\). (d) Co-implanted 360 keV Ag\(^+\) and I\(^+\) implanted, each implanted to a fluence \(1 \times 10^{16}\) cm\(^{-2}\), resulting in a total fluence of \(2 \times 10^{16}\) cm\(^{-2}\). The arrows indicate the interface between the bombardment-induced altered layer and the 6H-SiC substrate. Nano-cavities are visible at the interface.
Fig. 6. Heavy Ion ERDA results of I and Ag co-implanted at room temperature.

Fig. 7: Heavy Ion ERDA results of I and Ag co-implanted at room temperature and annealed at 1500 °C for 30 h.