Synergistic effects of iodine and silver ions co-implanted in 6H-SiC

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Abstract

Motivated by the aim of understanding the release of fission products through the SiC coating of fuel kernels in modern high temperature nuclear reactors, a fundamental investigation is conducted to understand the synergistic effects of implanted silver (Ag) and iodine (I) in 6H-SiC. The implantation of the individual species, as well as the co-implantation of 360 keV ions of I and Ag at room temperature in 6H-SiC and their subsequent annealing behavior has been investigated by Secondary Ion Mass Spectrometry (SIMS), Atom Probe Tomography (APT) and X-ray Photoelectron Spectroscopy (XPS). SIMS and APT measurements indicated the presence of Ag in the co-implanted samples after annealing at 1500 °C for 30 hours in sharp contrast to the samples implanted with Ag only. In samples implanted with Ag only, complete loss of the implanted Ag was observed. However, for I only implanted samples, some iodine was retained. APT of annealed co-implanted 6H-SiC showed clear spatial association of Ag and I clusters in SiC, which can be attributed to the observed I assisted retention of Ag after annealing. Such detailed studies will be necessary to identify the fundamental mechanism of fission products migration through SiC coatings.

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1. Introduction

The recent incident at Fukushima has prompted further scrutiny of the nuclear energy industry. Modern high temperature nuclear reactors hope to ensure improved safety through the coated fuel kernel design approach. This design involves coating the fuel kernel with successive layers of chemical vapour deposited (CVD) pyrolytic carbon and silicon carbide [1]. **The inner layer consists of a porous graphite buffer layer that absorbs gaseous fission products, accommodates thermal expansion and swelling of the kernel. A pyrolytic carbon layer is then grown on top of this followed by a SiC layer, and finally an outer layer consisting of pyrolytic carbon (OPyC).** In principle, the coating layers act as diffusion barriers to fission products produced in the fuel kernels. Many variants of the fuel kernels have been considered and include UO_2 , UC and combinations of the two such as UCO. Of all these layers, SiC is considered as the most important layer [2]. The significance of the SiC layer has stimulated extensive research into the diffusion of several fission products in SiC over the last couple of decades. Recent studies have shown that while the majority of fission products studied so far are retained in intact fuel coatings, the release of silver from intact fuel coatings remains a problem [3,4].

Earlier studies during the 1970's [5,6] showed that $^{110\text{m}}\text{Ag}$ appears to diffuse more easily through polycrystalline SiC layers than other fission products under reactor operating conditions. A similar trend was also observed in more recent studies [7,8]. The diffusion of Ag in CVD-SiC has been attributed to grain boundary diffusion [9-11] although the influence of the grain boundary structure on exact mechanism of the Ag transport remains unclear [10, 11]. Ag volume diffusion in crystalline SiC has been ruled out by several authors [5, 12-19]. **Quite recently Ag diffusion in 4H-SiC has been observed [14]. This was ascribed to an interstitially-driven and implantation-enhanced diffusion.** Iodine transport, via volume diffusion in SiC has also been studied [20,21]. Studies of I diffusion through polycrystalline SiC have also been performed [22]. Investigations by Audren *et al.* [20] did not show any diffusion of the implanted I in SiC after annealing up to 1000 °C. Furthermore, they also did not detect any noticeable I diffusion after subsequent irradiation of the iodine implanted samples with swift heavy ions. Isothermal annealing cycles at higher temperatures (up to 1300 °C) by Friedland *et al.* [22], revealed some anomalous diffusion behaviour of I implanted into 6H-SiC. Very little I loss (approximately 10%) through the front surface was observed despite the appreciable broadening of the I profile. The low loss was even more surprising when changes in the surface morphology as

seen from high resolution Scanning Electron Microscopy (SEM) images were taken into consideration [22]. Friedland *et al.* suggested that this low loss of I could point to some form of strong binding of the I within the SiC matrix or some form of compound formation. A recent study [23] involving the use of a multilayer diffusion couple also reveals the contrasting diffusion behaviour of I and Ag. For samples each separately implanted with europium, cesium, strontium, silver and iodine ions, the SiC barrier layer was able to retain all the fission products within the diffusion couple except silver.

Most of the previous studies have focused on the behaviour of silver in SiC without investigating the possible influences that other fission products may have on the diffusion of Ag. **Only recently some groups have studied the influence of palladium and the possibility of iodine co-incorporation on Ag transport in SiC respectively [24, 25]. Rutherford backscattering spectrometry (RBS) and heavy ion Elastic Recoil Detection Analysis (ERDA) studies have also been performed on co-implanted I and Ag into 6H-SiC [26].** In this study, new results on a microstructural investigation of the synergistic effects between Ag and I when ions of both elements are co-implanted in the same wafer at room temperature and subsequently thermally annealed are presented. The combined Secondary Ion Mass Spectrometry (SIMS), Atom Probe Tomography (APT) and X-ray Photoelectron Spectroscopy (XPS) results present a clearer understanding of the mechanisms of I assisted retention of Ag. **The non equilibrium concentrations involved in this study could enhance the Ag transport as the Ag can move via some sort of bulk transport mechanism which would be different to the transport of Ag at the lower concentrations in TRISO particles. Another primary difference between Ag release from TRISO particles and surrogate ion implantation diffusion studies is the influence of irradiation damage on Ag transport [14] where implantation effects could influence Ag transport. However, an attempt is made here to investigate the transport of Ag in SiC in the presence of another species which could provide insights into any possible synergistic effects.**

2. Experimental

Hexagonal 6H-SiC wafers from *Intrinsic Semiconductors*® were implanted with 360 keV ions of either Ag⁺ or I⁺ individually. In another set of wafers, I and Ag ions were co-

implanted into the same wafer. All the implantations were carried out at the Institut für Festkörperphysik, Friedrich-Schiller-Universität, Jena, Germany. The implantations were done at room temperature and the ion fluence for each element was $2 \times 10^{16} \text{ cm}^{-2}$ for Ag implantations and $1 \times 10^{16} \text{ cm}^{-2}$ in the case of I. For the full details of the ion implantation procedure, see Ref:[27]. For the annealing cycles, the samples were placed inside small graphite crucibles. Vacuum annealing was then carried out in a computer controlled *Webb 77* graphite furnace. The samples were annealed at 1500 °C for 30 hours.

SIMS measurements were performed in the Environmental Molecular Science Laboratory (EMSL) of the Pacific Northwest National Laboratory (PNNL), USA. The Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) depth profiling measurement was performed with a ToF.SIMS5 instrument from IONTOF GmbH (Germany). A 2.0 keV Cs^+ ion beam was employed as the sputtering beam and a 25 keV Bi^+ beam as the analysis beam. After depth profiling measurement, the depths of sputter craters were measured using a Dektak 6M stylus profilometer. The sputtering rate (nm/nA/s) was considered to be constant throughout the measurement.

APT specimen preparation and APT analysis was also conducted in the EMSL. The APT specimens were fabricated using the standard FIB lift-out procedure using a Helios Nanolab 600 dual-beam focused ion beam (FIB) instrument [28]. Atom probe analysis was then performed in a CAMECA LEAP 4000XHR atom probe tomography system using a 355 nm wavelength UV laser at 100 pJ pulse energy, 40 K specimen temperature and evaporation rate maintained at 0.005 atoms/pulse. The APT data was reconstructed and analysed using IVAS software.

XPS was performed using a Kratos Axis Ultra DLD spectrometer, which consists of a high performance Al $K\alpha$ monochromatic x-ray source (1486.6 eV) and a high resolution spherical mirror analyzer. The X-ray source was operated at 150 W and the emitted photoelectrons were collected at the analyzer entrance slit normal to the sample surface. The data acquisition was carried out in hybrid mode with analysis area of $700 \times 300 \mu\text{m}$. The survey spectra were recorded at pass energy of 160 eV with 0.5 eV step size and high resolution spectra were recorded at pass energy of 40 eV with step size of 0.1 eV. The pass energy of 40 eV in the $700 \times 300 \mu\text{m}$ analysis area is referred to the FWHM of 0.77 eV for Ag $3d_{5/2}$. The charge neutralizer with low energy electrons was used to exclude the surface charging effects and the

binding energy of C 1s at 284.8 eV was used as the charge reference. The chamber pressure was maintained at $\sim 5 \times 10^{-9}$ Torr during the measurements. XPS data was analyzed by CasaXPS software using Shirley background correction.

3. Results

SIMS depth profiling of the samples is shown in figure 1. Four signals, two from Ag signal in the single element implantation (as-implanted and annealed) and two from the Ag signal in the co-implanted sample (as implanted and annealed) are plotted together for comparison. The as-implanted profile shows the initial peak concentration of Ag in Ag only implanted SiC to be approximately 2%. After annealing at 1500 °C for 30 hours, virtually all of the implanted Ag has been lost (within the detection limits of the SIMS system) through the front surface in the Ag only implanted sample. This result is consistent with our RBS results presented in reference [26]. However, when I ions are co-implanted with Ag ions and annealed again at 1500 °C for 30 hours, SIMS Ag distribution shows that some Ag has been retained. For the co-implanted sample the peak concentration of the implanted Ag fell from a peak concentration of about 1.5% to approximately 0.4 %. This is consistent with Heavy ion ERDA results presented in reference [26]. This result demonstrates that the presence of I has a synergistic effect on the retainment of Ag in SiC. Iodine's role in enhancing the recrystallisation of SiC during annealing [27], could play an important role in the immobilisation of Ag.

APT was utilized to get a clearer picture of the Ag and I diffusion behaviour at atomic level. Figure 3(a) shows an SEM image of the APT needle specimen of the Ag and I co-implanted and annealed sample. APT analysis resulted in 7.8 million ion data capturing information up to 80nm depth from the top surface of the needle specimen. The entire APT reconstruction is shown in figure 3(b)) where Si (grey), C (brown) are predominantly visible. Ag only (blue) and I only (red) ion distributions are shown in figure 3(c) and (d) respectively from which multiple regions of clustering of Ag and I can be observed. These ion maps shows a higher concentration of both Ag and I towards the 80 nm region, consistent with the composition profile of the implants seen via RBS and ERDA [26] and SIMS (this paper). This is to be expected as the ion distribution peaks at the projected ranges of the ions which, predicted by SRIM and reported in reference [26], are approximately 97.1 nm and 107.3 nm for I and Ag,

respectively. A cluster of I ions is visible within the first 10 nm from the top surface of reconstruction, consistent with near surface peaks observed from RBS and SIMS measurements (figure 2). To further delineate the Ag and I clusters, isocomposition surfaces were plotted at 3 at% Ag (blue) and 3 at% I (red) as shown in figure 3(e). From the isocomposition surfaces shown in figure 3(e), a clear spatial association of Ag and I clusters can be noted. Examples of two such clusters with clear spatial association between Ag and I enriched regions are shown magnified in figure 3(f) and (g). Subsequently, to quantify the compositional changes going across the cluster shown in fig 3(f), a 1D concentration profile was plotted using a 1nm diameter cylinder (shown as inset in figure 3(g)). The composition profile given in fig 3(h) clearly highlights the presence of an I enriched region in the middle of two Ag enriched regions.

From the APT results, a clear spatial association of Ag and I is observed. To further understand if the Ag and I are in metallic state or have formed AgI compound, XPS analysis was conducted. XPS analysis was carried out on the surface of Ag and I co-implanted sample after annealing at 1500 °C for 30 hours to determine the chemical nature of Ag and I (figure 4). I 3d high resolution spectrum (figure 4 (b)) shows doublet peaks at 620.3 eV (I 3d_{5/2}) and 631.8 eV (I 3d_{3/2}), which can be ascribed to molecular I₂ [29, 30]. If iodine is in the form of AgI, I 3d_{5/2} peak should be at 618.4 eV associated with I⁻ [31]. **In fact, when compared to the as-implanted spectrum (figure 4(b)), the (I 3d_{5/2}) peak moved in the opposite direction. A similar shift to the higher energy side was observed for the Ag XPS peaks (figure (4a)).** Ag 3d spectrum (figure 4 (a)) exhibits doublet peaks at 368.9 eV (Ag 3d_{5/2}) and 374.9 eV (Ag 3d_{3/2}), which can be assigned to metallic Ag [31]. If Ag is in the form of AgI, Ag 3d_{5/2} peak should be at 367.2 eV assigned to Ag⁺ [32]. Thus, both I 3d and Ag 3d spectra suggest the absence of AgI compound in the annealed sample.

4. Discussion

Previous studies [9] have shown that Ag initially diffuses in damaged or amorphous layers of SiC but stops once the layers recrystallize. Loss of Ag in the single element Ag sample after annealing could be due to a different type of polycrystalline structure that forms on recrystallisation [27]. The presence of I in the co-implanted samples leads to a surface region on which the crystals grow larger than the Ag only implanted **samples** [27]. **Surfaces of**

samples implanted with iodine and even iodine co-implanted with Ag were more continuous and had fewer cavities than the surfaces of Ag only implanted samples after annealing [27]. The appearance of cavities on the surfaces after annealing might have implications for the nuclear industry. Recently it was proposed that these cavities might act as migration paths for implanted silver in SiC [4,12]. It is therefore expected that iodine likely to be retained in SiC while the large cavities observed on silver implanted samples could provide paths for release of silver. This may explain the observed loss of Ag in the Ag only implanted samples found in this study (see Figure.1). From a cross-sectional point of view, faceted voids were also observed in a recent High Resolution Transmission Electron Microscopy (HRTEM) study of Ag implanted and annealed polycrystalline SiC. [33]. Their study also showed that microstructural changes such as void formation in the annealed samples at temperatures similar to those used in this paper can result in a void mediated fission product transport scenario. Therefore the presence of iodine in the co-implanted samples which aids the recrystallisation of the damaged SiC resulting in a more continuous surface layer with fewer cavities/voids could be a significant contributor to the retainment of Ag.

The presence of iodine also leads to a more thermally stable near surface polycrystalline layer of SiC [26]. Raman spectroscopy measurements [34] have also shown that decomposition of SiC surface is more severe on Ag implanted samples than on I implanted samples after long time high temperature annealing. **The surface degradation is a result of a combination of the preferential sublimation of Si atoms on the surface leaving a carbon rich layer on the surface as well as severe topography occurring on the surface due to the differential thermal etching of different crystallographic surfaces [2].** The surface roughness increases initially because some crystal planes receded more than others because of sublimation and/or surface diffusion of the surface molecules. The latter resulted in the protrusion of some crystallites above others [2,27]. It has been shown that at high temperatures (above 1400 °C) the thermal etching of these surface crystallites is more severe on Ag only implanted samples than on surfaces of I implanted and Ag plus I co-implanted samples [26,27,34]. This stabilising effect the I has on reducing the etching/decomposition of the crystals could also play a role in the retainment of Ag.

The co-implantation process leads to possibly a greater degree of damage to the SiC than in the single element implantations. Studies have shown that for I only implantation [21], the implantation of the same fluence and energy of I ions used here results in an amorphous near surface region approximately 220 nm thick with total displacement damage of about 30 dpa at a depth of 70 nm. For Ag only implantation, Friedland *et al.*[9] reported the formation of an amorphous region approximately 260 nm thick, with total displacement damage of about 50 dpa at a depth of 80 nm. RBS data [26] shows that the co-implantation results in a larger amorphised region of about 290 nm. This combined with the higher concentration of impurity atoms from the double implantation could result in more trapping sites as compared to single implantation cases. This increase in trapping sites could play a role in the retainment of Ag and this effect needs to be explored further.

Conditions in the reactor differ from those in the surrogate ion implantation studies such as those used in this paper. The first discrepancy is on the damage (as mentioned in the introduction section) induced by room temperature implantations used here, where as in the reactor temperatures can be much higher than the threshold temperature for amorphization [4]. Another discrepancy is on the ion fluence used in the current study which results in the concentration of elements being above the solubility limit possibly leading to the formation of spatially segregated source terms [23] from which the mechanisms of diffusion can differ from that in actual TRISO particles. Precipitates of implanted Ag have been observed in previous studies [12,18,23]. The solubility limit of Ag in SiC at the temperatures similar to those used in this study has been estimated to be approximately $S(T) < 10^{-17}$ at/cm³ [14,35]. With the fluence used in this study, the concentration of Ag (C_{Ag}) is approximately $C_{Ag} > 10^{-22}$ at/cm³. Notwithstanding this, an attempt is made here to simulate the coexistence of Ag with other elements in SiC and the effect of this co-existence on the diffusion of Ag. In this case, the fluence used in this study (10^{16} cm⁻²) is equivalent to the fission product yield of silver at 20% burn up [23].

Recent work from the US TRISO fuel program [36,37] aimed at verifying fission product retention during normal irradiation conditions and also in conditions resembling accident scenarios provide insight into Ag release in actual TRISO particle. Results from post irradiation experiments (average temperatures ranging from about

950-1200 °C during irradiation) show complete loss of Ag from some particles and no loss from some particles in the same fuel compact of one of the compacts analysed. The authors suggest that the influence of a temperature gradient could be a factor in the release of Ag in some of the particles [36]. The authors also cite the absence of other fission products synonymous with SiC coating failure to conclude that the loss of Ag was through intact fuel coating [36]. As the damage induced during room temperature implantation is more than at these high temperature irradiations, the observed total loss of Ag in Ag only implanted samples (Figure. 1) could also be explained by Ag transport assisted by the damage retained on implantation. This is also supported by the results of heating experiments by Demkowicz *et al.* [37], at temperatures meant to simulate accident conditions. Ag release fractions [37] were characterised by a rapid release of a significant fraction of the compact inventory during the ramp up to 1600 °C (96% of all released Ag was released during the ramp up to 1600 °C). The early release of Ag during ramp up was put down to the Ag released from particles during irradiation but retained in the compacts. This temperature is similar to the temperature used in this current study (1500 °C) and the total loss of Ag in the current study could be due to the this temperature which is much higher than the (950-1200 °C) temperature ranges during the irradiation experiments in the US TRISO program. In this current study, the ramp up to the hold temperature of 1500 for 30 hours was also much sharper at 20 °C/min than the staggered approach used in ref [37].

The spatial association of Ag and I enriched regions observed from APT measurements are particularly interesting considering past reports of ions of individually implanted Ag and I into SiC have been known to form clusters after high temperature annealing cycles [12,18,23,38]. Although the XPS data suggests that both I 3d and Ag 3d spectra indicate the absence of AgI compound in the annealed sample, the binding energies of I 3d_{5/2} and Ag 3d_{5/2} for AgI in a host matrix like in SiC can be different from that of bulk AgI. Electronic binding energies of AgI nanoclusters into zeolites [39] showed that electronic binding energies had moved to higher energies as compared to electronic binding energies from bulk AgI. Li *et al.* have reported binding energy values of Ag 3d and I 3d for AgI/TiO₂ nanostructures similar to the binding energy values observed in this study [31]. They have assigned Ag 3d_{5/2} peak at 368.8 eV to metallic Ag nanoclusters, which constitute a very thin metallic Ag shell on AgI cores. They also observed I 3d_{5/2} peak at 620.1 eV, which was assigned to I₂.

The binding energy of the I 3d5/2 peak could also not give any concrete information in terms of I-Si compound formation. As mentioned earlier in the introduction of this paper, the low loss of I had been pointed to some strong binding effect or compound formation [8,22]. The angle resolved XPS analysis needs to be performed to obtain more information about the chemical state of Ag and I on the surface and near surface of the sample. This analysis should incorporate samples annealed over a wider temperature range starting from lower temperatures around 900 °C where SiC recrystallization is known to occur [40]. AgI has a melting point of 558 °C, a boiling point at 1506 °C and a known bond strength of around 234 kJ/mol [41]. Annealing from 900 °C, which is well below the boiling point of AgI [41], could also help to shed more light on the possible formation of AgI.

Results from APT show that the Ag and I precipitates that form are co-located. This maybe a result of the relatively large concentrations implanted in SiC compared to actual concentrations of fission products in TRISO particles. Londono *et al.* [25] reported *ab initio* calculations show that the binding Ag +I defects are approximately at least 8 eV. This high binding energy would make the sort of co-incorporation energetically unfavourable. However, with ion implantation reactions (co-incorporation) may be induced under implantation conditions.

Conclusions

The synergistic behaviour of iodine (I) and silver (Ag) ions co-implanted into 6H-SiC after annealing has been investigated by TOF-SIMS, APT and XPS. ToF-SIMS depth profiles after annealing at 1500 °C for 30 hours showed both I and Ag were still present in the co-implanted samples but complete loss of Ag was observed for the Ag only implanted samples annealed under the same conditions. These results suggest that I plays an important role in the retention of Ag in SiC. APT analysis clearly indicated the formation of both Ag and I clusters in the annealed co-implanted sample. Also a clear spatial correlation of Ag and I clusters was observed in the APT results. This could point to strong binding effects between Ag and I which can be the factor determining the retention of Ag in the co-implanted sample. Thus by utilizing multimodal chemical imaging we have clearly identified the reasoning for retention of Ag due to I in SiC, which we believe can be important for understanding the fission product transport through SiC.

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Figures

Fig 1: SIMS yield profiles from Ag ions in SiC normalized to Carbon 12. The profiles from SIMS measurements of the single element Ag implantation are: the as-implanted sample (●), the as-implanted of the co-implanted sample (▲), the co-implanted sample annealed at 1500 °C for 30 hours (□) and the single element Ag implanted sample also annealed at 1500 °C for 30 hours (◆).

Fig 2: I distribution profiles from SIMS measurements of the as-implanted of the co-implanted sample (grey curve) and from the co-implanted sample annealed at 1500 °C for 30 hours (black curve).

Fig 3: APT results from Ag and I co-implanted sample (a) SEM image of the final needle specimen (b) all ion map of the reconstruction showing Si (grey), C(brown), Ag (blue) and I(red) ion. (c)Only Ag ion distribution showing regions of clusters of Ag (d) Only I distribution showing regions of I clusters at similar locations of Ag clusters (e) 3 at% Ag and 3 at% I isocomposition surface showing the overall distribution of Ag and I clusters in the reconstruction (f, g) magnified views of two clusters showing the spatial correlation of Ag and I clusters (h) 1D composition profile across the clusters shown in (f) highlighting Ag enrichment on either sides of an I enriched cluster.

Fig 4: High resolution XPS spectra of (a) Ag 3d and (b) I 3d showing the binding energies for Ag 3d_{5/2} peak at 368.9 eV and I 3d_{5/2} peak at 620.3 eV, respectively from the co-implanted sample annealed at 1500 °C for 30 hours. Also included are the spectra from the as-implanted sample.