Diffusion of Fission Products through Silicon Carbide

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Abstract. Diffusion of silver and iodine through polycrystalline SiC layers produced by PBMR (Pty) Ltd for cladding of TRISO fuel kernels was investigated using Rutherford backscattering analysis and electron microscopy. Fluences of 2×10^{16} Ag$^+$ cm^{-2} and 1×10^{16} I$^+$ cm^{-2} were implanted at energies of 360 keV, producing an atomic density of approximately 1.5% at the projected ranges of about 100 nm. To obtain information on irradiation induced damage α–particle channeling measurements were performed on 6H-SiC single crystals implanted under similar conditions as the polycrystalline samples. The broadening of the implantation profiles and the loss of diffusors through the front surface during vacuum annealing at temperatures up to 1400 °C was determined. Fairly strong diffusion was observed after an initial annealing period at temperatures above 1200 °C, which is mainly due to implantation induced radiation damage. Diffusion was considerably reduced during further isothermal annealing. As no diffusion has previously been observed in single crystalline SiC at 1400 °C, the diffusor transport is obviously due to grain boundary diffusion and could be described by the Fick diffusion equation. Isochronal annealing up to 1400 °C exhibited an Arrhenius type temperature dependence. No abnormal loss through the surface as would be expected from the presence of nano-pores and/or micro-cracks was detected.

1. Introduction

Fuel elements of modern high-temperature nuclear reactors are encapsulated by a number of layers which serve as barriers to prevent fission product release. Recent reactor designs generally make use of fuel kernels surrounded by four successive layers of low-density pyrocarbon, high-density pyrocarbon, silicon carbide and high-density pyrocarbon, with silicon carbide being the main barrier for the metallic species. These so-called TRISO fuel particles retain quite effectively most of the important fission products like cesium, iodine, xenon and krypton at temperatures up to 1000 °C, although the release of silver seems to present a problem. Release studies from batches of fuel kernels or even entire fuel elements have produced largely differing results concerning magnitude and temperature dependence of silver transport through the particle coatings [1-3]. Recently our group measured silver diffusion coefficients in single and polycrystalline silicon carbide wafers [4], obtained from *Intrinsic Semiconductors* and *Valley Design Corporation* respectively. In that study broadening of a silver implantation profile during prolonged isochronal annealing has been determined from which diffusion coefficients were extracted. In all samples the first measurable broadening was observed at 1200 ℃ after a first annealing step of 10 hours. Longer annealing times and temperatures up to 1600 °C yielded no further broadening in the single crystalline samples, while it was significantly reduced in the polycrystalline samples. This enhanced initial diffusion is obviously due to implantation induced radiation damage, which was removed during the first annealing step. In polycrystalline silicon carbide diffusion coefficients exhibited Fickian characteristics and an Arrhenius type temperature depen-

dence. No diffusion in the single crystalline samples was observed up to 1600 °C. Instead a shift of the profile towards the surface accompanied by a simultaneous loss of silver occurred above 1450 °C. This is in agreement with the observations of ref. [5], who found no evidence of silver diffusion in single crystalline SiC at temperatures up to 1300 ^{0}C but a tendency of the silver to shift towards the surface at higher temperatures. According to our measurements the silver diffusion coefficient in 6H-SiC at 1300 °C is below 10^{-21} m^2 s^{-1}, from which one can conclude that the observed diffusion in the polycrystalline samples is mainly due to grain boundary diffusion while volume diffusion can be neglected.

Currently design studies for high-temperature nuclear reactors operating at temperatures significantly above 1000 °C are under way to enhance their efficiency, especially in view of process heat applications for hydrogen generation. It therefore becomes necessary to investigate transport behaviour of fission products at temperatures above 1000 °C, where little reliable information is available. In this study we investigate silver and iodine diffusion through silicon carbide layers produced by *PBMR (Pty) Ltd* in a coater, operated under similar conditions as used for coating dummy fuel kernels consisting of zirconium oxide. The results are compared with those obtained for the commercial wafers.

2. Experimental Method

The deposition of SiC on polycrystalline SiC wafers was done in the Research Coater Facility of PBMR, Pelindaba. This facility consists of a Chemical Vapour Deposition (CVD) coater that takes a charge of up to 1 kg of kernels. The diameter of the particles present while the wafers were being coated was around 710 µm. A charge of 900 g of particles was used in this case. A graphite shaft with nine horizontal rods was placed

FIG. 1. Sample holder for the CVD coater at PBMR (Pty) Ltd. Substrates of commercial polycrystalline silicon carbide wafers are mounted in grooves between the horizontal rods.

in a fixed upright position in the centre of the reaction tube inside the coater *(FIG. 1)*. The wafers were secured in slots between the horizontal rods. The CVD deposition was carried out at a temperature of around 1500 ºC, as measured on the outside of the reaction tube. A mixture of methyl trichlorosilane and hydrogen was constantly fed into the bottom of the reaction tube causing the particles to fluidize and SiC to be deposited on

the surface of the particles and the wafers. After the coating had been completed and the coater had cooled down, the particles were extracted from the top of the coater and the target holder and wafers were lowered out through the bottom of the coater. The microstructure of the deposited SiC layer was investigated by scanning electron microscopy (SEM) employing a *Jeol 5800* instrument. SEM images of the deposited layer with a thickness of approximately 10 μm are shown in *FIG. 2*. The material consists of a network of relatively large crystallites with a rudimentary columnar structure along the growth direction. The crystallites exhibit numerous stacking faults and twins.
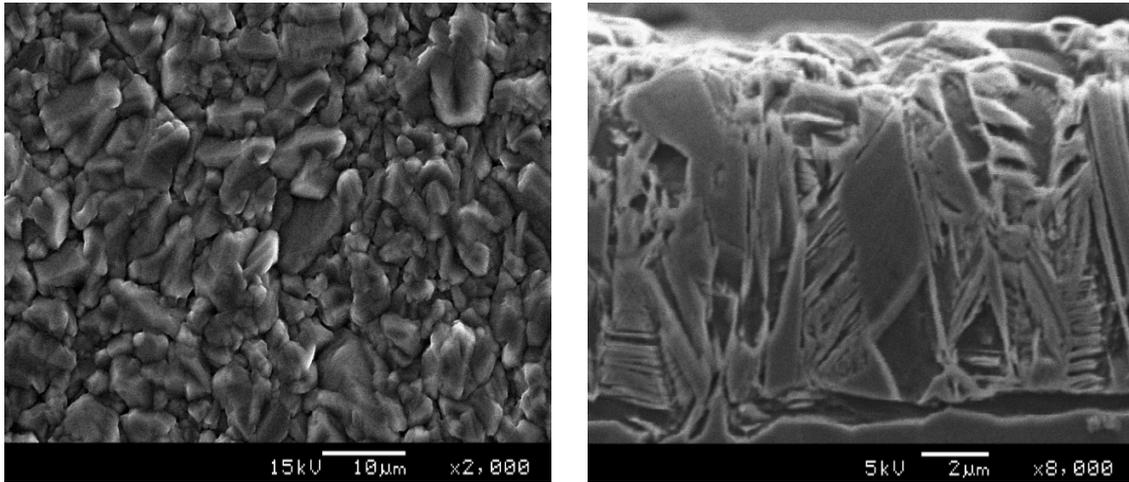

FIG. 2. SEM images showing the untreated top surface (left) and a polished and etched cross-section (right) of the deposited silicon carbide layer.

This columnar characteristic is much clearer developed in the commercial wafers studied earlier [4]. The difference is probably due to the relatively thin layer deposited in the current investigation.

Into the coated wafers 360 keV ions were implanted at temperatures ranging from room temperature (RT) to 600 °C with a fluence of either 2×10^{16} Ag^+ cm^{-2} or 1×10^{16} I^+ cm^{-2} and a flux not exceeding 10^{13} cm^{-2} s^{-1}. High implantation temperatures were chosen to reduce irradiation damage. The above fluences introduce displacement damages of ~50 dpa at 80 nm and ~30 dpa at 70 nm respectively. α–Particle channeling reveals complete amorphization of the surface regions up to depths of ~260 nm and ~225 nm for the silver and iodine implantations at RT in 6H-SiC. It also shows that the well-known radiation hardness of SiC above 300 °C [6] leaves the crystal structure intact if implanted above that temperature, although high densities of extended defects are observed.

The implanted wafers were vacuum annealed in a computer controlled *Webb Red Devil* graphite furnace for periods ranging from 5 to 60 hours. Isochronal as well as isothermal annealing studies at temperatures up to 1400 °C were done. Depth profiles of the implanted ions before and after annealing were obtained by Rutherford backscattering spectrometry (RBS) at room temperature using α-particles with energies of 1.6 and 1.8 MeV. The analyzing particle beam was collimated at a spot of 1mm diameter and the current of approximately 20 nA was measured directly on the target. A ring-shaped electrode in front of the target was kept at a negative potential of 200 V to suppress secondary electrons. Backscattered particles were observed at 165° by a surface barrier

detector telescope with an acceptance angle of 2°. Sufficient counting statistics was obtained by collecting an integrated charge of 8 µC at 1.6 MeV and 9 µC at 1.8 MeV. Energy calibration was obtained from the observed spectral shift of the silicon edge
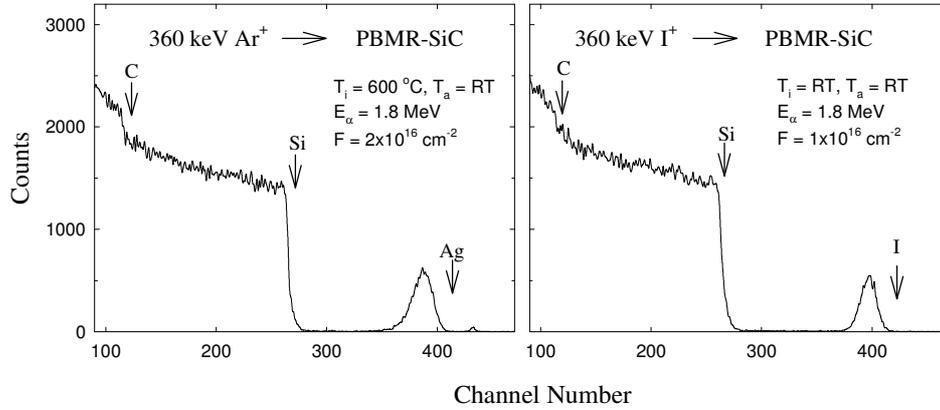

FIG. 3. RBS spectra of implanted samples before annealing. Arrows indicate the positions of the surface signals from carbon, silicon and the implants.

between the two beam energies. Typical RBS-spectra are shown in *FIG. 3*. Energies of the backscattered particles are converted to a depth scale by using the energy loss data of Ziegler [7]. Depth resolution near the surface is limited by the system's energy resolution of 12 keV to approximately 15 nm for scattering from silver atoms. Because of energy straggling this value increases to almost 20 nm at a depth of 100 nm.

3. Results

As-implanted depth profiles are relatively well described by simulations obtained with the TRIM-98 code [7] assuming displacement energies of 35 eV and 20 eV for the silicon and carbon atoms respectively [8]. Experimentally observed projected ranges of 114 nm for silver and 98 nm for iodine are in reasonable agreement with the theoretical estimates of 107 nm and 99 nm respectively. Range straggling, however, is about 50% larger for the RT implantations than predicted and even twice as large for implantations at 600 °C. This points to strong irradiation induced diffusion during high-temperature implantations where also the higher distribution moments differ more from Gaussian ($\beta = 3$; $\gamma = 0$) than observed for the RT implantations. However, to a first approximation, the depth profile can still be considered as an almost normal distribution. Fick's diffusion equation for the dilute limit leads to a particularly simple solution if the original profile at time $t_0 = 0$ can be described by a Gaussian distribution [9]. In that case the concentration profile after annealing for a time t stays a normal distribution in an infinite medium and is given by

$$C(x,t) = K \ [\pi D \ t]^{-1/2} \ \exp(-x^2/4Dt).$$

In this equation K is an adjustable constant, while the position of the maximum concentration is unchanged at $x=0$. Defining the profile width $W(t)$ as the full width at half maximum (FWHM), the following relationship between the final and original widths holds:

$$[W(t)]^2 = 4Dt \ln(2) + [W(0)]^2.$$

Hence, the diffusion coefficient D is directly obtained from the slope of a plot of $[W(t)]^2$ versus annealing time at constant temperature. *FIG. 4* displays depth profiles
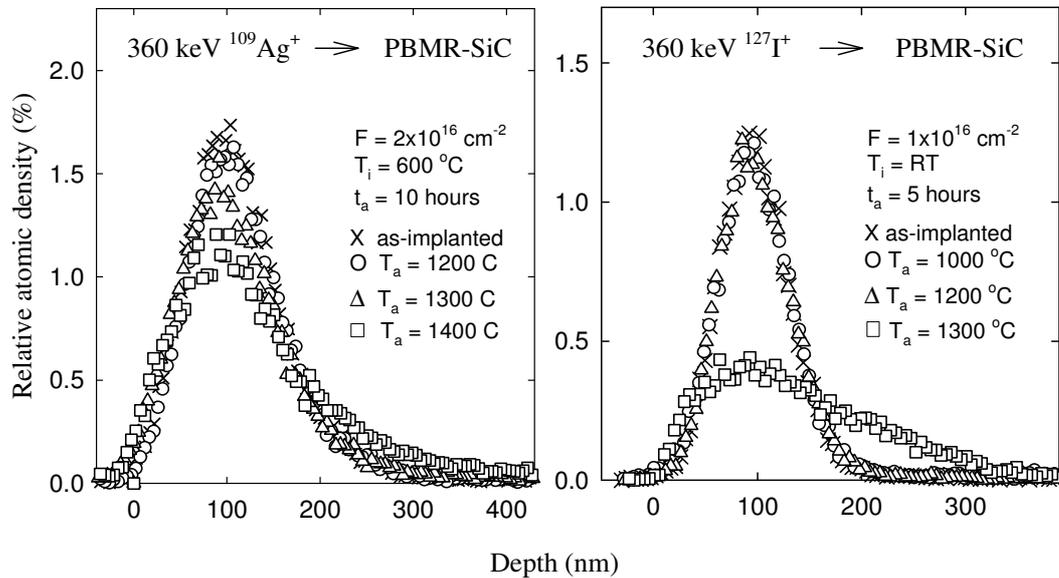

FIG. 4. Depth profiles in PBMR produced CVD-SiC before and after isochronal annealing for silver and iodine implantations at 600 °C and at RT respectively.

before and after isochronal annealing. In the peak region the shapes of the silver profiles are approximately Gaussian, allowing an analysis in terms of the procedure discussed above. However, the suddenly increased iodine diffusion at 1300 °C with a 20% loss to the surface is somewhat surprising and needs further experimental verification. No profile broadening could be detected below 1200 °C for both species, as it is obviously below the detection limit of our system.
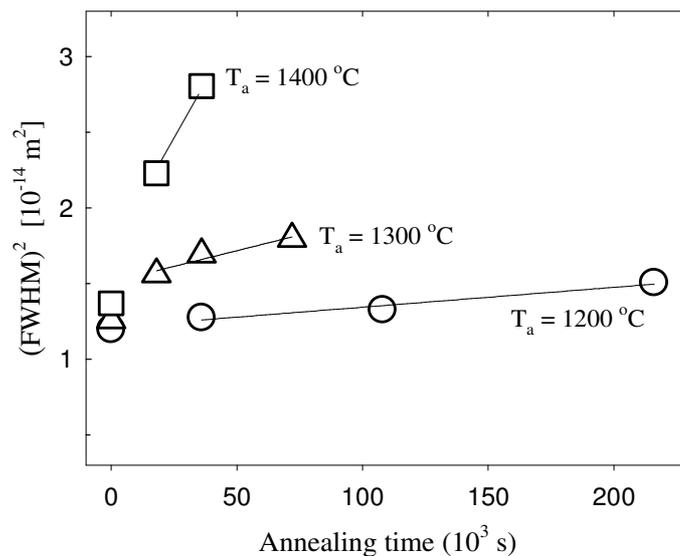

FIG. 5. Isothermal annealing curves for silver implantations

Isothermal annealing curves for silver are displayed in *FIG. 5*. Diffusion coefficients were determined from the slopes, excluding the first annealing cycle where radiation

damage effects are present. The percentage of retained silver after each annealing cycle was directly determined from the RBS spectra by normalizing the integral of the silver peak to the heights of the silicon edge. This is applicable as long as the depth interval per channel for the silicon signal stays constant. The temperature dependence of the observed loss is reconcilable with the increasingly larger fraction of the broadened distribution reaching the surface where the diffusors evaporate.

4. Discussion

All annealing curves display an initial broadening, which is significantly larger than found at subsequent annealing steps. A similar observation was also made for commercial polycrystalline and single crystalline samples implanted at 350 °C and RT respectively [4]. This phenomenon has been interpreted as enhanced diffusion in the initially highly damaged lattice structure, which anneals out during the first annealing cycle above 1000 °C. The current results seem to prove that even at an implantation temperature of 600 °C irradiation induced damage plays still an important role. From these initial slopes effective diffusion coefficients could be calculated for the damaged material. This, however, would be a rather meaningless exercise as the structural evolution of the damage structure during this first annealing stage is difficult to quantify. The only conclusions one can draw is that diffusion is enhanced in defective SiC and that most of the damage annealing is completed after the initial annealing step. A reduced but linear profile broadening is observed after that first cycle, from which one can conclude that Fickian diffusion conditions prevail after the initial annealing step. The diffusion coefficients obtained from fitting the experimental data to a straight line yields the following values for silver:

$$D_{1200} = (4.7 \pm 0.5) \times 10^{-21} \ m^2 \ s^{-1}$$
$$D_{1300} = (1.5 \pm 0.4) \times 10^{-20} \ m^2 \ s^{-1}$$
$$D_{1400} = (1.2 \pm 0.2) \times 10^{-19} \ m^2 \ s^{-1}$$

These results can be reconciled with those of ref. [11] who found no diffusion in a similar experiment after annealing at 1180 °C for 30 minutes. According to the above results the diffusion coefficient at that temperature is of the order of $10^{-21} \ m^2 \ s^{-1}$ and the expected profile broadening after such a short annealing time would be difficult to detect by RBS analysis. Assuming Arrhenius type temperature dependence, a theoretical fit of the experimental data yielded the following values for the frequency factor and activation energy:

$$D_o = (2.4 \pm 0.3) \times 10^{-9} \ m^2 \ s^{-1}$$
$$E_a = (5.5 \pm 0.5) \times 10^{-19} \ J.$$

These results are plotted in *FIG. 6* together with the results obtained previously for the commercial CVD samples [4]. The diffusion coefficients compare quite well, while the activation energy is approximately 20% higher. In view of the extremely low upper limit for the diffusion coefficient in defect-free single crystalline silicon carbide [4,12], the diffusion in CVD-SiC can almost entirely be associated with grain boundary diffusion. A rough estimate from *FIG. 2* of the relatively small fraction of grain boundary area exposed at the surface shows that grain boundary diffusion must be many orders of magnitude larger than volume diffusion. The quoted statistical errors are obtained

for a particular sample. As the diffusion depends on the random distribution of grain sizes, differences between individual samples can be significantly larger. Our results
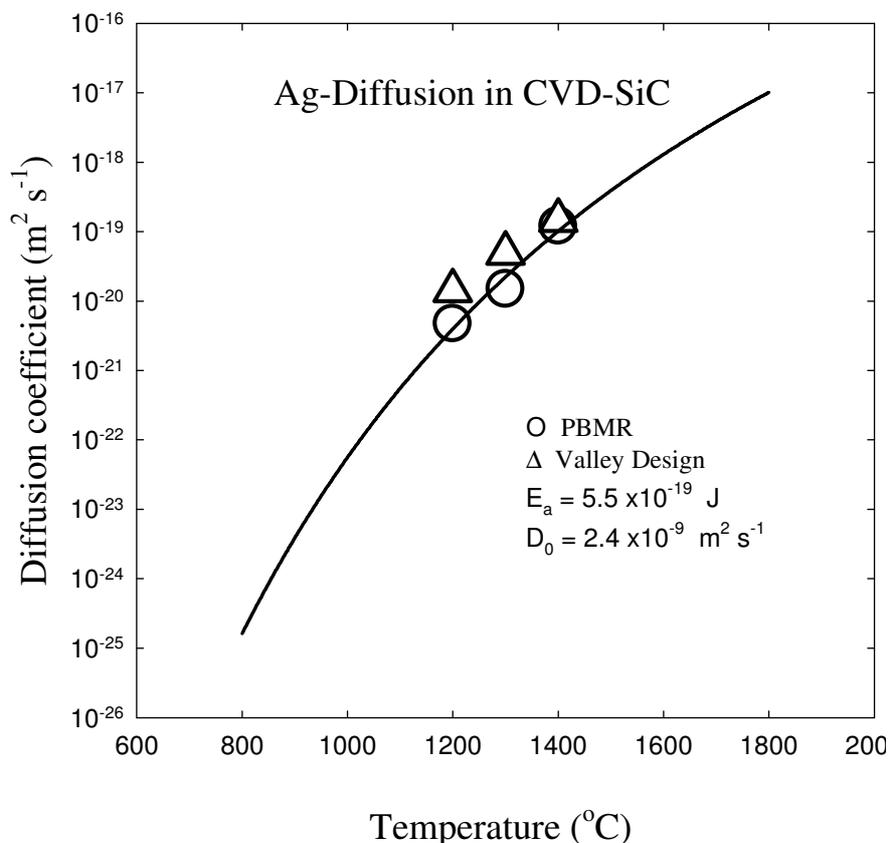

FIG. 6. Experimental silver diffusion coefficients in CVD-SiC. The solid line represents a theoretical fit assuming Arrhenius type temperature dependence.

are in variance with the findings of ref. [12], who observed no sign of silver migration via either inter- or intra-granular paths. No iodine diffusion was observed at 1000 C° by ref. [13], which agrees with our results.

5. Conclusion

As volume diffusion in silicon carbide can safely be neglected at typical operating conditions of high temperature nuclear reactors, the transport of [110m]Ag into the primary cooling system will only depend on the grain and mechanical structure of the silicon carbide coatings of fuel kernels. Diffusion coefficients below 10^{-20} m^2 s^{-1} at 1200 °C measured in this investigation are small enough to prevent any significant contamination of the cooling medium. At the typical maximum temperature of 1000 °C encountered inside a fuel kernel of a gas-cooled high-temperature nuclear reactor, the diffusion coefficient of silver in samples studied in this work would be less than 10^{-22} m^2 s^{-1}. The fractional release from fuel kernels with intact silicon carbide coatings of typically 35 μm thicknesses during their total residence time in the core would be infinitesimal ($\ll 10^{-23}$/annum). The fact that high silver losses from fuel elements have been reported in the literature must therefore be either due to SiC coatings with structural imperfections or diffusion enhancing impurities in their grain boundaries. The latter is obviously not applicable to the PBMR coatings. However, one has to bear in mind that

the current study makes use of coatings deposited on polycrystalline SiC substrates. The deposition of SiC on pyrolithic carbon might introduce stresses parallel to the interface leading to mechanical imperfections.

6. Acknowledgements

7. References

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