

CHAPTER 6 REVIEW OF PREVIOUS RESULTS

Since the detection of silver in the primary circuit of the test reactors i.e. the Dragon Reactor in the United Kingdom, the Jülich Arbeitsgemeinschaft Versuchsreaktor (AVR) in Germany and the Peach Bottom in the United States, many studies have been carried out on the possible migration paths of FPs through the coating layers, especially SiC (which is the main barrier of fission products). Most of the previously reported investigations have been performed using the batch and individual inventory methods. Only a few have been carried out utilising the implantation and diffusion couple methods, which are the methods used in this thesis. However to obtain the full picture of the migration of silver in SiC one needs to understand the previous results on silver migration investigated by all the methods and all the assumptions made in arriving at their results.

In the batch method, large populations of either loose fuel particles or those in the fuel element are heated together and the total amounts of released FPs are measured. From the released FPs the diffusion coefficients are calculated using analytical and numerical solutions for diffusion and release from spherical shells. All the calculations are performed by assuming that the particles in the batch behave exactly the same. In the individual inventory experiments the FPs of each fuel particle are measured before and after annealing using gamma counting. The FPs release measurements on the batches of fuel elements which provide useful information on the overall performance, but these do not furnish enough information on the performance of the individual particle. Individual particle measurements provide a more detailed image of fission transport. This type of measurement is time consuming because more time is required to count each particle. For example, counting times up to 8h are required to obtain reliable counting statistics. The demand on resources limits the number of particles that can be individually counted to evaluate the release of fission products. Therefore, small populations of particles, sometimes just 10 to 25, are investigated and assumed to be representing much larger batches.

In ion implantation, the ion of interest (silver in this study) is implanted into one of the coating layers of interest (SiC in this study) and its migration is investigated by comparing the ion's depth profiles before and after treatment.

The majority of the previous results indicate that the migration path of silver is diffusion in SiC; however the reported diffusion coefficients differ by many orders of magnitude. The ion implantation method has just been described while in the diffusion couple method the substance of interest (silver in our case) is coated on the substrate; then annealed. The annealed couple is thereafter analysed for any in-diffusion. In this chapter some results of the previous studies are discussed according to their investigation methods.

6.1 BATCH MEASUREMENTS

In this section the previous results gathered from the batch method are discussed and their diffusion results are summarised in table 1.

Nabielek et al. annealed TRISO particles that were irradiated in a reactor (with neutrons) at 1500 °C: the total FPs released were measured every 10 days up to 210 days [Nab77]. The results after annealing indicated that the release of silver began after 10 days of annealing, with cesium and strontium still being retained. The silver release curve as a function of annealing time was plotted: its shape contradicted that of the silver diffusion in SiC. At the beginning of the annealing, the release of silver was equivalent to a diffusion coefficient of about $10^{-16} \text{ m}^2\text{s}^{-1}$, and as the annealing continued the silver release curve was equivalent to a diffusion coefficient of about $10^{-15} \text{ m}^2\text{s}^{-1}$. From these results Nabielek et al. concluded that the silicon carbide layer was slowly becoming transparent to silver as the annealing time lengthened, allowing an increase in the silver released. Therefore, the proposed physical mechanism for this change in the SiC properties during annealing indicated that silver migration did not entirely take place by a diffusion mechanism.

In another investigation, Nabielek et al. [Nab77] performed post irradiation annealing between 1140 °C and 1240 °C for both shorter and longer annealing times. A noticeable increase in the release of silver was observed. From these results it was

suggested that SiC was only an effective barrier below 1200 °C, and no diffusion coefficient was calculated by the authors [Nab77].

The FPs' release behaviour in BISO (this is a particle similar to the TRISO particle explained in chapter 1 although SiC is not its coating layer) and TRISO particles were investigated by Brown et al. [Bro76]. In this investigation both BISO and TRISO particles were annealed at 1500 °C and the FPs released were measured. The results indicated instant release of silver in BISO particles while, in the TRISO particles the release of silver began after 16 days of annealing. From the results the diffusion coefficient of silver in silicon carbide was calculated:

$$D_{\text{SiC}}(1500\text{ °C}) = 1.5 \times 10^{-16} \text{ m}^2\text{s}^{-1} \quad \dots 6.1$$

Amian et al. [Ami83] investigated the FPs release behaviour from the TRISO particles which were previously irradiated with fast neutrons fluences from $< 0.5 \times 10^{25} \text{ m}^{-2}$ to $8.2 \times 10^{25} \text{ m}^{-2}$ at temperatures ranging from $< 400\text{ °C}$ to $< 1055\text{ °C}$: the burnup values for these particles ranged between 2.3% and 12.1% FIMA. In this investigation different particle types of fuel kernel materials with only slight variations in coating dimensions were used. Before the post irradiation, isothermal annealing at temperatures between 1000 °C and 1500 °C under vacuum was performed, and the FPs content of each particle was measured. After annealing was completed the particles' FPs were measured. By combining all the results a diffusion equation for silver in silicon carbide was derived [Ami83]:

$$D_{\text{SiC}} = 4.5 \times 10^{-9} \exp[-218\text{kJ mol}^{-1}/(\text{RT})] \text{ m}^2\text{s}^{-1} \quad \dots 6.2$$

The diffusion coefficients from different batch tests carried out by Amian et al. scattered over more than one order of magnitude at any annealing temperature. The large scatters in the diffusion coefficient data were suggested as resulting from the variations in the silicon carbide microstructure, which differ from coating to coating. Within the range of the burnup and fast fluence of the tested fuels, the dependence of silver diffusion on those variables within the scatter of data has not been found. From the experiments performed and the calculated diffusion coefficients, the authors concluded that the grain boundary diffusion was responsible for silver diffusion in

polycrystalline SiC, not the volume of diffusion through grains. Therefore, the scatter in the data was understood to be also the result of grain boundary diffusion, since such diffusion depends on the microstructure of the sample, which varies from sample to sample and from manufacturer to manufacturer.

Table 1: Pre-exponential factors and activation energies and diffusion coefficients of silver in silicon carbide (SiC) from different authors.

Type of Particle	Temperature (°C)	$D_0(\text{m}^2\text{s}^{-1})$	E_a (kJmol ⁻¹)	Diffusion Coefficient or Diffusion Equation (m ² s ⁻¹)	Source
TRISO	1500			10^{-16} and 10^{-15}	[Nab77]
TRISO	1140, 1240				[Nab77]
BISO and TRISO	1500			1.5×10^{-16}	[Bro76]
TRISO	1000:1500	4.5×10^{-9}	217.7	$D = 4.5 \times 10^{-9} \exp\left(\frac{-218\text{kJ}}{RT}\right)$	[Ami83]
TRISO	1200, 1350 and 1500				[Bul84]
TRISO	1600 :1800				[Sch91]
TRISO	1400			8.0×10^{-17} to 2.0×10^{-16} and 9.9×10^{-17} to 7.3×10^{-17}	[For82]
TRISO	1600:1900				[Min93]

Bullock [Bul84] measured the release of silver and other FPs at 1200 °C, 1350 °C and 1500 °C. This was carried out by isothermal annealing (at these three temperatures) the previously irradiated TRISO particles (five different types, at 900 °C, to burnups in excess of 20% FIMA). The five TRISO particles investigated were undergoing three changes in the fuel kernel material and two changes in the coatings. The five

coated particle fuels were: UO_2 ; UC_2 ; UCO ; and a mixture of UO_2 and UC_2 ; denoted as UC_2 ; UO_2 with solid ZrC over-coating on the kernel denoted as $\text{UO}_2^*(1)$; and UO_2 with ZrC dispersed in the buffer layer surrounding the kernel, denoted as $\text{UO}_2^*(2)$. The FPs released were measured up to an annealing time of about 10,000 hours [Bul84]. The results of this test revealed the strong temperature dependence of the breakthrough times, i.e. as the temperature increased, the fission product breakthrough times decreased dramatically. These breakthrough times also appeared to depend on the type of fuel particle tested. $\text{UO}_2^*(1)$ particles did not release any FPs during the annealing test while all the other types released silver with breakthrough times from about 30 h to 8,000 h. This long delay time before the release of silver was explained by the fact that no silver escaped during irradiation. This was based on the fact that, if silver had escaped during this process it would have been distributed throughout the particle and if that had been the case, silver escape during annealing would have occurred sooner than observed. No diffusion coefficient was calculated by the author.

Schenk et al. performed post-irradiation annealing of spherical fuel elements containing 16,400 fuel particles per element at temperatures between 1600°C and 1800°C . The content of FPs before and after annealing was measured [Sch90]. The results indicated that the fuel elements released a greater fraction of their original silver than any other fission product. This high quantity of silver release was said to be indicating the mobility of silver in SiC and no diffusion coefficient was calculated from these results. The fractional release values were derived by comparing the total amount of silver released during annealing with the measured inventory before annealing and were found to become greater with higher annealing temperature [Sch90]. Since measurements of silver release from the collection of coated fuel particles inside an element do not provide any insight into the mechanism controlling silver transport through SiC , the diffusion coefficients were not calculated from the silver release data. Through calculating equivalent failures (broken SiC) from the fractional release values, it was found that a mechanism resulting in a complete silver loss could produce the same results regarding the release of silver. Hence no diffusion coefficient was calculated.

In another attempt at understanding the migration path of silver in SiC , Förthmann et al. measured the fractional release of silver from UO_2 TRISO-coated fuel particles.

This was performed during post-irradiation annealing of these particles at 1400 °C. In these investigations Förthmann et al. focused on the relationship between the calculated diffusion coefficients and SiC coating parameters. The said parameters, such as density, grain size, microstructure, and light reflectivity, indicated no clear relationship with the silver released. However, a range of diffusion coefficients corresponding to the range of deposition temperatures and carrier gas used during SiC deposition was reported [For82].

Förthmann et al. also annealed seven types of previously irradiated fuels, compressed with matrix graphite at 1400 °C, over different annealing times. The results indicated the unprompted release of silver. Its curve provided a steady contribution of silver before the general breakthrough of this FP. This was thought to be due to uranium contaminating the outside of the silicon carbide layer. This suggestion was based on the fact that silver produced outside the SiC layer would be released almost immediately, compared to that produced inside the SiC. In the SiC deposited in pure hydrogen, the diffusion coefficient increased with the deposition temperature from $8.0 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ to $2.0 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$, with deposition temperatures ranging from 1300 °C to 1550 °C [For82]. What was also observed was that the SiC microstructure consisted of a striated structure with free silicon when the deposition temperature was 1300 °C, a crystalline structure with small crystalline size when this temperature was 1400 °C, and large columnar crystals when the deposition temperature was 1500 °C.

The results reported by Förthmann et al. indicated no significant influence of the presence of free silicon in the SiC deposited at 1300 °C on silver diffusion as suggested by Nabielek et al. [Nab77]. In the SiC deposited in pure hydrogen, the silver diffusion coefficient appeared to increase as the SiC became more columnar. However, the total change in the diffusion coefficients on SiC deposition temperature was much smaller than the range observed in the literature. Hence a definite trend was not confirmed. What was also found from these results is that the residual stress within the SiC coatings was different for different SiC grain structures and that this may play a role in the performance of SiC as the main barrier to solid FPs.

The results of SiC deposited in a mixture of argon and hydrogen indicated a decrease in diffusion coefficient from $9.9 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ to $7.3 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ as the deposition

temperature increased from 1300 °C to 1550 °C. In this type of deposition, the SiC deposited at 1300 °C consisted of a crystalline structure with small crystallite sizes, of small and uniformly distributed crystallite when the deposition temperature was 1400 °C and of coarse-grained but not columnar grains when this temperature was 1500 °C. The results of Förthmann et al. identified no relationship between microstructure and silver release [For82]. From the results, the authors found that the trend of diffusion coefficient was changing with respect to deposition temperature, especially for SiC deposited in pure hydrogen. The values of diffusion coefficients reported in these study [For82] were all within the range of diffusion coefficients reported by other authors. The small variations of these results relative to the literature suggested that the microstructure associated with the change in SiC deposition was not the primary contributor to silver transport in SiC.

Minato et al. conducted a post-irradiation annealing of TRISO particles in the temperature range 1600 °C to 1900 °C [Min93]. The burnups of the fuels were 3.6 % FIMA, which corresponded to the designed maximum burnup in the HTTR. The two samples A and B were irradiated at different average temperatures, i.e. 1250 °C and 1510 °C respectively. The results of these tests revealed no pressure vessel failure, no palladium attack or thermal decomposition of SiC. It was, however, found that ¹³⁷Cs, ¹³⁴Cs, ^{110m}Ag, ¹⁵⁴Eu and ¹⁵⁵Eu were released from the coated particles through the coating layers during post irradiation annealing. The diffusion coefficient of ¹³⁷Cs was calculated from the release curves based on the diffusion model, assuming a one layer coated fuel particle [Min93]. No silver diffusion coefficient was calculated from the fractional release but the measurements of fractional release suggested that the diffusion coefficient of ^{110m}Ag in SiC was larger than that of ¹³⁷Cs, which agreed with most results found in the literature.

In summary, the previous published batch results have suggested that silver migrates via diffusion through intact silicon carbide layers in the coated fuel particles. This suggestion has been justified by the fact that silver was released from the coated fuel particles while the volatile fission gases and cesium were retained. This suggestion has also been motivated by the results of coating failures, i.e. where both the pyrolytic carbon layers and the SiC layer have failed and the kernel is exposed. During coating failure cesium and silver escape from the fuel particles at typical operating

temperature. Therefore, all the published results have been interpreted as representing the diffusion-controlled release of silver through intact silicon carbide layers. Moreover, the calculated activation energies for diffusion coefficients in SiC fall in the same range as the activation energies for grain boundary diffusion of other fission products [Ami83]. Thus the current interpretation of silver migration indicates that silver diffuses along grain boundaries in intact silicon carbide at typical operating temperatures. However, the variations in the reported diffusion coefficients are not consistent with grain boundary diffusion and other observations, which has raised doubts about diffusion as the dominant mode of silver transport.

6.2 INDIVIDUAL INVENTORY MEASUREMENTS

In this section previous results on individual inventory measurements are discussed. Nabielek et al. also measured the individual silver content of particles. The particles investigated appeared intact and retained all their cesium and other FPs but considerable changes in silver content were observed [Nab77]. The variation in silver release data was resulting from the availability and accessibility of free silicon on the SiC grain boundaries, which enhanced silver diffusion.

Bullock conducted a post isothermal annealing at temperatures of 1200 °C, 1350 °C and 1500 °C on coated particles with different fuels as discussed in section 6.1 [Bul84]. Ten particles from each of the five irradiated fuels were randomly selected for post isothermal annealing. From the selected particles, the individual contents of silver, cesium, europium and cerium were measured before and after annealing. These individual fission product inventories were then normalized to the ^{106}Ru inventory (a chemically stable fission product in the fuel particle) before annealing. The calculations of inventories were also performed after annealing. The results indicated close agreement between the experimental and theoretical values for ^{134}Cs and ^{137}Cs inventories. This indicated that cesium was not released during irradiation. However, about 25% less silver, 15% cerium and 25% more europium than predicted were found. The highly nonuniform release of silver per particle was also noted. The majority of the annealed particles released more than 50% of their original silver while one particle retained all of its original silver [Bul84]. Cesium was mostly retained, with about three particles from the two batches losing their entire original

silver. This behaviour, i.e. from completely retained silver to complete release did not agree with diffusion as the transport mechanism. If diffusion had been the transport mechanism, identical particles in the same test would have produced similar results. For example, at 1500 °C it was found that some particles retained their entire silver inventory, while others experienced total release of silver. This indicated that SiC was still a useful barrier up to 1500 °C.

The UO₂ particles that experienced the greatest silver release consisted of columnar, large-grained SiC. The UO₂*(1) particles that retained all silver and other FPs comprised laminar structured SiC but the ZrC coating on the fuel kernel may also have assisted the retention. The UCO particles also comprised laminar SiC and good silver retention. However, the UC₂ particles also consisted of laminar SiC timely released silver. This indicated that laminar SiC was not the only reason for silver retention. The results also demonstrated that silver breakthrough times increase significantly as the annealing temperature decreases. Measurements of the FPs before the annealing provided the total amount of the silver in each particle at the beginning of each test, but the exact location or distribution of this silver was not known. Silver not already released from the fuel kernel into the coating layers must diffuse through the kernel and coatings before it reaches the SiC. The particles irradiated under the same conditions should indicate the same location and distribution of silver. However the lack of knowledge of the initial location made it impossible to determine the contribution of the retention of silver because of the delay in the fuel kernel and the SiC layer. Bullock [Bul84] also found that SiC microstructures within a given batch of fuel particles were similar after etching but that silver release differed from particle to particle within a batch. Hence, the variations in microstructure may have contributed to the silver released between batches but did not by themselves explain the large variations in silver release within the batches. These variations were considered to be due to short-circuit paths or cracks in the SiC layers.

Pearson et al. [Pea80] [Pea82] performed a test on the interaction of silver in UO₂ TRISO-coated particles having 3.3 wt% of silver, which is 100 times more than the silver expected during the normal operation of medium-enriched UO₂ to 20% FIMA. This was done to ensure that silver was detectable after annealing, while taking into consideration the loss from the kernel during the coating process. In this test silver

was mixed with UO_2 during the manufacture of the fuel kernel before coating (standard TRISO coating). The silver-doped fuel particles were annealed on a graphite wafer in three different ranges of temperature: 1550 to 1900; 1400 to 1750 and 1250 to 1500 °C for 25; 260 and 3528 h respectively. After annealing the particles were mounted and then polished to the midplane. SEM identified several locations of silver interaction with the SiC in many of the particles, which was inconsistent with the diffusion process. On the colder side of the particle, silver was found along the PyC-SiC interface [Pea80].

Pearson et al. [Pea82] also investigated silver interaction with SiC in TRISO particles with 1.26 wt% silver mixed with UO_2 fuel kernel at the maximum temperature of 1500 °C. SEM results indicated no silver penetrating SiC but extensive swelling in the SiC was reported [Pea82]. TEM results after annealing for 2000 h indicated no microstructural changes either on the hot or the cold side of the particles, and also no second-phase nodules and no grain boundary films [Pea80]. Due to the lack of measurements of particle silver inventories, the release of silver was not mentioned. Hence, from the results, it was not clear whether silver was released or not.

Minato et al. performed a test on the particles that were deconsolidated from irradiated fuel elements [Min98] [Min00]. The fission product inventory of the individual particles before and after annealing was measured. The results of gamma measurements after irradiation indicated that gamma rays from ^{95}Zr , ^{106}Ru , ^{134}Cs , ^{137}Cs and ^{144}Ce were dominant. Using the activity ratios of mobile FPs (such as silver and cesium) to chemically stable FPs (such as ruthenium and zirconium), the comparisons between the fuel particles inventories were made while accounting for individual variations in fuel kernel size and burnup. In this investigation, during an accident condition test (ACT), solid FPs released from the particles were collected regularly and counted. The amount of ^{85}Kr release was monitored as an indication of through-coating particle failure during heating. In the first accident condition (ACT-1), 100 particles were annealed at 1600 °C for 73.6 h. This test was initially planned to run for 1000 h but it was stopped, owing to the high rate of particle failures and contamination caused by the release of FPs. The amount of ^{85}Kr indicated four through-coating particle failures during annealing at 1600 °C for 5h, 28 h, 44 h and 50 h [Min98] [Min00]. It was also found that five particles lost significant cesium during

annealing, while a total of about 22 particles lost part of their OPyC layer and three of the five particles that lost significant cesium also lost part of their OPyC layer or experienced cracks in their OPyC layers. Silver release was investigated on six particles (out of 100 particles); the results indicated that two out of six lost more silver than cesium. The fission product release curves evaluated from seven measurements during annealing revealed similar shapes for both silver and cesium, which indicated that silver and cesium were released within 5-20 h. Although this suggested that silver and cesium were released at the same time, most likely from the same particles, the long gap between deposition cup readings left uncertainty about the individual behaviour of silver and cesium.

Two other accident condition tests, i.e. ACT-3 and ACT-4, were conducted. Their aim was to measure the diffusion of silver through intact SiC layers. In these investigations, each test was limited to 25 particles to accommodate long counting times, i.e. 8 h, to measure silver inventories. During annealing the particle identities were maintained so that the fission product inventories measured could be compared before and after annealing. In ACT-3 25 particles were annealed at 1800 °C for 270 h. No significant fission gas release was detected during annealing by the gas monitoring system, which indicated no through-coating failure during this test. However, the total inventory measurements of the 25 particles before and after annealing indicated that the particles lost an average of about 47% of their silver compared to about 7% of their cesium.

In ACT-4 25 particles were annealed at 1800 °C for 222 h. The results also indicated the considerable variation in the retention of the fission products. The 25 particles released more silver than cesium, i.e. about 69% of their silver was lost compared to 16% of their cesium. Based to these results the authors concluded that silver diffuses faster than cesium in SiC. However, the variation in the fractional release was noted among 25 particles in ACT-3 and ACT-4, which raised a question as to whether diffusion was the silver transport mechanism [Min98] [Min00].

6.3 ION IMPLANTATION

Batch measurements and individual inventory measurements discussed in section 6.2 and section 6.3 do not furnish extensive information about the behaviour of FPs in each coating layer. In ion implantation, an ion of interest (silver in this study) is implanted into one of the coating layer of interest (SiC in this study) and its migration is investigated by comparing the ion's depth profiles before and after treatment. The treatment may be the annealing of the sample or irradiation of the sample after implanting. This method provides additional information on the behaviour of FPs in a specific coating layer. However, implantation creates a great deal of damage depending on the implantation temperature, which influences the migration behaviour of the fission products. This section discusses the previous diffusion results of silver implanted in SiC.

In addition to the study of total silver release from fuel particles, the migration of implanted silver into CVD-SiC has been studied by various researchers. Nabielek et al. [Nab77] investigated the migration of silver implanted in a silicon carbide disk. The silver was implanted with a peak concentration equivalent to a relative atomic percent of 1.8 % ^{109}Ag into SiC, positioned at about 80 nm underneath the SiC surface. After annealing the sample at 1180 °C for 30 minutes, it was reported that the mobility of silver was too small to be detectable [Nab77]. The SiC contained some pores and had a density of 3.18 gcm^{-3} , within the range of typically characterized SiC and close to the theoretical SiC density (3.21 gcm^{-3}). The implanted silver concentration was in the range of typical concentrations reached at 12% FIMA. Nabielek et al. suggested that the silver was trapped inside the SiC grains; hence the lack of migration was due to the extremely low silver diffusion rate within these grains. From the small movement of atoms in the ion implantation experiment, the upper limit for the diffusion coefficient of silver in SiC at 1180 °C was calculated:

$$D_{\text{SiC}} (1180 \text{ }^\circ\text{C}) \ll 10^{-19} \text{ m}^2\text{s}^{-1} \quad \dots 6.7$$

This value is much lower, approximately more than two orders of magnitude lower, than the other diffusion coefficients for silver in SiC reported in the literature.

MacLean et al. investigated the migration of implanted silver with energies between 93 MeV and 161 MeV (which correspond to silver's projected range of 9 μm and 12 μm respectively) on a flat plate of SiC 0.3 cm thick. The SiC plate were chemically vapour deposited (CVD) by the Coorstek company: the reported density was 3.21 gcm^{-3} with grain sizes of the order of 3-10 μm , preferably oriented in a direction perpendicular to the SiC surface. XRD (X-ray diffraction) analyses on a polished SiC sample confirmed that the Coorsek CVD SiC contained crystalline β -SiC with a strong preferred orientation so that the (111) planes were parallel to the surface and long, dendritic SiC grains, perpendicular to the surface, were evident in AEM analyses [Mac04].

In order to encourage diffusion, the implanted samples were annealed at 1500 $^{\circ}\text{C}$ for longer times, i.e. between 200 h and 500 h, in a vacuum, using a Webb graphite furnace. The annealing conditions for selected samples are shown in table 2. Before and after annealing the samples were analysed using XPS to measure the silver concentration profile, and SEM and AEM to investigate silver distribution within SiC. The XPS results indicated no measurable change in the silver concentration profiles after annealing, while the SEM and AEM results showed that silver was forming precipitates after annealing. AEM analyses indicated that silver was residing in amorphous SiC after implantation and that the silver precipitates were located between recrystallized SiC grains after annealing. Therefore, the SEM and AEM results indicated that silver did not migrate out of its original deposition zone.

From these results MacLean et al. calculated the upper limit of the silver diffusion coefficient in SiC:

$$D_{\text{SiC}}(1500 \text{ }^{\circ}\text{C}) = 5 \times 10^{-21} \text{ m}^2\text{s}^{-1} \quad \dots 6.8$$

which is a value that is of about 6 orders of magnitude smaller than the other values reported in the literature, even though the annealing had been performed at a higher temperature for a longer time.

Table 2. Annealing conditions of some of the samples studied by MacLean et al. [Mac04].

Sample ID	Implanted fluence(atoms/cm ²)	Temperature (°C)	Time(h)	Analysis techniques
2b	1.9×10 ²¹	1500±15	210±0.25	XPS profiles
5a	2.1×10 ²¹	1500±15	480±0.25	AEM
6a	2.6×10 ²¹	N/A	N/A	AEM

Jiang et al. implanted 2 MeV Ag²⁺ ions on 0001- oriented 6H-SiC single crystalline wafers at -63 °C and 600 °C temperatures to a fluence of 5×10¹⁶ cm⁻². Complete amorphization occurred on the surface region, up to a depth of 748 nm for the implantation at -63 °C, while a highly crystalline structure was retained after implantation at 600 °C [Jia04]. To study the response of the implanted silver in crystalline and amorphous states of SiC, Jiang et al. irradiated the two wafers (implanted at 600 °C and at -63 °C) with 5.4 MeV Si⁺ ions to a fluence of 5×10¹⁵ cm⁻² at 600 °C. RBS-C was used to study the diffusion of silver and radiation damage respectively.

The results indicated that Ag implants were very immobile in SiC. Silver atoms did not diffuse in any phase of SiC (crystalline or amorphous) in the presence or absence of external ion irradiation at or below 600 °C. At 1300 °C, the implanted silver did not move in a single crystalline structure of SiC but appeared to migrate towards the surface in completely amorphised SiC. This behaviour was thought to be related to a less dense structure of fully amorphised material that provided diffusion paths for the implanted silver at a high temperature (1300 °C). No diffusion coefficient of silver was calculated in this study [Jia04]. However, these results are inconsistent with that of MacLean et al. which might be due to structural differences in the material studied, i.e. CVD-SiC for Maclean et al. and Nabielek et al. [Mac04][Nab76] and 6H-SiC for Jiang et al. [Jia04].

6.4 DIFFUSION COUPLE METHODS

The diffusion couple method is widely used in investigating the in-diffusion of a particular material into a substrate. In this method the substance of interest is coated on the substrate to form a diffusion couple. For in-diffusion investigation the diffusion couple is then post annealed to a temperature below the substance's melting point in order to avoid evaporation of the substance, or the diffusion couple is manufactured in such a way that silver would remain in the substrate surface above its melting point (for example, encapsulation is used in this thesis). This section discusses the results of previous silver-SiC diffusion couple methods.

The normal diffusion couple consisting of a diffusing metal and the substrate is not applicable to a silver diffusion experiment owing to the low melting point of silver, which will cause silver on SiC to evaporate from the surface or escape through any open edges rather than diffusing into SiC at temperatures near or above 960 °C. These factors have hindered silver-SiC diffusion couple studies.

In addition to the study of migration of implanted silver in silicon carbide, MacLean et al. investigated the migration of silver using the diffusion couple [Mac04]. MacLean's diffusion couples were hollow shells fabricated from either graphite or SiC. Two half shells were fabricated with an overlapping seam, coupled together to form a 1.9 cm hollow sphere with 0.076 cm thick walls. Silver powder (99.9995% purity) was placed inside one half and enclosed inside the shell to form the diffusion couple. Another coating was deposited on the outside of the joined half shells.

The diffusion couples were annealed at temperatures between 1050 °C and 1700 °C for periods between 2h and 1760 h. Mass loss measurements after annealing indicated silver had been released from the diffusion couples, but no silver was detected during concentration profile measurements in SiC. However, leak test results indicated the presence of cracks in many of the SiC coatings, which were assumed to have provided pathways for silver. The crack sizes were estimated by means of the vapour flow model.

A detailed summary of most of the work done on the release of silver in a high temperature reactor can be found in [Han04][Pet04] while summaries of the FPs released in the Jülich AVR reactor are contained in [Nab08].

Most of the results reported here stem from the batch and individual inventory measurements. Only a few result from ion implantation, which is used in our study. The only study that is directly related to ours is that by Jiang et al [Jia04]. Therefore, our results will be compared to it.

6.5 REFERENCES

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