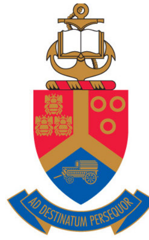
Diffusion of silver in 6H-SiC

by

Thulani Thokozani Hlatshwayo



Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY (PhD) {PHILOSOPHIAE DOCTOR} in Physics

in the Faculty of Natural and Agricultural Sciences at the University of Pretoria

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Supervisor/Promoter: Prof. J.B. Malherbe

Co-supervisor: Prof. E. Friedland

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Summary

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SiC is used as the main diffusion barrier in the fuel spheres of the pebble bed modular reactor (PBMR). The PBMR is a modern high temperature nuclear reactor. However, the release of silver from the fuel spheres has raised some doubts about the effectiveness of this barrier, which has led to many studies on the possible migration paths of silver. The reported results of these studies have shown largely differing results concerning the magnitude and temperature dependence of silver being transported through the fuel particle coatings. Results from earlier investigations could be interpreted as a diffusion process governed by an Arrhenius type temperature dependence. In this study, the silver diffusion in 6H-SiC was investigated using two methods.

In the first method a thin silver layer was deposited on 6H-SiC by vapour deposition while in the second method silver was implanted in 6H-SiC at room temperature, 350 ^{o}C and 600 ^{o}C to a fluence of 2×10^{16} silver ions cm^{-2}. Finally the effect of neutron irradiation on the diffusion of silver was investigated for the samples implanted at 350 ^{o}C and 600 ^{o}C.

Silver depth profiles before and after annealing were determined by Rutherford backscattering (RBS). Both isothermal and isochronal annealing were used in this

study. Diffusion coefficients as well as detection limits were extracted by comparing the silver depth profiles before and after annealing. The radiation damage after implantation and their recovery after isothermal and isochronal annealing were analysed by Rutherford backscattering spectroscopy combined with channelling.

The results of in-diffusion of silver into 6H-SiC at temperatures below the melting point (960 °C) using un-encapsulated 6H-SiC samples with 100 nm deposited silver indicated no in-diffusion of silver; however, disappearance of silver occurred at these temperatures. For the encapsulated samples, no in-diffusion of silver was observed at 800 °C, 900 °C and 1000 °C but silver disappeared from the samples' surface and was found on the walls of the quartz glass ampoule. This disappearance of silver was established to be due to the wetting problem that existed between silver and SiC.

The room temperature implantation resulted in a completely amorphous surface layer of approximately 270 nm thick. Epitaxial re-growth from the bulk was already taking place during annealing at 700 °C and the crystalline structure seemed to be fully recovered at 1600 °C, for samples that were sequentially isochronally annealed from 700°C in steps of 100 °C up to 1600 °C. However, no silver signal was detected at this temperature, which left certain doubts regarding the crystalline structure of the samples at this temperature. This was speculated to be due to thermal etching of the top original amorphous layer while the deeper amorphous layer was epitaxial re-growth from the bulk. The decomposition of SiC, giving rise to a carbon peak in the RBS spectra due to evaporation of Si, was clearly observed on the same samples at 1600 °C. Isothermal annealing at 1300 °C for 10 h cycles up to 80 h caused epixatial re-growth from the bulk during the first annealing cycle (10 h). No further epitaxial re-growth from the bulk was observed up to 80 h. This was believed to be due to the amorphous layer re-crystallising into crystals that were randomly oriented to the 6H-SiC substrate.

No diffusion of silver was observed at temperatures below 1300 °C but silver seemed to form precipitates at these temperatures. Diffusion of silver towards the surface accompanied by silver loss from the surface began at 1300 °C and was very high at 1400 °C, with silver profiles becoming asymmetric and closer to the surface. The loss of silver was already taking place at 1100 °C. This loss was found to be due to the

following: diffusion of silver towards the surface; the mass flow of silver via holes that were observed to be becoming larger with higher annealing temperatures on SiC surfaces and thermal etching of SiC. Isothermal annealing at 1300 ^{o}C for 10 h up to 80 h caused diffusion of silver during the first annealing cycle, while no further diffusion was observed for any further annealing at the same temperature up to 80 h. The diffusion coefficient was not calculated due to the lack of information on the structural evolution of SiC during the first annealing cycle. Isothermal annealing at 1300 ^{o}C and 1350 ^{o}C for 30 minute cycles up to 120 minutes caused high diffusion during the first cycle and reduced diffusion during the second cycle, while no diffusion was observed for any further annealing longer than the second cycle. The higher diffusion during the first 30 minutes was due to ion induced amorphization. The diffusion of silver in amorphised SiC was measured at different temperatures in the range 1300 ºC to 1385 ^{o}C and yielded to $D_0 \sim 1.4 \times 10^{-12}$ m^{2}s^{-1} and $E_a \sim 3.3 \times 10^{-19}$ J. These values were found to be approximately the same as the values of silver diffusion in polycrystalline CVD-grown SiC found by our group which were due to grain boundary diffusion: $D_o \sim 4{\times}10^{-12}$ m^2 s^{-1} and $E_a \sim 4{\times}10^{-19}$ J.

Implantation of silver at 600 ^{o}C retained crystallinity although distortions occurred in the implanted region while implantation at 350 ^{o}C also retained crystallinity but more distortions occurred as compared to silver implanted at 600 ^{o}C. This was caused by the fact that at 600 ^{o}C, the displaced atoms were more mobile because of their higher thermal energy than at 350 ^{o}C. The higher thermal energy increased the probability of the displaced atoms combining with their original lattice sites. Annealing of these samples at 1300 ^{o}C, 1350 ^{o}C and 1500 ^{o}C caused the annihilation of some defects but certain others were retained.

No diffusion of silver was observed during annealing of the samples (implanted at 350 ^{o}C and at 600 ^{o}C) at 1300 ^{o}C, 1350 ^{o}C and 1500 ^{o}C but silver moved towards the surface at 1500 ^{o}C. The upper limit of the diffusion coefficient of $D < 10^{-21}\ m^2 s^{-1}$ was obtained at 1300 ^{o}C. The movement of silver towards the surface was found to be due to thermal etching at 1500 ^{o}C. Neutron irradiation of these samples caused no silver diffusion but silver ^{110m}Ag, due to ^{109}Ag capturing a neutron during neutron irradiation, was detected in the samples.

DECLARATION

I, Thulani Thokozani Hlatshwayo, declare that the thesis, which I hereby submit for the degree of PhD in Physics at the University of Pretoria is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Signature: ……………………………………………………

Date: …………………………………………………………

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ABBREVIATIONS

ACT-Accident Condition Test

AEM-Analytical Electron Microscopy

AVR-Arbeitsgemeinschaft Versuchsreaktor

BCA-Binary Collision Approximation

BISO-Bistructural Isotropic

CAB-Core and Bonds (Model)

CFE- Cold Field Emitter

CVD-Chemical Vapour Deposition

EBSD-Electron Backscattered Diffraction

EDS-Energy Dispersive X-ray Spectroscopy

FIMA- Fissions per Initial Metal Atom

FP-Fission Product

FWHM-Full Width at Half Maximum

HTGR –High Temperature Nuclear Gas Reactor

HTTR-High Temperature Test Reactor

IPyC- Inner Pyrolytic Carbon

MCA-Multi-Channel Analyzer

MD-Molecular Dynamics

OPyC-Outer Pyrolytic Carbon

PBMR-Pebble Bed Modular Reactor

PyC-Pyrolytic Carbon

RBS-Rutherford Backscattering Spectroscopy

RBS-C- Rutherford Backscattering Spectroscopy combined with Channelling

SA PBMR-South African Pebble Bed Modular Reactor

SCA-Single Channel Analyser

SEM-Scanning Electron Microscopy

SFE-Schottky Field Emitter

TEM-Transmission Electron Microcopy

TFE-Thermal Field Emitter

TRIM-TRansport of Ions in Matter

TRISO-TRistructural ISOtropic

XPS-X-ray Photoelectron Microscopy

XRD-X-ray Diffraction