Cesium and Silver Diffusion in SiC for TRISO Applications

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INTRODUCTION

TRistructural-ISOtropic (TRISO) fuel is the preferred fuel for the Very High Temperature Reactor (VHTR). TRISO fuel is a ceramic based spherical fuel. In the construction of TRISO fuel the SiC layer serves as the main fission product barrier to metallic fission products, however, during operation ^{110m}Ag and ^{137}Cs have been observed to release causing maintenance and safety issues. To ensure safe and efficient operation an understanding of the kinetics and transport mechanism for Ag and Cs diffusion in the SiC layer must be known. Previous experimental work has not provided repeatable results, reporting diffusion coefficients varying orders of magnitude.[1-5] While fractional release measurements of TRISO particles has shown a microstructural dependence on the retention of the Ag and Cs fission product inventories.[6] These observations suggests grain boundary (GB) diffusion may be responsible for fission product release.

DESCRIPTION OF THE ACTUAL WORK

Ion implantation diffusion couples were fabricated to investigate the diffusion of Ag and Cs in SiC. In the design Ag and Cs ions were implanted in SiC substrates, 6H single crystal from Cree, Inc. and polycrystalline CVD-SiC from Rohm and Haas. The CVD-SiC samples are included to investigate the contribution of GBs to diffusion while the 6H single crystal sample serves as a control to directly measure volume diffusion. The samples were implanted with Ag^+ and Cs^+ at 400 kV to a fluence of $2x10^{16}$ at/cm^2 at 300°C at the Michigan Ion Beam Laboratory. The implantations yielded a maximum implantation peak of ~2.6 at% at ~125 nm for Ag and ~2.8 at% at 120 nm for Cs according to SRIM calculations. The temperature of 300°C was selected to avoid irradiation induced amorphization of the SiC.[7]

The implanted samples were exposed to elevated temperatures to induce thermal diffusion in a W-mesh vacuum furnace capable of temperatures up to 1700°C with a heating and cooling rate of 1000°C/hour and an operational vacuum of ~$3x10^{-5}$ torr. The selected exposure conditions were 1300-1500°C for times ranging 10-24 hours. To mitigate decomposition of the SiC surface, which occurs at temperatures above 1500°C, the samples were enclosed in a graphite cylinder with SiC caps. The system serves to limit the decomposition by sacrificing the container to saturate the vapor pressure of C(v) and Si(v) in the exposure chamber.

Analysis of the implantation samples was completed using Secondary Ion Mass Spectroscopy (SIMS) and Rutherford Backscattering Spectroscopy (RBS). SIMS is a highly sensitive depth profiling technique capable of achieving nm depth resolution and detection limits of 1 part-per-billion (ppb), making SIMS the ideal technique for depth profile measurements in ion implantation studies. RBS is employed to measure depth profiles necessary to calculate relative sensitivity factors required to correlate real concentration to SIMS intensity. Depth profiles of Cs in SiC were obtained by a time-of-flight SIMS (ToF-SIMS) (IONTOF GmbH, Germany) at Environmental and Molecular Science Laboratory at Pacific Northwest National Laboratory. Ag in SiC depth profiles were initially measured by ToF SIMS at PNNL, but, due to detection limitations the analysis was shifted to magnetic sector SIMS. Ag in SiC depth profiles were measured by Evans Analytical Group, Sunnyvale, CA. RBS measurements were made at the University of Wisconsin's Ion Beam Laboratory User Facility.

ANALYSIS

Initial RBS results indicated a loss of Si from the surface of the implanted CVD-SiC samples exposed to temperatures 1400°C and above. This result was also corroborated by a shift in depth of the maximum concentration peak observed in both RBS and SIMS. Interpretation of the SIMS depth profiles from the CVD-SiC samples is not feasible due to the observed surface decomposition. This phenomenon was not observed in the 6H single crystal samples. Figure 1 shows the SIMS depth profiles for Ag/6H-SiC system as implanted and exposed to 1500°C for 10 hours. Figure 2 shows the SIMS depth profiles for Cs/6H-SiC as implanted and exposed to 1400°C and 1500°C for 10 hours. In Figure 1 the detection limits reached were $1x10^{15}$ at/cm^3 (1 ppb). A comparison of the Ag distribution in the as implanted sample with the exposed sample shows a shoulder in the exposed sample suggesting a solubility limit of ~$1x10^{16}$ at/cm^3 at 1500°C, this value is reasonable as it is within the reported values of the solubility limits of other impurities (Al, P, N, and B) in 6H SiC[8] and the values of Ag in bulk SiC calculated by *ab initio* simulations.[9] The Ag intensity past the as-implanted Ag signal (at ~1100 nm) is indicative of Ag impurity diffusion, suggesting Ag volume diffusion is active at 1500°C. In the Cs/6H SiC system the detection limits were ~3x10^{17} at/cm^3 and no indication of impurity diffusion was observed. The bimodal distribution observed in the high [Cs] peak is due to redistribution along the high damage region from irradiation induced defects and recrystalization of an amorphous layer observed in the Cs/SiC system.[10]

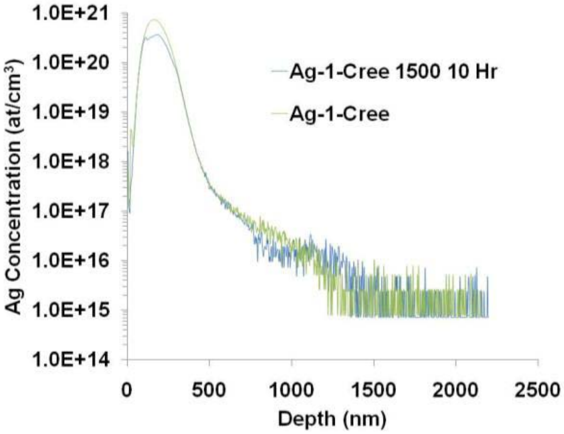

Figure 1) Magnetic Sector SIMS (EAG) depth profile of Ag/6H-SiC, as-implanted and exposed to 1500°C for 10 hours

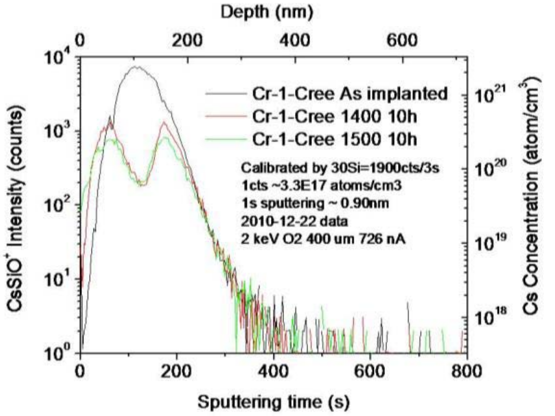

Figure 2) ToF SIMS (PNNL) depth profile of Cs/6H-SiC, as-implanted and exposed to 1400 & 1500°C for 10 hours

RESULTS

The preliminary SIMS results show promise concerning the measurement of impurity diffusion in the Ag/SiC and Cs/SiC systems. The measured change in the Ag concentration in the Ag-1-Cree 1500°C 10 hrs sample suggests impurity volume diffusion to be active; this is further supported by the measurement of a reasonable solubility limit for the system. These results are a promising start for the investigation of the diffusion kinetics of Ag in SiC and to the authors knowledge the first reported experimental values of the solubility limit for the Ag/6H-SiC system. Future analysis of Ag implanted CVD-SiC will show the contributions of grain boundaries by comparison with 6H samples at identical exposure conditions. No Cs impurity diffusion was observed, this is not surprising as a comparison of the Ag system (Figure 1) suggests the solubility limits likely exists below the system detection limits. High temperature exposures could allow for measurement of Cs diffusion if the solubility limit exceeds detection limits above 1500°C.

This work is supported by DoE NERI Grant Award No. DE-FC07-07ID14823. The submitted paper is a result of activities conducted by the author under a cooperative agreement funded by the U.S. Government under award No. NRC-04-07-120. Accordingly, the U.S. Government retains a nonexclusive, royalty-free, license to publish, reproduce, and to authorize others to do so for U.S. Government purposes. Part of this research was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research located at Pacific Northwest National Laboratory (PNNL).

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