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Observations of Ag diffusion in ion implanted SiC

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ABSTRACT

The nature and magnitude of Ag diffusion in SiC has been a topic of interest in connection with the performance of tristructural isotropic (TRISO) coated particle fuel for high temperature gas-cooled nuclear reactors. Ion implantation diffusion couples have been revisited to continue developing a more complete understanding of Ag fission product diffusion in SiC. Ion implantation diffusion couples fabricated from single crystal 4H-SiC and polycrystalline 3C-SiC substrates and exposed to 1500–1625 °C, were investigated by transmission electron microscopy and secondary ion mass spectrometry (SIMS). The high dynamic range of SIMS allowed for multiple diffusion régimes to be investigated, including enhanced diffusion by implantation-induced defects and grain boundary (GB) diffusion in undamaged SiC. Estimated diffusion coefficients suggest GB diffusion in bulk SiC does not properly describe the release observed from TRISO fuel.

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1. Introduction

The development of advanced nuclear reactor concepts has prompted a need for materials with high performance under extreme environments. Silicon carbide (SiC) possesses high temperature strength, chemical inertness, and a low neutron cross-section making it an ideal material for advanced reactor core components [1]. SiC has found a prominent role in the design of tristructural isotropic (TRISO) coated particle fuel. The TRISO fuel construction, as identified by the US DOE Advanced Gas Reactor Fuel Development Program, consists of a mixed uranium-dioxide and uranium-carbide fuel kernel surrounded by a approximately 100 μm carbonaceous buffer layer and successive isotropic layers of approximately 35 μm inner pyrolytic carbon (IPyC), approximately 40 μm chemical-vapor-deposited (CVD) SiC, and approximately 35 μm outer pyrolytic carbon (OPyC) [2]. In the TRISO fuel design the CVD-SiC layer acts as a structural component and as a barrier to fission products and radioisotopes not stabilized in the fuel kernel.

While modern TRISO fuel has demonstrated excellent retention of fission products and radioisotopes, variable release of ^{110m}Ag from intact particles has continued to be observed [3]. This release of Ag from intact TRISO particles represents a legacy problem, which has been a focus of research since the 1970s [4,5]. Comprehensive reviews of the reported literature related to Ag release from TRISO fuel and Ag diffusion in SiC are presented by van Rooyen et al. [6] and Malherbe [7]. No consensus has been reached concerning the mechanism responsible for Ag release from TRISO fuel, however, it is suggested that the release is influenced by the SiC layer microstructure as particles with large columnar-grained SiC layers have been observed to release a larger fraction of Ag fission product inventory relative to particles with fine-grained SiC layers [8]. The two primary competing hypotheses for the observed release are grain boundary dependent transport [4,9–15] and micro-crack vapor transport [16,17]. The understanding of the Ag release mechanism from TRISO fuel is derived from Ag release measurements from irradiated TRISO fuel [4,5,18–24], surrogate Ag diffusion studies [9–14,16,17,25], and computation simulation studies [15,17,26,27]. The measured diffusion coefficients for release from TRISO fuel are observed to be orders of magnitude greater than the surrogate diffusion and simulations studies. The reason for the observed discrepancy is not explicitly known.

A primary variable between the TRISO release and surrogate diffusion studies is the influence of irradiation damage on observed Ag transport. Molecular dynamics simulations by Méric de Bellefon and Wirth [27] have postulated that irradiation induced microstructural defects and variations in grain boundary (GB) network of the SiC layer may significantly influence the observed Ag transport in SiC. Similarly, in surrogate ion implantation studies, implantation effects have also been observed to influence the redistribution of Ag in SiC implanted at room temperature to 600 °C [9,10,13,28]. The reported surrogate diffusion studies focus on investigation of Ag diffusion in unirradiated SiC or in the case of

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ion implantation diffusion studies, SiC substrates with an irradiated implantation layer adjacent to unirradiated SiC. This variation in SiC substrates and experimental methodology may contribute to the reported discrepancies in Ag diffusion coefficients (D^{Ag}) obtained from surrogate studies and those from TRISO release analysis.

Additionally, the physical properties of SiC which make it an ideal fission product barrier material for nuclear fuel applications also present challenges for investigating impurity diffusion behavior for high atomic number elements in SiC, notably due to low impurity solubility limits (S), $S(T) < 1 \times 10^{17}$ at/cm^3 at 2150 °C [29], and large migration energy barriers [30]. For diffusion studies, these challenges require high temperature exposures to drive diffusion to measurable diffusion depths and concentrations by available analysis techniques.

For the temperatures of interest to TRISO operations and accident conditions, 800–1600 °C [31], elemental Ag is primarily in the liquid phase with a high vapor pressure. This is an issue for traditional diffusion couple designs as it leads to possible Ag dissolution in $Ag_{(l)}$ [32] and difficulty in maintaining a consistent diffusion surface. Ion implantation diffusion couples provide a consistent, buried Ag source for investigating diffusion in SiC at elevated temperatures where diffusion in the implanted substrate is indicated by an extension of the implanted species past the implantation peak after thermal exposure and has been observed for B and Al in SiC [33,34]. In this study, ion implantation diffusion couples are investigated by secondary ion mass spectrometry (SIMS) depth profiling; SIMS provides an expanded dynamic range of Ag detection relative to previously reported Ag ion implantation studies [9,10,13,16,17]. The expanded dynamic range allows for the investigation of Ag diffusion phenomena at Ag concentrations of approximately 1×10^{20}–1×10^{15} at/cm^3, yielding additional insight to further understand Ag release from TRISO fuel.

2. Materials and methods

2.1. Implantation and thermal exposure

Polycrystalline CVD 3C-SiC from Rohm and Haas (standard grade SC-001) and single crystal 4H-SiC wafers 4° off (1 0 0 0) from Cree, Inc. were used as ion implantation substrates for diffusion studies. Polycrystalline 3C-SiC samples were prepared from bulk samples and were polished to an arithmetic surface roughness (R_a) < 10 nm using successively finer diamond polishing media and a final polish of 0.05 μm colloidal silica. The single crystal 4H-SiC wafers were obtained from Cree, Inc. with a R_a < 10 nm. Roughness values were measured using a Zygo optical profilometer. The polycrystalline 3C-SiC substrates were implanted with two separate dose conditions, 400 kV Ag^+ to 1×10^{14} ion/cm^2 and 5×10^{14} ions/cm^2, at 300 °C at the Michigan Ion Beam Laboratory (MIBL) through the Advanced Test Reactor National User Facility (ATR-NSUF) program. The single crystal 4H-SiC substrates were implanted to a dose of 5×10^{14} ions/cm^2 at identical conditions to the polycrystalline 3C-SiC substrates. The implantation dose and the 300 °C implantation temperature were selected to avoid amorphization of the SiC substrate during implantation. Following Ag implantation a 200–250 nm diamond-like-carbon (DLC) coating was deposited on the SiC implantation surface to protect the sample during thermal exposure.

Individual samples, approximately 8 mm × 8 mm, were cut from the bulk implanted substrates for thermal exposure. Individual samples for thermal exposure were mated with an as-polished 3C-SiC sample using graphite paste to further protect the implantation surface. The samples were sealed in a thick-walled quartz ampoule with excess coarse SiC powder to limit surface decomposition [35]. Approximately, 0.05 g of Ag foil were encapsulated in the isolated sample chamber along with the diffusion sample to limit Ag out-diffusion from the Ag implanted SiC substrates. Samples were exposed to 1500–1569 °C in an MTI GSL 1600X-80 tube furnace and at 1625 °C in a Lindberg Blue tube furnace. The self-contained samples were inserted and removed at temperature followed by a quenched step to limit diffusion contributions during transient heating and cooling. Temperatures were monitored with an external Type-B thermocouple placed in the center of the tube furnace hot zone. After thermal exposure, the ion implantation substrates were investigated by transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and SIMS to understand the change in Ag distribution. Table 1 shows the ion implantation diffusion couples investigated in this study.

2.2. S/TEM analysis

S/TEM samples for investigation were prepared by traditional focused ion beam (FIB) lift-out techniques using a Zeiss CrossBeam Dual Beam FIB/SEM at the at the University of Wisconsin-Madison Materials Science Center (UWMSC). The FIB lift-out technique provided cross-sectional TEM samples of the SiC structure along the implantation and diffusion direction. Bright Field (BF) TEM analysis was performed using a Technai TF-30 at 300 kV. Selected area diffraction (SAD) patterns of the implantation layer and unaffected SiC beyond the implantation layer were obtained using a 300 nm aperture. Annular Dark Field (ADF) micrographs were obtained using a FEI Titan aberration-corrected STEM at the UWMSC to provide additional mass-contrast to aid in resolving the nature of the Ag after implantation and thermal exposure.

2.3. SIMS analysis

SIMS analysis was conducted using a Cameca IMS 7f-GEO magnetic sector SIMS. Depth profiles were obtained for Ag in SiC by rastering a 5 keV O_2^+ ion beam over a 200 × 200 μm area with a 33 μm diameter optically gated analysis area. The SIMS analysis was performed at the Institute of Critical Technology and Applied Science Nanoscale Characterization and Fabrication Laboratory at Virginia Tech. ^{107}Ag intensity was measured as a function of time and the measured intensity was correlated to Ag concentration ([Ag]) using a relative sensitivity factor of 1.10–1.32 $\times 10^{23}$ at/cm^3 calculated from the as-implanted (AI) SiC substrates using the isotope ^{28}Si as the bulk SiC reference intensity. Relative sensitivity factors were determined for all AI substrates (polycrystalline 3C-SiC 1×10^{14} ions/cm^2 and 5×10^{14} ions/cm^2, and single crystal 4H-SiC 5×10^{14} ions/cm^2) where the range in relative sensitivity factors is representative of minor experimental variations for each AI substrate. Crater depths were determined by measuring the SIMS sputter crater using a Zygo optical profilometer to correlate sputtering time with depth.

3. Results and discussion

3.1. S/TEM analysis

Fig. 1 shows a BF-TEM comparison of the implantation zone for the polycrystalline 3C-SiC 5×10^{14} ions/cm^2 AI and 1569 °C 20 h

Table 1
Ion implantation diffusion couple exposure conditions for implantation doses of 5×10^{14} ions/cm^2.

Temperature (°C)	1500	1535	1569	1625
Time (h)	5, 10, 20[a]	10[a]	5, 10, 20	1

[a] Indicates 1×10^{14} ions/cm^2 also included.