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Radiation enhanced diffusion of cesium, strontium, and europium in silicon carbide

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ABSTRACT

The radiation enhanced diffusion (RED) of three key fission products in SiC: cesium, europium, and strontium was investigated following ion irradiation at a damage rate of 4.6×10^{-4} dpa s^{-1} at temperatures between 900° C and 1100° C. The radiation enhancement of diffusion was as large as 10^7 at 900° C, and dropped to a value of 1 by 1300° C for all but cesium grain boundary diffusion. Strontium and cesium exhibited several orders of magnitude enhancement for both mechanisms. Europium enhancement was greatest at 900° C, but dropped to the thermal rates at 1100° C for both mechanisms. The trends in the RED mechanism correlated well with the point defect concentrations suggesting that both carbon and silicon vacancy concentrations are important for fission product diffusion. These constitute the first radiation-enhanced diffusion measurements of strontium, cesium and europium in SiC.

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1. Introduction

Tristructural-isotropic (TRISO) coated fuel is the fuel form of choice for the Next Generation Nuclear Plant (NGNP) program that will demonstrate the technologies for fuel fabrication and qualification on an industrial scale. The fuel particles consist of kernels of uranium oxycarbide (UCO) or uranium oxide (UO_2) that are then coated with a porous carbon buffer, a pyrolytic carbon layer (PyC), a SiC layer, and a final PyC layer, to produce a nominally 1 mm diameter particle. These fuel particles are able to survive extreme environments of 900° C–1300° C under normal operating conditions and as high as 1600° C in accident situations [1]. During operation, several fission products (FPs): silver, strontium and europium in particular, have been observed to be released through intact SiC [2]. While significant research efforts have focused on quantifying and identifying a mechanism for silver release through the SiC [3–6], little is known about other FPs such as europium and strontium. Cesium, europium, and strontium all pose important radiological health concerns if released to the environment [7]. Cesium diffusion has been assumed to be negligible as high quality fuel has shown minimal cesium release, but this has not been verified.

Post-irradiation annealing of fuel has shown several features in FP release curves that can not be interpreted without knowing the FP distribution in the fuel *a priori*. The low solubility of most FPs and low melting and boiling temperatures compared with the temperatures of interest makes diffusion couples very difficult to construct [4,6]. Several studies have attempted to isolate thermal and radiation enhanced diffusion (RED) for FPs with little success. Ion implantation has been used to introduce FPs into SiC, but this is complicated by the introduction of trapping sites due to radiation damage from the implantation [8], and the likely change in diffusion mechanisms due to the very high concentrations necessary to measure the diffusion profiles [3,5,9–11]. One study investigated silver diffusion via ion implantation and SIMS at lower concentrations, but could not establish if those concentrations were above or below the solubility limit [12]. Spherical diffusion couples made using the same coaters for TRISO particle production have shown that grain boundaries play an important role in silver diffusion through SiC, but these experiments have been conducted at very high silver concentrations (pure silver at the interface) that are not

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relevant under fuel operating conditions [6]. The spherical geometry also limits the analytical techniques for concentration profiling to those with poor sensitivity, significantly reducing the accuracy of the measured diffusion coefficients.

Recently a novel diffusion couple was developed that maintains a thin film geometry to allow the use of depth profiling techniques, introduces FPs into PyC adjacent to SiC without causing radiation damage in the SiC and at concentrations that would be relevant to TRISO fuel, recreates the PyC/SiC interface, and allows for the isolation of thermal diffusion [13]. This design was used to study the thermal diffusion of cesium, strontium, and europium between 900° C and 1300° C reported in [14]. This thin film geometry is well suited to conduct controlled RED experiments using ion irradiation to emulate neutron irradiation. This study investigated the role of radiation on fission product diffusion and examines how this diffusion data fits with the fission product release measurements.

2. Experimental method

2.1. Materials

Details of the novel diffusion couple design were reported in Ref. [13]. The diffusion couple is a substrate of high purity CVD β-SiC (grain size: 1.8 μm) obtained from Rohm and Haas Inc., that was coated with 300 nm of PyC. The FP of interest: cesium, europium, or strontium was then implanted into the PyC. A final coating of plasma-enhanced CVD (PECVD) SiC sealed the diffusion couple to allow the FP to have sufficient residence time at the interface to diffuse into the SiC substrate. For this study, all three FPs were implanted at 400 keV to a total fluence of 10^{16} cm^{-2}. The energy was chosen to ensure that the FP remained within the PyC and did not penetrate the SiC substrate, allowing for the calculation of purely thermal diffusion coefficients within the SiC and the controlled measurement of RED as performed in this study.

2.2. Ion irradiation

High temperature irradiations were performed using a 3 MV Pelletron accelerator at the University of Michigan Ion Beam Laboratory. Fig. 1 is a schematic of the irradiation chamber that was designed to allow for accurate dose and temperature monitoring. Temperature was monitored using both a thermocouple mounted on the sample surface and a 2D infrared pyrometer. Damage level was monitored using a Faraday cup inserted directly in front of the stage. A 4.5 MeV Si^{++} beam was raster scanned over a set of tantalum slits that define the irradiation area at 1019 Hz horizontally and 117 Hz vertically.

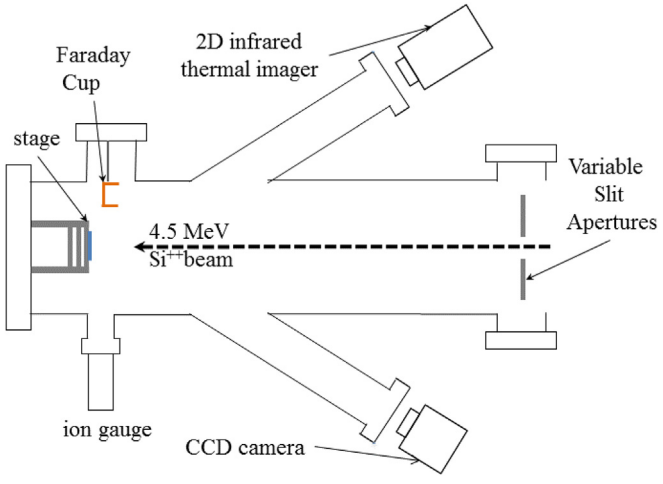

Fig. 1. Schematic of the irradiation chamber. A 4.5 MeV Si^{++} beam is used to irradiate the sample. A Faraday cup that can be inserted directly in front of the sample is used to measure dose. A set of variable slit apertures is used to control the irradiation area. A thermocouple on the stage and the 2D infrared thermal imager are used to monitor temperature. A CCD camera allows for monitoring of the entire setup. An ion gauge placed close to the stage monitors vacuum in the chamber.

Dose-rate was calculated at the PyC/SiC substrate interface in the SiC using the Stopping Range of Ions in Matter (SRIM) code in quick Kinchin-Pease mode [15,16] with a silicon atom displacement energy of 35 eV and a carbon atom displacement energy of 20 eV [17]. A resistive graphite heater on the stage provides the majority of the heating, but the addition of beam-heating was required to reach the peak-temperature of 1100°C. This bounded the damage rate to at minimum 4.6×10^{-4} $dpa\,s^{-1}$. Fig. 2 shows the damage and implanted ion concentration as a function of depth. Between the PyC/SiC substrate interface at 350 nm and a depth of 1000 nm the implanted silicon concentration was minimal and the change in dose only varies by a factor of two. While this could affect the diffusion kinetics, the majority of the effect should be within the first 300 nm as witnessed in the thermal diffusion study, where the dose only varies by a factor of 50%.

The sample temperature was monitored using a thermal imager and a thermocouple attached between the lip of a graphite shim and the diffusion couple surface. After initial heating, the 2D infrared pyrometer was calibrated to the surface emissivity using the thermocouple. The ion beam adds nearly 200° C of temperature increase due to beam heating as verified using the pyrometer. The thermocouple is protected from the beam and does not see this temperature increase. The surface temperature varied by 15° C across the irradiated area.

2.3. Time of flight ion mass spectrometry

Time of flight secondary ion mass spectrometry (ToF-SIMS) was used to profile the cesium, europium, and strontium concentrations for diffusion measurements using an Ion-TOF SIMS 5 at the Georgia Institute for Electronics Tech and Nanotechnology (IEN). All ToF-SIMS spectra were acquired analyzing for positive ions using 25 keV Bi^+ to sputter material for analysis and 5 keV O^+ to sputter material for depth profiling. The sputtered craters were 100 μm × 100 μm while only the center 50 μm × 50 μm was analyzed to prevent edge effects that would reduce the depth

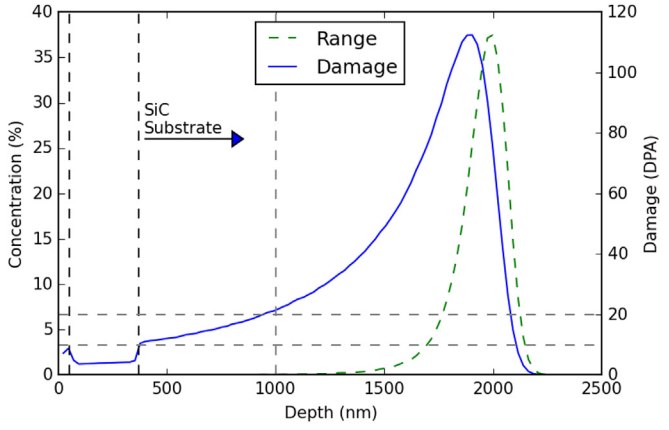

Fig. 2. SRIM calculation of 4.5 MeV Si^{++} into the diffusion couple. The layers are differentiated by vertical dashed black lines. Horizontal grey lines mark the 10 and 20 dpa dose points which correspond to the PyC/SiC interface and 650 nm into the SiC substrate, within which all the RED is limited.