Ag out-surface diffusion in crystalline SiC with an effective SiO₂ diffusion barrier

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Abstract

For application of tristructural isotropic (TRISO) fuel particles in high temperature reactors, release of radioactive Ag isotope (^{110m}Ag) through SiC coating layer is a safety concern. To understand the diffusion mechanism, Ag ion implantations near the surface and in the bulk were performed by utilizing different ion energies and energy-degrader foils. High temperature annealing was carried out on the as-irradiated samples to study the possible out-surface diffusion. Before and after annealing, Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry (SIMS) measurements were employed to obtain the elemental profiles of the implanted samples. The results suggest little migration of buried Ag in the bulk, and an out-diffusion of the implanted Ag in the near-surface region of single crystal SiC. It is also found that a SiO₂ layer, which was formed during annealing, may serve as an effective barrier to reduce or prevent Ag out diffusion through the SiC coating layer.

1. Introduction

Silicon carbide (SiC) is a promising structure material under harsh environment due to its superior physical and chemical properties, including high mechanical strength, excellent chemical stability, outstanding dielectric properties, low thermal expansion, as well as small neutron absorption cross-section [1-8]. In high-temperature nuclear reactors, SiC is employed as one of the four coating layers in the tristructural isotropic (TRISO) coated particles to provide structural strength and dimensional stability in high temperature, high radiation environments. It is also expected that the SiC layer serves as the first containment barrier to withhold the radioactive fission products, especially, atoms such as Cs, Xe, and Ag, from releasing out of the fuel particles. However, it has been reported that at the operation temperature of high temperature gas-cooled reactor (HTGR), Ag atoms, include one of its isotope ($^{110\text{m}}\text{Ag}$), release from intact TRISO particles [9-10]. The half-life of $^{110\text{m}}\text{Ag}$ is 253 days and releases a highly energetic γ upon decay. Deposition of the released $^{110\text{m}}\text{Ag}$ may lead to serious safety issues as well as other practical operational issues within the nuclear plant.

To reduce or prevent the release of Ag from the SiC coating layer in TRISO, it is of crucial importance to develop a fundamental understanding of the diffusion mechanism. A simple Fickian diffusion model, in which the diffusion rate increases with temperature has been investigated [10-12]. However, the predicted diffusion coefficients are not in good agreement with each other, significant difference of several magnitudes still exists. On the other hand, evidence has been proposed that the grain structure is a key issue in Ag diffusion. Petti *et al.* compared Ag release from TRISO particles with different SiC grain size, samples containing small equiaxed grains shows lower diffusion rate than the ones contain larger columnar grains [13]. Khalil *et al.*'s *ab initio* calculation suggests that the Ag diffusion coefficient is $3.7 \times 10^{-18} \text{ m}^2/\text{s}$ in the $\Sigma 3$ grain boundary, compared to $3.9 \times 10^{-29} \text{ m}^2/\text{s}$ in the bulk [14]. In addition, low energy (360 keV) Ag ion implantation experiment performed by Friedland supports a Fickian grain boundary diffusion mechanism [15]. However, it is worth noting that, in Friedland's experimental work, the Ag distribution profile is

only ~100 nm in depth. Employing the ATLAS accelerator facility, Maclean *et al.* performed high-energy implantation to produce Ag profiles buried deeper than 10 μm inside the polycrystalline SiC bulk. After 210 and 480 hours annealing, no Ag migration was observed [16]. It raises the possibility that besides the grain boundary, the out-surface diffusion also plays an important role in the release of Ag at high temperature. Friedland *et al.* [12] and Jiang *et al.* [17] have experimentally observed Ag diffusions toward the surface in both crystalline and amorphous SiC at high temperature, respectively. Recently *ab initio* calculations also suggest that Ag prefers to absorb at the surface, and the mobility of Ag is relatively high on the surface [18].

In the present work, Ag profiles near the surface as well as buried inside the SiC bulk are produced by varying Ag ion energy in combination with energy-degrader foils. Annealing is applied to initiate the migration of Ag atom and simulate the operation condition of HTGR. Before and after annealing, RBS spectra were collected for each sample. Taking advantage of the elastic collisions between the incident ions and target atoms, which provide mass selectivity, RBS is a widely utilized non-destructive technique for determining target composition. Moreover, because of the electronic stopping power, the energy of the detected He ions decreases with increasing depth at which the ion is backscattered, which provides reasonable depth resolution. Through the combination of mass and depth resolution, RBS measurements provide Ag distribution profiles, and any redistribution of the Ag is easily determined from changes in the RBS elemental spectra.

2. Experimental

Single crystal 4H-SiC wafers grown by Cree, Inc. were used in this study. The Ag implantation was performed employing the 3.0 MV electrostatic tandem accelerator facility within Environmental Molecular Sciences Laboratory (EMSL) at the Pacific Northwest National Laboratory (PNNL) [19]. The Ag ion implantation was carried out at a tilt angle of 10° off the surface normal to avoid channeling effects. In order to

compare the near-surface out-diffusion with the diffusion in the bulk, Ag profiles at different depth were produced by implantation utilizing varied ion energies produced by passing the incident ion beam through Al foils with different thickness. (a) The buried Ag profile was produced by 2.0 MeV Ag implantation to an ion fluence of $1.6 \times 10^{16} \text{ cm}^{-2}$ in a bare SiC wafer (sample 1). (b) In order to produce a shallower Ag distribution near the surface (sample 2), a nominal 1.5 μm Al foil was attached in front of the SiC wafer as the energy degrader foil. Implantation with 4.0 MeV Ag^+ to an ion fluence of $2.4 \times 10^{16} \text{ cm}^{-2}$ was carried out with the Al foil. Both implantations were performed at 650 K, which is higher than the critical temperature for amorphization of 4H-SiC (450 K) [20]. After ion implantations, the Al foil was removed, samples were annealed at 1273 K for 48 hours in an Ar atmosphere. Before annealing, the disorder profiles were determined by RBS channeling measurements along the $\langle 0001 \rangle$ direction using a 2.0 MeV He^+ beam and a backscattering angle of 150° . The Ag distribution profiles before annealing were determined from the RBS spectrum at random geometry. After annealing, both RBS and Time-of-Flight secondary ion mass spectrometer (ToF-SIMS) measurements were performed to obtain the distribution of Ag and other elements.

3. Results

Virgin and random RBS spectra of the pre-implanted SiC sample are shown in Fig. 1a. The virgin spectrum refers to the RBS measurement along the $\langle 0001 \rangle$ direction for the pristine single crystal SiC before irradiation, and represents the nominally defect-free level or a level associated with the low concentration of intrinsic defects. The random spectrum, obtained by off-axis rocking of the sample, is equivalent to the backscattering spectrum for fully amorphous SiC. The ratio of the scattering yield between virgin and random spectrum is less than 3%, which suggests the high crystalline quality of the starting crystals. Prior to the measurements of the as-implanted SiC, an energy calibration was performed using Mo, Au and intrinsic SiC samples to determine the linear relation between the channel number and the

energy of the backscattered He ion. The RBS results for sample 1 (bare SiC) and sample 2 (Al foil attached SiC) before annealing are shown in Fig. 1b and 1c in solid lines. Employing the energy calibration result, each peak (or edge) is attributed to certain elements, which are Si, C and Ag respectively. The peaks corresponding to the implanted Ag are shown in details in the insets. It can be seen in sample 2 that the Ag peak shifts to higher channel numbers, indicating that the Ag distribution is relatively close to the surface. On the other hand, the Ag peak of sample 1 is located at a lower channel number and partly overlaps with the silicon edge, which indicates a buried Ag profile is produced.

After annealing at 1273 K in Ar atmosphere, the RBS measurements were performed on both samples under identical experimental conditions. The annealing results are shown in Fig. 1b for sample 1 and (c) for sample 2 as dashed lines, along with the RBS spectrum before annealing (solid lines). A new peak appears at channel number ~ 340 , which is attributed to the oxygen at the surface. According to Fig. 1c, carbon is found depleted at the surface layer after annealing, because the carbon edge shifts to lower channel number in the RBS spectrum. The silicon edge does not shift, and the reduced RBS yield suggests that the atomic concentration of Si decreases. Regarding the appearance of the O peak after annealing, the growth of a SiO₂ thin layer on the surface is indicated. With regard to the Ag distribution, as shown in the inset image of Fig. 1b, after annealing there is no evidence of the migration of Ag, which is buried in the bulk (sample 1). On the contrary, a decrease in the RBS yield is observed for the Ag profile in sample 2 (Fig. 1c), which may be attributed to a decrease in the Ag concentration due to Ag release from the SiC surface. The Ag edge shifts to a lower channel number, similar to the carbon, and the implanted Ag is found depleted in the near-surface region.

From the RBS spectra, the SiO₂/SiC structure, as well as Ag concentration profiles can be determined by utilizing the SIMNRA code [21], and the results are shown in Fig. 2a and 2b, for samples 1 and 2, respectively. The Ag concentration profiles

confirm that during annealing there is no observable migration of the buried Ag, both in sample 1, and for sample 2 beyond 350 nm in depth. On the other hand, as illustrated in Fig. 2b, in the surface region of sample 2, the concentration of Ag decreases after annealing. The reduction of Ag may be attributed to Ag out-diffusion, in which Ag first migrates towards the surface and then desorbs from the sample.

As discussed in the introduction, RBS is a commonly used, non-destructive technique to provide depth distribution profiles for elements. However, the depth resolution and elemental sensitivity of RBS is relatively poor for light elements such as O and C. While the Ag ion fluence reaches 10^{16} cm^{-2} , the scattering yield is still low because of the limited backscattering cross-section for medium mass atoms. In SIMNRA, the concentration of Ag is determined by simulating the target layer by layer with varied thickness and Ag concentration to fit the RBS spectrum. The accuracy of the simulation is, therefore, limited by the resolution and detection efficiency of RBS. In order to better evaluate the Ag diffusion, [SIMS measurements were carried out after annealing to provide elemental profiles with better depth resolution and higher sensitivity](#). Unlike RBS and the SIMNRA simulation, SIMS cannot determine the atomic concentration in units of atom/cm^{-3} or at. % without a reference. In order to obtain the Ag concentration profiles, two assumptions are proposed: First, there is little release of Ag in sample 1, which is supported by the RBS results. If the total amount of the implanted Ag is assumed to be a constant ($1.6 \times 10^{16} \text{ cm}^{-2}$), the conversion of SIMS yield (counts) to Ag concentration can be determined. The second assumption is that the sensitivity of SIMS for Ag remains constant between the measurements for sample 1 and sample 2. As a result, even though the implanted Ag may deposit in the Al foil or be released from sample 2, the Ag concentration can be estimated by comparing the SIMS yield of sample 2 to sample 1. Based on these assumptions, the Ag concentration profiles are determined and overlaid with the RBS results, as presented in Fig. 2.

4. Discussion

The SIMS determined Ag profiles are in good agreement with the RBS results. It is confirmed that the implanted Ag diffuses towards the surface and is released out of sample 2. Inside the SiC bulk, no migration is detected for both samples. As MacLean *et al.* suggested, surface diffusion through a nano-crack may play a crucial role in the release of Ag from a SiC coating layer [16]. The surface diffusion mechanism has also been studied recently by *ab initio* calculations [18]. The calculations were carried out using Density Functional Theory (DFT) within the framework of general gradient approximation, as implemented within the Vienna Ab Initio Simulation Package (VASP) [22]. All calculations were spin-polarized, and the exchange-correlation terms were described using Perdew and Wang (PW91) functional [23-24]. The interaction between ions and electrons was described using the projector augmented wave method [25]. A supercell consisting of six Si layers, six C layers and a vacuum region of 16 Å was used. The dangling bonds of the bottom atoms were saturated by hydrogen atoms. Convergence with respect to a plane-wave cutoff energy of 450 eV and a Monkhorst-Pack *k*-point sampling of 3×3×1 were verified. The fourth surface layer was taken as the bulk-like state and Ag diffusion from the fourth surface layer to the surface state was studied. The diffusion pathway along the direction perpendicular to the surface was fixed and complete structural optimizations were then performed. The energy profiles relative to the surface state for Ag diffusion from the fourth to first slab layer are shown in Fig. 3 (original presented in ref. 18), in which the configuration at the A point represents Ag adsorption on the surface, and B, C, D and E points correspond to Ag adsorbed in the first, second, third and fourth surface layer, respectively. It turns out that Ag diffusion from the fourth layer to surface state is an exothermic process and easily takes place, i.e., Ag migration from the surface state into bulk SiC needs to overcome a huge energy barrier. The energy barrier for Ag desorbing from the surface is determined to be 0.85 eV. It is worth noting that for real materials that experience ion irradiation, defects are produced and accumulated, and the damaged crystals are at a relatively unstable state due to both damage and local ionization. Vacancies and local charge re-distribution may modify the migration barriers and provide easy paths for Ag out-diffusion to occur. Such complexity is

beyond the capacity of the DFT calculation. However, the DFT result provides important indication that firstly, if redistribution of Ag occurs, the net diffusion of Ag is suggested to be from the bulk to the surface. Secondly, in a high temperature environment, the energy barrier may be overcome so that Ag desorption takes place. The loss of Ag from the SiC surface may keep the concentration gradient. As the result, diffusion may continue and eventually create a concentration difference that can be experimentally observed.

Besides the decrease of Ag concentration at the surface region, by taking advantage of its high depth resolution, SIMS provides detailed elemental profiles for Si, C and O. Inspection of the results from sample 2, a sharp interface located at ~55 nm can be clearly observed in the Ag distribution profile, at which the Ag concentration rapidly drops to ~0. An accumulation of Ag at the deeper side of the interface indicates that the Ag diffusion towards the surface is obstructed. According to the SIMS yields, O and C profiles are plotted in Fig. 4 and overlaid with the Ag yield. In Fig. 4a, the depletion of carbon at the surface region confirms the formation and growth of the SiO₂ layer during annealing. For the O concentration, three spots with different irradiation histories were measured by SIMS, including: (a) virgin SiC at which neither ion implantation nor RBS measurements have been performed, (b) sample 1 at which the implanted Ag atoms were buried inside the SiC bulk, and (c) sample 2 with Ag profile at the surface region. For all three spots, SiO₂ layers are formed, but with varying thickness. At spot (a), the thickness of the SiO₂ layer is less than 10 nm, which agrees with the study of Vickridge *et al.* that the oxidization rate of single crystal SiC is relatively low [26]. For sample 1 and sample 2, the incident ions, as well as the recoils, lead to displacements of the target atoms, which result in damage to the crystalline structure. At the surface, the SRIM predicted displacement doses are 9.2 dpa (displacements per atom) and 41 dpa for sample 1, and sample 2, respectively. The displacement energies are 35 eV for Si, and 20 eV for C in the SRIM simulations [27]. While the SiC was not fully amorphized at 650 K according to the RBS channeling measurement, continuing displacement due to further irradiation will

induce more damage to the crystal lattice [20, 28], which may be responsible for the increased thickness of SiO₂ layer because the defects may enhance the diffusion of O. For sample 2, the Ag and O profiles are plotted in Fig. 4b. The interface between the SiO₂ layer and SiC substrate is located at 55-60 nm, and as discussed above, the Ag concentration rapidly drops to ~0 at 55 nm. These results indicate that the SiO₂ film may work as an effective diffusion barrier to obstruct the Ag out-diffusion. The statement is in agreement with insignificant diffusion coefficient for Ag in SiO₂ reported by Nason *et al.* [29].

The idea of using SiO₂ as the barrier to withhold Ag from releasing out of the SiC coating layer is interesting because the thermal oxidation of SiC is relatively economical and easy to achieve. The growth mechanism has been intensively investigated [30-31]. In an effort of further exploring the potential of SiO₂ in reducing Ag release, near-surface implantation should be performed by employing a similar method, as for sample 2, where various ion fluences can be used in implantation to obtain Ag profiles from shallow to deep. Annealing at higher temperatures with longer time may be carried out to further confirm if the Ag diffusion can be stopped by the SiO₂ layer under extreme condition over a long time. The formed SiO₂ and the SiC lattice can be studied by high resolution TEM to determine the nano-scale structures as well as the concentration or distribution of the defects and cracks, and their relation to the Ag diffusion as well as the oxidization.

5. Conclusions

The release of a radioactive Ag isotope from the SiC coating layer in TRISO fuel particle can result in serious safety concerns in the operation of high temperature fission reactors. To investigate the diffusion mechanism, Ag ion implantations were performed to obtain Ag distribution profiles both buried inside the bulk and at the surface region of single crystal 4H-SiC. After implantation, high temperature annealing was carried out. The RBS results before and after annealing suggest that a

SiO₂ layer forms on the surface of SiC. While no migration is observed for the buried Ag, out-diffusion of the Ag in the surface region is evident. The Ag release out of the SiC wafer may be attributed to the relatively low adsorption energy at the surface. The out-diffusion of Ag at the surface is confirmed by the SIMS measurements. According to the SIMS results, there is no Ag concentration in the SiO₂ layer, and Ag diffusion is obstructed by the thin SiO₂ layer, which may serve as an effective barrier to prevent Ag from diffusing out of SiC coating layer.

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Figures and figure captions

Fig. 1. RBS spectrum of (a) virgin and random spectrum of the single crystal 4H-SiC wafer used in this study, and (b) sample 1 (c) sample 2 before (solid line) and after (dash line) annealing. Edges corresponding to Ag, Si, C and O are indicated.

Fig. 2. Ag distribution profiles (in atomic percentage) determined from the RBS (squares for before and tritangles for after annealing) and SIMS (solid line, after annealing) measurement results of (a) sample 1 and (b) sample 2.

Fig. 3. Adsorption energy of Ag at the surface (A), 1st to 4th layer (B-E) and at the free state (F). High energy barrier exists for Ag to diffuse into the bulk SiC, and an energy barrier of 0.85 eV is needed to overcome for the Ag at the surface to desorb from the SiC sample. [The original plot was presented in ref.18.](#)

Fig. 4. SIMS determined (a) O yield of the virgin spot, sample 1 and sample 2, and C yield of sample 2. (b) O and Ag yields of sample 2, the abrupt decrease of O and increase of Ag yields are detected at an interface locates at 55-60 nm.