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Morphological study of borosilicate glass surface irradiated by heavy ions☆

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ABSTRACT

Borosilicate glass is a candidate material for radiation waste formation and other optical applications in various fields. To understand the radiation effect of borosilicate glass, heavy ion (Ar^{q+}, Kr^{q+} and Xe^{q+}) irradiations were used to simulate the alpha and recoiled nuclei irradiations in this study. The surface morphology of glass has been compared to ion irradiation doses and ion energies. The surface topography evolution of irradiated samples is characterized by optical microscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM) and secondary ion mass spectrometry (SIMS). Micro-bumps are observed on the sample surface after irradiation with 5 MeV Xe^{q+} over 5×10^{13} ions·cm^{-2}. The size and density of the bumps increases with increasing irradiation dose. At a low dose, bumps are on the nanometer (nm) scale and rather rare. While the dose is higher than 9×10^{15} ions·cm^{-2}, the size of bumps is on the scale of a few microns, and the density is saturated. However, the height of the bumps increases from a few nm to over 150 nm with further irradiation. The distribution of micro-bumps is nearly homogeneous. The bumps are condensed and swell up, and there is no crystallized structure according to the TEM diffraction pattern. Element migration and concentrations are observed with SIMS imaging. The arrayed micro-bumps are a new finding, and they might be used to change the surface properties. Bump formation is caused by phase separation, and volume swelling is induced by ion irradiation.

1. Introduction

Geological disposal is one of the final solutions for high-level nuclear waste (HLW) treatment. HLW is usually in the liquid phase and needs to be transitioned into a solid state [1]. The most important requirement for making high-level waste appropriate for disposal in a geological repository is the structural durability [1]. Borosilicate glass is a candidate material for immobilizing HLW due to its good chemical stability and high resistance to radiation. Irradiation is a key parameter; not only is it the main cause of atomic displacement in glass structures under disposal conditions, but the radiolysis processes generated by the field in the aqueous solution could also affect the leaching behavior in nuclear glass [2]. Because of the minor actinides (Np, Am and Cm) contained in the glass, alpha decay, beta decay, gamma decay, recoil nucleus and fission fragments can affect the glass properties. Radiation particles, such as alpha, recoil nucleus and fission fragments, contribute the most to the radiation damage in the glass. Normally, accelerator ion irradiation of material is used to simulate heavy particle damage and to evaluate the structural durability of material. However, ion irradiation only induces a radiation effect on a surface or near-surface region. Thus, the morphological study of an ion-irradiated surface is essential to evaluating the structural durability of glass with HLW. Some studies on surface topography and phase separation have been performed. G. Battaglin et al. used 42.5 keV Ar ion to irradiate silicate glass, simulating the effect of heavy ion, and they observed bumps that consisted of argon accumulation [3]. X.D. Chen studied alkali silicate and Na-borosilicate glasses, which were implanted *in situ* with 50 keV Xe ions, and reported on a possible mechanism for bubble formation [4]. O. Gedeon et al. studied the morphology evolution with an increasing electron irradiation dose [5]. K. Jurek et al. studied the evolution of a borosilicate glass surface and compositional changes with electron irradiation, and they observed two distinct bumps as well as alkali ion migration [6]. However, few studies on the surface morphology of MeV-ion-irradiated borosilicate glass have been performed. Although this morphology is an important aspect of irradiation effects for borosilicate glass, many

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studies have instead concentrated on the electron and low energy heavy ions. Because the sample surface area is required to determine the leach rate, it is important to determine whether the surface morphology reflects the surface variation of the glass samples that are treated with heavy ion irradiation. To study the effects of high energy heavy ion, we used 5 MeV Xe ions and 2 MeV Ar ions to irradiate borosilicate glass in this study. AFM, SIMS and TEM were used to study the evolution of the microstructure and composition as a function of heavy ion irradiation.

2. Experiment

Borosilicate glass samples that were 1 mm × 10 mm × 10 mm were used in this study. The borosilicate glass compositions are as follows: 70 ± 5 wt% SiO_2, 17 ± 3 wt% Na_2O, 5 ± 1 wt% Al_2O_3, 4 ± 1 wt% B_2O_3, and 4 ± 1 wt% CeO_2. After ultrasonic cleaning in de-ionized water for 10 min followed by air-drying, the glass samples were mounted on a quadrangular prism target holder and irradiated with 5 MeV Xe^{23+} ions and 2 MeV Ar^{16+} ions, which were generated using a 320 kV electron cyclotron resonance (ECR) ion source in the National Laboratory of Heavy Ion Accelerator, Lanzhou. Ion beams with X and Y two-dimensional scanning were used to homogeneously irradiate the samples. The irradiation field was extended to 18 mm × 18 mm. The ion flux was approximately 6.0×10^{11} $cm^{-2}\cdot s^{-1}$, and five fluences, which ranged from 5.0×10^{13} to 2.0×10^{16} ions·cm^{-2}, were applied to the glass samples. The penetration range of 5.0 MeV Xe ions in this borosilicate glass is approximately 2.0 μm, which was calculated using the SRIM 2008 code [7].

The surface topography of the glass was examined using atomic force microscopy (AFM, MFP-3D-SA, Asylum Research) in tapping mode. The sensitivity of tip deviation and scanner resolution is smaller than 0.1 nm. The images and roughness parameters of the surface were analyzed using IGOR PRO 6.04A software. The mean roughness (*MR*) is the arithmetic average of the absolute values of the surface height deviations measured from the mean plane: $MR = \frac{1}{n}\sum_{i=1}^{n}|Z_i|$.

The element distribution was measured using a TOF-SIMS5 spectrometer (IONTOF GmbH, Münster, Germany) in the Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory. An O^{2+} beam with kinetic energy of 1.0 keV was used as a sputter beam, which was scanned on a 300 × 300 μm^2 area to remove surface contamination before data collection. A 25.0 keV Bi^+ beam was used as an analysis beam for data collection, which was scanned on a 60 × 60 μm^2 or 30 × 30 μm^2 area at the center of the O^{2+} sputter crater. The lateral resolution was approximately 300 nm. Transmission electron microscopy (JEM-2010 TEM) was used to study the bump cross section. TEM samples were polished to less than 10 μm at first; then, they were milled to an electron transparent thickness using the ion milling system.

3. Results and discussion

3.1. AFM images

Fig. 1(a) shows the plane surface morphology of the pristine borosilicate glass obtained from the AFM measurements. Fig. 1(b)–(f) show the plane surface morphology variations with increasing Xe ion irradiation fluence. Fig. 2(a)–(f) show the 3D surface morphology of the pristine borosilicate glass and Xe-ion-irradiated glass; the *MR* of the pristine glass surface is approximately 0.9 nm. Fig. 1(g)–(i) show the plane surface topography of the Ar-ion-irradiated glass. Fig. 2(g)–(i) show the 3D morphology of the Ar-ion-irradiated glass. Compared with pristine glass, there are several small bumps on the Xe-ion-irradiated borosilicate glass in Fig. 2(b) and (c), indicating that some small bumps were formed after irradiation. However, there were no radical variations for the surface morphology up to these two fluences. Their *MR* are 1.7 nm and 1.8 nm. When the Xe-ion-irradiated fluence reaches 4.0×10^{15} ions·cm^{-2}, as shown in Fig. 2(d), the surface morphology changes significantly. Numerous small and several large bumps can be found on the sample surface. The large bumps are scattered throughout the glass sample surface, and the base diameters of the well-defined micro-bumps are approximately 1–6 μm. The *MR* of this sample increases to 15.9 nm, and irradiation induced almost one order of magnitude change for the glass surface roughness. In addition, the bumps in Fig. 2(d) have different sizes. The smaller bumps were formed first, then, the smaller bumps were transformed into larger bumps during ion irradiation. The different sizes indicate the formation process of the bumps. Therefore, the fluence between 3.0×10^{15} and 5.0×10^{15} ions·cm^{-2} might be the critical fluence for achieving significant changes in this borosilicate glass. The large bumps distribute homogenously on the surface of the irradiated glass while the irradiation fluence exceeds 9.0×10^{15} ions·cm^{-2}, as shown in Fig. 2(e) and (f). However, compared with Fig. 2(e) (9.0×10^{15} ions·cm^{-2}), there are two bigger bumps in Fig. 2(f) (2.0×10^{16} ions·cm^{-2}). It should be noted that the base diameter of two large bumps is approximately 10 μm, which is much larger than for other bumps. Also, the height of these two bumps is much higher than the others. For these two fluences (9.0×10^{15} ions·cm^{-2} and 2.0×10^{16} ions·cm^{-2}), the *MR* are 39.9 nm and 52.6 nm, respectively. However, for Ar-ion-irradiated borosilicate glass, there are several small bumps on the sample observed in Fig. 2(h) and (i), while the fluences reach 7.7×10^{15} ions·cm^{-2} and 1.67×10^{16} ions·cm^{-2}. The *MR* of these two samples are 1.5 nm and 11.2 nm, respectively. The number of bumps and *MR* of the Ar-ion-irradiated borosilicate glass are smaller than those of the Xe-ion-irradiated borosilicate glass.

The evolutions of *MR* for the pristine and irradiated samples are plotted in Fig. 3. The *MR* of Xe-ion-irradiated glass is shown in Fig. 3(a), and the *MR* of Ar-ion-irradiated glass is shown in Fig. 3(b). For borosilicate glass, the *MR* barely changes, while the fluence is less than 10^{15} ions·cm^{-2}, then, it increases steeply while the fluence exceeds this point. Compared with the *MR* of pristine glass, the *MR* of Xe-ion-irradiated glass is increased by approximately 55 times for the maximum fluence. However, the *MR* of Ar-ion-irradiated glass is increased by approximately 11 times for the maximum fluence in this study.

3.2. SIMS results

To investigate the relationship between the chemical structure and surface morphology evolution, secondary ion mass spectrometry (SIMS) was used to characterize the surface morphology evolution. The SIMS results for the pristine and irradiated borosilicate glass are shown in Fig. 4. Compared with the element mapping of pristine samples, the distribution of elements on the glass surface significantly changed with Xe ion irradiation. The relative sodium content increased in the bumps, as shown in Fig. 4 (a) and (b), while the relative aluminum and silicon contents reduced in the bumps, as shown in Fig. 4(c) and (d) and Fig. 4(e) and (f), respectively. There was no observed significant change in the oxygen content, as shown in Fig. 4(g) and (h). The results demonstrate that phase separation was induced by Xe ion irradiation.

3.3. TEM results

TEM images of irradiated borosilicate glass at 9.0×10^{15} ions·cm^{-2} are shown in Fig. 5. The white rectangular frame was a bump on the sample surface. As shown in Fig. 5, the base diameter of the bumps on the top surface is approximately 4 μm, which is consistent with the AFM result in Fig. 2(e). No crystalline phase or bubbles could be found in the bump area (see the electron diffraction pattern image in the upper right corner of Fig. 5(a)).

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