FINAL REPORT
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Characterization of Helium Bubble Formation and Microcracking in Borosilicate Glass
Using Small-Angle Scattering Techniques

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1. Introduction

Work performed under NEER sponsorship at UIUC included two primary activities, small-angle x-ray scattering measurements and molecular dynamics simulations. The first activity is currently the Ph.D. project of one UIUC student, Alexander Terekhov, while the second activity encompassed the M.S. thesis work of another UIUC student, Maria Okuniewski. Significant results from both research activities are presented in this report.

2. Small-angle x-ray scattering of He bubbles in borosilicate glass

Small-angle x-ray scattering measurements were performed to study He bubble formation in borosilicate glass. Helium is very insoluble in solids, a consequence of the closed s1 electron orbital and associated lack of a significant electronic interaction required for interatomic bonding. The radioactive decay of actinides occurs predominately by alpha particle emission, a process that leads to He introduction in waste storage media. The other consequence of the decay process is bombardment of the matrix by heavy-ion recoils.

Small angle scattering is the result of constructive interference of the scattered radiation over an angular range from approximately 0.005 to 1 degrees. This technique is sensitive to structural heterogeneities that exist over length scales from approximately 10 to 1000 Å. The effect of He implantation, specifically the formation of He bubbles as a function of dose, was investigated with SAXS. Helium was implanted over an energy range of 1.5 to 2 MeV to give a uniform depth distribution over a few thousands of Angstroms. The samples were 100 micron thick borosilicate glass supplied by Dow Corning. Two sets of samples were prepared and measured in June of 2002 and August of 2004. The SAXS data were acquired at the Advanced Photon Source using the BESSRC 12-ID beam line. The energy of the incident x-ray beam was approximately 9.6 keV, corresponding to a wavelength of 1.3 Å.

The net SAXS responses from samples with different He implantation doses are shown in Figure 1. The background scattering from a zero-dose glass sample was subtracted to give the net response. The data in Fig. 1 indicate the on-set of significant SAXS response above a dose of approximately 1×10^{15} He/cm². This dose corresponds to a local He concentration of 400 atomic parts per million (appm). Doses were

determined by a direct measurement of the incident beam current over the course of the implantation. The local He concentration is a calculated quantity determined using measured dose, the half-width of the implanted He depth profile obtained from a TRIM simulation [1], and the atomic number density of the glass (approximately 8.3×10^{22} atoms/cm³). The 400 appm level does not represent the solubility limit of implanted He since a net SAXS response was observed for doses greater than approximately 1×10^{14} He/cm². This is clear in Fig. 2, the SAXS response from the low-concentration samples in Figure 1. Thus, the He solubility limit with respect to bubble formation in borosilicate glass is at or slightly above 40 appm.

The SAXS response from the He bubbles can be modeled with the single particle form factor for a sphere averaged over a distribution of sphere radii. This model also must include inter-particle interference via the structure factor. The Percus-Yevick hard sphere interaction potential [2] combined with the Schulz particle size distribution function [3] was used for the fitting model. Fits to the SAXS data for selected doses are shown in Figure 3. The fitting parameters are the mean sphere radius of the distribution, the distribution width, and the volume fraction of the spherical heterogeneity (the He bubbles in this case). The dependence of the mean radius and volume fraction versus implantation dose are shown in Figure 4. Two sets of data are shown, one from a series of samples measured in 2002 and different series of samples measured in 2004. Both sample sets track together, demonstrating reasonable reproducibility. The clearest trend in these data is the systematic increase in volume fraction with dose. A less obvious trend is the increase in bubble radius with dose, at least for doses above approximately 2×10^{15} cm⁻².

The effect of annealing on He bubble formation was also investigated. Two sets of samples with doses of 9.4×10^{14} cm⁻² and 9.4×10^{15} cm⁻² were annealed for two hours at 373, 473, and 573 K. The mean radius and volume fraction values determined from the fits to these data are shown in Figure 5. Annealing evidently induces further He bubble precipitation since higher volume fraction values are found. The mean radius appears to decrease with annealing; an observation that is somewhat counterintuitive and requires further study.

Figure 1. SAXS response given by the intensity versus Q ($Q=4\pi/\lambda \sin\theta/2$, where λ is the wavelength and θ is the scattering angle) from a series of He implanted borosilicate glass samples. The implantation dose varies systematically from 9.4×10^{13} (lowest curve) to $2.8 \times 10^{16} \text{ cm}^{-2}$. The corresponding local He concentration varies from 40 to 11200 appm. The on-set of significant scattering is marked by the thick line.

Figure 2. SAXS response from the low concentration samples shown in Figure 1. The He implantation dose varies systematically from 9.4×10^{13} to $2.3 \times 10^{15} \text{ cm}^{-2}$ in this figure. The corresponding local He concentration varies from 40 to 1000 appm. The two dose levels discussed in the text are identified by the thick lines.

Figure 3. Fits to selected SAXS curves from Fig. 1 using the Percus-Yevick hard sphere potential and Schulz distribution. The fits yield the mean radius of the distribution and the volume fraction of the He bubbles.

Figure 4. Mean radius and volume fraction determined from fits to the SAXS response versus He dose. The two data sets correspond to 2002 (dotted lines) and 2004 (solid lines) measurements. A different set of samples were used in each set.

Figure 5. Mean radius and volume fraction determined from fits to the SAXS response versus annealing temperature for two He implantation doses. The data indicate a trend of increasing volume fraction with annealing but are inconclusive with regard to the mean radius dependence on annealing temperature.

Helium bubble stability during heavy ion bombardment was studied with molecular dynamics simulations and is presented in the next section. These simulations demonstrate that bubbles are stable with respect to heavy ion bombardment. A series of SAXS measurements were also performed to investigate bubble stability under heavy ion bombardment. This required both He implantation and overlapping heavy ion bombardment. However, the range of heavy ions is much less than the range of helium. The He implantation energy was therefore reduced to 5 keV to allow the heavy ions (Kr at 2 MeV) to deposit displacement energy at the depth of the implanted He. Three sets of samples were prepared, two sets with a combination of He implantation and Kr bombardment (one set each for two different Kr doses) and a third set with just Kr bombardment. The third set represents the background scattering from Kr implantation only. The two Kr bombardment doses investigated were 4.1×10^{15} and 4.1×10^{14} ions/cm².

The effect of Kr bombardment (high dose) is shown in Fig. 6 for a He implantation dose of 2.8×10^{16} ions/cm². These data demonstrate a synergistic effect from the Kr bombardment; the scattering response from the He-only sample is much lower than the residual scattering from the sample with both He implantation and Kr bombardment after subtraction. We suspect that Kr bombardment either brings out He trapped in solution or shifts the He bubble distribution to smaller sizes, thereby increasing the scattering response at high Q . This synergistic effect is a function of He dose. This is shown in Fig. 7, the net or residual scattering responses for samples with different He

implantation doses. The synergistic effect is largely absent below a He dose of 1×10^{15} ions/cm².

The effect of low Kr dose is shown in Fig. 8, again for a He dose of 2.8×10^{16} ions/cm². Here the synergistic effect is small, even for the largest He dose investigated. The residual or net scattering responses for all samples with the low Kr dose level are shown in Figure 9 and demonstrate that the effect is absent for all He doses. Thus, the synergistic effect requires both high He implantation dose and high Kr bombardment dose. Of course, this is exactly what would be expected of a synergistic effect. Further SAXS and molecular dynamics studies are planned to identify the source of this effect.

Figure 6. Intensity versus Q for 5 keV He implantation (dose= 2.8×10^{16} ions/cm²) plus 2 MeV Kr bombardment (dose= 4.1×10^{15} ions/cm²) sample (upper thick solid line) together with the sample irradiated with 5 keV He only (lower thick solid line). The net scattering response (Kr-only background scattering and He-only scattering subtracted) is shown as the thin solid line.

Figure 7. Net scattering response for 5 keV He implantation samples with Kr- and He-only scattering subtracted. The two highest He implantation doses (2.8×10^{16} and 1.4×10^{16} ions/cm²) show the most significant synergistic effect.

Figure 8. Intensity versus Q for 5 keV He implantation (dose= 2.8×10^{16} ions/cm²) plus 2 MeV Kr bombardment (dose= 4.1×10^{14} ions/cm²) sample (upper thick solid line) together with the sample irradiated with 5 keV He only (lower thick solid line). The net scattering response (Kr-only background scattering and He-only scattering subtracted) is shown as the thin solid line.

Figure 9. Net scattering response for 5 keV He implantation samples with Kr- and He-only scattering subtracted. Very little, if any, synergistic effect is observed for the low Kr dose bombardment.

3. MD simulations of void and He bubble stability. Molecular dynamics simulations are ideally suited for atomic-level investigations of displacement cascade damage. This is because the time scales of the damage events (sub-picosecond) are easily within the temporal resolution of MD. The disadvantage with MD simulations is that the duration of a given simulation is limited to of order 100 picoseconds. Another limitation is the total number of atoms in the simulation cell. Both the duration of a simulation and the number of atoms in the simulation cell are constrained by the cpu clock speed and total cpu time available. MD simulations of He and void stability were performed recently under NEER sponsorship. The parallel MD code PARCAS [4] was used in for this study. The results described below comprised an MS thesis for a student (Maria Okuniewski) in the Nuclear, Plasma, and Radiological Engineering Department at UIUC and have recently been published [5].

The simulation cell used for the MD simulation consisted of 50,000 atoms of amorphous Si (a-Si). Amorphous Si was chosen as a model system for nuclear waste glass for two reasons. First, a well-established melt-quench procedure exists for the creation of an amorphous simulation cell. Second, the Stillinger-Weber interatomic interaction potential is known to reproduce critical properties of a-Si [5]. Helium bubbles with a 20 Å diameter were introduced into the a-Si via MD by the following procedure. First an fcc lattice of He with the Lennard-Jones potential was heated to 500 K and then rapidly cooled to quench in the gas phase. The gas pressure was set with a constant-pressure boundary condition during a relaxation MD run of the He simulation cell. A 20

Å diameter spherical region of this cell was then extracted and placed into a 20 Å void in the a-Si cell to create a He bubble at the desired internal pressure.

The He bubble volume versus simulation event number (one displacement cascade per simulation event) is shown in Fig. 10 for different internal gas pressures under 2 keV Xe bombardment. These data are a measure of the bubble stability since stable bubbles maintain volume. The data in Fig. 10 indicate that bubbles with pressures greater than 0.01 kbar are stable with respect to collapse under heavy ion bombardment. The bubble collapse mechanism identified in the MD simulations was not a ballistic effect where He atoms are ejected from the bubble. Rather it was convective flow into the bubble/void; convective flow induced by local melting of the a-Si associated with the displacement cascade [5]. The internal He pressure acted to inhibit this flow, at least for pressures greater than 0.01 kbar.

These data demonstrate that He bubbles, once formed, will be stable with respect to heavy ion bombardment. One limitation of the MD simulations was the incident ion energy. The heavy-ion recoils from alpha decay have higher energies, in the range of a few hundred keV. However, the higher recoil energy is not expected to influence the stability. The 2 keV events completely engulfed the 20 Å-diameter He bubbles; greater incident ion energy will only result in a larger displacement cascade, not greater damage energy density. The characteristic He bubble radii determined from the SAXS measurements (Fig. 4) are of order 10 Å. The MD simulation therefore represents the conditions expected during the bombardment of He bubbles by actinide recoils.

Although void stability is not necessarily an issue in waste storage media, it was a natural extension of an investigation of He bubble stability. The void volume versus simulation event number is shown in Fig. 11 for different incident Xe ion energy. Voids are unstable with respect to collapse for all incident energies simulated. The void closure rate on a per-dpa basis, $dr/de(d\phi/de)^{-1}$, can be found assuming the a-Si responds as a visco-elastic medium [5]. The corresponding closure rate is given by,

$$\frac{dr}{de} \left(\frac{d\phi}{de} \right)^{-1} = \frac{\gamma}{2\eta\dot{\phi}}. \quad (1)$$

where r is the void radius, e is the event number, γ is the surface energy, η is the viscosity, and $\dot{\phi}$ is the fluence rate in units of ions per second. Note that dr/de is given by the slope of the Fig. 11 data by after conversion from volume to radius. Analysis of the void closure data in Fig. 11 allows the radiation-induced viscosity to be determined, $1/(\eta\dot{\phi}) \sim 2 \times 10^{-8} (\text{Pa dpa})^{-1}$ [5]. This value is significantly higher than the universal value of $3 \times 10^{-9} (\text{Pa dpa})^{-1}$ found for metallic glass and glassy SiO_2 [6].

Figure 10. Helium bubble volume for different internal gas pressures versus simulation event number. The zero pressure case, a void, is shown for comparison. The stabilizing effect of internal pressure is seen above 0.01 kbar, where the volume decreases from the initial value (volume associated with the 20Å diameter bubble) and then levels off. The incident particle was a 2 keV Xe ion.

Figure 11. Void volume versus simulation event number for different incident Xe energies. The slope after conversion to dr/de is related to the radiation induced viscosity of the visco-elastic medium. The baseline open volume is the open volume inherent to the a-Si disordered simulation cell.

The visco-elastic flow process represented by Eqn. 1 is actually a stress relaxation mechanism; displacement cascade damage induces a visco-elastic flow that acts to relieve internal stress. An internal *tensile* stress exists when voids are present that is relieved by this flow. Void closure is the natural consequence. *Convective* flow into the void was also observed in the MD simulations at high incident ion energy. This effect increased the effective radiation-induced viscosity determined from the high-energy closure data in Figure 11.

Convective flow into a void is shown in Figure 12. This figure is a series of four snapshots of MD simulations taken during a k 2 keV heavy ion displacement event and demonstrates convective flow of Si atoms. The origin of this flow is local melting of the a-Si in the vicinity of the void. An elongated morphology develops that inhibits further convective flow into the void during uni-directional bombardment, thereby resulting in a stable void [5]. Isotropic bombardment does not lead to an elongated void morphology; voids were therefore found to be unstable with respect to isotropic heavy ion bombardment [5].

Figure 12. Cross sectional views of a 2-keV Xe bombardment event. The four frames correspond to (a) 0.025 ps, (b) 0.5 ps, (c) 2 ps, and (d) 60 ps snapshots. The views shown are cuts through the $y = 0$ plane. The direction of Xe is shown in (a) as traveling from left to right. The white arrows point to Si atoms that have flowed into the void. An elongated morphology evolves with time and is illustrated by the white outlines in the lower right hand corner of each slice. These outlines are traces of the open volume that have been shifted down and over for better illustration. Notice the three smaller vacancy clusters that develop at 0.5 ps and then disappear.

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