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Modeling defect production in silica glass due to energetic recoils using molecular dynamics simulations

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Abstract

Silica is one of the candidate materials for final focusing mirrors in inertial fusion reactors. These materials will be exposed to high irradiation fluxes during operation. Radiation damage results in point defects that can lead to obscuration, that is, degradation of the optical properties of these materials. A basic understanding of defect production and migration in these materials is, however, limited. In this paper we present molecular dynamics simulations of defect production in silica glass due to energetic recoils. We compute the oxygen deficient centers generated during irradiation at energies between 1 and 5 keV and identify the mechanisms for production and recombination at short time scales.

1. Introduction

Fused silica is one of the components considered in fusion reactor designs. In the case of inertial fusion energy, silica is one of the candidate materials for the final optics. In the case of magnetic fusion energy silica, will be used mostly for diagnostics. In both cases this material will be exposed to the effects of radiation, neutrons and ions, generated during normal operation of the plant. It is therefore important to understand the effects of radiation on these materials. There is an experimental evidence of obscuration of the material due to radiation. Both neutron and gamma radiation can produce electronic defects that can act as color centers, absorbing the light and reducing transmission [1,2]. Payne and coworkers have shown that neutron irradiation produces oxygen deficient centers (ODCs) that can be converted into E′ centers after gamma irradiation [2]. They have also observed a significant reduction in the absorption coefficient of irradiated samples through high temperature annealing (>350 °C) [2]. Understanding the mechanisms of production and annealing of these defects is the main goal of this study, in an effort to identify methods for reducing or minimizing the concentration of these defects during radiation, and predict the lifetime of these materials.

2. Approach

We use molecular dynamics simulations to study the defects produced in fused silica by energetic atoms, such as those produced during neutron irradiation. Fused silica is an amorphous system, formed by silicon atoms tetrahedrally bonded to oxygen atoms. The interatomic potential used for our calculations is the one developed by Feuston and Garofalini [3]. This potential was fitted to reproduce the structure factor measured experimentally by neutron diffraction. It includes a screened Coulomb potential, a pair potential, Born–Mayer type and a three-body term, of the same type as the one used by Stillinger and Weber for their interatomic potential for silicon [4]. The simulations were performed using a parallel molecular dynamics code, with system sizes up to two million atoms, on the ASCI Blue SP2 machine and Compaq EV67 clusters at Lawrence Livermore National Laboratory.

The initial fused silica is constructed by a melting and quenching procedure, starting from a beta-cristobalite

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structure. The initial beta-cristobalite is melted to a very high temperature (7000 K) for about 25 ps. Then the temperature is reduced by scaling the velocities of the atoms in incremental steps of 1000 K, from 7000 to 1000 K, relaxing for 25 ps on each step. Finally the temperature is reduced from 1000 to 300 K and again the system is relaxed for another 25 ps. At this point we calculated the structure factor, the bond angle distribution, coordination and ring statistics, which shows good agreement with experimental measurements of fused silica glass, as explained in previous works [5].

Using the starting fused silica glass at 300 K we study the production of defects due to energetic recoils. The energetic recoil is selected close to the center of the box and given a random direction. We have studied recoils of energies 1, 2 and 5 keV.

Due to the amorphous nature of the material studied, identification of point defects is not unique, and therefore a definition of a point defect must be described. For each atom in our cell we calculate the coordination, considering a cut-off of 2.0 Å between first and second nearest neighbors distance (1.6 Å is the bond length in silica glass). In a glass with no defects all silicon atoms will be fourfold coordinated while all oxygen atoms will be twofold coordinated. Wherever a threefold coordinated silicon atom is identified, we consider that there is a site for an ODC. We should point out that these could be both a true ODC, or a stretched Si–O bond. Both types of defects will result in an electronic defect observable experimentally.

The 2.0 Å cut-off length used to identify nearest neighbors lies at the minimum of the radial distribution function $g(r)$ between the first and second peaks. Nevertheless, thermal fluctuations in the amorphous supercell result in the fluctuation in numbers of ascounted ODCs. In order to quantify the stable defect population, final irradiated structures are quenched and defects are re-counted. This effect can be observed in Fig. 1 where along the track of the ion (solid lines) it is clear that ODCs are formed (crosses). Most of these ODCs will be stable for several picoseconds. Far form the cascade some ODCs are also identified, however these change in time, therefore being related to temperature fluctuations. The final number of ODCs quoted in this paper refers to the numbers after quenching the structure, that is, eliminating the temperature fluctuations, and therefore considering only those produced by the energetic recoils.

3. Results

Fig. 1 shows the resulting damage due to a 1 keV recoil atom in silica. The solid lines show the path of the energetic atoms. Red crosses represent the position of ODCs. Fig. 2(a) shows the evolution of the number of

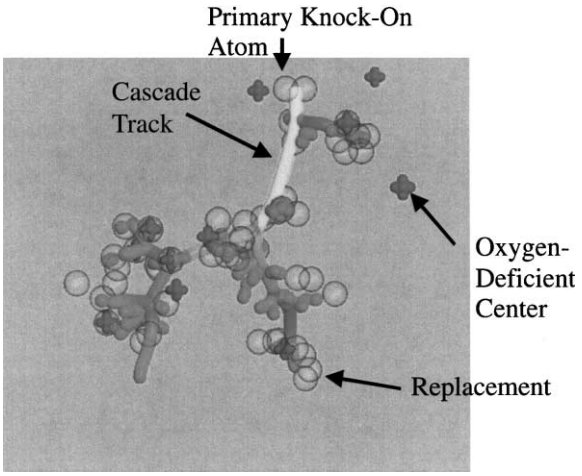

Fig. 1. 1 keV cascade in silica. Red circles represent ODCs. Blue circles are oxygen atoms that have changed from their original positions due to the radiation. Lines show the path of the energetic recoils.

ODCs as a function of time. Note that these defect counts are of structures subject to thermal fluctuations. Hence, they are slightly higher than the final stable defect production values calculated after quenching. Observe that, as seen in other materials, such as metals, there is a first increase of the number of defects produced in the cascade, followed by a recovery stage and a final constant number of defects. In order to understand how this recovery occurs we have followed the position of those oxygen atoms displaced by the energetic atoms. Most of the displaced oxygen atoms find a threefold coordinated silicon close by, restoring the damage and reducing the total number of ODCs, but resulting in a replacement with respect to their original locations. Only a few of the defects remain as ODCs. This is also clear in Fig. 2, where the number of replacements is plotted together with the number of ODCs. Observe the correlation between ODC production and replacements; when the number of ODCs decreases, the number of replacements increases. This is observed at all energies computed, 1 keV (Fig. 2(a)), 2 keV (b) and 5 keV (c). The number of defects reaches a steady-state value after a few picoseconds (below 2.5 ps as shown in Fig. 2). Most of the replacements occur during the first picosecond. The range of these ions is very close to those calculated by a binary collision model such as TRIM [6], 14 nm for 2 keV vs. 16 nm with TRIM, 27 nm for 5 keV vs. 30 nm with TRIM.

The final number of defects produced for each of these energies is: 3, 7 and 19 respectively. We should point out that there is an initial concentration of ODC before irradiation, corresponding to 2.7×10^{18} defects/cm^3. However, this has not been included in the number

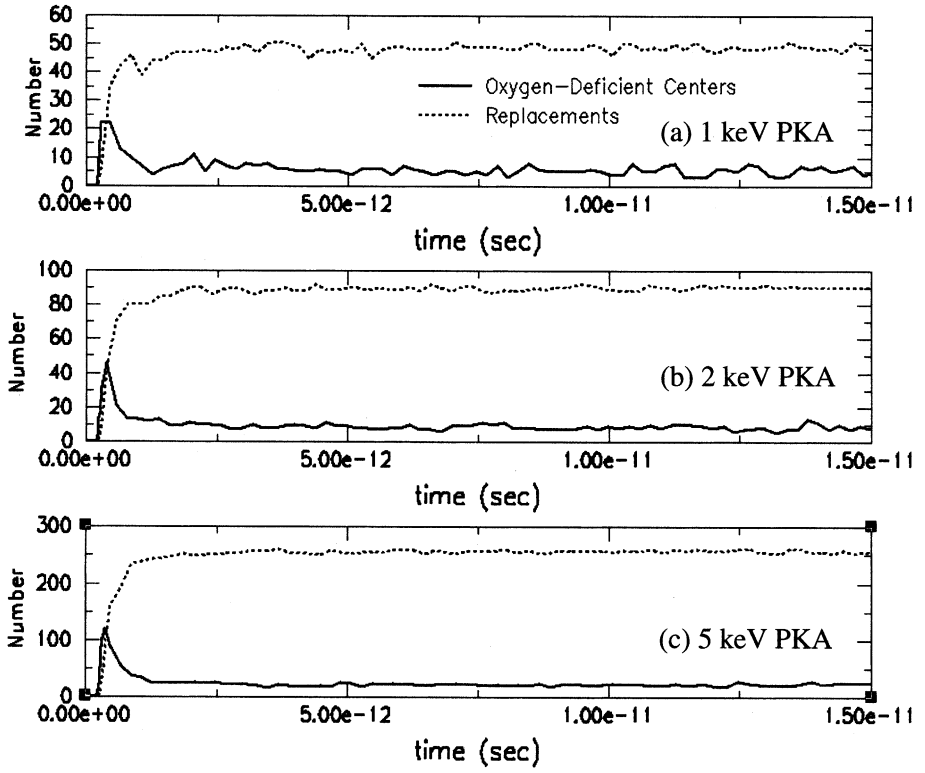

Fig. 2. Time evolution of the number of ODCs produced during the cascade evolution for (a) 1 keV, (b) 2 keV and (c) 5 keV recoils. In the same plot we include the number of replacements (oxygen atoms that end up in a different position than originally).

of defects quoted above, to identify solely those that are produced due to irradiation. Considering a modified Kinchin–Pease type of model [7], $N_D = 0.8E_D/(2E_{th})$, where N_D is the number of defects produced, E_D is the total deposited energy and E_{th} is the threshold displacement energy or minimum energy to produce a defect, we can estimate the value of E_{th}. The value obtained from these calculations is between 105 and 133 eV. Notice that this value is much larger than the threshold displacement energies measured in metals. However, we should point out that only one type of defect is being tracked in these simulations. Other possible defects, such as non-bridging oxygens, will also be produced during irradiation. The threshold displacement energy derived here is the effective threshold displacement energy for production of ODCs. As shown also in Fig. 3(a), in this case for 5 keV, those defects produced by the energetic recoils are clearly identifiable, since they follow the track of the energetic ions. Fig. 3(b) shows the tracks of the displaced atoms during the collision cascade. Dark lines represent the oxygen atoms being displaced while light tracks (not to be confused with the shadowing) are the silicon atoms. It is clear that the collisional cross section is larger for the case of oxygen than for silicon atoms, as expected.

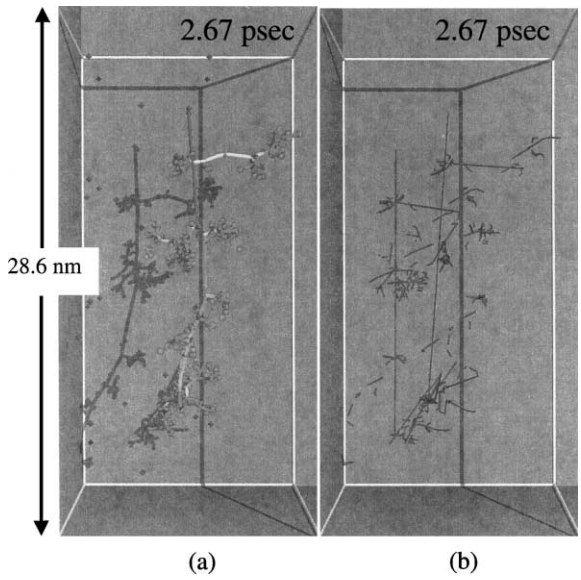

Fig. 3. 5 keV recoil in silica, (a) number of ODCs (black) and replacements (dashed), and track of energetic atoms, (b) dark blue tracks are displaced oxygen atoms and red tracks are displaced silicon atoms.

4. Discussion

We have studied the production of defects in fused silica during irradiation using molecular dynamics. Our simulations show that ODCs are formed in the energies studied (between 1 and 5 keV). From these simulations we estimated a value of ~117 eV for the threshold displacement energy of production of ODCs. Experimental measurements of absorption of silica glass after irradiation at 1 MeV show that the number of ODCs produced is on the order of 188 per neutron. Considering that the deposited energy is 110 keV, the number of defects predicted by our simulations is 376 (using the NRT model and 117 eV threshold energy). The factor of 2 higher values obtained from this model, with respect to those estimated experimentally, can be due to two possible effects: (a) in our model both true ODCs and stretched Si–O bonds are accounted for in the total number of defects and (b) the simulation times are only on the order of picoseconds. Some room temperature recovery can exist for times comparable to the experimental dose rates, which will decrease the total number of defects. It is also possible that the efficiency for defect production decreases at higher recoil energies, as observed in the case of metals. All these possibilities are being explored.

We have also identified a mechanism for recovery of damage produced during irradiation, where large numbers of ODCs are produced at very short times but are annealed out through a replacement mechanism. Only those oxygen atoms displaced long distances from the original positions with produce stable ODCs. The recovery of this damage through annealing at high temperatures (600 K) is currently being studied, as a possible method of restoring the optical properties of the material after irradiation.

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References

[1] R.A.B. Devine, IEEE Trans. Nucl. Sci. 41 (1994) 452.
[2] C.D. Marshall, J.A. Speth, S.A. Payne, J. Non-Cryst. Solids 212 (1997) 59.
[3] B.P. Feuston, S.H. Garofalini, J. Chem. Phys. 89 (1999) 5818.
[4] F.H Stillinger, T.A. Weber, Phys. Rev. B 31 (1985) 5262.
[5] A. Kubota, M.J. Caturla, J.S. Stölken, M.D. Feit, in: Optics Express, vol. 8, Optical Society of America, 2001.
[6] J.F. Ziegler, J.P. Biersack, U. Littmark, in: J.F. Ziegler (Ed.), The Stopping and Range of Ions in Solids, vol. 1, Pergamon, New York, 1985.
[7] M.J. Norgett, M.T. Robinson, I.M. Torrens, Nucl. Eng. Des. 33 (1975) 50.