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Molecular dynamics study of structure transformation and H effects in irradiated silica

F. Mota [a,b,*], M.-J. Caturla [c], J.M. Perlado [b], J. Mollá [a], A. Ibarra [a]

[a] Materiales Para Fusion. Ciemat. Avda Complutense 22, Madrid 28040, Spain
[b] Instituto de Fusion Nuclear, UPM, Madrid, Spain
[c] Universidad de Alicante, Dep. Fisica Aplicada, Alicante, Spain

A B S T R A C T

Fused silica is a key component in a number of diagnostics for the Safety and Control Systems of the ITER machine as well as in the final focusing optics of lasers for inertial fusion and it will be exposed to high radiation fields (neutron and gamma) in both environments. Silica properties of interest are closely related to the presence of defects and its changing structure. On the other hand, some experimental results show that radiation damage depends on its hydrogen content. In this work we present molecular dynamics (MD) simulations to study the effects of displacement cascades on the ring size distribution and on the presence of the hydrogen atoms. Changes in the ring size distribution and variation of the local relative densities have been observed to be a function of the primary knock-on atom energy. And on the other hand, the effects of the hydrogen atoms in the evolution of numbers of defects have been determined.

1. Introduction

Vitreous silica is a material of great importance, both from the point of view of the fundamental physics, due to its use as model structure, and from the point of view of its great variety of technological applications. The electrical, dielectric and optical properties, characteristic of vitreous silica, together with its chemical inertness and thermal stability are the main factors that determine the great versatility of applications of this material. Fused silica is a candidate material for optical and radio-frequency diagnostic systems in magnetic confinement fusion reactors and as final optics in inertial confinement fusion reactors [1–5]. In both cases this material will be exposed to high radiation fields, both neutrons (with energy up to 14 MeV) and gamma rays. Radiation induces optical absorption, creating point defects that can act as colour centers [6]. These defects which determine in last instance the properties of the material may be detected, among other methods, by studying the optical absorption bands or its photoluminescence. At the present time there is abundant information on the different defects and their optical properties [7]. In spite of this, we have to increase the knowledge of them and especially about of their evolution under irradiation.

Molecular dynamics (MD) is a computer simulation technique that allows one to obtain information on the atomic structure of the system and on its physical properties. It has proved to be useful in the description of solid networks as well as the defects produced by irradiation at keV energies in metals and semiconductors [8,9]. However the number of MD studies in oxides and in particular, in amorphous systems, is more reduced. The objective of this work is the study through MD of the lattice structure modification and the defects variation that occur in fused silica produced by radiation.

2. Simulation modelling

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 [10,11]. This potential was fitted to reproduce the structure factor of this amorphous system as determinated experimentally through X-ray diffraction and neutron scattering data.

The different vitreous silica materials studied in this paper were generated starting with the cubic β-cristobalite structure. The initial amorphous structure was generated by melting a beta-cristobalite lattice of SiO_2 (at 7000 K) and subsequently quenching down to 300 K (in step of 1000 K). The whole process takes a simulation time total of 50 ps (in simulations steps of 0.5 fs). This procedure was used previously in similar studies [12,13]. Simulations have been performed using a parallel molecular dynamics code MDCASK [14]. This code has been run in parallel computer SGI Altix 3700 (96 Itanium 2 processors at 1,3 GHz). In these calculations a simulation box with a total of 192000 atoms was used, that occupies a volume of approximately $15 \times 15 \times 15\ nm^3$. Hydrogen

* Corresponding author. Address: Materiales Para Fusion. Ciemat. Avda Complutense 22, Madrid 28040, Spain.
E-mail address: fernando.mota@ciemat.es (F. Mota).

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(1 at.%) was added in order to study the influence of these impurities on the displacement cascades.

Once the initial amorphous structure was constructed and cooled to room temperature (300 K), we identified the defects in the bulk. Periodic boundary conditions were used with a temperature bath control to keep the final temperature at 300 K through scaling the velocities of the atoms close to the border of the simulation box.

In order to verify the structure we calculated the correlation function, the structure factor, the bond angle distribution and the ring size distribution. There is also experimental information on these properties in the literature [10,12,15]. A good agreement between calculations and experimental data was obtained. In fused silica the ring structures are formed by the bonds Si–O and its size is defined by the number of these bonds encountered in the rings. Three samples of rings, 3, 4 and 6 sizes may be observed in Fig. 1. Such structures are usually called medium range order (MRO).

In order to reproduce the neutron irradiation damage we simulated directly an energetic silicon atom that has acquired its kinetic energy by neutron impact, which is the so-called Primary knock-on Atom (PKA). This PKA is chosen in the top of the box to simulate the radiation exposure and the chains of collisions caused by PKA so-called displacement cascades. The radiation damage may change with the energy of the PKA. In this work, range of energies from 400 eV to 3.5 keV was studied. The time step selected to study displacement cascades was 0.1 fs and the total number of steps to each cascade have been 40 000 steps (4 ps). The result for each PKA energy reported in this paper is the statistical result of five simulations.

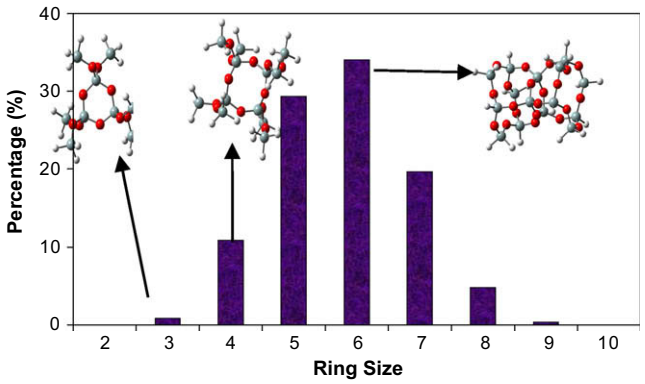

Fig. 1. Fused Silica ring size distribution obtained following the melting of the beta-cristobalite and subsequent quenching down to 300 K. A diagram of the typical ring shape is also shown.

3. Result and conclusion in ring size distribution

The typical amorphous silica ring size distribution can be seen in Fig. 1. The ring size distribution is centered in size 6, in excellent agreement with previously reported MD studies [12,16].

In this work, the change of the ring size distribution under displacement energy is analyzed. The procedure consisted in the calculation of the ring size distribution following the production of the cascade by the energetic PKA. In the last decade, many reports have emphasized the importance of the smaller three and four membered ring. These strained rings have peculiarly exhibited reduced activation barriers to chemical reaction and bond scission [17]. The smaller rings are close to planar and present vibration frequencies that can be detected by Raman spectroscopy. Raman experiments and simulation of compressed and irradiated vitreous silica have shown enhancement of the the D1 and D2 lines associated with rings of size 4 and 3, respectively [18–20].

We have observed that the typical ring size distribution (Fig. 1) changes with increasing PKA energy. In fact, the evolution in the number of rings, shown in Figs. 2 and 3, indicates that the number of the smallest and biggest rings increases with increasing PKA energy. In addition, a comparison between these two figures indicates a partial recovery when the simulation box is subjected to a 300 K annealing process. That is, the number of defects decreases if the system is subjected to an annealing process, as it could be observed in previous work [6,21].

The change of silica structure under pressure has been studied elsewhere [12,22] one of the results being a ring size distribution change as a function of the pressure. In fact, the number of smallest and biggest rings increases with increasing pressure. These results are quite similar to ours. This effect is associated with the increase of the relative density in different areas of the bulk. Thus we can think that the structure silica under irradiation could behave similar form.

One may conclude that both effects occur as a result of the displacement cascades. Indeed, oxygen depleted areas appear along the PKA path, leaving these regions with low relative atomic concentrations, while other regions in the vicinity of the same PKA

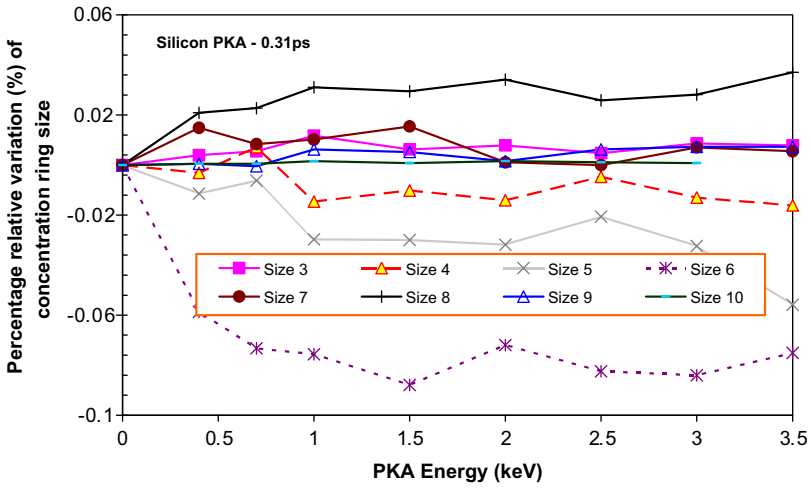

Fig. 2. The Percentage variation of ring for different ring sizes as a function of the PKA energy. Calculations were performed 0.31 ps after the starting of displacement cascades. The total number of rings registered is 384305.

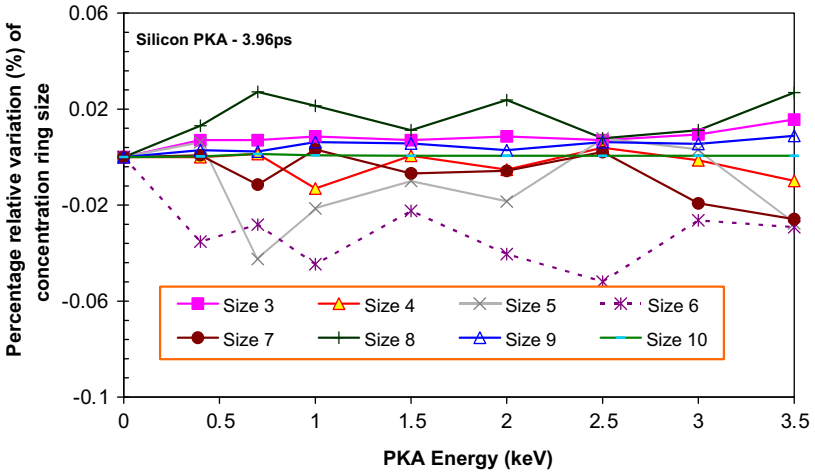

Fig. 3. The percentage variation of ring for different ring sizes as a function of the PKA energy. Calculations were performed following the cascade development and the annealing process (3.96 ps). The total number of rings registered is 384305.

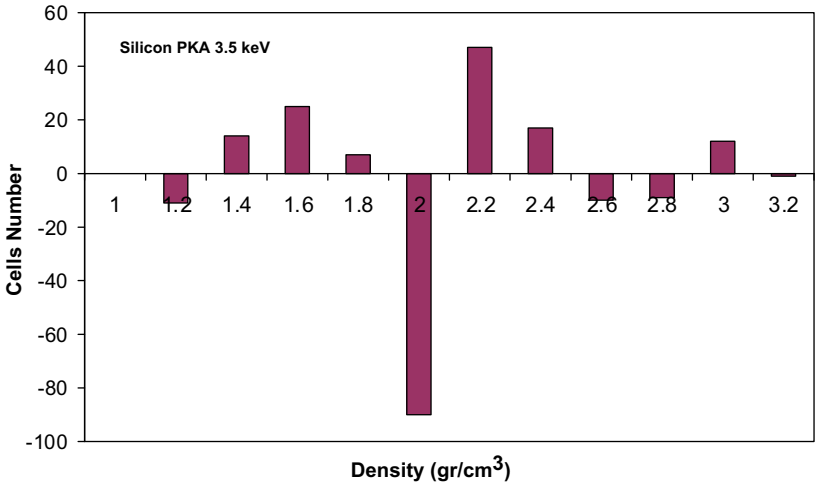

Fig. 4. The number of cells that change their density after the displacement cascade due to a silicon PKA with an initial energy 3.5 keV. The size of each cells is $7.16 \times 7.16 \times 7.16$ Å. The total number of unit cells in whole simulation box is 8000.

path exhibit high concentrations. This happens because it is easier to displace oxygen atoms than silicon atoms.

To prove it we divided the bulk of the simulation box in cells with a size equal to one lattice unit, that is, $7.16 \times 7.16 \times 7.16$ Å^3, and we calculated the relative atoms concentration (relative atoms density) in each one. This has been calculated before and after of the displacement cascades and we have registered the variation between both situations. The number of cells that change their relative atoms density after the displacement cascade due to silicon PKA with an initial energy 3.5 keV is shown in Fig. 4. It is possible to appreciate that the number of cells with density 2 g/cm^3 decrease and the cells with density higher and lower increase, as we wanted to prove.

4. Result and conclusion, defects with H impurities

To analyze the defects in presence of H atoms we generated the simulation box with a 1% of H atoms. These H atoms were implanted randomly into the materials, in those positions that do not coincide with other atoms of the lattice; the annealing process lets H atoms to move to their more stable positions in the bulk of the simulation box. It is possible to see in Fig. 5, the production of defects as a function of the PKA energy. In Fig. 5a we represent the defects without H atoms. The defects can be explained as follows: (1) Si3: Silicon with three oxygens as nearest neighbors; (2) Si5: Silicon with coordination 5: silicon with five oxygens as nearest neighbors; (3) O1: Oxygen with coordination 1: one silicon as nearest neighbor; (4) O3: Oxygen with coordination 3, oxygen with three silicon as nearest neighbors. These defects were already reported in older own work [13,23]. The defects in presence of H atoms, Fig. 5b, are basically of two types, H atoms binding with an oxygen atom with coordination 1 [7,24], that is, the H atom is binding to a O1 defect being H–O–Si or H–O, theirs schema representation. The H–O–Si≡, and O–H are two different form to represent the H atom binding with a oxygen atom. The H–O–Si≡ is determined by the coordination of the oxygen atom while the O–H is determined by the coordination of the H atom, but we must also bear in mind that the oxygen atom could have any coordination. The other possible state is a H atoms without any binding (free H). The free H (H with coordination zero) and H–O=2Si both correspond to free H atoms but H–O=2Si correspond to H atoms when its nearest neighbor is an oxygen (O2) (Si–O–Si).

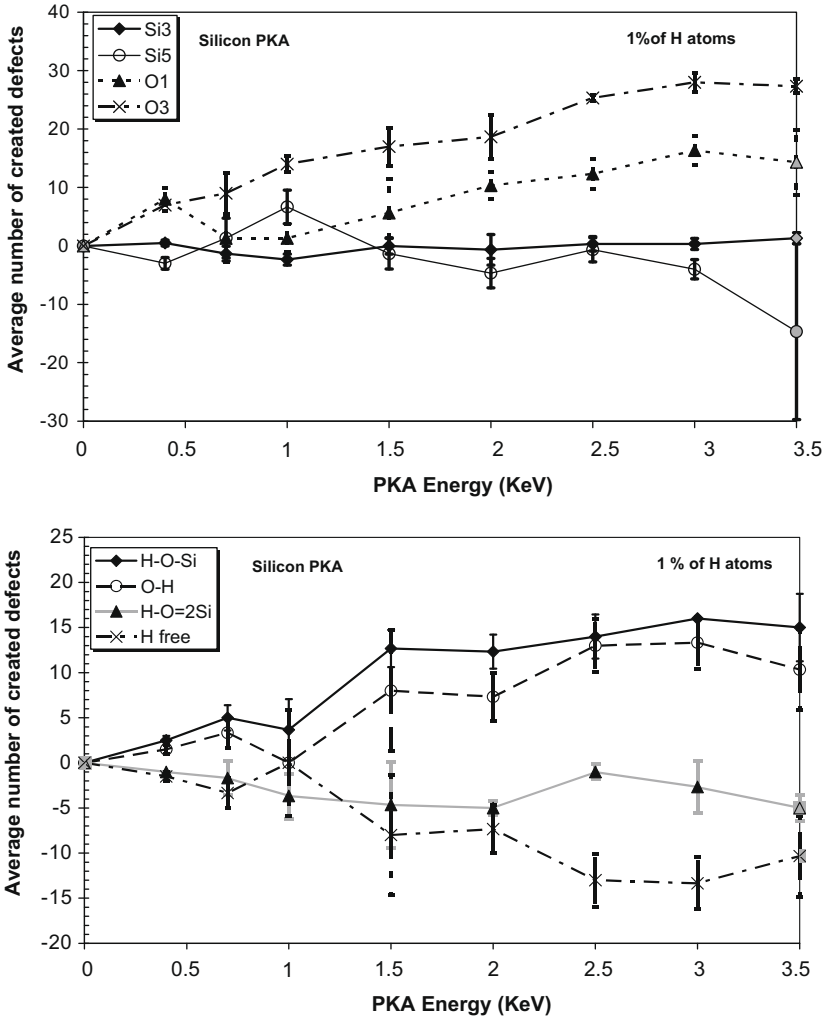

Fig. 5. Average number of defects produced by the PKA as a function of its initial energy, in the simulation box containing 1% at H. (a) Si5, Si3, O3 and O1 defects and (b) H–O–Si, O–H, H–O=2Si H free, that is Hydrogen related defects. As example, the whole damage in the simulation box to PKA initial energy 3.5 keV is 180 atoms displaced (vacancies). In the simulation box the total numbers of atoms is 192 000 atoms.

But it is absolutely clear that in both kind of defects, the number of defects, both without H atoms and with H atoms, increases with increasing PKA energy.

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