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Amorphization of α-quartz and comparative study of defects in amorphized quartz and Si nanocrystals embedded in amorphous silica

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ABSTRACT

Ion irradiation of α-quartz renders the crystal SiO_2 structure amorphous. The enormous amount of structural defects produced after ion irradiation give a chance for photoactive intrinsic defects to be formed. These may be responsible for the photoluminescence in irradiated α-quartz. On the other hand, the radiation defects are not stable, and thus, an alternative structure where the defects of interest can be stabilized is required. The stabilization of the defects can be achieved in the structures of amorphous silica with embedded Si nanocrystals (NC), thanks to the unique structure of the formed interface. By means of Molecular Dynamics (MD), we analyze defects in both amorphized α-quartz and Si-NC/a-SiO_2 interfaces formed by 1.1, 2.4 and 4 nm diameter NC's. In the simulation, we employ a classical interatomic potential and a potential, which takes into consideration a charge transfer between Si and O atoms. We show that although the number of silanone bonds Si=O in irradiated quartz is higher, they are also found in a Si-NC/a-SiO_2 interface without the necessity of preceding irradiation of the sample. We also compare the defects in irradiation-amorphized quartz and the three sizes of Si-NC/a-SiO_2 interfaces. Analysis of the charges showed that the charge state of coordination defects depends on the type of atoms in the near neighborhood.

1. Introduction

Ion beam modification of materials is widely applied to design new properties applicable for optoelectronics. In this respect, the SiO_2 compound as a key part of the modern electronic industry, is the most apparent candidate for tailoring optical responses in Si-based electronics. Significant attention has been paid lately to the possible increase of optical properties of amorphous silica by forming nanoparticles inside of the matrix [1]. Si ions implanted into amorphous SiO_2 clearly separate in a phase into small Si nanocrystal (NC) balls with a diameter depending on temperature of post-implantation annealing [2]. However, the nature of the optical responses observed in these structures is still under debate. Splitting the energy levels in Si quantum dots (nanoparticles) due to the quantum confinement effect can explain the intense photoluminescence spectra with blueshift, see for example [3,4]. In the same time, there is a strong opinion that the origin of luminescence in Si-NC's comes from the interface between Si nanoclusters and amorphous silica, as it is a favorable region to create radiative recombination centers for excitons [5–7]. Although the interface defects form prevalently non-radiative states for excitons, the combination of particular coordination defects can form a so called silanone bond (a double Si=O bond) that introduces the radiative states for excitons inside of the bandgap [7].

Ion irradiation of α-quartz causes amorphization of the crystal structure, rendering the α-quartz into a vitreous silica-like structure. The intrinsic defects that remain in the matrix after the ion irradiation are of particular interest due to the fact [8,9] that some of them have a photoactive nature as well. Although both amorphized α-quartz and vitreous silica with embedded Si-NC's are close in the structure and have similar defects, the different origin of the defects may lead to the certain peculiarity, which must be taken into account while the expected properties of the structures are designed. However, determining the detailed defect structure from experiments is very difficult, and thus atomistic simulations have a crucial role for understanding the origin of Si–O defects.

In the present work we utilize the Molecular Dynamics technique to amorphize the α-quartz, aiming to compare the intrinsic defects in amorphized α-quartz structure without excess of Si

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atoms with defects in pristine amorphous silica after embedding a small Si-NC in it. We also apply a charge-optimized many-body potential to both structures to observe the difference in charge transfer between the atoms involved into formation of the defects of certain type.

2. Methods

2.1. Molecular Dynamics simulation of α-quartz amorphization

By means of classical Molecular Dynamics (MD) code *parcas*, we simulated the process of ion irradiation of perfect α-quartz crystal structure by ^{23}Na ions of 50 keV energy. Although we simulated the ion irradiation process by adding a certain energy to an atom randomly chosen within a computational cell, the added energy was also chosen randomly from the realistic recoil spectrum for a Na^+ ion in an α-quartz. The simulations were started from perfect α-quartz, and every new recoil produced damage over the results from the previous recoil until the full amorphization of the cell was achieved. The details of the simulation method we applied for the α-quartz amorphization can be found elsewhere [10]. In the present work, we considered the amorphization complete at the dose when the radial distribution function of atoms in the amorphized cell approached the shape of the same function in pristine amorphous silica cell, constructed in the same manner as in [11].

In Fig. 1a we compare the radial distribution functions of atoms in the different cells: the α-quartz crystal irradiated with a low dose (D_{irr} = 0.5 eV/atom), the α-quartz when the amorphization is complete (D_{irr} = 6.8 eV/atom), and the pristine amorphous silica. The latter was built applying WWW Monte-Carlo technique with the subsequent relaxation with the Watanabe–Samela potential [11]. All the curves are compared to the similar function measured experimentally in a vitreous silica sample [12]. The radial distribution function of the amorphized α-quartz and the amorphous silica show satisfactory agreement with the experimental function. Interestingly, we find the appearance of the Si–Si nearest neighbor peak around 2.44 Å only in the cell of the amorphized α-quartz, but not in any of the other analyzed cells. Apparently, the irradiation process stimulates the formation of oxygen-free spots inside of the quartz crystal. We have also plotted the Si–O–Si bond angle distributions for the same samples (Fig. 1b). The bond angle distributions of the pristine amorphous silica and the amorphized quartz are very close to each other in shape, but with both peaks, slightly shifted to smaller angles compared to the experiment. However, this small difference does not affect the main conclusions of the present work.

2.2. Atomistic models of Si-NC's embedded in amorphous silica cell

With the goal of elucidating the nature of the defects, which are of identical type but of different origin, we constructed three models of 1.1, 2.4 and 4 nm Si-NC's embedded into the amorphous silica cell and compare these to the irradiation-amorphized quartz. To increase the statistical reliability of the observed results, we constructed 10 Si-NC embedded structures of each size. Every structure was made to differ from the others by shifting the insertion position of the same Si-NC into the same amorphous silica cell, taking into account the periodic boundaries of the cell. The construction procedure is described in details in [11]. During the amorphization process of α-quartz and construction of NC atomistic models, we applied classical interatomic potentials of Stillinger–Weber type for Si–Si interaction and Watanabe–Samela potential [14,15] developed for Si–O mixed systems to describe the interaction between Si and O atoms.

2.3. Dynamic charge equilibration

To complement the study of defects nature, we have also applied the charge-optimized many-body (COMB) potential for Si/SiO_2 and amorphous silica [16], which has been further developed compared to [17]. Both potentials take into account the charge transfer between Si and O atoms in silicon dioxide compounds, while the more recently developed one replaces the point charge model and the electrostatic cut-off function with Coulomb integrals over Slater 1s orbital [18] and by treating the electrostatic interactions using the real-space direct summation of modules.

The dynamic charge equilibration was made to proceed as follows. Since the electrochemical potential, μ_i, for each atom is the change in energy with respect to its electron density, which, in turn, is equal to the electronegativity with a negative sign, then:

$$\mu_i = \frac{\partial E}{\partial \rho} = -\chi_i \tag{1}$$

Following the approach of Rappe and Goddard [19], the energy of a neutral atom as a function of partial charge, q_i, may be expanded to second order as:

$$E(q_i) = E(0) + \chi_i q_i + \frac{1}{2} J_i q_i^2 \tag{2}$$

The first derivative of energy with respect to charge is defined as negative of the electronegativity, χ_i, and the second derivative is often defined as the atomic hardness or the Coulombic self interaction, J_i. Electronegativity and atomic hardness are atomic properties often associate with orbital population and electronic

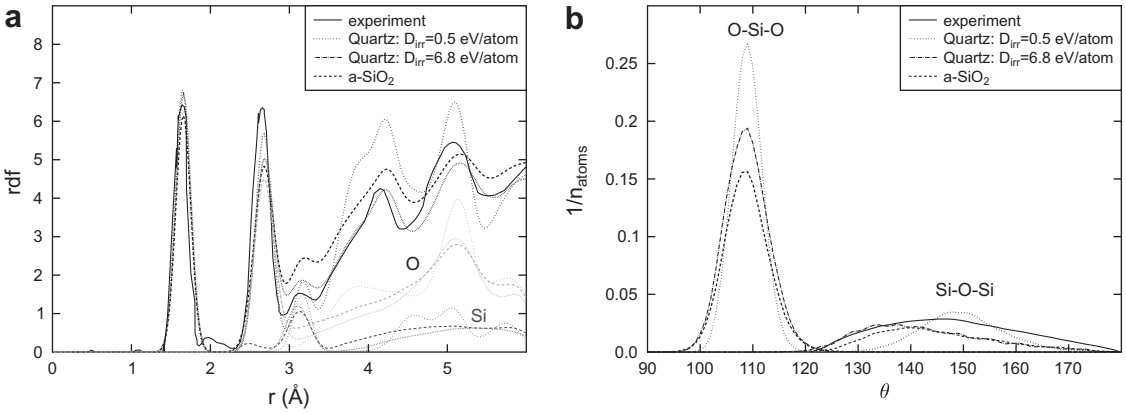

Fig. 1. (a) Radial distribution of atoms and (b) bond angle distributions in the different computational cells compared to the experiment. The experimental results are from Ref. [12] in (a) and from Ref. [13] in (b). The thinner gray lines show Si atoms and light gray lines show O atoms decomposed from the distributions of all atoms in the cells.