Amorphization of $\alpha$-quartz and comparative study of defects in amorphized quartz and Si nanocrystals embedded in amorphous silica

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A B S T R A C T

Ion irradiation of $\alpha$-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 $\alpha$-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 $\alpha$-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.

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 nanocrystals 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 $\alpha$-quartz causes amorphization of the crystal structure, rendering the $\alpha$-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 $\alpha$-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 $\alpha$-quartz, aiming to compare the intrinsic defects in amorphized $\alpha$-quartz structure without excess of Si
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 a-quartz amorphization

By means of classical Molecular Dynamics (MD) code parcas, we simulated the process of ion irradiation of perfect a-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 a-quartz. The simulations were started from perfect a-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 a-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 a-quartz crystal irradiated with a low dose ($D_{irr} = 0.5$ eV/atom), the a-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].

2.2. Atomic models of Si-NCs 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 a-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, $\mu$, 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:

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

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:

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

The first derivative of energy with respect to charge is defined as negative of the electronegativity, $\chi_i$, 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

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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.
polarizability, i.e., Mulliken electronegativity. They were defined in terms of Kohn–Sham theory [20], where $\chi_i$ and $J_i$ are, respectively, the first and second derivative with respect to electron density around each atom.

At equilibrium, the electron density around each atom redistributes in such a way that the chemical potential and, thus, the electronegativity (Eq. (1)), at each site is equal. As the system evolves, the electron density redistributes from sites with low electronegativity to those with a high one, essentially, fluctuating in response to the local environment. If we account for change in the atomic volume, then the variation in electron density corresponds to change in partial charge. The equilibrium partial charges for all atoms are, then, those that satisfy the condition where the electronegativity is equal at all sites provided that the total charge with in the system is constant. With the COMB formalism, the partial derivative of energy with respect to charge is non-linear and thus does not have a unique solution. Instead the partial charges are selected as those that minimized the energy with respect to charge, with the constraint that total charge is conserved.

3. Analysis of defect structures

We have made a quantitative analysis of the coordination defects present in amorphized quartz and in the Si-NC/a-SiO$_2$ interface. In the present analysis, we have made a particular difference in the cut-off parameters for the atoms of different type. Having studied the Fig. 1a and also similar functions for the amorphous silica cells holding the Si-NCs, we defined the cut-off parameters for every atomic pair inside of the analyzed cells. Thus, we chose 1.8 Å for the Si–O pairs, 2.66 Å for the Si–Si pair and 2.45 Å for O–O pair (the latter has been taken as same as the O–O interaction cut-off in the Watanabe–Samela potential [14]). While analyzing all atoms in the cell, atoms of the same type nearby are considered as those that minimized the energy with respect to charge, with the constraint that total charge is conserved.

Table 1 summarizes the results obtained with the Watanabe–Samela and COMB potentials. The results are shown in Table 1, where these structures are marked with an asterisk. After relaxation the radial distribution functions slightly changed the shape, thus we increased the cut-off distance for Si–O pair to 2.2 Å, while the other cut-off parameters were set to 2.45 Å. Even with these cut-off parameters, there is a difference in the observed numbers of the defects. If we account for the presence of NCs and the NC–SiO$_2$ interfaces, assuming that the nature of these defects is photoactive.

Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>Undercoord. %</th>
<th>Overcoord. %</th>
<th>Suboxides %</th>
<th>Silanone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (&lt;4b)</td>
<td>4.85</td>
<td>6.97</td>
<td>1.5</td>
<td>0.32</td>
</tr>
<tr>
<td>O (&lt;2b)</td>
<td>2.66 ± 2.66</td>
<td>5.4 ± 2.4</td>
<td>1.7 ± 0.39</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>Si (&gt;4b)</td>
<td>2.96 ± 0.5</td>
<td>3.86 ± 0.6</td>
<td>2.23 ± 0.4</td>
<td>0.39 ± 0.1</td>
</tr>
<tr>
<td>O (&gt;2b)</td>
<td>7.9 ± 1.2</td>
<td>9.56 ± 0.7</td>
<td>1.16 ± 0.2</td>
<td>9.0 ± 0.5</td>
</tr>
<tr>
<td>Si=O</td>
<td>18.15</td>
<td>5.35</td>
<td>0.24</td>
<td>3.21</td>
</tr>
<tr>
<td>SiO</td>
<td>16.48</td>
<td>1.45</td>
<td>4.68</td>
<td>12.08</td>
</tr>
</tbody>
</table>

Surprisingly, the number of the structural defects does not change significantly with the size of the NC, and switching from the NC to the amorphized but uniform structure of α-quartz. Although the smallest NC (1.1 nm in diameter) has no crystal order after being embedded into an amorphous structure, it does not exhibit the increase of relative number of the defects. On the contrary, the structure grows more flexible to saturate the dangling bonds natural for the free-standing NC. The number of silanone bonds, although much smaller in the absolute value compared to the amorphized α-quartz structure, appears in the investigated interfaces with a certain probability. The stabilization of these bonds due to the presence of a NC gives a good ground for the stable contribution of these bonds into the optical properties of the NC/a-SiO$_2$ interfaces, assuming that the nature of these defects is photoactive.
found to be 2.73e for Si and –1.47e for O. The close presence of extra oxygen atom raises the value of the charge state for Si up to 2.84e and the deficiency of oxygen decreases it to 2.18e (undercoordinated Si atom with 1 Si and 1 O neighbors). Similarly, Si vicinity affects the charge state for O atoms, such that charge can change between –0.73 (1 Si and 1 O neighbors) and –1.7 (3 Si neighbors). In the case of the interface formed by 2.4 nm Si-NC in a-SiO₂, the charge states for the defected atoms can be diminished due to the presence of neutral states within the NC. Here, the charge changes for Si defects between 0.08e (only 2 Si neighbors) and 2.68e (3 O neighbors) and for O defects between –0.09e (more than 2 O neighbors, but 1 Si neighbor) and –1.68e (4 Si neighbors).

4. Conclusions

Using Molecular Dynamics simulations, we analyzed defects in both amorphized α-quartz and Si-NC/a-SiO₂ interfaces formed by 1.1, 2.4 and 4 nm diameter NCs. We employed a classical interatomic potential as well as a potential that takes into consideration a charge transfer between Si and O atoms. We showed that although the number of silanone bonds Si=O in irradiated quartz is higher, they are also found in a Si-NC/a-SiO₂ interface without the necessity of irradiation of the sample. We also compared the defects in irradiation-amorphized quartz and the three sizes of Si-NC/a-SiO₂ interfaces. Analysis of the charges showed that the charge state of coordination defects depends on the type of atoms in the near neighborhood.

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