Simulation of Silica Cluster Overcharging

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The interaction of an e-beam with silica glass has been simulated using the $27SiO_2$ cluster, charged from 0 to -18 by a PM3 semiempirical quantum chemical method. The structures of the charged $27SiO_2$ silica clusters and their physicochemical characteristics, namely the heat of formation, relative volume, electron density of states distribution, gap between HOMO and LUMO and charge distribution, have been derived and analyzed in order to study the processes occurring on the atomic level at an e-beam-irradiated surface. The overcharging of the silica cluster led to its expansion by 30% in volume and evaporation of the charged species, followed by cluster densification. The silica cluster expansion should lead to structural changes in the neighbouring silica glass areas.

Key words: Silica Glass; E-Beam Irradiation; Computer Simulation; EDOS.

1. Introduction

Silica-based glasses have useful optical and electrical properties enabling many scientific and technological applications [1, 2]. It has been demonstrated that low energy electron irradiation of silica glass leads to a network compaction with the formation of nanoscale spots, possessing an increased refractive index and enriched with luminescent centres [2 – 6]. This can be used in important fields of electron beam (e-beam) techniques, such as electron beam lithography (EBL), to produce integrated circuits by direct e-beam writing [4, 5]. Thus changes of the silica network by electron bombardment are of special interest. However the electron-silica interaction mechanism is not clarified. According to physical arguments, the e-beam irradiation of insulators induces an electric field due to the trapping of charges within the interaction volume. During electron irradiation, focused on a selected area of silica glass, a nanoparticle of the insulating material may become positively or negatively charged, depending on the acceleration voltage. Physical continuum models [7 – 9] are not developed to describe the processes which occur at atomic level, and therefore the structure of the e-beam-induced defects can not be explained by these models.

The interaction of the e-beam with the silica glass may be represented as a set of the following processes, which might occur sequentially or simultaneously:

1. Trapping of charges in the interaction volume, which induces an electric field. The electron trapping and emission lead to charging of the surface negatively or positively, correspondingly.
2. Initiation and genesis of structural defects, e. g. low-coordinated atoms (so-called dangling bond sites), nonbridging oxygen atoms, E′-centres and peroxy linkages.
3. Formation of electron-hole pairs. Most of these pairs quickly recombine; a few electrons and holes move, respectively, to the conduction and valence bands before they are trapped in the localized level (which may be interpreted in terms of structural defects).
4. Electron-stimulated desorption of constituents, in particular oxygen, from the surface of electron-irradiated silica (energy $>$ 100 eV), which may contribute to volume reduction.

Thus, a strong correlation between charge trapping and damage (bond breaking) in insulators has been suggested [7 – 9]. It has been predicted that electron

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bombardment produces an electric field that may result in electromigration of mobile charged species. So, after an e-beam exposure, the chemical composition may be affected. Also, the spatial structure of the silica glass is altered due to the interaction with the e-beam.

The experimental data of the e-beam-treated silica glass are the following. It has been shown earlier by studies of an e-beam-irradiated silica glass surface that nanospots occur at the places of the e-beam treatment due to volume reduction [2 – 6]. Raman spectra prove that the structure of the silica glass is changed not at the nanospot but in the adjacent areas. The question is, whether the changes in the atomic structure of silica occur during irradiation or later – at the stage of excessive charge dissipation.

Analysis of the trapping of charges should be a starting point in the study of the interaction of the e-beam with the silica glass. Computer simulation can increase the knowledge about the charge trapping in the insulator, induced by the e-beam. An application of quantum chemical (QC) methods on silica nanoparticles has proved to be effective [10 – 12].

Since the rate of the charge dissipation in the insulator is rather low, we might assume that in a certain period of time the e-beam-treated area of the silica glass is overcharged and preserves the excessive charge. This area is nanosized, so it can be considered in terms of the cluster approach.

Recently, results of a close examination of a QC investigation on changes in an Au nanoparticle spatial structure upon charging have been reported in [13]. However, the methodology proposed there can not be applied directly to the problem of the present paper because of the low symmetry of an amorphous SiO_2 cluster. Therefore one may compare the effect of overcharging on metal and oxide nanoparticles, studied by different models.

In the present work we focused on the examination of an overcharged $27SiO_2$ cluster, performed by QC simulation.

2. Computational Methodology

The $27SiO_2$ cluster described in [10, 11], representing the silica glass nanoparticle, has been used as starting model to simulate the interaction of the e-beam with a local silica area. The $27SiO_2$ cluster used is completely amorphous, characterized by a broad distribution of bond lengths, angles and coordination numbers of atoms [10, 11].

The $27SiO_2$ nanoparticle with charges from 0 to -18 has been simulated by consecutive addition of negative charge with complete QC optimization at each step. The charged $27SiO_2$ clusters QC simulation has been performed by the semiempirical method PM3 [14] with the QuChem program [15].

The PM3 method is an extension of the modified neglect of diatomic overlap (MNDO) semiempirical methods line, particularly of the AM1 method. As all semiempirical methods, the PM3 method is set up with the same general structure as a Hartree-Fock calculation, in that it has a Hamiltonian and a wave function [16 – 20]. The core electrons are not included in the calculation. Their effect is considered in the core function – an empirical parameterized formula. The Löwdin transformation is applied, in order to avoid the time-consuming calculation of three- and four-centre integrals.

The physicochemical characteristics of the charged $27SiO_2$ clusters, namely the heat of formation ($\Delta_f H$), the relative volume (V_R), the electron density of states (EDOS) distribution, the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the charge distribution, have been derived and analyzed.

The change of the cluster volume on the charging of clusters has been estimated by the formula $V_R = V/V_0$, where V_R is the relative volume of a cluster, $V = \left(\frac{1}{n}\sum_i^n\sum_j^n r_{ij}\right)^3$ is the volume of the simulated cluster, V_0 is the volume of the starting $27SiO_2$ cluster (see above), equal to 303.2058 Å^3, r_{ij} is the interatomic distance and n is the number of atoms in the cluster [21].

3. Results and Discussion

Since silica glass is an insulator, a negative electric charge accumulates at its surface upon the e-beam irradiation, slowly dissipating to the neighbouring areas. Therefore one can imagine the changes in the spatial structure of an e-beam-irradiated area of the silica glass as a set of $27SiO_2$ clusters charged differently.

A consecutive addition of a negative charge to the $27SiO_2$ nanoparticle with complete QC optimization (for the Cartesian coordinates please communicate with the authors) at each step leads to an increase of the bond lengths in the $27SiO_2$ nanoparticle. This causes the expansion of the nanoparticle, which can be seen from the growth of the relative volume up to 30% upon addition of the charge -15 (Fig. 1a). Changes

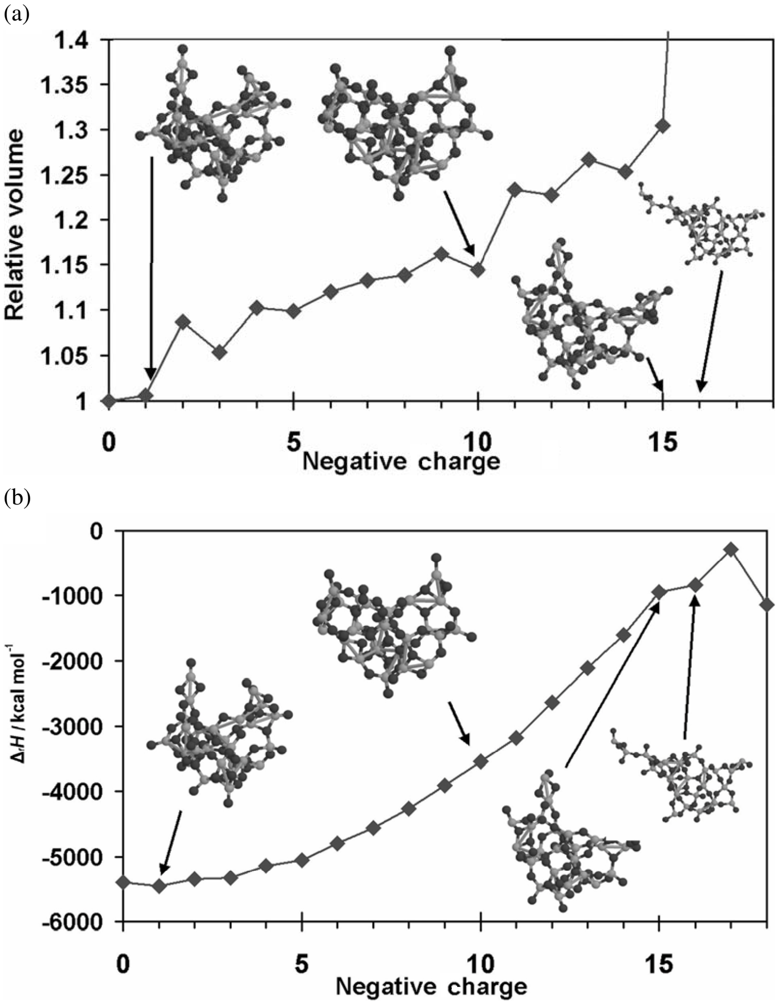

Fig. 1. (a) The relative volume and (b) the heat of formation against the charge of the $27SiO_2$ cluster. The insets demonstrate the corresponding QC-optimized spatial structures of the clusters (black, O atoms; grey, Si atoms).

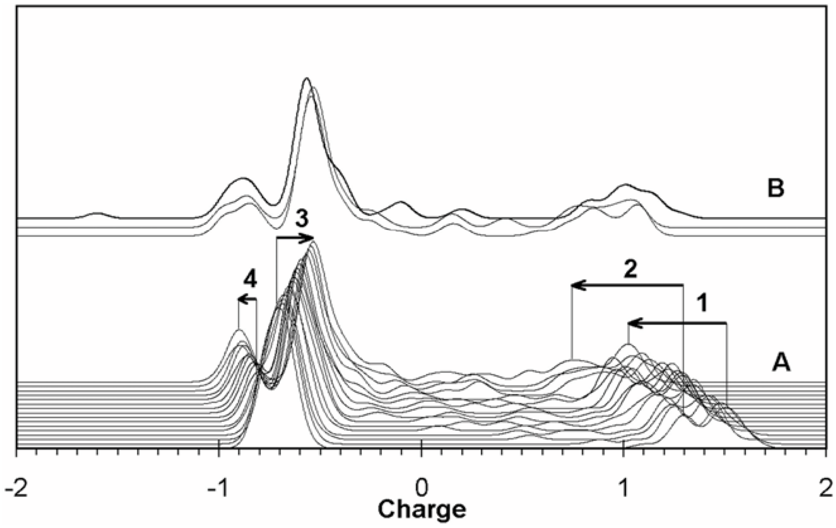

Fig. 2. The QC-derived distribution of charge on atoms in the $27SiO_2$ cluster with total charges from 0 to −15 (A – from bottom to top) and from −16 to −18 (B – from bottom to top). Arrows indicate the trends in the changes of the charge localization: 1, for 4-fold coordinated Si atoms; 2, for 3-fold coordinated Si atoms; 3, for bulk O atoms; 4, for surface O atoms.

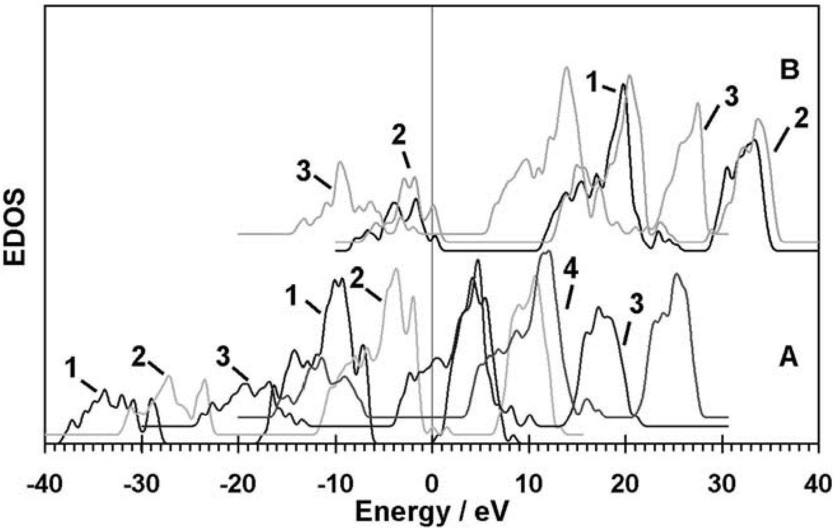

Fig. 3. The QC-derived electron density of states (EDOS) distribution in the $27SiO_2$ cluster with total charges: 0 (A1), −3 (A2), −7 (A3), −11 (A4), −15 (B1), −17 (B2), −18 (B3).

in the spatial structure of the $27SiO_2$ nanoparticle are illustrated by insets in Figure 1. Further increase of the charge leads to dissociation of the silica nanoparticle and desorption of the smaller overcharged silica species (with the total charge −6), which can be approximately described by the reaction

$$Si_{27}O_{54}{}^{18-} = Si_{25}O_{49}{}^{12-} + Si_2O_5{}^{6-}.$$

The overcharged silica species like $Si_2O_5{}^{6-}$, formed upon the dissociation, evaporate and leave from the irradiation site. Also, the increase of the charge leads to the growth of the $27SiO_2$ $\Delta_f H$ value (Fig. 1b), i. e. the energy of the e-beam is partially accumulated by the silica nanoparticle.

Figure 2 demonstrates the changes in the charge distribution on atoms upon an increase of the total charge. It is clearly seen that the excessive negative charge is mainly distributed on the Si atoms. Also, after a certain cluster charge value the O atoms become differentiated by their charge, i. e. the surface O atoms accumulate more of electron density.

The QC-evaluated data on the electronic structure of the charged $27SiO_2$ nanoparticles are summarized in Fig. 3 and Table 1. The EDOS of the neutral $27SiO_2$ nanoparticle consists of three bands. The σ-parts of bonds are mainly situated between −39 and −28 eV. The band between −18 and −6 eV contains mainly π-parts of bonds, while antibonding bands lie between 0 and +9 eV.

As one can see from Fig. 3, the electronic bands shift systematically to higher energy upon increase of the negative cluster charge. The gap between the HOMO and the LUMO energies (Table 1) decreases from 7.28 eV to 4.06 eV for the neutral and −17 charged clusters, respectively. At the charge of −18, when the $27SiO_2$ nanoparticle dissociates, the energies of the electronic bands partially relax to the lower energies, since electronic excitation localizes mainly on the $Si_2O_5{}^{6-}$.

Table 1. The QC-derived highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, and the HOMO-LUMO gap of the negatively charged $27SiO_2$ nanoparticle.

Negative charge	HOMO energy, eV		LUMO energy, eV		HOMO-LUMO gap, eV	
	Alpha spin	Beta spin	Alpha spin	Beta spin	Alpha spin	Beta spin
0	−6.65	−6.65	0.63	0.63	7.28	7.28
1	−3.06	−4.64	3.04	2.91	6.10	7.54
2	0.70	0.70	4.85	4.85	4.15	4.15
3	1.53	0.83	6.89	6.04	5.36	5.21
4	4.60	4.60	8.31	8.31	3.70	3.70
5	5.70	5.15	10.52	10.62	4.82	5.47
6	8.31	8.31	11.30	11.30	2.99	2.99
7	10.27	10.27	14.15	14.14	3.88	3.87
8	12.01	12.01	16.39	16.39	4.38	4.38
9	13.75	13.73	17.93	17.93	4.18	4.20
10	15.76	15.76	20.30	20.30	4.54	4.54
11	17.25	17.25	21.46	21.35	4.21	4.09
12	19.36	19.36	23.39	23.39	4.02	4.02
13	21.45	21.45	25.13	25.13	3.68	3.68
14	22.81	22.81	27.06	27.06	4.25	4.25
15	25.33	24.63	29.07	29.24	3.74	4.61
16	23.72	23.72	27.92	27.92	4.20	4.20
17	24.81	24.82	28.88	28.74	4.06	3.93
18	21.04	21.04	22.29	22.29	1.25	1.25

The HOMO of the neutral $27SiO_2$ nanoparticle is mainly localized on the surface of 1-fold coordinated O atoms, while the LUMO is distributed on several bulk Si atoms. With the increase of the negative charge the contribution of the Si atoms AO to the HOMO grows steadily, until at the charge of -13 the HOMO is almost completely formed by the surface Si atoms. An analogous behaviour is observed for the MO, forming the electronic band below the HOMO.

After evaporation of the charged species the remaining silica nanoparticle decreases in volume, retaining almost the same spatial structure (the atomic connectivity in the silica clusters remains similar). At the same time, according to this model the expansion of the charged SiO_2 nanoparticle in a glass should create pressure-induced deformations in the neighbouring parts of the silica glass. The pressure, induced by the expanding charged cluster obviously should be compensated by pressure of the bulk material on the cluster itself [13]. This should alter the structure of the irradiated and interfacial areas and change their spectral properties, as observed experimentally for e-beam-irradiated silica glasses [4–6].

4. Conclusions

The QC simulations show that the overcharging of the $27SiO_2$ cluster leads to its expansion by 30% and evaporation of the charged species, followed by the densification of the nanoparticle. The structure and characteristics of the remaining nanoparticle, i. e. the bond lengths, angles and coordination number distributions, remain unchanged, but the pressure-induced deformations caused by the nanoparticles expansion should alter the structure of the irradiated and interfacial silica glass areas.

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