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Adsorption characteristics of F and Cl atoms on fused silica surface defects

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ABSTRACT

F and Cl atoms are always brought by the process of wet etching for fused silica devices, which dramatically influence the performance of the devices. The adsorption characteristics of F and Cl atoms with two main fused silica surface defects (E', NBOHC) were investigated on the basis of first-principle methods. Through the comparison of absorption capacity of different surface defects, we found that E' has larger capability to adsorb halogen atoms than NBOHC, and F atom is easier to be trapped by surface defects than Cl atom. Furthermore, the electronic structure and the bonding nature for surface defects are also studied and the calculations show that the introduction of F and Cl atoms will lead to the disappearing of defect states in band gap. And this adsorption process of F and Cl atoms on fused silica surface can be considered to chemical adsorption.

1. Introduction

Fused silica as high quality optical material is widely used in microelectronic, optoelectronic and optic devices. In the construction of these applications and the manufacture of glass, the fused silica surfaces play a significant role. Similar to the internal defects in fused silica, there are partial same defects exist on the surface of fused silica [1–4]. Silicon dangling bond (E') and oxygen dangling bond (usually named as non-bridging oxygen hole center, NBOHC) are two main kinds of intrinsic defects on fused silica surface. E' center is a stable defect which may be transformed from the surface oxygen vacancy center (ODC(I)) [5,6]. The optical adsorption band for surface E' center is located at 5–6 eV. NBOHC defect is usually formed by the disconnect of Si—O bond or Si-OH bond, whose optical adsorption band is at 2 eV [7].

The surface defects in fused silica can cause apparent absorptions and are often detrimental for the performance of optical devices. To improve the anti-laser damage ability of fused silica surface, some preprocessing methods are used to reduce or eliminate various impurities and defects. Wet chemical etching, such as hydrochloric acid (HCl) etching and hydrofluoric acid (HF) etching, is one of the important procedures for fused silica surface post processing. Although wet chemical etching can remove absorbing impurities on fused silica surface, some new impurities, such as F and Cl atoms, are introduced by the etching process [8,9].

Theoretical studies have been devoted to reveal the nature of the fused silica surface defects. The silica surface defects can trap and stabilize the metal atoms or clusters close to the surface [10–13]. D. Costa et al. have studied the effect of different types of hydroxyl groups on the adsorption of glycine at silica surface [14]. Water molecule reacts with the two-membered rings at the silica surface through an activation barrier and results in two silanol groups [15,16]. The interaction of metal clusters with SiO_2 surface shows that paramagnetic defects are the most efficient adsorption site [17]. Although the F and Cl atoms play an important role in the performance of SiO_2-based optical devices [18], there are few comprehensive studies about the adsorption behavior of F and Cl atoms on fused silica surface.

Considering the extensively intrinsic defects on fused silica surface, there is the blank about F and Cl atoms adsorbed at these surface defects. In order to reveal the adsorption mechanism between F and Cl atoms and intrinsic defects, the atomic structures, adsorption energy, electronic states, as well as bonding nature are performed by using first-principle method. Compared with the adsorption of F and Cl atoms on fused silica surface, the F atom can be adsorbed easier at E' center and NBOHC than Cl atom. The adsorption energy of E' center was always larger than NBOHC, which means that E' center is better to adsorb F and Cl atoms. And the introduction of F and Cl atoms led to the disappearing of defect states in band gap.

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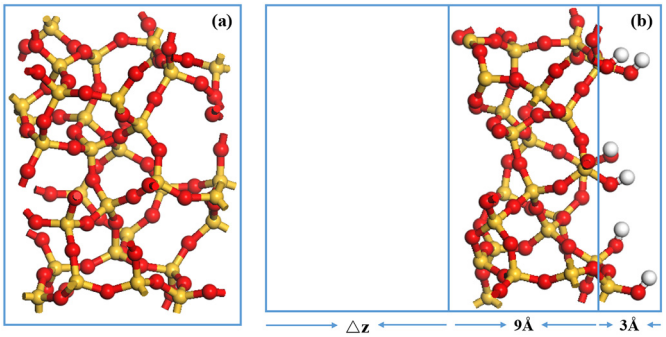

Fig. 1. (a) The initial fused silica model; (b) The obtained silica surface model.

2. Structure models and computational methods

A combination of classical molecular dynamics (MD) simulation and *ab initio* molecular dynamics (AIMD) optimization is used to generate a fused silica surface model [19,20]. A $2\times2\times2$ crystal silica supercell containing 96 atoms was chosen as initial model. The fused silica model (see Fig. 1(a)) was produced by melt-quench method used in classical MD calculations, whose simulated mass density of 2.20 g/cm^3 is agrees well with the experimental result [21]. We cut the system vertically by only cutting silicon-oxygen bonds to generate an interface. These free oxygen atoms are saturated by hydrogen atoms. And then we fixed atoms which is 3 Å away from this interface, to avoid the atoms mobile because of the force field role. Next we add a vacuum layer of $\Delta z = 10$ Å on the top of fused silica model and thus generate a free surface at around 9 Å. The atom positions and cell dimensions of fused silica surface model was relaxed using AIMD at constant temperature (400 K) based on a microcanonical ensemble. After the geometry optimization, we obtained the surface model containing 57 oxygen, 25 silicon, and 6 hydrogen atoms, as shown in Fig. 1(b). The obtained silica surface is full of O dangling bond (NBOHC) and Si dangling bond (E').

The nudged elastic band (NEB) method [22] is used to study the adsorption process of F and Cl atoms on fused silica surface. The adsorption energy where the positive E means the better absorption ability was calculated by the following formula

$$E = E_{ad} + E_{sub} - E_{ad/sub} \quad (1)$$

where $E_{ad/sub}$ is the total energy of the slab model with the impurity on the substrate; E_{ad} and E_{sub} refer to the energy of the impurity and the clean substrate, respectively. The calculations have been performed in the framework of density functional theory (DFT) by using the Vienna *ab initio* simulation package (VASP) based on the plane-wave pseudopotential [23,24]. General gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) was adopted to describe the electron correlation [25]. The quasiparticle GW0 approximation [26] are adopted to calculate electronic structure properties for these surface defects.

3. Result and discussion

3.1. Geometry of the amorphous silica surface

The physical properties of amorphous silica surface strongly depend on its atomic structures. Therefore, the microscopic features of the silica surface region were analyzed using ring distributions, bond lengths and bond angles. In our model, the fused silica surface is constructed by $(SiO_2)_n$ rings with different sizes, which is in agreement with the calculation of hydroxylated surface of amorphous silica [20]. The ring sizes vary from three- to seven-membered with the distribution of 1:3:2:2:1, respectively. We also analyzed the distributions of bond lengths and bond angles of silica surface model. Fig. 2(a) shows that Si—O bonds range from 1.60–1.70 Å located at the center of 1.65 Å, which is consistent with the average Si—O bond length in amorphous silica [21]. Fig. 2(b) shows that the Si-O-Si angles range from 125° to 165°, having a maximum around 150°-160°. The distribution of O-Si-O angles, as is presented in Fig. 2(c), is relatively gathered from 104° to 116°, agreeing with the fact that Si atoms are fourfold coordinated to form a rigid SiO_4 tetrahedra.

3.2. Adsorption of F and Cl atoms on E' center

The adsorption energy of adsorbate-substrate is a crucial characteristic that allow one to estimate the role of the surface active centers in anchoring. In order to avoid the influence of other defects on the adsorption of F and Cl atoms on fused silica surface E' center, NBOHC defect was saturated by hydrogen atoms. When Cl atom adsorbed at E' center, a covalent Si—Cl bond is created, the calculated adsorption energy is 3.73 eV. When F atom adsorbed at E' center, a covalent Si—F bond is formed, the adsorption energy is 5.93 eV, which is similar to previous experimental results [27,28]. Larger adsorption energy value indicates that F atom can be adsorbed easier at E' center than Cl atom. This trend is comparable with M.Seel's work [29], in which the interaction of fluorine and chlorine with the Si (111) surface was studied. We further analyzed the change of the bond length during the adsorption process. The Si—Cl bond is calculated at 2.03 Å, which is 6.5% shorter than the sum (2.17 Å) of atomic radii of Si and Cl atoms. This result shows that the force between Si and Cl atoms is small. The calculated Si—F equilibrium distance is 1.60 Å. Relative to the sum (1.89 Å) of atomic radii of Si atom and F atom, the length shortens 15.3%, which illustrates that there are strong force between Si atom and F atom.

The total density of states (TDOS) for the E' center structure, E' adsorbed Cl model and E' adsorbed F model are calculated respectively shown in Fig. 3. The GW0 approximation is used to estimate quasiparticle energies of the system, which can describe accurately the experimental results relative to DFT method [30]. For the E' center, as shown in Fig. 3(a), there is an unoccupied defect state at 5.26 eV. To analyze the contribution of band structure, the partial density of states (PDOS) are introduced to search the origin of defect states. The corresponding PDOS of the Si atom and the adjacent O atoms for E' center are plotted in Fig. 3(a). The PDOS shows that the unoccupied defected state at 5.26 eV is from the mixture of Si 3 s and Si 3p and O1 2p and O2 2p and O3 2p orbitals, where O1, O2 and O3 are the adjacent O atoms of Si atom for E' center. However, when E' center adsorbed Cl atom, as is presented in Fig. 3(b), the unoccupied defect state result from E' center disappeared. Similar phenomenon happened when E' center adsorbed F atom. One immediate conclusion is that F and Cl atoms can eliminate the E' defect on the fused silica surface.

To better comprehend the electron distributions and bonding natures of the adsorbate and substrate, the relative partial differential charge density are studied. Fig. 4 showed the differential charge density for the free E' defect, the complex of E' adsorbed Cl and E' adsorbed F. It can be seen that there are more electrons transfer from Si atom to F atom because F atom has a large electronegativity than Cl atom. But the adsorption between E' center and F or Cl atom does not change much the charge distribution of nearby Si atom. Therefore, the Si atom of above three configurations shows same characteristics of sp^3 orbital hybridization. To quantitative analysis the transfer charge, we further analyzed the Bader charge population. Bader analysis involves only the outer electrons of atoms. When Cl adsorbed at E' center, 0.69e electrons transfer from Si atom to Cl atom. When F adsorbed at E' defect, there is about 0.8e electrons transfer from Si atom to F atom. The transfer of charge was observed in the adsorption of F and Cl atoms on E' defects, this adsorption process can be considered to chemical adsorption. Considering the larger adsorption energy, F atom can get more electrons from Si atom, therefore it can be adsorbed easier on E' center than Cl atom.