

Adsorption of O adatoms on hydrogenated Si cluster

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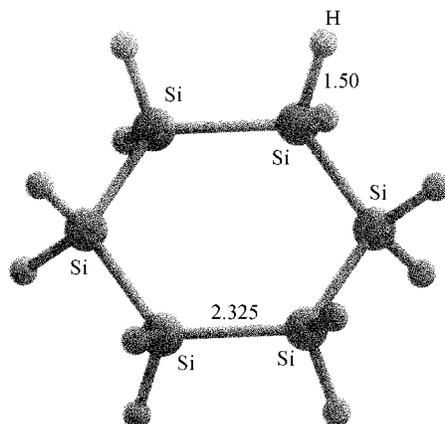
Abstract. – The adsorption of an O adatom on the most stable hydrogenated Si cluster (Si_6H_{12}) has been explored for the first time by using first principles. Two interesting adsorption configurations are found: In the first one, a striking feature is the substitutional adsorption: the O adatom forms a bond with a Si atom in the substrate cluster, which releases a H atom, and the H atom is in turn bonded to the adatom, exhibiting a similar feature to the Si adatom on the hydrogenated Si(100) surface. In the second one, the O adatom breaks the Si-Si bond and is bridge-bonded to two Si atoms, which not only exhibits the key structural feature for Si oxide clusters with ring and chain structure, but also displays the characteristics of oxidation of the Si(001) surface and oxygen impurities in bulk silicon. The latter structure is more stable than the former.

Introduction. – Silicon oxide is the most abundant substance on Earth and is important in many technological areas. The understanding of the structure, bonding, surfaces and defects in silicon oxide could aid the development in diverse applications such as catalysts, amorphous materials, environmental sciences, and electronic device physics. Among the various studies, oxygen adsorption on the Si surface is important, not only because it is an initial stage of oxidation of the materials, but also because its microscopic understanding provides a basis of silicon technology. Many experimental and theoretical works have been done to reveal the atomic and electronic structures of oxygen on Si surfaces. Among them, it is interesting to mention the cluster model method (Si_6H_{12}), used by Batra *et al.* [1] to mimic the oxygen-adsorbed Si(001) surface, where the H atoms are used to terminate the bonds of the Si atoms which extend into the crystal, and the Si-Si distances and orientations were taken from the bulk crystal geometry. It is concluded that a hollow bridge site is most favorable energetically for the oxygen adsorption, which was confirmed by using complicated methods [2, 3]. This simple cluster model method has shed some light on this important subject. In recent years, with the advent of flexible and precise experimental techniques, real hydrogenated Si clusters are produced [4-7], and one may intuitively expect that hydrogenation would help the recovery of the tetrahedral bonding network by saturating the dangling bond. Moreover the hydrogenated Si clusters can also be regarded as a model of porous silicon [8], therefore many theoretical

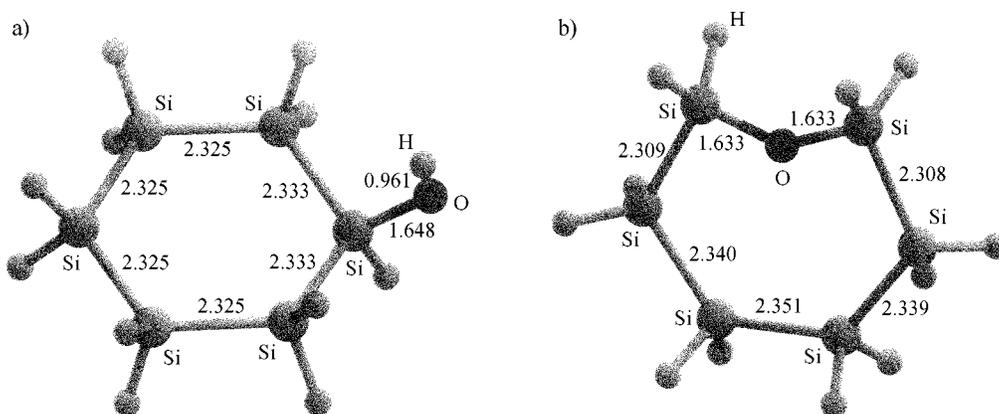
researches have also been performed [9,10]. Especially, the stable structures of hydrogenated Si clusters have been determined [4], and it is found that among neutral hydrogenated Si clusters Si_6H_{12} is the most stable. What about the adsorption of the O adatom on this real and most stable hydrogenated Si cluster and not on the cluster model for bulk as used by Batra *et al.* [1]? Besides, the oxidations of Si clusters and ultrafine Si particles have also been studied recently [11-14], by using anion photoelectron spectroscopy and *ab initio* calculations; the chain and ring structures were determined for the silicon oxide clusters with different Si:O stoichiometries. In addition, the clusters containing Si, O and H were also used to simulate possible defects in amorphous silicon [15], and what is more important is that nanosize Si-O-H clusters have novel optical properties which attract much attention nowadays [16,17]. Therefore, studies for the adsorption of O adatoms on the hydrogenated Si cluster are highly desirable.

Theoretical method. – Our calculations are based on density-functional theory; the exchange correlation energy of valence electrons is adopted in the form of Ceperley and Adler [18] as parameterized by Perdew and Zunger [19]. The ion-electron interactions are described by pseudopotentials, the silicon potential is generated in the norm-conserving pseudopotential scheme of Troullier and Martins [20], the reference configuration is chosen as $3s^23p^1$, the cut-off radius for both s and p orbitals is taken to be 1.6 a.u., and s and p orbitals are treated as nonlocal components. This potential gives a lattice constant of 5.37 Å for the bulk diamond silicon and for the Si_3 cluster, and produces an isosceles triangle configuration with bond length 2.172 Å and bond angle 77.65° , in agreement with *ab initio* molecular-orbital calculations [21]. However, for oxygen, due to the lack of the corresponding core states for cancellation, the tightly bound $2p$ valence wave functions are sharply peaked. As a result, in the conventional norm-conserving pseudopotential scheme, a relatively hard pseudopotential has to be generated and a relatively large number of plane-wave basis functions are required in the calculations. Therefore, in our calculations, the potential of oxygen is generated in the ultrasoft pseudopotential scheme introduced by Vanderbilt [22]. The $2s^22p^4$ configuration is used as the reference state to construct the oxygen potential for both s and p orbitals; the cut-off radius is 1.28 a.u. In order to improve the transferability, two reference energies are set to be the eigenvalues of orbitals; the other parameters are given in Liu *et al.* [23]. In this way, for the O_2 molecule, the bond length is 1.205 Å, in good agreement with experiment. For the H_2O molecule, this potential gives a H-O bond length of 0.961 Å and a $\angle\text{HOH}$ bonding angle of 104.9° , also in agreement with experimental results. 40 Ry has been used as cut-off energy in the plane-wave expansion of the pseudo-wave-functions, which is large enough to obtain convergence. The minimization of the total energy over the degrees of freedom of electron densities and atomic positions is performed using the conjugate-gradient iterative minimization technique [24]. In the optimizations, the cluster is placed in a cubic cell with edge length of 16 Å; this size is sufficiently large to make dispersion effects negligible. The structure optimization was symmetry unrestricted, and the optimization was terminated when the forces acting on the atoms are less than 0.03 eV/Å.

Results and discussions. – It has been found that the most stable structure for the Si_6H_{12} cluster is cyclohexasilane [4,10]. We have also obtained this structure as shown in fig. 1, where the Si-Si bond length is about 2.325 Å and the Si-H bond length is 1.50 Å. We have searched the possible adsorption sites in the whole range over the hydrogenated Si_6H_{12} cluster: we have placed an oxygen atom at one site and then performed geometry optimization according to the calculated force acting on atoms. We have next chosen another site and repeated this procedure. In this way, two adsorption configurations are found, as indicated in fig. 2(a) (type I) and fig. 2(b) (type II). In type-I configuration, a striking feature is the

Fig. 1. – Structure of the Si_6H_{12} cluster.

substitutional adsorption: the O adatom forms a bond with a Si atom in the substrate cluster, which releases a H atom, and the H atom is in turn bonded to the adatom. This kind of substitutional adsorption has also been found recently for the Si adatom on the hydrogenated Si(100) surface [25]. This similarity in adsorption between the hydrogenated Si_6H_{12} cluster and the hydrogenated Si(100) surface could be attributed to this fact: in the hydrogenated Si_6H_{12} cluster, H atoms have terminated the dangling bonds, and the Si atoms favor the bulklike sp^3 bonding even in this small cluster [4]. The adsorption energy for O in this configuration is 8.57 eV, which is greater than that for the O adatom on Si(100) surface (8.2 eV) [2]. The Si-O bond length is 1.648 Å, whereas in the Si(001) surface the bond length between the oxygen and the nearest Si atom is 1.68 Å [2]. The contraction of the bond length in the cluster results in a larger adsorption energy. The bond length between O and H is 0.961 Å, close to that in H_2O .

Fig. 2. – Structures for adsorption configuration I (a) and configuration II (b) of O on the Si_6H_{12} cluster.

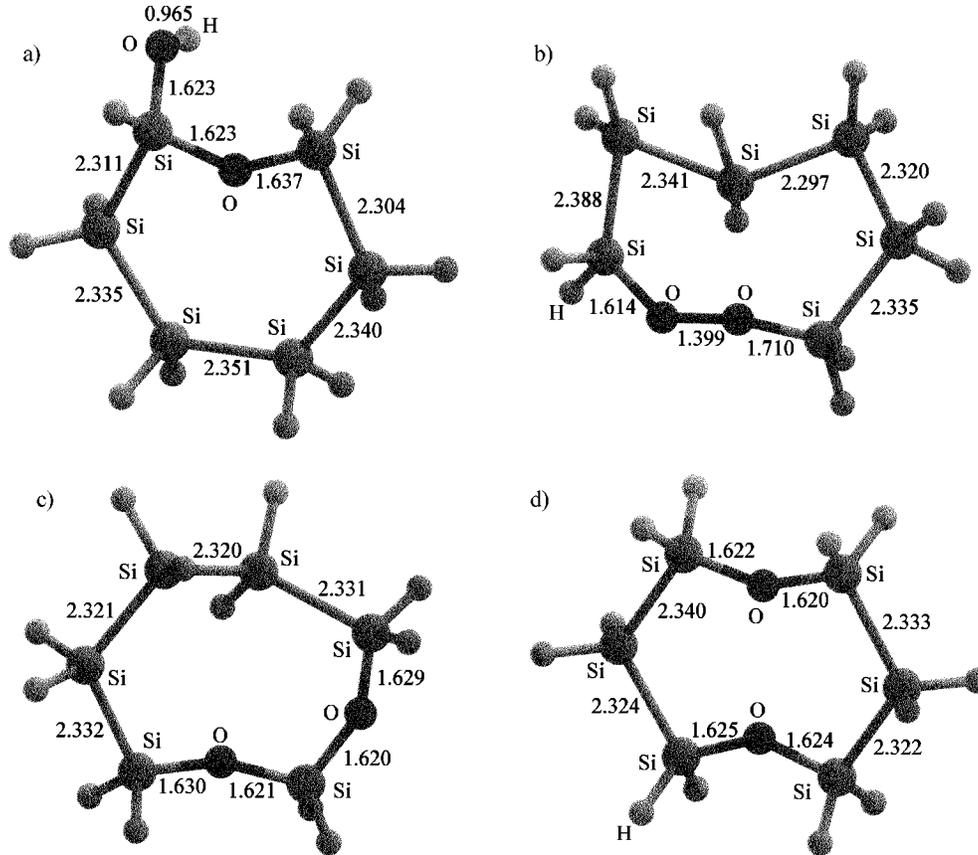


Fig. 3. – The structures for adsorption configuration with two O atoms. Si-O-Si-O-H configuration (a), Si-O-O-Si configuration (b), Si-O-Si-O-Si configuration (c) and Si-O-Si-Si-Si-O-Si configuration (d).

In type-II configuration, the O adatom breaks the Si-Si bond and is bridge-bonded to two Si atoms. The Si-Si bond length is 1.633 Å, the Si-O-Si angle is 144.3°, which are close to those (1.60 Å and 144°) in the case of the O impurity in bulk Si [26] and in the case of the Si/SiO₂ interface [27]. The adsorption energy is 9.238 eV, greater than that in type-I configuration, and is more stable. Recently, Filonov *et al.* [16] studied the oxygen effect on the optical properties of the Si₁₄H₂₄ cluster, in which 14 Si atoms are at their positions corresponding to the diamond crystal sites, and all the silicon dangling bonds at the surface are passivated by 24 hydrogen atoms that remove the dangling-bond states from the band-gap energy region. They used the self-consistent semiempirical molecular-orbital method, to simulate the presence of oxygen atoms in the cluster. They adopted two possible structural models: in model 1, the surface hydrogen atoms are replaced with OH-group terminators (similar to the type-I configuration in this paper, and what is more important is that our calculations have confirmed that the O atom will automatically replace the H atom to form the OH-group terminator); in model 2, oxygen atoms are inserted into the cluster in between Si-Si bonds, thus creating Si-O-Si dimer bridges (similar to the type-II configuration in our study). According to the total-energy calculation, they also found that the structure of model 2 is more stable than that of model 1, in agreement with our calculation.

In Si oxide clusters with ring and chain structures, the key structural feature is that oxygen is a bridge site bonded to two Si atoms, as has been found experimentally and theoretically [11, 12]. What about the situation in the hydrogenated Si cluster? To this end, the geometry optimizations for adsorbed O atoms have been extended to the case of two oxygen atoms. The four possible structural configurations are shown in fig. 3. In the first one, one oxygen replaces the H atom, another oxygen atom breaks the Si-Si bond, forming a Si-O-Si-O-H configuration (fig. 3(a)), the adsorption energy per O atom is 9.09 eV. In the second one, the two oxygen atoms are nearest neighbors forming a Si-O-O-Si configuration (fig. 3(b)), and the adsorption energy per O atom is decreased to 5.21 eV. In the third one, the two oxygen atoms are the bridge sites bonded to two Si atoms, forming a Si-O-Si-O-Si configuration (fig. 3(c)), and the adsorption energy per O atom is increased to 9.613 eV. For the last one (fig. 3(d)), the two oxygen atoms form a Si-O-Si-Si-O-Si configuration, and the adsorption energy per O atom is 9.346 eV, less than that in the third one. We can see that the most stable configuration is that in which two oxygen atoms have a common bridge site, which is similar not only to the case of Si_mO_n clusters [11, 12], but also to the cases of oxidation of the Si(001) surface and oxygen impurities in bulk Si. It has been found recently that in the initial layer-by-layer oxidation of Si(001) surfaces the O atoms on the uppermost layer will migrate to the back bonds [28], and as impurities in bulk silicon, the O atom breaks a silicon-silicon $\langle 111 \rangle$ bond and forms two silicon-oxygen bonds in bridging configuration [29, 30]. Therefore, despite the different coordination number and the different symmetry for O atoms in the Si cluster, in the hydrogenated Si cluster, in the Si bulk and on the Si surface, the local environment for O atoms shares some similarities. Comparing the adsorption energy for configurations in fig. 2(b), fig. 3(c) and fig. 3(d), we can see that the adsorptions of oxygen with higher stoichiometries are preferable, being in agreement with experiment, in which the silicon oxide clusters with higher Si:O stoichiometries are found [11, 12].

In summary, oxygen adsorption on the most stable hydrogenated Si cluster (Si_6H_{12}) has been studied for the first time, which not only exhibits similar adsorption features of hydrogenated Si(001) surface, but also displays the characteristics of silicon oxide clusters, the oxidation of Si(001) surface and oxygen impurities in bulk silicon.

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