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DFT Investigation of O₂ Adsorption on Si(001)-(2×2×1):HXiao-yan Deng^{a,b}, Chun Yang^{a*}, Ming-xiu Zhou^a, Wei-fei Yu^c, Jin-shan Li^c

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A novel model was developed to theoretically evaluate the O₂ adsorption on H-terminated Si(001)-(2×2×1) surface. The periodic boundary condition, the ultrasoft pseudopotentials technique based on density functional theory (DFT) with generalized gradient approximation (GGA) functional were applied in our *ab initio* calculations. By analyzing bonding energy on site, the favourable adsorption site was determined. The calculations also predicted that the adsorption products should be Si=O and H₂O. This theoretical study supported the reaction mechanism provided by Kovalev *et al.* The results were also a base for further investigation of some more complex systems such as the oxidation on porous silicon surface.

Key words: Si(001)-(2×2×1):H, O₂, Density functional theory (DFT), Adsorption site

I. INTRODUCTION

Thin Si films have many important technical applications in solar energy conversion and the art of the microelectronics. In ultra-large scale integrated circuit (ULSI) devices, thin oxide films have become significantly important materials. Porous silicon has attracted considerable attention recently because it is a kind of potential candidate material for Si-based optoelectronic devices and explosive materials [1], in which the oxidation of H-terminated porous silicon surface plays a key role. So it is necessary to make the oxidation process clear by theoretical investigation.

Recently, some correlative experimental [2-9] and theoretical [10-14] studies were designed to investigate the surface oxidation effect on H/Si surface. Most of them only focused on the optical properties. The adsorption process of O₂ on H/Si surface is still nuclear, because there are so few studies done on it. Especially, there are no first-principles studies or simulations applied to interpret the oxidation process of H-terminated Si surface. Some published experimental data [2-4] indicated that the products of oxidation reactions are Si=O and Si-O-Si, while the O₂ adsorption process on Si(001)-(2×2×1):H is not clear yet.

In this work, we investigated the process of the partial oxidation on Si(001)-(2×2×1):H, in order to study the favourable adsorption site on Si(001)-(2×2×1):H and the adsorption product. Furthermore, this study could provide instruction for the theoretical investigation of oxidation on hydrogen-terminated porous silicon surface.

II. THEORETICAL METHOD

Our computational work was based on the density functional pseudopotential method [15]. The nonlocal generalized gradient approximation (GGA) of Perdew and Wang 91 (PW 91) [16] functional was applied to calculate the exchange-correlation potential. The total energy calculations were all carried by the modified version of CASTEP 2.2 software [17]. The plane-wave basis set was used in our computation. According to the Bloch's theorem, in the reciprocal space, the electronic wave functions at each *k*-point can be expanded in terms of a discrete plane-wave basis set. In principle, an infinite number of plane waves are required for such expansion. However, the plane waves with small kinetic energies are more important than those with large kinetic energies. So, an appropriate cutoff energy can be chosen. Then we only need to take account of the plane waves that have kinetic energies smaller than the cutoff energy. The cutoff energy was 120.0 eV. To ensure the convergence, the finite basis set correction was applied. The Brillouin zone *k*-point was 4×4×4.

This work was performed through three steps. In the first step, we gave an overview of the possible oxidation product after the adsorption reaction on H-terminated Si surface. Then the possible results were inputted as initial information in the calculation. After analysis and comparison, we can get the most reasonable choice. In the second step, we focused on the energies, which were calculated for all possible adsorption sites to show which site was the favourable adsorption site. In the third step, we discussed the structural and electronic properties of Si(001)-(2×2×1):H surfaces before and after adsorption.

The elements involved in this adsorption reaction are silicon, hydrogen, and oxygen. According to studies [2-14], Si=O [2-4], Si-O-Si [2-4], and H₂O [2] are the most possible experimental products of O₂ adsorp-

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tion on H/Si surface. For example, Kovalev *et al.*'s report [2] showed that the final experimental products of the explosive reaction are SiO₂ and H₂O by infrared vibrational adsorption spectroscopy investigation. Ikeda *et al.* [3] investigated the surface reactions of H-terminated Si(001) surfaces with oxygen by high-resolution electron energy loss spectroscopy to clarify the initial oxidation process of H-terminated Si surface. These authors inclined to believe that the possible products are Si=O, Si-O-Si and H₂O. Although the experiments could provide us what the possible reaction products were, they could not answer what the most possible reaction products were and what the reaction details were in the adsorption process. In this work, we want to answer such questions in atomic scale.

III. RESULTS AND DISCUSSION

A novel model was developed to theoretically evaluate the O₂ adsorption on H-terminated Si(001)-(2×2×1) surface. The substrate under H-terminated Si(001)-(2×2×1) surface consists of 4 layers Si atoms. The geometry of the Si(001)-(2×2×1):H surface was optimized from a regular hydrogen-terminated Si(001)-(2×2×1) surface. The optimized surface model is shown in Fig.1. The local electron density is also shown in Fig.1. After optimization, we can see that, the flat Si surface is not flat anymore. The stepped and kinked surface appeared after geometry optimization. Rough surfaces are much more chemically active than flat surfaces. These factors can contribute to the enhanced reactivity [14].

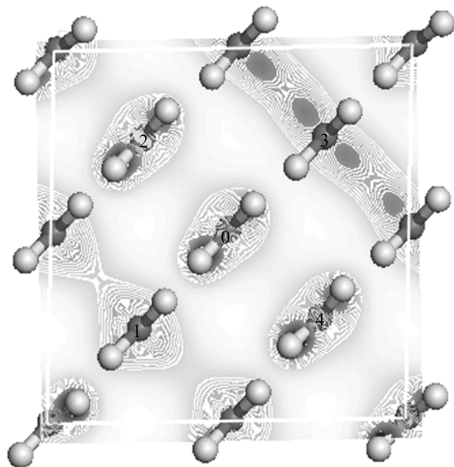
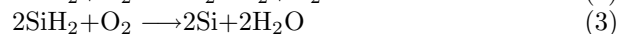
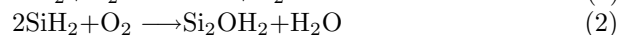


FIG. 1 The model of H-terminated Si(001)-(2×2×1) surface. The gray ball denotes H and the dark ball denotes Si. The numbers of 0, 1, 2, 3, and 4 denote 5 Si atoms' sites, respectively.

The possible configurations of oxidized Si(001)-(2×2×1):H surfaces are very complicated. In order to simplify the complicated problem, we only dealt with a single oxygen molecule attached to the Si(001)-(2×2×1):H surface. According to the possible reaction

products, we designed three possible reactions with different products: (i) the final reaction products were Si=O and H₂O; (ii) the final reaction products were Si-O-Si and H₂O; (iii) the final reaction products were two H₂O. The three reactions are expressed respectively as follows:



Taking periodic boundary conditions into account, only 5 sites need to be calculated. We denote them site-0, site-1, site-2, site-3, and site-4, respectively (shown in Fig.1). So, taking account of all the three possible reaction processes, we only need to deal with 21 reactions as follows: (i) Five cases with products of Si=O and H₂O on the sites: site-0, site-1, site-2, site-3, and site-4. (ii) Eight cases with products of Si-O-Si and H₂O between every two sites: (site-0, site-1), (site-0, site-2), (site-0, site-3), (site-0, site-4), (site-1, site-2), (site-2, site-3), (site-3, site-4) and (site-4, site-1). (iii) Eight cases with products of two H₂O between every two sites: (site-0, site-1), (site-0, site-2), (site-0, site-4), (site-0, site-3), (site-1, site-2), (site-2, site-3), (site-3, site-4) and (site-4, site-1).

We obtained the adsorption energies of the 3 possible reaction processes: 8.89-9.11 eV, 3.36-7.74 eV and 3.17-4.47 eV. For comparison, all the adsorption energies were got under the same conditions. It is obvious that the adsorption energy with products of Si=O and H₂O (the first reaction process) is higher than that of the others. The bonding to the surface structure with the highest adsorption energy should be achieved first. So, the first case with the highest adsorption energy is the most reasonable reaction process: one oxygen atom of oxygen molecule attached to a single silicon atom forming a double bond: Si=O, and the other oxygen atom connected with two hydrogen atoms forming H₂O molecule on the surface. This reaction mechanism agrees well with that proposed by Kovalev *et al.* [2].

Now, we have already determined that the first reaction process is the reasonable one. Subsequently we will determine which site is the favourable adsorption site in the first reaction process. Table I shows the adsorption energies of every site in the first reaction process. We can see that the adsorption energy of site-4 is higher than those of the other sites. As we all know, as a gas molecule is near the surface, it will undergo an attractive potential whose intensity will depend on the electronic and atomic structures of the surface. The site with the highest adsorption energy has the strongest attractive potential, so the chemical bond is always formed on the site with the highest adsorption energy. According to the above analysis, we concluded that site-4 is the favorable adsorption site.

The formation of a chemical bond in adsorption must be accompanied with the charge transfer and form a covalent or an ionic bond. The charge transfer depends on the nature of the adsorbate and the substrate. The ex-

TABLE I Adsorption energies of O₂ on different sites

Adsorption sites of Si	Total energy/eV	Adsorption energy/eV
site-0	-4125.53	8.89
site-1	-4125.68	9.04
site-2	-4125.68	9.04
site-3	-4125.72	9.08
site-4	-4125.75	9.11

tent of the charge transfer can describe the adsorption ability of oxygen on H/Si surface [14]. Table II shows the atom charges population before and after adsorption on site-4. We can see that, before adsorption, the site-4 atom lost 0.31 electrons, in which 0.24 electrons were transferred to the two neighbor H atoms combined with Si, and the others were transferred to the substrate. After adsorption, the site-4 atom and O atom combined to form Si=O double bond, and the site-4 atom lost 0.94 electrons, in which 0.89 electrons were transferred to the neighbor O atoms combined with site-4, and the other were transferred to the substrate. Comparing the charge transfers before and after adsorption, it is obvious that the charge transfer from site-4 to O after adsorption is far more than that from site-4 to H before adsorption. The more stable Si=O double bond substituted for the Si-H bond. It is also interpreted by the bigger electronegativity of the oxygen atom. The results are in good agreement with those in the work [3].

TABLE II The atom charges population analysis before and after adsorption on site-4

	Element	Population		Net charge/e
		s orbit	p orbit	
Before adsorption	H	1.12		-0.12
	Si(site-4)	1.30	2.39	0.31
After adsorption	H	1.12		-0.12
	O	1.94	4.95	-0.89
	Si(site-4)	1.24	1.82	0.94

IV. CONCLUSION

The density functional theory were used to analyze the energy and the electronic property of the O₂ adsorption on Si(001)-(2×2×1):H surfaces in the atomic scale. The rough surfaces obtained by the geometry optimization are much more chemically active than the flat surfaces. Based on the calculations, the ability to adsorb O₂ molecule of the Si atom(site-4) is the strongest. So, it is the favourable adsorption site. The electrons are transferred from the Si atom(site-4) to the O atom and the H atom. The Si=O double bonds structure is the most stable structure after oxygen reaction on surface

Si(001)-(2×2×1):H. Our results accord with the reaction mechanism in the work [2]. The calculations also predicted that the adsorption products should be Si=O and H₂O. Huge adsorption energies obtained (~9 eV) also indicate that the H/Si surface is a good candidate for energy conversion materials [2]. This work provided a theoretical interpretation on the explosive reaction [2] in atomic scale and theoretical instruction for the study of porous silicon products [18-20] and will contribute to investigation on more complex systems.

V. ACKNOWLEDGMENTS

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- [1] L. M. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
- [2] D. Kovalev, V. Yu. Timoshenko, N. Künzner, E. Gross and F. Koch, *Phys. Rev. Lett.* **87**, 068301 (2001).
- [3] H. Ikeda, K. Hotta, S. Furuta, S. Zaima and Y. Yasuda, *Appl. Surf. Sci.* **104/105**, 345 (1996).
- [4] R. R. Koropecski, R. D. Arce and J. A. Schmidt, *Phys. Rev. B* **69**, 205317 (2004).
- [5] B. G. Yacobi, R. W. Collins, G. Moddel, P. Viktorovitch and W. Paul, *Phys. Rev. B* **24**, 5907 (1981).
- [6] G. Mauckner, K. Thonke and R. Sauer, *J. Phys.: Condens. Matter* **5**, L9-L14 (1993).
- [7] V. P. Markevich, L. I. Murin, J. L. Lindström, A. G. Ulyashin, R. Job, W. R. Fahrner and V. Raiko, *J. Phys.: Condens. Matter* **12**, 10145 (2000).
- [8] S. Miyazaki, A. Mouraguchi and K. Shiba, *Thin Solid Film* **297**, 183 (1997).
- [9] R. B. Wehrspohn, J. N. Chazalviel, F. Ozanam and I. Solomon, *Thin Solid Film* **297**, 5 (1997).
- [10] M. D. Halls and K. Raghavachari, *J. Phys. Chem. B* **108**, 19388 (2004).
- [11] Z. D. Xu, J. C. Ding, Z. Q. Du and W. X. Chen, *Chin. J. Chem. Phys.* **8**, 457 (1995).
- [12] J. T. Arantes, R. H. Miwa and T. M. Schmidt, *Phys. Rev. B* **70**, 235321 (2004).
- [13] I. Vasiliev, J. R. Chelikowsky and R. M. Martin, *Phys. Rev. B* **65**, 121302 (2002).
- [14] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, New York: Wiley-Interscience Publication, (1993).
- [15] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- [16] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- [17] H. Huang and G. H. Gilmer, *J. Appl. Phys.* **84**, 3636 (1998).
- [18] L. T. Caham, *Appl. Phys. Lett.* **63**, 337 (1993).
- [19] L. Pavesi, Y. F. Chen, A. Shih and S. C. Lee, *Phys. Rev. B* **65**, 195307 (2002).
- [20] H. J. Li, S. Qu, Z. J. Jian, J. C. Peng and J. N. Xiang, *Chin. J. Chem. Phys.* **13**, 492 (2000).