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1993 J. Phys.: Condens. Matter 5 2897

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The bonding characterization of Br on Si(100) 2×1

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Received 15 December 1992

Abstract. The bonding characterization of Br on the Si(100) surface has been studied by the atom superposition and electron delocalization molecular orbital theory, using 2×1 symmetric- and buckled-dimer models for this surface. From the total energy minima, we have found two stable adsorption sites for Br bonding in the symmetric-dimer model. One is along the surface dangling bond, with a Br–Si bond length of 2.16 Å and a bond angle of 19° to the surface normal; the other is the bridge site with a Br–Si bond length of 2.13 Å. In the buckled-dimer model, Br is predicted to adsorb onto the dangling bonds and further to enhance the buckling. The calculated bond lengths and angles are in good agreement with the recent x-ray standing-wave (XSW) experiment. Moreover, we give a new explanation for the low coherent fraction f_c in the XSW study.

1. Introduction

The study of the adsorption of halogen atoms onto a silicon surface is of both fundamental and technological importance, especially in view of the potential application of halogens (e.g. F_2 and Cl_2) as an etching agent in the manufacture of patterned silicon substrates for very-large-scale integrated circuits. Meanwhile, the simplicity of the expected monovalency of halogens may help us to learn how the chemisorption depends on the reconstruction of the substrate and how the chemisorption itself influences the surface relaxation. Numerous studies of this field have been carried out to try to obtain a better understanding of the interface structures and properties [1–8]. The interest mainly focused on the adsorption of fluorine and chlorine on Si(100) and Si(111) surfaces [1–5], while the interaction of bromine with silicon surfaces has been much less studied. Recently, some efforts have appeared to shed light on the interface structure. Materlik and co-workers, using an x-ray standing-wave (XSW) experiment, have studied Br adsorption on Si(111) 1×1 and 7×7 [6, 7] and Si(100) 2×1 surfaces [8].

For Br adsorption on the Si(100) 2×1 surface, an off-normal adsorption geometry has been proposed [8], just like many experimental results for F [1] and Cl [3, 4] on this surface. The 2×1 LEED pattern is maintained up to saturation coverage [8], suggesting that Br atoms bond to the surface without breaking the dimer bonds. A low coherent fraction coefficient f_c was found in this XSW study [8]; $f_c = 0.13 \pm 0.02$ at room temperature (RT), 0.32 ± 0.02 at 490°C and 0.42 ± 0.02 at 690°C , while for Br adsorption on Si(111) 1×1 and 7×7 , f_c is 0.96 and 0.76, respectively, at RT [7]. These workers suggested that the low f_c on

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Si(100) 2×1 was caused by the Br adsorption on surface defects, steps and buckled dimers [8].

The present work is to develop a deeper insight into the bonding mechanism for Br adsorption on Si(100) 2×1 . We hope to find a new explanation for the low coherent fraction in the XSW study and to determine whether the surface buckling remains or not or whether it is even enhanced after Br adsorption.

2. Models and method

In this paper, a four-layer silicon cluster model $\text{Si}_{31}\text{H}_{36}\text{Br}$ is adopted to simulate the Br bonding and migration on Si(100) 2×1 . For the Si(100) surface, we use both the 2×1 symmetric- and asymmetric-(buckled-)dimer models reported by Roberts and Needs [9]. For the symmetric model, the displacements of the first-layer Si atoms making up each dimer are 0.331 Å in the $[\bar{1}00]$ direction (closer to the second layer) and ± 0.803 Å in the $[0\bar{1}1]$ direction (to form dimers), and the second-, third- and fourth-layer Si atoms also have some small displacements with respect to their unreconstructed bulk places; for the 2×1 asymmetric-dimer model, the buckling angle is about 6.9° , and the displacements of the above four-layer atoms are more complex. Details have been given in [9]. The H atoms in the cluster are used only to saturate the bulk Si dangling bonds (DBs) as in most of the studies concerning silicon surfaces.

The atom superposition and electron delocalization molecular orbital theory is used in the present calculation. This fast semi-empirical method has been applied to the study of adsorption on both metal and semiconductor surfaces and has proved to be reliable in determining the bonding geometries and force constants [10–12]. The parameters used in calculations are listed in table 1 [13–15].

Table 1. Atomic parameters used in the calculation: n , principal quantum number; I_p , ionization potential; ζ , the Slater orbital exponents.

Atom	s orbital			p orbital		
	n	I_p (eV)	ζ (au)	n	I_p (eV)	ζ (au)
Br	4	21.80	2.638	4	9.85	2.257
Si	3	14.68	1.634	3	8.08	1.428
H	1	11.60	1.200	—	—	—

3. Results and discussion

In order to determine the role that the buckling plays in Br adsorption and conversely the influence upon buckling by Br adsorption, we adopted both 2×1 symmetric- and asymmetric-dimer models for calculation. Other models in [9], such as the $p(2 \times 2)$ alternating buckled-dimer and the 2×4 and 2×2 missing-dimer models, are not included in the present study because the 2×1 LEED patterns are maintained in the Br adsorption process [8]. We begin with Br adsorption using the 2×1 symmetric-dimer model.

For each adsorption site, including the pedestal A, bridge B, cave C, valley bridge D, side bridge E, atop F and 'original' atop G (figure 1), we calculated the total energy (TE)

of the cluster versus the adsorption height in detail. The pedestal, cave, valley bridge and side bridge sites are found to be unfavourable since there are no binding energies for the Br atom on these sites, while the bridge, atop and 'original' atop sites are capable of adsorbing a Br atom with binding energies of 1.11 eV, 0.68 eV and 1.23 eV, respectively. When the Br-Si bond length l and angle θ to the surface normal near the original atop site are carefully varied, further calculations show that the most favourable site is along the DB with $l = 2.16 \text{ \AA}$, $\theta = 19^\circ$ and a binding energy of 1.232 eV (figure 2).

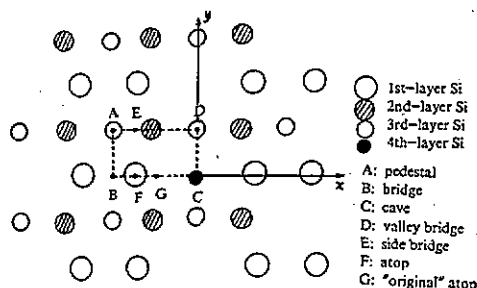


Figure 1. Cluster model $\text{Si}_{31}\text{H}_{36}\text{Br}$ for Br adsorption on the Si(100) 2×1 surface and the possible adsorption sites: A, pedestal; B, bridge; C, cave; D, valley bridge; E, side bridge; F, atop; G, 'original' atop. For convenience, the H atoms saturating the bulk DBs are not plotted.

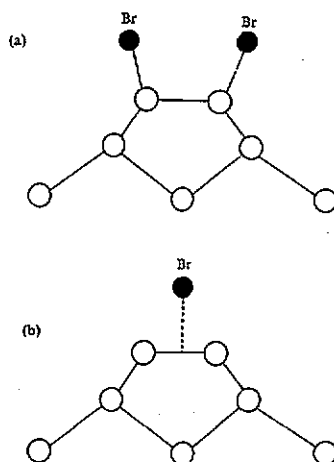


Figure 2. Schematic diagrams of the Br adsorption geometries on the DB site and bridge site.

In order to obtain this bond length and bond angle, we have used a Morse-type expression to simulate the TE curve versus the bond length (bond angle, adsorption height, etc) near the equilibrium values [16]:

$$E(x) = E(x_0) + [a + b(x - x_0) + c(x - x_0)^2] \{1 - \exp[-\alpha(x - x_0)]\}^2$$

where x is the bond length (bond angle, adsorption height, etc), $E(x)$ is the TE at x , and x_0 , $E(x_0)$, a , b , c and α are the parameters to be determined. Using this optimum technique, we may find the accurate bond length, binding energy and force constant ($k = (d^2E/dx^2)|_{x=x_0} = 2a\alpha^2$). The bond length of 2.16 \AA as is obtained above for Br adsorption on Si(100) 2×1 is in good agreement with the xsw result of $2.20 \pm 0.05 \text{ \AA}$. This value is also consistent with the semi-empirical estimation using the equation

$$d_{\text{cov}} = r_{\text{Si}} + r_{\text{Br}} - c|x_{\text{Si}} - x_{\text{Br}}|$$

for the bond length d_{cov} in covalent bonding [17, 18] of two atoms with covalent radii $r_{\text{Si}} = 1.11 \text{ \AA}$ and $r_{\text{Br}} = 1.14 \text{ \AA}$ and electronegativities $x_{\text{Si}} = 1.8$ and $x_{\text{Br}} = 2.8$. The constant c is 0.06 \AA [17, 18]. From this estimation the bond length is 2.19 \AA , 0.03 \AA larger than the present calculation. Certainly, our bond length also needs further confirmation by experiments and more reliable calculations, such as *ab initio* methods. The bond angle 19°

is very close to the ideal tetrahedral angle (19.47°), indicating that the Br adatom is along the DB of the surface dimer atoms. Similarly, we use the same cluster model for Si(100) and have found that the H adatom bonds to a DB with a bond length of 1.56 \AA and a bond angle of 22° to the surface normal; these are more reliable than our previous results for H on Si(100) using a smaller two-layer cluster model [15]. We have also found that the behaviours of Br and H adatoms on Si(100) are very similar. The stretching and bending frequencies of the Br–Si bond are calculated to be 165 cm^{-1} and 41 cm^{-1} , respectively. This stretching frequency is somewhat less than that of SiBr_4 (249 cm^{-1}). Since there are no HREELS results on Br/Si(100) 2×1 , direct comparison is difficult for us now. However, our calculation for H/Si(100) 2×1 revealed that the Si–H stretching frequency is 2124 cm^{-1} , as found in this work and our recent work on $\text{C}_2\text{H}_2/\text{Si}(100) 2 \times 1$ and $\text{C}_2\text{H}_4/\text{Si}(100) 2 \times 1$ [19], in excellent agreement with the HREELS result of about 2120 cm^{-1} [20]. If we assume that the Si–Br and Si–H bonds have the same force constants, the Si–Br stretching frequency may be estimated to about 240 cm^{-1} ($2120\sqrt{M_{\text{H}}/M_{\text{Br}}}$), in reasonable agreement with our calculation result.

Except for the DB site, the bridge site is found to have a binding energy of 1.11 eV , only 0.12 eV less than that of the DB site. The bond length is 2.13 \AA and the perpendicular vibrational frequency is 330 cm^{-1} (see figure 2). In order to determine the stability of this site and further the Br site-to-site mobility, we calculated the binding energies and adsorption heights for various positions between the bridge and DB sites. The results are shown in figure 3. It is obvious that the bridge site is a stable equilibrium site, and the migration barrier for the Br adatom transition from the bridge site to the DB site is about 0.8 eV . This high migration barrier indicates that Br adatoms cannot easily migrate between the two adsorption sites. Thus, Br adatoms may be adsorbed on the bridge sites even at temperatures above RT. Meanwhile, considering that there is no adsorption on the pedestal, cave, valley bridge and side bridge sites, etc, we can draw the conclusion that the mobility of Br adatoms on Si(100) is very poor, and the adsorption is very localized.

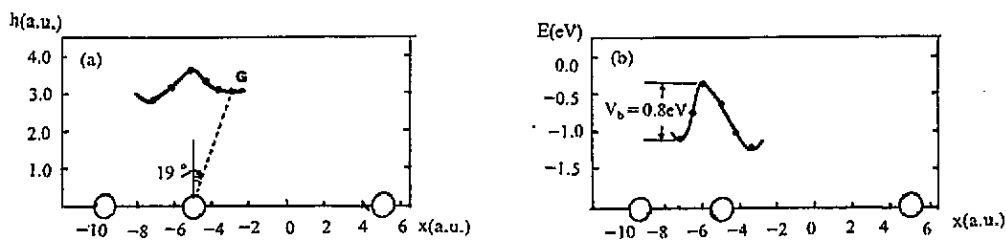


Figure 3. Adsorption heights and the corresponding total energy for a Br adatom on various positions between the bridge site and the neighbour DB site. Here, we have adopted the total energy for a Br atom as zero at infinity.

Since a scanning tunnelling microscopy (STM) study [21] and first-principles calculations [9] have both shown that non-buckled and buckled dimers coexist on the Si(100) surface, a buckled-dimer model must be included in our calculation. Detailed calculations have been performed for Br adsorption on the buckled-dimer surface. Br atoms are found to adsorb onto the DB with a bond length of 2.16 \AA (the same as for the symmetric-dimer model) and a bond angle of 16° to the surface normal. As we know, the surface buckling angle is about 6.9° ; thus one may expect the bond angle to decrease to 12° [8]. This difference between our calculation result and the expected value is under further investigation. The binding

energy increases to 1.75 eV, 0.52 eV larger than that for the non-buckled-dimer model; meanwhile, the stretching and bending frequencies increase to 217 cm^{-1} and 66 cm^{-1} , respectively. This indicates that the Br adsorption may stabilize the buckling of the surface. This is similar to the findings of Hashizume *et al.* [22] in their STM studies on Li and K adsorption on Si(100) 2×1 , where the Li and K adatoms stabilize the buckled dimerization of this surface. Our result is also consistent with the recent report on the origin of the buckling of Si(100) by Tsuda *et al.* [23] using *ab initio* Hartree–Fock molecular orbital calculations. In their opinion, the buckling comes from an imbalance of the electric charge distribution on the surface. The most stable geometry is symmetric for the electrically neutral case, but asymmetric or buckled for the negatively or positively charged cases [23]. In the present study, approximately $0.25e$ charge transfers are found between Br and Si atoms owing to the different electronegativities for Si (1.8) and Br (2.8). Thus, a buckled-dimer geometry may be favoured and enhanced. Of course, a comprehensive study must include surface relaxation in the calculation, whereas it is difficult for cluster methods to include the adsorbate-induced reconstructions of the substrate because of its finite cluster sizes. However, we expect that the relaxation will further lower the total energy of the system, i.e. increase the binding energy again; thus we think that the conclusion for the stabilization of the buckling may be unchanged.

Finally, we discuss briefly the low coherent fraction f_c in the XSW experiment [8], which indicates that a significant percentage of Br atoms are adsorbed at sites with randomly distributed distances to the (400) planes [8]. It was suggested that this resulted from the Br adsorption on defects, steps and buckled dimers, but that the adsorption must be along the DBs, and the bridge, cave, valley bridge and pedestal sites were all discarded. Our calculation results give a new reason for the low coherent fraction; although the defects, steps and buckled dimers (discussed above) do contribute to the random fraction, the two independent adsorption sites, i.e. the DB site and the bridge site, may play an important role. The Br adatoms on the two different adsorption sites have certainly different distances to the (400) planes. Furthermore, the high migration barrier of about 0.8 eV limits the migration from the bridge site to the DB site to a great degree, which explains well the low increase in f_c with increasing temperature, from 0.13 at RT to 0.32 at 490°C to 0.42 at 600°C . On the other hand, the very different situation of Br on Si(111) also provides us with some evidence. The coherent fraction f_c is 0.96 ± 0.07 for Br/Si(111) 1×1 and 0.76 ± 0.03 for Br/Si(111) 7×7 at RT [7]. The high coherent fractions confirm unambiguously one adsorption site for Br on Si(111) while, for Br on Si(100) 2×1 , f_c is much smaller. Although the chemical etch and anneal may not leave the Si(100) surface as well ordered as Si(111) [23], it is reasonable to think that the coexistence of the two stable adsorption sites for Br on Si(100) 2×1 may be a more important cause of this much lower f_c than the effect of surface defects. In fact, the coexisting adsorption sites have also been found by Craig and Smith [2] in their SLAB MINDO study for Cl and F adsorption on Si(100) 2×1 .

4. Conclusions

The adsorption, migration and vibration properties of Br adatoms on the Si(100) 2×1 surface have been studied in this paper. Some important results are summarized as follows.

(1) There are two adsorption sites for Br on the Si(100) 2×1 symmetric-dimer surface. One is along the surface DB with an Si–Br bond length of 2.16 \AA and a bond angle of 19° to the surface normal. The other is the bridge site with a bond length of 2.13 \AA . The binding

energies of the two sites are close, while the migration barrier between the two sites is as high as 0.8 eV.

(2) In the 2×1 buckled-dimer model, Br adatoms adsorb onto the DBs of the buckled dimer and further stabilize the buckling, which is similar to Li and K adsorption on this surface.

(3) The coexistence of two adsorption sites gives a new and perhaps more important cause for the low coherent fraction f_c of the XSW experiment. That is to say, not only surface defects and buckled dimers, but also the second stable site (i.e. the bridge site) contribute to the low coherent fraction.

Acknowledgments

This work was supported by the National Science Foundation of China and by the Science Foundation of the National High Pure Silicon and Silane Laboratory, Zhejiang University.

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