Structure of Si(111)$3 \times 2$ Induced by Alkaline-Earth Metals

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We have performed total-energy calculations to study the atomic and electronic structure of the Si(111)$3 \times 2$ surfaces induced by the adsorption of alkaline-earth metals (AEMs). Not only Ba but all other AEMs such as Mg, Ca, and Sr are found to induce a Si reconstruction into the honeycomb chain-channel structure. The structural and the electronic properties tend to follow the atomic size of the “AEM”. The Mg atom is an exceptional case, for instance, showing a much smaller binding energy compared to other AEM atoms. The deviation of Mg is attributed to its significantly large ionization energy.

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I. INTRODUCTION

Adsorption of alkali metals (AM = Li, Na, K, Rb) and alkaline-earth metals (AEM = Mg, Ca, Ba) on Si(111) and Ge(111) surfaces was known to induce the $(3 \times 1)$ reconstruction, as observed in low-energy electron diffraction (LEED) [1–5]. The $3 \times 1$ surfaces of Si(111) and Ge(111) induced by AMs have been extensively investigated both experimentally and theoretically [1, 2, 6–14]. A consensus on the detailed atomic geometry of the Si(111)$3 \times 1$-AM surface has been reached after a long debate. It is the so-called “honeycomb chain-channel (HCC)” model consisting of nearly planar honeycomb chains separated by empty channels in the topmost layer [15–17]. The coverage of AMs is 1/3 monolayer (ML). A similar reconstruction was suggested for the Si(111)$3 \times 1$-AEM LEED phase based on the similarity in LEED $I$-$V$ curve observed for Mg [3]. Also, the metal coverage has been assumed to be 1/3 ML, the same as that of the Si(111)$3 \times 1$-AM surface.

However, in a series of previous works on the Ba/Si(111) system [18–20], we have found that the Si(111)$3 \times 1$-Ba LEED phase indeed has a $3 \times 2$ periodicity with a Ba coverage of 1/6 ML and the HCC substrate structure. From the similarity in the Si substrate reconstruction between the Si(111)$3 \times 2$-Ba and the Si(111)$3 \times 1$-AM surfaces deduced from the filled-state scanning tunneling microscopy (STM) images, we examined the models proposed for the Si(111)$3 \times 1$-AM surface [20]. Figure 1 shows those models: (a) the HCC [15,16], (b) the extended Pandey chain (EPC) [21], (c) the Seiwatz chain [22], and (d) the double-$\pi$-bonded chain (D$\pi$C) [23] models. To accommodate the experimentally determined 1/6 ML AEM coverage, every other atom in the AEM row was removed from the original models, leading to a $3 \times 2$ unit cell. The HCC structure was found to be the most favorable among various candidate structures, similarly to the case of AM/Si(111). We then proposed that the HCC structure is commonly adopted for the other AEM atoms. A divalent rare-earth atom, Sm, was also shown to induce the $3 \times 2$ HCC reconstruction [24].

In this paper, we examine our previous proposition by employing ab initio calculations to investigate the atomic and electronic structure of the Si(111)$3 \times 2$-AEM (AEM=Mg, Ca, Sr) surface. Similarly to the Ba case, the other AEM atoms are found to induce the HCC reconstruction. Then, we discuss the differences in the detailed properties of the Si(111)$3 \times 2$ reconstruction for different AEM adsorbates.

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II. CALCULATION METHODS

Total-energy calculations were carried out within the local density approximation (LDA) by using the Vienna *ab initio* simulation package (VASP) [25]. Plane waves up to energies of 250, 400, 226, and 150 eV were included to expand the wave functions for the (Mg, Ca, Sr, and Ba)/Si(111) systems, respectively. The atoms, except Sr, were represented by ultrasoft pseudopotentials as provided with VASP [26]. Electron-ion interactions for Sr were described using the projector augmented wave (PAW) potential [27, 28]. In the surface calculation, the theoretical lattice constant of 5.39 Å was used. The Si(111)3 × 2-AEM surface was modeled by using a repeated slab geometry. The slab consisted of an AEM atom (1/6 ML), a surface Si layer, four subsurface Si layers, and an H layer passivating the bottom surface. The surface layer contained different numbers of Si atoms for different structure models. For the surface Brillouin-zone integration, we used a 2 × 3 grid in the Monkhorst-Pack special *k*-point scheme. Gaussian broadening with a width of 0.02 eV was used to accelerate the convergence in the *k*-point sum. We determined the relaxed atomic positions by minimizing the total energy and the Hellmann-Feynman forces: Atomic positions were relaxed until the residual forces were smaller than 0.01 eV/Å with the bottom Si and H layers kept fixed.

### III. RESULTS AND DISCUSSION

In order to compare surface structures with different silicon coverages, we consider the surface formation energy $\Delta E_s$ (relative to the HCC model) for each model, which is defined by

$$\Delta E_s = E_{\text{tot}}(\text{model}) - N_{\text{Si}}E(\text{Si}) - E_{\text{tot}}(\text{HCC}),$$

where $N_{\text{Si}}$ is the change in the number of Si atoms referred to the HCC model ($N_{\text{Si}} = 0, 4, -4, 0$ for HCC, EPC, Seiwatz, and DπC, respectively). $E_{\text{tot}}(\text{model})$ is the total energy of a specific model and $E(\text{Si})$ is the Si bulk energy. In a previous work, it was found that the HCC structure is the most favorable for the Ba case and that the DπC model is unstable [20].

Since AEM atoms such as Mg, Ca and Sr belong to the same group, group II, as Ba, the HCC structure is expected to be favorable for other AEM cases. This is confirmed by the calculated surface energies ($\Delta E_s$) presented in Table 1, where the band gap ($E_g$) for various structures are also listed. For comparison, we list the values of $\Delta E_s$ and $E_g$ that were previously calculated for the Si(111)3 × 2-Ba surface [29].

Table 1. Surface energies ($\Delta E_s$) per (3 × 2) unit cell (relative to the HCC model having the lowest energy) and band gaps ($E_g$) calculated for various structures. The energies are given in eV. For comparison, we give the previous results for the Ba case.

<table>
<thead>
<tr>
<th></th>
<th>HCC $\Delta E_s$</th>
<th>EPC $\Delta E_s$</th>
<th>Seiwatz $\Delta E_s$</th>
<th>HCC $E_g$</th>
<th>EPC $E_g$</th>
<th>Seiwatz $E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.0</td>
<td>0.61</td>
<td>0.67 (0.83)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6 (0.4)</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0</td>
<td>1.01</td>
<td>0.98 (1.15)</td>
<td>1.0</td>
<td>0.6</td>
<td>0.6 (0.4)</td>
</tr>
<tr>
<td>Sr</td>
<td>0.0</td>
<td>1.02</td>
<td>0.99 (1.15)</td>
<td>1.0</td>
<td>0.6</td>
<td>0.6 (0.4)</td>
</tr>
<tr>
<td>Ba</td>
<td>0.0</td>
<td>0.81</td>
<td>0.84 (1.00)</td>
<td>0.9</td>
<td>0.6</td>
<td>0.6 (0.4)</td>
</tr>
</tbody>
</table>
Table 2. Total energies ($\Delta E$) at different sites relative to the $T_4$ site in the HCC structure with 1/6 ML AEM.

<table>
<thead>
<tr>
<th></th>
<th>$T_4$</th>
<th>$H_3$</th>
<th>$B_2$</th>
<th>$C_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$ (eV/Mg)</td>
<td>0.0</td>
<td>-0.03</td>
<td>0.14</td>
<td>1.16</td>
</tr>
<tr>
<td>$\Delta E$ (eV/Ca)</td>
<td>0.0</td>
<td>0.09</td>
<td>0.33</td>
<td>1.11</td>
</tr>
<tr>
<td>$\Delta E$ (eV/Sr)</td>
<td>0.0</td>
<td>0.08</td>
<td>0.27</td>
<td>1.11</td>
</tr>
<tr>
<td>$\Delta E$ (eV/Ba)</td>
<td>0.0</td>
<td>0.01</td>
<td>0.15</td>
<td>0.86</td>
</tr>
</tbody>
</table>

and $H_3$ sites are almost degenerate for the Ba/Si(111) system. The surface energies in Table 1 are referred to the HCC model with the Mg, Ca, Sr, and Ba adsorbates located at the $H_3$, $T_4$, $T_1$, and $T_4$ sites, respectively.

In Table 1, note that the values in the parentheses of the last column represent those for the original Seiwatz model. The original Seiwatz model can be further relaxed by allowing the Ba atoms to move along the chain direction on the surface. This lowers the energy by about 0.16 eV/(3×2). Similarly to the Ba case, the Drz structure is unstable for the examined AEM atoms. This structure relaxes to a structure (not shown), which is higher in energy than the other structures. As a result, we found that the HCC structure is the most favorable for the Si(111)3×2 surface, suggesting a similar Si reconstruction. The band gap of Sr is almost the same as that of Ca. The band gap corresponds to the π-π* band split in these systems [30].

There is a large body of experimental data on the Si(111)3×2 surfaces induced by different AEMs [18,31–37]. Most of these data are mainly from photoelectron spectroscopy (PES) [31–33] and STM [18,34–37] measurements. The electronic bands mapped using PES are well matched with those calculated for the HCC model applied to the AM-induced Si(111)3×1 surface [15,16]. The filled-state STM images obtained for Ca [36,37] and Ba [18] are also quite similar to those for the AM-induced Si(111)3×1 surface, suggesting a similar Si reconstruction. The empty-state STM data commonly show an obvious 3×2 periodicity of the adsorbed metal atoms [18,20,34,37]. All these data can be accounted for by presuming that the AEM-induced Si(111)3×2 surface adopts the HCC structure with 1/6 ML of metal coverage, as directly confirmed for the Ba case [18]. Our calculations find that the HCC model is more favored in energetics over other available structural models for all other AEMs, strongly supporting our presumption.

For the lowest energy configuration (the HCC structure) of each AEM atom, we calculate the binding energy for adsorption, $E_b$ [38]:

$$E_b = - [E_{tot}(HCC) - E_{AEM} - E_{tot}(clean) - N_{Si}E(Si)],$$

where $E_{AEM}$ and $E_{tot}(clean)$ are the total energies of the free AEM atoms and the unreconstructed clean surface, respectively. $N_{Si}$ is the difference in number of the Si atoms between the clean and the HCC 3×2 surfaces, which is equal to 8. The binding energies are listed in Table 3 along with the structural parameters. The binding energies for Ca, Sr, and Ba are within about 0.3 eV, while that for Mg is much smaller compared to other AEM cases. In the AEM/Si(111) systems, the AEM atoms are fully ionized and have a charge state of 2+. The ionization energy is larger for smaller AEM atoms. The energy gain from the Coulomb interaction between the AEM ion and the dangling bond electrons of the surrounding Si is also larger for smaller AEM atoms because of the shorter AEM-Si distance (see Fig. 2 and Table 3).

The increased Coulomb energy gain seems to be largely compensated by the ionization energy cost in Ca, Sr, and Ba, yielding the similar binding energies. However, the smallest of the examined AEM atoms, Mg, constitutes an exceptional case by having a much smaller binding energy. We conjecture that the deviation of Mg is due to its significant ionization energy. The ionization energy to remove two electrons is 22.67 eV for Mg, which is much larger than those of other AEM atoms: 17.98, 16.72, and 15.21 eV for Ca, Sr, and Ba, respectively [39]. The energy cost for the ionization of Mg may compensate for a significant part of the energy gain obtained from the Mg-Si Coulomb attraction, leading to the smallest binding energy.

Figure 2 shows the schematics of 3×2 HCC structures with AEM atoms at the $T_4$ and $H_3$ sites. Detailed
structural parameters (indicated in Fig. 2) are summarized in Table 3: $z_i$ is the height of the AEM atom from the surrounding top-layer Si atom labeled $i$, while $d_i$ is the distance between the AEM atom and the Si atom labeled $i$. $db1$ and $db2$ represent the lengths of two inequivalent Si (double) bonds. In the relaxed structure, the Mg, Sr, and Ca atoms lie at positions of nearly equal distance from the top-layer Si atoms (labeled 1, 2, and 3) within about 1 – 2 %, while the Ba atoms lie within about 0.3 %. It is worthwhile to note that the equilibrium AEM-Si bond lengths tend to shorten in order of Ba, Sr, Ca, and Mg. The smaller Mg atom naturally forms a shorter AEM-Si bond compared to other larger elements. Such a trend has been observed in a theoretical investigation of AM/Ge(111) [38].

On the other hand, the heights ($z_i$) of the AEM elements relative to the top-layer Si atoms are very different and tend to be lower in order of Ba, Sr, and Ca, except Mg. The height of Ca is almost equal to that of the Si top layer, while those of Sr and Ba are about 0.2 – 0.3 and 0.6 – 0.7 Å, respectively. The height of Mg is exceptionally high (about 0.5 Å) even though Mg has the smallest ionic radius among the AEM elements considered. This can be understood in terms of a narrowing of the channel width between the honeycomb chains. Due to the strong Mg-Si Coulomb interaction, the distance in the $x$ coordinate between the Si atoms labeled 1 and 2 (or 3) surrounding the Mg atom becomes shorter by 0.2 – 0.5 Å compared to other AEM cases. This narrowing of the channel width may cause the Mg atoms pushed to lift up; thus, the height of the Mg atoms becomes exceptionally high.

The existence of Si double bonds in the honeycomb chains of the AEM/Si(111) systems, except for Mg, is manifest in $db1$ and $db2$ of Table 3. The bond-length reduction is largest in the Ba case compared to the bulk value of 2.33 Å. The Si double bonds tend to be slightly weakened in order of Ba, Sr, and Ca. For the Mg case, the $db2$ bond (= 2.28 Å) is considered to be a double bond, while the $db1$ bond (= 2.33 Å) is the single bond, slightly buckled (0.1 Å). This is consistent with the fact that Mg distorts the honeycomb chain significantly by pulling the surrounding Si dangling bonds.

In summary, we studied the atomic and electronic structure of Si(111)3 × 2 surfaces induced by the adsorption of alkaline-earth metals. Similarly to the Ba case, the HCC structure is also found to be the most favorable among various structures for the cases of Mg, Ca, and Sr. Therefore, the HCC structure is confirmed to be the common structure for the AEM-adsorbed Si(111) surfaces with 1/6 ML AEM coverages. Different AEM atoms reveal a trend in their structural and electronic properties that can be easily understood in terms of the atomic size and the ionization energy. The Mg constitutes an exceptional case due to its significantly large ionization energy and its strong interaction with Si dangling bonds.

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REFERENCES

[29] The band gaps shown in Table 1 are obtained by using the tetrahedral method, which corrects some of the band gap values reported in Ref. 20. Especially, the band gap for the HCC model is corrected to 0.9 eV, which is still smaller than the experimental value (1.0 eV).