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First-principles study of lithium adsorption on Si(1 0 0)2 × 1 and Ge(1 0 0)2 × 1 surface at 1.0 monolayer coverage

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Abstract

First-principles calculations based on density functional theory have been carried out to determine the atomic structure and electronic properties of the Si(1 0 0)2 × 1–Li and Ge(1 0 0)2 × 1–Li adsorption systems at 1.0 monolayer (ML) coverage. For the Si(1 0 0)2 × 1–Li chemisorption system, the lowest energetic configuration is that one Li atom resides at the T3′ (which is displaced along the positive *y*-axis from the valley bridge (T3) site by 0.90 Å) and the other resides at pedestal (HH) site. For the Ge(1 0 0)2 × 1–Li chemisorption system, the most stable configuration is found to be that one Li atom resides at HH site and the other one will penetrate deeply into the substrate surface. Chemisorption of the lithium atoms is found to result in a minimum energy configuration characterized by symmetric dimers in agreement with the results of high-resolution core-level photoelectron spectroscopy. The adsorption systems show semiconducting surface characterization.

Keywords: First-principles calculation; Lithium adsorption; Atomic structure

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1. Introduction

The interaction of alkali metals (AM) with semiconductor surface has been intensively studied for a long time due to both the fundamental interest and possible technological applications [1,2]. Several questions concerning the basic properties of the AM–semiconductor adsorption system remain controversial. These include the actual adsorption sites of the AM atoms, saturation coverage and the nature of the bond between the AM atoms and the substrate, and whether the AM atoms penetrate deeply into the substrate subsurface.

Of all the alkali metals, potassium and sodium on the Si(1 0 0) and Ge(1 0 0) surface have been widely investigated experimentally and theoretically [3–15]. Cesium and Rubidium on the Si(1 0 0) surface also been investigated [16–22]. However, Lithium, the lightest one of the alkali metals, has attracted much less interest. There is little theoretical calculations have been carried out for the adsorption of lithium on the Si(0 0 1) surface [23–27], although some experimental work devoted to studying were reported this system [28–35]. There's no report about the adsorption of lithium on Ge(1 0 0) surface. The small size of lithium makes Li adsorption in Si significantly different compared to the other alkali metals. The small size of the Li atoms leads to a higher ability to intermix and react with a semiconductor surface. In a combined Auger electron spectroscopy, low-energy electron diffraction (LEED), and electron energy-loss spectroscopy measurement of the Si(1 0 0)–Li system, it was shown the Li intermixes with the substrate at room temperature [36]. Johansson et al. [34] and Grehk et al. [31] investigated the Si(0 0 1)2 × 1–Li system for low (<1.0 ML) and high (>1.0 ML) Li coverage using high-resolution core-level photoelectron spectroscopy. They showed that the Si surface reconstruction changed from asymmetric to symmetric dimers for a Li coverage of 1.0 ML, and that beyond this coverage the Li atoms

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reacted with the substrate indicating the possibility of silicide formation. Kleine et al. [33], however, on the basis of similar experiments, argued against the creation of silicides and suggested that Li multilayers were formed. Results obtained from the metastable de-excitation spectroscopy (MDS) and thermal desorption spectroscopy (TDS) experiments of Hongo et al. [30] supported silicide formation and suggested that intermixing of the Li adatoms with the substrate starts at coverages of about 1.0 ML.

Using first-principles molecular-dynamics study of the Si(1 0 0)–Li surface, Morikawa et al. showed that the Li can adsorb beyond one monolayer and that at 2 ML the Si–Si dimerization disappears completely [23], and the most energetically favorable structure for 1.0 ML coverage would result from the two Li atoms sitting essentially at the pedestal (HH) and valley bridge (T3) sites. Theoretical calculations carried out by Ko et al. [37] predicted that chemisorption of the Li atoms at the pedestal (HH) and cave sites (T4) at the coverage of 1 ML. However, the energy difference between the T4-HH and T3-HH site adsorptions is extremely small, 0.01 eV per 2×1 unit cell. For Li adsorption either at the T4-HH or T3-HH sites, the Li atoms are well separated from each other and the dangling-bond orbital of the Si dimers are fully occupied. Apart from the symmetric positions, asymmetric positions also been predicted to be more energetically stable. Kobayashi et al. [24] predict that the Li adatoms occupied asymmetric positions 0.36 Å from the pedestal site HH along the HH-T3 direction in Fig. 1, and 1.00 Å from the valley bridge site T3 along the T3–T4 direction in Fig. 1. Shi et al. [25] predicted that for the lowest energy configuration the second lithium atom lies at the T3′ site which is displaced along the positive y-axis from the T3 site by 0.82 Å.

In the present work, ab initio plane-wave pseudopotential total energy method based on DFT were used to investigate the adsorption of Li-adsorbed Si(1 0 0) and Ge(1 0 0) surfaces at a coverage of 1 ML with the $p(2\times1)$ structure chosen as the substrate. The minimum energy Li adatom configuration and the nature of the AM–semiconductor bond were investigated.

2. Methods

Our calculations have been carried out using the ab initio total-energy within the density functional theory (DFT) framework. The interaction between ions and electrons is described using the ultrasoft pseudopotentials introduced by Vanderbilt [38] and provided by Kresse and Hafner [39]. The general gradient approximation functional proposed by Perdew and Wang known as PW91 [40,41] is untilized. The influence of different K-point sampling and plane-wave cutoff energy was explored in a series of test calculations and this lead to the calculations being performed with $6\times6\times1$ K-point sampling and a cutoff energy of 350 eV. The 2×1 periodic cell consisted of eight layers of silicon (or germanium) and a vacuum region of 24.6 and 26 Å for Si and Ge, respectively. All of the coordinates of the silicon (and germanium) atoms in the top four layers of the slab, plus those of the chemisorbed lithium atoms, were allowed to vary, while the atoms in the bottom four layers were fixed at the bulk truncated positions with each atom saturated by two H atoms.

The pseudopotentials of Si, Ge and Li atoms all have been tested. For bulk properties, the optimized lattice constant was 5.468, 5.766 and 3.445 Å for Si, Ge, and Li, respectively. These values are in agreement with experimental values of 5.43, 5.657 and 3.51 Å.

3. Results and discussion

3.1. Clean Ge and Si(1 0 0)2 × 1 surface

We determined the stable geometry of the Si(1 0 0)2×1 and Ge(1 0 0)2×1 surface before performing the adsorption calculations. We found an asymmetric dimer structure with a bond length $d_{\text{Si–Si}} = 2.30$ Å and a buckling angle of $\Phi_{\text{Si–Si}} = 17.6°$ for the clean Si(1 0 0) surface. These values are in good agreement with the results of the first principles calculations by Northrup [42], Uchiyama [43] and Ramstad et al. [44]: $d_{\text{Si–Si}} = 2.29$ Å and $\Phi_{\text{Si–Si}} = 17.5°$, $d_{\text{Si–Si}} = 2.28$ Å and $\Phi_{\text{Si–Si}} = 18.5°$, $d_{\text{Si–Si}} = 2.26$ Å and $\Phi_{\text{Si–Si}} = 18.3°$, respectively. These values are also in agreement with the experimental result [45]: $d_{\text{Si–Si}} = 2.24 \pm 0.08$ Å and $19 \pm 2°$.

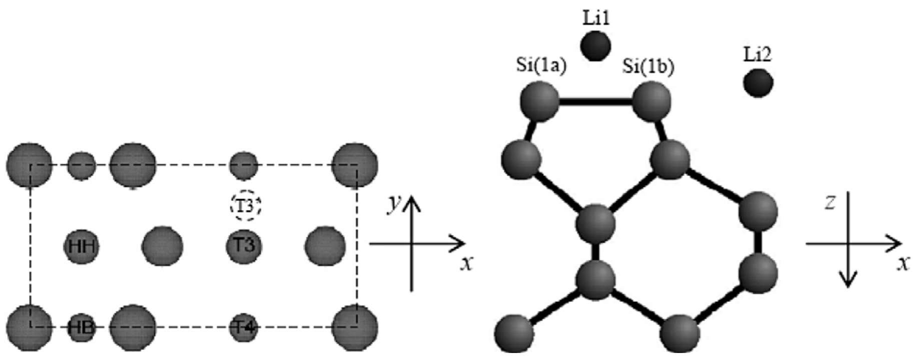

Fig. 1. Top and side view of the Si(1 0 0)2 × 1 structure. The pedestal, valley bridge, cave and bridge site are denoted by HH, T3, T4 and HB, respectively. The Si atoms from the first layer to the fourth layer are presented by dark gray balls with decreasing size for the top view.