First-Principles Study of Silicon-Embedded Ni(110)

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First-principles total energy calculations were performed to investigate stable atomic structures for the displacive adsorption of silicon on the Ni(110) surface. Gibbs free energies were compared for 0-4 silicon atoms embedded into the top layer in a 2×2 unit for the Ni(110) surface. When a half monolayer of Si was embedded, the p(1×2) structure had the lowest energy, and the c(2×2) structure had only 13 meV/1×1 higher energy than the p(1×2) structure. By extending to a 4×2 unit, the c(4×2) structures had almost the same energy with the p(1×2) structure. Alternating Si-Ni chains along the close-packed [1 1 0] row play an essential role to stabilize these structures. Si and Ni are alternatively aligned in separate [110] rows forming a p(2×1) structure, which had 276 meV/1×1 higher energy than the p(1×2) structure. For the p(2×1) structure, unique one-dimensional electronic bands derived by the Si-3s states were formed along the [110] direction. [DOI: 10.1380/ejssnt.2017.96]

Keywords: Density functional calculations; Compound formation; Surface relaxation and reconstruction; Nickel; Silicides

I. INTRODUCTION

Interaction between Si and Ni has drawn much attention since the beginning of surface science because Ni-Si compounds, frequently called Ni-silicides, have potential uses for advanced silicon microelectronic devices [1]. Since the lattice constants between Si and NiSi2 have a marginal difference, Ni-silicides can be epitaxially grown on Si substrates. An abrupt interface, which can be formed between Si and metallic NiSi2, is a prototypical metal-semiconductor junction. The study of carrier transports across interfaces showed that Schottky barrier heights are critically influenced by the details of bonding configurations between Si and NiSi2 [2, 3]. Inspired by this fact, atomic geometries and electronic states at the interface have been studied experimentally and theoretically scrutinized with a wide variety of techniques.

Most such studies, however, have focused on the thin Ni-silicide films that form on silicon substrates. The interfaces are usually formed by depositing Ni onto Si substrates, followed by a thermal treatment that leads to epitaxial Si-rich silicide overlayers. Ni-silicides may also be formed by Si deposition onto Ni substrates, and in this case Ni-rich silicides might be formed [4-7].

We address the very initial stage of silicide formation on a Ni(110) surface by focusing on the stable atomic configurations of Si-induced surface superstructures for Si coverage less than 1 ML. To seek the stable atomic configurations of Si-embedded Ni(110) surfaces and examine their electronic states, we applied the first-principles ab initio total energy calculation. We found that when a half monolayer of Si is embedded in the Ni(110) surface, the p(1×2), c(4×2) structures have almost the same adsorption energies, and the c(2×2) structure was only 13 meV/1×1 higher than the other superstructures. A common feature for these superstructures is alternative Si-Ni chains along the close-packed [1 1 0] row. If Ni and Si are formed with alternatively separated rows, our calculations show 276 meV/1×1 higher energy than the mixed-atom row. For the separated row structure, the Si row had a unique one-dimensional free-electron like dispersion along the [1 1 0] direction derived by the Si 3s states in the electronic band structure.

II. COMPUTATIONAL METHODS

We employed the first-principles calculation code based on the density functional theory [8], and used the projector-augmented wave (PAW) method for the Ni and Si potentials [9]. The spin-resolved local density functional was amended by the generalized gradient approximation (GGA) [10]. Before calculating the surface structures, we evaluated bulk fcc nickel and found that the lattice constant was reproduced within +0.2% compared to the experimental lattice constant and the cohesive en-
energy was 4.735 eV/atom. We then constructed a (110) oriented slab model with 2×2 and 4×2 surface unit cells in accordance with experimentally observed superstructures [7], and they are shown in Fig. 1. Si was embedded by replacing part of the Ni in the topmost layers. The slab was a 11 layers thick with 0.63-nm vacuum gaps on both sides. Except for the middle layer, all atoms were fully relaxed until the force fell below 0.1 eV/μm, and the wave function and the charge density were iterated until the total electron energy was converged to 10 μeV in the unit cells. We sampled a two-dimensional k-mesh \((k_x, k_y)=10\times12\) and \(5\times12\) along the [001] and [110] directions for the 2×2 and 4×2 unit cells, respectively. The cut off energy was set to 337 eV for all the calculations. We used the Methfessel-Paxton method to evaluate the partially filled electronic bands [11] and optimized the smearing energy width to \(\sigma=0.12\) eV.

### III. RESULTS AND DISCUSSION

We first recalculated the Ni(110) surface and compared it to our previous study because we adopted an improved functional here [12]. Our calculation showed the layer spacing between the first to the second \((d_{12})\) shrunk by -10.48%, which is slightly improved from -11.10% in the previous calculation. The second to the third \((d_{23})\) and the third to the fourth \((d_{34})\) spacings were +2.62% and +0.21%, respectively, which are also somewhat closer to the experimental layer spacings [7]. The surface energy was 1.238 eV/1×1 in this calculation.

We next calculated the surface models where one to four surface Ni atoms were replaced by Si in the surface 2×2 unit cell for several configurations as shown in Fig. 2. For the two Ni atoms replaced by Si, i.e., a half monolayer of Si coverage, three different configurations are possible. Here we define a Si configuration as `align` when the Si atoms are aligned along the [001] direction and form a p(1×2) reconstruction, `separate` when they are aligned along the [1¯10] direction and form a p(2×1) reconstruction, and `stagger` when they are obliquely lined up and form a c(2×2) reconstruction. For all the configurations, the calculations were performed for 2×2 unit cells with identical k-points.

Because the number of constituent atoms is different for these models in Fig. 2, the total energies were compared using bulk cohesive energies for Ni and Si. When the cohesive energies of Ni and Si are denoted by \(E_{Ni}^{slab}\) and \(E_{Si}^{slab}\), respectively, the total energies for different numbers of embedded Si can be written,

\[
E_{total} = E_{slab} - N_{Ni} E_{Ni}^{slab} - N_{Si} E_{Si}^{slab},
\]

where \(N_{Ni}\) and \(N_{Si}\) are the numbers of Ni and Si atoms in the slab, respectively. We calculated the cohesive energies for the bulk Ni and Si using the same cut off energy as the slab calculations and respectively found 4.735 and 5.413 eV/atom for the bulk Ni and Si with optimum lattice constants. These values are somewhat larger than...
The respective cohesive energies, 4.44 eV/atom for Ni and 4.63 eV/atom for Si in the literature [13]. When the energy of the Ni(110) surface is taken as a reference, the relative energies of these Si-embedded structures in Fig. 2 can be compared using Eq. (1), and they are shown in Fig. 3 as a function of the Si coverage. In Fig. 3, $E_{\text{rel}}$ refer to a 1×1 surface unit cell.

For a half monolayer of Si, the three Si configurations in Fig. 2(c) are possible in the 2×2 unit cell, and their relative energies are indicated by different symbols in Fig. 3. For these structures, $\text{align}$ is the most stable ($\Delta E=0$ eV/1×1), and $\text{stagger}$ has slightly higher energy of $\Delta E=13$ meV/1×1 than $\text{align}$, whereas $\text{separate}$ has $\Delta E=276$ meV/1×1 higher energy than $\text{align}$. This indicates that the Si-Si bond along the close-packed [\(1\bar{1}0\)] direction is not favorable, but Si and Ni are alternatively aligned in the row. Referring to the energies of the $\text{align}$ and $\text{stagger}$ structures, $E_{\text{total}}$ decreases almost linearly as a function of Si coverage up to 0.5 ML and deviates upward beyond 0.5 ML. Decreasing $E_{\text{total}}$ from the Ni(110) surface ($E_{\text{rel}} < 0$) by embedding Si is direct evidence of positive mixing energy between Si and Ni even in the top surface layer. Bulk Si and Ni are miscible each other and form several stable Ni-silicides [14], and their formation energy has a positive curvature with Si composition [15]. For surface compounds, $E_{\text{rel}}$ is minimum around 0.5 ML indicating that Si coverage around 1 ML is not stable. Indeed, our previous scanning tunneling microscopy (STM) study showed an instability for Si deposition beyond 0.5 ML [7].

The 2×2 structures for a half monolayer of Si coverage can be extended along the [001] direction to form 4×2 superstructures in accordance with experimentally observed superstructures [7]. The low-lying energy structures such as $\text{align}$ and $\text{stagger}$ in Fig. 2(c) were employed as building blocks and extended along the [001] direction as shown in Fig. 4. In addition to simply extending $\text{align}$ and $\text{stagger}$, alternating them, called a $\text{cross}$, and doubling $\text{align}$ by one unit along the [001] direction, called a $\text{shift}$, can be constructed. We calculated the total energies for these structures with optimized atomic geometries. The relative energies referenced to $\text{align}$ are indicated in Fig. 4. The total energies were within 13 meV/1×1 for all the structures, indicating that they almost degenerated. The tenancy slightly higher energy for $\text{stagger}$, in which the embedded Si is obliquely aligned, is the same with the 2×2 unit cell. Referring to the accuracy of the present calculation, we cannot determine the true ground states among $\text{align}$, $\text{shift}$, and $\text{cross}$. Indeed we observed that those structures coexisted in our scanning tunneling microscopy study [7]. The crucial point for the stability of these structures is Si-Ni alternating chains along the [110] direction. Elimination of the Si-Si bond is an essential element of stabilizing the Si-Ni surface silicide.

On optimized atomic geometry, the top Si have more inward relaxation compared to the topmost Ni for all Si-embedded structures. For the low-lying energy structures in Fig. 4, all the Si was 19-20 pm lower than the top Ni. Higher energy structures such as $\text{separate}$ were only 13 pm lower relative to the top Ni row. The atom movements relative to the clean Ni(110) surface are illustrated in Fig. 5 for $\text{align}$ as an example of atomic geometry. The inward relaxation of Si affects the surrounding atoms; i.e., a 9.7 pm inward movement of the embedded Si at the top layer induces a 2.6 pm inward movement of Ni underneath and a 10.6 pm outward movement of Ni adjacent to the depressed Si in the [110] row. This outward movement of the top layer Ni pulls up underneath the Ni by 2.6 pm, resulting in the total undulation of the third layer of 5.2 pm. Although the surface atoms were displaced in the surface-normal direction, lateral displacements were

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FIG. 6. Partial density of states (PDOS) of Ni for (a)surface and bulk, and (b)Si-embedded structures. Labels, align, stagger, and separate correspond to those shown in Fig. 2. (c)PDOS of Si for Si-embedded structures. Labels correspond to those shown in Fig. 2 (d)The band structure of minor spin for separate. One-dimensional bands are indicated by colored broken lines. (e)Charge distributions for separate in the (110) plane (top panel) and the (001) plane (bottom panel) including Si.

less than 1 pm for all atoms, indicating that virtually no lateral displacement was induced by the embedded Si. The up-and-down movements of the surface atoms along the [110] direction are coherent in the [001] direction for align, but they are alternate for other structures, such as stagger, leading to a distortion of the surface layers, which might be one reason why the surface structures that do not align along the [001] direction have slightly higher energies than align.

We next discuss the electronic band structures of these surface structures. The partial density of states (PDOS) decomposed with spherical harmonics are displayed in Figs. 6(a) and (b) for surface Ni and Si, respectively. For the Ni(110) surface, the PDOS for the top Ni are compared with the Ni at the center of the slab, that is thought to be bulk, in Fig. 6(a). The width of the 3d-derived bands at the surface layer was about 3.3 eV compared to 4.8 eV for the bulk Ni, again slightly narrowed due to the lack of counterpart, as discussed previously [12]. The PDOS at the top Ni sites for align, stagger, and separate are compared in Fig. 6(b). The exchange splittings of the d-components were 0.46 and 0.48 eV for align and stag-
The PDOS for the top Si for align, stagger, and separate are compared in Fig. 6(c). The Si 3s components of these structures were isolated and localized around -8 to -10 eV from $E_F$, but the 3p components were spreaded around -5 to 5 eV and they were minimum around $E_F$. This suggests that the Si 3p states are hybridized with the Ni 4s and 4p states as well as the 3d states, but the Si 3s is rather isolated from the Si 3p bands. A prominent feature for the Si 3s PDOS for separate is due to the one-dimensional nature of the local density of states. The band structure of separate is depicted in Fig. 6(d) for the minority spin. The bottom of the Si 3s band has almost no dispersion along the $\Gamma - \frac{1}{2} Y$ direction (the [001] direction), but clear parabolas are seen for the $\Gamma - \frac{1}{2} X$ direction (the [110] direction). Similar parabolic band dispersions were also seen for the majority spin (not shown here). The effective masses for the lowest three parabolas are 1.18$m_0$, 1.05$m_0$, and 1.15$m_0$ from the lowest band, where $m_0$ is the free electron mass. The charge distribution of the lowest 3s bands that is indicated by a red broken line in Fig. 6(d) is displayed in Fig. 6(e). The charge is confined around the surface Si along the [110] row. This is direct evidence that the bands have a one-dimensional character.

We now discuss the implication of the present results. For a half monolayer of Si, alternating Si and Ni in close-packed [110] rows have lower energy than the separated configuration. A few metal-embedded superstructures, such as Sn/Ni(110) [16, 17], Mn/Ni(110) [18, 19], were previously reported on the Ni(110) surface, and only the c(2×2) superstructure was stabilized for both surfaces. This shows a marked contrast to the present Si/Ni(110) where p(1×2) coexists with c(2×2). For the Sn/Ni(110) surface, the atomic radius of Sn is about 20% larger than that of Ni, leading to compressive stress both in the [001] and [110] directions. The surface stress can be partly relieved by the outward relaxation of Sn, and 40±3 pm protrusion was reported by low-energy electron diffraction (LEED) and 33±6 pm by medium-energy ion scattering (MEIS) [16] as well as 47 pm by the first-principles calculation [17]. This stress can be further relieved by alternately locating Sn along the [001] direction to stabilize the c(2×2) configuration. For the Mn/Ni(110) case, the atomic radius of Mn depends on the magnetic states, and a ferromagnetic state gives a larger atomic radius [18, 19]. The outward relaxation of Mn was 30±3 pm by surface x-ray diffraction [18] and 26 pm by the first-principles calculation [19]. Therefore, similar compressive stress to the Sn/Ni(110) surface is expected, again stabilizing the c(2×2) configuration. For the present case, although the bond lengths between Si and Ni for typical bulk Ni-silicides are larger than that of the Ni-Ni distance, the atomic radius of Si is smaller than that of Ni, leading to inward relaxation [22]. This leads to tensile stress along the [001] direction, but since its amount is small, the energy gain by alternately locating Si along the [001] direction is also negligible. This is another reason why p(1×2) is also stabilized with the c(2×2) configuration.

Compared to the Ni surfaces, the Si-adsorbed Cu surface has been extensively studied because Si-Cu has a fundamental importance for metal-semiconductor interface formation. On the Cu(110) surface a Si-embedded c(2×2) structure is formed for a half monolayer of Si. Similar to Si/Ni(110), Si was embedded into the top layer and had an inward relaxation of 24 pm by LEED [20], 26±4 pm by x-ray photoelectron diffraction combined with LEED analysis [22], and 13 pm [21] and 24 pm [23] by first-principles calculations. These inward relaxations of embedded Si resemble the present calculation for the Si/Ni(110) surface and experimental observations [7]. Curiously, even for an STM observation, no p(1×2) structure has been seen on the Si/Cu(110) surface [24]. One possible explanation is that for the Si/Ni(110), Ni 3d is located near $E_F$ and takes part in the bonding to Si 3p, but for the Si/Cu(110) surface, Cu 3d is almost intact even if embedded in the [110] row [23]. The embedded Si in the row is therefore diagonally bonded to the Si in the adjacent row through second-layer Cu, forming a c(2×2) structure in the top layer [22]. This directional bonding stabilizes the c(2×2) structure more than the straight p(1×2) structure. On the Ni(110) surface, however, due to the strong covalent bond between Si and Ni, the order of Si in the adjacent [110] row scarcely affects the formation energy. This explains why the p(1×2) also stabilized on the Si/Ni(110) surface.

One-dimensional electronic states for the Si 3s-derived bands in separate are another important finding for the Si/Ni(110) surface. Although one-dimensional bands will provide opportunities for unique electronic properties [25], the separate structure has higher energy than other structures such as align and stagger, and therefore it is not easy to align Si in a [110] row. However, if the separate structure could be synthesized by manipulating the surface atoms or employing surface steps, it would have an unique electronic properties.

IV. CONCLUSION

We performed a first-principles calculation for Si-embedded Ni(110) surfaces and found that p(1×2) and c(2×2) structures are the most stable in a 2×2 unit cell in good agreement with experimental observations [7]. When the 2×2 unit cell was extended to the [001] direction to form a 4×2 unit cell, the mixed structures between the p(1×2) and c(2×2) superstructures also had total energy close the p(1×2) and c(2×2) structures, and these structures were again experimentally observed. A common feature for these structures is alternating Si-Ni chains in the close-packed [110] row that plays an important role for stabilizing these surface structures. As was previously pointed out [7], the alternating Si-Ni chain resembles the atomic structure of the (110) plane for bulk $\beta_1$-Ni$_3$Si and its lattice constant is only 0.5% smaller than that of the p(1×2) structure on the Ni(110) surface. Therefore it may be possible to grow epitaxial Ni-silicide films on the c(2×2) and/or the p(1×2) structure if Si and Ni are simultaneously deposited with stoichiometric composition.
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