Structural and Electronic Properties of Ordered Single and Multiple Layers of Na on the Si(111) Surface

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Na-induced 3×1 reconstruction on the Si(111) surface was studied using a scanning tunneling microscope and other tools. Atomic images showed that this surface consisted of Na zigzag chains separated by a missing row, which covered the bulk-terminated Si(111) 1×1 substrate at the coverage of $\frac{2}{3}$. Upon further deposition, a Na multilayer was grown following the Stranski-Krastanov mode. Tunneling *I-V* curves showed that the first layer of Na was insulating but the insulator-metal transition occurred in the second layer. We propose, based on the structural analysis, that this transition represents a two-dimensional Mott-Hubbard system.

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Alkali metal overlayers have been studied intensively because of their importance in technology and science. In particular, the interface structure and the coverage-dependent metallization of alkali metal overlayers on semiconductor surfaces remain a controversial subject. As an example, Aruga, Tochihara, and Murata [1] proposed that a plasmon peak from the K overlayer on the Si(100) 2×1 surface was due to one-dimensional metallic K chains formed at the saturation coverage of $\frac{1}{2}$ monolayer (ML). However, from their angle-resolved photoemission study, Enta *et al.* [2] argued that this surface was semiconducting at the saturation coverage. In a subsequent experiment using x-ray photoelectron diffraction, Abukawa and Kono [3] proposed that the saturated K coverage was not $\frac{1}{2}$ but 1 ML so that there were an even number of valence electrons per surface unit cell, which would render the surface semiconducting in a single-particle picture. The structure of this surface is still under dispute. In another example, the insulating Cs monolayer on the GaAs(110) surface has been attributed to the two-dimensional Mott system [4]. According to the surface schematic in that Letter [4], deduced from a scanning tunneling microscopy (STM) image at low Cs coverages [5], there is an unpaired electron per surface unit cell, which would render the surface otherwise metallic. A similar result was obtained from the Cs-covered InSb(110) surface [6]. However, because Cs forms clusters above monolayer coverage on these surfaces, a clear structural analysis in connection with the electron correlation effect was rather difficult [4].

In this Letter, we report the first observation of an atomically resolved Na overlayer on the Si(111) surface at full monolayer coverage. The system we studied was the Na-induced 3×1 reconstruction on the Si(111) surface. Recently, this surface has attracted a renewed interest because of its inactivity against oxidation [7], contrary to the general belief that alkali metal adsorption should enhance surface chemical reactivity. Therefore, a detailed documentation of this surface should have new bearing on the alkali-metal-adsorbed semiconductor surfaces. The atomic image of the 3×1 surface showed that this surface consists of a single layer of Na zigzag chains separated by a missing row formed on the Si(111) 1×1 substrate. Further Na deposition at room temperature resulted in an ordered multilayer film through island formation. Tunneling spectroscopy showed that the first Na layer was insulating but an insulator-metal transition occurred in the second layer.

The experiment was performed using a UHV STM equipped with LEED/AES (Auger electron spectroscopy) optics, and a field-ion microscope (FIM) for *in situ* tip cleaning and manipulation [8]. The base pressure was typically $\leq 4\times10^{-11}$ Torr. Tips were fabricated by electrochemically etching the (111) oriented W wire. Si(111) samples (boron doped, 3 Ω cm) were degassed at 700 °C overnight and repeatedly annealed to 1220 °C for cleaning. After obtaining the 7×7 structure, Na was deposited using SAES getter sources on the surface heated at 360 °C. Before STM measurements were performed, the 7×7 to 3×1 conversion was confirmed with a LEED observation which showed a gradual replacement of the 7×7 spots by the 3×1 spots. Further deposition after the conversion was completed did not induce formation of any new structure, indicating that the Na coverage of the 3×1 surface represents the saturation coverage at this temperature. The Na multilayer was grown by dosing Na onto the initial 3×1 surface kept at room temperature. STM images were obtained in constant-current mode with bias voltages applied to the sample. The work function change was determined by the secondary electron cutoff using the LEED/AES gun.

At the initial stage of Na deposition at 360 °C, long channels of the 3×1 structure formed at the step edges [9]. The unconverted region was disordered but the dimer chains could be easily distinguished. Upon further exposure, the 3×1 region expanded by converting adjacent 7×7 unit cells (denoted as *domino growth*) until the growth front reached the step edge at the other end of the terrace. The image of the completed 3×1 surface [Fig. 1(a)] shows that the entire 7×7 surface is replaced by three equivalent domains of the 3×1 structure. In addition, one can see newly formed island structures and meandering step edges. As will be discussed below, these features are the result of Si adatom diffusion. An atomic image in Fig. 1(b) shows that the 3×1 structure consists of zigzag chains separated by a missing row along the dimer chain direction of the original 7×7 surface. The interatomic distance of Na, as determined using the calibrated piezo scanner, showed that the Na overlayer was well commensurate with the Si(111) 1×1 plane. There are two Na atoms per 3×1 unit cell, and thus the (saturation) coverage is uniquely determined to be $\frac{2}{3}$ ML in units of Si(111) 1×1 top layer atoms.

To determine the Na bonding site and to elucidate its interface properties, we annealed the 3×1 surface to sublimate the Na overlayer and to disclose the underlying Si substrate. At about 420 °C, Na atoms began to desorb, initially from the step edges as shown in Fig. 2(a). One could then see, from the unveiled Si region, the presence of subunit cells of the 9×9, 5×5, and 7×7 structures as well as the disordered Si adatom structure. This image also shows interesting chain structures along the domain boundary, which was observed quite often. We assigned these bright spots in the chain to the Si adatoms. From this image, it is clear that the Na overlayer is a single layer and that Na does not intermix with Si. A complete recovery of the 7×7 surface was achieved at about 700 °C. These results suggest that, upon the 3×1 reconstruction, the Si 7×7 substrate converted to the bulk-terminated 1×1 structure. In general, epitaxial layers grown on the hexagonal-close-packed surface form three domains rotated relative to each other by 120° [Fig. 1(a)] due to the symmetry imposed by the substrate. The Si(111) surface reconstructs to the 2×1 structure when cleaved. However, it is not likely that the 2×1 is the structure of the Si top layer under the Na overlayer, because one cannot accommodate the 3×1 overlayer on the 2×1 substrate while keeping the Na bonding site consistent. The total energy calculation for the K adsorbed Si(111) surface also showed that the 1×1 substrate was more stable than the 2×1 substrate [10]. There are more adatoms on the 7×7 structure than necessary to fill the corner holes for the conversion to the 1×1 structure [11]. Therefore, the excess Si adatoms would diffuse to the step edge or coalesce to form islands shown in Fig. 1(a). The 3×1 structure initially formed at the step edges and expanded into the terrace through the chain reaction. This is because the breakup of the dimer chain, a barrier to the Si atom diffusion, is easier at the step edge and at the growth front than in the midterrace.

By extrapolating the Na region into the Si region in the same image of the annealed surface [Fig. 2(a)], we determined that Na atoms adsorb on top of the second-layer Si atoms (T_4 site). The schematic of the 3×1 surface is displayed in Fig. 2(b). The diagram also shows a possible bonding site of the Si adatom chain shown in Fig. 2(a).

In the general case of room-temperature deposition of alkali metals on semiconductors, the work-function change saturates without going through a minimum. The increase in the work function and the concomitant metallic signal are usually detected when the second layer is grown at cryogenic temperatures. To our surprise, however, our STM images showed that a highly ordered Na multilayer could be grown by room-temperature deposition onto the 3×1 surface, i.e., the Na first layer. For the second-layer growth, Na atoms nucleated homogeneously, *on top of the missing Na rows of the first layer* [Fig.

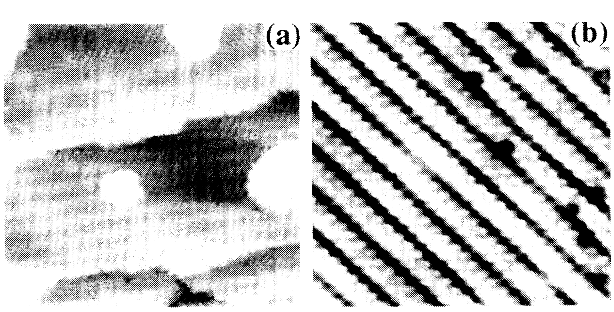

FIG. 1. (a) STM image (430×480 Å^2) of the Na-induced 3×1 surface. The black dots are vacancy defects. $V_s = -2.5$ V, $I_t = 20$ pA. (b) Atomic image (90×100 Å^2) of the Na zigzag chains. $V_s = -1.6$ V, $I_t = 20$ pA.

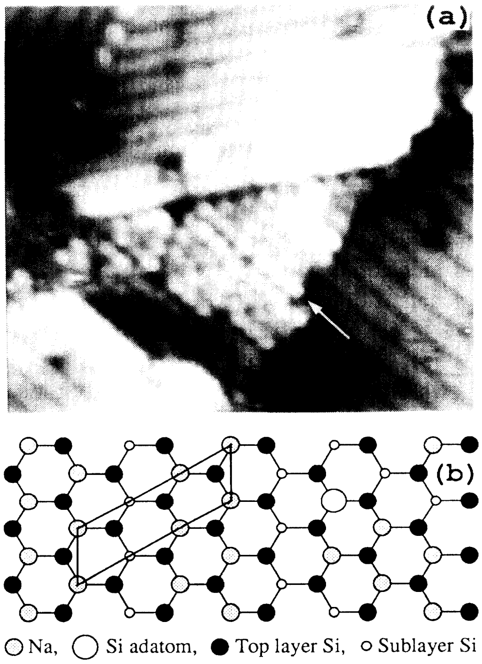

FIG. 2. (a) Si(111) 3×1-Na surface (140×180 Å^2) after annealing to 420 °C to partially desorb the Na overlayer. Note that the white arrow (missing Na row) is aligned with the Si adatom row occupying T_4 site. $V_s = -1.6$ V, $I_t = 20$ pA. (b) A schematic top view of the Si(111) 3×1-Na surface.

3(a)], to form an epitaxial layer of the 3×1 structure [Fig. 3(b)]. The 3×1 LEED pattern from the second layer was almost as perfect as that of the first layer. In Fig. 3(b), some of the individual Na atoms are resolved, which shows that the second-layer Na chains are not zigzag but linear. This means that the coverage of the second layer alone is $\frac{1}{3}$ ML. Upon further deposition, third-layer Na chains nucleated inhomogeneously, *over the top of the missing Na rows of the second layer*, and eventually a multilayer film was grown through island formation [Fig. 3(c)]: The growth of the Na multilayer followed the Stranski-Krastanov mode. As the third layer was formed, LEED showed a streaky 3×1 pattern arising from the irregular spacing between the chains. The schematic side view of the first and second layers based on the STM images is drawn in Fig. 3(d).

We have also deposited other alkali metals onto the heated Si(111) 7×7 surface, and found that K induced a poor-quality 3×1 structure but Li and Cs did not. This result suggests that the highly ordered Na multilayer on the Si(111) 1×1 substrate was possible due to the small lattice mismatch between the bcc Na(110) and the Si(111) planes. A detailed structural analysis of the Na multilayer together with the results from other alkali-metal-induced structures will be presented elsewhere [12].

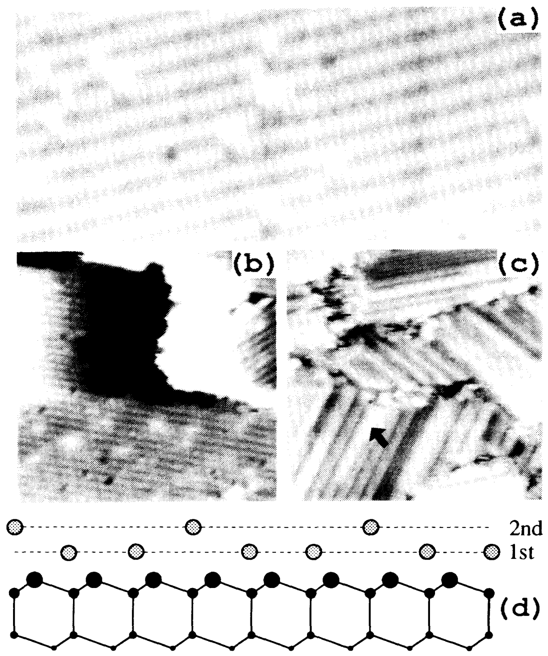

FIG. 3. (a) STM image of the early stage of Na second layer (230×105 Å^2). $V_s = -3$ V, $I_t = 20$ pA. (b) A completed epitaxial second layer (350×370 Å^2). The shadow is due to the background subtraction. $V_s = 1.6$ V, $I_t = 20$ pA. (c) A Na multilayer (350×480 Å^2). The arrow marks a fourth layer. The sample bias voltage was only -0.1 V. $I_t = 20$ pA. (d) A schematic side view of the first and second layers of Na. Dotted and filled circles denote Na and Si atoms, respectively. The broken lines are a guideline.

Theoretical studies by Batra and Ciraci [10] and by Northrup [13] suggested that alkali metals make a strong ionic bonding on the Si(111) 1×1 surface, and as a result the work function decreases by as much as 2.7 eV. However, our measurement showed that the work function decreased by only about 1.6 eV for the Na first layer. This small work-function decrease implies that the present interface is polarized covalent but not ionic, which agrees with the recent theory of Ossini, Arcangeli, and Bisi [14].

An attempt to image the Na first layer using low bias voltages resulted in the tip-surface contact. Indeed, the tunneling I-V curves obtained from the first layer exhibited a distinct energy gap, as seen in Fig. 4. As the second layer was formed, however, we could obtain the image with decreasing bias voltages. This is consistent with the I-V curve (Fig. 4) obtained from the completed second layer, which shows a closing of the gap: The insulator-metal transition occurred when the second layer was formed. The ideal Si(111) 1×1 surface is metallic because of the dangling-bond surface states [15]. In a single-particle picture, the Na-covered 3×1 surface also would be metallic because there is an unpaired electron per surface unit cell [Fig. 2(b)], which contradicts our results. We propose that the Na overlayer on the Si(111) 1×1 surface represents a two-dimensional Mott-Hubbard insulator: When the coverage is very low, each Na atom is isolated and forms a surface molecule with Si substrate atoms. One can think of two electronic states associated with such a molecule: a donor state to remove an electron from the molecule and an acceptor state to add an electron to the molecule [16]. These two states are separated by the Coulomb repulsion energy U, which gives rise to the tunneling gap [17,18]. As the coverage increases, the distinction between these two states becomes smaller. However, the I-V curve (Fig. 4) obtained from the Na first layer [Fig. 1(a)] shows that the two states are still separated at the $\frac{2}{3}$ ML coverage. Upon further deposition, the second-layer Na atoms adsorb over the missing rows, bridging the Na zigzag chains of the first layer. As a result, the donor and acceptor states

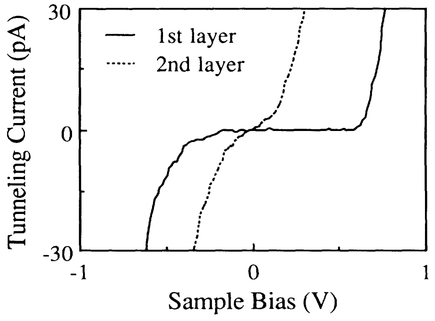

FIG. 4. Spatially averaged tunneling I-V curves obtained from the first and second layer of Na.

broaden into bands with the accompanying further decrease in the energy difference between them. When the second layer is completed, the wave functions of adjacent Na atoms overlap sufficiently over the entire surface. At this stage, the donor and acceptor states will overlap and the surface becomes metallic. Since the tunneling spectroscopy is surface sensitive, the observed metallic signal is due to the Na overlayer metallization.

The work function continued to decrease by about 3.8 eV until the completion of the second layer [12]. This is probably due to the relaxation or charge redistribution at the interface upon the second-layer formation. The work function increased, when the third layer started to form, which indicates that the film exhibits bulk properties (such as free electron excitation) from the third layer.

In conclusion, we have obtained the atomic structure of the single and multiple layers of Na on the Si(111) surface. We also showed that the Na first layer was insulating but the insulator-metal transition occurred as the second layer was formed at 1 ML coverage. We propose that the nature of this transition can be understood on the basis of the two-dimensional Mott-Hubbard system.

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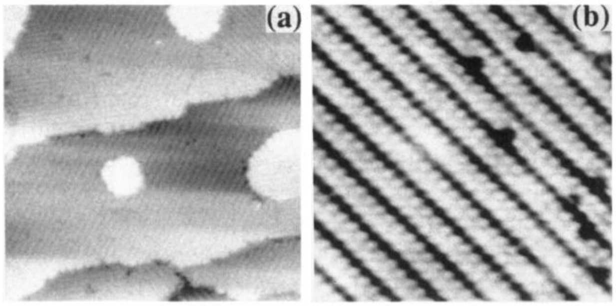

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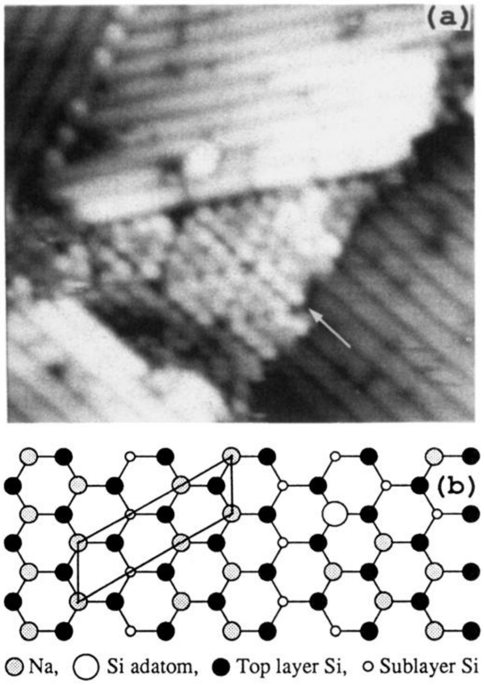

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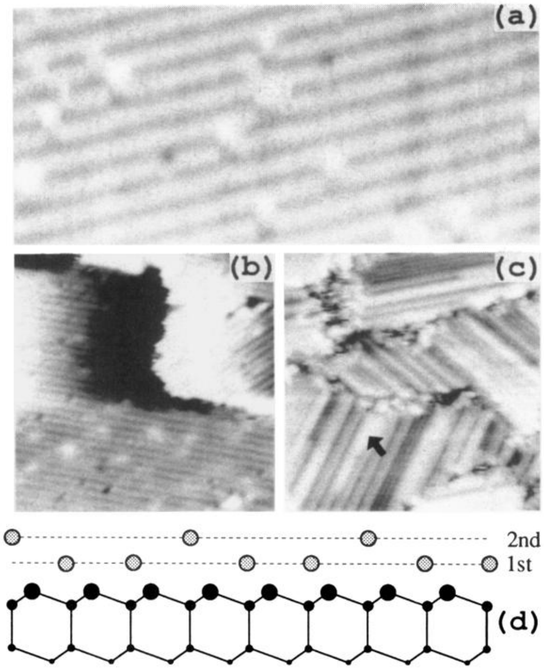

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