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Origin of the semiconducting nature of the Na-adsorbed Si(111) surface

Ki-Dong Lee and Jinwook Chung

Department of Physics, and Basic Science Research Institute, Pohang University of Science and Technology, Pohang, 790-784, Korea

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The change of electronic properties induced by Na adsorption on the Si(111)-(3×1) surface has been investigated by using high-resolution electron-energy-loss spectroscopy. We find that the initially (3×1) surface at 1/3 monolayer (ML) develops into an ordered (6×1) phase at 1/2 ML while keeping the surface semiconducting. The surface further transforms into another (3×1) phase at 2/3 ML still exhibiting the semiconducting nature before turning into a metallic phase at saturation. We ascribe this semiconducting nature of the surface above 1/3 ML to the bipolaronic effect primarily caused by the onsite electron-electron correlation. [S0163-1829(98)50204-4]

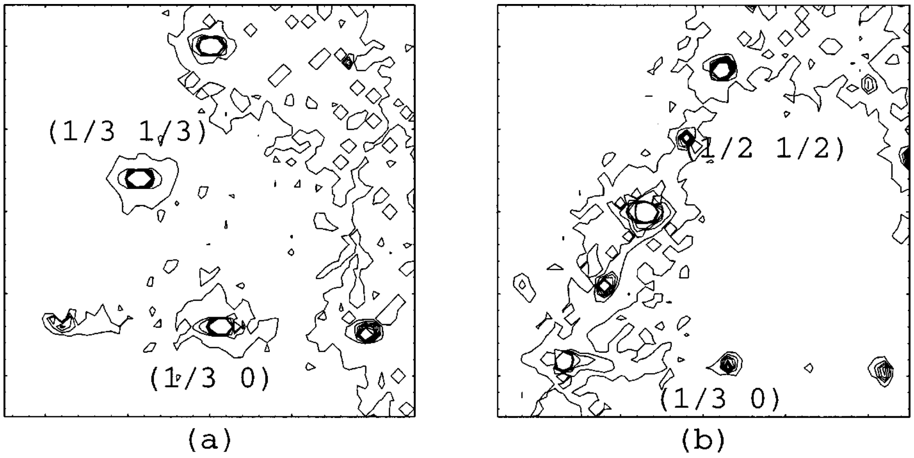
Alkali metal (AM) adsorption on semiconductor surfaces has been one of the classical problems in surface physics. Up until now, most studies have been performed with the expectation of tractability in understanding the surface phenomena induced by AM adatoms due to the rather simple electronic configuration of AM atoms. The nature, however, shows surface phenomena much more complicated to understand than expected. In particular, the change of electronic properties induced by AM adatoms remains unresolved despite the extended research efforts to date. Recent study on the electronic property of the AM/GaAs surface reveals a typical example of the complexity which requires a theory beyond a simple Bloch theory of band structure to understand the nature of the surface.[1–3] In addition, evidence of Mott insulating state has been suggested for the K/Si(111)-$\sqrt{3}\times\sqrt{3}R30°$-B surface.[4]

The AM-induced (3×1) reconstruction of the Si(111) surface has been studied extensively.[5–12] Jeon and co-workers reported a scanning tunneling microscopy (STM) study of the Na-induced (3×1) structure of the Si(111) surface, and proposed a 2/3 monolayer (ML) for the Na coverage.[5] This assignment of Na coverage predicting a metallic phase within the framework of the Bloch theory, however, conflicts with their own experimental observation that the surface remains semiconducting with an energy gap of 0.8 eV. The authors then proposed a Mott-Hubbard mechanism to resolve the contradiction. A later photoemission study confirmed the semiconducting nature of the surface.[6,7] Recently, a general consensus has been reached that the coverage is a 1/3 ML for the (3×1) surface.[7–10]

In this paper, we report high-resolution electron-energy-loss spectroscopy (HREELS) results for the Na adsorption on the Si(111) surface at room temperature. We find that although the semiconducting nature of the (3×1) surface at 1/3 ML can be understood in terms of the simple Bloch picture, the semiconducting nature of the surface above 1/3 ML may be ascribed to the surface polaronic effects as invoked also for the AM/GaAs surfaces.[2]

The experiment was carried out in an UHV chamber with a base pressure better than 3×10^{-11} mbar. A p-type B-doped Si(111) single-crystal surface was cleaned through several cycles of flashing at 1175 °C and annealing at 800 °C. The surface thus prepared showed a very sharp and bright (7×7) low-energy electron diffraction (LEED) pattern with a low background. The cleanness of the surface was also checked by x-ray photoemission spectroscopy (XPS) and HREELS. Na adatoms were evaporated by using commercial SAES dispensers which were thoroughly outgassed to minimize any impurity effects. The coverage was controlled indirectly by measuring the work function change, $\Delta\phi$, which was determined from the shift of secondary electron tail in XPS spectra. The electronic excitation spectra were obtained by using a Leybold ELS-22 spectrometer. The primary energy of the incident electron was 15.0 eV with energy resolution of 20 meV. The LEED data were collected from a spot-profile-analysis (SPA) LEED system. Adsorption of Na on the substrate kept at 400 °C produces a well-ordered and bright (3×1) LEED pattern [see Fig. 1(a)]. Further adsorption of Na at room temperature forms a (6×1) ordered phase [Fig. 1(b)] for a very narrow coverage range near $\Delta\phi=-2.0$ eV, which transforms into a (3×1) phase again.

The evolution of the loss spectra with increasing Na coverage is presented in Fig. 2 with $\Delta\phi$ shown in the inset. The measured $\Delta\phi$ versus deposition time curve is quite similar to that of Weitering and co-workers[8] except that the minimum is more pronounced in our data. The presence of the minimum indicates the formation of the second Na layer and is a typical sign of the metallization of the surface as confirmed by our electron-energy-loss (EELS) data. The bottom spectrum shows clearly the semiconducting feature of the (3×1) surface with an energy gap of 1.2 eV, as also reported by Weitering and co-workers.[8] Upon increasing the adsorption of Na, the energy gap decreases gradually and becomes 0.4 eV near the minimum of $\Delta\phi=-2.48$ eV, where the formation of the first Na layer is completed. Just above this coverage, one finds two relatively sharp loss peaks at 0.8 and 1.4 eV (S_3 and S_4 in Fig. 2). These peaks appear to develop earlier when the surface shows the (6×1) phase. As discussed later, regarding the excitations associated with these loss peaks, it is important to note that the loss energies remain unaltered while the intensity of the peaks grows with increasing Na coverage. At $\Delta\phi=-1.92$ eV passing the minimum, the gap is filled with the excitation continuum revealing the metallicity of the surface. A new loss peak S_5



(a) (b)

FIG. 1. Contour plots of the LEED pattern for the Na/Si(111)-(3×1) structure at 1/3 ML (a) and the (6×1) structure at 1/2 ML (b) at room temperature. The half-order LEED spots are clearly visible between the third-order spots in (b).

at 2.7 eV appears near saturation, which is a surface plasmon of the metallic surface.

Before discussing the origin of the semiconducting property of the surface above 1/3 ML, we first discuss structural models for the ordered structures induced by Na adsorption. For the (3×1) phase at 1/3 ML, two models, a so-called Seiwatz model and an extended Pandey model, have been considered.[7,10] We only consider the Seiwatz model in the present work and the validity of the extended Pandey model in interpreting our data is briefly discussed later. In Fig. 3(a), the atomic arrangement of the Seiwatz model first proposed by Weitering and co-workers[8] is depicted. It consists of the top-layer Si chains along the $[110]$ direction with empty channels between them, which accommodates the 1/3 ML of Na adatoms. According to the pseudopotential total-energy calculations,[10] the Si chains in this model are buckled, and Na atoms occupy the threefold T_4 sites. The buckling of Si chains induces a charge transfer from the lowered to the raised Si atoms resulting in a large energy gap as in Si(001) and Ge(001) surfaces.[13] From the band structures calculated by Jeong and Kang,[10] the loss S_1 in Fig. 2 may be attributed to the interband transitions from the dangling bond states of the second-layer Si atoms and the filled states of the raised Si atoms (big solid circles) to the vacant states of the lowered Si atoms (empty circles) in the Si chains. The loss peak S_2 also observed by Tihkov and co-workers[11] may be a transition to a Na-derived empty state.

The structural model for the (6×1) shown in Fig. 3(b) is constructed assuming that the (3×1) surface at $\Delta\phi=-0.91$ eV has 1/3 ML of Na adatoms. This is reasonable since Okuda and co-workers[12] and Weitering and co-workers[8] estimated the Na coverage as 1/3 ML at $\Delta\phi=-0.6$ and -1.0 eV, respectively. On the other hand, the coverage at the minimum in $\Delta\phi$ is estimated as 2/3 ML.[8] We assign the coverage of the (6×1) surface at $\Delta\phi=-2.07$ eV as 1/2 ML, which may be justified by the structural models sketched in Fig. 3(b). One easily finds that the (6×1) structure can be formed by adding more adatoms at the threefold sites in the vacant rows of the Si chains in the (3×1) structure [Fig. 3 (a)]. The additional Na atoms then form double Na rows in one channel between Si chains, while neighboring channels have only one Na row to produce a (6×1) periodicity. Further adsorption of Na naturally fills the remaining threefold sites resulting again in a (3×1) periodicity with the coverage of 2/3 ML as in Fig. 3(c).

With the structural models in Fig. 3, the semiconducting nature of the (3×1) structure at 1/3 ML can be understood easily in the simple Bloch band picture since it contains an even number of electrons in the surface unit cell. The same electron counting for the (6×1) at 1/2 ML and the (3×1) at 2/3 ML with the structural models in Fig. 3, however, gives an odd number of electrons, 9 and 5, respectively, which

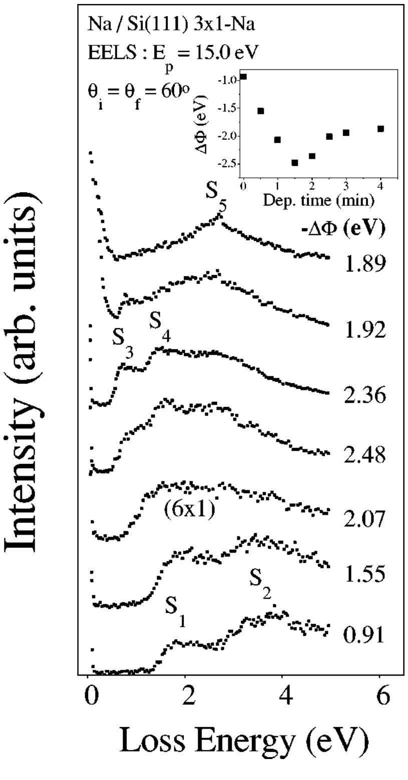
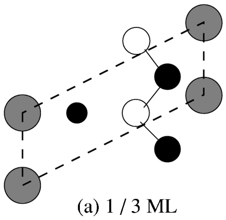
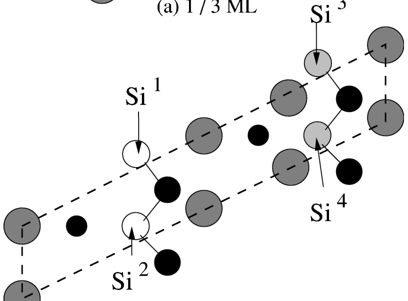


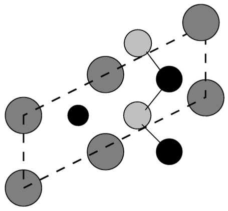
FIG. 2. Progressive change of EELS spectra with increasing Na coverage obtained at specular geometry ($\theta_i=\theta_f=60°$). The inset shows the change of work function as a function of deposition time. Note that the surface becomes briefly a (6×1) near $\Delta\phi=-2.07$ eV, while it is (3×1) otherwise.



(a) 1 / 3 ML



(b) 1 / 2 ML



(c) 2 / 3 ML

FIG. 3. Structural models for the (3×1) at 1/3 ML (a), (6×1) at 1/2 ML (b), and (3×1) at 2/3 ML (c). Note that there are 9 and 6 electrons per unit cell for the (6×1) and (3×1) at 2/3 ML, respectively. Si^{1} and Si^{2} are the empty lowered Si atoms while Si^{3} and Si^{4} are the singly charged lowered Si atoms in the Si chains.

predicts a metallic phase in contradiction to our data in Fig. 1. Therefore we have to go further than the simple Bloch picture to explain the semiconducting surface above 1/3 ML. Moreover, Weitering and co-workers pointed out that even the (3×1) at 1/3 ML might not be understood properly without considering the electron-electron correlation effects.[7] Recent studies, both theory and experiment, on the AM/GaAs(110) surfaces stress the importance of electron-electron correlation as well as electron-lattice coupling in understanding the electronic properties of AM-induced semiconducting surfaces.[1–3]

As pointed out previously,[7] the (3×1) surface has several common features with a GaAs(110) surface. In a buckled Seiwatz chain model, the lowered Si atoms within the Si chains (Si^{1} and Si^{2} in Fig. 3) have empty dangling bond states, which are likely to interact with additional Na atoms above 1/3 ML. The charge transfer from Na adatoms to the empty dangling bond states may cause a local lattice distortion since the charge distribution becomes different from the buckled chain structure where the empty lowered Si atoms exist. In this case the surface may become semiconducting by forming single-polaron-type localized electrons. Alternatively, as in Na/GaAs(110),[2] a singly charged lowered Si atom, for example Si^{3} in Fig. 3, may transfer its charge to neighboring Si atoms of the same kind, Si^{4}, when Si^{4} acts as a so-called negative U center where U is the onsite Coulomb repulsion. Such a charge transfer then gives rise to a so-called Mott-Hubbard insulating phase. A bipolaronic insulating phase becomes more plausible when the Mott-Hubbard state couples with a local lattice distortion to reduce further the total energy of the surface. This is more likely to happen especially for the (3×1) structure at 2/3 ML where all the empty lowered Si atoms are occupied by Na 3s electrons.

The notion of bipolaronic interaction is supported by recent theoretical[10] and experimental[6] studies where the surface bands associated with Na adsorption are rather flat, so that one may anticipate a significant electron-phonon coupling. As a result of the bipolaronic interaction, the surface bands become narrower so that U can be larger than the bandwidth of the surface bands. Such a narrowing of a surface band due to the polaronic interaction was already reported in a theoretical study of Si(111)(2×1).[14] In this regime, the Hubbard correlation becomes important and governs the electronic property of the surface. We estimate the effective Coulomb repulsion $U^* \approx 0.8$ eV from the loss energy of the loss peak S_3 in Fig. 2. The loss peak S_4 near 1.4 eV may then be a transition from the filled Si to the empty Si surface bands. Interestingly, the spectral changes in Fig. 2 are very similar to those reported for the Cs/GaAs(110), which was considered as a Mott-Hubbard insulator.[1] For the Cs/GaAs(110), U^* was estimated to be 0.4 eV. A recent photoemission and inverse photoemission study of K/Si(111)$-\sqrt{3}\times\sqrt{3}R30°$-B reveals two narrow surface bands near E_F, which were identified as the lower and upper Hubbard band separated by a Hubbard gap of 1.3 eV.[4]

The discussions so far are based on the buckled Seiwatz model, which reproduces the surface bands closer to the experimental data than does the extended Pandey model.[7,10] Since the bandwidth of the empty dangling bond states in the extended Pandey model is larger than that predicted by the Seiwatz model,[10] one anticipates that the electron correlation effect may be less important in the extended Pandey model. Further adsorption of Na greater than 2/3 ML results in the growth of a second Na layer and the surface becomes metallic simply through the overlayer metallization.[5] The top spectrum in Fig. 2 shows a metallic excitation continuum filling up the energy gap. The excitation S_5 at 2.7 eV is a surface plasmon of the metallic layer, which approaches the surface plasmon energy of a bulk Na metal when the Na layer grows further. The growth of a Na second layer was reported previously in the STM study by Jeon and co-workers.[5] They showed that a semiconductor-to-metal transition occurs with the formation of a second Na layer consistent with our observation.

In conclusion, we find that the Na adsorption above 1/3 ML produces two ordered surface structures which remain semiconducting before the formation of the metallic second layer. The semiconducting nature of the surface for Na coverage greater than 1/3 ML is understood in terms of a bipolaron model where electron-electron correlation plays an important role in determining the electronic property of the surface.

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