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Spectroscopic interpretation for Na-induced phase transitions on Na/Si(1 1 1)3 × 1

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Abstract

Na adsorption at room temperature causes the Na/Si(1 1 1)3 × 1 surface with Na coverage of 1/3 monolayer (ML) to transit into the Na/Si(1 1 1)6 × 1 surface at 1/2 ML and sequentially into the Na/Si(1 1 1)3 × 1 surface at 2/3 ML. The phase transition was studied by Si 2p core-level photoemission spectroscopy. The detailed line shape analysis of the Si 2p core-level spectrum of the Na/Si(1 1 1)3 × 1 surface (2/3 ML) is presented and compared to the Na/Si(1 1 1)3 × 1 surface (1/3 ML) which is composed of Si honeycomb chain-channel structures. This suggests that as additional Na atoms form atomic chains resulting in the Na/Si(1 1 1)3 × 1 surface (2/3 ML), the inner atoms of the Si honeycomb chain-channel structure is buckled due to the additional Na atoms.

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1. Introduction

Interests in one-dimensional (1D) structures continue to grow, fueled by exotic 1D phenomena such as Luttinger liquid and Peierls instability and the importance of nano-wires in nano-scale devices [1–7]. Various metals on the Si(1 1 1) surface induce atomic-scale 1D structures with interesting phenomena. The In zig-zag chain on the In/Si(1 1 1)4 × 1 surface shows a metal-insulator Peierls transition [8,9]. The double honeycomb Si chain on the Au/Si(1 1 1)5 × 1 surface yields exotic phenomena such as a self-doping and an inhomogeneous quantum wire [10,11]. Besides, most of alkali metals (AM's) and alkali earth metals (AEM's) on the Si(1 1 1) surface were found to produce the same 1D structure, the honeycomb chain-channel (HCC) structure on the AM/Si(1 1 1)3 × 1 [12–14] and AEM/Si(1 1 1)3 × 2 surfaces [15].

In the early years, the AM/Si(1 1 1)3 × 1 surfaces attracted interests because the insulating property of the AM/Si(1 1 1)3 × 1 surfaces were ascribed to a Mott–Hubbard insulator (MHI) [16], although their insulating property is now understood to be a simple band insulator with even electron numbers in the 3 × 1 cell [13,14]. For this reason, many structure models of the AM/Si(1 1 1)3 × 1 surfaces have been suggested and debating. The conflicting structure models were settled down by X-ray diffraction (XRD) experiments, which finally reaches the HCC model composed of 1D Si HCC's and Na chains, as shown in Fig. 1a [12–14]. Recently, low energy electron diffraction (LEED) found that Na adsorption at room temperature (RT) induces the phase transition of the Na/Si(1 1 1)3 × 1 surface with Na coverage (θ_{Na}) of 1/3 ML (3 × 1-I hereafter) into the Na/Si(1 1 1)6 × 1 surface with 1/2 ML and sequentially into the Na/Si(1 1 1)3 × 1 surface with 2/3 ML (3 × 1-II hereafter) [17,18]. Besides, electron energy loss spectroscopy found that the insulating property of the 3 × 1-II surface is to be beyond a single-electron band picture because of odd electron numbers in the 3 × 1 cell.

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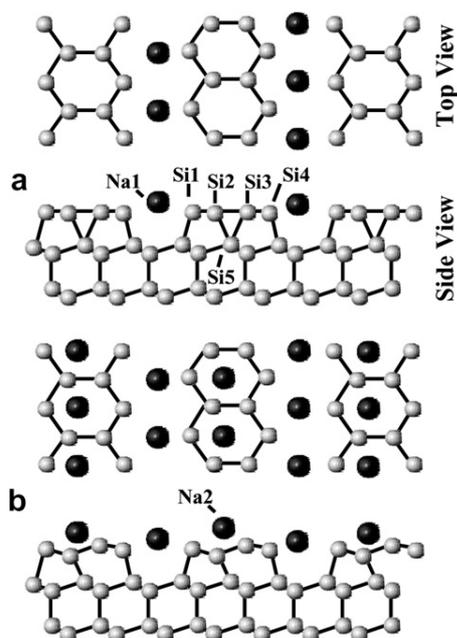


Fig. 1. Side and top views of the structure models of (a) the 3×1 -I surface ($\theta_{\text{Na}} = 1/3$ ML) and (b) the 3×1 -II surface ($\theta_{\text{Na}} = 2/3$ ML), where gray and black circles represent Si and Na atoms, respectively. Na atoms on the 3×1 -I surface and additional Na atoms on the 3×1 -II surface are denoted as Na1 and Na2, respectively.

More recently, the insulating property of the 3×1 -II surface was suggested to be a MHI with an effective on-site Coulomb repulsion of 0.8 eV by scanning tunneling microscopy, photoemission spectroscopy, and density functional theory calculations, while the additional Na atoms on the 3×1 -I surface were found to be adsorbed on the HCC's without driving a drastic surface reconstruction [17].

Si 2p spectra were measured using a photon energy of 130 eV at the 2B1 spherical grating monochromator beamline of the Pohang Light Source, Korea. The nominal energy resolution was better than 140 meV. In order to quantify Si 2p spectra, they were fitted using the spin-orbit-split Voigt functions with a Lorentzian width of 0.085 eV for all components and Gaussian widths of 0.45 and 0.38 eV for surface and bulk components, respectively. The relative binding energy of a surface component with respect to that of the bulk component will be written briefly by a surface core-level shift (SCLS). A clean Si(111) 7×7 surface was prepared by the repeated cycles of annealing at 700 °C and flashing at 1200 °C, as confirmed from the well-defined non-integer spots of the 7×7 phase and the nonexistence of O 1s and C 1s core-level spectra. Na atoms were deposited from a commercial SAES dispenser. Relative θ_{Na} was calibrated by the work function change which was measured from the secondary electron cut-off of the normal-emission spectrum.

The main feature of the structure model for the 3×1 -I surface (see Fig. 1a) is the HCC, where Na atoms are bonded to the outer Si atoms (Si1 and Si4) of the HCC

[13,14,17]. Based on the HCC model, Kang et al.'s [13] and Erwin et al.'s [14] theoretical calculations reproduced completely various experimental results for the 3×1 -I surface. This disclosed that the highest-occupied and lowest-unoccupied bands originate from the saturated dangling bonds of the outer Si atoms of the HCC and the π^* anti-bond between the inner Si atoms (Si2 and Si3) with sp^2 bonds of the HCC, respectively [13,14]. This also turned out that the two surface components of the Si 2p spectrum of the 3×1 -I surface, as shown in Figs. 2 and 3, are due to the outer and inner Si atoms of the HCC with gains and depletions of charge, respectively [13].

Fig. 2 shows θ_{Na} -dependent Si 2p spectra along the (3×1 -I) $-(3 \times 1$ -II) phase transition. The two surface components, denoted as S1 and S2, of the Si 2p spectrum of the 3×1 -I surface are noticed from the line shape. The line shape evolves gradually and consistently up to 0.93 ML without a drastic change. Na adsorption at RT on the 3×1 -I surface reduces the intensity of the S1 component. Consequently, the Na adsorption grows up two new components, denoted as S3 and S4, respectively: the S3 component with a positive SCLS is located near the S1 component, while the S4 component with a negative SCLS is shown as a shoulder. The S3 and S4 components develop fully at 2/3 ML and are noticed up to 0.93 ML. In order to quantify the θ_{Na} -dependent Si 2p spectra, they were fitted using the spin-orbit-split Voigt functions, as shown in Figs. 3 and 4. The two surface components of the Si 2p

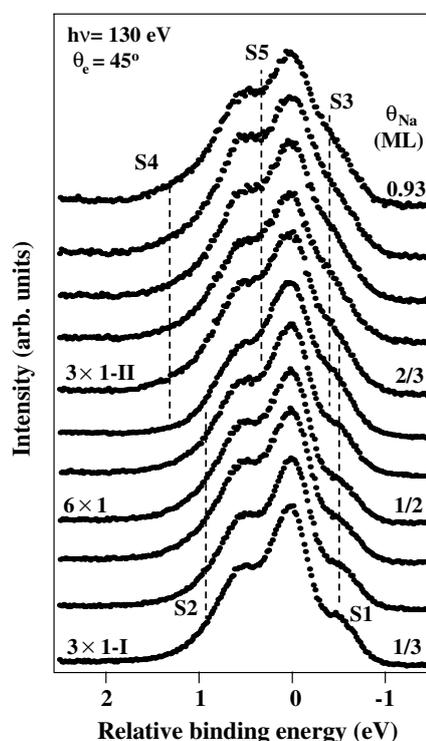


Fig. 2. θ_{Na} -dependent Si 2p spectra measured using a photon energy ($h\nu$) of 130 eV at an emission angle (θ_e) of 45°. The variations of surface components are guided by dashed lines, respectively.

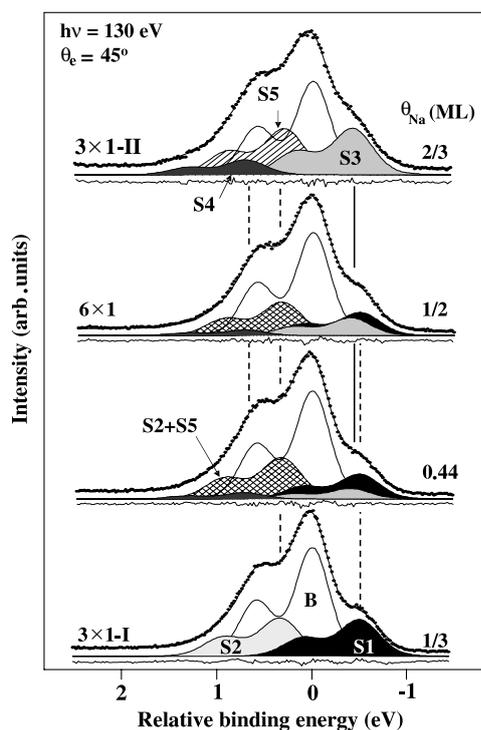


Fig. 3. Variations of Si 2p spectra along the $(3 \times 1\text{-I})$ – $(3 \times 1\text{-II})$ phase transition. Surface components are filled by different patterns and guided by lines. The residual between experimental and fitted data is included under each spectrum.

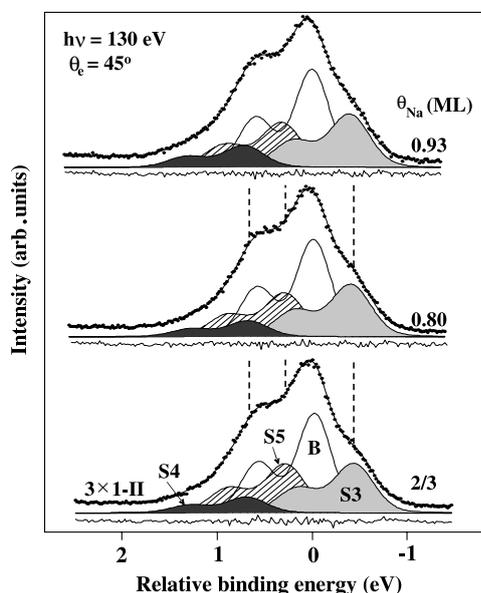


Fig. 4. Variations of Si 2p spectra above $2/3$ ML. Surface components are filled by different patterns and guided by lines. The residual between experimental and fitted data is included under each spectrum.

spectrum of the $3 \times 1\text{-I}$ surface were found to have SCLS's of -0.59 (S1) and 0.33 eV (S2), respectively, which is consistent with previous experiments [19–21]. Recently, the Si 2p line shapes of the AM/Si(111) 3×1 surfaces were rein-

vestigated with a higher resolution, which also reveals that the $3 \times 1\text{-I}$ surface has two surface components with SCLS's of -4.0 and 0.24 eV [22]. Based on the HCC model, the S1 and S2 components originate from the inner and outer Si atoms of the HCC [13,22], as described above. Besides, the intensity of the S1 component is equal to that of the S2 component. This can be also explained by the HCC model because both the inner and outer Si atom numbers of the HCC are two in the 3×1 cell [13,22].

With increasing θ_{Na} at RT, the $3 \times 1\text{-I}$ surface transits into the 6×1 surface and sequentially into the $3 \times 1\text{-II}$ surface. Fig. 3 shows the detailed curve fitting analysis of the Si 2p spectra of the Na/Si(111) surfaces ranging from $1/3$ to $2/3$ ML. The Si 2p spectrum of the $3 \times 1\text{-II}$ surface is fitted well with three surface components, denoted as S3, S4, and S5. The S3 and S4 components with SCLS's of -0.39 and 0.72 eV, respectively, are noticed from the line shape, as discussed above. The S5 component with a SCLS of 0.57 eV is needed to fit the line shape near the bulk component B. The Si 2p spectra below $2/3$ ML are fitted with the surface components (S1–S5) of the $3 \times 1\text{-I}$ and $3 \times 1\text{-II}$ surfaces. This is because STM experiments found that additional Na atoms on the $3 \times 1\text{-I}$ surface are adsorbed on identical sites and occupy fully the identical sites resulting in the $3 \times 1\text{-II}$ surface [17]. The curve fitting analysis reveals that, with increasing θ_{Na} up to $2/3$ ML, the S1 component fades and disappears at $2/3$ ML, while the S3 and S4 components are gradually grown up. On the other hand, the variation of the S2 component is not obvious because it has nearly the same SCLS with the S5 components. Above $2/3$ ML (see Fig. 4), no noticeable change was observed in line shapes. For this reason, the Si 2p spectra above $2/3$ ML are fitted with the same number of surface components with the $3 \times 1\text{-II}$ surface; the S3 and S4 components are marginally enhanced above $2/3$ ML. This indicates that the Si structure of the $3 \times 1\text{-II}$ surface may be robust for additional Na atoms.

To understand the atomistic origins of the surface components, the structure models of the 6×1 and $3 \times 1\text{-II}$ surfaces need to be introduced. Fig. 1b shows the structure model of the $3 \times 1\text{-II}$ surface, based on the HCC model of the $3 \times 1\text{-I}$ surface [17]. The structure model is suggested from experimental and simulated STM images; additional Na atoms, denoted as Na2, were found to be adsorbed on the HCC without breaking up the HCC structure [17]. In STM experiments, the Na2 atoms were observed as identical bright protrusions between the inner atoms of the HCC up to $2/3$ ML [17]. The adsorption site of the Na2 atom is thus unique until the $3 \times 1\text{-II}$ surface forms through the 6×1 surface. This naturally leads to the conclusion that the 6×1 surface is produced when the Na2 atoms occupy the unique adsorption sites of every second HCC's, and the $3 \times 1\text{-II}$ surface forms when the unique adsorption sites are fully occupied. Besides, the density functional theory calculations found that the Na2 atoms cause the inner atoms (Si2 and Si3) of the HCC to be buckled resulting in a charge transfer from the Si2 atom to the

Si3 atom [17], as observed on the asymmetric Si dimers of the Si(100)2 × 1 surface [23]. Consequently, the two Si atoms (Si1 and Si5) bonding to the lower Si2 atom form sp³-like bonds, and the upper Si3 atom comes to have a half-filled dangling bond [17].

The bucklings of the inner atoms of the HCC are quite related to the variations of the surface components of the Si 2p spectra. Fig. 5 shows the θ_{Na} -dependent intensity ratios (I_S/I_B) of the bulk (I_B) and surface (I_S) components. It is notable that the gradient of I_{S1}/I_B is nearly $-1/2$ times that of I_{S4}/I_B and $-3/2$ times that of I_{S3}/I_B . Based on the HCC model of the 3 × 1-II surface, a Na2 atom produces a buckled Si2–Si3 pair in the 3 × 1 cell resulting in a charge depletion of the Si2 atom and a charge gain of the Si3 atom. In this case, Na adsorption on the 3 × 1-I surface should split the S2 component into two surface components with smaller and larger SCLS's, respectively, than that of the S2 component and with the half intensity of the S2 component. The S4 component of the 3 × 1-II surface has a larger SCLS than that of the S2 component and its intensity is nearly the half of the S2 component. We thus assign the S4 component as due to the lower Si2 atom of the buckled Si2–Si3 pair. The upper Si3 atom of the buckled Si2–Si3 pair is expected to produce a surface component with the same intensity with the S4 component, which seems not to be matched with any surface components of the 3 × 1-II surface. Here, we need to elaborate the disappearance of the S1 component on the 3 × 1-II surface. Because no surface component with a larger SCLS than that of the S1 component is observed on the 3 × 1-II surface, it is obvious that the Na2 adsorption depletes the charge of the outer atoms (Si1 and Si4) of the HCC shifting the S1 component to the higher binding energy side. These suggests that the Si1, Si3, and Si4 atoms could produce the S3 component, which is supported by the intensity ratio of the S3 and S4 components, $I_{S3}/I_{S4} \approx 3$. The S5 component, developing fully on the 3 × 1-II surface, may originate from the Si second layers, as observed on the Na/Si(100) surface [23]. On the other hand, the 6 × 1 surface is composed of

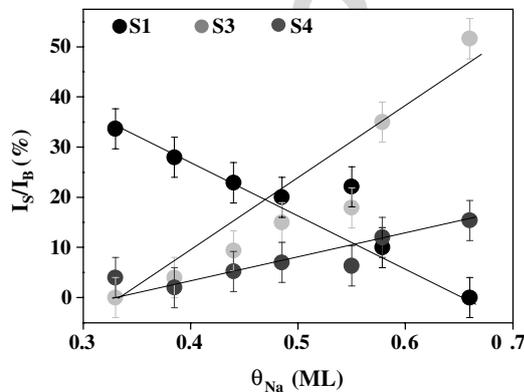


Fig. 5. Intensity ratios (I_S/I_B) of the bulk component (I_B) and the surface components (I_S) for the S1 (black circle), S3 (light gray circle), and S4 (dark gray circle) components. We note that I_S/I_B 's change linearly up to 2/3 ML.

the alternate HCC's with and without the Na2 atoms, respectively, as discussed above [18]. Thus, the half intensities of the surface components of the 3 × 1-I and 3 × 1-II surfaces should contribute to the Si 2p spectrum of the 6 × 1 surface, which is nearly consistent with the intensities of the surface components of the 6 × 1 surface (see Fig. 3).

In summary, we measured θ_{Na} -dependent Si 2p spectra along the (3 × 1-I)–(3 × 1-II) phase transition. The Si 2p spectrum of the 3 × 1-I surface is composed of two surface components with SCLS's with -0.59 (S1) and 0.33 eV (S2), respectively. Additional Na atoms on the 3 × 1-I surface grow up two new surface components with SCLS's of -0.39 (S3) and 0.72 eV (S4), respectively. Besides, the intensity ratios (I_S/I_B) of the bulk and surface components changes linearly with increasing θ_{Na} : the gradient of I_{S1}/I_B is nearly $-1/2$ times that of I_{S4}/I_B and $-3/2$ times that of I_{S3}/I_B . The spectral variations can be explained by two charge transfer mechanisms due to additional Na atoms: (i) the buckling of the inner atoms of the HCC and a consequent charge transfer between the inner atoms and (ii) the charge depletions of the outer atoms of the HCC. The charge transfer mechanisms suggest that the S3 component is due to the outer atoms and the lower atom of the inner atoms of the HCC and the S4 component originates from the lower atom of the inner atoms of the HCC.

Acknowledgements

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