

Photoemission spectroscopy study of Na-induced phase transitions on Si(1 1 3)

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Abstract

We reinvestigate the Si 2p spectrum of clean Si(1 1 3)3 × 2 to testify two competitive structure models, i.e. adatom-dimer-interstitials and oppositely puckered models, in comparison with recent theoretical calculations. This reveals that only the adatom-dimer-interstitials model reproduces the surface components of the Si 2p spectrum. After decorating Na atoms on clean Si(1 1 3)3 × 2 at room temperature, the 3 × 2 phase was found to transit into the 3 × 1 phase by low-energy electron diffraction and photoemission spectroscopy experiments. We will discuss the (3 × 2)–(3 × 1) phase transition on the adatom-dimer-interstitials model.

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1. Introduction

Studies of semiconductor surfaces have focused on low-index surfaces such as Si(1 0 0) and Si(1 1 1) for several decades. Recently, high-index Si surfaces have taken interests and have shown exotic phenomena such as one-dimensional growths of metal atoms and unusual stabilities of some high-index Si surfaces. Intrinsic anisotropy makes high-index Si surfaces more useful in fabricating one-dimensional structures [1–5]. In addition, the unusual stability of some high-index surfaces is interesting because high-index surfaces usually facet into low-index surfaces [6–8]. The Si(1 1 3) surface is one of the stable high-index surfaces with its intrinsic reconstructed surface and without a facet [7]. Theoretical calculations show that the energetic stability of Si(1 1 3) is comparable to Si(1 1 1) and Si(1 0 0) [9]. Moreover, some high-index surfaces are stabilized by forming facets including {1 1 3} after chemical (or thermal) treatments [10–12].

Further studies of Si(1 1 3) have been limited by conflicting structure models of clean Si(1 1 3)3 × 2. First,

Dabrowski et al. [13] introduced interstitial (I) atoms, inserted selectively in tetramers, to produce the 3 × 2 translational symmetry using scanning tunneling microscopy experiments and ab initio total energy calculations, which is called the adatom-dimer-interstitial (ADI) model (see Fig. 1(a)). Another model explaining the 3 × 2 phase is Wang et al.'s [14] oppositely puckered (OP) model (see Fig. 1(b)), where the tetramers are alternatively buckled to generate the 3 × 2 translational symmetry. This was supported by photoemission spectroscopy, Kikuchi electron holography, and X-ray diffraction [15–17]. In this report, we reinterpret the Si 2p spectrum of clean Si(1 1 3)3 × 2 to testify the ADI and OP models and compare it with the previous theoretical calculations [18]. This suggests that only the ADI model can explain the surface components of the Si 2p spectrum. In addition, Na adsorptions on clean 3 × 2 at room temperature (RT) were found to induce a (3 × 2)–(3 × 1) phase transition, which is explained on the basis of the ADI model.

2. Experimental

The photoemission measurements were performed at the beamline BL-18A of Photon Factory, high-energy

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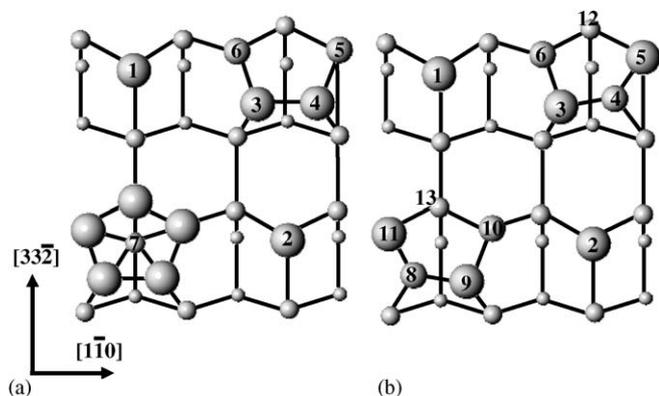


Fig. 1. Atomic structure models of (a) Dabrowski et al.'s ADI [13] and (b) Wang et al.'s OP 3×2 models [14].

accelerator research organization (KEK). The nominal energy resolution is better than 150 meV at an angle-integrated mode. Si 2p spectra were measured using a photon energy of 135 eV and fitted with a Lorentzian width of 80 meV for all components and Gaussian widths of 300 and 350 meV for bulk and surface components, respectively. The clean Si(1 1 3) 3×2 surface was prepared by the repeated cycles of annealing at 800 °C and subsequential flashing at 1200 °C, as confirmed by the low-energy electron diffraction (LEED) patterns with clear non-integer spots. Na atoms were deposited using well-degassed Na dispenser, and relative Na coverage (θ_{Na}) was calibrated by a work function change ($\Delta\phi$) which was measured using a secondary electron cut-off in the normal-emission PES spectrum. We estimate that all Si dangling bonds of clean Si surfaces at a minimum work function are saturated by alkali-metal (AM) adsorbates. In addition, the number of Si dangling bonds of clean Si(1 1 3) in the 3×2 unit cell is six and ten on the ADI and OP models, respectively. This suggests that θ_{Na} at a minimum work function is roughly 0.5 and 0.8 ML on the ADI and OP models, respectively. In this report, we assign θ_{Na} at a minimum work function as 0.5 ML because the ADI model is compatible to our experiments.

3. Results and discussion

Fig. 2 shows a work function change and a phase transition as increasing θ_{Na} . The non-integer spots of the $\times 2$ periodicity begin to fade away at 0.12 ML and subsequently disappear at 0.25 ML, while the non-integer spots of the $3 \times$ periodicity keep nearly the same intensities. Consequently, the work function is reduced rapidly at initial θ_{Na} and the gradient of $\Delta\phi$ varies abruptly at $\theta_{\text{Na}} = 0.12$ and 0.5 ML. Recently, scanning tunneling microscopy experiments of Na on Si(1 1 1) at RT suggested that a change of a gradient of $\Delta\phi$ is closely related to a structure transition [19]. This implies that (i) the Na-induced Si(1 1 3) surface undergoes structure transitions at $\theta_{\text{Na}} = 0.12$ and

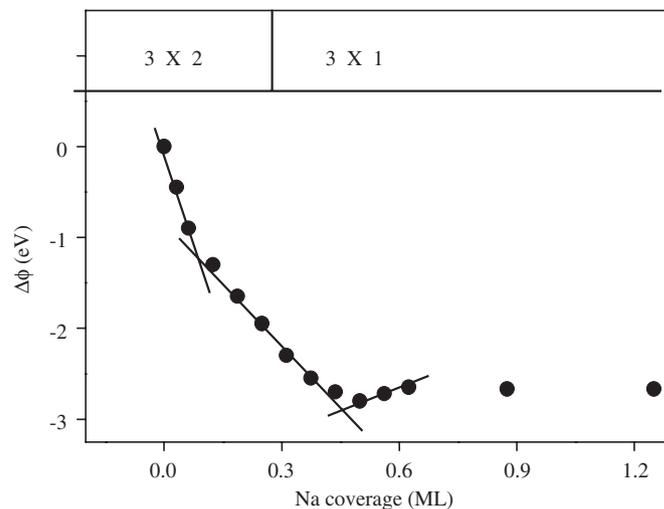


Fig. 2. Work function changes ($\Delta\phi$) of Na/Si(1 1 3) as increasing θ_{Na} at RT with the (3×2) – (3×1) phase transition.

0.5 ML and (ii) the Na-induced 3×1 phase begin to form at $\theta_{\text{Na}} = 0.12$ ML and has optimal θ_{Na} between 0.12 and 0.5 ML.

To get further insight into the (3×2) – (3×1) phase transition, we measured Si 2p spectra as increasing θ_{Na} , as shown in Fig. 3. The line shape of the Si 2p spectrum of clean 3×2 reveals the existence of the two surface components S1 and S2 with negative and positive surface core-level shifts (ΔBE), respectively. Initial Na adsorptions begin to make the S1 and S2 components fade gradually and, at $\theta_{\text{Na}} = 0.07$ ML, nearly disappear. Consequently, the new surface component S3 evolves and has a maximum intensity at 0.10 ML, which is observed from the change of the line shape near $\Delta\text{BE} = 0.3$ eV. At higher θ_{Na} , another new component S4 begins to grow and its intensity is gradually enhanced as increasing θ_{Na} . For a quantitative analysis, the Si 2p spectra were fitted as shown in Fig. 4. The Si 2p spectrum of clean 3×2 (see Fig. 4(a)) is fitted well with four surface components; S2 ($\Delta\text{BE} = 0.72$ eV), C2 (0.30 eV), C1 (−0.21 eV), and S1 (−0.61 eV). Moreover, the exact binding energies of the Na-induced S3 and S4 components are found to be 0.26 and −0.32 eV, respectively, from the analysis of the Si 2p spectra at $\theta_{\text{Na}} = 0.10$ and 0.61 ML.

Before further discussing about the (3×2) – (3×1) phase transition, we need to interpret the Si 2p spectrum of clean 3×2 to testify the structure models. Recently, the Si 2p surface core-level shifts of clean 3×2 were calculated using the ADI and OP models (see Fig. 1) [18]. Hereafter, we will call a Si tetramer with an interstitial as a Si pentramer. The calculations suggest that Si adatoms (Si1 and Si2) and Si tetramers (Si3, Si4, Si5, and Si6) of the ADI model produce surface components with ΔBE s between 0.5 and 0.7 eV, and the interstitials of Si pentramers (Si7) provide a surface component with a $\Delta\text{BE} = -0.6$ eV. For the OP model, it was found that surface components with ΔBE s between 0.4 and 0.8 eV originate from Si adatoms (Si1 and Si2) and

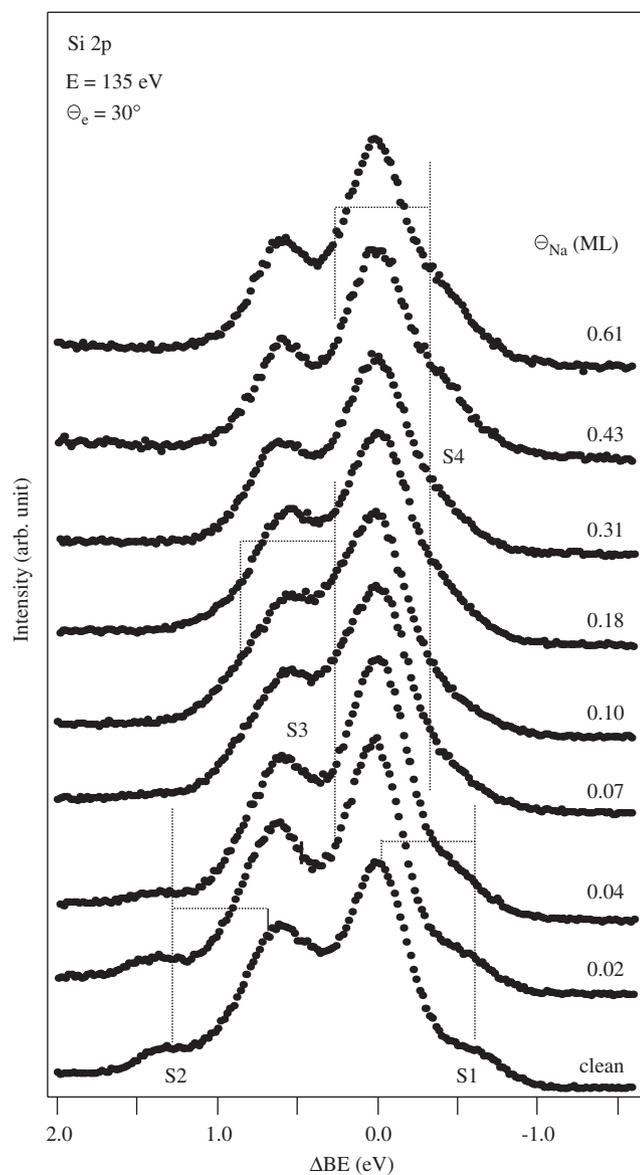


Fig. 3. Si 2p spectra of the Na adsorption on RT Si(113) with a photon energy of 135 eV and an emission angle (θ_e) of 30° . The variations of the S1–S4 surface components are guided by dotted lines.

upper atoms of Si tetramers (Si3, Si5, Si9, and Si11), and a surface component with a $\Delta BE = 0.2$ eV is due to lower atoms of Si tetramers (Si12 and Si13). The S2 component with a $\Delta BE = 0.72$ eV is reproduced by both structure models. However, the OP model cannot provide a surface component corresponding to the S1 component with a $\Delta BE = -0.61$ eV, while the ADI model explains well the existence of the S1 component. This suggests that only the ADI model is compatible with the experimental Si 2p spectrum and the S1 and S2 components originate from Si interstitials and Si tetramers + Si adatoms, respectively.

AM adsorptions on Si surfaces at RT have been found not to induce an abrupt reconstruction, as observed on AM/Si(111) [19,20] and AM/Si(100) [21,22]: the bound-

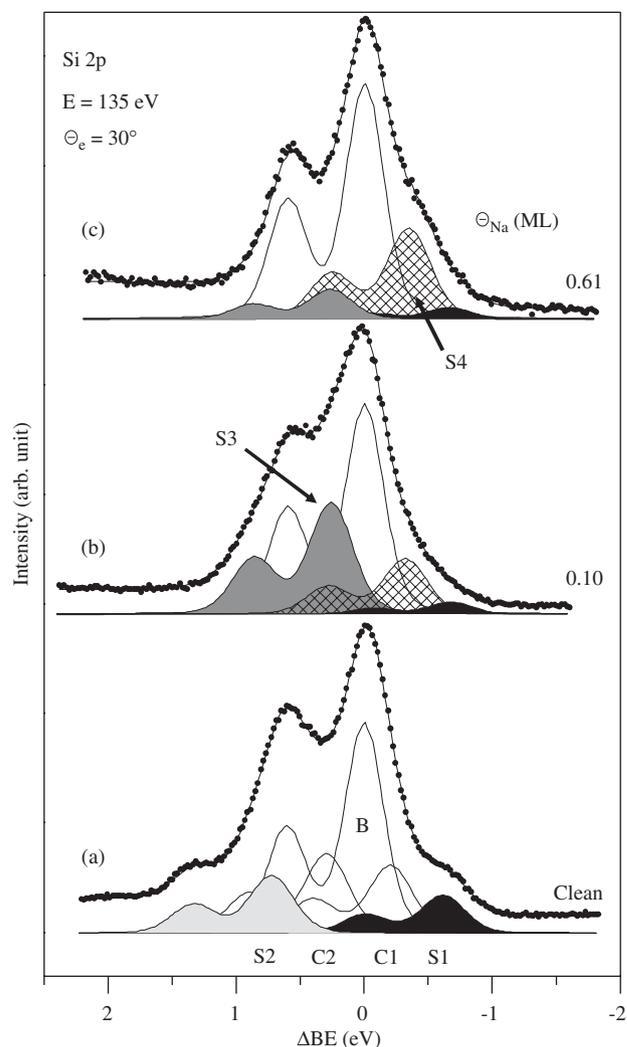


Fig. 4. Si 2p spectra, at representative $\theta_{Na} =$ (a) 0, (b) 0.10, and (c) 0.61 ML, with a photon energy of 135 eV and an emission angle of 30° . The surface components are filled by different colors or patterns.

ary of the 7×7 unit cell on Si(111) is kept, while the buckling angle of a Si dimer on Si(100) is raised or lowered but the dimer structure is maintained. Na adsorptions on clean Si(113) 3×2 , thus, are expected not to break the building blocks of clean 3×2 . For this reason, we will explain the (3×2) – (3×1) phase transition on the basis of the ADI model. At first, Na-induced surface components at RT were reported to locate at a $\Delta BE \simeq -0.3$ eV on both Na/Si(100) [22] and Na/Si(111) [20]. In addition, the S4 component locates at a $\Delta BE = -0.32$ eV and its intensity is proportional to θ_{Na} . This leads naturally to the interpretation that the S4 component originates from the Si tetramers and/or the Si adatoms bonding with Na adsorbates. In comparison to the S4 component, the S3 component has a maximum intensity at $\theta_{Na} = 0.10$ ML with a positive ΔBE . The S3 component, thus, may be due to charge redistributions of unsaturated Si tetramers and/or the Si adatoms without Na–Si bonds. A remaining problem is that “the coexistence of Si pentamers and tetramers cannot produce

the 3×1 phase.” The interstitial of Si pentramer should eject to satisfy the 3×1 phase. However, the ejection of the Si interstitial may need a high activation energy in comparison to a thermal energy at RT. This suggests that Na adsorptions at RT produce a disorder 3×1 phase rather than a order 3×1 phase. Similar disorder phases were observed on alkaline-earth metals (AEM) on Si(1 1 1) [23]. The AEM/Si(1 1 1) surfaces form 3×2 phases with short-range orders along the $\times 2$ direction, which results in 3×1 LEED patterns. For this reason, we suggest that the 3×1 LEED pattern of Na/Si(1 1 3) at RT originates from a 3×2 phase with a short-range order along the $\times 2$ direction.

4. Conclusions

We reinterpret the Si 2p spectrum of clean Si(1 1 3) 3×2 in comparison with the theoretical calculations. This suggests that only the ADI model explain well the two surface component S1 and S2 with ΔBEs of -0.62 and 0.72 eV, respectively. This leads to the interpretation that the S1 and S2 components originate from Si interstitials and Si tetramers +Si adatoms, respectively. Na adsorptions on clean 3×2 at RT were found to induce the (3×2) – (3×1) phase transition. Na adsorptions produce the two distinct surface components S3 and S4 with ΔBEs of 0.26 and -0.32 eV, respectively. The θ_{Na} dependence of the S4 component indicates that it is due to the Si tetramers and/or the Si adatoms bonding with Na adsorbates. To form an order 3×1 phase, the Si interstitials are required to eject from the Si pentramer, which needs a larger activation energy than a thermal energy at RT. This implies that the (3×2) – (3×1) phase transition is an order–disorder one, where the disorder may come from a short-range order along the $\times 2$ direction.

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References

- [1] Segovia P, Purdie D, Hengsberger M, Baer Y. Nature 1999;402:504.
- [2] Ahn JR, Yeom HW, Yoon HS, Lyo I-W. Phys Rev Lett 2003;91:196403.
- [3] Ahn JR, Yeom HW, Cho ES, Park C-Y. Phys Rev B 2004;69:233311.
- [4] Losio R, Altmann KN, Kirakosian A, Lin J-L, Petrovykh DY, Himpsel FJ. Phys Rev Lett 2001;86:4632.
- [5] Crain JN, Kirakosian A, Altmann KN, Brombergre C, Erwin SC, McChesney JL, et al. Phys Rev Lett 2003;90:176805.
- [6] Baski AA, Erwin SC, Whitman LJ. Science 1995;269:1556.
- [7] Knall J, Pethica JB, Todd JD, Wilson JH. Phys Rev Lett 1991;66:1773.
- [8] Gai Z, Zhao RG, Sakurai T, Yang WS. Phys Rev B 2001;63:085301.
- [9] Eaglesham DJ, White AE, Feldman LC, Moriya N, Jacobson DC. Phys Rev Lett 1993;70:1643.
- [10] Baski AA, Saoud KM, Jones KM. Appl Surf Sci 2001;182:216.
- [11] Gibson JM, McDonald ML, Unterwald FC. Phys Rev Lett 1985;55:1765.
- [12] Hirayama H, Hiroi M, Ide T. Phys Rev B 1993;48:17331.
- [13] Dabrowski J, Müssig H-J, Wolff G. Phys Rev Lett 1994;73:1660.
- [14] Wang J, Horsfield AP, Pettifor DG, Payne MC. Phys Rev B 1996;54:13744.
- [15] Chang CY, Chou YC, Wei CM. Phys Rev 1999;59:R10453.
- [16] Hwang CC, Kim HS, Ihm KW, Park CY, An KS, Kim KJ, et al. Phys Rev B 2001;64:045305.
- [17] Mizunoa Y, Akimotoa K, Aoyamaa T, Suzukia H, Nakaharaa H, Ichimiyaa A, et al. Appl Surf Sci 2004;237:40.
- [18] Lee G-D, Yoon E. Surf Sci 2004;559:63; Lee G-D, Yoon E. Phys Rev B 2004;68:113304.
- [19] Wu K, Fujikawa Y, Nagao T, Hasegawa Y, Nakayama KS, Xue QK, et al., Phys Rev Lett 2003;91:126101.
- [20] Paggel JJ, Neuhold G, Haak H, Horn K. Surf Sci 1998;414:221.
- [21] Johansson LSO, Reihl R. Phys Rev Lett 1991;67:2191.
- [22] Chao Y-C, Johansson LSO, Uhrberg RIG. Phys Rev B 1997;55:7198.
- [23] Lee G, Hong S, Kim H, Shin D, Koo J-Y, Lee H-I, et al. Phys Rev B 2001;63:056104.