

## Electronic structure of the single-domain Si(001)2×1-K surface

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A single-domain Si(001)2×1-K surface has been made by K deposition onto a room-temperature single-domain Si(001)2×1 substrate. Angle-resolved ultraviolet photoelectron spectra have been measured for the single-domain Si(001)2×1-K surface. The work on the single-domain surface has made it possible for the first time to identify the existence of two surface-state bands and dispersions of the two bands. The resulting surface-state bands are in principle consistent with a recently proposed K double-layer model [T. Abukawa and S. Kono, *Phys. Rev. B* **37**, 9097 (1988)] rather than with the more widely believed one-dimensional alkali-metal-chain model.

It is known that alkali-metal adsorption on semiconductor surfaces has remarkable characters in negative electron affinity and catalytic reactions on semiconductor surfaces. For the last several years, the Si(001)2×1-K surface has been extensively studied by various experimental<sup>1-5</sup> and theoretical<sup>6,7</sup> techniques. In previous papers, we performed angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) studies of the Si(001)2×1-K (Refs. 8 and 9) and -Cs (Ref. 9) surfaces. Our results were in contradiction with a generally accepted model for the Si(001)2×1-alkali-metal surfaces, i.e., one-dimensional alkali-metal-chain (ODAMC) model.<sup>6,7</sup> In recent x-ray photoelectron-diffraction (XPD) studies,<sup>10,11</sup> Abukawa and Kono denied the ODMC model and proposed an alkali-metal double-layer model. The double-layer model was qualitatively consistent with our previous results.<sup>8,9</sup>

However, the previous studies were performed on double-domain (DD) Si(001)2×1 substrates which made the identification of surface-state dispersion ambiguous.<sup>8,9</sup> Therefore, further studies of the Si(001)2×1-alkali-metal surfaces in terms of surface electronic structures were hampered by the ambiguity. In the present study, a single-domain (SD) Si(001)2×1 substrate is used and the surface states are definitely identified for a single-domain Si(001)2×1-K surface.

The experiments were performed in a UHV chamber (base pressure of  $\sim 5 \times 10^{-11}$  Torr) equipped with the same experimental apparatuses as described in Refs. 8 and 9, except for an added Si evaporation source for an epitaxial Si growth. The energy and angle resolutions of the ARUPS system were  $\sim 0.1$  eV and  $\pm 1.5^\circ$ , respectively. A mirror-polished Si(001) wafer ( $25 \times 3.5 \times 0.38$  mm<sup>3</sup>), whose surface normal was off from the [001] orientation by  $\sim 3'$  along  $[\bar{1}10]$  and by 0 to  $\sim 30'$  along [110] directions, was used. This wafer was etched, preoxidized,<sup>12</sup> and annealed at  $\sim 1000^\circ\text{C}$  in the UHV chamber. No contaminants were observed by Auger electron spectroscopy, and low-energy electron-diffraction (LEED) patterns showed a DD 2×1 periodicity. In order to prepare a SD surface, we grew epitaxial Si layers

( $\sim 1000$  Å) onto this wafer at  $\sim 500^\circ\text{C}$  and then annealed at  $\sim 1000^\circ\text{C}$  for 20 min. After several times of repeating this procedure, LEED spots of the minor domain reduced in intensity to  $\lesssim 10\%$  of those of the major domain as determined by a spot-intensity measurement. The LEED spots were rather sharp, and splittings of spots due to regular arrays of steps were not observed. This indicated that the terrace width of the obtained SD Si(001) surface was sufficiently wide for ARUPS measurements and certainly wider than those of vicinal samples.<sup>13,14</sup> Properties of the SD surface have been reported in detail elsewhere.<sup>15</sup> K was deposited onto a room-temperature SD substrate from a chromate dispenser (SAES getter) under a pressure of  $\sim 6 \times 10^{-10}$  Torr, and a SD Si(001)2×1-K surface was realized. Behaviors of LEED patterns, Auger intensity ratio, and work function change with K-deposition were identical to those for the DD surface.<sup>8,9</sup>

We first observed ARUPS spectra for the SD Si(001)2×1 substrate and found that a weak metallic structure, which had appeared around normal electron emissions for the DD surface,<sup>8,9</sup> completely disappeared. It indicated that surface defects and domain boundaries for the SD surface were considerably reduced. However, with initial deposition of K onto the clean SD surface, a metallic peak at around normal emissions appeared and developed as it had happened for the DD surface.<sup>8,9</sup> The rest of the spectral profile did not change essentially, also consistent with the result for the DD surface.<sup>8,9</sup> We infer that the metallic peak at the initial K deposition is due to 4s electrons of K atoms dispersely adsorbed on the SD surface. With further K deposition, the metallic peak disappeared and the whole surface electronic structures changed to those for a K-saturated SD 2×1 surface.

Figure 1 shows representative ARUPS spectra for the K-saturated SD 2×1-K surface as excited by unpolarized He I light. ARUPS spectra as excited by unpolarized Ne I light were also measured (results not shown). Figure 2 shows diagrams of the binding energy ( $E_b$ ) versus the wave vector parallel to the surface ( $k_{\parallel}$ ) obtained from the ARUPS spectra in Fig. 1 and the other ARUPS spectra.

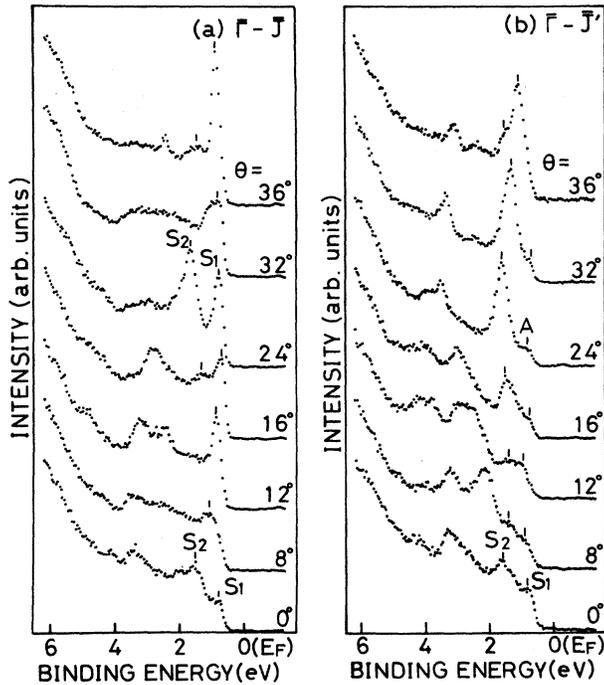


FIG. 1. ARUPS spectra of the K saturated single-domain Si(001)2 $\times$ 1-K surface. Excitation photon energy is 21.2 eV (HeI). The polar angle,  $\theta$ , of electron emission is changed along (a)  $\bar{\Gamma}$ - $\bar{J}$  (short side) and (b)  $\bar{\Gamma}$ - $\bar{J}'$  (long side) of the 2 $\times$ 1 surface Brillouin zone. The surface-state peaks above  $E_b \approx 2$  eV are marked with bars.

In Fig. 1, there are of course differences between the two series of the ARUPS spectra along  $\bar{\Gamma}$ - $\bar{J}$  (short side) and  $\bar{\Gamma}$ - $\bar{J}'$  (long side) directions of the surface Brillouin zone (SBZ). We confirmed that when we superposed two spectra for the two directions  $\bar{\Gamma}$ - $\bar{J}$  and  $\bar{\Gamma}$ - $\bar{J}'$  at a same polar angle, resulting spectrum resembled a corresponding spectrum of the DD 2 $\times$ 1-K surface.

As for the  $\bar{\Gamma}$ - $\bar{J}$  direction, to find surface-state dispersions is rather straightforward. First we notice two dominant structures  $S_1$  and  $S_2$  at the  $\bar{\Gamma}$  point of the second SBZ. Any surface-state dispersion along  $\bar{\Gamma}$ - $\bar{J}$  direction is symmetric about  $\bar{\Gamma}$  and  $\bar{J}$  points and surface-state dispersions are specified only by  $k_{\parallel}$ , i.e., independent of excitation light source. Therefore, two surface-state bands involving the  $S_1$  and  $S_2$  can easily be found and they are shown in Fig. 3: The NeI spectrum in Fig. 1 at  $\bar{\Gamma}$  point of the first SBZ has a peak at  $E_b \approx 2.0$  eV which is probably a bulk peak. Dashed lines in Fig. 3 represent ambiguous parts of the dispersion since peaks are not resolved or found there.

As for the  $\bar{\Gamma}$ - $\bar{J}'$  direction, we can definitely identify a surface-state band at  $E_b \approx 1.6$  eV at  $\bar{J}'$  point. Interpretation of the structure  $A$  around  $\bar{J}'$  point in Figs. 1(b) and 2(b) is very critical in the determination of surface-state bands. As noted, we have a minor-domain contribution of  $\approx 10\%$  of the major domain in actual spectra. By subtracting 10% of the spectral profile at  $\theta = 24^\circ$  of Fig. 1(a) (minor-domain contribution) from that at  $\theta = 24^\circ$  of Fig.

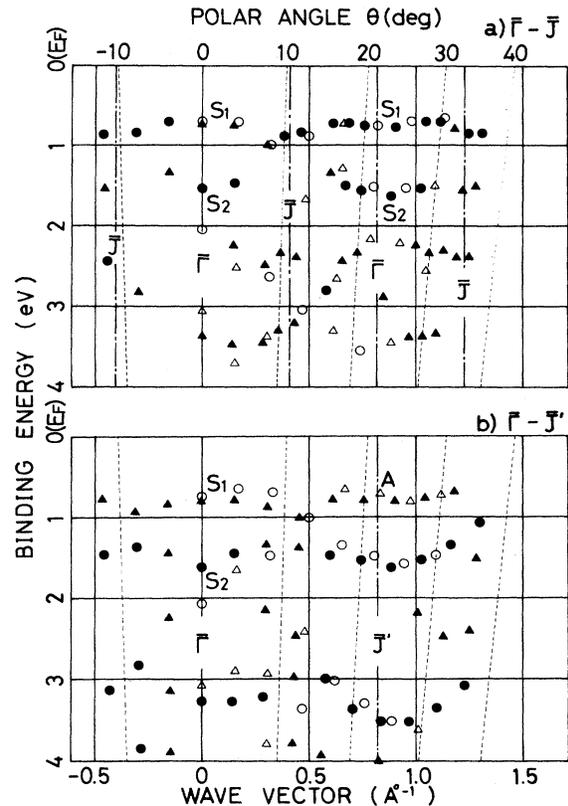


FIG. 2. Band dispersions ( $E_b$  vs  $k_{\parallel}$ ) obtained from the ARUPS spectra in Fig. 1 and others not shown. Solid (open) symbols are plotted from results of HeI (NeI) excitation. Circles stand for strong or clear peaks and triangles stand for weak or broad structures in actual spectra. Polar-angle scale is for HeI excitation.

1(b) (major-domain spectrum), we could prove that the structure  $A$  is due to the  $S_1$  peak of the minor domain. Therefore, surface-state dispersion along the  $\bar{\Gamma}$ - $\bar{J}'$  direction becomes as shown in Fig. 3. The dashed lines are again ambiguous parts of the dispersion.

In the previous deduction of surface-state dispersion from the result of a DD surface,<sup>9</sup> we considered that the

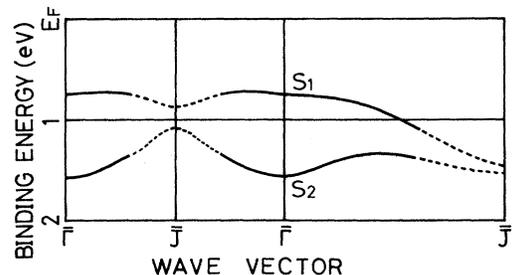


FIG. 3. Surface-state dispersions for the full-coverage, single-domain Si(001)2 $\times$ 1-K surface as deduced from Figs. 1 and 2. Dashed lines represent dispersions that are somewhat ambiguous.

$S_2$  band near the  $\bar{\Gamma}$  point of the second SBZ would be due to the  $S_2$  band near the  $\bar{J}'$  point of the other domain. This is incorrect.

The  $S_1$  and  $S_2$  bands are completely filled states, thus the full-coverage Si(001) $2\times 1$ -K surface is semiconducting. This is consistent with the expectation from the one-monolayer, double-layer model of Abukawa and Kono,<sup>10</sup> whose K coverage is equal to the atomic density of a truncated Si(001) $1\times 1$  surface. Namely, we may consider that the obtained two band states  $S_1$  and  $S_2$  originate from the two K 4s valence electrons and from the two Si dangling bonds in the  $2\times 1$  unit cell. The surface-state dispersion presently determined can serve as a guideline to further clarify the structure of the Si(001) $2\times 1$ -K surface.

In conclusion, we found that the K saturated Si(001) $2\times 1$ -K surface is semiconducting and that the two surface-state bands  $S_1$  and  $S_2$  disperse between  $\sim 0.7$  and

$\sim 1.6$  eV below the Fermi level. The  $S_1$  and  $S_2$  bands probably originate from the two K 4s valence electrons and two Si dangling bonds in the  $2\times 1$  unit cell. The obtained electronic structure is, in principle, consistent with the one-monolayer K double-layer model recently proposed by photoelectron diffraction.<sup>10,11</sup>

*Note added in proof.* It is worthwhile to note concerning the preparation of a single-domain Si(001) $2\times 1$  surface that the major and minor  $2\times 1$  domains can be exchanged by switching the polarity of the applied direct current for the wafer annealing. Cycles of the switching improved the quality of the single domain surface.

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