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Photoelectron diffraction study of Si(001)2×1-K surface: Existence of a potassium double layer

T. Abukawa and S. Kono
Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan
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X-ray photoelectron diffraction patterns of K 2*p* core levels have been measured for the Si(001)2×1-K surface. From a kinematical analysis of the diffraction patterns, it is concluded that a sawtooth-type arrangement of the potassium double array is present over the substrate. This is in disagreement with an existing assumption of the one dimensionality of the alkali-metal–Si(001) systems.

Adsorption of alkali metals on Si(001) surfaces has been of much interest in surface science.[1] The Si(001)2×1-K surface is one of the most extensively studied ordered surfaces of this kind.[1-4] A basic idea about this surface is that a one-dimensional array of alkali atoms is present over the ridge of Si dimers as is schematically shown in Fig. 1(a). Theoretical calculations of electronic structures are based on this kind of one-dimensional-alkali-chain (ODAC) model.[3,4] Recent angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) work, however, suggests that the amount of K atoms over the substrate could be twice as much as that for the model in Fig. 1(a).[5] In the present x-ray photoelectron diffraction study, this is confirmed and it is further suggested that arrays of K atoms are like those in Fig. 1(b) although the relationship of the K arrays to the substrate is not determined by the present study.

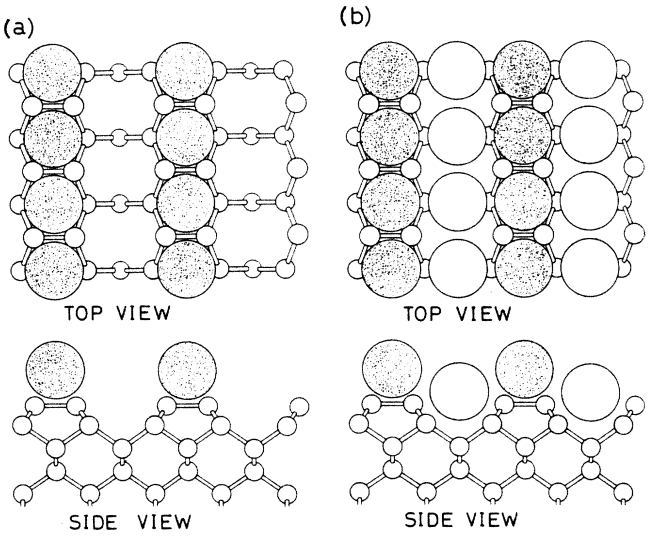

FIG. 1. Schematic illustration of models for the Si(001)2×1-K surface; (a) generally assumed one-dimensional-alkali-chain (ODAC) model, (b) presently proposed model except that relationship to the substrate is an assumption. K atoms are represented by large circles (shaded circles represent the upper K array, and open circles represent the lower K array). The assumed dimerized Si substrate is drawn as a ball-and-stick structure. The radius for K atom is the mean of the atomic and the ionic radii of K, and the radius for Si is arbitrary.

Experiments were performed using a VG ADES 400 photoelectron spectrometer which was basically equipped with a hemispherical electron analyzer, a twin anode (Al, Mg) x-ray source, low-energy electron-diffraction (LEED) optics and a sample manipulator under a base pressure of 5×10^{-11} Torr. A Si(001) wafer (*p* type, 20–40 Ω cm, 0.5×8×8 mm^3) was preoxidized and cleaned *in situ* by cycles of Ar^+ bombardment and annealing at ~1000 °C. After the *in situ* cleaning, two-domain 2×1 LEED patterns were observed with no trace of contaminants as checked by x-ray photoemission spectroscopy (XPS). K was deposited onto a room-temperature substrate from a chromate dispenser (SAES getter) under a pressure of $\sim5\times10^{-10}$ Torr.

The amount of K adsorbed on the substrate was monitered by K 2*p* XPS intensity; it showed an initial linear increase and saturation at a constant value in the same manner as was observed previously by Auger-electron spectroscopy[5] (AES). Evolution of LEED patterns was also similar to the previous observation including the appearance of a two-domain 3×2 pattern.[5] Azimuthal x-ray photoelectron diffraction (XPD) patterns were measured for a Si(001)2×1-K sample prepared at the K-adsorption stage just after saturation. For the measurement of azimuthal XPD patterns, photoelectron intensity of K 2*p* levels as excited by Mg *Kα* lines was measured for every 2.1° azimuth (ϕ) at a constant electron take-off angle (θ_t) (cf. inset of Fig. 2). Dotted-dashed lines in Figs. 2 and 3 are experimental XPD patterns for the Si(001)2×1-K surface. Because of a two-domain structure of the 2×1 surface, the resulting experimental patterns are fourfold symmetric. The anisotropy in the XPD patterns is defined as $(I_{max}-I)/I_{max}$ and is about 30% for the experiment at $\theta_t\approx13°$–15°. The amount of experimental anisotropy of 30% is very high for the adsorbate core levels; it is normally about 20% at most. This indicates presence of scatterer atoms above the level of emitter K atoms.

Formalism of a kinematical calculation with a spherical-wave and a plane-wave emitter has been described previously.[6] Partial-wave phase shifts (up to $l=24$) were calculated for a muffin-tin potential con-

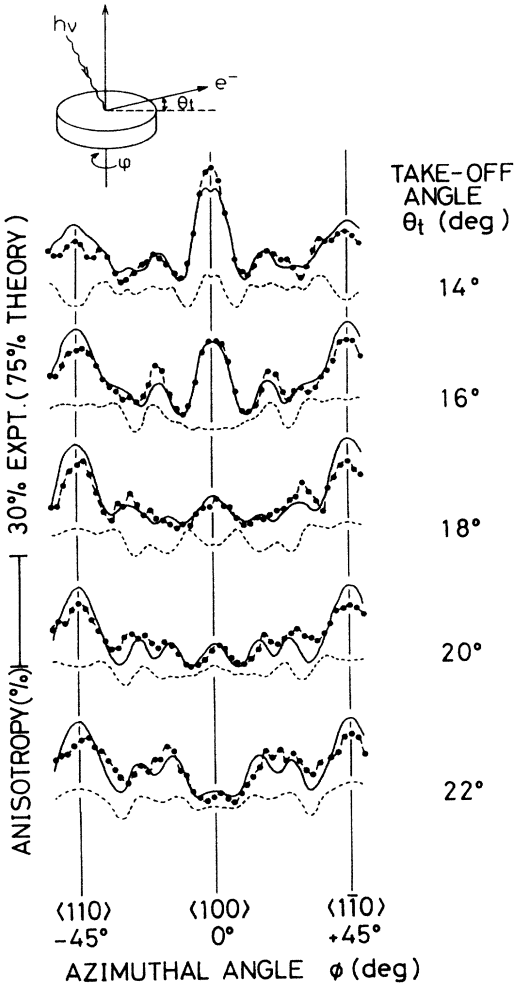

FIG. 2. Azimuthal x-ray photoelectron diffraction patterns of K $2p$ core levels for the Si(001)2×1-K surface. Dot-dashed lines are experimental. Solid lines are the results of the kinematical calculations for the K cluster in Fig. 1(b). Dashed curves are the results of the kinematical calculations for the generally assumed one-dimensional K chain model as in Fig. 1(a). Inset shows geometry of the measurements.

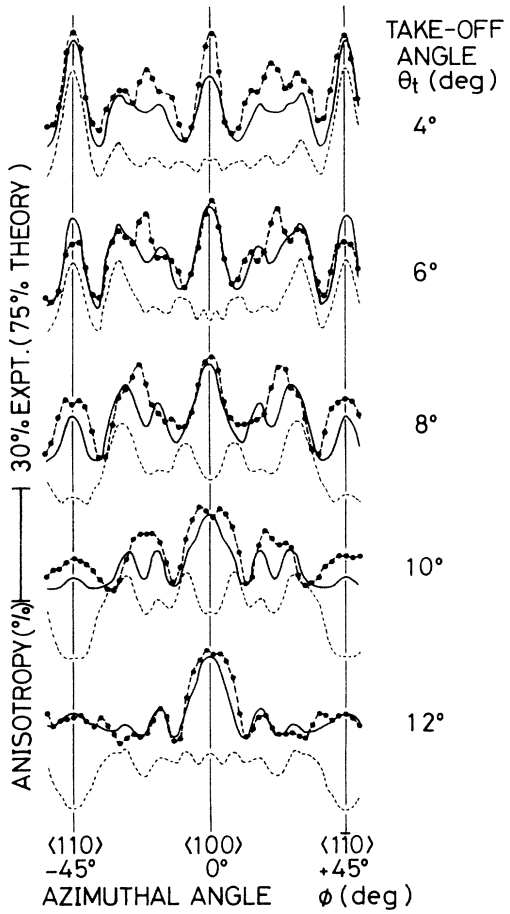

FIG. 3. The same as in Fig. 2 but for $4^0 \leq \theta_t \leq 12^0$.

structed from Roothaan-Hartree-Fock atomic wave functions.[7] Kinetic energy of K $2p$ photoelectron was set at 967 eV inside the solid. Inner potentials ranging from 5 to 15 eV were tested to find an optimum fit to the experiment for each structural model. Other input parameters were identical to those in the previous analysis.[6]

Of various structural models tested including the one in Fig. 1(a), so far the best agreement with experiment is reached for a K-double-layer model shown in Fig. 1(b). Symmetric dimers of the substrate Si(001)2×1 surface are arbitrarily placed in this model (see the explanation below). In this model, there are two types of K array aligned next to each other (the upper and the lower) with vertical separation of 1.1 ± 0.1 A. Resulting plane-wave kinematical calculations for this model are shown as solid-line curves in Figs. 2 and 3 for an inner potential of 9.0 eV. Results of spherical-wave kinematical calculations were almost identical to those of the plane wave. Agreement between the calculation and the experiment is remarkable for $\theta_t \geq 12°$. For $\theta_t \leq 10°$, calculated curves show a two-peak structure at $\phi \approx \pm 20°$ although experimental curves do not show exactly the same structure around $\phi \approx \pm 20°$. However, the general tendency of experimental patterns is well reproduced by the calculation for the K double-layer model even for $\theta_t \leq 10°$. In order to demonstrate the superiority of the K double-layer model over the ODAC model, results of plane-wave kinematical calculation for a K cluster of the ODAC in Fig. 1(a) are shown in Figs. 2 and 3 as dashed curves. Input parameters in the calculation are the same as for the K-double-layer model. The dashed curves do not reproduce the experiment; especially for $8° \leq \theta_t \leq 18°$, the calculations are very different from the experiment. For these take-off angles, forward scattering of the electron emitted from the lower K layer by the upper K layer plays an important role in the K double-layer model. This forward scattering is absent for the ODAC model.

We have tested the effects of the substrate by placing several types of substrate, such as the symmetric-dimer Si(001)2×1 surface as in Fig. 1, underneath the several types of K overlayer. However, the correspondence between experiment and calculation becomes worse if the vertical distance between the lowest K layer and the first Si layer becomes less than ~0.5 Å, for which forward

scatterings by the Si layers become comparable to forward scatterings within the K layers. Thus, the K double layer in Fig. 1(b) appeared to be the unique possibility from the present study.

The structure of the substrate Si layers and the registry of the K double layer to the substrate are other problems to be solved. Information about surface electron structures ARUPS (Ref. 5) and inverse photoemission studies[8] must be helpful in determining these problems by aid of theoretical calculations of the surface state dispersion. However, in the two-domain Si(001)2×1-K surface, it is expected that a relatively large fraction of surface is covered by disordered area due to domain boundaries. Unsatisfactory parts of the agreement of XPD patterns for $\theta_t \leq 10°$ in Fig. 3 may be related to this defective area of the surface. The result of ARUPS work[5] might also be affected by the defective area of the surface. A single-domain clear Si(001)2×1 surface is known to occur.[9] It is of great interest to see if a single-domain Si(001)2×1-K surface can be made on a single-domain clean Si(001)2×1 surface and to see how results of XPD and ARUPS, etc., improve. Work towards this end is under way in our laboratory.

Finally it is worthwhile to comment on the previous interpretation of angle-resolved electron energy-loss spectra of Aruga, Tochihara, and Murata,[2] which is based on the ODAC model. As pointed out by Ciraci and Batra,[4] the loss peak is not necessarily due to collective excitations of electrons. Instead, the loss peak can be interpreted by band-to-band transitions among the surface electronic states of the semiconducting Si(001)2×1-K surface[5] with the surface structure such as in Fig. 1(b).

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[1]For example, see J. E. Ortega, E. M. Oellig, J. Ferron, and R. Miranda, Phys. Rev. B **36**, 6213 (1987), and references therein.

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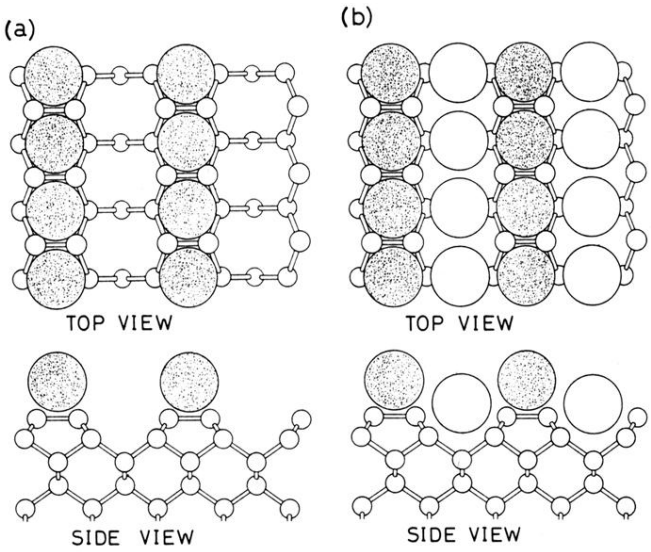

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