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Angle-resolved photoelectron-spectroscopy study of the Si(001)2×1-K surface

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Angle-resolved ultraviolet photoelectron spectra for the Si(001)2×1-K surface have been measured as a function of K coverage. It is found that the Si(001)2×1-K surface is semiconducting at saturation K coverage, in contrast to previous interpretations of electron-energy-loss spectra based on a metallic Si(001)2×1-K surface. It is further inferred that the saturation coverage of K for the Si(001)2×1-K surface is one monolayer instead of half a monolayer as generally assumed for alkali-metal/Si(001) surfaces.

Alkali-metal adsorption on low-index semiconductor surfaces has been studied extensively for the last decade from academic and technological points of view.[1] A basic assumption about the electronic properties of these adsorption systems is that the alkali-metal provides its outermost *s* electrons to the substrate and the surface becomes metallic at saturation alkali-metal coverages.[1-5]

Of alkali-metal–semiconductor systems, the Si(001)2×1-K surface is the system for which the most quantitative analyses have been given.[2-5] For a saturation K coverage on the Si(001)2×1 surface, Aruga *et al.*[2] measured angle-resolved electron-energy-loss spectra to obtain a dispersive loss peak around the loss energy of 1.8 eV. Tsukada and co-workers[3] interpreted the dispersion, based on a first-principles band-structure calculation, as due to an interband plasmon excitation between K $4s$-like and K $4p_x$-like bands of one-dimensional metallic K chains. Nakayama *et al.*[4] further gave a general analysis of a collective excitation of electrons to show a linear frequency-momentum dependence for the one-dimensional metallic surface. Ciraci and Batra[5] later pointed out that the loss peak is not necessarily due to collective excitations and that the metallic surface originates from active dangling bonds from the substrate. Common to these interpretations is the existence of a nearly one-dimensional metallic surface.

Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) is a powerful tool for investigating the electronic structures of surfaces. It is rather surprising that essentially no ARUPS measurements have been reported for alkali-metal–semiconductor systems. In this Brief Report we report ARUPS spectra of Si(001)2×1-K surface for the first time and show that the surface is semiconducting at full K coverage.

Experiments were performed with a UHV photoelectron spectrometer which basically consists of a hemispherical electron analyzer, a He I resonance lamp, a cylindrical-mirror Auger analyzer, and LEED optics.[6] The base pressure of the chamber was $\sim 5\times10^{-11}$ Torr and the energy and angle resolutions of the spectrometer were ~ 0.1 eV and $\sim \pm 1.5°$, respectively. A Si(001) wafer (p type $20\sim40\ \Omega\,\mathrm{cm}$, $0.5\times4\times25\ \mathrm{mm}^3$) was pretreated[7] and cleaned *in situ* by cycles of Ar^+ bombardment and annealing at $\sim 900\,°\mathrm{C}$. After cleaning, no contaminants were observed in the AES spectra, and LEED showed clear two-domain 2×1 patterns. K was deposited onto a room-temperature substrate from a chromate dispenser (SAES getter) under a pressure of $\sim 6\times10^{-10}$ Torr.

First, we describe the characterization of the Si(001)2×1-K surface. Figure 1 shows change in work function Φ and Auger electron intensity ratio $I(\mathrm{K}(LMM))/I(\mathrm{Si}(LMM))$ as a function of the duration of K deposition. The work functions were measured from the low-energy cutoff of an ARUPS spectrum for a negatively biased sample. Φ decreases almost linearly up to $\Delta\Phi=-3.3$ eV at $t=4$ min, then increases very slowly. The AES ratio increases almost linearly up to $t=4$ min and then stays essentially constant. The LEED patterns observed throughout were those for the 2×1, except for a weak additional two-domain 3×2 pattern for only $\Delta\Phi\approx-1.9$ eV. These results are in qualitative agreement with the recent results of Oellig and Miranda.[8] However, in Ref. 8 it is reported that the saturations of $\Delta\Phi$ and K AES intensity do not coincide with each other, which disagrees with our results. In our experiment both the $\Delta\Phi$ and the AES ratio were measured on the same sample prepared under the same condition.

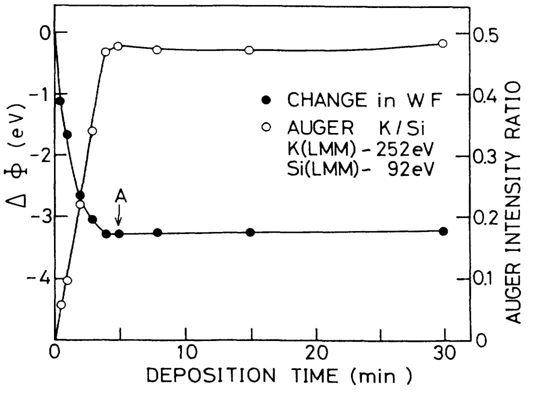

FIG. 1. K-deposition dependence of the change in work function (WF) and Auger electron intensity ratio $I(\mathrm{K(LMM)})/I(\mathrm{Si(LMM)})$ for K/Si(001). Work function for the clean Si(001)2×1 was ~ 4.8 eV.

This makes our measurement more precise than that of Ref. 8. It is also to be noted that the breaks in the Si LMM Auger intensity curve in Fig. 2(a) of Ref. 8 are quite ambiguous; without the straight lines, the dots form a smooth curve. Therefore, the conclusion of a layer-by-layer growth of K deduced in Ref. 8 is very doubtful. Tochihara[9] also reported the work function change upon K adsorption on a Si(001)2×1 surface. His result did not show minimum in $\Delta\Phi$ and the absolute value of $\Delta\Phi$ was much less than ours and that of Ref. 8. We suppose Tochihara's sample had more imperfections such as defects and contaminants.

ARUPS spectra were measured for both the clean and K deposited samples; ARUPS spectra for the K saturated 2×1-K surface were measured at the stage of the arrow *A* in Fig. 1. Figures 2(a) and 2(b) show representative ARUPS spectra of the saturation Si(001)2×1-K surface measured at the polar angles θ along ⟨110⟩ and ⟨010⟩ directions, respectively: Incident light is at 45° along the opposite azimuth. For each spectrum, the cleaning and K deposition was carried out each time since the surface appeared rather unstable. Figures 3(a) and 3(b) summarize the binding energy, E_b, versus the wave vector parallel to surface, $k_\parallel$, for the clean 2×1 (open symbols) and the saturation 2×1-K (solid symbols) surfaces. We note that the spectra and $E_b - k_\parallel$ diagrams for the clean 2×1 surface are essentially identical to those of a recent ARUPS work on the Si(001)2×1 surface.[10] It is reported that some of the structures in the clean 2×1 surface for $E_b \gtrsim 2$ eV can be ascribed to the direct-transition peaks or peaks due to the one-dimensional density of states in bulk bands.[10] The structures for $E_b \lesssim 2$ eV are mainly surface originated.[10]

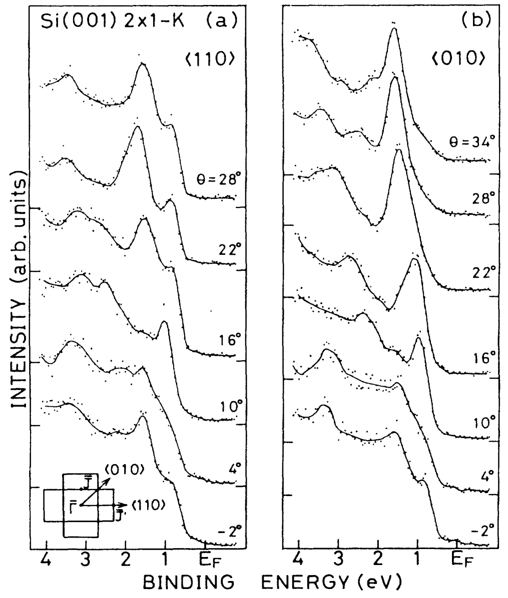

FIG. 2. Representative He I ($h\nu = 21.2$ eV) ARUPS spectra of the saturation Si(001)2×1-K surface as a function of polar angle θ. Azimuths are along (a) ⟨110⟩ and (b) ⟨010⟩ directions. Inset shows relation to two-domain 2×1 surface Brillouin zone.

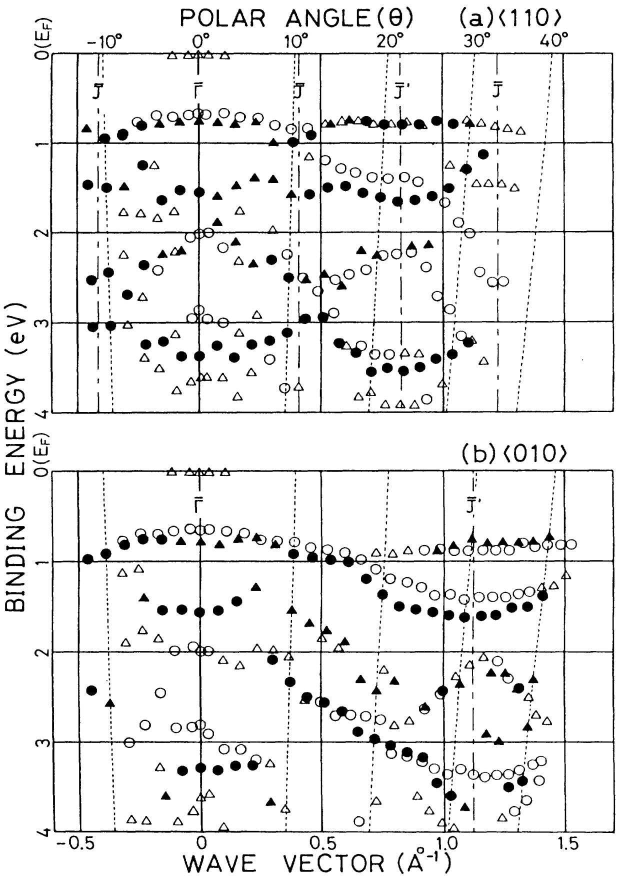

FIG. 3. E_b vs $k_\parallel$ plot for the clean Si(001)2×1 (open symbols) and the saturation Si(001)2×1-K (solid symbols) surface. (a) along ⟨110⟩ azimuth (b) along ⟨010⟩. Circles correspond to clear peaks or shoulders in actual spectra and triangles correspond to broad unclear structures. Denoted polar angles are for the saturation 2×1-K surface.

In Figs. 2 and 3 we first notice that there are structures which close the Fermi level, E_F, for the clean 2×1 surface but no such structures exist for the saturation 2×1-K surface. The structures just below E_F for the clean 2×1 surface are known for Ge(001)2×1 surfaces to be due to disorders on the room-temperature sample:[11] The surface order changes with temperature as $c(4\times 2)$ (low temperature)$\leftrightarrow 2\times 1$ (high temperature) and the metallic structures disappears for low temperatures.[11] For the K-saturated 2×1 surface in Figs. 2 and 3, even this metallic peak disappears with no traces of metallic surface band which is a prerequisite in Refs. 3–5. Therefore, the dispersive electron-energy-loss peak observed by Aruga *et al.*[2] should be attributed to a surface band-to-band transition of the semiconducting 2×1-K surface.

The properties of the clean Si(001)2×1 surface are now rather well known. Recent STM works[12,13] finally revealed that the clean 2×1 surface is composed of symmetric and asymmetric dimers of Si atoms together with vacancies of these dimers. The metallic surface peaks found in Figs. 2 and 3 should originate from the vacan-

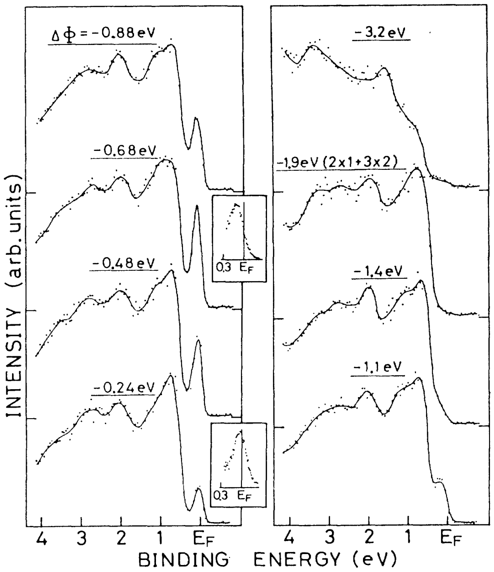

FIG. 4. Normal-emission ARUPS spectra (He I) for the various stages of K adsorption on the Si(001) surface. Incident light is at ∼45° along ⟨110⟩ azimuth. The $\Delta\Phi$'s are the measures of the degree of K adsorption (cf. Fig. 1). The insets are the expanded spectra near the E_F for $\Delta\Phi = -0.24$ and -0.68 eV.

cies to be consistent with the result for the Ge(001)2×1 surface. K adsorption on the 2×1 surface is assumed to take place on the rows of the symmetric and/or asymmetric dimers.$^{3-5}$ However, the Si(001)2×1 surface, in reality, contains a rather large fraction (probably ∼10%) of vacancies.^{12,13} Therefore, it is of interest to see how the metallic peak changes as a function of the K coverage.

Figure 4 shows normal emission ARUPS spectra as a function of K coverage. The noted $\Delta\Phi$ are a measure of K coverage (cf. Fig. 1). The metallic peak of the clean surface developes as K adsorbes up to $\Delta\Phi \approx -0.7$ eV and recedes off for $\Delta\Phi < -0.7$ eV. Coincided with the intensity increase of the metallic peak for $\Delta\Phi \gtrsim -0.7$ eV is a slight shift of the peak to the higher binding-energy side, as is well demonstrated in the insets for $\Delta\Phi = -0.24$ and -0.68 eV. Polar angle dependence of ARUPS spectra for $\Delta\Phi = -0.68$ eV showed no dispersion of the metallic peak and the intensity of the peak decreases with increase in θ and becomes zero for $\theta > 30°$. Except for the change in the metallic peak, the other structures in the spectra do not show any essential changes up to $\Delta\Phi = -1.9$ eV. On going from $\Delta\Phi = -1.9$ to $\Delta\Phi = -3.2$ eV (saturation K coverage), the spectra display a substantial change.

From these experimental findings, the following view of the growth of the Si(001)2×1-K surface can be drawn. Since Φ decreases substantially at an almost linear rate and K uptake increases also almost linearly up to the saturation of K coverage, the K atoms are nearly ionized upon the adsorption up to the saturation coverage. The 4*s* electrons donated from K atoms seem to be consumed first by filling the empty states localized at the vacancies. This is indicated by the intensity increase of the vacancy-derived metallic peak with K deposition for $\Delta\Phi \gtrsim -0.7$ eV. The observed nondispersiveness of the peak also coincides with the disordered nature of the vacancy. The slight shift of the metallic peak for $\Delta\Phi \approx -0.7$ eV as compared to that for $\Delta\Phi = -0.24$ eV indicates that more vacancy states are occupied by electrons donated from K atoms for the higher coverage. Between $\Delta\Phi \approx -0.7$ and -1.9 eV, the K adsorption seems to cause rearrangement of the Si dimers to eliminate the vacancies, which is indicated by the decrease in the metallic-peak-intensity and by no other changes in the spectra for these coverages. It is also possible that the observed 3×2 LEED pattern is an indication of a well-ordered K overlayer on the dimerized substrate. Presence of 3×2 overlayers was also suggested for Cs/Si(001) surface.^{14} From $\Delta\Phi \approx -1.9$ eV, the surface electronic structure appears to change to very different structures of that of the saturation Si(001)2×1-K surface.

It is to be noted that the coverage of K for $\Delta\Phi \approx -1.9$ eV, for which the 3×2 pattern is observed, is about $\frac{1}{3}$ of the saturation in Fig. 1. If the 3×2 order is an indication of $\frac{1}{3}$ monolayer (ML) [ML being the surface atom density of a truncated Si(001) surface] coverage of K of a dense 3×2 overlayer of Ref. 14, the saturation coverage for 2×1 K becomes 1 ML. If the 3×2 corresponds to $\frac{1}{6}$ ML of a dilute 3×2 of Ref. 14, the saturation coverage is $\frac{1}{2}$ ML. However, if one takes $\frac{1}{2}$ ML of K on the Si 2×1 surface, the resulting surface is metallic as is the case in Refs. 3 and 5. If one takes 1 ML of K on the Si 2×1 surface, the resulting surface would be semiconducting since the number of surface valence electrons per the 2×1 unit cell in this case is always a sum of even numbers. The conservation of valence electrons at the surface would be held since the bonding between Si and K atoms is expected to be weak. However, whether the substrate Si forms chains of dimers even for the 1 ML saturation 2×1-K surface is another problem. If it is the case, one can expect an additional surface band near the E_F which is filled by electrons from K 4*s*. This additional band seems absent in Figs. 3(a) and 3(b). However, little can be said from the present ARUPS alone about the geometry of the substrate.

In summary, angle-resolved UPS spectra for the Si(001)2×1-K surface have been measured for the first time as a function of K coverage. It is shown that the K-saturated 2×1 surface is not metallic in contrast to the theoretical analyses for this surface$^{3-5}$ and the general assumption for alkali-metal/Si systems.^{1} The measured work-function change and K-uptake change indicate that K atoms are nearly ionized on the surface for the whole coverages. Observed behavior of surface-state peaks with K coverage indicates that the 4*s* electrons of K atoms fill the empty states of substrate vacancies at an early stage of K adsorption. For the full K coverage, it is suggested that the measured electronic structure of the Si(001)2×1-K surface is explained by a 1 ML K-covered surface with or without the dimerization of the substrate Si atoms.

[1] For example, A. Franciosi, P. Soukiassian, P. Philip, S. Chang, A. Wall, A. Raisanen, and N. Troullier, Phys. Rev. B **35**, 910 (1987), and references therein.

[2] T. Aruga, H. Tochihara, and Y. Murata, Phys. Rev. Lett. **53**, 372 (1984).

[3] M. Tsukada, H. Ishida, and N. Shima, Phys. Rev. Lett. **53**, 376 (1984); H. Ishida, N. Shima, and M. Tsukada, Phys. Rev. B **32**, 6246 (1985).

[4] M. Nakayama, T. Kato, and K. Ohtomi, Solid State Commun. **50**, 409 (1984).

[5] S. Ciraci and I. P. Batra, Phys. Rev. Lett. **56**, 877 (1986).

[6] T. Yokotsuka, S. Kono, S. Suzuki, and T. Sagawa, Surf. Sci. **127**, 35 (1983), the RHEED optics are replaced by LEED in the present experiment.

[7] J. Henderson, J. Electrochem. Soc. **119**, 772 (1972).

[8] E. M. Oellig and R. Miranda, Surf. Sci. **177**, L947 (1986).

[9] H. Tochihara, Surf. Sci. **126**, 523 (1983).

[10] A. Goldmann, P. Koke, W. Mönch, G. Wolfgarten, and J. Pollmann, Surf. Sci. **169**, 438 (1986).

[11] S. D. Kevan and N. G. Stoffel, Phys. Rev. Lett. **53**, 702 (1984); S. D. Kevan, Phys. Rev. B **32**, 2344 (1985).

[12] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985).

[13] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).

[14] R. Holtom and P. M. Gundry, Surf. Sci. **63**, 263 (1977).