Measurement of Overlayer-Plasmon Dispersion in K Chains Adsorbed on Si(001)2×1

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The overlayer-plasmon dispersion in a K adlayer on Si(001)2×1 has been measured by angle-resolved electron-energy-loss spectroscopy. The dispersion of the interband-plasmon mode shows an azimuth-dependent anisotropy, which is in good agreement with recent theories that assume a strongly anisotropic electronic structure. Besides, the intraband-plasmon mode was observed, which identifies a metallic character of the K chains. It is proposed that the K chains adsorbed on Si(001) are in the nature of a one-dimensional metal.

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Adsorption of alkali-metal atoms on solid surfaces has been intensively studied in regard to its prototypical nature as well as technological applications. One of the most conspicuous features of alkali-metal-atom adsorption is excitation of plasmons in high-coverage monolayers observed by electron-energy-loss spectroscopy (EELS).[1-5] A microscopic theory of the overlayer plasmon has been developed by Newns,[6] who has analyzed the dielectric response of an electron gas confined to a thin film using a "particle in a box" model for the one-electron wave function. Measurement of the dispersion relation of overlayer plasmons, however, has been reported only by Jostell[2] for Na, K, and Rb adlayers on Ni(001). The dispersion relation observed in K and Rb monolayers showed a shallow energy minimum, which was in fairly good agreement with calculations of Newns.[6]

Previously we have reported the observation of the overlayer-plasmon excitation in Cs and K adlayers on Si(001)2×1.[4,5] It has been certified by Auger-electron spectroscopy, low-energy electron diffraction (LEED),[5] and synchrotron ultraviolet photoelectron spectroscopy[7] that the amount of intermixing between alkali-metal adlayers and silicon substrate is insignificant. This is in contrast with the case of transition-metal adsorption on Si, where intermixing due to diffusion and silicide formation plays an important role. On the basis of the LEED observation and other experiments, a geometric model shown in Fig. 1 has been established for the alkali-metal-atom overlayer on Si(001)2×1 at saturation coverage.[8] Alkali-metal atoms are arrayed in parallel linear chains along the [110] azimuth of the substrate. In this Letter, we present the angle-resolved EELS measurements of the overlayer-plasmon dispersion relation, i.e., plasmon energy $\hbar\omega$ versus momentum transfer parallel to the surface $q_{\parallel}$, in a potassium monolayer on the Si(001)2×1 surface. The measured dispersion relation exhibits an azimuth-dependent anisotropy, reflecting the anisotropic band structure. The relevance of the result to recent theories of the overlayer plasmon[9,10] is discussed. Moreover, we have found a longitudinal plasmon mode, which can be directly connected with the metal-insulator (Mott) transition[11] in the adlayer. We propose here that the K chains adsorbed on Si(001)2×1 are in the nature of a one-dimensional metal.

The experiments were performed in a Mumetal-shielded vacuum chamber with a base pressure of 1×10^{-8} Pa. EEL spectra were recorded with our constructed spectrometer which consists of a 127° deflector-type electron monochromator and a hemispherical deflector-type analyzer. The monochromator is fixed in position, whereas the analyzer and sample can be rotated independently about a common latitude axis θ. This allows independent variation of incident angle θ_i and exit angle θ_s in

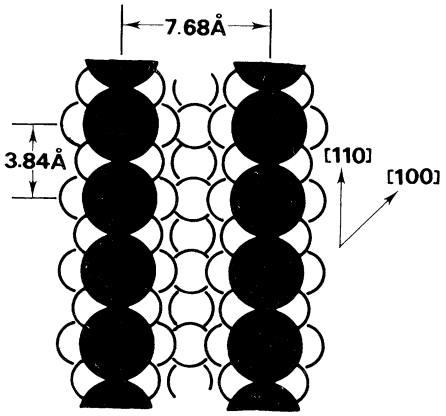

FIG. 1. The linear-chain arrangement of K atoms (solid circles) adsorbed on the Si(001)2 ×1 surface (open circles) at the saturation coverage.

the plane of incidence, both angles measured from the surface normal. The angular and energy resolutions were set to 0.5° and 0.2 eV, respectively. A commercial Si(001) wafer (p type, $\sim 20\ \Omega$ cm) of $8\times10\times0.4$ mm^3 was treated as prescribed by Henderson.[12] The sample was cleaned *in situ* by resistively heating to ~ 1550 K and then cooling slowly (1–3 K/s) down to ~ 320 K. This procedure yielded a sharp and well-contrasted 2×1 two-domain LEED pattern and an Auger spectrum with a trace of carbon as a sole impurity. The C(272 eV)/Si(92 eV) peak-to-peak ratio was below 1×10^{-3}. K deposition was carried out by using a SAES dispenser (from S.A.E.S. Getters). The pressure was maintained below 2×10^{-8} Pa during the whole experiment. The peak-to-peak height of the *LMM* Auger peak of potassium increased linearly with the deposition time until a saturation coverage, which corresponds to monolayer completion, was attained. At saturation, LEED showed a clear 2×1 two-domain pattern, whose intensity profile was different from that of the clean Si(001)2×1 surface. A typical EEL spectrum is presented in Fig. 2 for the K-covered Si(001) surface. There is seen a prominent peak due to the excitation of overlayer plasmons.[5]

Angle-resolved EELS is a suitable technique to search the dispersion relation of surface excitations. By recording EEL spectra with fixed E_p and θ_i in a series of off-specular angles, a momentum transfer $q_\parallel$ associated with a given energy loss can be scanned. From the energy and momentum conservation law for inelastic scattering,[14] $q_\parallel$ is determined as

$$q_\parallel = (2m/\hbar)^{1/2}[(E_p-\hbar\omega)^{1/2}\sin\theta_s - E_p\sin\theta_i], \qquad (1)$$

where m is the electron mass. In this work, the measurements were carried out with $E_p=43.8$ eV, $\theta_i=45.5°$, $39°\leq\theta_s\leq50°$ in the [110] azimuth, and with $E_p=39.8$ eV, $\theta_i=45.5°$, $38°\leq\theta_s\leq51°$ in the [100] azimuth. Figure 3 shows typical EEL spectra measured for a sequence of θ_s in the [110] and [100] azimuths. The prominent plasmon loss peak slightly disperses in energy with varying θ_s; besides, a shoulder is evidently seen in each spectrum for $\theta_s=43°$ and 50° in the [100] azimuth. Perceptible swell in the lower-energy-loss side of the main plasmon loss peak is also seen for $\theta_s=44°$ and 48° in the [110] azimuth.

The observed dispersion characteristics in each azimuth are represented in Fig. 4. The heavily drawn curve shows the dispersion obtained from a cubic least-squares fit to the loss energies recorded for $q_\parallel<0.25$ Å^{-1}.[15] The observed dispersion

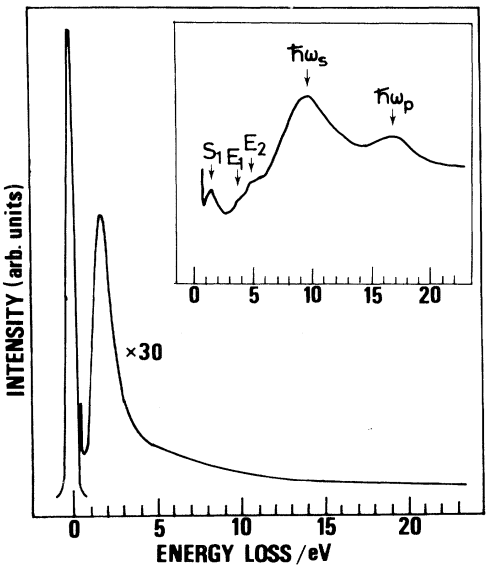

FIG. 2. A typical angle-resolved EEL spectrum for the K-covered Si(001)2×1 surface for $E_p=43.8$ eV, $\theta_i=\theta_s=45.5°$ in the [110] azimuth. The inset is for the clean Si(001)2×1 surface with $E_p=80.0$ eV, $\theta_i=\theta_s=45.5°$ in the [110] azimuth. The energy location features are in good agreement with a previous observation from Ref. 13.

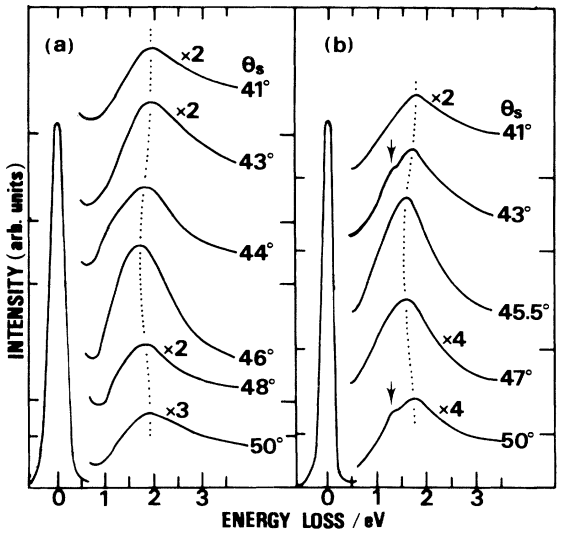

FIG. 3. Typical angle-resolved EEL spectra measured for a sequence of θ_s: (a) with $E_p=43.8$ eV, $\theta_i=45.5°$ in the [110] azimuth, and (b) with $E_p=39.8$ eV, $\theta_i=45.5°$ in the [100] azimuth. The dotted line shows the dispersion of the main plasmon loss peak. The arrow indicates a shoulder.

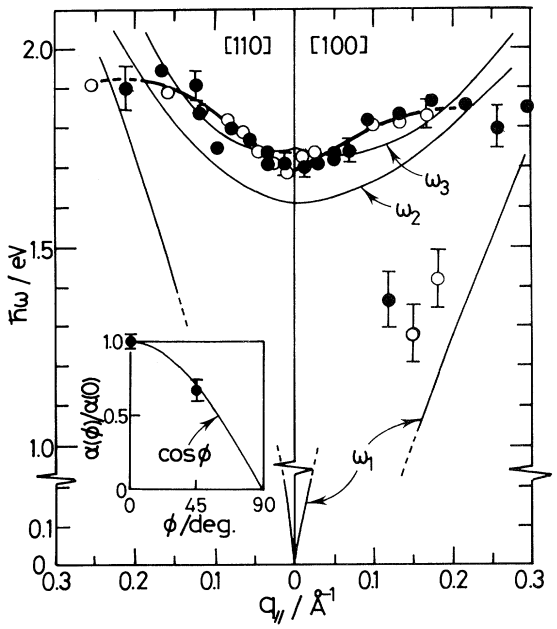

FIG. 4. The overlayer-plasmon dispersion relation. The open and solid circles represent the measured data with positive and negative $q_{\parallel}$ values, respectively. The thick line indicates the experimental dispersion curve (see text). The thin lines represent the theoretical dispersion relation from Ref. 9. The inset shows the angular dependence of the dispersion.

clearly shows an azimuth-dependent anisotropy: Along the [110] azimuth, the plasmon energy disperses from ~ 1.7 to ~ 1.95 eV in a small $q_{\parallel}$ region ($q_{\parallel} < 0.2$ Å^{-1}), whereas along the [100] azimuth the plasmon energy disperses from ~ 1.7 to ~ 1.85 eV in almost the same $q_{\parallel}$ region. It should be noted that in a small $q_{\parallel}$ region, the dispersion relation in both azimuths exhibits a nearly linear dependence on $q_{\parallel}$, $\hbar\omega(q_{\parallel}) = \hbar\omega(0) + \alpha q_{\parallel}$. In the inset of Fig. 4, the value of α obtained for $q_{\parallel} < 0.1$ Å^{-1} is plotted against the angle between $\vec{q}_{\parallel}$ and the chain axis, ϕ.

The interatomic distance between adjacent K atoms is 3.84 Å along the chain, while the spacing between adjacent chains is 7.68 Å. The K radius of 1.92 Å, which is $\sim 17\%$ shorter than the radius of K metal, 2.31 Å, is short enough for K valence electrons to form delocalized bands in the chains,[16] whereas the spacing between adjacent chains seems to be a little too long. The observed angular variation of the plasmon dispersion coefficient shows a cosine dependence, $\alpha(\phi) = \alpha(0)\cos\phi$.[9,17] This is an evidence that the K chains are like a one-dimensional metal rather than an anisotropic two-dimensional one.

The shoulder observed in several spectra is assigned to a collective intraband mode, which is essentially longitudinal oscillation along the potassium chains. Jostell tentatively assigned a similar shoulder seen in EEL spectra for K and Rb monolayers to a one-electron excitation.[2] However, for a one-electron type of excitation, the excitation will be restricted close to $q_{\parallel} = 0$. That this shoulder is not observed at small $q_{\parallel}$ values can be explained as follows. Since this mode is a "zero sound" mode, the intensity of this mode goes to zero at $q_{\parallel} \to 0$, and in a small $q_{\parallel}$ region this mode should be merged into interband excitation continuum. The broadening of the shoulder in the spectra taken in the [110] azimuth can also be attributed to the mechanism as is suggested above. MacRae *et al.*[1] suggested that the appearance of overlayer plasmons implies a Mott transition in Cs adlayers on W(001). Later, a direct connection was ruled out[6] between the Mott transition and the excitation of the interband-plasmon mode, which in principle exists in an atomic model of the alkali-metal layer. In the present case, the collective intraband mode, i.e., the longitudinal plasmon mode, was observed; its appearance really identifies a metallic character of the K chains.

Since the Si(001)2×1 surface is a "two-domain" structure, the potassium chains are laid parallel to the [110] and [$\bar{1}$10] azimuths. The EEL spectra in the [110] azimuth then contain overlayer-plasmon excitations with $\vec{q}_{\parallel}$'s both parallel and perpendicular to the chains, while the spectra in the [100] azimuth are composed of overlayer-plasmon excitations with $\vec{q}_{\parallel}$ at an angle of 45° with the chains. In the observed EEL spectra for the [110] azimuth, however, no evident peak or shoulder due to the excitation of overlayer plasmons with $\vec{q}_{\parallel}$ perpendicular to the chains is seen. This is, perhaps, because of weaker response of the modes to the excitation perpendicular to the chains.[18]

Starting from a simple "parallel-rod model" for the one-electron wave function, Tsukada, Ishida, and Shima[9] have derived the dispersion relation of three overlayer-plasmon modes, represented as ω_1, ω_2, and ω_3 in Fig. 4, in parallel potassium chains. In a small $q_{\parallel}$ region, the ω_1 mode almost comes from the 4*s*-4*s* collective intraband mode, the ω_2 mode from the 4*s*-4p_y, and the ω_3 mode from the 4*s*-4p_z collective interband mode. In a small $q_{\parallel}$ region ($q_{\parallel} \leq 0.15$ Å^{-1}), the experimental dispersion curve roughly coincides with the ω_3 mode, which has been calculated to be considerably more intense than the ω_2 mode.[9] However, an evident disagreement can be found in the slope of each dispersion curve at $q_{\parallel} \to 0$. The slope of the

theoretical dispersion curve of the ω_3 mode is slightly negative at $q_{\parallel}=0$, which is analogous to the B mode derived by Newns[6]; on the contrary, the experimental curve shows a positive dispersion in a small $q_{\parallel}$ region. Very recently Nakayama, Kato, and Ohtomi[10] discussed general properties of the overlayer-plasmon dispersion relation in detail. They showed that the dispersion of an interband-plasmon mode is linear in $q_{\parallel}$ for small $q_{\parallel}$ values, and that positive dispersion can be expected when an adsorbate structure has low symmetry, just as the present system. Their result well agrees with the present observation. Thus the observed main plasmon loss peak is explained by the K $4s$-$4p$ collective interband mode, which is essentially an oscillation transverse to the plane of the overlayer.

In conclusion, two overlayer-plasmon modes in K chains adsorbed on Si(001)2×1 have been observed by angle-resolved EELS. The dispersion of the more intense plasmon mode shows an azimuth-dependent anisotropy. At $q_{\parallel}\rightarrow 0$ this mode is assigned to the transverse oscillation, and the other to the longitudinal oscillation along the K chains. The results are in good agreement with recent theories.[9,10] It has been proposed that K chains adsorbed on Si(001)2×1 are in the nature of a one-dimensional metal. Inquiries into intriguing properties of a one-dimensional metal, i.e., valence-band structure[19] and the Peierls transition[20] at low temperature, are in progress.

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