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# Dispersion of the dangling-bond surface states of Si(111)-(7×7)

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Low-energy-loss spectroscopy with wave-vector resolution has been applied to study transitions between dangling-bond surface states of the Si(111)-(7×7) surface. Evidence of the dispersion of these surface states within the (7×7) surface Brillouin zone is obtained for the first time. Comparison with angle-resolved and inverse-photoemission spectroscopy data is also discussed.

Despite extensive theoretical and experimental investigations of well defined Si(111) surfaces, the true nature of the different superstructures, (2×1) on the cleaved (111) surface and (7×7) after annealing, is not definitively settled. An important impact in this field is due to the $\pi$-bonded chain model suggested by Pandey[1] for the (2×1) superstructure. For this structure, all spectroscopic results so far are in good agreement with the conclusion from the chain model although very recently it is still questioned.[2]

For the (7×7) superstructure, the situation is particularly interesting although very complex. In recent years, most impressive experimental and theoretical efforts have dealt with this superstructure. However, no definitive conclusion could be achieved.[3] The complexity of the large unit mesh with 49 atoms prevents any unambigous structural model.[4] Although an important progress has been brought by recent results of the scanning tunneling microscopy technique[5] giving information on the real space of the (7×7) surface, so far no direct evidence can be found on the energy dispersion of the surface states of the dangling bonds within the (7×7) surface Brillouin zone (SBZ) because of its very small extension in the $\vec{k}$ wave-vector space ($\sim 0.155$ Å$^{-1}$).

In this study, we apply electron-energy-loss spectroscopy (ELS) with wave-vector resolution to measure the transition energy $\hbar\omega$ between occupied and empty dangling-bond surface-state bands in dependence on the wave-vector transfer $\vec{q}_{\parallel}$ parallel to the surface. Our technique allows wave-vector transfers throughout half of the (7×7) SBZ (see below) and our first results show evidence of the dangling-bond surface-state dispersion which could not be obtained so far with angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) experiments. Since in ELS the observed electron transitions are related to the creation of a hole, i.e., influenced by electron hole interaction, the transition energies $\hbar\omega$ do not necessarily give direct information about the one-electron states being mapped in the band structure. Meanwhile, however, first results from inverse photoemission on the (7×7) superstructure are now available[6] and a rough comparison of the energetic position of occupied electronic surface states [from ultraviolet photoelectron spectra (UPS)] and empty states (from inverse photoemission) with transition energies (from these results) between these states is also possible.

All experiments were performed in an ultrahigh vacuum (UHV) chamber equipped with standard low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) (with a CMA analyzer) techniques. The high-resolution electron-loss spectrometer consists of two 180° hemispherical electrostatic condensors with their optics used as monochromator and analyzer, respectively. Both the sample and the analyzer can be rotated around the axis normal to the incidence plane and the sample can also be rotated around the normal to its surface in order to orient the crystallographic direction along the investigated SBZ symmetry line. With this spectrometer, an energy resolution as low as $\sim 10$ meV could be achieved although during the experiments it was degraded to $\sim 30$ meV to improve the signal to noise ratio. This is largely sufficient for the present problem. The sample ($p$ doped, $10^{-1}$ $\Omega$ cm) was treated under UHV (base pressure $0.5\times10^{-10}$ Torr) by several annealing cycles until $\sim 1100$ °C. By this way, an atomically clean, well-ordered low background 7×7 surface could be produced as checked with AES and LEED techniques. ELS spectra were recorded with an incident angle $\theta_i = 45°$. Both specular ($\theta_r = \theta_i$) and off-specular ($\theta_r = \theta_i \pm \psi$) beams had been measured with several primary energies $E_0$ ranging from 5 up to 40 eV. This operation mode allows wave-vector-resolved ELS as demonstrated recently.[7] Two sample orientations had been used in order to probe the $\Gamma K'$ and $\Gamma M'$ of the (7×7) surface Brillouin zone. Some results are illustrated in Fig. 1. Only the elastic peak (0 energy reference) and the energy loss at $\sim 1.5$ eV are plotted and the following discussion will be focused on this loss peak.

From the present study and also from previous work,[8–11] it is evident that the loss structure near 1.5 eV is inherently related to the presence of the (7×7) superstructure. Slight contamination by residual ambient of the UHV chamber and submonolayer metal deposits cause the loss to vanish [dotted curve in Fig. 1(a)]. An interpretation in terms of electronic transitions between occupied and empty surface states is therefore obvious. With respect to the band structure of the states involved, one therefore has to account for wave vectors and wave-vector transfers $\vec{q}_{\parallel}$ parallel to the surface only ($\vec{q}_{\parallel} = \vec{k}_{0\parallel} - \vec{k}_{\parallel}$), where $\vec{k}_{0\parallel}$ and $\vec{k}_{\parallel}$ are the wave vectors parallel to the surface of the incident and analyzed electrons, respectively. These wave-vector transfers $q_{\parallel}$ can be determined from the scattering geometry ($\theta_i, \theta_r$) and the primary energy $E_0$. For an electron being scattered within the plane of incidence under an angle $\psi$ ($\psi = \theta_i - \theta_r$ is the deviation from specular direction), the $q_{\parallel}$ transfer of this electron follows from energy and wave-vector conservation as

$$q_{\parallel} = k_0[\sin\theta_i + (1-\hbar\omega/E_0)^{1/2}(\sin\psi\cos\theta_i - \cos\psi\sin\theta_i)] \ . \quad (1)$$

 

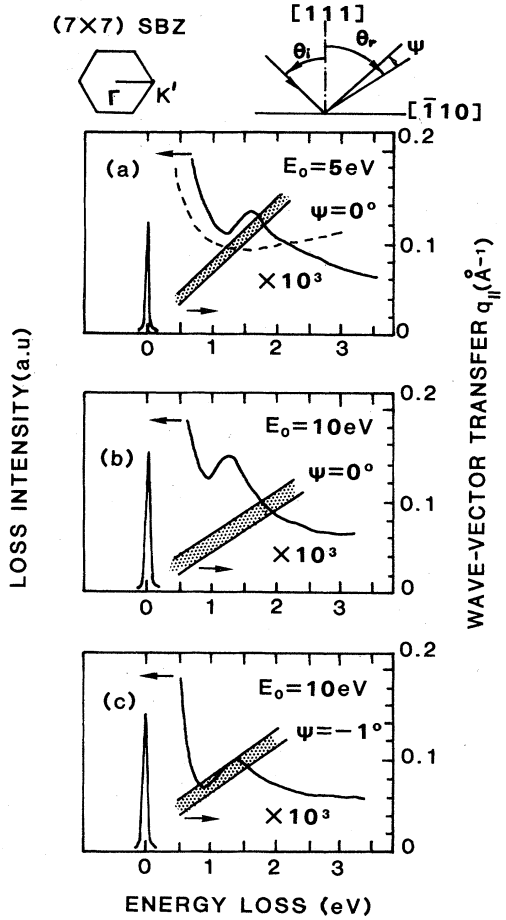


FIG. 1. Electron-loss spectra measured with different primary energies $E_0$ at different angles $\psi$ along the $\Gamma K'(7\times7)$ surface Brillouin zone. (a) and (b) spectra recorded under specular reflection ($\psi=0$) with, respectively, $E_0=5$ and 10 eV. The loss peak $\sim1.5$ eV involves transitions between occupied and empty surface states. The dotted curve in (a) shows the disappearance of this loss after a few hours under the $0.5\times10^{-10}$-Torr residual ambient. (c) Spectrum recorded under off-specular reflection, $E_0=10$ eV $\psi=-1°$. Shaded strips figured on each (a), (b), and (c) curve indicate the uncertainty in the wave-vector transfer $q_\parallel$.

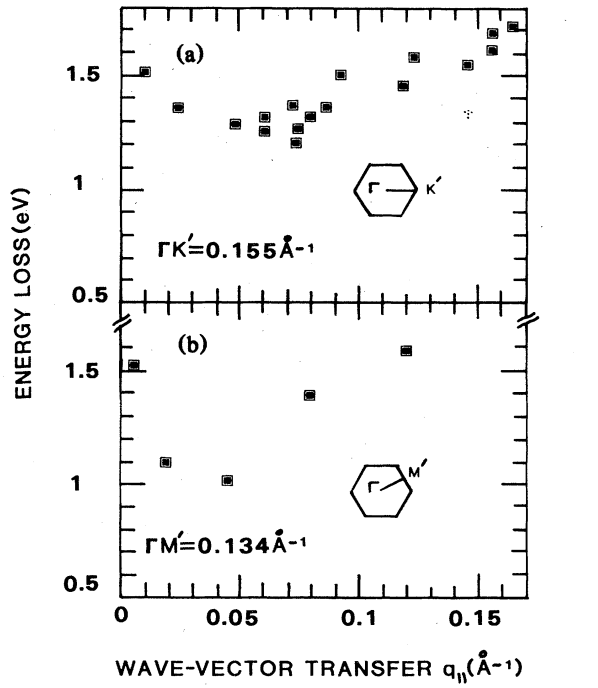


FIG. 2. Loss maxima positions $\hbar\omega$ plotted vs wave-vector transfer $q_\parallel$. The results derive from a compilation of several specular and off-specular data with various primary energies as exemplified in Fig. 1. (a) Results obtained when the $q_\parallel$ transfer is confined to the surface within the plane of incidence and parallel to the $\Gamma K'$ $(7\times7)$ surface Brillouin zone ([$\bar{1}$10] axis in direct space). (b) The $\Gamma M'$ $(7\times7)$ surface Brillouin zone is now scanned ([$\bar{2}$11] axis in direct space).

The finite angular aperture of the analyzer (typically $\pm0.5°$) determines the uncertainty in $q_\parallel$. Under the present conditions, it can reach values up to 0.03 $Å^{-1}$ but still small as compared with $q_\parallel$ itself. With a primary energy $E_0$ of 5 eV and scattering under specular direction ($\theta_i=45°$, $\psi=0°$), the $q_\parallel$ transfer at a loss energy of $\sim1.5$ eV reaches a value of about $\sim0.14$ $Å^{-1}$, i.e., approximately the length of the $\Gamma K'$ axis of the $(7\times7)$ surface Brillouin zone (inset Fig. 1). For $\hbar\omega/2E_0$ ratios smaller than $10^{-2}$, the $q_\parallel$ transfer [$q_\parallel\approx k_0\sin\theta_i(\hbar\omega/2E_0)$] is negligible as in an optical transition.

Equation (1) shows that a variation of either $E_0$ (with $\psi=0$) or $\psi$ (with $E_0$ constant), therefore, allows wave-vector transfer throughout half of the $(7\times7)$ SBZ. Several experiments had been done with $E_0$ varying in the range 5–40 eV and $\psi=\pm5°$. In Fig. 2, the observed loss maximum position, i.e., the transition energy $\hbar\omega$ is plotted versus the wave-vector transfer $q_\parallel$ as calculated from Eq. (1), along the $\Gamma K'$ axis [Fig. 2(a)] and the $\Gamma M'$ axis of the $(7\times7)$ SBZ [Fig. 2(b)]. The $\hbar\omega$ ($q_\parallel$) plot in Fig. 2 is the compilation of both specular and off-specular experiments. The plot demonstrates unambiguously for the first time that the dangling-bond state bands display a dispersion within the $(7\times7)$ SBZ. This result could not be obtained so far with ARUPS experiment due to the very small extension of the $(7\times7)$ SBZ. In ARUPS several groups[12–16] have observed two well separated occupied surface state bands at $\sim-0.9\pm0.1$ eV and at $\sim-1.9\pm0.1$ eV below the Fermi level $E_F$. The upper lying band has $\Lambda_1(s,p_z)$ symmetry with strong dangling-bond character and gives rise to strong emission for wave vectors near the center $\Gamma$ of the SBZ. The deeper lying states have $\Lambda_3(p_x,y)$ character and are likely involved in back bonding. In ARUPS, the dispersion of these bands could only be studied within the $(1\times1)$ Brillouin zone. With an uncertainty $\sim0.1$ eV, no dispersion had been found in the $(1\times1)$ SBZ. This last result does not mean that within the small $(7\times7)$ SBZ the surface state bands do not display any dispersion. Indeed we demonstrate for the first time that they do have a dispersion along the $(7\times7)$ SBZ. Another interesting comparison of the present results can be drawn up with ARUPS and inverse-photoemission data. The energetic width of the dangling-bond states, located at $-0.9$ eV below $E_F$ is about 0.5 eV. In inverse-photoemission Fauster and Himpsel[6] have found a band of empty surface states at $\sim+0.53$ eV above $E_F$ with an energetic width of about 0.4 eV. Symmetry and dispersion of these empty states have not been determined so far. The energetic distance between the occupied

dangling-bond band and the empty states is about $\sim 1.4 \pm 0.2$ eV. This value agrees well with the transition energy $\hbar\omega$ we have observed here with ELS ( $\sim 1.5$ eV at $q_{\parallel} = 0$). We therefore interpret the present loss structure in terms of electronic transitions between the $\Lambda_1(s,p_z)$ dangling-bond surface states and the empty states having been found in inverse photoemission (see Fig. 3). The relatively high width of the UPS and inverse-photoemission bands also explains at least part of the broadening which is seen in our loss data. The consistent interpretation of the ELS, ARUPS, and inverse UPS data, furthermore, strongly suggests that many-body effects (relaxation, shielding, electron-hole interaction) being involved in the different experimental methods in a different way are not very significant. Their overall contribution might be estimated to be smaller than 0.5 eV.

We have demonstrated with the wave-vector resolved ELS technique that a dispersion of the surface states within the very small $(7\times7)$ surface Brillouin zone does exist. This wave-vector resolved technique, when coupled with ARUPS, proves to be also a powerful tool with which to gather information on the empty states of two-dimensional electronic structures.

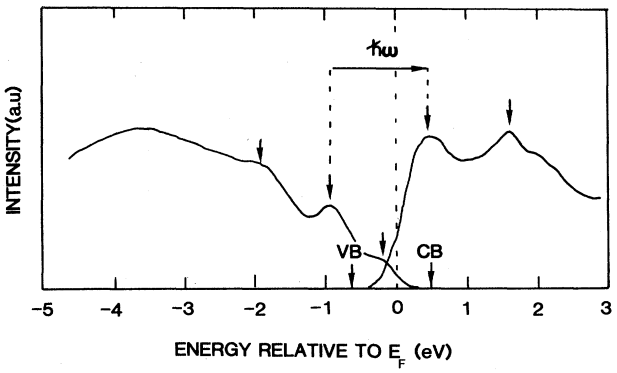


FIG. 3. Schematic energy diagram constructed from photoemission and inverse photoemission data (according to Refs. 6, 12–16). The $\hbar\omega$ arrow represents the loss discussed in this Rapid Communication. Other tic marks show occupied and empty surface states as revealed by UPS and inverse photoemission.

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