Electron-Phonon Interaction in Optical Absorption at the Si(111)2×1 Surface

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The temperature dependence of the optical absorption associated with surface states on the Si(111)2×1 surface is presented. The results indicate a behavior characteristic of localized excitations with a strong electron-lattice interaction, that is, a nearly Gaussian absorption that broadens roughly as the square root of the absolute temperature and shifts to lower energies upon increasing temperature. The frequency of the surface phonons that couple to the transition is smaller than hitherto assumed for the 2×1 surface.

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In recent years, the surface of Si(111)2×1 has been the subject of intensive research. The chain model of the 2×1 reconstruction,[1] that predicts the correct band dispersion observed in angle-resolved ultraviolet photoemission spectroscopy (ARUPS),[2] is now well established in its symmetry properties through optical anisotropy measurements,[3,4] ion scattering,[5] and scanning tunneling microscopy.[6] However, the arrangement of the atoms along the chains is still uncertain. Models of a dimerized[7] or a buckled[8] chain that explain the opening of the surface gap[9] have been proposed. The last model seems to be more consistent with dynamical low-energy electron diffraction studies.[10] Recently, the electron-phonon interaction[11] for various reconstruction models has been investigated theoretically, as well as the phonon structure of the surface.[12]

In this Letter we present measurements of differential reflectivity as a function of temperature that show a strong electron-phonon interaction affecting the optical transition across the surface gap. Such results give evidence of localization of the states involved in the transition. The phonons emitted have an energy much smaller than that hitherto associated with surface optical phonons.

Silicon samples with (111) orientation were cleaved at room temperature in ultrahigh vacuum (UHV) (pressure in the 10^{-10} Torr range) by use of the double wedge technique. In this way a good-quality (2×1) reconstructed surface is obtained with very high reproducibility. After cleavage the samples were brought to the required temperature and the reflectivity of the clean surface recorded as a function of wavelength. The surface was then fully oxidized, at that temperature, and a new reflectivity spectrum was taken. The ratio

$$\Delta R/R = (R_{\mathrm{clean}} - R_{\mathrm{ox}})/R_{\mathrm{ox}}, \qquad (1)$$

proportional to the imaginary part of the surface dielectric function, is shown in Fig. 1 versus the energy of the photons for three different temperatures, all of them well below that of the 2×1 → 7×7 transition.

It is seen from the curves of Fig. 1 that the dangling-bond peak displays a red shift with increasing temperature,[13] while its half-width increases considerably. Moreover, the shape of the curves is slightly asymmetric, being wider on the high-energy side, while their areas remain sensibly constant at the various temperatures. Figure 2 shows the temperature dependence of the full width at half maximum $W(T)$ of the curves of Fig. 1. It is seen that the width increases roughly as the square root of the absolute temperature.

Results of electron energy-loss spectroscopy show a 60-meV shift of the onset with increasing temperature

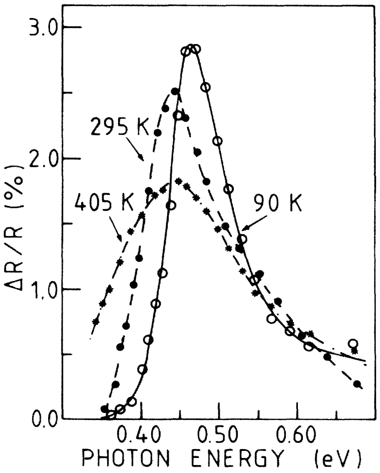

FIG. 1. Differential reflectivity as a function of the photon energy in Si(111)2×1 at three different sample temperatures.

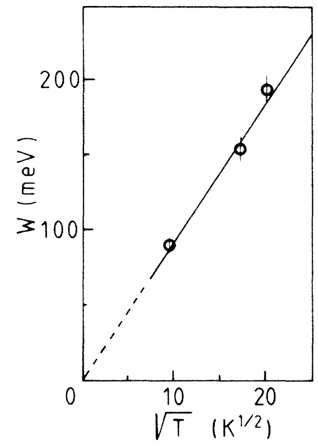

FIG. 2. The full width at half maximum of the curves of Fig. 1 vs the square root of the absolute temperature.

from 20 K to room temperature, while the position of the peak remains stationary.[14] A comparison of electron energy-loss spectroscopic and optical data is difficult because of the complexity of the loss processes undergone by electrons of 10 eV, as pointed out by the authors, though the general trend is in agreement with the present results.

The large broadening of the curves of Fig. 1 with temperature clearly shows that the electron-phonon interaction at the 2×1 surface is very strong. Moreover, their qualitative behavior as a function of energy resembles more closely a δ-like transition broadened by the phonons than a critical point in the joint density of states of dispersive surface bands. Such a behavior, namely, a nearly Gaussian absorption slightly asymmetric on the high-energy side, a $T^{1/2}$ dependence of the width at high temperature, and a red shift of the curves with increasing temperature, is characteristic of localized excitations.

On speculative grounds, one can try to compare the present results with the theory of localized transitions, i.e., the polaronic exciton or the F center.[15,16] In such theories the optical absorption is described as a vertical transition between electronic states, whose energy minima are displaced, in the configurational coordinate scheme, by the electron-lattice interaction. The half-width is proportional to $S^{1/2}$, where

$$S=\sum\nolimits_i (n_i+\tfrac{1}{2})a_i\omega_i/\hbar \qquad (2)$$

is the so-called Huang-Rhys factor that measures the strength of the electron-phonon interaction[17]; ω_i is the frequency of the ith vibrational mode, a_i its contribution to the displacement of the minima, and n_i the Bose-Einstein distribution function. In (2) the assumption has been made that ω_i does not depend upon the state of electronic excitation.

For an Einstein model with a single phonon frequency ω_0, the number of phonons emitted in the transition corresponding to the peak of the absorption curve at zero temperature is S, while the half-width is

$$W(T)=W(0)[\coth(\hbar\omega_0/2kT)]^{1/2}, \qquad (3)$$

which gives the $T^{1/2}$ behavior at high temperatures. Within such a model a red shift of the peak is explained by a softening of the mode when the electron is raised to the excited state, as well as by a change in the lattice parameter.[17,18]

The slope of the straight line of Fig. 2, representing the high-temperature expansion of Eq. (3), gives the ratio $W(0)/\hbar\omega_0$. Since $W(0)$ cannot be larger than 90 meV (the width at 90 K), an upper limit of approximately 15 meV is set for $\hbar\omega_0$, though a fitting of the functional relation (3) suggests a lower value around 10 meV.[19] In the same way a lower limit for the Huang-Rhys factor S can be found since $W(0)=C\hbar\omega_0 S^{1/2}$, where C depends on the shape of the curves and is $C=2(2\ln2)^{1/2}$ for a Gaussian.[16] It turns out that $S\geqslant7$, i.e., at least 7 phonons are created during the transition, which confirms that we are dealing with the case of a strong interaction and localized excitation. With $\hbar\omega_0=10$ meV one obtains in the same way $S=9$.

A model along similar lines has been proposed by Chen, Selloni, and Tosatti[11] for the fully buckled Hanemann structure of the 2×1 surface.[20] However, the assumption of a large phonon energy (~50 meV) and the neglect of the softening of the modes in the excited state led them to results in incomplete agreement with the experiments.

The assumption made in Eq. (3) of an Einstein model for the surface is of course very crude also in view of recent theoretical calculations of the phonon spectrum.[12] However, when more than one mode couples to the transition, the presence of the Bose-Einstein factor in S, together with the scaling of the a_i's with $1/\omega_i^2$,[15,18] considerably reduces the contribution of the phonons of higher energies. As an example, a phonon of 56 meV[21] gives a (nearly temperature independent) contribution smaller than one-tenth of that of a phonon of 10 meV that couples with equal strength. Therefore the experiments do not exclude the presence of phonons of higher energy, provided they couple with comparable or smaller strength.

Though the value obtained for the energy of the phonon might depend somehow upon the model, recent experiments of inelastic scattering of He atoms from Si(111)2×1 surfaces[22] give a value of 10 meV for the main surface phonon in the low-energy range, in agreement with the present results.

The strong electron-phonon interaction observed in the present work is in favor of reconstruction models displaying some polar character, like the buckled chain. In such a model atoms are raised and lowered along the chain and the electronic charge concentrates around the raised atoms. The optical transition corresponds to a charge transfer from a wave function centered on raised atoms to one centered on lowered atoms. Because of the change of charge distribution upon the transition, atoms move into new equilibrium positions, thus exciting the mode that modulates the buckling amplitude. In a recently developed theory of the surface vibrational spectrum of Si(111)2×1,[12] a mode that probably fits the above requirements would be the so-called rocking mode whose energy is found, however, at 33 meV. Detailed calculations are necessary to go beyond the simplified model assumed in discussion of the present results.

From the point of view of band theory, the optical transition of Fig. 1 occurs along the $\overline{JK}$ line of the surface Brillouin zone. Both theoretical calculations[23] and ARUPS[2] show that the dispersion is small along $\overline{JK}$ normal to the chains (x direction), and large parallel to the chains, for example, along $\overline{\Gamma J}$ (y direction). As a consequence, wave functions involved in the optical transitions are strongly localized in the x direction and delocalized in the y direction. They are obviously localized also in the z direction (normal to the surface). It has been suggested by Chen, Selloni, and Tosatti[11] that y localization may occur through polaronic effects caused by electron-phonon interaction. Polaron theory predicts a mass enhancement for the band electron (or exciton) of e^S.[15] Under these conditions flat polaron bands are singled out from ordinary bands giving rise to localized states.[24]

An apparent difficulty arises from the comparison with the results of Hansson and co-workers, who showed that in both Ge[25] and Si[26] the positions of the surface valence and conduction bands along $\overline{JK}$, detected by ARUPS, give rise to an energy difference equal, within the experimental accuracy of 50 meV, to that observed in optical absorption. The emission of S phonons in the optical transition with a total energy $\hbar\omega_0 S = 90$ meV seems to contradict that result. It should be mentioned, however, that the red shift of the peak of Fig. 1 by at least 20 meV at room temperature (where the ARUPS measurements have been taken) presumably reduces the vibrationally lost energy because of the softening of the modes. Furthermore, a close inspection of the data reported in Ref. 26 shows that the actual difference between the surface conduction and valence bands is slightly smaller (0.43 eV) than that observed in optical absorption (0.445 eV), thus reducing the above discrepancy to a value almost consistent with the experimental accuracy of ARUPS. Therefore, the conclusion of the above authors that excitonic effects in the optical absorption are not large maintains its validity.

In conclusion, the experimental results demonstrate that in Si(111)2×1, electron-lattice interaction is essential in describing surface processes, while the localized model outlined above seems to give a qualitatively correct picture of the surface optical transitions.

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