Polarization-dependent reflectivity of Si(111)-(2×1) surface above the gap

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(Received 22 October 1984)

Results of surface differential reflectivity with polarized light at photon energies above the gap are presented for Si(111)-(2×1) single-domain surfaces. They show an anisotropic behavior in the 2–3.5-eV range with a maximum when the electric vector is parallel to the $[\bar{2}11]$ direction of the reconstructed surface. The results are compared with those previously reported for energies below the gap and are interpreted in terms of transitions involving dangling-bond bands at different points of the surface Brillouin zone, in the framework of the Pandey model of the surface.

A large effort of work has been done in the last years on the properties of semiconductor surfaces by means of optical techniques. It is now well established that electronic transitions between surface bands can occur at energies both below[1] and above[2-4] the principal gap of the semiconductor. Such optical transitions have been observed in cleaved[1-3] and otherwise[4] prepared surfaces.

The Si(111)-(2×1) is one of the most extensively studied, both from the theoretical and experimental points of view.[5] Previous results of optical measurements have shown a strong peak at 0.45 eV and a broad structure between 2.0 and 3.5 eV.[1,2]

Very recently, optical techniques making use of polarized light have shown a strong anisotropy of the 0.45-eV peak (S_0) with maximum absorption along the $[0\bar{1}1]$ direction (from now on the y direction) for a single-domain (111)-(2×1) silicon surface.[6,7] Such measurements seem to support the so-called Pandey model[8] of the (2×1) reconstruction that predicts π-bonded chains in the $[0\bar{1}1]$ direction.

We report here results on the polarization dependence above the silicon principal gap that show a moderate anisotropy of the broad structure between 2.0 and 3.5 eV with the maximum along the $[\bar{2}11]$ direction (from now on the x direction).

Measurements were taken by the surface-differential-reflectivity method that consists of measuring the overall reflectivity of the sample before and after exposure to oxygen: The results are given in terms of $\Delta R/R$ [$\Delta R/R \equiv (R_{\text{clean}} - R_{\text{ox}})/R_{\text{ox}}$], i.e., the relative change of reflectivity for the clean and oxidized surface. The experiments were performed in a UHV chamber (base pressure 2×10^{-10} Torr) equipped with a four-grid low-energy electron diffraction (LEED) and coupled to an optical system by means of a CaF$_2$ window. The clean surfaces were prepared by cleaving silicon samples along the $[\bar{2}11]$ direction of the (111) plane, in order to obtain a single domain,[9] as controlled by LEED. A detailed description of the apparatus will be given elsewhere.

Figure 1 shows $\Delta R/R$ as a function of photon energy in the range 0.3–4.0 eV for light polarized in x and y directions, i.e., perpendicular and parallel to the chains, respectively. A remarkable difference between the two spectral regions, below and above the gap, is clearly evident.

The polar dependence of $\Delta R/R$ for two spectral points at 0.45 and 2.40 eV is plotted in Fig. 2. The S_0 peak shows a $\cos^2\theta$ behavior (solid line), θ being the angle between the

light electric vector **E** and the y direction. This behavior is as expected for a system with principal axes along x and y directions and anisotropy ratio 0:1 as shown in Fig. 1. On the contrary, the polar dependence of the $\Delta R/R$ at 2.40 eV can be fitted by const$+\sin^2\theta$ where the constant term arises from an isotropic contribution.

Though radically different in their polarization dependence, the various spectral structures behave in the same way with respect to exposure to oxygen as shown in Fig. 3, where $\Delta R/R$ at 0.45, 2.40, and 3.00 eV is reported as a function of oxygen exposure. The sticking coefficient for the initial stage of oxidation is found to be approximately 5×10^{-4}.[10]

The different polarization behavior for the S_0 peak and the spectral structure above the gap was predicted by Del Sole and Selloni,[11] who showed that, for the Pandey model, the S_0 peak originates from transitions along the JK direction of the two-dimensional surface Brillouin zone (SBZ) and can be excited only by light with **E** parallel to the chains, while the structure above the gap originates from transitions along $\Gamma J'$ and can be excited only with **E** perpendicular to the chains. Such a behavior is due to the different symmetry properties of the wave functions with
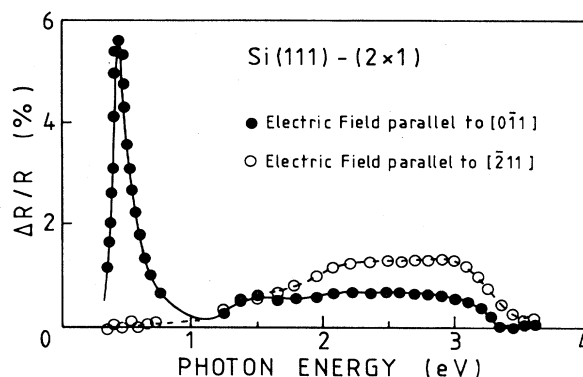

FIG. 1. Differential reflectivity spectra of a Si(111)-(2×1) single-domain surface. Light was polarized along the $[0\bar{1}1]$ (solid circles) and $[\bar{2}11]$ (open circles) directions, i.e., parallel and perpendicular to the π-bonded chains of Pandey model, respectively. R_{ox}, in the definition of $\Delta R/R$, is the saturation value of R after prolonged exposure.
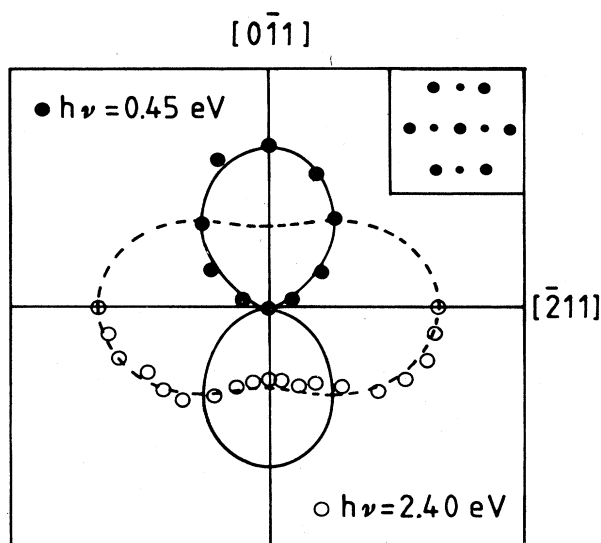
FIG. 2. Polar plot of the polarization dependence of $\Delta R/R$ at 0.45 eV (solid circles) and 2.40 eV (open circles). The solid and dashed lines are a $\cos^2$ and $\text{const} + \sin^2$ fitting to the data points, respectively. The inset represents a sketch of the LEED pattern (with integer and half-order spots) of the Si(111)-(2×1) face.

FIG. 3. Dependence of differential reflectivity vs oxygen exposure in langmuirs (1 L = 1×10^{-6} Torr sec) for a Si(111)-(2×1) surface. Data were taken simultaneously at three different photon energies: 0.45 eV (solid circles), 2.40 eV (open circles), and 3.00 eV (triangles). R_{ox} is, in this case, the value of R at a given exposure.

respect to the mirror plane containing the x direction.

These calculations substantially agree with the experimental results of Fig. 1, though a careful discussion is necessary for the structure around 2.5 eV. In this case the surface bands related to such transitions could be no more in the gap. An analysis of the projected bulk-band structure on the (111) plane together with angular-resolved photoemission results[12] and theoretical calculations[13] shows that an energy and **k** degeneracy between bulk and surface bands can occur. Under these conditions the surface states mix with bulk states and the mixture may show a different orbital composition with different matrix elements and reduced anisotropy. Contributions of other points of the SBZ near J' can also reduce the anisotropy. Of course a different interpretation assuming a completely anisotropic (narrower) transition centered around 2.8 eV superimposed to a broad isotropic band (possibly originating from back bonds) is also possible.

In order to clarify these points it is illuminating to evaluate, by means of the sum rules, the effective number of electrons associated with the two anisotropic components of the imaginary part of the surface dielectric tensor ϵ_x'' and ϵ_y''. Such components are directly related to the values of $(\Delta R/R)_x$ and $(\Delta R/R)_y$ (Refs. 14 and 15). Owing to the isotropic behavior of the system at sufficiently high ener-
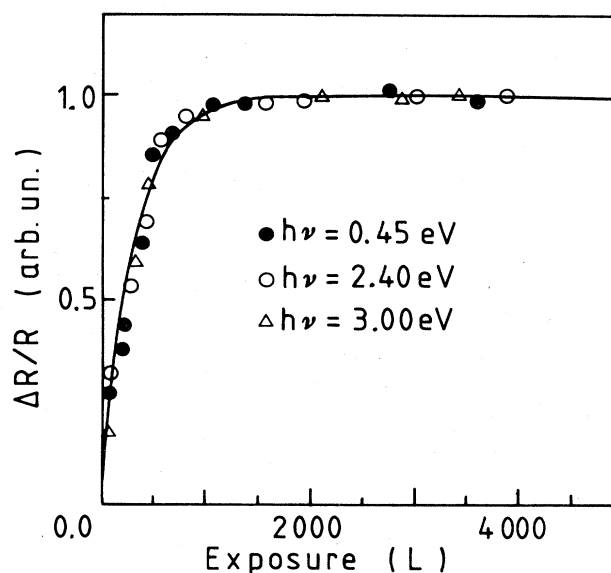
gies, it can be easily shown that

$$\int_0^\infty \omega \epsilon_x''(\omega)\, d\omega = \int_0^\infty \omega \epsilon_y''(\omega)\, d\omega$$

each being proportional to the number n_{eff} of the electrons taking part in the transition.

From the curves of Fig. 1 we can calculate the above integrals up to 3.8 eV. The corresponding values of n_{eff} are found to be ~ 1.5 and 1.0 electrons per surface atom, respectively. These results suggest that the dangling-bond electron has nearly exhausted its oscillator strength at 3.8 eV and that hybridization of the wave functions with bulk states is not very severe. Of course, such statements can only be rigorously proved by measurements of $\Delta R/R$ in a wider energy range, since in principle the structure around 2.5 eV, or part of it, could be due to mixing with bulk states or to back bonds.

In conclusion, the experimental results on the optical properties of the Si(111)-(2×1) in the 0.3–4.0-eV photon range show that most of the spectrum can be explained in terms of dangling-bond (DB) bands. The observed transitions display a polarization dependence that agrees with the symmetry properties of such states, as required by the π-bonding chain model. A partial mixing between the DB and bulk states is probably necessary to fully explain the experimental results.

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