Direct Measurement of the Polarization Dependence of Si(111)2×1 Surface-State Absorption by Use of Photothermal Displacement Spectroscopy

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(Received 19 December 1983)

The polarization dependence of midgap optical absorption (0.38–0.51 eV) by Si(111)2×1 single-domain surfaces has been measured directly by photothermal displacement spectroscopy. The absorption is strongest when the light is polarized perpendicular to the period-doubling direction of the 2×1 reconstruction and is reduced by at least 95% when the polarization is rotated by 90°. This result supports the π-bonded chain model of the Si(111)2×1 surface reconstruction.

PACS numbers: 73.20.-r, 68.20.+t, 78.20.-e

Upon cleavage at room temperature, the Si(111) surface reconstructs to a metastable 2×1 structure, with two surface atoms per surface unit cell. The exact nature of this reconstruction is an open question. Early models for the 2×1 reconstruction centered around a buckling mechanism[1] which involves raising and lowering of adjacent rows of surface atoms from their ideal bulk positions. Angle-resolved photoemission (ARPES),[2,3] however, shows a strong dispersive band along the $\bar{\Gamma}$-$\bar{J}$ direction in the surface Brillouin zone which is inconsistent with calculations based on the buckling model.[4] Recently, low-energy electron-diffraction (LEED)[5] and ion backscattering (IBS)[6] data have revealed additional inconsistencies with this model.

An alternative model involving π-bonded chains along the $\langle\bar{1}10\rangle$ direction of the Si(111)2×1 surface has been proposed by Pandey.[7] This model involves a major rearrangement of the atoms in the top few atomic layers. However, it has been shown[8] that the energy barrier to this reconstruction is less than 0.03 eV/surface atom. Band-structure calculations based on this model[7,8] predict the dispersive band seen in the photoemission data,[2,3] and the IBS measurements[6] are also consistent with this chain model. However, a second, less dispersive, band seen in ARPES,[3] and the dynamical LEED results,[5] appear inconsistent with Pandey's chain model. Variations on this model, including dimerized[9] and molecular[10] chains, have also been proposed.

The polarization dependence of the surface-state optical absorption is an important and straightforward test of semiconductor surface reconstructions, since it arises from symmetry considerations and is not critically dependent on calculations requiring accurate atomic positions, such as those required to simulate ARPES, LEED, and IBS data. Optical spectra of cleaved silicon with unpolarized light, as measured by reflectivity,[11] surface photovoltage (SPV), and surface photoconductivity (SPC),[12] show a surface-sensitive peak near midgap, around 0.45–0.47 eV. The absorption was originally taken to be evidence for the buckling model, since calculations[13] showed a similar gap between the full and empty dangling-bond states. However, in the context of the chain model, the optical absorption can be interpreted as a transition between the bonding and antibonding orbitals of the π-bonded chains. Although the buckling and chain models predict a similar optical gap, the predicted polarization dependence of the optical absorption is quite different. For the chain model, the absorption is maximal for light polarized parallel to the chains (along $\langle\bar{1}10\rangle$),[14] whereas the buckling model predicts the maximum absorption to occur for light polarized perpendicular to the rows of atoms (along $\langle 11\bar{2}\rangle$).[15]

The polarization dependence of SPV on the Si(111)2×1 surface has been reported at 0.33 and 0.6 eV.[12] The SPV at 0.33 eV was maximal for light polarized along a $\langle 11\bar{2}\rangle$ direction, and this has been taken as evidence for the buckling model.[12,15] However, the absorption near 0.33 eV has been shown to be cleavage dependent and may be dominated by step-state absorption.[16] The SPV at 0.6 eV was independent of the incident polarization. This may be due to excitations from the bulk valence-band maximum at Γ into unoccupied surface states.[17] The crucial test of the calculations in Refs. 14 and 15 is the polarization dependence of the strong dangling-bond absorption near 0.46 eV, an energy region not reported in Ref. 12.

Using a new technique, photothermal displacement spectroscopy (PTDS),[18] we have measured the polarization dependence of the Si(111)2×1 surface absorption peak. Unlike differential reflectivity and total-internal-reflection measurements, which require a difference spectrum between clean and oxidized surfaces, PTDS measures the optical absorption directly. A peak absorption at ~ 0.46 eV was observed. The magnitude of this absorption measurement agrees with that previously reported with reflectivity,[11] and the position of the peak is consistent with reflectivity,[11] SPV, SPC,[12] and electron energy-loss[19] measurements. As the polarization of the incident light is rotated in a single-domain region, determined from LEED to be reconstructed along the $[11\bar{2}]$ direction, the absorption is found to be highly peaked for light polarized in the $[\bar{1}10]$ direction (parallel to $\bar{\Gamma}$-$\bar{J}$). This result is predicted by the symmetric π-bonded chain model, and not by the strongly dimerized or molecular chain models, or by the buckling model for this surface.[14] We report a polarization dependence at 0.468 eV which is different from the SPV results[12] mentioned above, supporting the assignment of the 0.33- and 0.6-eV SPV signals as due to transitions involving different initial and/or final states from those contributing at the peak. In addition, we observe a linewidth which, like the SPV and SPC measurements, is smaller than that observed with reflectivity.[11]

Photothermal displacement spectroscopy is based on optical detection of the thermal expansion of a sample as it is heated by absorption of light. An optical absorption spectrum is generated as an intensity-modulated, tunable light beam (pump beam) is focused onto the sample. Following the absorption of light, excited electrons decay nonradiatively and the sample is locally heated. The change in slope of the sample surface due to local thermal expansion is detected through the deflection of a HeNe probe beam, which is measured by a position-sensitive photodiode. The signal, which is detected by phase-sensitive methods, is directly proportional to the surface absorption coefficient of the sample and is easily calibrated.[18] For the experiments reported in this Letter, the surface area probed was of diameter ~ 300 μm.

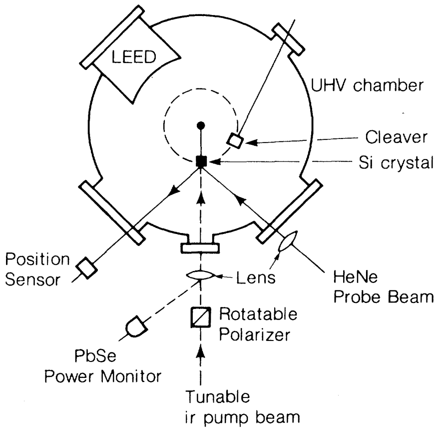

FIG. 1. Experimental configuration.

The experimental configuration is shown in Fig. 1. A Kr$^+$-pumped *F*-center laser serves as the pump beam. The beam is passed through a ZnSe Brewster-plate rotatable polarizer and a CaF$_2$ window into the UHV chamber, and is focused onto the Si crystal. The p-type ($\rho \sim 6$ Ω cm) Si samples were cleaved in UHV ($\sim 4\times10^{-10}$ Torr) along the $[11\bar{2}]$ direction. The pump and probe beams were aligned to probe a single-domain region as determined by LEED.

A peak in the optical absorption at ~ 0.46 eV was observed (see Fig. 2). For single-domain regions exhibiting sharp, unsplit LEED spots, a maximum absorption of 1.8%–2.4% was obtained for a $[\bar{1}10]$ polarization of the pump beam. The position of the

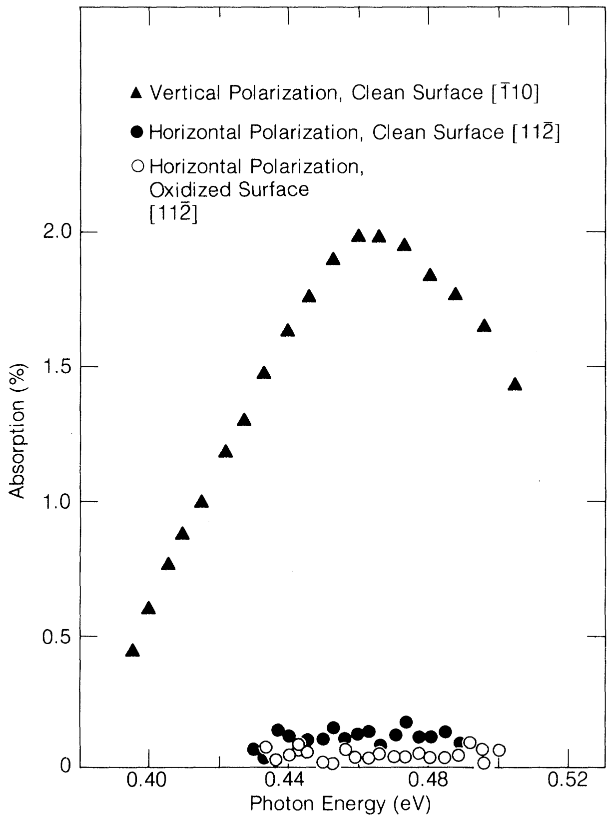

FIG. 2. Si(111)2×1 surface-state absorption spectrum. Saturation oxidation was obtained after ~ 1 h at 10^{-7} Torr.

line varied by 6 meV among three cleaves, with the smallest peak absorption occurring for the curve at the highest energy. The line shape was the same for the three cleaves. After oxidation, the absorption signal was reduced to less than 0.06% for all polarizations (see Figs. 2 and 3). This conclusively shows that the absorption seen was due to surface states on the Si(111)2×1 surface. The ~2% surface absorption measured with PTDS agrees with the 4% relative change in reflectivity ($\Delta R/R$) obtained by external reflectivity measurements.[11] Treating the surface as a 5-Å, uniform, dielectric layer[20] on bulk silicon, we calculate a 2.0% absorption of the incident beam in this surface layer when using the same surface dielectric function which results in a 4.0% $\Delta R/R$. It should be noted, however, that the reflectivity measurements previously reported[11] were for unpolarized light and an unspecified domain structure. A somewhat larger $\Delta R/R$ would be expected for polarized light reflected from single-domain surfaces.

We find that the absorption line shape obtained from PTDS is similar to that found in reflectivity,[11] but is narrower in linewidth. While the low-energy side of the reflectivity and the PTD spectra have the same dispersion, the PTD spectrum is shifted higher in energy by 25 meV. These differences may be due to the higher spatial resolution ($\leq 10^{-3}$ cm^2) and power densities (~2–40 W/cm^2) inherent in the PTDS experiment.

The polarization of the infrared pump beam was rotated through 360° at a photon energy of 0.468 eV (see Fig. 3). The sample region probed was determined by LEED to be single domain with the second-order spots occurring in the horizontal $[11\bar{2}]$ direction. The maximum signal was obtained with light polarized in the vertical direction (parallel to $[\bar{1}10]$). The signal decreases to less than 5% of the original for horizontal polarization. Spectra taken with horizontal $[11\bar{2}]$ polarization before and after oxidation are shown in Fig. 2.

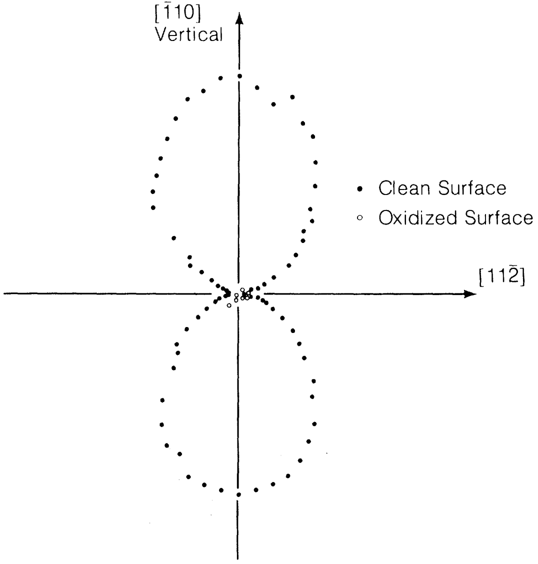

FIG. 3. Polar plot of the polarization dependence at 0.468 eV.

As can be seen from Figs. 2 and 3, the polarization dependence of the Si(111)2×1 surface-state absorption is very strong, with the absorption of $[\bar{1}10]$ polarized light stronger than that of $[11\bar{2}]$ polarized light by at least 20:1. No rotation of the major axes relative to the cleavage direction was observed. These results are confirmed by recent differential reflectivity measurements.[21] If the chain model is correct, the observed direction of the strong surface-state absorption is then parallel to the chains; if the buckling model is correct, the measured direction is parallel to the buckled rows of atoms. The dependence of the absorption on polarization angle seen with PTDS agrees with calculations by Del Sole and Selloni[14] for the symmetric π-bonded chain model proposed by Pandey,[7] and is not consistent with any of the other models tested. When these polarization results are combined with the ARPES data showing a large dispersion along $\bar{\Gamma}$-$\bar{J}$, it is evident that there is a large overlap of surface-state orbitals along this direction. Any correct model for the reconstruction of the Si(111)2×1 surface must account for the large anisotropy in the optical matrix elements between occupied and unoccupied surface states. From ARPES, these appear to be located along $\bar{J}$-$\bar{K}$ in the surface Brillouin zone, with the full state about 0.15 eV above the valence-band edge and the unoccupied states ~0.46 eV higher in energy.

Another interesting, though preliminary, result is the small blue shift of the surface peak with a smaller absorption signal. In the chain model, this could be interpreted as an increase in the surface optical gap as the chains are shortened by disorder of the surface. Further study of this effect is in progress.

Finally, photothermal displacement spectroscopy has been demonstrated to yield a spatially resolved, surface-sensitive, direct measurement of optical absorption by semiconductor surfaces in a UHV environment.

We thank P. Chiaradia for assistance and useful discussion; P. Chiaradia, A. Selloni, and R. Del Sole for communicating their results prior to publication; and R. S. Bauer for the silicon samples and the use of his cleaver during the early part of this experiment. This work was supported by the Defense Advanced Research Projects Administration under Contract No. 3343 and by the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

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