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December 1983

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Direct Measurement of the Polarization Dependence of Si(111)2×1 Surface Optical Absorption Using Photothermal Displacement Spectroscopy

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Abstract

The polarization dependence of mid-gap optical absorption (0.38-0.51 eV) by Si(111)2×1 single domain surfaces has been measured directly using 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.

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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 still 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, LEED[5] and ion backscattering (IBS)[6] data have revealed additional inconsistencies with this model.

An alternate model involving π-bonded chains along the $(\bar{1}10)$ 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 mid-gap, 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 anti-bonding 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 $\bar{\Gamma}$–$\bar{J}$);[14] whereas the buckling model predicts the maximum absorption to occur for light polarized perpendicular to the rows of atoms (along $\bar{\Gamma}$–$\bar{J}'$.)[15]

Using a new technique, photothermal displacement spectroscopy,[16] we have measured the polarization dependence of the Si(111)2×1 surface absorption. Unlike differential reflectivity and total internal reflection measurements, which require a difference spectrum between clean and oxidized surfaces, photothermal deflection spectroscopy 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[17] 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 many of the variations on the chain model, or by the buckling model for this surface.[14] In addition, we report a linewidth which, like the SPV and SPC[12] 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 illuminated portion of the surface is then displaced as the sample thermally expands. The resultant change in slope of the sample surface 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.[16] The volume of the sample probed is determined by the radius of the pump beam and the thermal diffusion length. For the experiments reported in this Letter, the surface area probed was of diameter ~ 300 μm.

The experimental configuration is shown in Fig. 1. A Kr^+ pumped F-center laser, tunable over the range 0.38-0.51 eV, serves as the pump beam. The beam is passed through a ZnSe Brewster plate rotatable polarizer, focused by a 20 cm CaF_2 lens, and passed through a CaF_2 window into the UHV chamber and onto the sample surface. 5mm×5mm×25mm, p-type (ρ~6 Ω-cm) silicon samples were cleaved in UHV along the $[11\bar{2}]$ direction using a carbide blade and copper anvil. The pump and probe beams were aligned to probe a single domain region of the surface as determined by LEED. The base pressure of the UHV chamber was ~$4x10^{-10}$ torr.

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% - 2.35% was obtained for a $[\bar{1}10]$ polarization of the pump beam. The position of the line varied by 6 meV among three cleaves, with the smallest peak absorption occurring for the curve at the highest energy. The lineshape 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 photothermal displacement was calibrated from the 64% absorption by bulk silicon (100% incident - 36% reflected) of Kr^+ 1.91 eV radiation. The same value was also obtained through comparison to thermoelastic theory.[16] This value 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[18] 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 lineshape obtained from photothermal displacement spectroscopy is similar to that found in reflectivity,[11] but is narrower in linewidth. While the low energy side of the reflectivity and the photothermal displacement spectra have the same dispersion, the photothermal displacement spectrum is shifted higher in energy by 25 meV.

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.

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 differential reflectivity measurements.[19] The polarization dependence of optical absorption between localized surface states should provide an unambiguous test of the validity of models proposed for the surface structure. Depending primarily on symmetry considerations, extensive calculations or assumptions are not required in order to compare the

experimental data with model predictions. 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 photothermal displacement spectroscopy agrees with calculations by Del Sole and Selloni[14] for the symmetric π-bonded chain model proposed by Pandey.[7] It is not consistent with any of the other models tested, including the π-bonded molecular chain,[10] strongly dimerized chain,[9] and buckling[1] models. When these polarization results are combined with the ARPES results 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. It should be noted that 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. The polarization dependence of surface photovoltage at 0.33 eV and 0.6 eV has also been reported.[12] The dependence at these energies is different from the 0.468 eV results reported here. This may be due to contributions from cleavage dependent step states[20] at 0.33 eV and transitions from the bulk valence band to unoccupied surface states[21] at 0.6 eV.

Another interesting, though preliminary, result is the small blue shift of the surface peak with a smaller absorption signal. Using 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 be a spatially resolved, surface sensitive, direct way of measuring optical absorption by Si(111), and should yield useful information from other semiconductor surfaces.

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FIGURE CAPTIONS

Fig. 1. Experimental configuration.

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

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

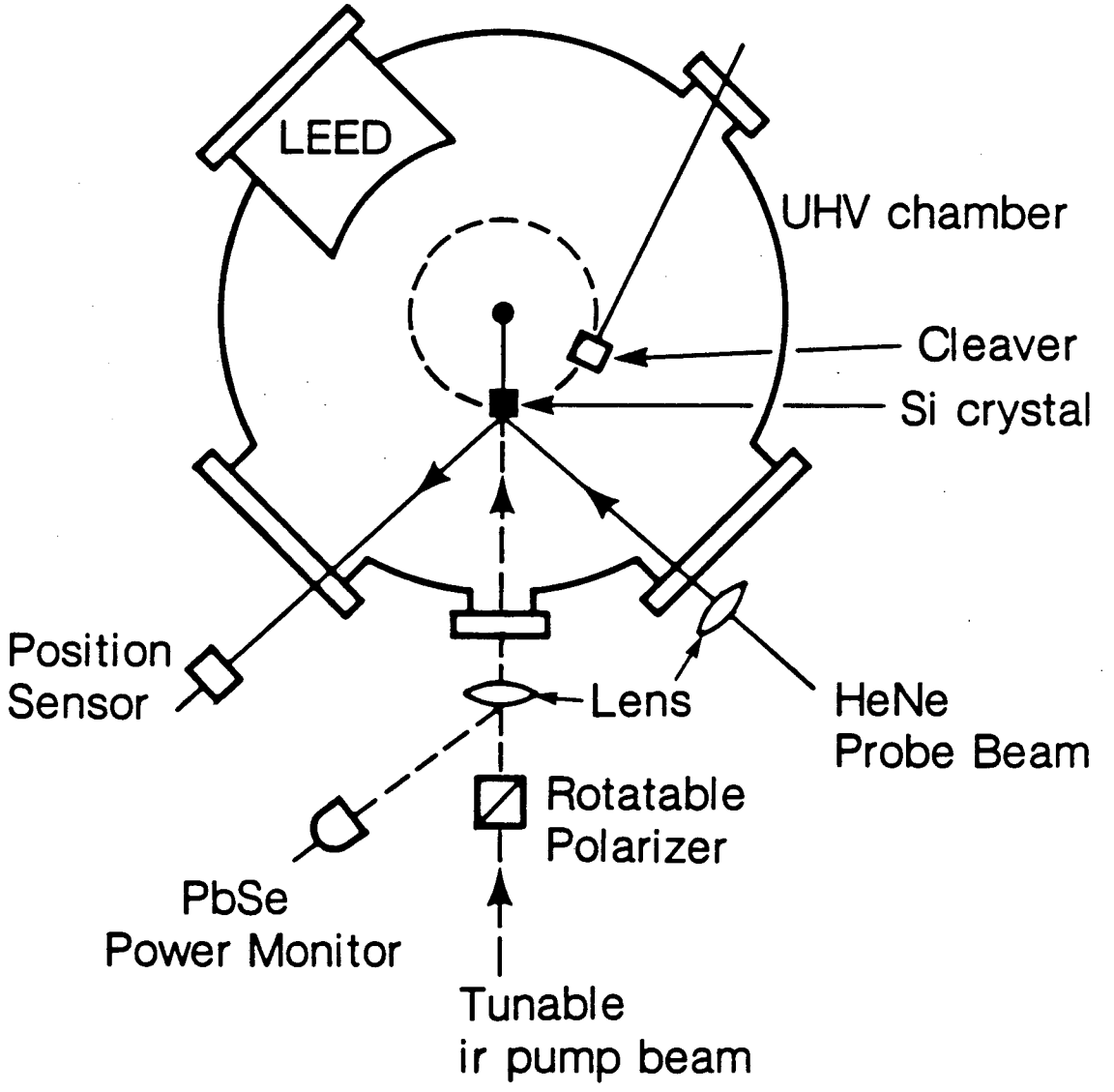

FIGURE 1

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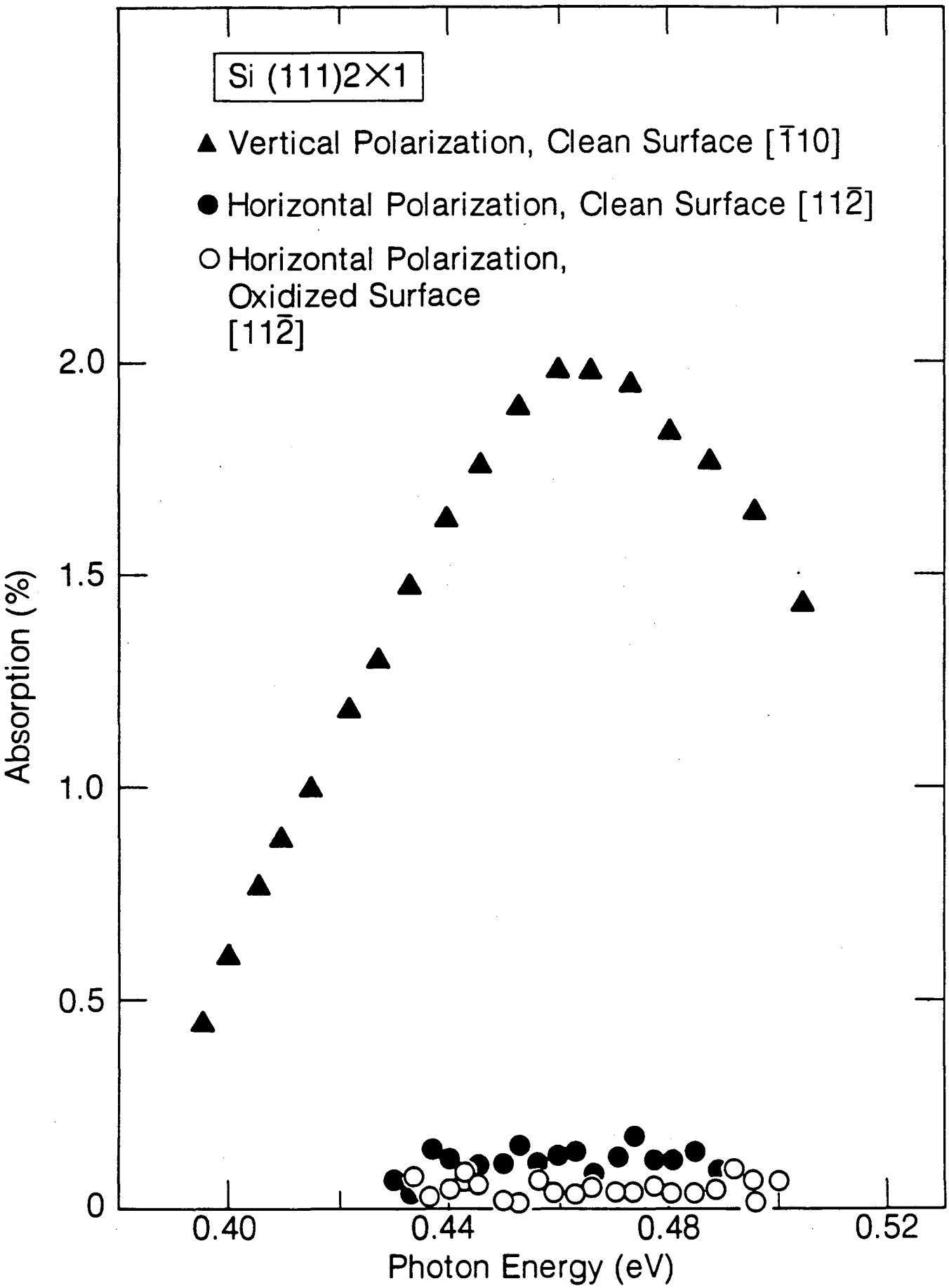

FIGURE 2

XBL 8312-6937

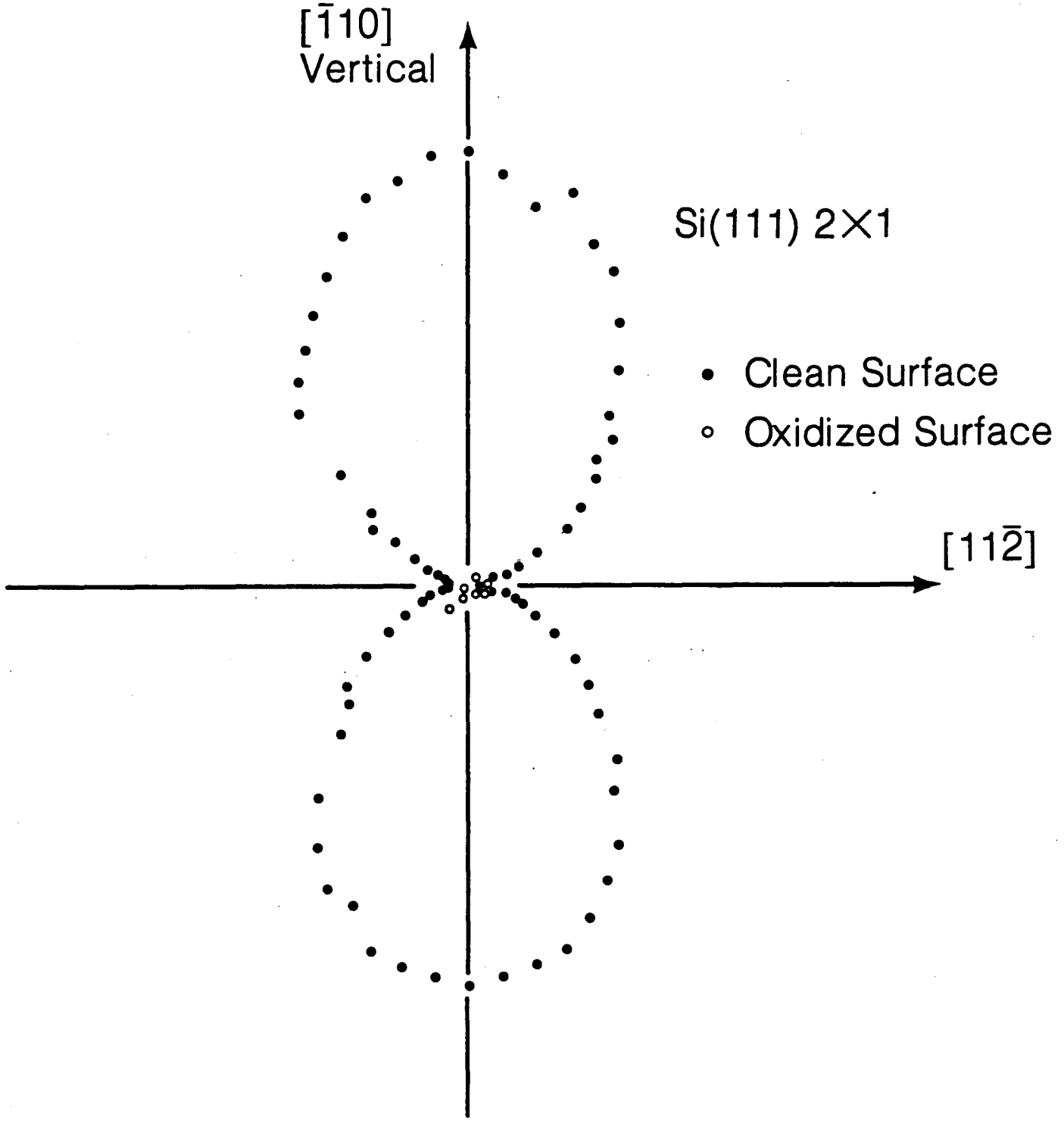

FIGURE 3

XBL 8312-6936

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