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Polarization dependence of Si(111)-2×1 surface-phonon and surface-state excitations

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Electron-energy-loss spectroscopy measurements for the Si(111)-2×1 surface have been performed to investigate the polarization of the dipole-excited surface-phonon and surface-state excitations. We have studied the dependence of the dipole scattering cross section on the azimuthal orientation of the crystal with respect to the scattering plane. Azimuthal asymmetry for dipole cross sections are reported and are in agreement with recent theoretical predictions on the origin and dynamics of the strong dipole-excited surface-phonon loss. Considerations of symmetry and measurements of finite-q vibrational linewidths and defect-dependent effects provide further insight into the vibrational and electronic structure of this surface.

There has been a continuing theoretical and experimental effort to resolve the geometric structure of the *in vacuo* cleaved Si(111) surface which exhibits a (2×1) reconstruction for temperatures $T < 450$ K. Experimental studies of surface-electronic properties using uv and x-ray photoemission (UPS[1] and XPS[2]), electron-energy-loss spectroscopy (EELS),[3,4] and optical spectroscopy[5–7] have been compared with theoretical predictions for various structural models.[8,9] Symmetry and structural information have been obtained by second-harmonic generation (SHG)[10] and low-energy electron diffraction (LEED),[11] respectively; direct structural imaging has recently been achieved with scanning tunneling microscopy (STM).[12] The majority of these studies support the validity of a tilted *π-bonded chain structure*[8] for the 2×1 reconstruction.

The experimental determination of the *static* structures of the 2×1 surface and the 7×7 surface, to which the 2×1 converts upon annealing, is important for comparison to theoretical calculations. In addition, the lattice dynamical structure of the surface can provide new insights into this surface phase transition,[13] the pinning of this transition by surface defects,[14] and the quantitative evaluation of electron-phonon coupling interactions.[4,15,16] The energy-loss spectrum of the cleaved Si surface is unique in that a sharp, strong dipole-excited loss at 57.5 meV is observed.[17] This loss lies below the top of the bulk phonon band. Upon first observation, this loss was assigned to a surface-phonon excitation arising from and localized in the reconstructed surface layer[17] (or from a bulk feature folded back due to the surface superstructure[18]). This conclusion was reached since removal of the surface reconstruction and of the surface-phonon loss occurs simultaneously. The eigenmode assignment of this dominant vibrational loss has remained unresolved, however.

Recently, Alerhand, Allan, and Mele[19] (AAM) performed a dynamical analysis of the (reconstructed) Si(111)-2×1 surface region using their tight-binding model[20] which predicts the static structure of the accepted (tilted) π-bonded chain. They assigned the previously observed loss at ~56 meV (Ref. 17) as a *longitudinal optical surface phonon polarized along the π-bonded chains* corresponding to the $\langle 01\bar{1}\rangle$ direction. Thus, in this model, the surface-vibrational mode is *polarized completely in the surface plane.* The strong dipole nature of the excitation observed in EELS, which by the surface-selection rule on a metal surface[21] would be expected to be screened if it is parallel to the surface, arises from virtual excitations to electronic states above the surface band gap. The calculation thus accounts for the screening of this parallel dipole and its strength is predicted to be relatively large with respect to the other optically allowed surface-phonon excitations. In addition, this surface excitation is split off from the bulk states by symmetry only at $\bar{\Gamma}$ in the surface Brillouin zone (SBZ) becoming resonant with the bulk band away from $\bar{\Gamma}$.[19]

Azimuthal-dependent inelastic electron scattering would be expected to exhibit an asymmetry in cross section for excitation of this mode if a (weakly screened) dipole component is polarized parallel to the surface. This arises due to the fact that the dipole scattering cross section is proportional to $|\mathbf{q}_\parallel \cdot \mathbf{u}|^2$ where $\mathbf{q}_\parallel$ is the parallel momentum transfer and $\mathbf{u}$ is the displacement coordinate of the normal mode. Parallel polarization of both the phonon and the electronic surface interband excitation is predicted by the AAM model along the chain direction ($\mathbf{x} \| \langle 01\bar{1}\rangle$).

We report, to our knowledge, the first azimuthal-dependent EELS measurements of the Si(111)-2×1 surface. They were performed in a chamber containing a $\theta - \phi$ angle-resolving EELS spectrometer, LEED optics, and a specially designed manipulator which provides for cleaving in the $\langle 2\bar{1}\bar{1}\rangle$ direction and flip-azimuthal rotation to vary the orientation of the crystal with respect to the incident EELS electron beam (ϕ_x). Electron scattering was studied on and off specular with the scattered beam in the plane of incidence ($\mathbf{q}_\parallel$ in the scattering plane). The spectrometer angular characteristics were measured at the start of each experiment in order to avoid inconsistencies in angular acceptance due to slight differences in the tuning of the electron optics. The sample was held near room temperature and background pressures were nominally in the mid-10^{-11}-Torr range.

Azimuthal asymmetry in the relative intensity of the

surface-phonon loss, indicative of a surface phonon with a component along $\langle 01\bar{1}\rangle$, has been observed. This asymmetry for a low-energy dipole-excited loss is found to be measurable but small due to the sharp angular dependence of the dipole scattering cross section and the finite angular aperture of the spectrometer.[22] Careful measurements of energy position and width of this loss for various azimuthal orientations has allowed us to rule out a possible feature from a second band. The azimuthal asymmetry of the phonon-loss intensity corresponds to observed asymmetry in the electronic-loss intensity; the position of the intrinsic gap remains fixed. We find a broadening of the phonon-loss off specular which suggests that the phonon is in a symmetry gap only at $\bar{\Gamma}$. In addition, we find that the energy position of the phonon loss is not greatly affected by defects, contrary to another recent study.[23]

EELS spectra of the Si(111)-2×1 surface with the scattering plane aligned in the $\langle 01\bar{1}\rangle$ direction ($\phi_x=0°$) for an incident beam energy $E_I\sim 6.9$ eV (contact potential difference uncompensated) are presented at the top of Fig. 1. The surface-phonon loss is found at 57.5 meV (off-specular measurement confirms that the loss is dipole excited) and the surface-interband excitation is centered at ~ 650 meV with the onset at ~ 350 meV corresponding to the minimum gap between $\bar{J}$ and $\bar{K}$ (see inset). The position of this onset indicates that a very low density of cleavage-induced defect states were present.[4,24]

We compare scattering in the $\langle 2\bar{1}\bar{1}\rangle$ direction ($\phi_x=90°$) also shown in Fig. 1. Besides a general decrease in the elastic scattering intensity we observe the following: (1) significant attenuation of the integrated interband loss *relative to the elastic intensity,* (2) a shift of the peak of the surface mode electronic state but *no shift in the surface band gap,* and (3) attenuation of the phonon loss *relative to the elastic intensity* with no shift ($\hbar\omega=57.5$ meV) and negligible broadening with respect to ϕ_x.

In order to analyze the observed azimuthal asymmetries, we must consider the range of $\mathbf{q}_\parallel$ collected by the instrument for various azimuthal orientations within dipole-scattering theory[25,26] applied to the phonon loss and the electronic loss. The assumption is made that the electronic-loss feature is fully polarized along the chains as found previously by theory[19] and experiment.[5,6] *The observations of asymmetry in relative intensities of both features ensures that we are scattering from a single domain region of the sample* and not near a region (e.g., near an edge) where LEED measurements typically can reveal rotated 2×1 domains.

We address the origin of the peak shift and the cause of incomplete attenuation in the electronic-loss band for allowed $\langle 01\bar{1}\rangle$ and forbidden $\langle 2\bar{1}\bar{1}\rangle$ scattering geometries. Normal-incidence optical-absorption experiments have obtained nearly complete attenuation when **A** is parallel to $\langle 2\bar{1}\bar{1}\rangle$, establishing that the electronic transition is polarized parallel to the surface along the chain direction.[5,6] The sharp surface-band-gap onset at ~ 350 meV for the losses in both scattering geometries indicates that the loss observed here in the forbidden geometry does not originate from defect excitations or due to a second band polarized along $\langle 2\bar{1}\bar{1}\rangle$. However, the peak shift makes it impossible to obtain a direct comparison of relative loss intensities at a given energy. Comparing the *integrated intensities* of these losses, we find an attenuation of ~ 8 for the electronic loss ($\sim$6-eV impact energy) between $\phi_x=0°$ and $\phi_x=90°$.

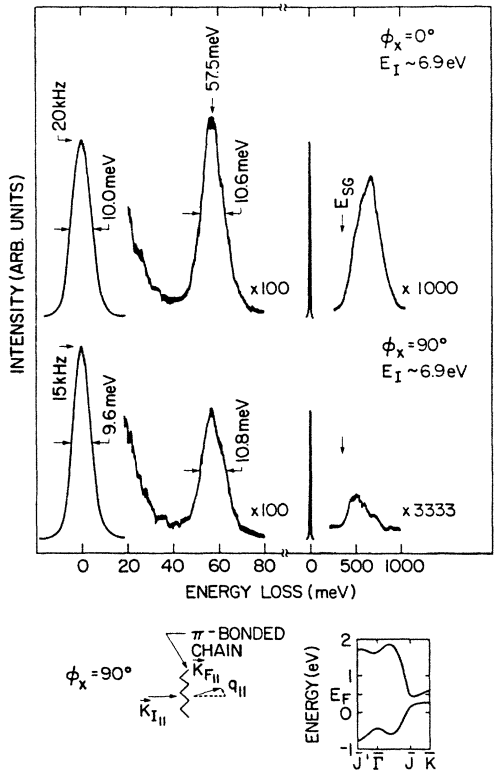

FIG. 1. EELS spectra for the surface phonon loss and the surface interband transition at $\phi_x=0°$ and $\phi_x=90°$ taken at $E_I\sim 6.9$ eV with $\theta_I=\theta_S=65°$. The angular acceptance was $\Delta\theta_{1/2}\sim 2.5°$ and $\Delta\phi_{1/2}\sim 2.0°$. E_{SG} denotes the position of the intrinsic surface band gap. Insets depict (left) direction of surface chain and scattering in forbidden geometry ($\phi_x=90°$) with view of a $\mathbf{q}_\parallel$ with transverse component collected by analyzer; (right) calculated surface bands from Ref. 8.

Since we are probing the momentum-dependent surface-loss function with electron scattering, the width and shift of the loss depends on the range of $|\mathbf{q}_\parallel|$ sampled by the instrument. Considering the finite angular acceptance of the spectrometer and the small-q nature of dipole scattering, we note that it is possible for inelastically scattered electrons deflected slightly away from the forward direction to be collected; such electrons have a component of $\mathbf{q}_\parallel=(q_{\parallel,\text{for}}, q_{\parallel,\text{trans}})$ transverse to the forward-scattering direction. This is illustrated in the inset of Fig. 1. If the crystal is oriented in the forbidden geometry, we can still collect a finite number of electrons which scatter with $q_{\parallel,\text{trans}}$ along the scattering plane which is capable of exciting the electronic loss. An instrument with infinite angular resolution should give exactly zero intensity for the forbidden geometry. Using the (modified) formalism of Sokcevic and co-workers,[25,26] we calculate[22] that an attenuation of $\sim$3–4 is expected for an electron impact energy of $\sim$6 eV and a loss energy of $\sim$500 meV for scattering within the spectrometer angular acceptance (FWHM in θ direction, $\Delta\theta_{1/2}$, $\sim 2.5°$ and FWHM in ϕ

direction, $\Delta\phi_{1/2}$, $\sim 2.0°$). In this situation, the approximate range of $q_{\parallel,\text{trans}}$ along the chain is $-0.03 < q_{\parallel,\text{trans}} < 0.03$ Å^{-1} while $q_{\parallel,\text{for}}$ for $\theta_I = \theta_S = 65°$ is $0.03 < q_{\parallel,\text{for}} < 0.06$ Å^{-1}.

The observed shift in the maximum of the electronic loss as a function of ϕ_x is consistent with our detailed study[24] of the q dependence of this band with the scattering plane aligned along the chains. In particular, with an incident beam angle of 65° and $\langle 01\bar{1} \rangle$ aligned along the scattering plane, 70° collection gives $|\mathbf{q}_\parallel| \sim 0$ and a peak position shifted toward the onset. This is the limiting condition to optical excitation where the transverse and longitudinal dielectric constants converge.[27] The trend for larger $|\mathbf{q}_\parallel|$ is that the electronic-loss peak moves toward higher energy while the gap position remains unchanged.

The analysis of the azimuthal dependence of the electronic loss carries through to the case of the surface phonon which is our main focus. The observed azimuthal attenuation of relative intensity of the phonon loss with respect to the elastic peak for scattering in a single domain region of the surface is ~ 1.7 for $E_I \sim 6$ eV and $\theta_I = \theta_S = 65°$. The ratio is reduced to ~ 1.0 when E_I is raised to ~ 11 eV. These results were reproducible for other (single domain) cleaves. The small attenuation observed with this spectrometer translates to an even smaller change for a spectrometer with larger angular acceptance (lower momentum resolution) as is more common; thus previous experiments where scattering in a single azimuthal direction was performed would not lead one to suspect any polarization-dependent behavior for the phonon loss.

Further evidence for the polarized behavior of inelastic electron scattering from the phonon is shown in Fig. 2, where the observed phonon intensities for $\phi_x = 0°$, 30°, 60°, and 90° relative to their respective elastic intensities are compared with calculation.[22] The data here were obtained from a different cleave from that of Fig. 1. Considering the critical dependence of the asymmetry on the angular acceptance which could vary somewhat (randomly) as the crystal is realigned, we consider the fit satisfactory, but place most emphasis on the observation and reproducibility of the asymmetry at these energies between $\phi_x = 0°$ and $\phi_x = 90°$ and the reduction of this asymmetry at higher beam energies for other cleaves.

The asymmetric behavior of the relative intensity of the phonon loss as a function of crystal azimuthal orientation observed for several one-domain cleaved surfaces at $E_I \sim 5$–6 eV directly implies that the dynamic dipole of the surface phonon contains a component parallel to the surface which is polarized along the chains. It is reasonable to relate this loss to the strongly dipole-active phonon which is predicted by AAM (at a slightly lower energy). In order to rule out a polarization component perpendicular to the surface in addition to the parallel component deduced by the asymmetry alone, one should consider the 2×1 surface symmetry predicted by AAM[19] and deduced by other experiments.[10,11] SHG[10] and LEED[11] have established the existence of one mirror plane on this reconstructed surface which is orthogonal to the π-bonded chains. Thus there exist only x and yz representations for the polarization. The phonon of interest is odd with respect to the mirror plane. This symmetry further implies that impact scattering is forbidden for both $\phi_x = 0°$ and $\phi_x = 90°$. In order to retain consistency with the existence of this mirror plane, *the dipole-excited phonon which we have characterized must be polarized purely parallel to the surface along the chains (in the x direction).*

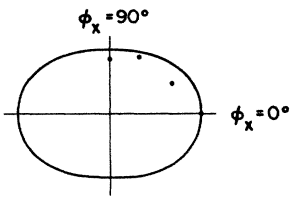

FIG. 2. Polar plot of calculated EELS relative cross section for $E_1 \sim 5$ eV, $\theta_1 = \theta_S = 65°$, $\Delta\theta_{1/2} = \Delta\phi_{1/2} = 2°$, $\hbar\omega = 0.055$ eV. Data points are relative intensities of phonon loss with respect to ϕ_x measured at $E_1 \sim 5.3$ eV, with $\Delta\theta_{1/2} \sim 2°$ and $\Delta\phi_{1/2} \sim 3°$, and normalized to the calculation at $\phi_x = 0°$. The azimuthal attenuation of the relative loss intensity is clearly observed. Uncertainty of the relative loss intensity is small; scatter is due to small variations in spectrometer alignment for each azimuthal orientation at same spot on crystal.

We note the following various possible alternative causes for the observed azimuthal behavior of the phonon loss which we can rule out as follows. (1) Becase of the C_s symmetry of the surface (single mirror plane) it might be argued that a perpendicular-polarized dipole loss is observed for all angles and a parallel-polarized loss is superimposed upon it in the allowed scattering geometry. Noting that only one strong phonon is predicted by AAM (by a factor of ~ 100), we have carefully measured the phonon energies and linewidths for both orientations in order to determine whether a second loss of a different origin is present. *Assuming that an accidental degeneracy does not occur, we find no evidence that two peaks are convolved together in the loss observed in the allowed scattering geometry.* (2) We have avoided contributions to the intensity in the forbidden geometry due to multiple domains by both careful alignment of the sample and consistency with the attenuation of the electronic-loss band as already discussed. Although the coherence length for the phonon mode is greater than that for the electronic loss since $|\mathbf{q}_\parallel|$ is smaller for the lower-energy phonon loss, the symmetry of the excitation is not broken by domain boundaries and chain truncations.[28] Furthermore, it has been found that the chains are rather long in defect-free regions of the sample.[12] (3) We consistently observe an attenuation of the elastic peak in the forbidden geometry with respect to the allowed geometry. Thus the absolute count rate of a particular loss is also reduced. This occurs due to a change in reflectivity as a function of scattering angle. For these dipole excitations, we have properly taken the ratio of the loss intensity to the elastic intensity[21,24–26] which removes any dependence on the value of reflectivity.

In the theory,[19,20] the Si surface phonon is found in a symmetry gap at $\bar{\Gamma}$. We have performed off-specular measurements to deduce the line shapes for $|\mathbf{q}_\parallel| \neq 0$ excitations to search for broadening at finite $|\mathbf{q}_\parallel|$. Since widths of the loss features can degrade somewhat in the off-specular mode due to instrumental constraints, we compare the width of the phonon loss to that of the quasielastic

peak in each spectrum. We observe that 5° and 10° (~7% of surface Brillouin zone) off-specular measurements with beam energy ~6.9 eV exhibit a broadening of the phonon loss by ~12 meV with no measurable dispersion. In the context of the AAM model, this suggests that the phonon band is indeed in a symmetry gap at $\bar{\Gamma}$ and that the band mixes with the bulk phonons as we move away from $\bar{\Gamma}$.

We briefly comment on the position of the phonon loss. By careful measurement of the position of the Stokes and anti-Stokes components of our spectra, we have reproducibly established that $\hbar\omega = 57.5$ meV for the surface-phonon loss for our single domain cleaves even with a small distribution of defects as deduced by the surface band gap. While most previous reports quote the loss at 56 meV, the present measurements were done with greater precision since it was recently reported that the loss can shift to as low as ~50 meV in the presence of defects with an apparent two-peak structure.[23] Even in cases where the electronic-loss spectra indicate a high level of defects and multiple domains were observed, we failed to notice a broadening or a shift to such a low value. The origin of the downshift of the loss to ~50 meV might be related to a distribution of small domains; typically the cleaves of the other study exhibited two domains as determined by LEED.[23]

We also note that the energy reported for the strong dipole-active band in the AAM model is predicted to be ~50 meV. The symmetry and dipole strength of this excitation causes us to make a correspondence with our observed loss at 57.5 meV where comparison of absolute vibrational energies between theory and experiment is not considered crucial.

Finally, we note that the azimuthal dependence of subband-gap electronic excitations arising from defects does not display a strong asymmetry. It is found that the relative loss intensities at ~350 meV (below the intrinsic surface band gap) in the forbidden and allowed geometries exhibit much reduced asymmetry. This implies that broken symmetry due to defects produces a z component for this electronic transition such that azimuthal attenuation of this defect electronic loss is greatly reduced.

We have presented the first EELS observation of azimuthal asymmetry for dipole-excited surface-phonon and surface-electronic-state losses. This is indicative of polarization of these excitations parallel to the Si(111)-2×1 surface and along the π-bonded chains. Our measurements and analysis of the azimuthal dependence of the dipole-scattering cross section provides a new means of obtaining polarization information of spectroscopic features in both the phonon band and in the surface-state-excitation region with EELS. More extensive azimuthal-dependent measurements are planned to obtain quantitative data in smaller angle increments over the range of ϕ_x. For example, smaller angular acceptance and reduced beam energies will improve the *momentum resolution* and enhance the asymmetry in relative intensities. Precise fits to dipole-scattering calculations will provide better information on the surface screening and permit the deconvolution of any impact-scattering contributions. In addition, the use of impact scattering has the potential to excite other phonon bands which might be fit to the AAM model to obtain a more complete picture of the dynamics at this reconstructed semiconductor surface.

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