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Temperature-dependent electronic excitations of the Si(111) 2×1 surface

N. J. DiNardo,* J. E. Demuth, W. A. Thompson, and Ph. Avouris
IBM Thomas J. Watson Research Center, Yorktown Heights,
New York 10598

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Electron-energy-loss measurements on cleaved Si(111) 2×1 surfaces show a temperature dependence in the position and shape of the absorption edge of the ~0.5-eV surface-state transition. The observed trends in the onset line shape provide experimental evidence for surface-state excitonic polarons. In addition, a lower-lying, defect-related surface-state transition at ~0.35 eV is studied at low temperature and found to have localized character.

Electron-phonon coupling at semiconductor surfaces has important consequences since it cannot only modify and/or obscure surface electronic structure at finite temperatures, but can provide a driving force for surface reconstruction. Evidence for such coupling between the electronic and vibrational states at the surface was recently observed in the electronic spectra of the Si(111) 7×7 surface.[1] However, the complexity of this surface—its unknown geometry and the large number of overlapping states and transitions observed—precludes a detailed understanding of their origin. On the other hand, the cleaved Si(111) 2×1 surface is structurally established[2] and has a simpler and generally understood surface electronic structure.[3] Furthermore, recent theoretical studies by Chen, Selloni, and Tosatti[4] have considered electron-phonon coupling effects on the surface state transitions of the Si(111) 2×1 surface. They predict the magnitude and characteristics of such effects for both the π-bonding chain model[3] and "ionic buckling" models.[5]

Here, we present the first measurements of the temperature-dependent electronic transitions of the Si(111) 2×1 surface which show features typical of excitonic effects expected for the π-bonded chain model. We also resolve the differences in the surface-state band gap found using optical[6-8] and surface photovoltage[9] methods as well as clarify the dependence of electron-energy-loss spectroscopy (EELS) spectra on cleavage defects, their relation to previous measurements,[7-11] and the nature of these defects.

The experiments were performed in an ion- and turbomolecular-pumped surface spectroscopy system which has been described previously.[12] The system provides for the combination of fixed-scattering angle EELS, angle-integrated ultraviolet photoelectron spectroscopy (UPS), using a cylindrical mirror analyzer (CMA), and low-energy electron diffraction (LEED). The chamber base pressure was 4×10^{-11} Torr. The EELS spectrometer was operated between 8- and 15-meV resolution with a beam of energy of 10.5 eV so as to provide high sample reflectivity and allow both high resolution and good signal to noise in the electronic loss region. Since the total scattering angle of the EELS spectrometer is fixed at 90°, changing the angle of incidence or collection is effected by rotating the sample manipulator on its axis; the scattering plane was set parallel to the $[01\bar{1}]$ direction (along $\bar{\Gamma}\bar{J}$). The cleavage assembly is incorporated onto the sample manipulator stage allowing for both cleaving and spectrsocopy to be performed between $T\approx25$ K and ≈900 K. Owing to the large thermal mass of the sample holder, we could not rapidly vary the sample temperature while spectroscopically probing it, but instead allowed for the sample to equibrate with the sample holder which was in contact with cold He gas, liquid nitrogen, or room temperature and monitored by a thermocouple. The sample bar ($3\times3\times20$ mm^3) was cut from a boule of single-crystal Si (B doping density $\approx10^{15}$/cm^3 supplied by Wacker Chemie) and then notched to permit cleavage along the $[2\bar{1}\bar{1}]$ direction. With our cleavage procedures, single-domain reconstructed surfaces over $\approx80\%$ of the sample were obtained in $\approx80\%$ of the cleaves. The angular deviation from the [111] direction of several cleaved surfaces was also measured by observing the deflection of specularly reflected focused He-Ne laser light over various parts of the sample. Angular deviations of ±1.5° were commonly observed on good single-domain cleaves. Particular areas with sudden topological changes could be correlated with increases "defect" density observed by LEED or EELS. Although UPS was also performed *in situ* the sampling area (~1 mm^2) was too large to isolate individual regions of different cleavage quality for detailed comparison with our EELS and LEED studies.

Electron-energy-loss spectra from our best Si(111) 2×1 cleaved surface are shown in Fig. 1 at 20 K (solid line) and

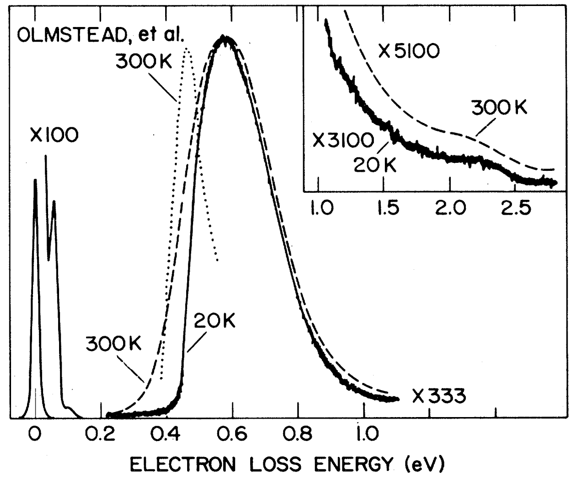

FIG. 1. Electron-energy-loss spectra of 2×1 Si(111) at 20 K (solid lines) and 300 K (dashed lines). The dotted line is the optical absorption as measured by Olmstead and Amer (Ref. 8). Both this and the room-temperature loss spectra have been scaled to the height of the low-temperature loss peak. The inset shows the higher-lying surface interband transitions.

at 300 K (dashed line). The large excitation peak centered near 0.6 eV corresponds to surface-state transitions along the $\bar{J}$ to $\bar{K}$ region of the surface Brillouin zone (SBZ) which have been widely studied before.[6–11] The peaks at 56 and 100 meV correspond to the surface phonon[13] and minute water contamination, $\lesssim 0.1\%$ of a monolayer,[14] respectively. In considering the temperature-dependent changes in the surface-state transition we must also consider the momentum transfer and range of wave vectors sampled in our EELS measurements which will modify the onset and peak positions from those measured optically. For comparison the optical transitions observed at 300 K by Olmstead and Amer[8] are shown by the dotted line in Fig. 1. Without knowledge of the topologies of the occupied and unoccupied surface-state band we cannot deconvolute the true optical $(\Delta q = 0)$ transitions from our EELS data. However, the sharpness of the onset we observe *at low temperatures* does allow us to place an accurate lower bound on the minimum gap of these surface-state transitions at the $\bar{J}$ point of the SBZ. Linearly extrapolating the onset of our loss peak to the background intensity yields a value of 0.43 ± 0.005 meV. A tabulation of our onset values as a function of temperature together with those of other measurements are presented in Table I. The excitation threshold for this surface excitation at 20 K together with the optical threshold measured at 300 K, indicates at least a 50-meV change in the onset between these temperatures. The temperature dependence of the onset we observe (Table I) also accounts for the differences found between the optical measurements at 300 K,[6–8] and the photovoltage or photoconductivity measurements at 130 K.[9]

Temperature-dependent changes in the surface-state bands which will affect EELS or optical absorption spectra can arise from both lattice contraction with decreasing temperature and the distortion of the lattice about the excitonic state, i.e., polaronic effects.[4] In the latter, the degree of coupling between the electronic excitations and the lattice phonons determines the nature of these changes; the magnitude of both contributions have been predicted by Chen, Selloni, and Tosatti for the π-bonding and ionic buckling models of the 2×1 Si(111) surface.[4] While the ionic buckling model (strong coupling case) is predicted to show a negligible net change in the peak or onset for optical adsorption, the π-bonded chain model (weak coupling case) is predicted to show a ~ 30-meV red shift in the peak of the optical adsorption and about an ~ 80-meV shift in its onset between 300 and 2 K. Our results are thereby consistent with Chen's calculation for the π-bonding model. While the calculated values may be uncertain due to the limitations of this theoretical model, the line-shape changes observed in our loss spectra are typical of the general features found in other excitonic-polaron systems.[15] We note that the higher-lying (~ 2 eV) surface-state transitions near the $\bar{\Gamma}$ point of the SBZ shown in the inset of Fig. 1 are nearly unchanged with temperature. It is suggested that these features will be particularly sensitive to temperature-dependent lattice distortions in the π-bonded chain due to the form of the eigenfunctions and calculated overlap integrals near the Γ point.[16] Thus, the weak changes observed in the peak between 2.0–2.5 eV (Fig. 1, inset) suggest little change in lattice constants. Furthermore, detailed LEED spectra at 20 and 300 K reveal identical fractional-order beam I-V profiles again suggesting no marked change in the π-bonding chain structure with temperature.[17]

As found in previous surface photovoltage[9] and room-temperature optical studies[7] additional excitations can be observed below the nominal surface-state gap which have been attributed to cleavage-induced defects on the surface. As

TABLE I. Details of surface-state transition features; other results are given for comparison.

		T (K)	Transitions			
			Surface state		Defect state	
			Onset	Peak	Onset	Peak
EELS						
	This work	300	0.34 ± 0.01	0.58 ± 0.02	Mixed	
	($E_0 \cong 10.5$ eV)	90	0.41	0.58	· · ·	
		20	0.43 ± 0.005	0.58 ± 0.01	~ 0.25	~ 0.35
	Matz *et al.* (Ref. 10) ($E_0 = 20$ eV)	300	0.31	0.55	~ 0.1	~ 0.36
	Rowe *et al.* (Ref. 11) ($E_0 = 50$ eV)	300	0.25	0.5	· · ·	· · ·
Optical						
Attenuated total reflection	Chariotti *et al.* (Ref. 6)	300	0.38	0.46	· · ·	· · ·
	Chiaradia *et al* (Ref. 7)	300	0.35–0.36	0.44	0.27	0.35
Photothermal displacement spectroscopy	Olmstead and Amer (Ref. 8)	300	0.37	0.46	· · ·	· · ·
Surface photovoltage or photoconductivity	Assman and Mönch (Ref. 9)	130	0.42	0.47	0.23	0.35

shown in Fig. 2 for a variety of different cleaves, we can observe similar states having an onset near 0.25 eV, *but only if examined at 20 K.* At room temperature these new states become merged into the excitonic-polaron edge of the surface-state transition, and enhance the onset intensity. For sufficient defect concentrations (e.g., the dash-dotted curve), these states tend to shift not only the onset but also the loss peak to lower energies when observed at 300 K.

Our LEED observations of these "defect" surfaces reveal that these states occur even for what appear to be good single-domain 2×1 regions of the surface, and vary in concentration over the surface regardless of whether single or multidomain cleaves were obtained. Dispersion measurements similar to those performed by Matz, Luth, and Ritz[10] were also performed at 20 K by changing the angles of incidence or collection. While the dispersion for the main transition is similar to that found earlier,[10] the "defect" transition shows little if any dispersion—indicative of its localized nature. Furthermore, these low-energy transitions cannot be considered to arise from excitations of defect-shortened, π-bonded chains since this effect would produce an opposite (blue) excitonic shift to that observed.[18]

In extreme cases these defect-derived losses were found to be most intense on stepped regions of the sample where visible distortions and splittings of the 2×1 diffraction spots are observed. In these cases, the room-temperature EELS spectra are dominated by these transitions as shown in the inset of Fig. 2. Here, we also find a peculiar inversion of the relative intensities of the defect-derived losses and the surface-state transition with increasing temperature. Although the details of this effect are not understood, these findings clarify significant differences between room-temperature EELS[10] and optical measurements[7,9] on such imperfect surfaces.

In summary, we present EELS results which show significant temperature-dependent changes in the surface-state excitations on Si(111) 2×1 which are characteristic of excitonic polaron systems, and in overall agreement with model calculations by Chen *et al.*[4] for the π-bonded chain model. We also show that defect states on this surface can also be directly observed by EELS at low temperatures.

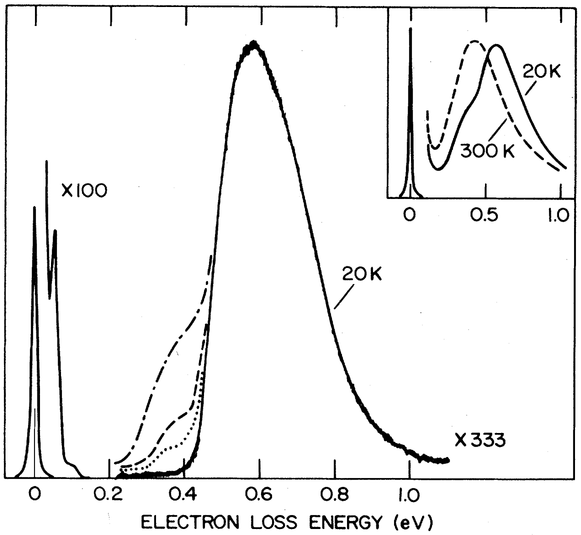

FIG. 2. Electron-energy-loss spectra obtained at 20 K for different 2×1 Si(111) cleaves. Here, each spectrum is scaled to the height of the low-temperature loss peak. The inset shows the low-temperature and corresponding room-temperature spectra of a particularly poor cleave.

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[*] Present address: Physics Department, Drexel University, Philadelphia, PA 19104.

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