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Helium atom scattering from the Si(111) surface at high temperatures

G. Lange, C. A. Meli,* and J. P. Toennies
Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, 37073 Göttingen, Germany

E. F. Greene†
Department of Chemistry, Brown University, Providence, Rhode Island 02912

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Helium atom scattering has been used to investigate the structure of the Si(111) surface in the temperature range from 900 to 1600 K. Even below the well-known (7×7) to ‘‘(1×1)’’ transition the adatoms become mobile, and, when the transition is reached near 1140 K, the specular- and integral-order diffraction peaks have sudden intensity changes, some up and others down, while the seventh-order peaks disappear. Above the transition the adatoms remain, moving rapidly on, and supported by, the ordered but relaxed, outer bilayer of the surface. A second transition, first reported by Ishizaka and co-workers occurs near 1470 K. The loss of all diffraction peaks and the attenuation of the specular peak indicate a completely disordered surface as the temperature approaches the melting point. [S0163-1829(97)01532-4]

INTRODUCTION

The Si(111) surface has been studied intensely[1] for scientific, technological, and aesthetic reasons. The nature of the equilibrium (7×7) reconstruction of Si(111) at room temperature was for many years an attractive yet difficult scientific puzzle; the dimer-adatom-stacking fault (DAS) solution of Takayanagi *et al.*[2,3] deepened interest in the subtle forces leading to this elaborate structure. In addition, the continual trend toward smaller and smaller electronic devices also has been a strong stimulus for investigators to study the surface and interface properties of Si.

Although the structure of the Si(111) surface at and below room temperature appears to be well understood, there continues to be a dispute about this and its other properties at elevated temperatures. There has been a technological component to this interest, due to the importance of high-temperature surface properties in processes such as surface reactions and film growth. However, such measurements are complicated by the need, for example, of heating the sample uniformly, understanding the effects of electric fields associated with the heating apparatus, complications caused by light emission from the sample, and vacuum degradation due to heating of the sample mount. Most importantly, thermal attenuation of the signals from probes used in surface science can lead to unacceptably low signal-to-noise ratios in measurements, and this has limited experimental results at high sample temperatures.

A disordering of the (7×7) reconstruction near 1173 K was noted over 30 years ago by Lander[4] using low-energy electron diffraction (LEED), and since then many different techniques have been used to probe this (7×7)→‘‘(1×1)’’ transition.[5–29] The quotation marks indicate that while the LEED pattern from the higher temperature structure is nominally (1×1), there is undisputed evidence of Si adatoms remaining on the surface. The (7×7)→‘‘(1×1)’’ transition has typically been observed to take place over the temperature range 1110–1140 K (Refs. 5, 6, 10, 13, 14, 18, 21, 22, and 29) with phase coexistence in this range[18,21,22] and with the range dependent on the average terrace width.[8] The (7×7) phase grows in from the upper edges of steps separating terraces. Symmetry considerations predict the transition should be first order,[30] in agreement with the observation of phase coexistence and the absence of broadening of the fractional-order peaks through the transition.[6,10,15,25] However, only three studies have detected measurable hysteresis through the transition,[25,26,29] and LEED and reflection electron microscopy results have been interpreted as suggesting second-order behavior.[6,8,31]

Florio and Robertson’s early work on both the high-temperature (Ref. 5) ‘‘(1×1)’’ and the Cl-stabilized (1×1) surfaces[32] led them to propose that the former is a bulklike termination with a 20% thinning of the top bilayer. Other experimental[15,33] and computational[34,35] results have supported this proposal. Phaneuf and Williams’s observation of broad, weak half-order diffraction peaks from the ‘‘(1×1)’’ surface was the first strong experimental indication of significant adatom coverage.[12] Since then, the direct observation of adatoms on the hot ‘‘(1×1)’’ surface with scanning tunneling microscopy[18,21,22] (STM) has made clear the dynamic behavior of the adatoms and steps. STM measurements of adatoms trapped by quenching the ‘‘(1×1)’’ structure[27] along with diffraction[15,24] and ellipsometry[19] measurements on the high-temperature surface, indicate coverage by 0.20–0.25 of a monolayer of mostly disordered adatoms, with some local (2×2) ordering.[16]

Recently, two additional changes in the surface structure of Si(111) have been reported by Ishizaka and co-workers using reflection high-energy electron diffraction (RHEED).[17,24] A decrease of the intensities of the seventh-order diffraction beams and an increase of the intensity of the specular beam near 830 K were interpreted as a (7×7)→(7×7) transition, in an unexplained relaxation of the DAS structure. Near 1410 K both the specular and first-order beams begin a sharp decrease to immeasurable levels.[24] This was attributed to a complete disordering of the surface; both surface melting and adatom-vacancy formation were mentioned as possible disordering mechanisms.

In the work presented here, we studied the Si(111) surface at high temperatures using He atom scattering. While an earlier experiment of this type has been reported,[14] the present work measures the behavior of the integral-order diffraction peaks and examines He scattering up to 1600 K. In this investigation we had specific goals in mind. We sought to characterize the (7×7)→"(1×1)" structural phase transition near 1140 K, and looked for evidence of the newly reported structural transition[17,24] near 1410 K. We also measured the incoherent elastic scattering and attenuation of the diffraction peaks with increasing surface temperature, since this knowledge is helpful in characterizing the disorder and dynamic properties of the surface. Finally, we wanted to compare the He scattering results from Si(111) to earlier results from Ge(111) (Ref. 36) to gain further insight into the properties of both surfaces.

APPARATUS AND PROCEDURE

The helium atom scattering apparatus is similar to that used earlier[36–38] with some modifications.[39] In brief, a highly monoenergetic helium atom beam with an energy spread of $\Delta E/E \sim 1\%$ is produced in a supersonic expansion and directed to the crystal at an angle Θ_i with respect to its normal. Rotation about this normal varies the azimuthal angle ϕ. The scattered atoms are detected by a differentially pumped mass spectrometer that is located at the end of a flight tube, with the angle between the incoming and outgoing beams fixed at 90°. Different momentum transfers ΔK parallel to the surface are probed by rotating the sample around an axis normal to the scattering plane to access different incident Θ_i and final Θ_f scattering angles. For time-of-flight (TOF) experiments the helium beam can be chopped with a variable-speed, variable-pulse-width chopper. In the Ge work this TOF filter greatly improved the signal-to-noise ratio for the measurements of the intensities of the elastic peaks.[36] Here it was used only to measure the incoherent elastic scattering [see Fig. 6(b)]. Apparently the stiffness of Si kept the inelastic background much lower than it was for Ge. Angular distributions of the total intensity were measured with incident energies (wave vectors k_i) between 11.3 meV (4.6 Å^{-1}) and 57.8 meV (10.5 Å^{-1}), but only ones with k_i equal to 5.4 Å^{-1} are shown in the figures here.

The Si(111) crystal[40] (n-type, phosphorus doped, 1.1 Ω cm, $12\times5\times0.38\ \mathrm{mm}^3$; commercial grown, cut, and polished, offcut 0.25°±0.2°) was mounted between two Mo clips attached to an xyz manipulator with provisions for sample tilt and azimuthal as well as polar rotations. The sample was resistively heated using dc current. The surface was prepared *in situ* with cycles of Ar-ion bombardment for 2 h at 300 K followed by a 5-min anneal at about 1275 K, until the surface was judged to be clean with Auger electron spectroscopy, and a reproducible, sharp, and intense (7×7) helium diffraction pattern was obtained. The sample temperature was measured to within ±5 K using an external optical pyrometer that was calibrated by melting the crystal after the experiments. The base pressure of the chamber was $<2\times10^{-8}$ Pa with the target at 300 K and $\sim3\times10^{-7}$ Pa for temperatures near 1600 K.

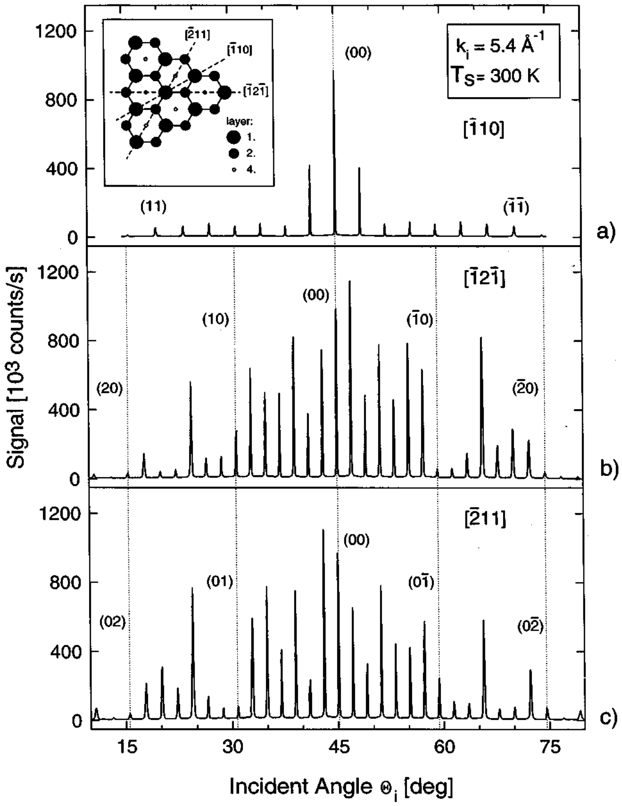

FIG. 1. Angular distributions of He scattered from the Si(111)(7×7) surface in (a) [110], (b) [121], and (c) [211] azimuthal directions. Incident wave vector $k_i = 5.4$ Å^{-1} ($E_i = 15.5$ mev); $T_S = 300$ K. Inset in (a) shows bulk-terminated Si(111) surface. High-symmetry directions studied are marked by dashed lines.

RESULTS

Diffraction scans of the total intensity of helium scattered from the Si(111) surface at room temperature are shown in Fig. 1. Three principal scattering azimuths were studied: the [110] direction, which leads to one diffraction scan that is symmetric about the (00) (specular) peak, and, in contrast, two others in the [121] and [211] directions, which give scans that are asymmetric about the specular peak and mirror images of each other. The symmetry properties of these diffraction scans are attributable to the threefold rotational symmetry of the surface below the adatoms; a schematic representation of the bulk-terminated (111) surface is shown in the inset in Fig. 1(a). The full width at half maximum is 0.013 Å^{-1} (0.02°) for the specular peak and as large as 0.028 Å^{-1} (0.04°) for the first-order diffraction peaks. The former corresponds to a domain width of at least 480 Å.

Diffraction scans at four different sample temperatures, for both the [110] and [121] scattering directions, are shown in Fig. 2. In all cases the sample was heated or cooled at about 10 K/min, and at least a 30-s equilibrium time was allowed before measurements were taken. All the seventh-order peaks remain present and sharp at 1065 K, though of lower amplitude, but by 1216 K all these peaks have vanished, and the relative heights of the integral-order peaks have changed drastically. In the single scan at 1603 K in the [121] direction, the integral-order peaks have also disappeared, with only a weak but sharp specular peak remaining.

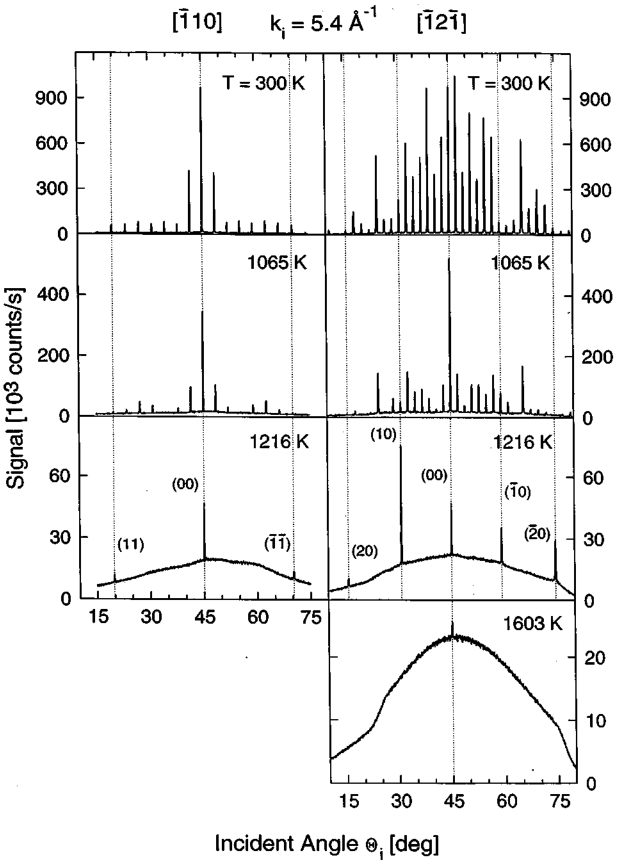

FIG. 2. Representative diffraction scans from Si(111) surface along [110] (symmetric) and [121] (asymmetric) directions at 300 K and three elevated temperatures. Incident wave vector $k_i = 5.4$ Å^{-1} ($E_i = 15.5$ meV). Dotted lines indicate positions of specular- and integral-order peaks.

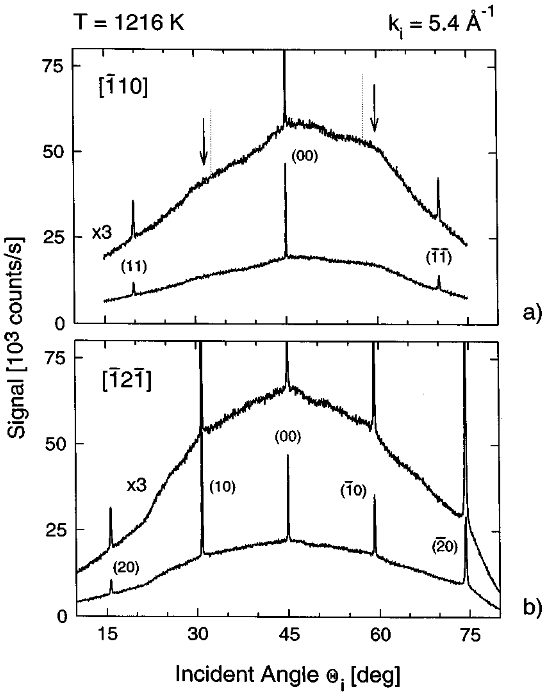

FIG. 3. Diffraction scans along $[\bar{1}10]$ and $[\bar{1}2\bar{1}]$ directions on Si(111) surface at 1216 K with unmagnified signals and magnified ones to show weak, broad, peaks in [110] direction indicated by arrows near nominal half-order positions (dotted lines). Incident wave vector $k_i = 5.4$ Å^{-1} ($E_i = 15.5$ meV).

No broadening of any of the integral-order or seventh-order peaks was observed at any temperature, but the adatoms have been found to be changing positions rapidly even at 743 K.[41]

Amplifying the intensities of the diffraction scans taken at a sample temperature of 1216 K also reveals additional features; see Fig. 3. Two weak, broad peaks are visible at approximately the half-order positions in the scan along the [110] direction. No analogous peaks are discernible along the [121] direction.

Figure 4 shows the intensity changes of the observable integral-order peaks in the three scattering directions used for temperatures near the (7×7) to "(1×1)" transition. In all three azimuths the specular intensity drops at the transition, while, surprisingly, the intensity of nearly all the integral-order peaks increases. Below and above the transition, which occurs in the range 1120–1150 K, the logarithms of the peak intensities show the linear attenuation with increasing temperature commonly seen in helium-atom scattering (HAS). However, comparison with the work of Ishizaka and co-workers[17,24] suggests that this linearity may not extend down to 300 K (see below). The intensities of all the seventh-order peaks between the specular and first-order peaks were also measured in all three azimuths; their behavior is qualitatively similar below the transition. Their logarithms also have a linear, but somewhat steeper, decay with increasing temperature to between 1000 and 1100 K, but there they begin to vanish more and more steeply as the transition is approached. Figure 5 shows examples for six selected seventh-order peaks. Selected integral-order and seventh-order peak intensities were measured on heating and cooling through the transition to look for hysteresis in the intensities. None was observable on the time scale of our measurements. No attempt was made to study the time dependence of the peak intensities or the effect of different heating and cooling rates on them. Our signal levels were constant during the measurements, which were reproducible, so they represent steady-state behavior for moderately slow heating and cooling.

Figure 6(a) shows the intensities of the specular, first-, and second-order diffraction peaks in the [121] direction through the temperature range 950–1600 K. Above the (7×7) to "(1×1)" transition the specular intensity is remarkably constant before it begins a weak attenuation with increasing temperature around 1350 K. In contrast, the logarithms of all the integral-order peaks attenuate at a faster, and greater than linear, rate above this transition and vanish abruptly near 1470 K. The disappearance of these peaks coincides with a kink in the intensity curve for the specular peak, which then continues to decrease linearly above 1470 K, up to 1600 K where the measurements were discontinued about 80 K below the melting point.

The incoherent *elastic* signal is presented in Fig. 6(b) through the same temperature range and in the same [121] scattering direction used in Fig. 6(a). This measurement was made by collecting only the elastically scattered He atoms (using TOF selection) with the incident angle set at 50°, i.e., between the (2/7 0) and (3/7) peaks. It gives a measure of the

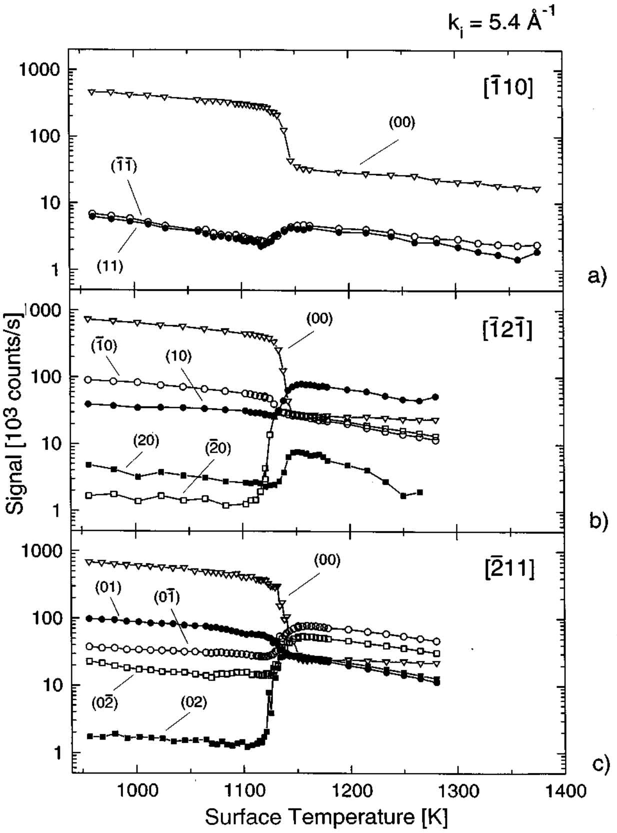

FIG. 4. Temperature dependence of signals measured for specular (00) peaks and for first- and second-order diffraction peaks for He scattered from Si(111) surface scanned along three principal directions. Incident wave vector $k_i = 5.4$ Å^{-1} ($E_i = 15.5$ meV).

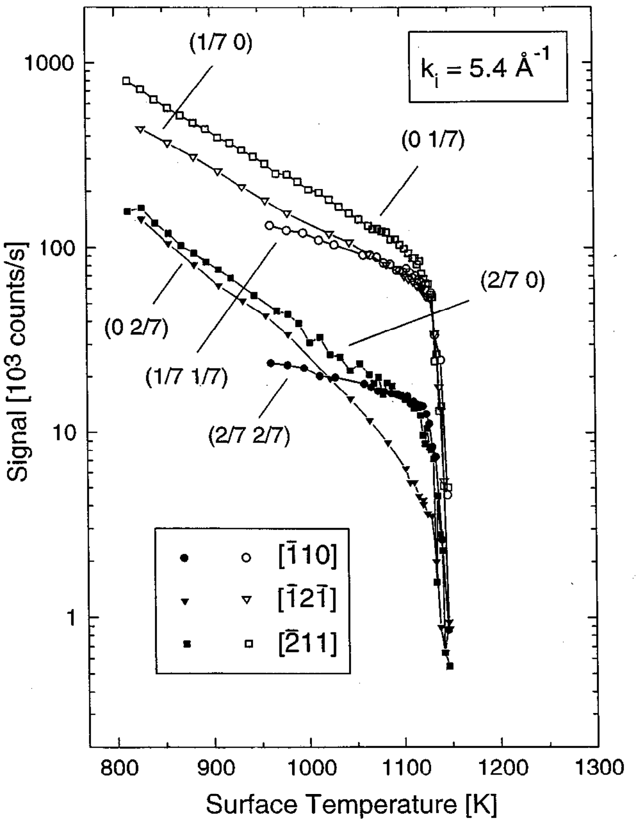

FIG. 5. Temperature dependence of signals of some seventh-order peaks for He scattered from Si(111) surface along three principal directions. Incident wave vector $k_i = 5.4$ Å^{-1} ($E_i = 15.5$ meV).

static disorder on the surface.[42] This incoherent elastic intensity increases slightly through the (7×7) to "(1×1)" transition up to about 1190 K and then decreases with increasing temperature. At about 1470 K, where the kink in the specular intensity was observed, the incoherent scattering also appears to drop at an increasing rate.

DISCUSSION

First we ask what we can learn about the surface from the HAS measurements illustrated in the figures. Because the thermal helium beam cannot penetrate below the top layer of the surface, the sharpness of the integral-order peaks to above 1400 K reveals that both the (1×1) structure of the top bilayer remains ordered and that the adatoms are dilute enough on the bilayer to permit the He beam to reach a substantial fraction of it. The sharpness of the seventh-order peaks reveals that at least some of the adatoms are well ordered up to the transition near 1140 K. Nevertheless, a comparison of the seventh-order peaks, e.g., (1/7 0) and (2/7 0), on heating from 300 to 1065 K (Fig. 2) shows that there is an 8- to 13-fold decrease in amplitude, while Fig. 5 shows that this decrease occurs almost entirely in the temperature range 800–1065 K. This would be consistent with the presence of a sharp turn downward on the intensity near 800 K like the one found in the RHEED work.[17,24] Perhaps at 1065 K a significant fraction of the adatoms responsible for the seventh-order peaks has been promoted from the sites they occupy in the DAS structure at 300 K to excited states in which they move freely over the surface and do not contribute to the diffraction peaks.

The absence of the seventh-order peaks above 1140 K shows that the whole DAS structure has been lost. But the faint, diffuse maxima near the half-order positions in Fig. 6(a) and similar maxima in half-order as well as others in $(3^{-1/2} \times 3^{-1/2})$ positions in the work of Iwazaki *et al.*[43] show that there is a small, residual tendency of the adatoms to take superlattice positions. The near constancy of all the specular peaks between 1140 and ~1470 K shows that the surface of the bilayer remains ordered, while the increasingly steep decline of the integral-order peaks as the temperature rises toward the second transition near 1470 K shows that the bilayer is finally becoming disordered. Above 1470 K the specular peak decreases more rapidly, suggesting that the surface gets rougher as it nears the melting point.[44] The kind of disorder calculated for the upper three layers of the Ge(111) surface at its transition near 1050 K (Ref. 45) is inconsistent with the sharp, integral-order peaks seen in HAS that show the bilayer of Ge(111) to be ordered. But it might provide a useful representation of the second transition observed here for Si(111) near 1470 K.

The most notable features of the temperature scans are the abrupt changes in magnitude seen near 1140 K (Figs. 4 and 6). These are either increases or decreases, reminiscent of, but not the same as, those seen for Ge(111) near 1050 K.[36] We propose that they are caused by a change in the spacing h between the two halves of the top bilayer when the adatoms suddenly become more mobile and allow the bilayer

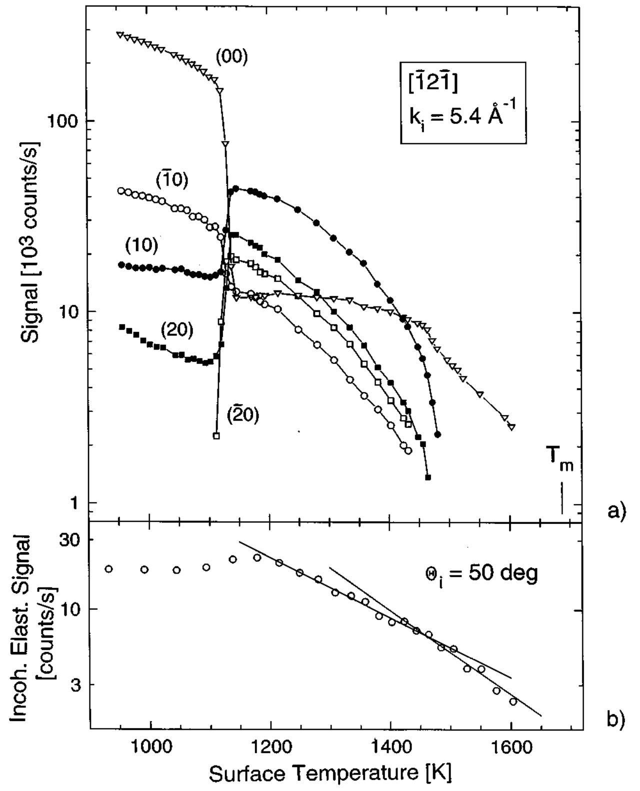

FIG. 6. Temperature dependence (a) for specular (00) peak, first- and second-order peaks (T_m melting point) and (b) incoherent elastic intensity in [121] direction through temperature range 950–1600 K. Incident wave vector $k_i = 5.4$ Å^{-1} ($E_i = 15.5$ meV).

to relax. There is both experimental[15,33] and computational[34,35] evidence to suggest that this relaxation consists of a decrease in h of about 20%. If the two levels of the bilayer lead to interference of the He beam, such a change in h would imply a related change in the magnitudes of the scattered signal depending on the wave vector k_i, the incident Θ_i, and the final Θ_f angles the He beam makes with the surface, and the periodicity of the surface in the scattering direction. Thus, the magnitudes of the scattered peaks could be expected to vary with the crystal (i.e., Ge or Si), the scattering direction (e.g., [110] or [211]) and the wavelength ($\lambda = 2p/k_i$) of the beam just as they are seen to do.

Similar abrupt changes in electron diffraction were seen by Ishizaka and co-workers[17,24] who found in RHEED experiments (primary electron energy 20 keV, glancing angle 1.7°, azimuthal direction [110]) on a Si(111) surface heated through the transition that their specular peak fell by a factor of 3 while their (10) peak rose by a factor of 3. We suggest that these changes may also be the result of changes in the diffraction of the electron beam caused by the thinning of the bilayer that occurs as it relaxes at the transition. The close parallel of the RHEED and HAS work extends to changes in the amplitudes of the seventh-order peaks at temperatures well below the transition. On heating their Si surface from 800 to 1000 K Ishizaka and co-workers found the sum of their three largest peaks, the (3/7 0), (4/7 0), and (5/7 0), fell gradually by a factor of 1.8, while in HAS we found an average fall (Fig. 5) of similar magnitude. Although the interpretation of these relatively less abrupt decreases in the fractional-order peaks is not clear, they cannot be caused by interference from the relaxation of the bilayer. Perhaps, as we mention above, they are related to the increasing mobility of the adatoms.

What can we say about the adatoms as the temperature rises through the first transition? Yang and Williams[27] deduce densities for the adatoms plus the bilayer of 2.08, 2.25, and 2.20–2.22 atoms per 1×1 unit cell or 0.24, 0.25, and 0.20–0.22 adatoms per (1×1) unit cell for the 7×7, 2×2, and ''1×1'' reconstructions, respectively. (Here we use 0.24 for the adatoms in the 7×7 reconstruction because the DAS structure has 12 adatoms in the 7×7 unit cell and some vacancies in the bilayer.) This near constancy of estimated adatom density and the nearly constant coherent elastic scattering over the range 1000–1200 K [Fig. 6(b)] seem consistent with the idea of a quasiequilibrium of the adatoms with the step edges.[27,28] This would leave the adatom density more dependent on the nature of the edges than of the adjacent terraces.

We conclude that the disordering of the Si(111) surface occurs in stages. The whole surface is well ordered at 300 K. Then as the temperature rises, the adatoms become gradually more mobile until at 1140 K the adatoms are disordered enough so the bilayer relaxes but stays ordered. Finally, at the second transition the whole surface disorders as the melting point is approached.

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[*] Also at 682 Whitney Avenue, New Haven, CT 06511.

[†] Author to whom inquiries should be directed.

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