High-Resolution Low-Energy Electron Diffraction Study of Pb(110) Surface Roughening Transition

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A clear Pb(110) surface roughening phase transition has been observed at $T_r \sim 415$ K, which is ~ 185 K below the bulk melting temperature, using the high-resolution low-energy electron diffraction technique. It is shown that the height-height correlation function diverges logarithmically at T_r. The measured value of the roughening transition temperature agrees remarkably well with recent molecular-dynamics calculations. Evidence of surface melting at about 520 K is also seen from the anomalous behavior in the diffraction intensity.

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Ever since Frenken and van der Veen reported[1] their important observation in the Pb(110) surface melting at 40 K below the bulk melting temperature using the high-energy ion-shadowing and -blocking techniques, a number of researchers[2-5] have further studied the disordering phenomena that occur in Pb surfaces using a variety of surface sensitive techniques such as x-ray scattering and low-energy electron diffraction. Whereas all subsequent experiments confirmed the existence of the disordering of the Pb(110) surface, there are serious disagreements as to the temperature at which the surface begins to disorder, and the nature of the disordering. In particular, x-ray scattering studies of the Pb(110) surface by Fuoss, Norton, and Brennan[4] showed that an initial liquid scattering occurred at a temperature below 300 K (at least 300 K below the bulk melting temperature which is 600.7 K). They also suggested a roughening of the surface at higher temperatures in addition to the partial melting of the surface.

Surface melting and surface roughening are two different disordering phenomena. In the case of surface melting, the atoms in surface layers lose both their two-dimensional (2D) crystal ordering and their resistance against 2D shearing; while during and after surface roughening, the surface atoms still occupy well-defined crystal lattice positions even though the surface width diverges on an atomic scale. The suggestion of the existence of a surface roughening by Fuoss, Norton, and Brennan in their experiment was based on the fact that the x-ray (112) "forbidden reflection" disappeared with increasing temperature. The same argument has been used to infer the existence of a surface roughening transition in the Cu(110) surface by Mochrie.[6] However, by a detailed beam-shape analysis in the He diffraction experiment carried out by Zeppenfeld *et al.*,[7] it was concluded that the Cu(110) surface does not undergo a thermal roughening transition up to 900 K. Zeppenfeld *et al.* concluded that the observation of an anomalous behavior in the x-ray reflection intensity is not a sufficient proof for the occurrence of thermal roughening.

In this paper, we report an observation of a clear surface roughening transition in the Pb(110) surface using the high-resolution low-energy electron diffraction (HRLEED) technique. From the diffraction beam-profile analysis, it is shown that the height-height correlation diverges logarithmically at ~ 415 K, which is defined as the transition temperature. We showed that fitting of the line shape of the beam profile is much more sensitive than using the width of the profile to detect the onset of surface roughening. An additional anomalous behavior in the diffraction beam intensity which does not involve the change of the beam shape has also been observed above 500 K. This may be related to the surface melting phenomenon reported by Frenken and van der Veen.

The experiment was performed in an ultrahigh-vacuum chamber with a base pressure in the middle range of 10^{-11} Torr. The Pb(110) sample is ~ 2.4 mm thick and is in the form of a disk with a diameter of 9 mm. The detailed operation of the high-resolution low-energy electron diffractometer has been described previously.[5,8,9] A single-pass cylindrical-mirror Auger analyzer was used to check the impurities at the Pb(110) surface. The surface was sputtered clean at room temperature using an argon-ion beam. After the sputtering, with only a mild annealing of the sample to 90°C, we obtained the narrowest diffraction beams as determined by full width at half maximum (FWHM) of the beam profiles. LEED showed a sharp (1×1) pattern.

The angular profiles of the (00), (10), and (01) beams were measured as a function of incident electron beam energy, E. All the profiles were smooth and had no shoulder structure or peak splitting. In Fig. 1, the FWHM of the (00) beam measured in both the [001] and $[1\bar{1}0]$ directions is plotted as a function of $S_\perp t$ (which in turn is a function of the incident electron beam energy), where $S_\perp$ is the momentum transfer perpendicular to the surface and t is the single-atomic-step height. At room temperature the FWHM is a constant value (0.02 Å^{-1}) without any oscillatory behavior. The FWHM at the out-of-phase diffraction condition is the same as that of the in-phase condition. This implies that

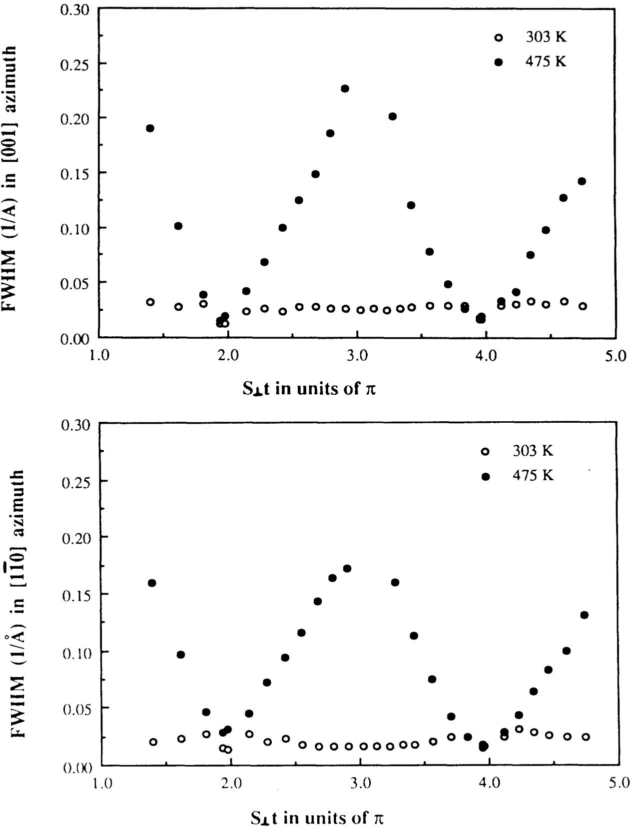

FIG. 1. The FWHM of the (00) beam, measured along [001] and [1$\bar{1}$0] directions are plotted as a function of $S_\perp t$ at 303 and 475 K. $S_\perp$ is the momentum transfer perpendicular to the surface and t is the step height.

the surface has a nondetectable density of steps.[10] Using the FWHM at the in-phase diffraction as our effective instrument response and taking into account the accuracy of our measurement of the profile's width, we estimate that the terrace width is at least 700 Å.[11] The surface misorientation angle is also nondetectable and is thus less than 0.1°.[9,12] This relatively "flat" sample is considered to be an excellent surface for the purpose of studying surface disordering phenomenon below the bulk melting temperature.

As the temperature is raised from room temperature, the FWHM changes drastically from a constant value to an oscillatory behavior, as seen in Fig. 1. Similar results were obtained for the (10) and (01) beam profiles. This oscillatory behavior is a clear indication of the roughening of the surface. From the period of oscillation we deduce that the surface contains single atomic steps with a step height of 1.75 ± 0.05 Å which is consistent with the bulk value. The average terrace width can be obtained from the amplitude of the oscillation.[10] It is estimated that the terrace width is ~300 Å at $T = 428$ K and ~35 Å at 475 K.

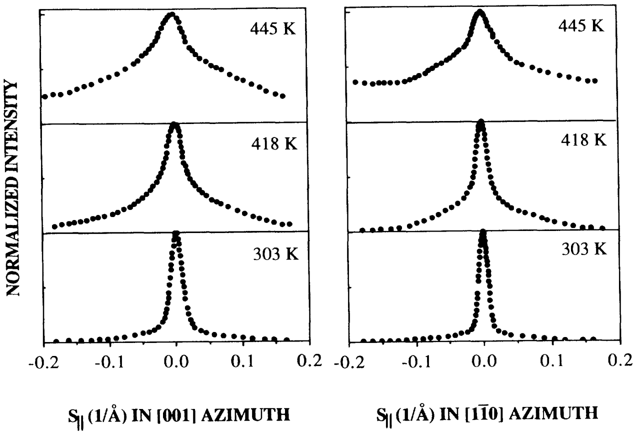

FIG. 2. Angular profiles of the (00) beam at 303, 418, and 445 K are plotted as a function of $S_\parallel$ at the out-of-phase diffraction condition, i.e., $S_\perp t = 3\pi$ or $E = 27.0$ eV. $S_\parallel$ is the momentum transfer parallel to the surface.

Figure 2 shows the evolution of the angular profiles measured along both the [001] and [1$\bar{1}$0] directions at different temperatures with $E = 27$ eV, which is the out-of-phase diffraction condition. The line shape is sharp at 303 K and develops a substantial tail at 418 K. An obvious increase in FWHM is observed at 445 K. In order to compare the measurements with theoretical predictions, a detailed analysis of the tails of the profiles is required.[7,13] Theories predict a logarithmic divergence in the height-height correlation function, $\langle [h(r) - h(0)]^2 \rangle$, in a surface roughening transition.[14] This gives a power-law behavior in the diffraction line shape in the form of $1/S_\parallel^{2-n}$, where $S_\parallel$ is the momentum transfer parallel to the surface and $n = x[1 - \cos(S_\perp t)]$ is an exponent.[15-17] The roughness of the surface is described by x. At the transition temperature, the value of x has been predicted to be close to 0.5. At the out-of-phase diffraction condition ($S_\perp t = \pi, 3\pi, \ldots$) the value of n would then be 1. For a fixed energy, the tail part of the intensity can be plotted as a function of $S_\parallel$ with the only adjustable parameter n.

Figure 3 shows the log-log plots of the (00) beam profiles in the [1$\bar{1}$0] direction at different temperatures using n as the fitting parameter. (Both the left- and right-side tails give a similar slope and only the fitting of the right-side tails is shown in the figure.) All the profiles used in the fit have been deconvoluted with the instrument response function which is taken to be the profile measured at the in-phase diffraction condition at room temperature. However, we point out that the exponents obtained from this fit are very close to those obtained without the deconvolution. This is due to the very fine angular resolution of the HRLEED system. The information extracted from the tail part of the angular profile at the out-of-phase condition is not significantly affected by the fine instrument response.

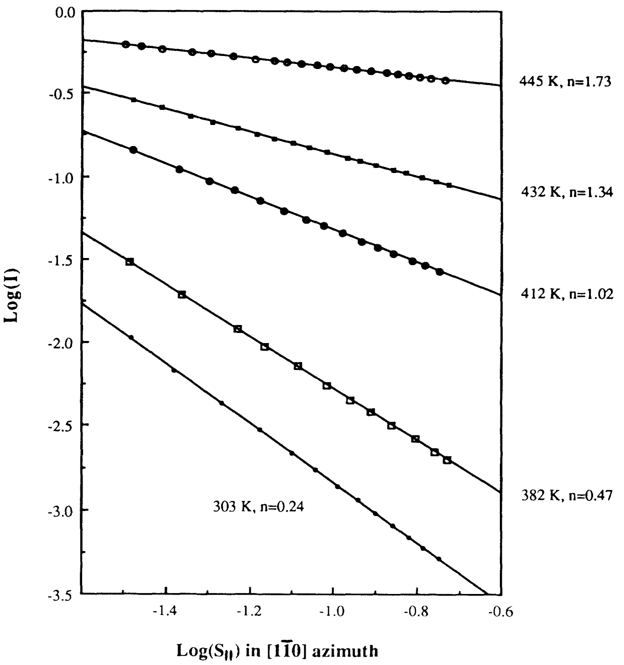

FIG. 3. The log-log plots of the tail part of the (00) beam profiles measured in the [1$\bar{1}$0] direction at $S_\perp t = 3\pi$ are shown at different temperatures. The slope of the plots is equal to $-(2-n)$. The data are taken from 2% to 10% of the Brillouin zone away from the center of the Bragg peak. Similar plots have been obtained for profiles measured in the [001] direction.

The data included in the fit shown in Fig. 3 extend from 2.0% to about 10% of the Brillouin zone away from the Bragg peak position. The slope is given by $-2+n$. In contrast to the Cu(110) experiment[7] using He diffraction where the slope never exceeded -2.5, our result shows that the slope does reach -1 and beyond. Figure 4(a) is a plot of the fitted value of n as a function of temperature. The transition temperature occurs at about 415 K where the slope becomes -1 or $n=1$. The measured transition temperature agrees remarkably well with a recent molecular-dynamics calculation[18] which predicts that for an fcc (110) surface, the surface should undergo a roughening transition at $0.7T_m$. For lead, $0.7T_m = 420$ K. n continues to grow as the temperature is raised beyond the transition temperature. At 480 K, the intensity dropped to the background level at this out-of-phase diffraction condition.

Below 360 K, n remains constant and is a very small number. For $T > 360$ K, n increases with temperature. The increase of n at around 360 K is not accompanied by an increase of the FWHM of the profile until the temperature reaches to about 400 K. Figure 4(b) shows the measured FWHM as a function of temperature in both [001] and [1$\bar{1}$0] directions. In fact, at the transition temperature defined by $n=1$, there is only a small increase (about 30%) in the FWHM. At 445 K, the FWHM increases to 3 times that measured at room temperature. It is seen that n is a much more sensitive parameter than FWHM to characterize the surface roughening phenomenon.

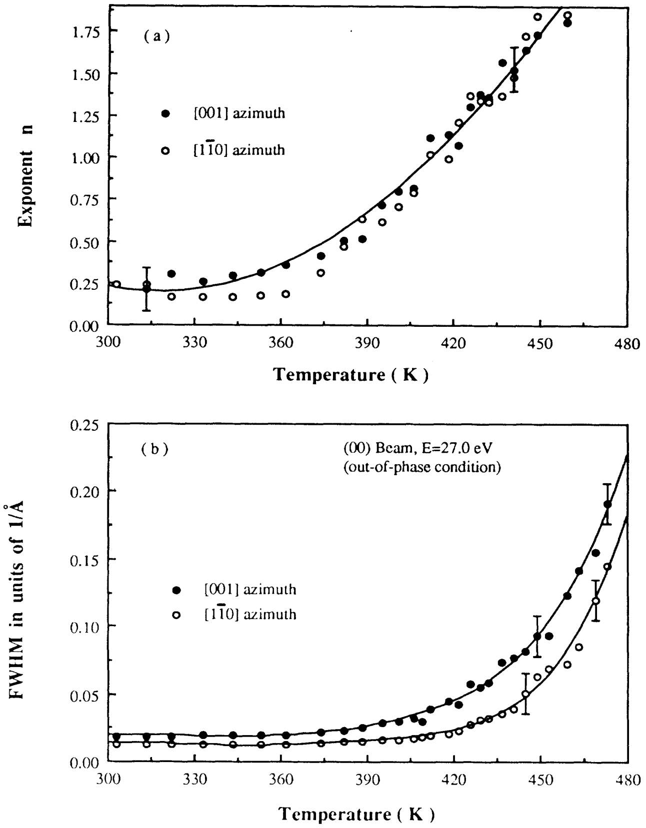

FIG. 4. (a) n obtained from the slope of the curves shown in Fig. 3 is plotted as a function of temperature. As n approaches 1, the height-height correlation function diverges to infinity. The solid curves are guidelines. (b) FWHM's of the (00) beam at the out-of-phase diffraction condition, i.e., $S_\perp t = 3\pi$ or $E = 27.0$ eV, for both the [001] and [1$\bar{1}$0] directions, are plotted as a function of temperature.

In contrast, the diffraction beam at the in-phase condition is not sensitive to the change of the surface due to steps created in the roughening transition. Figure 5 is a plot of the peak intensity as a function of temperature. At about 415 K, where the surface undergoes a roughening transition, the peak intensity behaves normally. No broadening of the profile is observed at any temperature. The peak intensity follows the familiar Debye-Waller decay due to the increasing surface lattice vibration. No anomalous behavior is observed in the peak intensity for temperatures below 500 K.

At temperatures higher than 520 K, a sudden reduction of the peak intensity is observed. The intensity decays to the background level as the temperature approaches 600 K. The angular profile still does not

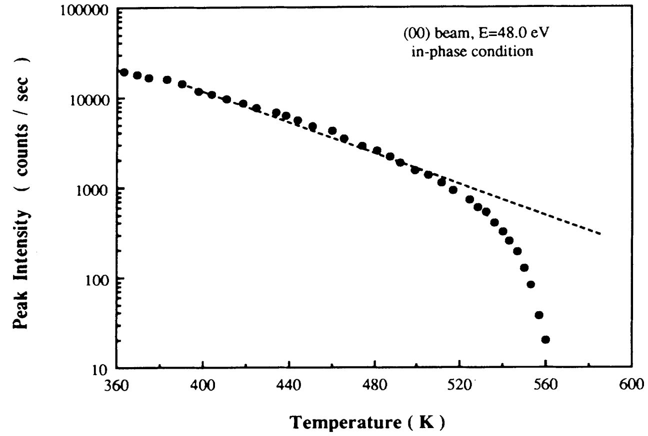

FIG. 5. The peak intensity of the (00) beam at the in-phase diffraction condition is plotted as a function of temperature. A sudden decrease in the intensity is observed at around 520 K.

broaden. The sudden reduction of the peak intensity occurs at a temperature very close to the surface melting temperature reported previously.[1,3] The behavior of the peak intensity at the in-phase diffraction condition at $T > 520$ K may therefore be interpreted as the effect of diffuse scattering (incoherent) from a molten layer of liquid which grows as the temperature is raised. When the liquid layer is as thick as the electron mean free path, the intensity diminishes. This occurs at around 560 K.

In summary, we have observed a clear surface roughening transition in Pb(110) surface at about 415 K using the HRLEED technique. The measured roughening transition temperature agrees very well with the predicted value of $0.7T_m$ by a previous molecular-dynamics calculation. Surface roughening cannot be easily detected by the high-energy ion-shadowing and -blocking techniques. Our results therefore complement those obtained by Frenken and van der Veen.[1] Also, from our data we see no sign of surface liquid formation below 500 K. It has been suggested[4,5] that surface imperfections such as steps that exist in the surface at low temperature may play an important role in the subsequent higher-temperature disordering phenomena. The substrate we used in the present experiment represents one of the best (with an average terrace width larger than 700 Å) metal surfaces we have ever prepared. We believe that both the surface roughening and melting transitions we observed in this experiment represent equilibrium phase changes free from severe finite-size effects.

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