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Collapsing of Thermally Induced Steps on the Pb(111) Surface

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Using high-resolution low-energy electron diffraction techniques we have observed an increase in step density near 550 K in a stepped Pb(111) surface. At room temperature the Pb(111) surface contained steps with an average terrace width of 63 Å. At 580 K, after the surface reached its maximum roughness, the steps suddenly collapsed and the surface appeared to be extremely flat. A possible explanation of the observed phenomenon is the occurrence of a surface melting phase transition which is induced by the thermally excited high density of steps.

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Recently, the nature of melting that occurs in surfaces below the bulk melting temperature has received increasing interest both theoretically[1-3] and experimentally.[4,5] According to recent microscopic theories,[1-3] surfaces can begin to disorder as one approaches the bulk melting temperature T_m, and the thickness of the disordered layer diverges at T_m. This prediction was first confirmed by Frenken and van der Veen in their observation of the melting of the Pb(110) surface by using high-energy ion-shadowing and -blocking techniques.[4] Since then, surface melting of Pb has further been studied by a number of researchers.[5-7] All of these experiments confirmed the existence of the premelting of the Pb(110) surface. However, there are serious disagreements as to the temperature at which the surface begins to melt and the exact portion of the surface being melted. Also, the x-ray scattering experiment performed by Fuoss, Norton, and Brennan[7] indicated that even the closed-pack Pb(111) surface displayed a weak disordering below the bulk melting temperature which was not observed in the works by Frenken and van der Veen,[4] Pluis *et al.*,[5] and Prince, Breur, and Bonzel.[6] Surface melting has also been observed in the Al(110) surface.[8]

Another important type of surface disordering that can occur at a temperature below the bulk melting temperature is the roughening of surface by creating a large number of surface steps. This phenomenon was predicted theoretically by Burton, Cabrera, and Frank,[9] and was recently observed numerous times at different surfaces.[10-12] In addition to surface melting and surface roughening phenomena, other forms of surface disordering can also occur.[13]

In this paper, we report a study of surface disordering phenomena which occur below the bulk melting temperature in a stepped Pb(111) surface using the high-resolution low-energy electron diffraction (HRLEED) technique. We found that the surface began to roughen at about 550 K, and the step density increased with increasing temperature. At ~580 K, the rough surface suddenly collapsed to form a very flat surface. All of these phenomena occurred below the bulk melting temperature of 600.7 K.

The experiment was performed in a UHV chamber equipped with a HRLEED system and a cylindrical mirror Auger-electron spectrometer (AES). The detailed operation of the HRLEED system has been described previously.[14,15] The instrument response function has a very narrow width of 0.007 $\AA^{-1}$. This narrow width (high angular resolution) allows us to measure accurately the surface defect density. The base pressure was $< 10^{-10}$ Torr. A pure single-crystal Pb sample with 6-mm diameter and 3-mm thickness was spark cut from a Pb ignot. Its x-ray Laue pattern indicated a typical fcc (111) single-crystal structure. A mixture of glacial acetic acid and a 30% hydrogen peroxide (2:1) was used to etch and polish the damaged surface region and a smooth, shiny surface was obtained. The surface temperature was measured by a type-*K* thermocouple embedded in the gap between the sample and the sample holder. The thermocouple was calibrated (by melting a similar sample) to provide a temperature reading within ± 1 K accuracy. The sample was heated by a hot pancake filament behind the sample. The Pb(111) surface was cleaned *in situ* by cycles of argon-ion bombardment and annealing (1 h at 570 K) until no impurity could be detected by AES. In all of the temperature-dependent measurements (both heating up and cooling down), at least $\frac{1}{2}$ h elapsed so that the sample reached thermal equilibrium before data were collected.

All of the angular distributions of the diffraction beam intensity (angular profiles) measured in this experiment were smooth. No splitting or shouldered structure was observed in the diffraction angular profiles within the range of the electron beam energy under consideration. Figure 1(a) shows the measured full width at half maximum (FWHM) of the specular beam intensity profiles along the $[1\bar{2}1]$ azimuthal direction as a function of the primary electron energy, E, for substrate temperature less than 550 K. The incident angle was 3.8° with respect to the normal. The broadening of the angular profile is a result of the interference between terraces of different levels. The minima of FWHM were located around $E = 36$ eV, which corresponds to the condition of an in-phase scattering of electrons from different ter-

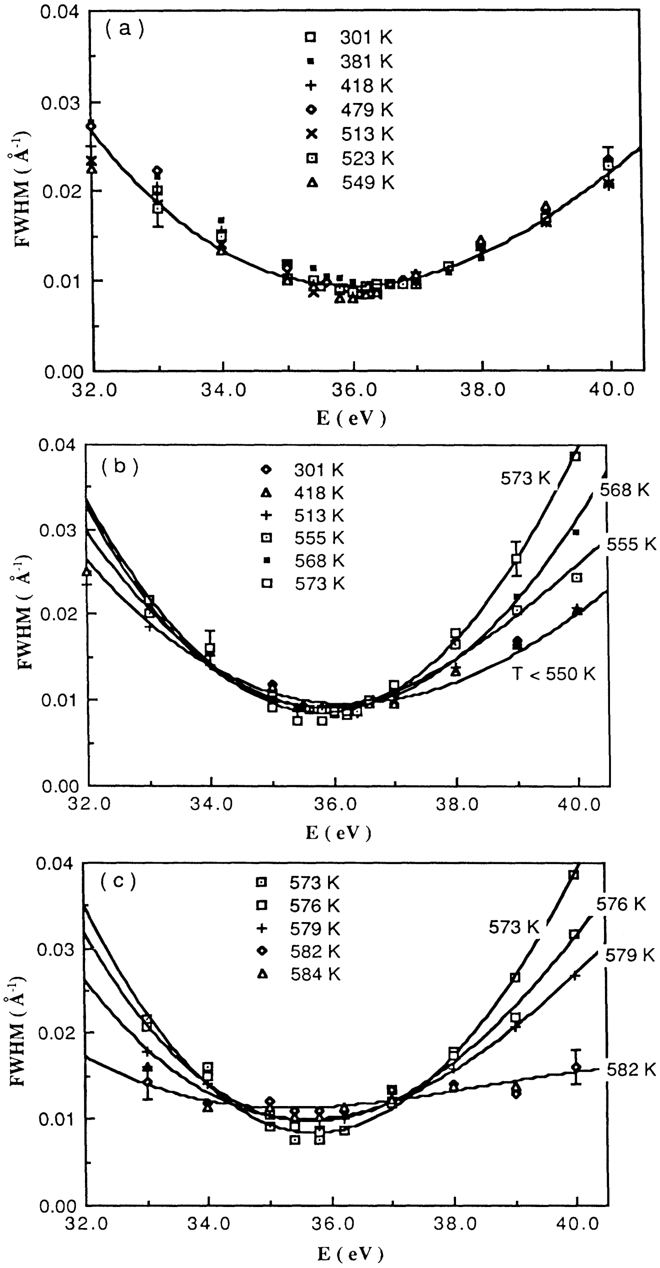

FIG. 1. The measured full width at half maximum (FWHM) of the specularly diffracted beam from the Pb(111) surface plotted as a function of the primary electron energy, E, for substrate temperature (a) less than 550 K, (b) between 550 and 573 K, and (c) between 573 and 584 K. The incident beam was 3.8° with respect to the normal.

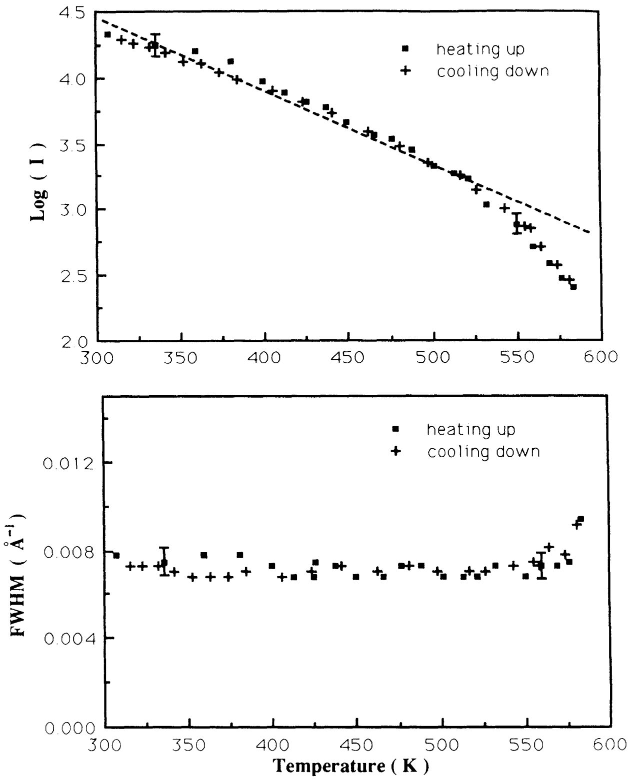

FIG. 2. The peak intensity and the FWHM of the specular beam measured as functions of temperature with a primary electron energy of 36 eV. Electrons are scattering in phase by different levels of terraces.

races.[16] The profiles broadened as one moved away from the in-phase scattering condition. The intensity became too weak to measure for $E > 41$ eV at elevated temperatures where the surface phase changes occurred. At $E = 40$ eV, the electrons scattered nearly out of phase between terraces of different levels and gave a large broadening effect.[16] Since the angular profiles showed a simple broadening effect (no splitting), the terrace width distribution must be rather random.[17] The average terrace width was obtained by comparing quantitatively the data shown in Fig. 1 and the calculated angular profiles from a well developed diffraction theory.[17] The average terrace width was found to be 63 ± 7 Å. As seen in Fig. 1, no obvious deviation of the FWHM or the beam shape could be detected for substrate temperature ranging from room temperature to 550 K. Since the beam shape does not change, we conclude that there is no step meandering effect below 550 K.[18] Therefore, the low-temperature stepped surface was a stable phase having an average terrace width of 63 Å.

As we increased the substrate temperature beyond 550 K, there was an obvious additional broadening of the angular profiles near the out-of-phase scattering condition, as shown in Fig. 1(b). The broadening reached its maximum value when the substrate temperature was 573 K. At this temperature, the average terrace width was estimated to be 34 ± 4 Å. The step density had become a factor of 2 more than that of the low-temperature phase.

More interestingly, as we further increased the substrate temperature, a sudden and rapid reduction of the FWHM was observed. As shown in Fig. 1(c), the FWHM of the profile shrank almost to its minimum

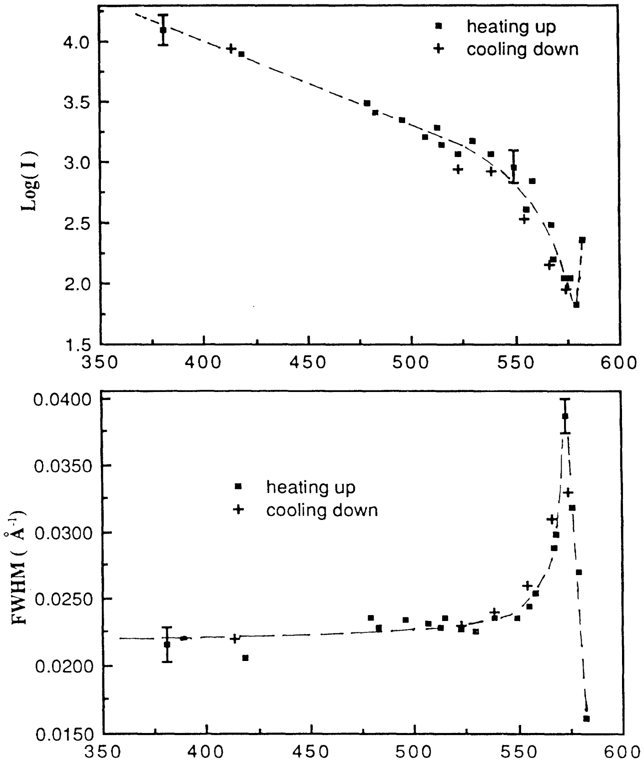

FIG. 3. The peak intensity and the FWHM of the specular beam measured as functions of temperature with a primary electron energy of 40 eV. Here electrons are scattered nearly out of phase by different levels of terraces.

value when the substrate temperature approached 582 K. At the nearly out-of-phase condition, the profile measured at 582 K was even narrower than that measured at room temperature before the surface underwent the roughening phase transition. Also, at 582 K, there was no significant difference in the measured FWHM at the in-phase and that of the out-of-phase scattering conditions. This is interpreted as the diffraction of electrons from a flat surface containing very few or no steps. Figures 2 and 3 are more detailed plots of both the peak intensity and the FWHM of the specular beam as functions of the substrate temperature for $E=36$ and 40 eV, respectively. The peak intensity was an integration of about 0.0003 Å^{-1}, i.e., 0.02% of the Brillouin zone which was typically much smaller than the FWHM ($\sim$0.01 Å^{-1} at the in-phase scattering condition) of the profile itself. All of the measured peak intensities and FWHM's were reversible in temperature. Some of the data obtained when the surface was cooled from the collapsed phase are shown in Figs. 2 and 3.

From the above data, we conclude that, at 582 K, all of the thermally induced steps, together with the low-temperature stable steps, collapsed to form a very flat surface which contained practically no steps. A plausible interpretation of the observed collapsing of surface steps would be the existence of a surface melting phase transition which is induced by the high density of thermally excited steps. The rough surface generated may serve as a precursor state for the subsequent melting transition. However, we should point out that we have as yet no definitive proof that the collapsed phase does contain a molten layer of Pb at the surface. For example, a surface containing a flat and immobile (amorphous) layer of Pb atoms would give the same diffraction characteristics.

At the in-phase scattering condition (Fig. 2), the peak intensity shows an obvious deviation from the Debye-Waller behavior at around 550 K, indicating a softening of the surface atomic vibrations. The intensity still persists for substrate temperature higher than 582 K, indicating that the flat, disordered phase contains a layer of surface atoms with a thickness less than the mean free path of the electron at that energy which is about 10 Å. There is an apparent broadening of the profile after the collapsing of the steps (substrate temperature > 580 K) at this in-phase scattering condition. One possible contribution to this broadening may come from nonsteplike defects such as dislocations at the "liquid"-solid interface.

At the nearly out-of-phase scattering condition (Fig. 3), the broadening reaches its maximum value at 573 K and suddenly drops to a very low value (lower than that obtained at room temperature) at 582 K. The peak intensity drops as the surface becomes rough (a result of out-of-phase interference between terraces of different levels), and recovers somewhat after the collapsing of steps.

Our results cannot be compared directly with those reported previously by other authors[4-7] on the study of the ordering of the Pb(111) surface. Unlike the previous experimental work, the step density of our sample at low temperature has been well characterized. Steps may be critical in controlling the surface disordering phenomena, both roughening and melting. Fuoss, Norton, and Brennan[7] reported the observation of an initial liquid formation at $\sim$220 K or $< \frac{1}{2} T_m$ on both Pb(110) and Pb(111) surfaces using a x-ray scattering technique. On the Pb(110) surface, roughening was observed together with the melting. They have conjectured that ". . . steps may be the source of the initial liquid fraction on these surfaces . . . ." On the Pb(111) surface, only very small and gradual disordering (melting) was observed, and the disordered portion was less than $\frac{1}{2}$ monolayer at 1° below the bulk melting temperature. Frenken and van der Veen,[4] Pluis *et al.*,[5] and Prince, Breuer, and Bonzel[6] did not observe anomalous behavior of the Pb(111) surface below the bulk melting temperature.

It would be interesting to see if the observed precursor state of roughening occurs before the surface melting (or other kinds of surface disordering) transition in other metal surfaces.

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