Time-Resolved Structural Study of Pb(100)

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Time-resolved reflection high-energy electron diffraction is used to study the structural behavior of Pb(100) subjected to 200 ps laser pulses. Analysis of the electron diffraction intensity indicates that residual order is present on the surface at a temperature of 615 ± 20 K, where the bulk melting temperature of Pb is 600.7 K. This implies that the disordered film that forms on Pb(100) is stable up to the bulk melting temperature and above.

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Since the initial work of Frenken and co-workers on Pb(110) [1], there has been a great deal of work performed to characterize the phenomenon of surface melting [2]. Surface melting is the formation of a disordered "quasiliquid" layer with thickness on the order of several atomic layers at temperatures below the bulk melting point T_m. Relatively few structural studies have been performed on fcc(100) surfaces near T_m [3-7]. A recent study on Pb(100) and vicinal surfaces using medium energy ion scattering (MEIS) showed that a limited amount of disorder began to form on Pb(100) at temperatures above 500 K, where T_m for Pb is 600.7 K [4]. The disordered layer thickness on Pb(100) was observed to increase logarithmically up to 2-3 K below T_m and then saturate at 1.3 monolayers, measured up to $T_m - 0.05$ K. The maximum amount of disorder on the vicinal surfaces increased with miscut angle from 1.9 to 3.5 monolayers on the 5° and 10° miscut surfaces, respectively. This is in contrast to the divergence of the disordered layer thickness of Pb(110) as T_m is approached. This behavior, where the disordered layer thickness is finite as T_m is approached, is known as incomplete surface melting. Incomplete surface melting cannot be explained by the mean-field theory used by Pluis, Frenkel, and van der Veen in their MEIS study of Pb [3(b)]. A recent model has been developed that includes the effect of the substrate on the disordered layer [8]. In this model, the ordered substrate induces a periodic density modulation in the disordered layer in a direction parallel to the solid-disordered layer interface. This modulation makes it energetically favorable for the surface to form disordered films with the thickness being an integral multiple of $2\pi/k_1$, where k_1 is the wave number corresponding to the first maximum of the structure factor of the bulk liquid. For Pb, $2\pi/k_1$ is approximately 2.86 Å [4]. The disordered layer that forms is stable up to T_m and does not act as a nucleus for further melting. The so-called layering model has proven successful in describing the disordering of Ge(111) [9], Pb(100) [4], and the (100) face of caprolactam [10].

Further experiments on Pb(100) with high-resolution low-energy electron diffraction (HRLEED) have shown a weak disordering at ~570 K [5]. This disordering is preceded by an anomalous surface expansion at $T \leq 480$ K and an abrupt generation of surface vacancies beginning at ~510 K. An anomalous surface expansion was also observed on Ni(001) using LEED [6]. An x-ray photoelectron diffraction study on Pb(100) demonstrated evidence for logarithmic growth of the disordered layer beginning at 585 ± 5 K and up to the highest temperature studied, $T_m - 2$ K [7].

Recently, there have been several molecular dynamics (MD) simulations modeling surface melting of fcc(100) surfaces [11-13]. The simulations by Häkkinen and Manninen examine the (110), (100), and (111) surfaces of copper, from 0 K to T_m [11]. This study, which uses effective-medium theory, allows for the direct comparison of the three low-index faces using the same MD potential and identical cell sizes. The results show pronounced disordering of Cu(110), weak disordering of Cu(100) just below T_m, and superheating of Cu(111). In addition, the high-temperature behavior of vicinal surfaces of Au(100) was studied using the many-body "glue" potential [12]. In both the studies of Cu(100) and the vicinal surfaces of Au(100), structural modulation in the disordered film was evident.

In the present Letter, we describe an experimental study of the high temperature structural behavior of Pb(100) using time-resolved reflection high-energy electron diffraction (RHEED). This technique, which has been described in more detail elsewhere [14], involves splitting the fundamental beam of a Nd:YAG laser ($\lambda = 1.06$ μm, 200 ps) into two parts. The first beam is amplified and interacts with the surface at near normal incidence, providing a pulsed heating source. The second beam is frequency quadrupled to the ultraviolet ($\lambda = 0.266$ μm) and is incident on the cathode of a photoactivated electron gun, producing electron pulses with a temporal width comparable to that of the fundamental laser pulse. The resulting electron beam is incident on the surface of the sample in the glacing angle RHEED geometry and probes the first few atomic layers. The energy of the electrons in the experiments reported here is 15 keV. The heating laser beam and the electron probe are temporally synchronized on the surface of the sample. An optical delay line is used to set different delay times

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between the heating laser pulse and the electron probe pulse. This allows RHEED patterns to be obtained throughout the pulsed heating process.

Our previous time-resolved RHEED experiments were performed on Pb(110) [15] and Pb(111) [16]. Pb(110) was seen to reversibly disorder below T_m, while Pb(111) sustained superheating to $\sim T_m + 120$ K. These experiments demonstrated the contrasting melting behavior of open and close-packed surfaces. Here we report on a study of the behavior of Pb(100), a surface that exhibits incomplete surface melting. The time-resolved RHEED measurements on Pb(100) that are presented here show that the residual surface order is lost at a temperature of 615 ± 20 K. The observation of residual order implies that the disordered layer that forms on Pb(100) does not nucleate further melting as T_m is approached and is stable at temperatures *above* T_m.

The Pb(100) sample was cut from a single-crystal rod aligned within 0.75° of the (100) orientation using Laue back reflection. The preparation of the surface is described elsewhere [16]. The experiments were performed in an ultrahigh vacuum chamber with a base pressure in the low 10^{-10} range. The sample was cleaned before each experiment with cycles of Ar^+ bombardment followed by annealing. Surface cleanliness was checked using Auger electron spectroscopy. Auger spectra were taken at elevated temperatures to insure that no high-temperature surface impurity segregation was occurring.

As an initial step in characterizing the structural behavior of Pb(100), measurements of the RHEED streak intensity were performed as a function of the surface temperature. A Hg arc lamp was used to excite the cathode of the photoactivated electron gun, producing a continuous electron beam. The 15 keV electron beam was incident along the ⟨001⟩ azimuth at an angle of 3°, resulting in a probed depth of ~5 Å, corresponding to ~3 monolayers. The diffracted electrons of the RHEED pattern were amplified by a microchannel plate which is proximity focused to a phosphor screen. The resulting RHEED pattern was lens imaged onto a linear-array camera for quantitative intensity analysis. In all of the experiments reported here the intensity of the (10) RHEED streak was examined. Line scans were taken through the center of the streak. A plot of the RHEED streak intensity normalized to that at 377 K is shown in Fig. 1. The inset is a plot of the data on a semilogarithmic scale. A qualitative difference is seen between these data and that obtained previously for Pb(111), which exhibited an exponential decrease in the diffraction intensity with temperature consistent with the Debye-Waller effect [16]. For Pb(100) we observe a nonexponential decrease in diffraction intensity from a temperature of ~475 K, over much of the temperature range in Fig. 1. The data are qualitatively very similar to that of Yang *et al.* obtained on Pb(100) using HRLEED [5]. This deviation from Debye-Waller behavior may initially be related to the anomalous surface expansion that they observed to occur below 480 K in the HRLEED study, in addition to the abrupt increase in vacancy concentration that they observed beginning at 510 K.

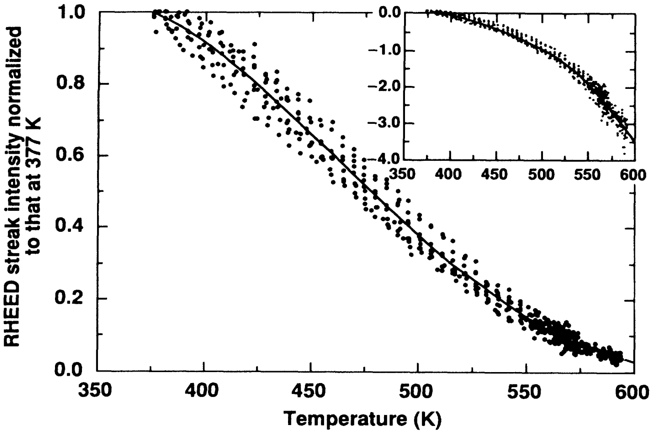

FIG. 1. RHEED streak intensity normalized to that at 377 K vs sample temperature. The orientation of the sample was the same as that for the time-resolved experiments. The inset is the data plotted on a semilogarithmic scale. In both plots, the solid line is a polynomial fit to the data. This RHEED intensity data are used to convert the normalized streak intensity of the time-resolved experiments to a surface temperature rise.

In order to determine the temperature rise induced on the Pb(100) surface by the heating laser pulse, time-resolved measurements were performed at the experimentally determined time of the minimum of the RHEED streak intensity, t_0, which is temporally close to the time of maximum surface-temperature rise. These two times do not coincide because of convolution effects that occur as a result of the finite pulse width of the electron probe. Such effects are most prominent near the temporal peak of the surface temperature profile where the rate of change of temperature with time is greatest. By examining solutions of a heat diffusion model for our experimental conditions and assuming an electron pulse width comparable to that of the fundamental laser pulse, we conclude that these effects can lower the experimentally measured peak surface temperature rise by approximately 20%. Measurements of the electron pulse width and space-charge broadening effects were previously performed on the photoactivated electron gun used in this study [14(b)]. For the initial experiments, the sample was biased at temperatures of 450 and 533 K, well below T_m. The angle of incidence of the electron beam on the surface and the azimuthal orientation of the sample were kept constant for all the RHEED streak intensity measurements. The RHEED streak intensity, normalized to that at 450 K is shown in Fig. 2 for various peak laser intensities. To convert the normalized streak intensity to a temperature rise, ΔT, the calibration of Fig. 1 is utilized. The inset of Fig. 2, where ΔT is plotted versus peak laser intensity, is the result of this conversion. A linear rela-

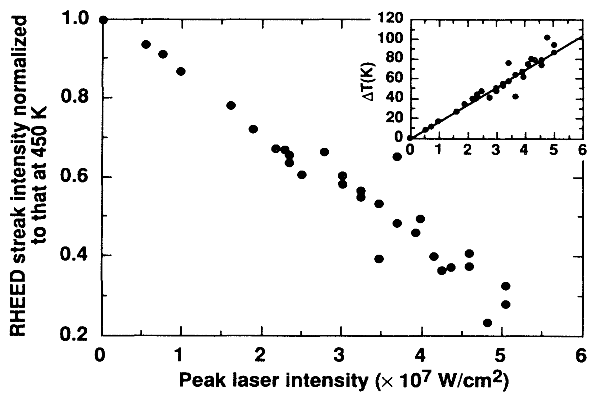

FIG. 2. Time-resolved RHEED streak intensity vs peak laser intensity on Pb(100) irradiated with Nd:YAG ($\lambda = 1.06$ μm, 200 ps) laser pulses. The sample was biased at a temperature of 450 K and the RHEED pattern was observed at the time of its intensity minimum. The inset is a plot of surface temperature rise, ΔT, vs peak laser intensity that is the result of converting the normalized streak intensity data to a ΔT using the calibration of Fig. 1. This is used to determine the surface temperature rise for data sets where the sample bias temperature is closer to T_m. The effect of convolution is not accounted for in these data.

tion between ΔT and peak laser intensity is observed which is consistent with classical heat diffusion. The maximum peak temperature in all of these sets is less than T_m. These sets give ΔT for a given peak laser intensity.

We next discuss experiments in which the RHEED streak intensity, normalized to that at a given bias temperature T_{bias}, was obtained for various peak laser intensities. Results are shown in Fig. 3 for four experiments representing bias temperatures successively closer to T_m, where the set in Fig. 3(d) is biased just 11 K below T_m. These sets were obtained at the time t_0. In each of the sets, the normalized streak intensity is observed to vanish at sufficiently high laser intensities, indicating that order has been lost in the probed surface layer. It is observed that as T_{bias} is raised, the peak laser intensity necessary to disorder the probed surface layers decreases from $\sim 4.3 \times 10^7$ W/cm^2 for $T_{\text{bias}} = 533$ K to $\sim 1.8 \times 10^7$ W/cm^2 for $T_{\text{bias}} = 590$ K. The peak surface temperature when the normalized RHEED streak intensity vanishes is obtained using the data of Fig. 2, which yields the surface temperature rise, ΔT, for a given peak laser intensity. In each of the sets of Fig. 3, the lowest peak laser intensity which corresponds to a vanishing RHEED streak intensity is converted to a temperature rise using the calibration of Fig. 2. When this is accomplished, we see that the peak surface temperature, $T_{\text{bias}} + \Delta T$, when order is lost in the probed layer is 607, 621, 611, and 619 K for Figs. 3(a)-3(d), respectively. The average peak temperature at which order is lost is $\sim 615 \pm 20$ K. The error bar accounts for (i) the spread of the static RHEED data, (ii) the spread of the temperature-rise data of Fig. 2, and (iii) the nonuniformity of laser heating, which is measured to be $\pm 25\%$ over the entire width of the sample. Our reported peak temperature does not account for convolution effects, which were mentioned earlier, and assumes that the thermal and optical properties of the sample do not change significantly over the considered temperature range. Including these effects in the analysis would lead to a somewhat greater peak surface temperature. In addition, since to a first approximation ΔT is proportional to peak laser intensity, the data of Fig. 3 suggest that the loss of residual order is not abrupt.

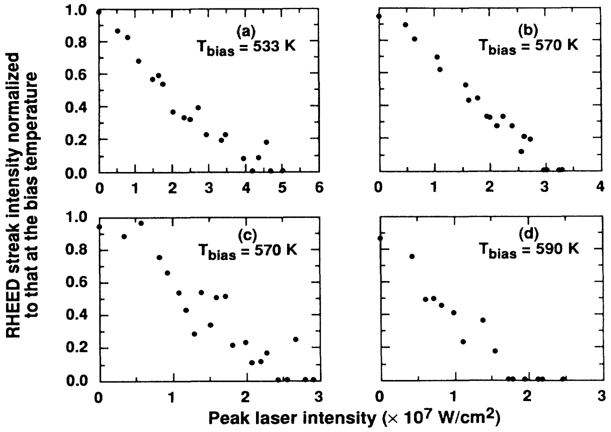

FIG. 3. RHEED streak intensity normalized to that at the sample bias temperature vs peak laser intensity. The streak intensity is observed to vanish for peak laser intensities above a certain threshold. This threshold is used along with the data of Fig. 2 to determine the surface temperature at which order is lost in the probed layers.

Further experiments were performed to examine the temporal behavior of the heating and disordering process. In these experiments, the normalized RHEED streak intensities were obtained at various delay times between the arrival of the heating laser pulse and the electron probe pulse at the surface of the sample. Results for varying sample bias temperatures and incident peak laser intensities are shown in Fig. 4. In Figs. 4(a) and 4(b), the sample was subjected to laser intensities sufficiently only to heat the surface but not cause disorder. These sets exhibit qualities consistent with laser heating with heating and cooling rates on the order of 10^{11} K/s: a rapid decrease in the streak intensity, as the surface temperature rises with the arrival of the heating laser pulse, followed by a rapid increase in streak intensity as the heat is conducted to the bulk of the crystal. In Fig. 4(c), sufficient laser intensity was provided to disorder the probed surface layer as is evident by the vanishing streak intensity near 1 ns. After disordering, the surface recrystallizes and cools as is seen from the increasing streak intensity for later times. Finally, in Fig. 4(d), the streak intensity remains suppressed for times ≥ 4 ns after the initial disordering.

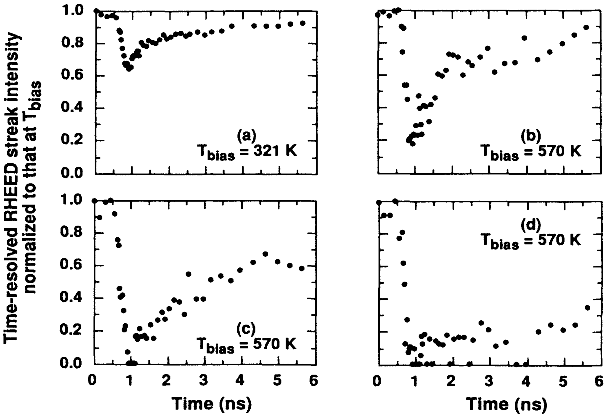

FIG. 4. Time-resolved normalized RHEED streak intensity on Pb(100) with different bias temperatures, T_{bias}, and peak laser intensities, I_p. (a) $T_{\text{bias}}=321$ K, $I_p=4.4\times 10^7$ W/cm^2. (b) $T_{\text{bias}}=570$ K, $I_p=2.3\times 10^7$ W/cm^2. (c) $T_{\text{bias}}=570$ K, $I_p=3.4\times 10^7$ W/cm^2. (d) $T_{\text{bias}}=570$ K, $I_p=5.1\times 10^7$ W/cm^2.

This is an indication of melting on the surface. In all of the experiments reported here, no surface damage was observed.

In conclusion, we have observed residual order to be present on Pb(100) at a peak surface temperature of 615 ± 20 K. Considering that the previously mentioned convolution effects lower the experimentally measured peak surface temperature, it is likely that residual order is present above T_m. At this high temperature, however, the surface most likely contains a high density of defects such as vacancies [5]. The presence of vacancies would be expected to lower the degree of superheating by providing nucleation sites for melting. Indeed, compared with the results obtained on Pb(111), where superheating to ~720 K was observed [16], the results on Pb(100) show evidence of residual order at a significantly lower surface temperature. Finally, these experiments show that there exists a barrier for the growth of the disordered layer thickness on Pb(100) at temperatures above T_m. At temperatures greater than our observed peak temperature, a second layering transition may occur that would result in a disordered layer thickness of $4\pi/k_1 \sim 5.7$ Å, a depth that exceeds the 5 Å probed by our electron beam.

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[1] J. W. M. Frenken and J. F. van der Veen, Phys. Rev. Lett. **54**, 134 (1985); J. W. M. Frenken, P. M. J. Maree, and J. F. van der Veen, Phys. Rev. B **34**, 7506 (1986).

[2] J. F. van der Veen, B. Pluis, and A. W. Denier van der Gon, in *Chemistry and Physics of Solid Surfaces VII*, edited by R. Vanselow and R. F. Howe (Springer-Verlag, Berlin, 1988), p. 455; J. W. M. Frenken, J. Vac. Sci. Technol. A **7**, 2147 (1989).

[3] (a) B. Pluis, A. W. Denier van der Gon, J. F. van der Veen, and A. J. Riemersma, Surf. Sci. **239**, 265 (1990); (b) B. Pluis, D. Frenkel, and J. F. van der Veen, Surf. Sci. **239**, 282 (1990).

[4] H. M. van Pinxteren and J. W. M. Frenken, Surf. Sci. **275**, 383 (1992).

[5] H.-N. Yang, K. Fang, G.-C. Wang, and T.-M. Lu, Phys. Rev. B **44**, 1306 (1991).

[6] Y. Cao and E. Conrad, Phys. Rev. Lett. **65**, 2808 (1990).

[7] E. A. Murphy, H. E. Elsayed-Ali, K. T. Park, J. Cao, and Y. Gao, Phys. Rev. B **43**, 12615 (1991).

[8] A. A. Chernov and L. V. Mikheev, Phys. Rev. Lett. **60**, 2488 (1988); A. A. Chernov and L. V. Mikheev, Physica (Amsterdam) **157A**, 1042 (1989).

[9] A. W. Denier van der Gon, J. M. Gay, J. W. M. Frenken, and J. F. van der Veen, Surf. Sci. **241**, 335 (1991).

[10] S. Chandavarkar, R. M. Geertman, and W. H. de Jeu, Phys. Rev. Lett. **69**, 2384 (1992).

[11] H. Häkkinen and M. Manninen, Phys. Rev. B **46**, 1725 (1992).

[12] G. Bilalbegović, F. Ercolessi, and E. Tosatti, Surf. Sci. **280**, 335 (1993).

[13] E. T. Chen, R.N. Barnett, and U. Landman, Phys. Rev. B **40**, 924 (1989).

[14] (a) H. E. Elsayed-Ali and G. A. Mourou, Appl. Phys. Lett. **52**, 103 (1988); (b) H. E. Elsayed-Ali and J. W. Herman, Rev. Sci. Instrum. **61**, 1636 (1990).

[15] J. W. Herman and H. E. Elsayed-Ali, Phys. Rev. Lett. **68**, 2952 (1992).

[16] J. W. Herman and H. E. Elsayed-Ali, Phys. Rev. Lett. **69**, 1228 (1992).