Superheating of Pb(111)

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Time-resolved reflection high-energy electron diffraction is used to study the laser-induced superheating of Pb(111). For a heating laser pulse width of ~180 ps, two regimes are observed depending upon the incident peak laser intensity. In the first regime, the time-resolved electron diffraction intensity indicates a transient superheating of the surface followed by cooling below the bulk melting temperature. In the second regime, which occurs at higher peak laser intensities, superheating is followed by melting. Superheating up to 120 K above the bulk melting temperature is observed.

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The superheating of solids has been attempted for many years. These studies have demonstrated that the free surface before melting and the solid-liquid interface after melting play a significant role in the kinetics of the melting process [1]. Solids with highly viscous melts such as quartz have been shown to readily superheat up to several hundreds of degrees above their bulk melting temperature T_m [2-4]. In these cases, the advance of the solid-liquid interface is limited by its propagation velocity rather than by heat flow.

The superheating of metals, however, has been more problematic. The viscosity of molten metals typically is many orders of magnitude lower than that of the solids considered in Refs. [2-4]. In addition, the phenomenon of surface melting [5], where some surfaces begin to disorder below T_m, makes it difficult to superheat. The primary factor governing surface melting is the interfacial free-energy difference between the ordered solid surface and the surface wetted by its melt, $\Delta\gamma$. For $\Delta\gamma > 0$, the free energy of the surface is reduced by the formation of a "quasiliquid" surface layer, while for $\Delta\gamma < 0$, the surface remains ordered. Superheating a surface for which $\Delta\gamma > 0$ is difficult since the disordered surface layer which forms below T_m serves as a vast nucleation site for melting into the bulk, thus precluding superheating. Experiments have shown that surface melting depends upon the degree of surface packing, with open surfaces demonstrating surface melting behavior. Closed surfaces such as the (111) surfaces of an fcc metal do not premelt. Recently this contrast was demonstrated on Pb(110) and Pb(111) [6], as well as on Al(110) and Al(111) [7].

Some metals, however, have been superheated by a number of means. Most of these involve bypassing the effect of the free surface in the melting process. Internal heating is one such approach. Single-crystal rods of Sn were superheated by 2 K by passing an electric current through them while preferentially cooling the surface to suppress melting [8]. Another approach has been to enclose one solid within another of higher bulk melting temperature. Ag spheres coated with Au have been superheated by up to 25 K for a time period of about 1 min [9]. X-ray diffraction was used to observe the superheating of Pb precipitates in Al [10]. In this case superheating was attributed to the lack of free surfaces. Superheating has been observed on small metal platelets that have extensive close-packed surfaces. Small platelets of Pb with extensive {111} surfaces were superheated by up to 2 K before melting after a time delay [11]. In a later study of Pb{111} platelets, superheating by ~3 K for periods of several hours was observed [12]. In these experiments, the shape of the platelets at different temperatures was studied with sufficient resolution to show that the superheated {111} surfaces were separated by curved regions consistent with localized melting at these regions. A theoretical study suggested that a molten region can exist between two nonwetting crystal surfaces at temperatures above T_m [13]. In addition, superheating was observed using platelets of Bi with extensive {0001} surfaces [14]. The work presented here is another approach to the superheating of metals. In contrast to the previous results on Pb{111} platelets, which showed that these could be superheated by a few degrees with slow heating rates, we show that the free Pb(111) surface can be superheated to a much higher degree using fast laser heating.

We next discuss the experimental setup. We employed pulsed laser heating along with time-resolved reflection high-energy electron diffraction (RHEED) to transiently heat the surface and probe the structure of the first few atomic layers at various times in the heating process. The fundamental wavelength of the Nd:YAG laser ($\lambda = 1.06$ μm) interacts with the surface at near normal incidence and is used as the transient heating source. The pulse width of the laser is about 180 ps. A small portion of the fundamental is frequency quadrupled to the ultraviolet ($\lambda = 0.266$ μm) and strikes the cathode of a photoactivated electron gun producing a pulse of electrons with comparable temporal width to that of the laser. This electron pulse probes the surface in the RHEED geometry. The heating pulse and electron probe pulse are well synchronized. This system is described in detail elsewhere [15] and has recently been used to study the time-resolved dynamics of surface disordering of Pb(110) [16].

The sample was cut from a single-crystal rod aligned in the (111) orientation using Laue backreflection. The surface was mechanically polished and then etched in a solution of 80% glacial acetic acid and 20% hydrogen peroxide (30% in water). The sample was then clipped to a resistively heated Mo base with a thermocouple placed between the retaining clip and the surface of the sample. The thermocouple was calibrated to the freezing and boiling temperatures of water and to the melting point of Pb ($T_m=600.7$ K) by melting a Pb sample *in situ*. The experiments were conducted in an ultrahigh vacuum chamber with a base pressure in the low 10^{-10} Torr range. Before each experiment, the crystal was cleaned with cycles of Ar^+ bombardment followed by annealing. Sample cleanliness was checked using Auger electron spectroscopy. Auger spectra were taken as a function of sample temperature to ensure that no high-temperature surface impurity segregation was occurring.

As a first step in understanding the temperature-dependent structural behavior of Pb(111), static RHEED measurements were performed. An arc lamp was used to produce electrons from the cathode of our photoactivated electron gun. This resulted in a stable electron beam that we used to probe the surface. The energy of the electrons was 18.2 keV, the angle of incidence was ~2°, and the beam was incident along the $\langle 01\bar{1}\rangle$ azimuth. The electron energy and angle of incidence give a probed depth of approximately two monolayers. The diffraction pattern was detected by a microchannel plate proximity focused to a phosphor screen, and the streak intensity was quantitatively analyzed by an optical multichannel analyzer. A graph of the RHEED streak intensity normalized to that at 407 K versus temperature is shown in the inset of Fig. 1. The data are plotted on a semilogarithmic scale. From this it is evident that the RHEED streak intensity follows an exponential decay in accordance with the Debye-Waller effect, where increased atomic mean-square vibrational amplitudes lead to decreasing elastic diffraction intensity. This should be contrasted to the behavior of the open Pb(110) surface, which has been shown to disorder below T_m [5,17,18]. Static RHEED measurements on Pb(110) have shown deviations from exponential Debye-Waller behavior at temperatures as low as 520 K [16]. From our measurements, we conclude that in contrast to Pb(110), Pb(111) does not experience surface premelting and remains ordered up to within 15 K of T_m in agreement with results from medium-energy ion scattering, which showed that Pb(111) remained ordered up to 0.5 K below T_m [6].

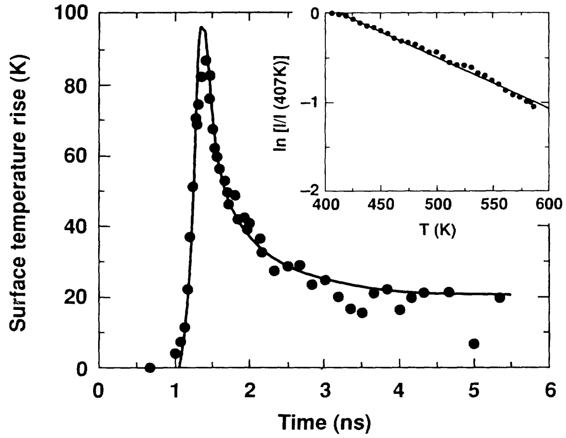

FIG. 1. Transient surface temperature rise of Pb(111) irradiated with Nd:YAG ($\lambda=1.06$ μm) laser pulses with a temporal width of 190 ps (FWHM) and a peak intensity of 3×10^7 W/cm^2. The experimental results were obtained from the transient surface Debye-Waller effect on RHEED intensity using the static calibration of the inset. Inset: The RHEED streak intensity plotted on a semilogarithmic scale showing Debye-Waller behavior up to 15 K below T_m, the maximum temperature studied. The orientation of the crystal was the same as that for the pulsed laser heating experiments.

We next discuss a time-resolved experiment that involved simple laser heating, where the peak surface temperature induced by the laser is less than T_m. The surface temperature rise on a sample biased at 493 K is shown in Fig. 1. The time-resolved RHEED streak intensity was converted to a surface temperature rise using the static RHEED calibration shown in the inset. The 190-ps laser pulse had a peak intensity of 3×10^7 W/cm^2, leading to an observed surface temperature rise of 90 K and a peak temperature of ~580 K. We next compare the data with a one-dimensional heat diffusion model:

$$C\frac{dT(z,t)}{dt}=K\frac{d^2T(z,t)}{dz^2}+I(1-R)\alpha e^{-\alpha z}f(t)\,,$$

where $T(z,t)$ is the temperature at distance z normal to the surface ($z=0$), t is time, $f(t)$ is the temporal profile of the laser pulse, which is assumed to be Gaussian, $C=1.58\times10^6$ J/m^{3}K is the heat capacity per unit volume [19], $K=32.2$ W/mK is the thermal conductivity [19], $\alpha=7.06\times10^7$ m^{-1} is the absorption coefficient [20], and I is the peak laser intensity in W/cm^2. The reflectivity R at $\lambda=1.06$ μm and 493 K was measured directly and found to be 0.79. The solid line in Fig. 1 is the solution of the model. The time-resolved temperature measurements, obtained from the RHEED streak intensity, are the result of the convolution of the temporal profile of the electron probe pulse with the actual temporal profile of the surface temperature. This convolution effect, which is not included in our analysis, is most significant for times near the peak of the temperature profile where the heating and cooling rates are highest. In Fig. 1, we set the temporal position of the experimental temperature profile by minimizing the mean-square difference between the experiment and the model for times between 1.5 and 2.5 ns, where convolution effects no longer play a significant role. Taking these effects into consideration, it is seen that the experimental data show agreement with that predicted from the classical heat diffusion model.

We next discuss laser heating experiments with the sample biased at 586 K ($T\approx T_m-15$ K) and transiently heated with varying peak laser intensities I_p. The experiments were performed at the time corresponding to the minimum of the normalized streak intensity, which is the experimentally determined time of maximum surface temperature rise. The pulse width of the laser was 170 ps and the same angle of incidence and azimuthal orientation were used as in the static RHEED measurements. We measured the RHEED streak intensity and normalized it to that at 586 K, as shown in Fig. 2. From the semilogarithmic plot in the inset of Fig. 2, two regimes are evident. For the first regime, where $I_p \leq 3.5\times10^7$ W/cm^2, the RHEED streak intensity follows an exponential decay with peak laser intensity, consistent with Debye-Waller behavior. The second regime, where $I_p \geq 3.5\times10^7$ W/cm^2, shows a deviation from exponential behavior indicating that the surface is experiencing disorder consistent with melting. To estimate the maximum superheating temperature before melting occurs, we obtained the peak temperature jump corresponding to laser intensity. The normalized streak intensity in the exponential region was transformed to a temperature jump ΔT by using the results of the static RHEED calibration in the inset of Fig. 1. For the lower I_p, the temperature jump ΔT leads to peak surface temperatures less than T_m. In the exponential Debye-Waller region, ΔT is proportional to the laser intensity; therefore, the lower values of the laser intensity and the corresponding temperature jumps can be used to make a correspondence between peak laser intensity and temperature. When this is done, we observe the departure from Debye-Waller behavior to occur when the surface is heated to a maximum temperature of ~720 K. In addition, the temperature-dependent RHEED streak intensity has a slope, when plotted on a semilogarithmic scale, equivalent to that from the static RHEED measurements within experimental error. Errors in determination of the slope can arise from the above-mentioned convolution effects, which are significant at the temporal minimum of the time-resolved diffraction intensity. This observation indicates that for peak temperatures less than 720 K, the surface remains ordered, cools below T_m, and behaves according to the Debye-Waller effect. Thus, we conclude that Pb(111) can be superheated by ~120 K using fast laser heating. In this context, superheating refers to a lattice mean-square vibrational amplitude in excess of that at T_m, which is still consistent with a Debye-Waller decrease in the elastic diffraction intensity. At higher temperatures melting occurs, resulting in a pronounced departure of the RHEED streak intensity from Debye-Waller behavior.

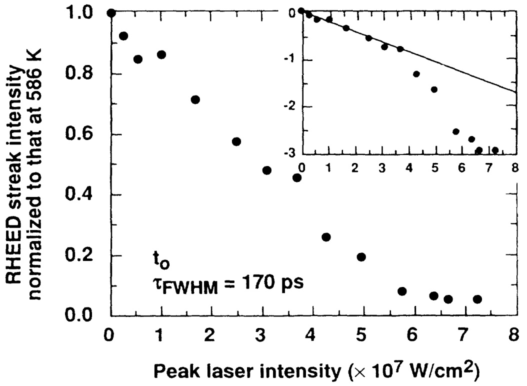

FIG. 2. Time-resolved RHEED streak intensity normalized to that at 586 K vs peak laser intensity obtained from pulsed laser heating at the minimum of the normalized streak intensity. Inset: A plot of the data on a semilogarithmic scale showing deviation from Debye-Waller behavior at $I_p \approx 3.5\times10^7$ W/cm^2. The corresponding peak temperature is ~720 K, approximately 120 K above T_m. The slope of the linear region is the same as the slope from the static RHEED measurements within experimental error.

The laser heating experiment with the sample biased at 586 K was also carried out at various times after the time of the minimum RHEED streak intensity, ranging from 500 to 4000 ps. At all of the delay times examined, deviation from Debye-Waller behavior consistently occurred above a peak laser intensity of about 3.5×10^7 W/cm^2, even at the longest delay time considered, 4000 ps. In fact, at 4000-ps delay, significant departure from Debye-Waller behavior was observed, leading us to conclude that this deviation is due to melting on the surface rather than surface anharmonicity.

We next discuss the temporal evolution of the RHEED streak intensity when the Pb(111) sample is biased at 586 K. The normalized RHEED streak intensity was obtained at various delays between the arrival of the laser heating pulse and the pulsed electron probe. Results for

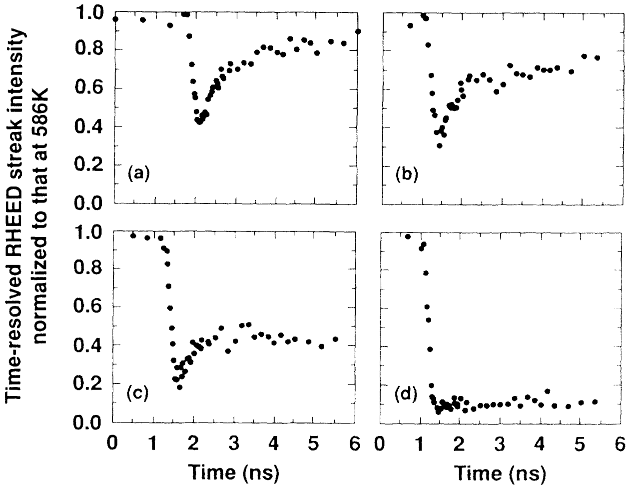

FIG. 3. Time-resolved normalized RHEED streak intensity of Pb(111) irradiated with Nd:YAG ($\lambda=1.06$ μm) laser pulses of varying peak laser intensity. Set (a) is consistent with classical heat diffusion and corresponds to a superheating of ~110 K. At higher peak laser intensities, the surface begins to melt and this is evident in the deviation of these sets from classical heat diffusion. By examining the initially fast rise in streak intensity after the intensity minimum in (b)-(d), the time from the minimum to the time at which deviation from classical heat diffusion occurs is seen to decrease with increasing peak laser intensity.

a peak laser intensity of $I_p \approx 3.3\times10^7$ W/cm^2 are shown in Fig. 3(a). These data are consistent with classical heat diffusion, showing a fast decrease in the diffraction intensity as the laser pulse heats the surface and a rapid recovery as the heat is conducted to the bulk. In Figs. 3(b)-3(d) the surface was heated with $I_p \gtrsim 3.5\times10^7$ W/cm^2, the threshold intensity for Debye-Waller behavior, as determined from Fig. 2. A qualitative difference in these sets is evident. As I_p is increased, the diffraction intensity fails to recover to what is expected from classical heat diffusion. We attribute this to melting on part of the surface. For the sets (b) and (c), the streak intensity exhibits an initially fast rise after the intensity minimum, similar to that seen in the nonmelting sets. In this time period the surface is most likely molten in some regions due to the nonuniformity of laser heating, which was measured to be $\pm18\%$ across the surface, and is a superheated solid in the remainder of the probed area. The excess surface temperature diffuses for some time τ, after which pronounced surface disorder occurs, as reflected in the failure of the streak intensity to recover.

To extract this time τ, we first compared the time-resolved RHEED intensity of the experiments that showed no melting and no superheating with those that were superheated but displayed no apparent anomalous behavior [see Fig. 3(a)]. This comparison showed good agreement, indicating that the superheated sets that do not show melting display behavior consistent with classical heat diffusion. Having verified this, we then compared the time-resolved RHEED intensity of the experiments that showed melting with those that did not and looked for the time at which deviation from the classical heat diffusion model occurred. A nonmelting, superheated set was normalized to a given melting set and subtracted from it. The resulting difference was then fitted with a polynomial and differentiated to observe the break from nonmelting behavior. The difference of this time and the time of the intensity minimum was identified as τ. The time τ was observed to decrease from ~1200 ps to <300 ps for peak temperatures of 130 and 215 K, respectively. This demonstrates the decreasing time duration of superheating with increasing temperature.

In conclusion, using time-resolved RHEED, we have observed the superheating of the free Pb(111) surface. The maximum superheating obtained was ~120 K. For superheatings ≤ 120 K, the surface was transiently superheated with no melting taking place. Evidently, melting is bypassed by the large heating and cooling rates, which are on the order of 10^{11} K/s. For superheatings above 120 K we observe deviation from Debye-Waller behavior indicative of melting. Time-resolved RHEED shows that the time at which pronounced deviation from classical heat diffusion is observed decreases with increasing peak temperature, indicating that in this regime the surface cooling rate is not rapid enough to overcome the time it takes to melt. It is conceivable that greater superheating could be observed with a larger heating rate. Finally, this work contrasts that done on the open Pb(110) surface where surface disorder could not be bypassed by fast laser heating [16].

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