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H. E. Elsayed-Ali

Old Dominion University, helsayed@odu.edu

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Surface Debye temperature measurement with reflection high-energy electron diffraction

H. E. Elsayed-Ali

Department of Electrical and Computer Engineering, Physical Electronics Research Institute, Old Dominion University, Norfolk, Virginia 23529-0246

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Measurement of the surface mean-square atomic vibrational amplitude, or equivalently the surface Debye temperature, with reflection high-energy electron diffraction is discussed. Low-index surfaces of lead are used as examples. Particular details are given about the temperature-dependent diffraction pattern of Pb(100) in the Debye–Waller region. The use of reflection high-energy electron diffraction for measurement of the substrate surface temperature in thin-film deposition chambers is suggested. © 1996 American Institute of Physics. [S0021-8979(96)08209-8]

I. INTRODUCTION

Monitoring of substrate temperature during thin-film deposition is often important for controlling the properties of the grown thin film. This measurement, however, is not necessarily straightforward. For example, in molecular-beam epitaxy, *in situ* measurement of the substrate temperature is complicated by the fact that the rotating holder does not permit good thermal contact between holder and thermocouples. A discrepancy of more than 70 °C between thermocouple reading and actual surface temperature was estimated.¹ Pyrometers can be used, however, they are sensitive to viewpoint transparency. Previously, it has been proposed that a surface phase transformation with a known critical temperature can be used for temperature calibration, and reconstruction in GaAs has been used for that purpose.¹ Here we show that the intensity of reflection high-energy electron diffraction (RHEED) is sensitive to surface temperature due to the Debye–Waller effect. The use of the Debye–Waller effect on the RHEED intensity provides a general method of surface temperature measurement for surfaces with known Debye temperature. Alternatively, RHEED can be used to study the vibrational properties of surfaces and epitaxial thin films with submonolayer sensitivity.

An understanding of the vibrational properties of surface atoms is of both fundamental and technological importance. For example, vibrational entropy is thought to contribute to the nature of surface segregation in alloys.^{2,3} The surface atom vibrational properties are also known to affect surface phase transformations such as the case for surface melting.^{4–6} Moreover, the vibrational properties of thin layers deposited on substrates provide information on the nature of interaction at the interface. It is well known that a surface does not behave as a simple termination of the bulk. One way in which this is manifested is in the increased vibrational amplitude of surface atoms. This is related to the asymmetric bonding and the reduced number of nearest neighbors that characterize a surface atom as compared with an atom in the bulk. Measurements of the enhanced vibrational amplitude of surface atoms have been carried out using low-energy electron diffraction (LEED).^{7,8} In the LEED studies, the Debye–Waller effect, which shows as a decrease in the elastic diffraction intensity with temperature and an

increase in background intensity, was used to characterize the surface thermal vibrations and to determine an effective surface Debye temperature Φ_D . In many of these studies, Φ_D was observed to increase with increasing incident electron beam energy. This is explained by the fact that higher incident electron energies lead to larger probed depths of the electron beam which, for high enough energy, approach bulklike characteristics.

RHEED represents another technique with which to determine surface Debye temperatures. The probed depth of the 10–20 keV electrons in the RHEED geometry, where the angle of incidence of the electron beam is typically 1°–5° with respect to the plane of the surface, is comparable to that of low-energy electrons (50–1000 eV) at near-normal incidence. Therefore, LEED and RHEED have comparable surface sensitivities. However, RHEED is much more widely used in thin-film growth studies, both as a qualitative structural probe and for thickness measurement and control using the well-known RHEED intensity oscillation.^{9–12}

II. DEBYE–WALLER EFFECT

The sensitivity of the diffraction intensity to temperature arises from the increase in the atomic vibrational amplitude with temperature. This is observed as a decrease in the elastic diffraction intensity with increased temperature. In the Debye–Waller treatment, atomic vibrations are assumed to be harmonic and the influence of multiple scattering events is ignored. In general, the harmonic vibration assumption is most valid for temperatures below the Debye temperature, however, this assumption is justified at higher temperatures when considering the intensity of the elastic diffraction peaks. Accordingly, the intensity attenuation of an elastic diffraction peak is described by¹³

$$I_n(T) = I_n(0) \exp(-MT), \quad (1)$$

where $I_n(T)$ is the n th-order diffraction intensity at temperature T , $I_n(0)$ is the n th-order diffraction intensity for a hypothetical rigid lattice, and

$$-MT = -\langle [\Delta \mathbf{k} \cdot \mathbf{u}(T)]^2 \rangle = -|\Delta \mathbf{k}|^2 \langle \mathbf{u}^2(T) \rangle \quad (2)$$

is the Debye–Waller factor. $\mathbf{u}(T)$ is the instantaneous displacement of an atom from its equilibrium position. The

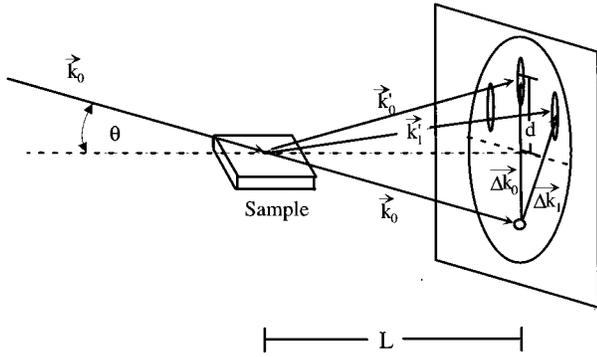


FIG. 1. This illustration shows how the parameters necessary for the calculation of the surface Debye temperature are obtained in RHEED. The incident electron beam, specular beam, and first-order diffracted electron beams are labeled \mathbf{k}_0 , \mathbf{k}'_0 , and \mathbf{k}'_1 , respectively. The momentum changes as corresponding to the 0th-order and the first-order diffraction are given by $\Delta\mathbf{k}_0$ and $\Delta\mathbf{k}_1$, and the ratio of their magnitudes is equivalent to the ratio of the measured distances from the transmitted beam. The angle of incidence θ is calculated from the specular spot.

separation performed in the second step of Eq. (2) is valid under the assumption of an isotropic vibrational amplitude. While this assumption is valid for atoms in the bulk, for surface atoms, anisotropy in the Debye temperature has been previously reported.⁸ In general, the vibrational amplitude of surface atoms perpendicular to the surface is larger than that in a direction parallel to the surface. For the low-order streaks (e.g., 00 and 01), $\Delta\mathbf{k}$ in the RHEED geometry is almost perpendicular to the surface. Therefore, for the low-order streaks we mainly measure the mean-square atomic vibrational amplitude perpendicular to the surface. For the n th-order diffracted beam, the momentum change resulting from the elastic scattering is

$$\Delta\mathbf{k} = \Delta\mathbf{k}_n = \mathbf{k}'_n - \mathbf{k}_0, \quad (3)$$

where \mathbf{k}_0 and \mathbf{k}'_n are the momentums of incident and n th-order elastically diffracted beams, respectively. $\langle\mathbf{u}^2(T)\rangle$ is the mean-square displacement of an atom from its equilibrium position. The slope M of $\ln[I(T)]$ vs T gives the surface Debye temperature and can be written as

$$M = \frac{|\Delta\mathbf{k}_n|^2}{|\Delta\mathbf{k}_0|^2} \frac{\langle\mathbf{u}^2(T)\rangle}{|\Delta\mathbf{k}_0|^2} = \frac{|\Delta\mathbf{k}_n|^2}{|\Delta\mathbf{k}_0|^2} \left(\frac{4\pi}{\lambda} \sin \theta \right)^2 \frac{3\hbar^2}{mk_B\Phi_D^2}. \quad (4)$$

For the specular spot, the momentum $\Delta\mathbf{k}$ is totally in a direction perpendicular to the crystal surface, while for $n > 0$ there is a parallel component of momentum transfer. The angle of incidence θ is defined from the plane of the surface, λ is the wavelength of the electrons, \hbar is Plank's constant divided by 2π , m is the atomic mass, k_B is Boltzmann's constant, and Φ_D is the surface Debye temperature. The parameters $\Delta\mathbf{k}_n/\Delta\mathbf{k}_0$ and θ are obtained from the diffraction pattern as demonstrated in Fig. 1. The distances from the specular spot to the shadow edge d and from the sample to the image plane L allow us to calculate θ . Providing one obtains $\Delta\mathbf{k}_n$, the effective surface Debye temperature, or

TABLE I. Parameters for the surface Debye temperature measurements using RHEED.

Face	E (keV)	θ ($^\circ$)	D_λ (\AA)
(110)	18.2	2.8	4.6
(100)	14.0	3.2	4.2
(111)	18.2	2.4	3.9

equivalently the component of $\langle\mathbf{u}^2(T)\rangle$ in the direction of $\Delta\mathbf{k}$ can be obtained from a measurement of the ratio $I_n(T)/I_n(0)$.

III. EXPERIMENT

We next demonstrate the use of RHEED to measure the surface Debye temperature of Pb(111), Pb(100), and Pb(110) surfaces. By observing the intensity attenuation of the RHEED streak maxima as a function of temperature, the dependence of $\langle\mathbf{u}^2(T)\rangle$, and hence Φ_D , on surface orientation is obtained. The surfaces were mechanically polished and chemically etched as discussed in previous publications.¹⁴ The experiments were performed in an ultrahigh-vacuum chamber with a base pressure in the low 10^{-10} Torr range. The samples were cleaned before each experimental run with cycles of Ar^+ bombardment for 30 min at 500 K followed by annealing for 5 min at 550 K. Auger electron spectroscopy was used to confirm the surface cleanliness of the samples. The samples were mounted on a resistively heated stage and the temperature was measured with two thermocouples mounted on the surface. Quantitative analysis of the RHEED streak intensity from the samples was carried out by imaging the phosphor screen detecting the RHEED pattern on an array detector interfaced to a personal computer.

The experimental conditions are given in Table I where E is the electron energy, θ is the angle of incidence of the electron beam measured from the surface of the sample, and D_λ is the depth probed by the electron beam. The probed

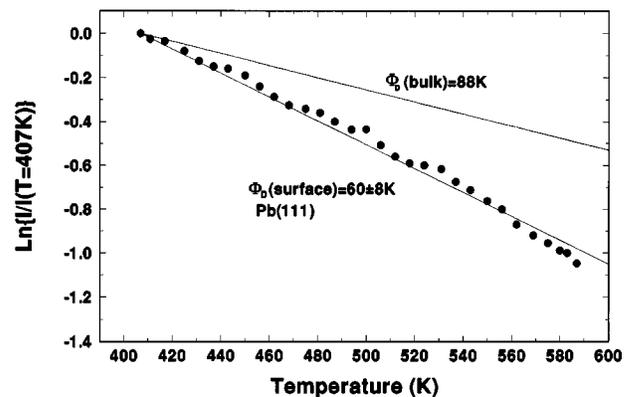


FIG. 2. RHEED intensity normalized to that at 407 K, $\ln[I(T)/I(T = 407 \text{ K})]$, is plotted vs temperature. The slope is used to obtain the surface Debye temperature of Pb(111). The line with smaller slope corresponds to that expected for a surface Debye temperature of 88 K, which is the Debye temperature of bulk Pb. The larger slope associated with the Pb(111) surface demonstrates the increased thermal vibrations of surface atoms relative to those of the bulk.

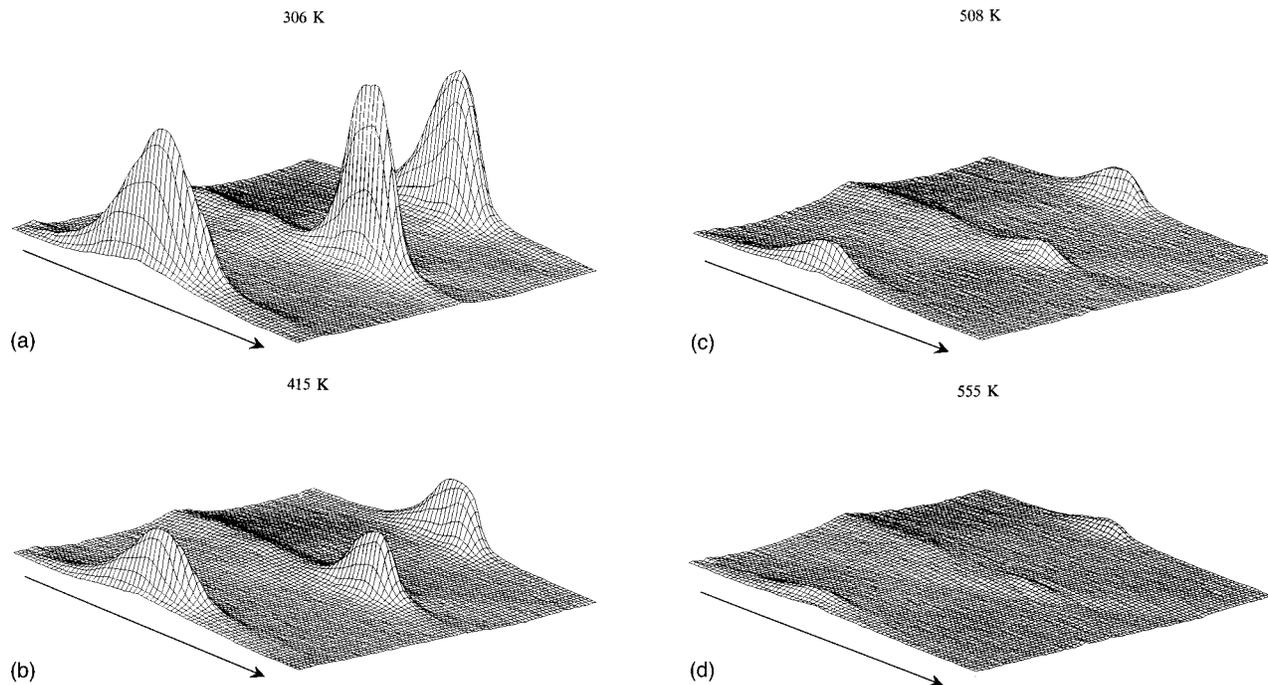


FIG. 3. Three-dimensional plots of RHEED patterns of Pb(100) obtained at different temperatures. The height of the streak profile represents the intensity of the streak (in arbitrary units). (a)–(d) show intensity of RHEED pattern at 306, 415, 508, and 555 K, respectively. The arrows are drawn along the RHEED streaks, and show the direction of increased momentum transfer perpendicular to the surface. The electron beam was incident along the [011] direction.

depth is obtained using an empirical relation between the electron energy and the inelastic mean-free path along with the measured angle of incidence of the electron beam.¹⁵

IV. RESULTS AND DISCUSSIONS

An example of a RHEED streak intensity measurement for the Pb(111) surface is given in Fig. 2 where the intensity of the 01 streak measured at its peak is shown as a function of temperature. The data are plotted on a semilogarithmic scale and shows an exponential decrease in the RHEED

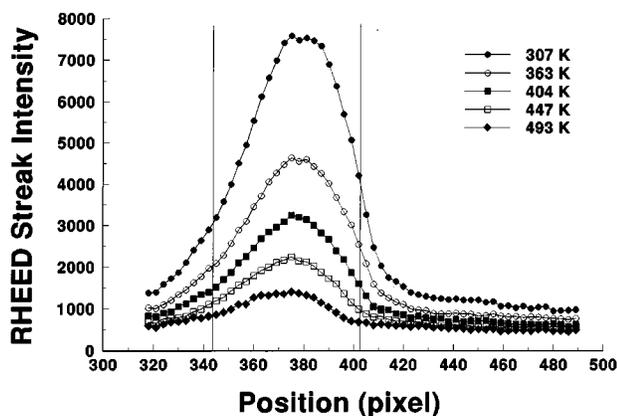


FIG. 4. RHEED intensity (in arbitrary units) along the 01 streak for Pb(100) is plotted for different temperatures varying from 307 to 493 K. Each location on the streak corresponds to different momentum transfer with respect to the incident beam, $\Delta\mathbf{k}$. The two vertical lines give the range of locations along each RHEED streak which we use to obtain the Debye–Waller curves.

streak intensity with temperature for the studied range, which extends up to $T_m - 15$ K. For comparison, the expected Debye–Waller reduction in the elastic diffraction intensity assuming a bulk Debye temperature of 88 K is plotted on the same graph. The effective surface Debye temperature is obtained from Eq. (4) using the experimentally determined slope of the RHEED streak intensity, the angle of incidence of the electron beam, and the momentum transfer corresponding to the considered location on the diffraction pattern. Only single scattering events are considered in this analysis. Moreover, since no electron energy filtering of the RHEED pattern was performed, the background includes inelastically scattered electrons. From the RHEED patterns obtained at room temperature, the intensity of the inelastically scattered electrons is much smaller than the elastic peaks. At the higher temperatures, the ratio of the intensity of an elastic peak to the background increases. Background subtraction from the elastic peaks was accomplished by measuring the background intensity midway between two RHEED streaks for each temperature and subtracting it from the elastic peak intensity measured at the same temperature. The observed larger slope of the RHEED data as compared with the slope predicted assuming a bulk Debye temperature implies that the surface atoms experience an increased vibrational amplitude relative to bulk atoms. The Debye–Waller behavior of surface atoms on Pb(111) is consistent with other experiments showing that this surface does not exhibit anharmonic surface vibration, thought to be a precursor to surface melting. The (110) and (100) surfaces displayed Debye–Waller behavior up to 520 and 550 K, respectively. At higher temperatures, deviation from Debye–Waller behavior occurred

TABLE II. The surface Debye temperature for Pb(100) calculated at different positions along the 01 streak.

$\Delta k_n / \Delta k_0$	$M (10^{-3} \text{ K}^{-1})$	$\Phi_D \text{ (K)}$
0.881	6.93	52.3
0.896	7.33	51.8
0.912	7.56	51.9
0.928	7.94	51.5
0.943	8.65	50.2
0.959	9.03	49.9
0.975	9.15	50.4
0.991	9.55	50.1
1.007	10.21	49.3
1.023	10.69	48.9
1.039	10.00	51.4

indicating the enhanced density of surface defects, anharmonicity in the atomic vibration,¹⁶ or enhanced inelastic processes which could dominate at higher temperatures.¹⁷ Anharmonicity and temperature generated surface defects would generally cause the Debye–Waller curve to bend downward, while enhanced inelastic scattering with temperature can cause the curve to bend upward. Thus, to obtain the surface Debye temperature it is important to conduct the measurement in a temperature range for which the simple kinematic Debye–Waller theory can apply.

Analysis of the exponential region of the data for Pb(110) and Pb(100) yields the effective surface Debye temperatures for these surfaces. A set of three-dimensional plots of RHEED patterns showing intensity changes with temperature for Pb(100) is shown in Fig. 3. The height of the profile is proportional to the RHEED intensity. The 00 order is in the center of the pattern. This set of plots shows the intensity of the RHEED pattern as a function of surface temperature, which is indicated on top of each diffraction pattern. The attenuation at a particular location on the streaks depends on the transfer of momentum, $\Delta \mathbf{k}$. In Fig. 4 the RHEED streak intensity along the 01 streak is plotted for different temperatures ranging from 307 to 493 K. The x axis represents the streak position as determined by the pixel number of the array detector observing the diffraction pattern. The y axis is the relative RHEED streak intensity. At higher temperatures, the temperature dependence of the streak intensity shows deviation from the exponential Debye–Waller behavior. In addition, anomalous surface expansion, which is to some degree occurring even at room temperature, starts to become significant enough to cause a noticeable shift in the peak of the streak location.¹⁸ These complications for this surface limits the Debye–Waller temperature region and makes it necessary to analyze only the lower-temperature data in order to extract from it the surface Debye temperature. Deviation from Debye–Waller behavior is even more noticeable in

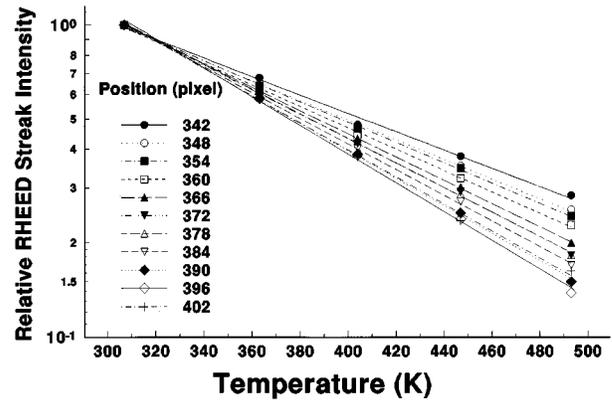


FIG. 5. The temperature dependence of the RHEED streak intensity for Pb(100) at different locations on the 01 streak. The Debye temperature corresponding to each curve is calculated in Table II.

Pb(110) which is well known to undergo surface premelting at temperatures significantly below the bulk melting temperature.^{4,5}

The temperature dependence of the RHEED streak intensity at different locations on the streak is displayed in Fig. 5. The position at which each Debye–Waller curve is obtained is indicated on the figure by the pixel number which corresponds to that shown in Fig. 4. Clearly the slope of each exponential curve is dependent on its location on the RHEED streak which determines $\Delta \mathbf{k}$. Analysis of Fig. 5 is given in Table II where the Debye temperature of Pb(100) is calculated using the temperature-dependent streak intensity at different locations along the 01 streak. In Table II, the amount of momentum transfer along the RHEED streak increases with the pixel number. ($\Delta \mathbf{k}_n / \Delta \mathbf{k}_0$ of 0.88 corresponds to pixel number 342, while that for $\Delta \mathbf{k}_n / \Delta \mathbf{k}_0$ of 1.039 corresponds to pixel number 402.) The value of the Debye temperature obtained from this set of data is 50.7 K. Analysis of the temperature dependent decay of the 00, 01, 0 $\bar{1}$ streaks obtained from three different sets of data indicates that the surface Debye temperature of Pb(100) is 49 ± 5 K.

Values of Φ_D for the three low-index faces of Pb are given in Table III along with values previously obtained from LEED.¹⁹ RHEED measurements reported here are for the temperature dependence of the 0th-order and the two first-order streaks. The momentum change for the n th-order streak $|\Delta \mathbf{k}_n|$ has components both perpendicular and parallel to the surface plane. To separate these components, a more detailed study which probes multiple crystallographic directions is necessary. The experimental errors in the reported RHEED measurements are due to the spread in the slopes of the semilogarithmic plots obtained for these measurements and the uncertainty in the angle of incidence and momentum transfers as measured from the RHEED pattern.

TABLE III. The Debye temperature for the low-index surfaces of lead.

Technique	Pb(110)	Pb(100)	Pb(111)	Reference
LEED	$37 \pm 20\%$ K	...	$55 \pm 20\%$ K, $49 \pm 20\%$ K	19
RHEED	30 ± 5 K	49 ± 5 K	60 ± 8 K	14, present work

V. CONCLUSION

We have demonstrated that RHEED is a comparable technique to LEED in probing the thermal vibrations of surface atoms. RHEED is suitable for submonolayer detection, with up to 0.1 monolayer mean thickness detection capability reported.²⁰ In addition, from a practical point of view, RHEED is the principle structural diagnostic tool in molecular-beam epitaxy. Its grazing angle of incidence makes it compatible with real-time observation of the surface quality during thin-film growth. Oscillations in RHEED intensity, in particular in the specular spot, has been extensively used to monitor and control layer-by-layer growth.^{9–12} Quantitative analysis of the Debye–Waller effect on the RHEED pattern provides the ability to monitor the effect of film thickness, with submonolayer accuracy, on the thermal vibrations of surface atoms. An understanding of the vibrational amplitude of surface atoms during film growth could be correlated with other technologically important parameters such as surface diffusion and substrate–adsorbate coupling. The simple analysis presented here, which ignores inelastic and dynamical scattering effects, is inadequate for a description of much of the temperature dependent vibrational behavior of the surface atoms. However, at some temperature range, the simple kinematic Debye–Waller analysis of the temperature dependence of the RHEED intensity seems to apply. We also point out that, for a surface with a known Debye temperature, the Debye–Waller reduction in the RHEED streak intensity with temperature can be used to obtain the substrate surface temperature in molecular-beam epitaxy or other high-vacuum thin-film deposition systems.

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