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Real-Space Direct Visualization of the Layer-Dependent Roughening Transition in Nanometer-Thick Pb Films

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By means of variable-temperature scanning tunneling microscopy and spectroscopy we studied the thickness-dependent roughening temperature of Pb films grown on Cu(111), whose electronic structure and total energy is controlled by quantum well states created by the spatial confinement of electrons. Large scale STM images are employed to quantify the layer population, i.e., the fraction of the surface area covered by different Pb thicknesses, directly in the real space as a function of temperature. The roughening temperature oscillates repeatedly with bilayer periodicity plus a longer beating period, mirroring the thickness dependence of surface energy calculations. Conditions have been found to stabilize at 300 K Pb films of particular magic thicknesses, atomically flat over microns.

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The surface roughening transition was introduced by Burton and Cabrera [1] more than 50 years ago in the framework of their classic theory of crystal growth. Below the roughening temperature T_R the surface of the crystal (in equilibrium with its own vapor) is atomically flat, while above T_R it is rough because the free energy to create a step vanishes. The roughening temperature is proportional to the surface energy per atom, and, thus, any physical factor contributing to the surface energy will influence T_R. The roughening temperature, accordingly, has been shown experimentally to depend on the surface orientation for He_4 [2] or Xe [3] crystals and also to be (monotonically) thickness dependent for films of Xe grown on Pd(111) [4,5]. In this latter case the population of the different layers as a function of temperature was deduced from the heights of the layer-dependent photoemission peaks [4].

Recently, the layer-dependent electronic energy contributed by quantum well states (QWS) to the total energy of ultrathin metallic films with confined electrons has been shown to influence the thermal stability of ultrathin metallic films deposited on semiconducting [6–8] or metal substrates [9], and the appearance of magic heights in the equilibrium distribution of metallic islands [10]. For films of Pb on Si(111) the critical temperature of superconductivity [11,12] or the surface diffusion barrier [13] has been shown to oscillate with bilayer periodicity and a superimposed beating period, related to the QWS periodicity imposed by the Fermi surface of Pb. For Pb/Si(111), a layer-dependent roughening temperature (or temperature of decomposition of every layer in favor of more stable heights) has been determined from the disappearance of the characteristic QWS in angular resolved photoemission (ARUPS) [6]. The T_R values reported show a single oscillation in the range of thicknesses explored [6]. The population of the different layers has been deduced from fits to x-ray reflectivity measurements as a function of temperature [7]. Reciprocal space techniques have the weakness of emphasizing the most probable configuration. Real space, local techniques such as scanning tunneling microscopy/spectroscopy (STM/STS), offer an invaluable insight on these nanosystems, often challenging the view obtained from averaging techniques, as illustrated recently in relation to the thickness dependence of the superconducting temperature for nanometer-thick films of Pb on Si(111) [12], where a real-space view of the superconducting gap has corrected previous inconsistencies [11].

We report here on a real space, direct determination of the layer dependence of T_R in the closely related QWS-controlled system of Pb/Cu(111). The temperature dependence of the population of each layer is determined by *in situ* variable-temperature STM from 98 K to 300 K, while, simultaneously, the energy of the QWS and their spatial distribution are measured by means of STS, which allows an unequivocal identification of the layer thickness. The layer-dependent T_R shows three periods of an oscillatory behavior with bilayer periodicity plus a first beating period. In the common thickness range our data are consistent with those obtained by means of ARUPS for Pb/Si(111), validating the analysis performed there [6] (contrary to the case of the superconducting temperature [11,12]) and generalizing the effect of electron confinement to metal substrates with an appropriate directional band gap. By choosing Pb thicknesses (8 or 10 ML) with the last occupied QWS far below the Fermi level (−0.9 eV), the layer dependence of T_R has been exploited to stabilize at 300 K films of Pb on Cu(111) that are atomically flat over lateral length scales of microns.

The experiments have been carried out in a UHV chamber with base pressure of 7×10^{-11} Torr that contains a variable-temperature STM and a rear view LEED optics. The Cu(111) crystal was cleaned by cycles of Ar^+ sputtering and annealing and displayed atomically resolved STM images. Pb was evaporated from a Knudsen cell on the sample while it was in the microscope at 98 K. The temperature of the substrate during and after the deposition was varied from 98 K up to 330 K. The polycrystalline W tips were routinely cleaned by ion bombardment and annealing. The STM images were recorded in the constant current mode with the tip sufficiently far away from the substrate ($V_b = -1.0$ V, $I_t = 0.1$ nA) to minimize a possible influence of the tip electrical field in the observed mass transport [14]. The dI/dV curves were obtained by numerical differentiation of the $I(V)$ curves. The experimental setup allows the *in situ* observation in real space of the structural transformations at atomic scale, as well as ramping the sample temperature and controlling it within 0.1 K.

Pb grows on Cu(111) at 300 K in the Stranski-Krastanov mode of growth, whereby 3D, (111)-oriented Pb islands grow on top of a (4 × 4) wetting layer, 1 ML high. In each of the 3D islands the electrons from the sp band of Pb are efficiently confined between the vacuum barrier and the gap in Cu along the $\langle 111 \rangle$ direction that goes from -1 to $+4$ eV around the Fermi energy [15]. The corresponding QWS resulting from the discretization of the band have been detected by local STS performed on top of islands [10,15] or by spatially averaging ARUPS [16]. The QWS determine the appearance of magic heights in the equilibrium height distribution [10,15] or *smaller* apparent step heights in He scattering [17], whenever they are far from the Fermi energy.

Upon lowering the temperature of deposition, the mode of growth changes to layer by layer. At 98 K, the surface diffusion is frozen enough so that even films with "forbidden" thicknesses can be stabilized. In fact, for Pb films deposited at 98 K, the surface morphology is the same independently of the thickness. Figure 1(a) illustrates it for a nominally 9 ML-thick film [18]. Most of the surface is covered by 9 ML, while a certain number of ramified islands (and voids) one monolayer high (deep), cover a small fraction of the surface. The islands have a dendritic shape indicating that at this temperature surface diffusion is essentially frozen.

Even if the substrate is completely covered, the local detection of the QWS states by STS allow a precise determination of the Pb local thickness. Figure 1(b) shows the corresponding tunneling spectra recorded at 98 K on the different regions of Fig. 1(a). There is a QWS right below the Fermi energy for 9 MLs, while for 8 and 10 ML films, the last occupied QWS (not shown) lies 0.9 and 0.6 eV below the Fermi level, respectively. All films with an even number of layers present an unoccupied QWS at $+0.65$ eV, first detected in metal-oxide-metal junctions of Pb [19]. The existence of this state facilitates the distinction between local thicknesses with even or odd numbers of layers. Even in the small islands and voids of Fig. 1(a) the STS spectra show the QWS for the corresponding thickness, demonstrating that the spatial distribution of the QWS maps precisely the lateral extension of the different local thicknesses.

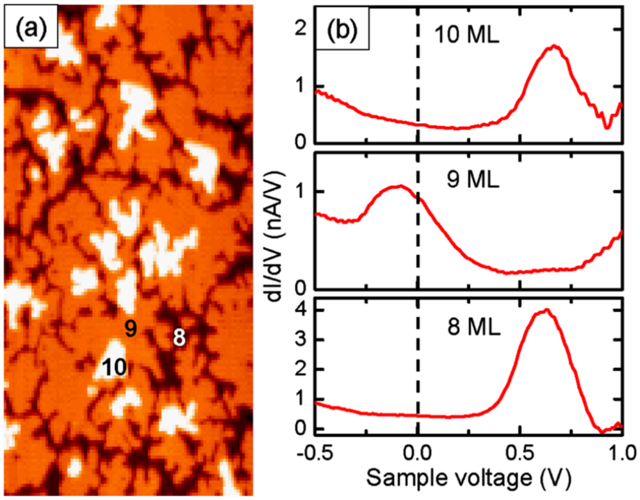

FIG. 1 (color online). (a) 88 nm × 155 nm STM image recorded *in situ* after deposition of 9 ML of Pb on Cu(111) at 98 K. (b) dI/dV curves showing the energy position of the QWS for different local Pb thicknesses around the Fermi level.

Variable-temperature STM is used to follow the evolution of the film morphology during annealing with a temperature ramp of 1 K per minute. Figure 2 illustrates the first morphological changes observed in the Pb films as their temperature increases. Figure 2(a) shows the large scale morphology of a 6 ML-thick film, which, as mentioned, is essentially identical to the one of 9 ML shown in Fig. 1. Notice, in particular, that the islands in the top layer and at steps show the dendritic shape characteristic of aggregation-limited growth with severely limited surface diffusion. Figure 2(b) shows that, at 180 K, diffusion along the step edges has already set in, and the islands have acquired a rounded shape. Since the activation energies for terrace and edge diffusion are rather similar, and the vapor pressure of Pb is so small, we considered that above this temperature, surface diffusion is operative and the

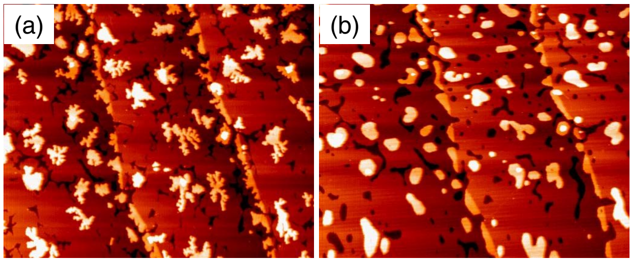

FIG. 2 (color online). Snapshots of STM movies showing the first stages of the evolution with the temperature of a 6 ML-thick Pb film on Cu(111) at: (a) 93 K and (b) at 180 K. The images are 200 nm × 130 nm.

films are in local equilibrium. Notice, however, that no vertical mass transport has taken place yet.

Increasing the temperature above 180 K produces additional changes in the morphology of the films. At temperatures that depend on the thickness, the basic excitation that leads to roughening (creation of adatom-vacancy pairs at steps) sets in, and the films break up by promoting atoms to higher layers. Reference [20] reproduces a STM movie of the thermal evolution of a film of 6 MLs of Pb. From an analysis of similar movies recorded for films of different thicknesses evaporated at 98 K, the layer population, i.e., the fraction of surface area covered by the different Pb thicknesses, can be calculated as a function of temperature. Figure 3 shows the evolution of the layer population observed during the annealing of 9 and 5 ML-thick films. The roughening temperatures are experimentally obtained for each layer from the maximum slope of the decay of its population with temperature, which yields similar results to the method based in the divergence of the height-height correlation function [4].

A summary of the experimentally determined roughening temperatures as a function of the film thickness is shown in Fig. 4, together with the total surface energy calculated for a 1D jellium (Pb) plus pseudopotential (Cu) system [21]. Three oscillations are observed. T_R oscillates with bilayer periodicity as a function of thickness and shows the first node of a longer beating pattern, whereby the films more stable change from odd to even number of layers. The first phase slip appears between 5 and 6 ML. Although the absolute values of roughening temperatures are still notoriously difficult to calculate [5], the relative changes depend only on the differences of the effective nearest neighbor interaction, and, thus, on the contribution to the surface energy of the layer-dependent QWS. In agreement with other calculations for freestanding Pb(111) films [22] or Pb on compressed Si(111) [6], the calculated surface energy curve shows bilayer oscillations with phase slips, whose positions depend sensitively on the electron reflectivity at the Pb/substrate interface. Thus, the calculated curve [21] has been shifted 2 MLs to adjust the positions of the first phase slip. The amplitude of the oscillations in T_R amounts to 60–110 K (40%), which should be compared with differences in the surface energy for neighboring layers of 7–20 meV/atom (10%) calculated with density functional theory for free standing Pb(111) films at their theoretical lattice constants [22]. The apparent step heights deduced from STM images (not shown) also oscillate with the thickness mirroring the density of states at the Fermi level and out of phase with T_R.

The layer-dependent behavior of T_R described here is consistent with the one reported for Pb/Si(111) [6], which was deduced from the disappearance of QWS detected by ARUPS. Our results confirm the validity of the analysis performed there [6] and extends the range of validity of these concepts to metal substrates. One significant difference is that the roughening temperature for 8 ML of Pb on Cu(111) is above 300 K, i.e., it should be possible, thus, to stabilize at 300 K an atomically flat film of Pb on Cu(111).

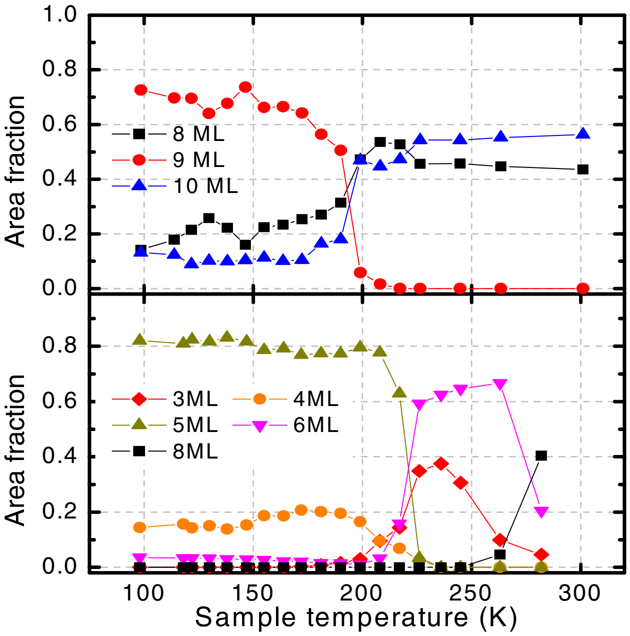

FIG. 3 (color online). Layer population (i.e., fraction of surface covered with different Pb thickness) as a function of the temperature, for an initial deposition of 9 (upper panel) and 5 ML (lower panel) of Pb on Cu(111) at 98 K.

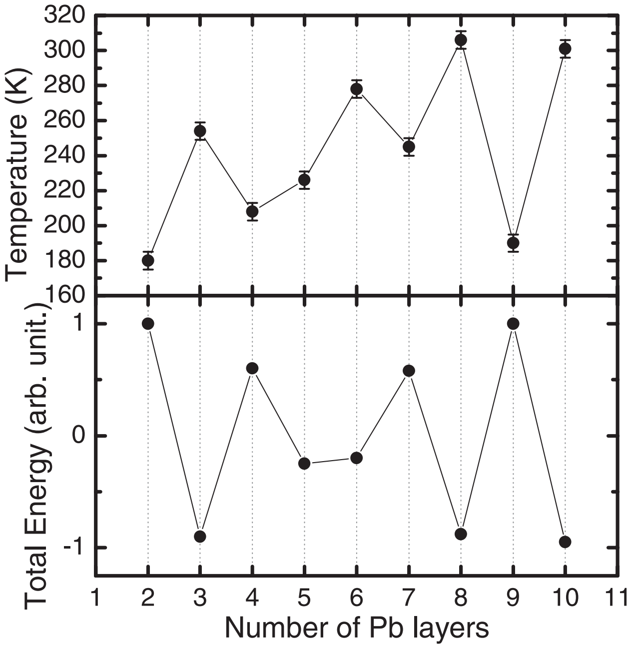

FIG. 4. Upper panel: experimentally determined roughening (breakup) temperature for different thicknesses of Pb/Cu(111). Lower panel: calculated oscillating part of the total surface energy as a function of the thickness for a 1D model [21]. The curve has been shifted 2 ML to fit the experimental phase slip.

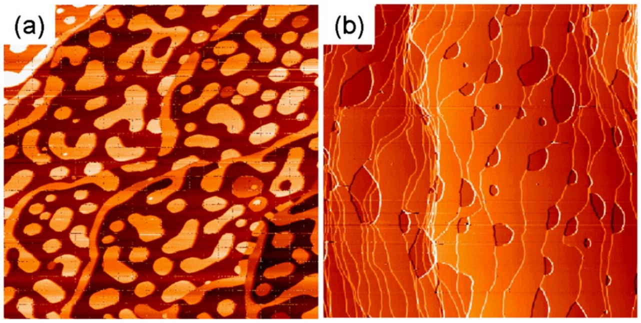

FIG. 5 (color online). Representative snapshots of STM movies showing the evolution with the temperature of Pb films of selected thicknesses: (a) decomposed 9 ML film at 200 K and (b) intact 8 ML film at 300 K. Images (a) and (b) are 500 nm × 500 nm and 1500 nm × 1500 nm, respectively.

As can be seen in Fig. 1(b), changing the initial thickness of Pb by 1 ML strongly modifies the electronic structure of the film in the vicinity of the Fermi level. The total surface energy and, thus, the thermal stability of the films, is severely affected by this difference in the electronic structure. Figure 5(a) shows that the 9 ML-thick film has roughened into 8 and 10 ML-high regions already at 200 K. A 9 ML film is particularly unstable because it has the last occupied QWS just below the Fermi energy. Figure 5(b) reproduces a 1.5 μm-wide STM image of a Pb film nominally 8 ML-thick, deposited at 98 K, annealed slowly to 300 K, and kept there for 22 hours. Contrary to the case of 9 ML, a 8 ML-thick film is still atomically flat at 300 K. The only changes observed during annealing are the rounding and disappearance of the 9 ML islands and the filling of the 7 ML voids present on the surface upon low temperature deposition. The film at 300 K reproduces the steps of the substrate underneath, having everywhere the same atomic thickness. The film, however, is in a metastable situation, and, if kept at 310 K, it evolves to its thermodynamically stable configuration, namely: a (4×4) wetting layer plus 3D islands. The process starts close to the step bunches of the Cu(111) substrate. The time that the film is trapped in the flat metastable state depends on the step density. A film recorded in the same area of the sample over 22 hours shows the time evolution of the surface covered by 8 ML and 10 ML of Pb [23].

In conclusion, the simultaneous determination in the real space of the local electronic structure (QWS) and the morphology for Pb films grown on Cu(111) has been used to determine quantitatively the evolution of the layer population with temperature. From this, the surface roughening temperature has been found to depend on the film thickness in a nonmonotonic fashion, oscillating with bilayer periodicity (plus a longer beating period). This extends previous observations in the reciprocal space for Pb/Si(111) [6] and mirrors the oscillatory behavior reported for the superconducting temperature [12] or the surface diffusion coefficient [13]. A clear correlation between the local electronic structure and the stability of the films is found. T_R oscillates with the thickness in opposition of phase with the total energy and the DOS at the Fermi level, i.e., films with QWS close to the Fermi level are energetically unfavorable, while films with low DOS at the Fermi energy film can remain atomically flat at 300 K. Considering that, at 300 K, metals often grow in the Stranski-Krastanov mode of growth on semiconductor and insulator surfaces, the kinetic pathway to atomically flat metal films facilitated by these quantum effects could be used in novel quantum devices requiring exceedingly perfect mirrors for atoms.

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[23] See EPAPS Document No. E-PRLTAO-97-082645 for a movie showing the time evolution at 300 K of a Pb film containing areas of 8 ML and areas of 10 ML. Real elapsed time 22 hours. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.