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Thermal stability of atomically flat metal nanofilms on metallic substrates

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Abstract

By means of variable temperature scanning tunneling microscope we studied the morphology and electronic structure of Pb films grown on Cu(1 1 1). Due to the spatial confinement of electrons, the islands display quantized energy levels. At 300 K, Pb forms 3D nanostructures with magic heights, that correspond to islands having a quantum well state (QWS) far from the Fermi energy. Below 100 K Pb grows in a quasi-layer-by-layer fashion. The QWS that develop in the films determine their total energy and, accordingly, their thermal stability. Films of particularly magic thickness are stable upon heating to 300 K.

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Electron confinement in nanostructures causes discretization of the quantum states available and the sequential population of these discrete states lead to transport, optical or magnetic properties that depend in magnitude on the size of the nanostructures. These Quantum Size Effects (QSE) were first predicted by Sandomirskii almost 40 years ago [1]. In ultrathin metal films, where electrons are confined in the perpendicular direction by suitable energy barriers (e.g. vacuum gaps in the substrate and image potential in the vacuum side), QSE reveal themselves, as oscillations in many physical properties with the film thickness. This is produced by the systematic variation in the density of states (DOS) at the Fermi level due to its periodic crossing by the quantum well states (QWSs) created by the confinement of electrons. Thus, the electron density inside and outside a metal film [2,3], the work function [4,5], the chemical reactivity [6,7]. the interlayer distances [8], the metallicity [9], the electrical resistivity in tunneling [10,11], the Hall coefficient [12], the superconducting transition temperature [13–15] or the intensity of the electron–phonon coupling [16] have been predicted or observed to oscillate with the thickness of metallic films with a periodicity of few monolayers.

A role of QSE in crystal growth was first postulated to explain an apparent alternation of single and double layer growth detected by means of He scattering during the low temperature deposition of Pb on Cu(1 1 1) [17]. More recently, the equilibrium height distribution of flat top Pb(1 1 1) nanoislands grown on Cu(1 1 1), as obtained from STM images, showed magic heights, i.e. certain heights appeared much frequently than others [18]. The characterization of the QWS in each Pb nanoisland by tunneling spectroscopy related the magic heights to the absence of occupied QWS close to the Fermi energy [18]. Islands with magic heights have been also observed during growth of Pb on Si(1 1 1) 7×7 [19]. This observations can also be understood in the framework of the electronic growth model first introduced by Zhang et al. [20] to explain the inverse Stranski–Krastanov mode of growth discovered for Ag on GaAs(1 1 0) [21], whereby a rough Ag film deposited at low temperature and consisting in nanoclusters, above a certain critical thickness smoothes into a flat film (with voids) upon annealing. The electronic growth model

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emphasizes the energy contribution of the QWS to stabilize certain thicknesses.

More recently, the occupancy of QWS has been shown to affect the morphology and thermal stability of thin metal films grown on semiconductors [22–24] and metals [25]. Atomically uniform films of Pb on Si(1 1 1) have been prepared at low temperature benefiting from quantum confinement [22], but the lateral scale of the atomically flat regions has not been reported. Both XRD reflectivity [23] and STM measurements [24] indicate that 2–3 atomic levels are almost equally occupied at low temperatures. The layer dependent thermal stability has also been determined by extracting the surface roughness from fits to X-ray reflectivity measurements as a function of the temperature [23].

In this paper we report the use of a variable temperature STM to study the influence of quantum size effects on the stability of atomically flat Pb films on Cu(1 1 1). The total energy of the Pb film oscillates with its thickness depending on the occupancy of the QWS and, therefore, not all the thicknesses are equally favorable. The relative stability of the different thicknesses is measured in real space by STM following the evolution of the surface morphology upon annealing from 98 to 300 K. Simultaneously, the position in energy of the QWS and their spatial distribution are measured by means of scanning tunneling spectroscopy. The presence of the QWS states allow a precise determination of the Pb local thickness in the images. A correlation between the energy of the last occupied QWS and the thermal stability of a given thickness can be determined. This effect allow us to stabilize at 300 K atomically flat films of Pb on Cu(1 1 1).

The experiments have been carried out in a UHV chamber with base pressure of 4×10^{-11} Torr. The chamber contains a variable temperature scanning tunneling microscope (STM) microscope with the capability to evaporate *in situ*, a rear view LEED optics that is also used for AES, ion gun and mass spectrometer. The Cu(1 1 1) crystal was cleaned by cycles of Ar^{+}sputtering and annealing. After cleaning, the sample displayed a sharp LEED pattern and atomically resolved high-quality 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 Cu(1 1 1) 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. These *in situ* experiment allows the direct observation in real space of the structural transformations at atomic scale, as well as a perfect control of the sample temperature. The dI/dV curves were obtained by numerical differentiation of the $I(V)$ curves.

Pb grows on Cu(1 1 1) at 300 K in the Stranski–Krastanov mode of growth (see Fig. 1), whereby 3D, (1 1 1)-oriented Pb islands grow on top of a wetting layer, just 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

Fig. 1. 1000 nm × 1000 nm STM image of the morphology of 2 ML of Pb deposited on Cu(1 1 1) at 300 K. The inset shows a 7.5 nm × 3 nm STM image with atomic resolution on the Pb wetting layer showing the 4 × 4 reconstruction.

Cu along the ⟨1 1 1⟩ direction that goes from −1 to +4 eV around the Fermi energy [26]. The confinement discretizes the band and the corresponding quantum well states (QWSs) can be detected by local tunneling spectroscopy performed on top of islands of different heights [18,26] or by ARUPS [27].

The theoretical position in energy of the QWS can be predicted using a phase accumulation model and assuming that the Pb nanocrystallites behaves as 1D wells [26]. For room-temperature depositions the island height distribution can be correlated with the position in energy of the last occupied QWS. In particular, islands of 9 and 18 ML, that present a QWS just below the Fermi level, were never observed [18].

Upon lowering the substrate temperature during the Pb deposition, the mode of growth changes towards a layer-by-layer type, as atomic diffusion becomes progressively frozen. At 98 K the growth occurs almost ideally layer-by-layer and the Pb films cover uniformly the substrate. At this temperature even the films with a ''forbidden'' thickness, which were not observed in the equilibrium distribution of heights can be stabilized. Fig. 2(b) shows an STM image measured at 98 K after the deposition of 9 ML of Pb, which displays small dark areas where the layer number 9 is not complete (i.e. corresponding to layer number 8) and dentritic, ramified islands corresponding to a local thickness of 10 ML. Fig. 2(a) shows the corresponding tunneling spectra recorded on top of different regions. For 9 MLs, there is a QWS at the Fermi energy (as predicted by the 1D well model) [18]. All the films having an even number of layers present an unoccupied QWS at +0.65 eV (see Fig. 2(a)). This state was already detected by Jaklevic and Lambe in Pb-oxide-Pb junctions deposited at low temperature [10]. Even in the small islands and voids shown in Fig. 2(b) the STS spectra show the QWS for the corresponding thickness, this result demonstrate that the spatial distribution of

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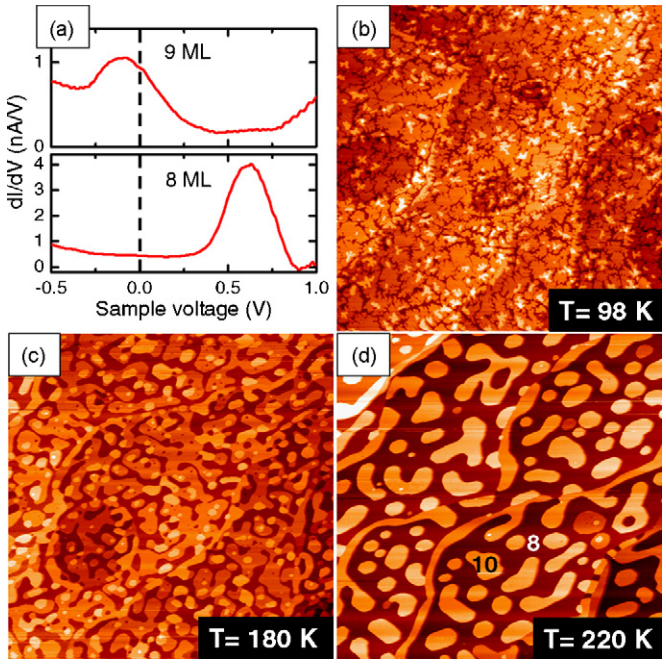

Fig. 2. (a) dI/dV curves showing the energy position of the QWS for different Pb thicknesses around the Fermi level. The presence of the predicted occupied QWS close to the Fermi level for 9 ML of Pb is clearly demonstrated. (b), (c) and (d) show snapshots of a movie illustrating the evolution with the temperature of a 9 ML Pb film. The size of the images is 500 nm × 500 nm.

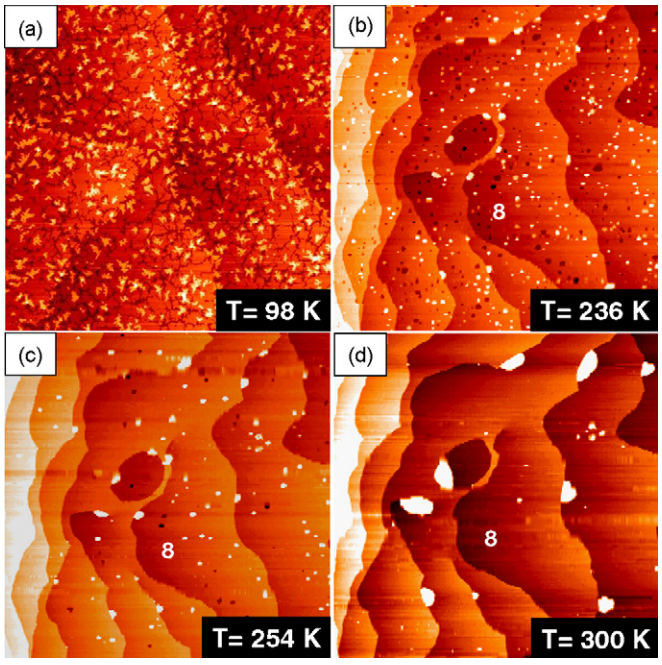

Fig. 3. (a) 500 nm × 500 nm STM image showing the morphology of 8 ML of Pb deposited on Cu(1 1 1) at 98 K. (b), (c) and (d) show snapshots of a movie illustrating the evolution with the temperature of a 8 ML Pb film. The size of the images is 1000 nm × 1000 nm.

the QWS corresponds with the spatial extension of a given thickness and allow us to determine unequivocally the local Pb thickness.

A variable temperature STM is now used to follow the evolution of the film morphology during annealing with a temperature ramp of 1 K per minute. Special care was taken to carry out all the experiments with the same temperature ramp to make them comparable. Panels (b), (c) and (d) in Fig. 2 shows some selected, large-scale STM images that illustrate the morphological changes observed in the 9 ML Pb film as its temperature increases. The film, initially flat on the atomic scale (Fig. 2), starts to decompose at 180 K (Fig. 2(c)) into 8 and 10 ML-high regions. At 220 K only 8 and 10 ML-high areas can be seen (Fig. 2(d)). From this temperature up to 300 K the surface remains covered by 8 ML and islands of 10 ML.

Changing the amount of Pb deposited by just 1 ML results in a very different electronic structure. For 8 ML film the only QWS close to the Fermi level is unoccupied at +0.65 eV and the last occupied QWS lies 0.9 eV below the Fermi level. The evolution of the film morphology with the temperature changes dramatically. The initial surface morphology after depositing 8 ML of Pb is identical to the one obtained for 9 ML. Most of the surface is covered by 8 ML. There are some dendritic islands and voids one monolayer high or deep, respectively, which cover a small fraction of the surface (see Fig. 3(a)). Fig. 3(b), (c) and (d) shows snapshots of the film morphology during the annealing process. Contrary to the 9 ML-thick film, the 8 ML film is stable up to room temperature and the only change observed is the rounding of the islands and voids originally present on the surface. In the areas were the original Cu(1 1 1) surface presents step bunches the film becomes unstable around 280 K. Presences of steps bunches is very difficult to avoid in standard (1 1 1) fcc metallic surfaces.

There have been theoretical studies of the relative stability of ultrathin Pb films [29]. The theoretical calculations show a bilayer periodicity with a superimposed beating pattern in the stability versus thickness curve. The beating pattern is due to the difference between the interlayer distance in Pb and the wavelength of the electrons at the Fermi level. The existence of this beating pattern means that the number of Pb layers that are stable changes from even to odd after certain number of layers [28]. Close to the thickness where the periodicity in the stability changes, the difference in energy between the stable and unstable layer is very small and therefore the evolution of the film morphology with the temperature is quite complicated. We evaporated 5 ML of Pb at low temperature, thickness close to where the periodicity in the stability changes. Fig. 4 shows a summary of the behavior with the temperature of a 5 ML Pb film. Around 220 K the 5 ML areas start to disappear and the surface is covered mostly by 3 and 6 ML. At 240 K, the 3 ML areas disappear while 8 ML starts to appear. Finally, around 280 K the surface is covered by the wetting layer, and 6 and 8 ML-high islands.

Films of different thicknesses have been grown at low temperature and their thermal stability determined by STM. A summary of the stability temperatures for each film is shown in Fig. 5. The stability of the layers oscillate with the thickness. Each Pb layer becomes unstable at a different temperature. The films with non-magic heights (i.e. 2, 4, 5, 7 or 9 ML), which are atomically flat at low temperatures because they are trapped by kinetic constraints, decompose into more stable heights (i.e. 6 and 8 ML-high islands) at lower temperatures. The layers

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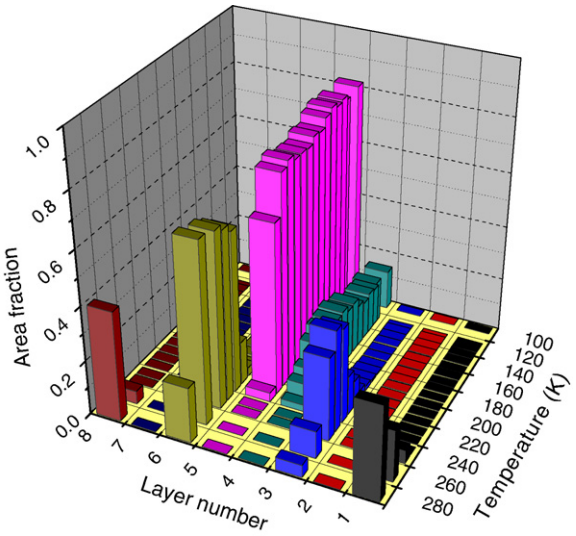

Fig. 4. Evolution with the temperature of the fraction of surface covered with different Pb thickness for an initial deposition of 5 ML at 98 K. The histogram has been constructed by analyzing STM images 500 nm wide recorded on the same spot during the slow (1 K/min) annealing of the film.

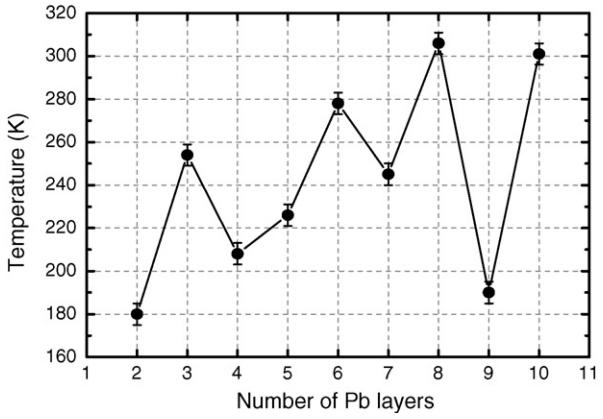

Fig. 5. Experimentally determined break-up temperature for different thicknesses of Pb/Cu(1 1 1).

whose thickness correspond to magic heights (i.e. 3, 6, 8 or 10 ML) are stable to higher temperatures. Below 5 ML the even thicknesses are more stable and above are the odd ones. In the curve shown in Fig. 5 is clear the existence of the beating pattern and between 4 and 5 ML the even layers changes from be stable to be unstable.

In conclusion, we take advantage of the spatial resolution of the STM/STS to measure in real space, and simultaneously, the morphology and electronic structure of Pb films grown at low temperature on Cu(1 1 1). We found that the spatial distribution of the QWS states strictly corresponds to the lateral extension of the different local thicknesses. We found also a clear correlation between the local electronic structure and the stability of the films. The 8 ML film is so stable that it can be heated to 300 K and still remains atomically flat, because it has no QWS close to the Fermi level. On the contrary the 9 ML is energetically unfavorable due to the presence of an occupied QWS just below the Fermi level. As soon as the atoms have enough mobility the film splits in 8 and 10 ML areas. For any thickness the real space images and spectroscopic data determine precisely the evolution with the temperature. Considering that, at 300 K, metals grow in the Stranski–Krastanov mode of growth on most semiconductor and insulator surfaces, the quantum effect reported here could be used to stabilize flat metallic film of specific heights on many different substrates.

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