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ScienceDirect
Applied Surface Science 254 (2007) 12–15
applied surface science
www.elsevier.com/locate/apsusc

Thermal stability of atomically flat metal nanofilms on metallic substrates

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Available online 20 July 2007

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.

PACS : 68.35.−a; 68.60.Dv; 68.47.De; 68.37.Ef

Keywords: Quantum size effects; Metallic films; Scanning tunneling microscopy; Scanning tunneling spectroscopy

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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doi:10.1016/j.apsusc.2007.07.112

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

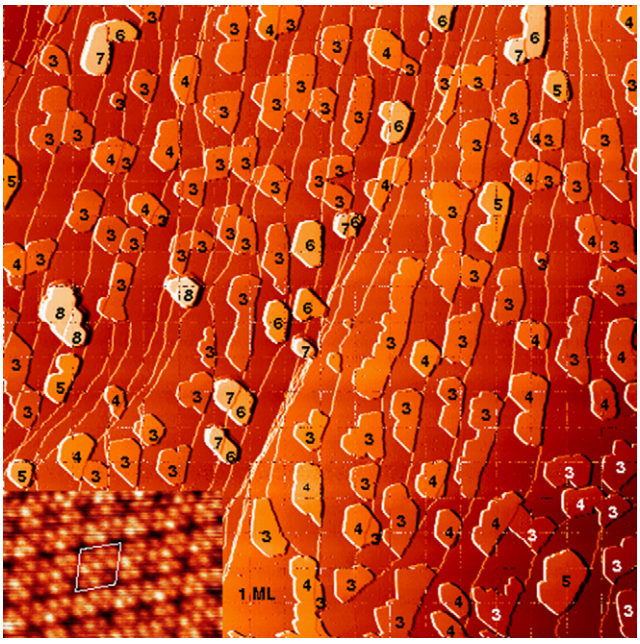

Fig. 1. 1000 nm × 1000 nm STM image of the morphology of 2 ML of Pb deposited on Cu(1 1 1) at 300 K. The inset shows a 7.5 nm × 3 nm STM image with atomic resolution on the Pb wetting layer showing the 4 × 4 reconstruction.

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