Self-organization of Pb thin films on Cu(111) induced by quantum size effects

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Electron confinement in thin films of Pb on Cu(111) leads to the formation of quantum well states, formed out of the upper valence band of Pb. Their evolution as a function of film thickness is characterized in angle-resolved photoemission and can be interpreted in terms of a straightforward quantum well model. This permits an identification of film growth mode at low temperatures. Bringing the films into thermal equilibrium by annealing induces strong changes in the spectra. Their interpretation demonstrates that specific "magic" layers are preferred because of total energy minimization induced by the arrangement of quantum well states with respect to the Fermi level.

I. INTRODUCTION

Quantum well states, resulting from electron confinement in small artificial structures, offer access to an interpretation of many interesting physical properties of matter under conditions of reduced dimensions. Moreover, a study of quantum well states may give insight into physical properties of bulk materials that are difficult to access otherwise. In general, there is a connection between the occupancy of quantum well states and surface/thin film properties, which leads to an oscillatory behavior of these properties as a function of film thickness, as predicted by Schulte in 1975,[1] and later studied by means of self-consistent calculations by Feibelman and Hamann.[2] Among the predictions, specific "critical" and "magic" thicknesses, preferred over others because of their lower total energy[3] (similar to magic cluster sizes[4]), have found considerable interest. In an experimental demonstration of this effect, Luh and co-workers showed that silver films of 1, 2, and 5 monolayer (ML) thickness are stable, whereas others disproportionate into $N \pm 1$ monolayer thickness when brought into equilibrium.[5] They supported their findings using a calculation of the total electronic energy in the film. For the Pb/Si(111) system, islands of 7 monolayer (ML) thickness were found to be most stable over a wide range of coverages and substrate temperatures.[6] Evidence for the increased occurrence of specific island heights was also found in a scanning tunneling microscopy/spectroscopy study of Pb/Cu(111) by Otero *et al.*[7]

Here we examine quantum well states in the Pb/Cu(111) system, and analyze their electronic structure and its interplay with film morphology, using angle-resolved photoemission. This technique has been shown to be well-suited for the study of the energies of quantum well states in metal films, and to characterize the dynamics of electron motion, interface electron reflectivity, phase shifts, and related aspects.[8] We find that at low temperature, epitaxial layers are grown.

Upon annealing, these rearrange into islands of different height influenced by quantum size effects, in that the stable layers have the topmost occupied well state further removed from the Fermi level than the less stable ones.

II. EXPERIMENT

All experiments were carried out in a stainless steel ultrahigh vacuum chamber, with a base pressure of below 1×10^{-10} mbar. Pb films were deposited from a water-cooled Knudsen cell, at a pressure of 3×10^{-10} mbar, onto a Cu(111) sample held at 100 K, and cleaned before deposition by ion bombardment and annealing. Photoelectrons were excited by photons from beamline TGM 4 of the Berliner Speicherring-Gesellschaft für Synchrotronstrahlung (BESSY) storage ring. Their energy was analyzed in two separate hemispherical analyzers, an OMICRON AR65 with three channeltron detectors and a PHOIBOS 100 (SPECS GmbH), permitting recording of energy-vs-angle images using a channel plate and charge coupled device camera readout. This latter instrument also served to observe changes in valence band features in real time during annealing, permitting a better observation of changes induced by the annealing process.

III. RESULTS AND DISCUSSION

The fact that electron confinement in Pb films lead to the occurrence of quantum well states, formed out of the *s-p* electrons in the topmost valence band of Pb,[9] can be directly inferred from the set of valence band photoelectron data shown in Fig. 1. Spectra recorded for depositions equivalent to thicknesses from 3 to 15 ML (where 1 ML corresponds to a density of 9.43×10^{14} atoms/cm^2) exhibit several well-defined lines, which are absent in spectra from bulk Pb(111);[9] moreover, the lines shift in binding energy upon increasing the layer thickness, which confirms that they arise
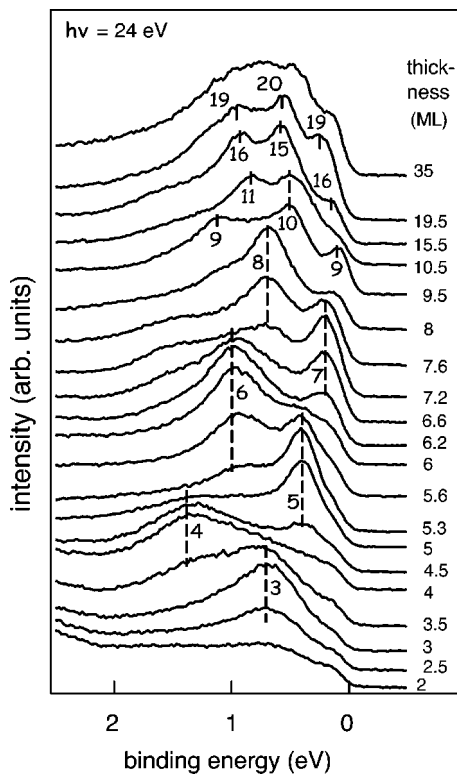
FIG. 1. Valence level spectra from Pb layers on Cu(111) deposited at 100 K, for different depositions as indicated, recorded in normal emission at a photon energy of 24 eV.
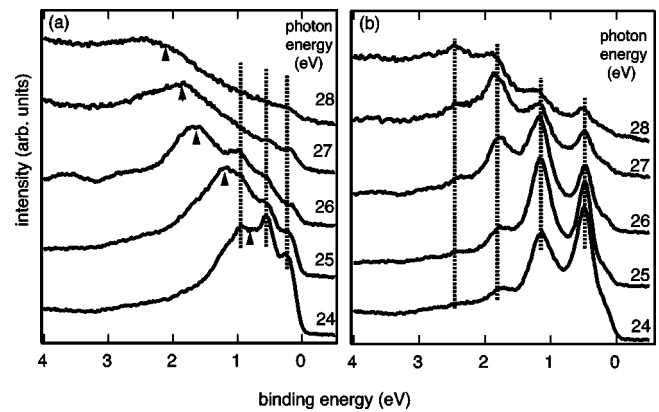

FIG. 2. (a) Set of spectra from an unannealed 19.5 ML Pb film, recorded in normal emission as a function of photon energy. Dotted lines indicate observed peaks due to quantum well states. (b) Same set of data after annealing the layers to room temperature. Note the increased peak-to-valley ratio, and the energy shift of quantum well peaks.

from individual quantum well states. The binding energies of the peaks can be used to identify the layer thickness from which the specific quantum well state arises, through the well-known phase accumulation model.[10,11] This is based on the concept that one electron "round trip" within the layer, including the phase shift at the Pb-vacuum (Φ_b) and Pb–Cu (Φ_c) interface must be equal to a multiple of 2π, i.e., $n \cdot 2\pi = 2k \cdot d + \Phi_b + \Phi_c$, where k is the electron wave vector and d the film thickness. With plausible assumptions on the (energy-dependent) magnitude of Φ_b and Φ_c, and taking into account that $d=na$, where a is the interlayer distance, the electron wave vector can be unambiguously determined. On the basis of the dispersion of the band from which the quantum well states are formed, the energies for specific states can be derived as a function of thickness. Calculations on this have been performed previously[7,12,13] and the peaks in Fig. 1 are marked correspondingly. Turning to the 7.2 ML spectrum in Fig. 1, we note that the peak spacing is 0.5 eV, whereas a quantum well with this width would lead to an energy separation of states of about 1.5 eV. This implies that the peaks at 0.2 and 0.7 eV belong to two different film thicknesses, and from a phase accumulation analysis these are 7 and 8 ML, respectively. Furthermore, by analysis of the observed peaks it is clear that a layer starts to grow only when the previous layer is finished, therefore avoiding the growth of successive odd or even layer thicknesses as observed for Pb on Si(111).[14] The growth mode can thus be interpreted in terms of layer-by-layer growth as suggested by Braun and Toennies,[15] similar to other quantum well systems.[16,17] Note that the observed development of quantum

well peaks with coverage does not support the concept of bilayer growth suggested for this system by Hinch *et al.*,[18] since in a spectrum for a specific coverage there are peaks from consecutive even and odd numbers of layers.

Annealing of Pb layers induces remarkable changes to the photoelectron spectra, as shown from a comparison of spectra from as-deposited and annealed films for different photon energies in Fig. 2, for a thickness of 19.5 ML. A broad peak ranging from E_F up to 1.5 eV binding energy (E_B) occurs for the as-deposited film [Fig. 2(a)], with several smaller, quantum-well derived peaks superimposed. This feature develops into a set of sharp and well-defined peaks, with a large peak-to-valley ratio, reaching up to about 3 eV E_B. The effect of annealing [Fig. 2(b)], leading to a preference of one specific layer thickness, can be directly seen from the separation of quantum well peaks indicated by dotted lines. The spacing of 0.66 eV is characteristic for a 22 ML thick quantum well. This comparison is made for several photon energies, centered at 26 eV. The first observation is that the features identified as quantum well states do not shift with photon energy (and thus with the normal component of the wave vector), confirming again the confinement in the surface normal direction. The broad peak in the unannealed film, however, on which the quantum well peaks are superimposed, does move with photon energy, and so does the envelope of the sharp peaks in the spectrum from the annealed surface. By comparison with the direct bulk band transition[9] indicated by the triangles, it is clear that the broad feature in Fig. 2(a) has a strong bulk character, and that the modulation of intensities in Fig. 2(b) is likewise induced by a bulk transition.

The apparent contradiction of having bulk and quantum well features in the spectrum from a thin film is resolved when considering that the wave function of a quantum well state consists of the Bloch function from bulk Pb modulated by the quantum well state envelope wave function.[8,19] Hence photoemission from quantum well states is most intense at a photon energy where there is a direct bulk transition, and the intensity decreases for higher or lower photon energies. This

behavior is observed for all four indicated quantum well state peaks of the annealed film in Fig. 2(b). Mugarza *et al.* have used such intensity modulations to map the unoccupied band structure of Cu(100) by studying thin Cu films on Co(100).[20] However, when there are regions on the probed surface where there is a relatively large amount of disorder, the peaks from quantum well states in this region will not be well defined and only a feature representing the direct bulk transition will be observed. This leads us to the plausible conclusion that the as-deposited film has a higher amount of disorder than the annealed layers.

A band gap occurs between $E_B = 0.85$ eV and E_F in Cu(111), hence one might expect that the quantum well states in the Pb film can only exist in this gap because outside this region there is no confinement. However, in Fig. 2(b) quantum well peaks are observed even at 2.5 eV binding energy, these are not broadened enough to be classified as mere resonances, besides this they have a constant energy spacing characteristic of this quantum well. The electrons appear to be confined over the whole energy range of the upper Pb valence band. Similar observations have been made in other metallic quantum well systems.[17,21] This observation can be explained by considering that coherent reflection on both sides of the metal film need not be total. Whether this reflection is due to the absence of electronic states in the substrate, or due to scattering at the interface, is of no immediate concern as long as the coherent backward scattering is large compared to transmission through the interface and incoherent scattering in multiple directions. Due to the large lattice mismatch between Pb and Cu, 4.95 and 3.61 Å, respectively, transmission will be limited, leaving the incoherent scattering as the main competitor for coherent backward scattering. As observed above, the disorder in the annealed layer is much smaller as in the unannealed layer, hence a lack of order appears to be the prime reason for incoherent scattering. This directly explains why the quantum well peaks in the unannealed layer are primarily observed in the relative substrate gap and are of a lower intensity as in the annealed layer. The relatively low incoherent scattering of the annealed layer creates a condition for good confinement for a large energy range extending beyond the relative substrate gap. Such confinement in the absence of a band gap has also been observed in other quantum well systems.[22]

The data in Fig. 2 are taken from a relatively thick film (19.5 ML); in the unannealed film peaks due to 19 and 20 ML are dominant (Fig. 1). The effect of annealing on the quantum well signature is shown for several film thicknesses in Fig. 3. It is obvious that such annealing-induced rearrangement is not limited to thick films, but occurs for thinner films also, and shows equally dramatic effects on the spectra. The spectra for the as-deposited films (dashed lines) exhibit clear lines in an energy range right up to the Fermi level, for example, the 8.5, 10.5, and 17 ML films. Upon annealing, two processes can happen: either an existing peak increases, and the others vanish, or an entirely new peak occurs (17 ML). In either case, features with spectral weight at higher binding energy now dominate the spectrum. That structural changes are induced by annealing is also apparent from the intensity of the Cu 3d peak at 3 eV binding energy (not shown here). This intensity increases markedly for spe-
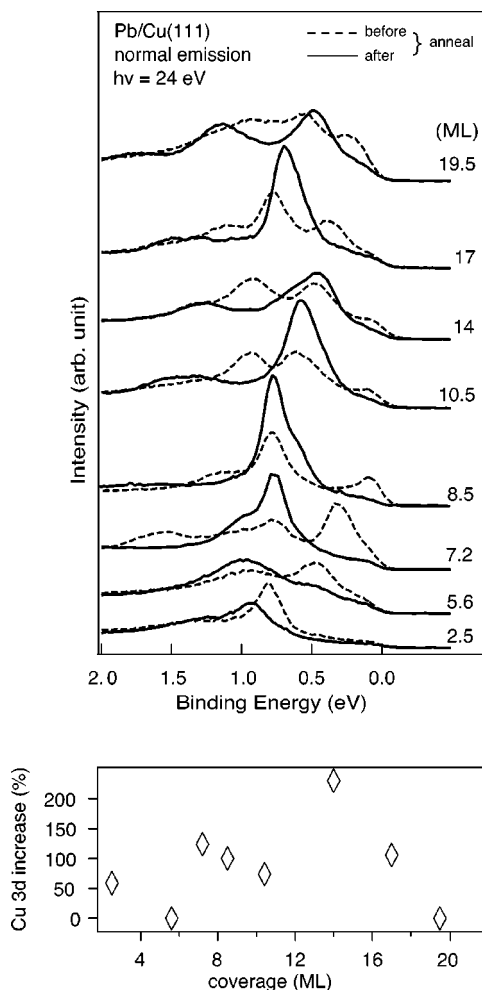

FIG. 3. Close-up of spectra near E_F of as-deposited Pb films (dashed lines) of different thickness, and changes induced by annealing (solid lines), recorded in normal emission at a photon energy of 24 eV. (Bottom) Increase in the Cu 3d line upon annealing relative to the intensity before annealing, demonstrating the formation of islands in this process.

cific coverages, suggesting that here more change occurs and the deposited thicknesses are therefore less stable. Its intensity increase is shown at the bottom of Fig. 3. This can only be explained by a breaking up of the Pb layer into islands with a well-defined height by diffusion of Pb atoms. A similar process was observed in the case of Pb/Si(111),[23] where a considerable mass transport onto the top of the islands occurs.

It is a specific advantage of valence level photoelectron spectroscopy that the electronic mechanism responsible for the layer rearrangement can be directly inferred from the spectra, along with the process of island formation and narrowing of height distribution. While the latter are reflected in the narrowing of features and the disappearance of sets of peaks, the former is clearly inferred from the fact that in each case a lowering of the energy of the highest occupied quantum well state occurs. The reason for this process can be identified when considering the total energy of the film, by adding up all electron energies in quantum well states from the bottom of the well. The energy of the topmost occupied
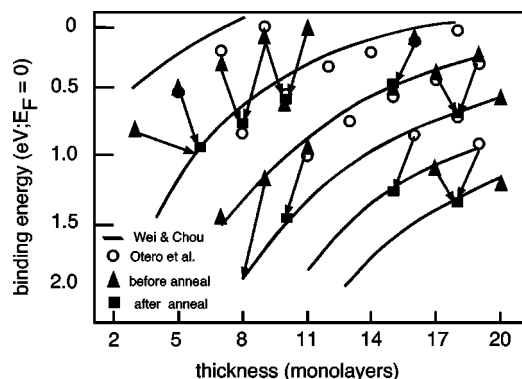
FIG. 4. Energies of quantum well peaks in the valence band spectra for different thickness, derived from calculations within the phase accumulation model, (lines) DFT calculations (Wei and Chou), (circles) an infinite potential well model (Otero *et al.*), and experimental data from photoemission (this work), (triangles) before anneal, and (squares) after anneal.

state can be lowered by changing the thickness to a width where the next higher state is just above the Fermi level;[24] or in other words, the islands rearrange their height to avoid the presence of quantum well states at the Fermi level.

We can put this finding on a more quantitative basis by analyzing peak energies in our spectra of as-deposited and annealed Pb films. The observed peak binding energies are compared, in Fig. 4, to results from two models, i.e., the free-standing slab calculations by Wei and Chou (solid lines),[13] and considerations of the energetics of quantum well states based on the Fermi surface of Pb by Otero *et al.* (circles).[7] There is a good correspondence between our experimental results and the predicted energies at higher thickness, where the relative influence of the interfaces, which is difficult to incorporate into the model, is smaller. From the comparison it follows that, after anneal, the preferred heights in Pb films on Cu(111) are 6, 8, 10, 15, 18, and 22 ML. At these coverages the quantum well states are far away from the Fermi level.

The observed preferred heights correspond very well with the STM results presented by Otero *et al.*,[7] where preferred heights are observed for 6, 8, 10, 11, 15, and 17 ML. The 11 ML high island turns out to be very unstable from our results and will bifurcate into 10 and 15 ML islands when annealed. The reason for this discrepancy can be found in the fact that at 11 ML, there is a state right on the Fermi energy. This state will, depending on the exact configuration, either fall just below or above E_F, yielding an energetically favorable or unfavorable situation influenced by just a small change in the boundary conditions at the interface. This is confirmed by Otero *et al.* in the observation that the density of step edges has a profound effect on the observed preferred heights. A similar line of reasoning may explain why in this research a preferred height is observed for 18 ML islands, whereas the STM results yield 17 ML as a preferred height. The next branch of quantum well states passes through the Fermi level around 18 ML. Besides this it has to be noted that Otero *et al.* use room temperature deposition, whereas here deposition at 100 K is followed by annealing. It is well-known that the details of the preparation recipe can have a pronounced influence on film morphology.[25]
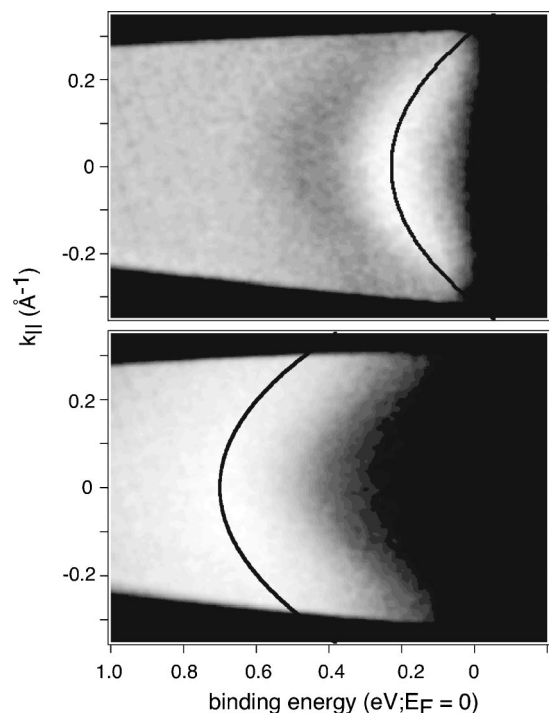

FIG. 5. Display of the dispersion $E(k_\parallel)$ of quantum well states for a 7.2 ML thick film, recorded from an unannealed film (top) and after annealing (bottom), showing the effect of annealing in reducing the binding energy of the topmost quantum well level. The solid lines give parabolic fits with specific effective masses (see text).

The electrons are confined in the direction perpendicular to the surface, but in the direction parallel to the surface no confinement exists, due to the relatively large lateral size of the islands compared to the coherence length of the electron. In this direction one therefore expects a dispersive behavior of the electrons. In Fig. 5 two plots of intensity vs parallel wave vector $k_\parallel$ are shown as grayscale images, for an as-deposited and an annealed 7.2 ML film in the ΓK direction. The solid line parabolas are nearly free electron-like fits to individual ARUPS spectra and are placed on the grayscale images for a graphical comparison. The in-plane effective mass of confined electrons $(m_\parallel^*)$ is described using a parabolic dispersion, $E(k_\parallel) = h^2 k_\parallel^2 / 8 \pi^2 m_\parallel^*$ near $k_\parallel = 0$. The effective masses derived from this fit are $1.6 m_e$ and $1.4 m_e$, respectively. From the analysis of other coverages it follows that the effective mass increases gradually from $1.1 m_e$ to $1.6 m_e$ depending only on binding energy but not on island height. This corresponds very well to the effective mass found in band structure calculations,[26] which over an extended range of binding energy are in the region of $0.6–1.6 m_e$. A similar increase in the effective mass towards the Fermi level has also been observed for Ag on Si by Matsuda and Ohta.[27]

IV. CONCLUSIONS

In summary, we have investigated the formation of quantum well states in Pb films grown on Cu(111) under different conditions. Quantum well states are clearly identified in valence level photoemission, and are related on the basis of

their observed binding energies to specific layer thicknesses using the phase accumulation model. Strong changes are observed upon annealing of the Pb layers, with a concomitant sharpening of quantum well features. An analysis of annealing-induced changes on the peak binding energies shows that the layer reorganizes into specific preferred heights; already from a visual inspection of peak energies with annealing it can be seen that an electronic driving mechanism is in place here. From this process we derive the layer widths which are particularly stable, using an analysis of quantum well state energies within the phase accumulation model.

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