Nonuniform Quantum-Confined States and Visualization of Hidden Defects in Pb(111) Films

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The spatial dependence of the differential conductivity of ultrathin Pb films deposited on the Si(111)7 × 7 surface has been studied by low-temperature scanning tunneling microscopy and spectroscopy. Pb films are characterized by the presence of quantum-confined states for conduction electrons and, correspondingly, maxima of the differential tunneling conductivity. The energy of these states is determined mainly by the local thickness of the Pb layer. It has been found that the tunneling conductivity within atomically smooth terraces can be spatially inhomogeneous, and the period of small-scale modulation coincides with the period of the Si(111)7 × 7 reconstruction. Large-scale inhomogeneities of the tunneling conductivity have been detected in sufficiently thick Pb films. They are manifested in the gradual shift of the quantum-confined levels by about 50 meV at a distance of about 100 nm. Such inhomogeneities of the tunneling conductivity and, correspondingly, the density of states in Pb films can be attributed to the presence of intrinsic defects of the crystal structure, e.g., local electrical potentials and stresses.

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INTRODUCTION

Due to the miniaturization of logical elements, sensors, and conductors connecting them, the effects of discreteness of the electric charge and disorder, as well as quantum confinement effects, affect the transport properties of nanoelectronic devices [1].

Convenient objects for study of quantum-confined effects in metallic nanostructures are thin Pb films and islands (see [2–14] and references therein). Electronic states are studied using low-temperature scanning tunneling microscopy and spectroscopy (STM/STS) [2–9], as well as transport [10, 11] and photoemission [12–14] measurements. Peaks of the differential tunneling conductivity for some values of the potential Un of the sample, as well as maxima of the conductivity for some values of the potential difference or photoemission maxima for some photon energies, were detected in thin Pb films. In particular, the energies $E_n = eU_n + E_F$ of local maxima of the conductivity with respect to the Fermi level depend on the local thickness of the Pb layer and correspond to the quantum-confined energy levels for an electron in a one-dimensional potential well bounded by the metal–vacuum and metal–substrate interfaces (Fig. 1). The observed effect is usually interpreted in terms of the resonant tunneling through quasi-stationary levels at $E = E_n$. The energy spectrum $E_n$ of a particle in a one-dimensional well with a constant potential is determined by the Bohr–Sommerfeld quantization rule [4]

$$\varphi_1 + \varphi_2 + 2k_{\perp}d = 2\pi n.$$  

(1)

Here, $\varphi_1$ and $\varphi_2$ are the phase shifts of an electron wave at reflection from the upper and lower interfaces, respectively; $k_{\perp,n}$ is the spectrum of allowed values of the transverse wavenumber; $d$ is the thickness of the layer; and $n = 0, 1, \ldots$ is the integer index. The ab initio theory of quantum-confinement phenomena in Pb(111) films was developed in [15]. Quantum-confined effects are observed not only in Pb but also in Ag, Cu, In, Sn, and Sb [16–20].

We emphasize that the analysis of features of resonant tunneling in solid-state nanostructures is an important diagnostic tool similar to other methods based on interference of waves (optical, mechanical, electron, etc.). The authors of [4] demonstrated the possibility of visualizing the structure of atoms of the lower interface under the metal layer by scanning tunneling microscopy due to the lateral coordinate dependence of the phase $\varphi_2$. The authors of [9] showed the possibility of visualizing defects invisible on a topographic image such as monatomic-height steps of a substrate and foreign inclusions. Estimates show that the thickness of a monolayer for the Pb(111)
surface is \( d_{\text{ML}} = 0.285 \text{ nm} \) and the Fermi wavelength is \( \lambda_F = 0.394 \text{ nm} \); i.e., the ratio \( \lambda_F / d_{\text{ML}} \) is close to 4/3 [5]. Consequently, electronic states near \( E_F \) in the form of standing waves have the following property [5, 7, 9]: the energy of a state with the number of zeros \( n \) for a film with the local thickness \( N d_{\text{ML}} \) should be close to the energy of a state with the number of zeros \( n + 3 \) for a film with the thickness \( (N + 2)d_{\text{ML}} \) (see Fig. 1). Indeed, in measurements at a fixed energy, the displacement of a tip from one region to the other whose thicknesses differ by \( d_{\text{ML}} \) can lead to a sharp change in the differential conductivity [3, 5, 9], which makes it possible to identify regions of the surface with an even or odd number of monolayers [9]. The \( U_n - d \) diagrams allow the reconstruction of the spectrum \( E(k_L) \) and the estimation of the thickness of the wetting layer and the effective mass and velocity of electrons [3, 5, 6, 9]. Analyzing the temperature dependence of the width of resonant tunneling peaks, the authors of [6] estimated the lifetime for various scattering mechanisms.

In this work, we report the low-temperature STM/STS study of spatial inhomogeneities of the differential tunneling conductivity of thin Pb films. This study makes it possible to reveal a correlation between local electronic properties and the positions of structural defects. When studying large surface regions, different scanning rates in the \( x \) and \( y \) directions in the sample plane, as well as the parasitic motion of the tip along the \( z \) axis caused by a change in the temperature of a piezoelectric motor, can distort a feedback signal map interpreted as a topographic image. In particular, the height of atomically flat terraces can differ from the height of the monolayer, and terraces on the topographic image can look like nonplanar. We propose a simple method for the visualization of regions with visible and hidden defects based on the synchronous measurement of topography and differential tunneling conductivity directly in the process of scanning. This makes it possible to distinguish topographic images with artifacts caused by imperfection of an instrument and a processing procedure from images of real defects. We believe that revealed large-scale inhomogeneities of the differential conductivity on terraces with a nominally constant height can be attributed to the presence of inhomogeneities of the crystal structure and can indicate, e.g., the presence of local electrical potentials and stresses.

**EXPERIMENTAL PROCEDURE**

The electrophysical properties of Pb nanostructures were studied on a UHV LT SPM Omicron Nanotechnology ultrahigh-vacuum measuring complex. The thermal deposition of Pb (Alfa Aesar, purity of 99.99%) was performed on the reconstructed Si(111)7 × 7 surface at room temperature, a pressure of \( 3 \times 10^{-10} \text{ mbar} \), and a rate of about 0.5 nm/min for a time varied from 5 to 40 min.

The topography of prepared Pb islands was studied by scanning tunneling microscopy at a temperature of 78 K in the regime of a given tunneling current \( I \) at a constant potential \( U \) of the sample with respect to the tip of a tunneling microscope. Tungsten wires with apex cleaned by electron bombardment in ultrahigh vacuum were used as tips. Topographic images were processed by removing the global tilt through the subtraction of a plane specified by three reference points. The electronic properties of Pb islands were studied by scanning tunneling spectroscopy, which involves the measurement of series of the \( I(U) \) and \( G(U) \) characteristics at a fixed position of the tip. Here, \( G = dI / dU \) is the differential tunneling conductivity of the tip—sample contact. Furthermore, maps of local differential conductivity were obtained by bias-modulation tunneling spectroscopy. Using a Stanford Research SR 830 lock-in amplifier, we measured the oscillating component of the tunneling current, which appeared when the ac voltage \( U = U_0 + U_1 \cos(2\pi f_0 t) \), where \( f_0 = 7285 \text{ Hz} \), was applied to the sample. Under the condition \( U_1 \ll U_0 \), the amplitude of current oscillations at the modulation frequency \( f_0 \) is obviously proportional to the differential conductivity \( G(U_0) \). If \( f_0 \) is much higher than the feedback response frequency (~200 Hz), the ac voltage applied to the sample does not lead to artifacts on topographic images. This method [9] makes it possible to synchronously obtain topographic images in the regime of holding of the average current \( I_0 \) and the dependences of \( G \) on the lateral coordinates \( x \) and \( y \) at a given \( U_0 \) value.

**RESULTS AND DISCUSSION**

It is well known that the growth of Pb on the Si(111)7 × 7 surface at room temperature occurs...
through the Stranski–Krastanov mechanism: a disordered wetting layer with a thickness of about 1 nm first appears and, then, two-dimensional Pb islands with the upper facet corresponding to the (111) plane are formed. It was shown in [2–9] that the local conductivity $G$ depends nonmonotonically on $U_0$ (Fig. 2b). In particular, voltages $U_n$ corresponding to the conductivity peaks on the $G(U_0)$ dependence depend on the local thickness of the Pb film and boundary conditions for the wavefunction.

Figure 2a shows the topographic image of the surface and differential conductance map $G(x,y,U_0)$ for two different energies recorded simultaneously with the topographic image at the forward (Fig. 2c) and backward (Fig. 2d) directions. Since the interval $\Delta E$ between neighboring maxima on the dependence $G(U_0)$ is 185 meV (Fig. 2b) and the Fermi velocity is $v_F = 1.8 \times 10^4$ cm/s [2, 9], the local thickness of the island is estimated as $d = \pi \hbar v_F/\Delta E \approx 19$ nm $\approx 70$ ML. The local thickness of the film in region I is larger than the thicknesses in regions II and III by 1 and 2 ML, respectively. As a result, at different energies, the tunneling conductivities in regions I and III are almost the same and significantly differ from the conductivity in region II (Figs. 2c, 2d). It is noteworthy that the continuous variation of the height of the film near the center of a screw dislocation does not result in the smooth variation of the tunneling conductivity. Indeed, the conductivity changes drastically upon crossing a line invisible on the topographic image that corresponds to the hidden part of the dislocation loop line on the surface of the sample.

Figure 2a shows the topographic image of the surface shown in panel (a) obtained at $U_0 = 400$ pA. The dashed line shows the projection of the dislocation loop line on the surface of the sample. Here and below, the symbols $\otimes$ mark reference points used to align the image. (b) Dependence $G(U_0)$ for points inside regions I and II; the vertical dashed straight lines indicate the $U_0$ values at which maps (c, d) are obtained. (c, d) Differential conductivity maps $G(x,y,U_0)$ for the surface shown in panel (a) obtained at $U_1 = 40$ mV, $f_0 = 7285$ Hz, and $U_0 = (c) 500$ and (d) 600 mV. Light and dark regions correspond to higher and lower tunneling conductivities, respectively.

**Fig. 2.** (Color online) (a) Scanning tunneling microscopy image of the surface of the Pb island ($175 \times 175$ nm, average potential of the sample $U_0 = 500$ mV, average tunneling current $I_0 = 400$ pA). The dashed line shows the projection of the dislocation loop line on the surface of the sample.
a 32 × 32 grid (grid spectroscopy) with a step of 0.36 nm. Figure 4a shows the \((x, y)\) map of the conductivity for \(U_0 = 490 \text{ mV}\). Several typical local dependences \(G(U_0)\) are shown in Fig. 4b. We note that local tunneling spectra include either a set of pronounced peaks or weak peaks, depending on the point of measurement. To analyze the dependence of the position and height of resonant peaks on the energy and coordinate, it is convenient to exclude a nonresonant background. To do this, we averaged all 1024 spectral curves over the area of the sample and, then, the average conductivity \(\langle G(U_0) \rangle\) shown by the thick line in Fig. 4b was approximated by a third order polynomial to exclude traces of quantum-confined levels. The approximating polynomial \(B(U_0)\) (background) is shown by the dashed line in Fig. 4b. Figures 4c and 4d show the difference between the local conductivity and nonresonant background \(B(U_0)\) as a function of the voltage \(U_0\) and \(y\) coordinate for \(x = (c) 3\) and (d) 7 nm. It is clearly seen that regions with pronounced peaks of the differential conductivity alternate with regions where peaks are absent, weak, or shifted to a different energy.

Figure 5 shows the topographic image and differential conductivity maps for the Pb island for which the monatomic-height terraces have the form of centric circles. The conductivity in regions I and IV is close to the maximum conductivity, whereas the conductivity in regions II and III is close to the minimum conductivity. This indicates the presence of a hidden monatomic-height step in the substrate, which ensures a sharp change in the conductivity within one Pb terrace (transitions I–III and II–IV in Fig. 5b). In addition, we detected terraces with a smooth variation of the conductivity at a fixed energy (e.g., transitions V–VI in Fig. 5b or I–II and III–V in Fig. 6b). The appearance of regions with the smooth variation of the differential conductivity seems surprising because the thickness of films in elementary models should be equal to an integer number of monolayers and, therefore, the tunneling conductivity should also change discretely. The appearance of gradual contrast on \(G(x, y, U_0)\) maps cannot be due to the modification of the shape of the apex of the tip in the process of scanning because regions with sharp and smooth boundaries are observed simultaneously. Figures 5c and 5d show the cross sections of the topographic image and tunneling conductivity maps along the A–B axis close...
To analyze features of the differential conductivity of domains of Pb films with gradual large-scale inhomogeneities depending on coordinates and energy, we study the region of the surface of the island with a height of about 60 ML with three monatomic-height steps. The topographic image is shown in Fig. 6a. The detailed analysis of sections along lines I–II and III–IV indicates the monotonic variation of the height of the terraces by 0.2\(d_{\text{ML}}\) in the interval from \(y = 0\) to \(y = 100\) nm, according to the variation of colors in Fig. 6a. The tunneling conductivity map shown in Fig. 6b indicates the presence of sharp boundaries, e.g., at the transition from region I to region III, whose heights differ by one monolayer. However, the transition from region I to region II (or III–IV) is accompanied by the smooth variation of the tunneling conductivity: the conductivity for \(E_0 = 900\) meV decreases at the I–II transition and increases at the III–IV transition (Figs. 6b, 6c). A series of measurements of local current–voltage characteristics and differential tunneling conductivity spectra were performed on the 32 × 32 grid in this region and the nonresonant background was excluded using the above procedure. The results of these measurements indicate that the motion along the \(y\) axis is accompanied by the smooth shift of quantum-confined levels toward higher energies by about 50 mV (Figs. 6d, 6e). In other words, the tip relocation along line I–II at an energy of 900 meV (vertical dashed straight line in Fig. 6d) is accompanied by a smooth transition from a local maximum on the dependence \(G(U_0)\) to a local minimum, which corresponds to a decrease in the tunneling conductivity (Figs. 6b, 6c). Similarly, a smooth increase in the conductivity is observed at the motion along line III–IV at an energy of 900 mV (Fig. 6e). A constant differential conductivity with a sharp jump at the edge of the terrace is observed at the motion in the horizontal direction between regions V and VI (Fig. 6f). Consequently, the monotonic variation of the height of terraces is accompanied by change in the electronic properties of the sample and is manifested in the systematic shift of quantum-confined levels in the interval from \(y = 0\) to \(y = 100\) nm. It is remarkable that the observed shift of the levels is close to the estimated displacement \(\delta E_0\) of the bottom of the conduction band caused by the variation of the electron density.

In the simplest model (1) of localized electronic states in a one-dimensional potential well, the smooth shift of quantum-confined levels can be caused, first, by the monotonic variation of the thickness \(d(x, y)\) of the Pb layer; second, by the shift of the bottom \(E_0(x, y)\) of the conduction band; and, third, by a change in the boundary conditions at the metal–substrate interface. The last circumstance apparently explains the small-scale inhomogeneity of the electronic properties. We suggest that the mechanical stresses of the crystal structure, which arise in the process of growth of Pb structures and can change both the energy \(E_0\) and the height of terraces, are most likely responsible for the appearance of regions with a smooth inhomogeneity of the tunneling conductivity.

Fig. 5. (Color online) (a) Scanning tunneling microscopy image of the surface of the Pb island (460 × 460 nm, \(U_0 = 700\) mV, \(I_0 = 400\) pA). (b) Differential conductivity map \(G(x, y; U_0)\) of the same surface region at \(U_0 = 700\) mV and \(U_1 = 40\) mV; the arrow indicates the position of the monatomic step in the substrate. (c, d) Profiles of the topographic image and differential conductivity along the A–B dashed line in panel (a); the horizontal dashed straight lines correspond to the levels of Pb terraces. (e, f) Profiles of the topographic image and differential conductivity along the C–D dashed line in panel (a); the dashed circles indicate the unavoidable artifacts of processing of the topographic image.
CONCLUSIONS

We have shown that a change in the local thickness of the Pb film by one monolayer because of the presence of monolayer-height steps on the lower or upper interface results in abrupt spatial variations (with a typical scale of about several nanometers) in the average differential tunneling conductivity at a given energy. The observed small-scale modulation of the tunneling conductivity (with a typical scale of about 3 nm) is due to the effect of the periodic potential of the substrate for which the Si(111)7 × 7 reconstruction has been used. Furthermore, we have detected large-scale variations of the differential tunneling conductivity within one terrace of the Pb island, which are manifested as the smooth change in the energies of quantum-confined levels by about 50 meV at spatial scales of about 100 nm. Large-scale inhomogeneities of the electronic properties can possibly be caused by spatially inhomogeneous internal stresses of thin Pb films, which can result in unquantized changes in the thickness of the Pb layer, which differ from an integer number of monolayers. The systematic analysis of the dependence of the differential conductivity on the coordinates and energy is a convenient method for studying the intrinsic defects of Pb nanostructures.

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