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Angle-resolved photoemission of ultrathin Pb films on Si(111)-(6×6)Au: quantum size effect

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The electronic band structure of extremely thin (from 1 to 8 monoatomic layer (ML) thick) epitaxial Pb(111) films grown at low temperatures in ultrahigh vacuum (UHV) condition on Si(111)-(6×6)Au substrate is studied with angle-resolved photoelectron spectroscopy (ARPES). The morphology of the Pb film is determined with scanning tunneling microscopy (STM). Normal-emission photoelectron spectra recorded at the sample temperature of 130 K reveal quantum well states (QWS) characteristic of quantization perpendicular to the film surface. The energies of these states as a function of the number of the Pb(111) monoatomic layers are determined and compared with calculated in terms of the Bohr–Sommerfeld phase accumulation model.

Keywords: quantum wells, Pb, angle-resolved photoelectron spectroscopy.

1. Introduction

When the thickness of the film is comparable with the de Broglie wavelength of electron confined in, the motion of the electrons is quantized in the direction perpendicular to the surface. Theoretical works show (SCHULTE [1] and TRIVEDI *et al.* [2]) that in such two-dimensional systems the energy spectrum splits into the subbands and the work function, the electron density, and the inner potential depend on the film thickness. These effects are well known as so-called quantum size effect (QSE). Several experiments confirmed occurrence of such phenomenon. Already JAKLEVIC *et al.* [3, 4] were studying tunneling in metal–insulator–metal junctions. They observed electron standing wave states in 100 to 1000 Å Pb, Mg, Au, Ag thick texturized films. Other experimental techniques show electrical resistivity oscillations (JAŁOCHOWSKI *et al.* [5–7]) as a function of the thickness of ultrathin Pb films. A suitable experimental method for the determination of the QSE electron energy levels in ultrathin films is angle-resolved photoelectron spectroscopy (ARPES). This method was recently successfully applied for studying the QSE in thin Ag [8–10], Cu [11], Mg [12],

Pb [13, 14] metallic films. In the first photoemission experiments on Pb quantized films, JAŁOCHOWSKI and BAUER [13] studied QSE during the growth of ultrathin Pb films onto Si(111)-(6×6)Au substrate at low temperatures. Their study clearly showed the thickness dependent band structure quantization.

In the present work, we extend studies of the Pb ultrathin films grown on Si(111)-(6×6)Au substrates by performing energy and angle highly resolved photoemission measurements. The experimentally determined energies of the quantum well states (QWS) are compared with calculated in terms of the Bohr–Sommerfeld phase accumulation model.

2. Experimental

The experiments were performed in the ultrahigh vacuum (UHV) chamber with the base pressure below 8×10^{-11} mbar. The ARPES apparatus consisted of a high-intensity helium lamp with a polarizer as a HeI photon source (E = 21.22 ev) and electron energy analyzer VGX900IC. The Si(111) sample was mounted on a precise manipulator which enabled its rotation around two axes – in the plane of the sample, and perpendicular to it. The samples were cooled with liquid nitrogen to about 130 K.

Before experiments the Si(111) substrate was cleaned by heating shortly up to about 1500 K, applying the direct current heating. This procedure was repeated several times, until the Si(111)-(7×7) surface reconstruction was well developed and the sample was free of residual SiC. The cleaning of the substrate was fully controlled by reflection high electron energy diffraction (RHEED).

Si(111)-(6×6)Au reconstruction was obtained by deposition of about 1.3 monoatomic layers (ML) of Au onto Si(111) at room temperature, and subsequent annealing at about 1000 K. The amount of deposited Au and Pb was determined with the aid of a precise quartz crystal monitor.

During photoemission measurements the electron energy analyzer was set to full width half maximum (FWHM) energy resolution equal to 60 meV, and FWHM of the analyzer acceptance angle was equal to 2 deg. The morphology of the ultrathin Pb films deposited onto Si(111)-(6×6)Au at low temperatures was studied using scanning tunneling microscopy (STM) type Omicron VT.

3. Results and discussion

The Pb ultrathin films under investigation were composed of polycrystalline domains with well defined thickness. The samples deposited at 130 K grow in a layer-by-layer mode. Figure 1 shows STM scans of two samples with the fractional top layer coverage – in the intermediate state, when two surfaces with different thicknesses are exposed. In Fig. 1**a** the 1 ML thick islands are formed on the Si(111)-(6×6)Au substrate. The average diameter of these islands is about 5 nm. Single Pb atoms between islands, not attached yet to the islands, can also be seen. Further deposition results as first in the formation of smooth 1 ML thick film and then new 1 ML thick islands grow, Fig. 1**b**.

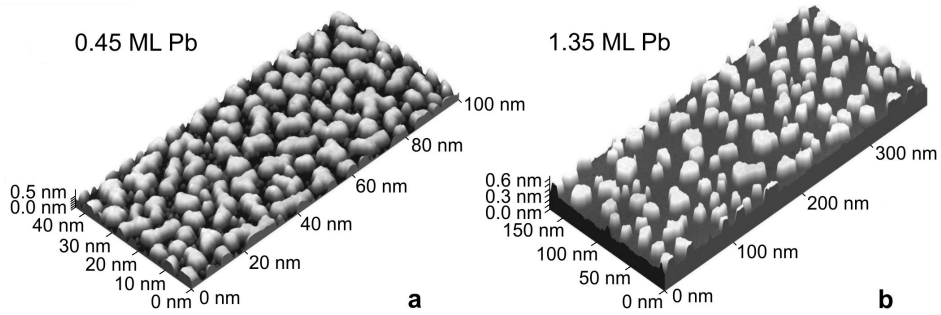

Fig. 1. STM topographic images of the ultrathin Pb films deposited on Si(111)-(6×6)Au surface. The samples were deposited and measured at 170 K. The average Pb thickness is equal to 0.45 and 1.35 ML in (**a**) and (**b**), respectively. The sample bias and the tunneling current were equal to: –1.6 V and 0.1 nA (**a**), and –1.2 V and 0.1 nA (**b**).

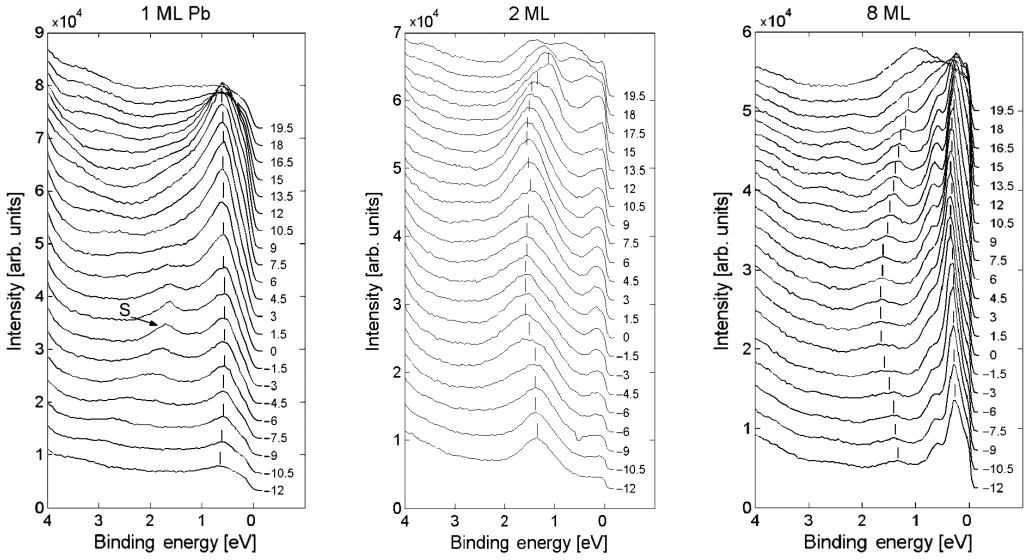

Fig. 2. Angle-resolved photoemission spectra of the Pb films deposited on Si(111)-(6×6)Au with thickness 1, 2 and 8 ML. The off-normal angle varies from –12 to 19.5 deg. The bars indicate positions of the QWS peak. For 1 ML thick sample the structures originating from the substrate are marked with *S*.

At low temperatures the scenario repeats several times, thus allowing production of the Pb film with desired integer number of the Pb monolayers. Such samples are suitable for study of the quantum size effects with ARPES.

Figure 2 shows examples of the ARPES spectra for the Pb films with thickness equal to 1, 2, and 8 ML. The polar angle (the angle between the sample normal and the analyzer entrance slit) varies from –12 to 19.5 deg and lies in the [110] plane. The spectra show clearly thickness-dependent features which are well described as the QSE

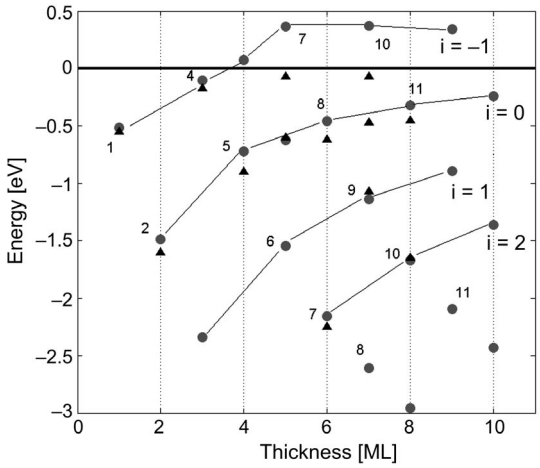

Fig. 3. Measured (triangles) and calculated (dots) energies of the QWS states in the ultrathin Pb samples. The lines connect the states with $i = 3N - 2n = -1$, 0, 1 and 2.

states. The energies of these states are marked in Fig. 2 by short bars. For the 1 ML thick sample only one QSE state at about 0.55 eV of binding energy is visible. In this sample, the other strongly dispersive feature visible at about 1.5 eV (marked by *S*) originates from the Si(111)-(6×6)Au substrate. The experimentally determined energies of the QSE states for all measured samples with the thicknesses ranging from 1 to 8 ML of Pb are presented in Fig. 3. These energies are marked by triangles.

In order to describe the quantization condition in the quantum wells (QW) we use the Bohr–Sommerfeld phase accumulation model [15]. According to this model the electron plane wave propagates inside the quantum well and it is reflected backward with additional phase shifts Φ_B and Φ_C, for surface–vacuum and surface–substrate interface reflection, respectively. Thus, the quantization condition is given by:

$$2k(E)Nd + \Phi_B(E) + \Phi_C(E) = 2\pi n \tag{1}$$

where $k(E)$ is the wave vector perpendicular to the surface, d is the thickness of a single monolayer taken to be 2.685 Å, N is the number of monolayers, Φ_B and Φ_C are the phase shifts at the boundaries, and n is the principal quantum number of the QWS. The phase shift at the vacuum side is well known and approximated by Wentzl–Kramers–Brillouin formula [16]:

$$\frac{\Phi_B(E)}{\pi} = \sqrt{\frac{3.4\ [\mathrm{eV}]}{E_V - E}} - 1 \tag{2}$$

where E_V is the work function, and E is the energy of the QWS. Both energies are expressed in eV unit. The phase shift at the substrate can be determined experimentally if one finds QWS at the same binding energy for various film thicknesses. These states

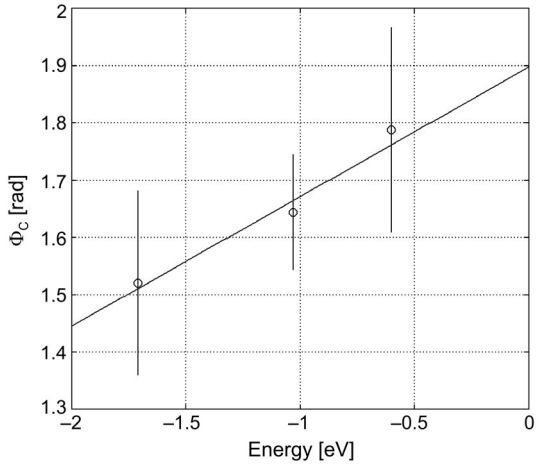

Fig. 4. Phase shift of electrons reflected at QW–substrate interface as a function of the QWS binding energy.

must have the same phase shifts since the total phase shift depends only on energy. Applying Eq. (1) for 2 films with different thicknesses we obtain wavevector k for the QSE level with energy E:

$$k = \pi \frac{n_2 - n_1}{N_2 - N_1}. \tag{3}$$

After inserting this value, and the phase shift from Eq. (2), back into Eq. (1), we obtain the phase shift for a particular energy at the substrate–sample interface. Figure 4 shows phase shifts determined for three pairs of the QWS. The numerical fit of the linear dependence $\Phi_C = Ea + b$ allows coefficients a and b to be determined. They are equal $a = 0.2262$ rad/eV and $b = 1.8971$ rad. For comparison, MANS *et al*. [14] obtained linear dependence with $a = 0.34$ rad/eV and $b = 3.1$ rad for the Si(111)-(7×7)–Pb interface. For the Pb–Si(111)-(6×6)Au interface these values are slightly different. Knowing Φ_C and Φ_B we calculated the QSE energies for all the thicknesses under study. These energies are marked in Fig. 3 by circles. The number near each circle indicates the corresponding principal quantum number. The QWS are connected by the thin lines labeled $i = -1, 0, 1, 2$ satisfying the condition $3N - 2n = i$. Each of these lines has the property that it brings a new quantum state as the thickness increases by two monolayers. The number of antinodes for each bilayer increment increases by three.

4. Conclusions

The electronic structure of the QWS in the ultrathin Pb grown onto Si(111)-(6×6)Au films has been extensively studied. The energies of the QWS are determined and

compared with the calculated within the Bohr–Sommerfeld phase accumulation model. The phase shift at the substrate–quantum well interface has been determined.

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