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Work Function Oscillation of Pb Quantum Islands on Cu(111) Surface: Observation by Gundlach Oscillation

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The Gundlach oscillation in scanning tunneling spectroscopy is used to measure the work function of Pb quantum islands grown on a Cu(111) substrate. The results reveal that the work function varies in oscillation with island thickness, which can be attributed to the existence of the quantum well states within the islands. The undulation of the work function is consistent with the theoretical calculations for a thickness from 6 to 15 atomic layers. While the island is grown layer-by-layer, it is found that the work function decreases (increases) whenever one (two) subband(s) is(are) added to the occupied states of the island.

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The work function of an electronic system characterizes crucial physical and chemical properties of the system. Recent studies have shown that the work function is a significant factor in the fabrication of solar cells [1], organic thin film transistors [2], and metal-oxide semiconductors (MOS) [3, 4]. For instance, in the design of an MOS, the work function of the metal layer can affect the charge trapping, and, in turn, determines the performance of the MOS. Therefore, a precise way of measuring the local work function of a thin film or nanostructure becomes essential in the current industrial trend of scaling down devices. Using scanning tunneling microscopy (STM) and spectroscopy (STS), one can obtain the local work function by measuring the apparent barrier height [5]. However, the general measured error with this method can be as high as 0.3 eV; thus, this method is not accurate enough for an industrial application.

An alternative choice is to observe the Gundlach oscillation in STS [6], which is a phenomenon of field-emission resonance through standing-wave states in the tip-sample gap [7, 8]. Previous studies have demonstrated that the Gundlach oscillation can be exploited to study the dynamics of electrons at surfaces [9, 10] as well as to observe the electronic properties of diamond [11], reconstructed surfaces [12–14], oxide layers [15], and graphene [16]. In a previous study [17], the phenomenon of the constant energy shift (ES) emerging from the high-order peaks of the Gundlach oscillation was demonstrated. This constant ES directly reflects the work function difference between the film and its substrate. It has been found that the work functions of the noble metallic and magnetic films can be measured with a precision of less than 0.02 eV, which is much better than the precision achieved by detecting the apparent barrier height. It has also been clarified that this method can be exploited for the dielectric thin films [18] grown on the metallic substrate [17]. In order to explore whether this technique derived from the Gundlach oscillation can be applied to other kinds of film, in this work, the Pb islands grown on a Cu(111) surface possessing quantum well (QW) states [19–21] were studied.

Because of the existence of the QW states [22–31], several physical properties of the Pb films may change with the film thickness [32–37], and one notable property is the work function. Wei *et al.* performed the first principle calculation for the free-standing Pb films and predicted that the work function should reveal a bilayer oscillation with thickness [38]. Qi *et al.* observed the behavior of the bilayer oscillation in the work function of Pb films on an Si(111) substrate by measuring the tunneling barrier height with STM [39]. Recently, the first principle calculations of the work function of Pb films on a Cu(111) surface were performed by Jia *et al.* [40]. This theoretical result provides a reference for the investigation using the Gundlach oscillation measurements in our work. The results of our study demonstrate that the phenomenon of a constant ES indeed occurs on the Pb films and varies with film thickness, implying that the Gundlach oscillation can be utilized to measure the work function of a thin film with QW states. Furthermore, the variation of the work function not only reveals the bilayer oscillation, but it also agrees with the theoretical calculation of Jia *et al.* [40] for thicknesses from 6 to 15 atomic layers.

Previous studies have shown that Pb can be grown into flat islands with (111) orientation on a Cu(111) surface at room temperature, and the electronic structures of the islands involve the QW states [19, 20]. In our experiment, the Cu(111) surface was treated with cycles of ion beam sputtering and annealing at 600 °C. To create the Pb islands, Pb was evaporated onto the Cu surface at room temperature with a flux of 0.03 monolayer (ML) per minute. To observe the Gundlach oscillation requires the differentiation of the Z-V spectrum, which was accomplished by a numerical method. In this experiment, a homebuilt STM, operating at 4.3 K, was used to acquire the Z-V spectrum of the Pb islands.

The inset in Fig. 1(a) is a typical topographic image of the Pb islands grown on a Cu(111) surface with a coverage of 2.1 monolayer (ML). Before the island's formation, about 1 ML Pb is consumed in wetting the substrate. The rest of the Pb grew into islands above the wetting layer. Here the island thickness is measured relative to the Cu(111) substrate, i.e., including the 1-ML wetting layer. Owing to the existence of the wetting layer, it is not possible to measure the absolute work function of the Pb island using the Gundlach oscillation unless the work function of the wetting layer is known [17]. Hence, only the work function difference between the island and the wetting layer can be measured. Figure 1(a) shows the average dZ/dV-V spectra taken on the wetting layer and the island with a thickness of eight layers, respectively. The numbers marked close to the peaks denote the order of the Gundlach oscillation. It is apparent that the ES exists between peaks of the same order. However, the measured ES as a function of the order shown in Fig. 1(b) does not appear as a constant. This is due to the fact that the quantum phenomenon of the transmission resonance is manifested in the spectrum of the wetting layer (marked by an arrow), displacing the following Gundlach oscillation peaks to higher energies [41, 42]. Therefore, it is not a good choice to measure the work function difference in reference to

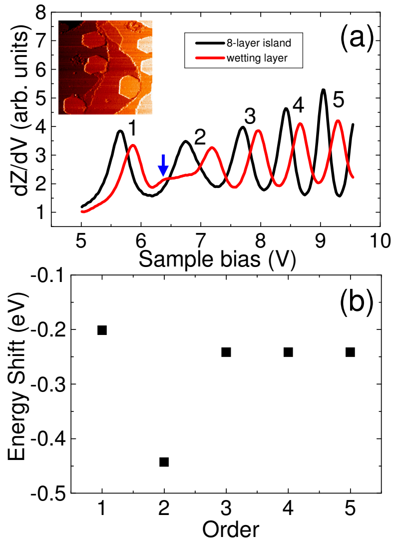

FIG. 1: (color online) (a) Average dZ/dV-V spectra of the wetting layer and the eight-layer island. Distinct peaks marked by numbers are the Gundlach oscillations. Inset: topographic image of Pb islands on a Cu(111) surface at room temperature. (b) Energy shifts between peaks of the same order as a function of the order for spectra in (a).

the Gundlach oscillation peaks of the wetting layer. Fortunately, Fig. 1(a) shows that the signal of the transmission resonance disappears in the spectrum of the island. Hence, the theoretically-predicted work function undulation can still be investigated experimentally by observing the Gundlach oscillation.

Figure 2(a) shows the average dZ/dV-V spectra acquired on the islands of six and seven atomic layers in the energy range from 0.5 to 9.5 eV above the Fermi level. In this wide energy range, not only the Gundlach oscillation peaks (marked by numbers), but also the peaks of the empty QW states below the vacuum level [21] are observed. The energies of the QW states, like the fingerprint of the island, are sensitive to the thickness. Thus, besides direct measurements of the island thickness on the STM topographic image, one can also distinguish the thickness by the QW states [43]. Moreover, because of the existence of the QW states, the lowest (zero) order Gundlach oscillation peak reflecting the quasi-image-potential state in the tunneling gap is quenched [21]. The observed Gundlach oscillation peaks in Fig. 2(a) thus belong to the higher orders and reveal the ES for the same order. To measure the ES, the peaks of the thinner island are always used as the reference here. The ES as a function of the order, which is displayed with the squares in Fig. 2(c), exhibits a constant level with a tiny variation of 0.01 eV due to energy resolution. This indicates that the behavior of the constant ES can appear on Pb islands. Therefore, the work function difference of six-layer and seven-layer islands is 0.09 eV because the majority of ESs are equal to 0.09 eV. Figure 2(b) depicts the average dZ/dV-V spectra acquired on 16-layer and 17-layer islands. It can be seen that the Gundlach oscillation peaks in both spectra nearly

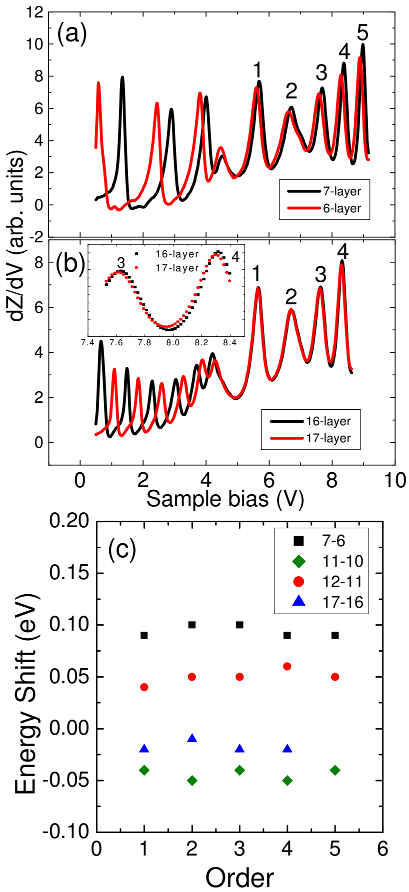

FIG. 2: (color online) (a) and (b) are the average dZ/dV-V spectra acquired on the 6-layer and the 7-layer islands as well as the 16-layer and the 17-layer islands, respectively. Peaks marked by numbers are related to the Gundlach oscillation. Other peaks are quantum well states. The inset in (b) shows the zoom-in spectra of peaks 3 and 4. (c) Energy shifts between the Gundlach oscillation peaks as a function of the order for the cases in (a), (b), and the ones of the 10- and 11-layer islands as well as the 11- and 12-layer islands (spectra not shown).

overlap while their QW state peaks are clearly separated. Careful inspection, as evidenced from the zoom-in spectra of peaks 3 and 4 in the inset, presents the minute energy difference of -0.02 eV between the peaks. It implies that the accuracy of the work function measured with the Gundlach oscillation can be better than 0.02 eV. The work function difference of -0.02 eV is thus obtained from the majority of the same ESs (displayed by triangles) in Fig. 2(c). Moreover, although the energy of the Gundlach oscillation peak is sensitive to the electric field in the tip-sample gap, it is emphasized here that this subtle difference of -0.02 eV is independent of the electric field in our observation.

Figure 2(c) also shows the constant ES appearing in the cases of the 10-layer and 11-

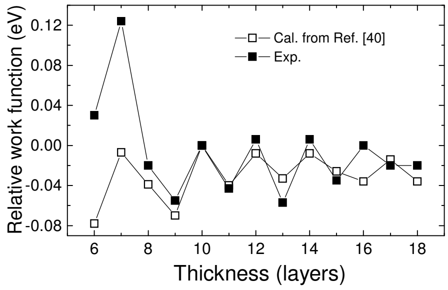

FIG. 3: The measured relative work function as a function of thickness in this study, marked by solid squares. The data marked by open squares are the relative work function from Ref. [40].

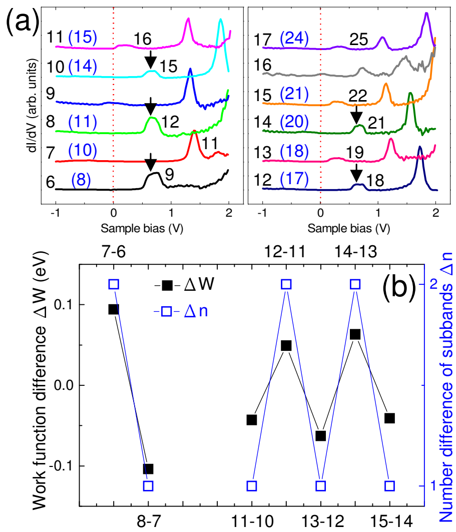

FIG. 4: (color online)(a) dI/dV-V spectra taken on islands of thicknesses from 6 to 17 layers. Except for the spectra of 9-layer and 16-layer thicknesses, in each spectrum, the peak marked by number is the lowest unoccupied quantum well states and the number of the subbands is marked in the parenthesis. (b) The number difference Δn of occupied subbands and the work function difference ΔW of the adjacent thicknesses, marked by open and solid squares, respectively.

layer islands as well as the 11-layer and 12-layer islands. Note that Fig. 2(c) displays the ES of the islands of adjacent thicknesses, but the value can be either positive or negative. This indicates that the work function is undulated with the thickness, as predicted by the first principle calculation [40]. Therefore, we measure the constant ES of adjacent thicknesses for thicknesses from 6 to 18 layers.

The relative work function is obtained by choosing the work function of the 10-layer island as the reference, as depicted in Fig. 3. It can be seen that the work function of the island, marked by solid squares, indeed varies in bilayer oscillation with the thickness. In addition, there appears to be a crossover at the nine-layer thickness; after which, the even-number thickness has a higher work function in comparison with that of the adjacent odd-number thickness. However, the trend is just reversed before the crossover. In Fig. 3, the result is compared with the work functions calculated (open squares) by Jia *et al.* [40] by choosing the 10-ML work function as the reference. It turns out that the variations of the measured values display a consistent trend with the calculated results for the thickness from 6 to 15 layers. In particular, the crossover in the calculation also occurs at the nine-layer thickness, exactly as what we have observed.

It is believed that the work function oscillation originates from the quantum size effect; i.e., the existence of the QW states. Recently, Qi *et al.* [39] studied the system of Pb/Si(111) and demonstrated that the work function oscillation can be directly related to the energy of the highest occupied QW state. Here it was determined that an additional correlation between the work function variation and the quantum number of the lowest unoccupied quantum well state (LUQWS). Figure 4(a) shows the dI/dV-V spectra in the range from -1 to 2 V of the sample bias for Pb islands of varied thicknesses. The number H at the left-hand side of each spectrum represents the thickness in terms of atomic layers. The dotted line at 0 V is the Fermi level, and thus the LUQWS of each thickness is the peak marked by a number corresponding to its quantum number n [21] in each spectrum. The quantum number of the LUQWS is assigned as in the following description. In Fig. 4(a), a QW state in the 6-, 8-, 10-, 12-, and 14-layer islands at $\sim$ 0.6 eV above the Fermi level, indicated by an arrow, is obviously independent of the thickness. According to our previous study [21], the wavevector k of this constant state is equal to nπ/Hd. Since n and H are integers, one can find that some wavevectors are independent of H, e.g., k= π/d for any H value and k= π/2d for any even H value. The constant state only appears in the even-number-layer islands, indicating that its wavevector could be equal to π/2d, 3π/2d, 5π/2d, and so on. Since the Fermi level has been determined experimentally in the band structure [44, 45], one can be sure that the constant state should correspond to E(π/2d) in the second band of the reduced zone in the [111] direction, and thus the wavevector is 3π/2d. Substituting this k of 3π/2d into the quantized condition of the quantum well state: kHd= nπ, the corresponding quantum numbers for fixed states can be determined. Other QW states can then be numbered accordingly. However, the LUQWSs of 9-layer and 16-layer islands cannot be easily identified, because a peak appears near the Fermi level. Therefore, these two thicknesses are not included in the following discussion.

Since the quantum number of the LUQWS is known, the number of the occupied subbands in the island of each thickness can be obtained, which is n$-$1 marked in the parenthesis in Fig. 4(a). In principle, the work function is physically related to the electronic structure of the occupied subbands. Once the number of subbands varies with the film thickness due to the quantum size effect, the electronic structure of the Pb film may redistribute with the thickness. The work function can thus change with the thickness accordingly. For example, Schulte performed a self-consistent calculation for a jellium slab to demonstrate that, as the thickness increases, a local minimum (cusp) in the work function occurs whenever a subband drops below the Fermi level [46]. This calculation implies that the work function variation could also be explained with the change in the number of occupied subbands. Figure 4(b) shows the number difference Δn of occupied subbands and the work function difference ΔW of the adjacent thicknesses, marked by open and solid squares, respectively. It can be seen that ΔW is positive (negative) whenever Δn is two (one), indicating they are coherent. Therefore, the work function increases (decreases) whenever two (one) subbands are added to the occupied state as the island thickness grows by one atomic layer.

In summary, it has been shown that the Gundlach oscillation can be applied to measure the relative work function of the Pb islands involving the QW states. The precision of this method can be better than 0.02 eV, and thus the subtle variation of work function in Pb islands of different thickness can be detected. The work functions of the Pb quantum islands reveal the bilayer oscillation, which is consistent with the theoretical prediction for thicknesses from 6 to 15 layers. By observing the LUQWS and counting its quantum number, it is found that the bilayer oscillation can be directly related to the number of occupied subbands added as the film grows one more layer.

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