Atomic-layer-resolved local work functions of Pb thin films and their dependence on quantum well states

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The thickness dependence of the local work function (LWF) and its relationship with the quantum well states (QWSs) are studied. The measured LWF shows an oscillatory behavior between adjacent layers with a period of 2 ML and, in addition, an envelope beating pattern with a period of 9 ML. Scanning tunneling spectroscopy investigations reveal that the oscillatory LWF correlates perfectly with the formation of the QWSs: the higher the occupied QWS is, the smaller the LWF is. Through the role of the LWF, this study establishes the importance of quantum size effects in thin films for surface reactions and catalysis.
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Work function, defined as the minimum energy required for an electron to escape from the surface, is one of the most fundamental properties of a metal, as it determines the degree of difficulty of emitting electrons and moreover the reactivity of the surface of the metal. With the recent development of lower-dimensional electronic devices, measuring the local work function (LWF) of a metal becomes more and more important in order to know what might be happening on the electrons via geometric confinement.[1] The LWF changes due to alkali metal adsorption,[2] crystallographic orientation,[3] and surface steps[4] have been theoretically and experimentally studied. It reveals that the changes are closely related to the local density of states. Spatial confinement of the electronic motion by a one-dimensional potential well could also lead to a modification of the local density of states (DOS), forming the so-called quantum well states (QWSs). Such an electronic property, as theoretically predicted 30 years ago by Schulte, was confirmed recently by experiments and found to also play an important role in modifying the fundamental physical properties of the films ranging from magnetic coupling in superlattices[5] to growth properties.[6]

Extensive studies of the QWSs have been done on metals also because electrons near the Fermi level E_F have a short de Broglie wavelength, which makes the DOS rather sensitive to the thickness of the film. The LWF, as it greatly depends on the electronic DOS, should also show similar quantum behavior due to the change in local thickness. There have been a number of theoretical work predicting an oscillatory behavior of the work function over film thickness in such systems as Pb/Cu(111) (Ref. 7) and metal films.[8] A recent experiment has measured the atomic-layer-resolved quantum oscillations in the work function on Ag/Fe(100).[9] However, QWS modulated LWF in other systems has not been systematically studied experimentally. This is because measuring the LWF would require high spatial resolution, namely, to bring the probe close enough to the homogeneous and defect-free areas on the surface.

In the past, several approaches such as photoemission from adsorbed xenon,[10] two-photon photoemission spectroscopy,[11] and local Kelvin cantilever[12] have been developed to study the LWFs. Nonetheless, it has been shown that the scanning tunneling microscopy (STM) with a lock-in technique is, to date, the most powerful tool for imaging the morphology, as well as the LWF with atomic resolution, for example, for Au/Cu(111) (Ref. 13) and Pd/Cu(111).[14] As a matter of fact, Binnig and Rohrer are the first to measure the LWF for metal and semiconductor, following their early development of the STM.[15] LWF is closely related to the potential barrier between the STM tip and the sample surface. Hence, one can measure the LWF by changing the STM tunneling distance and then monitoring the response in the current.

Pb/Si(111) is also an ideal system for studying the QWSs. With the unique relationship between Fermi wavelength λ_F and the interlayer distance along the [111] crystallographic direction: $\lambda_F \approx 4d$, a bilayer modulation behavior can be expected or in other words, a monolayer (ML) change in N can induce dramatic change in the DOS near the E_F. As has been demonstrated, the physical properties of Pb/Si(111) such as the superconductivity transition temperature,[16] thermal stability,[17] and surface energy[18] strongly depend on the electron density function and its modulation by the layer thickness N. There has been a theoretical prediction of the LWF change as a function of the thickness of the Pb films by Wei and Chou,[19] but no experimental work has yet followed.

In this letter, we examine LWF of Pb islands on vicinal Si(111)7×7 substrate. The islands are wedge shaped with flattop surfaces,[20] which allow us to continually measure the LWF as a function of N. Our images reveal an even-odd oscillatory pattern of the work function and, on top of it, a 9 ML envelope beating pattern over a wide range of N. Scanning tunneling spectroscopy (STS) study was also carried out to track the evolution of the QWSs with N. We found that the highest occupied QWS (HOQWS) has the same oscillatory

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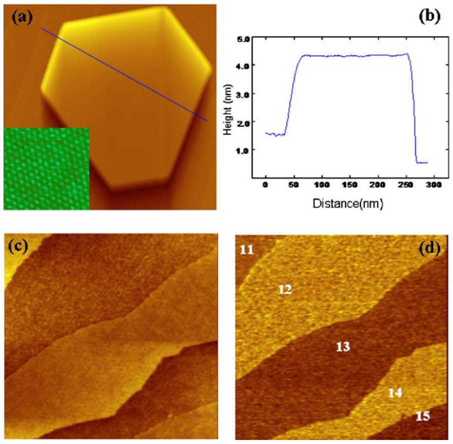

FIG. 1. (Color online) (a) STM image of a Pb island taken at $V=-0.8$ V and $I=0.1$ nA. Image size: 500×500 nm^2. Insert is a 5×5 nm^2 atomic resolution image ($V=0.4$ V, $I=0.1$ nA). (b) A line plot along the blue line in (a) to show the height profile. (c) The topographic and (d) local work function images taken simultaneously ($V=-2$ V, $I=0.1$ nA). The bright area has a larger work function than the dark area. Image size: 337×337 nm^2.

behavior as the LWF, and the two are perfectly anticorrelated: namely, larger LWF corresponds to lower HOQWS.

The experiments were performed in an ultrahigh vacuum STM-MBE system made by Unisoku Co. The temperature range for scanning is from 2.2 to 300 K, and the data presented here were collected at 77 K under LN_2 cooling condition with a base pressure$=1\times10^{-10}$ mbar. An SPM1000 controller (RHK Co.) was used. We obtain 7×7 reconstruction of Si(111) by flashing the *n*-type substrate to 1200 °C after degassing for 8 h at 500 °C. Pb deposition rate at room temperature is about 0.3 ML/min, and the growth mode follows that of Stranski-Krastanov: a 2–3 ML thick wetting layer followed by Pb island formation due to lattice mismatch between Pb and Si. The thickness of the islands is determined by the growth time.

When measuring the LWF, a sinusoidal ac voltage at 2.0 or 3.0 kHz was superimposed on the *z*-axis piezo of the tip to modulate the distance between the tip and sample surface. Response tunneling current was selected by the lock-in amplifier to yield the LWF images. The morphology and LWF images were collected simultaneously. STS measurement was made by using the modulation signal to sample bias at the same frequency of 2.0 or 3.0 kHz and the bias ramping from −1.5 to 1.5 V to record the differential tunneling current by lock-in.

Figure 1(a) is a typical image of the Pb islands with thickness *N*, from left to right, between 11 and 15 ML beyond the wetting layer. The inset shows the atomic resolution STM for the top surface. A line scan through Fig. 1(a) is shown in Fig. 1(b), which reveals the flattop nature of the Pb island despite that it is on top of a stepped Si substrate.

Figures 1(c) and 1(d) show the topography and LWF images of the island taken simultaneously. A sinusoidal ac voltage at 0.1 V was superimposed to modulate the tip-sample distance change within 0.7 Å. Buried interfacial structures were observed on the topographic images, which has been explained in terms of a nondiffractive scattering of the quantized electrons in the QWSs.[21] From the LWF image, we can see clearly the difference in terms of *N*: even layers (12 and 14 ML) have larger work functions than odd layers (11, 13, and 15 ML). This implies that electrons in the 12 and 14 ML regions need more energy to escape from the

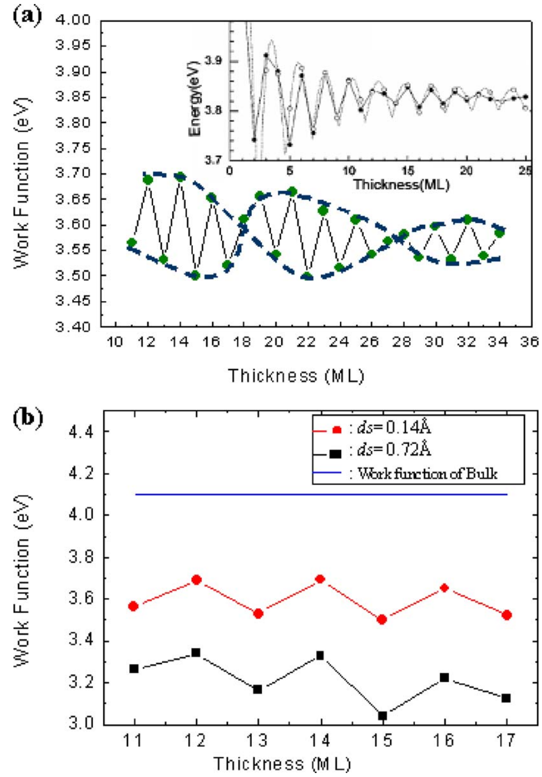

FIG. 2. (Color online) (a) Measured Pb local work function (LWF), showing a strong dependence on local film thickness N. Inset is the theoretical prediction in Ref. 19. (b) A comparison of the LWF measured with modulation bias of 0.1 V, modulation distance of 0.72 Å and that with modulation bias of 0.02 V and modulation distance of 0.14 Å.

surface than those in their respective neighboring regions.

The LWF image in Fig. 1(d) was obtained as a perturbation to the natural logarithm of the current ($d\ln I$) modulated by the change of the distance between tip and sample (ds) and is strictly speaking not the LWF. According to the tunneling theory, the relationship between the current and potential barrier ϕ, which defines the LWF, can be described as $I\propto\exp(2\sqrt{2m\phi}/\hbar)$. Therefore, the LWF can be written as

$$\phi\approx0.95\left(\frac{d\ln I}{ds}\right)^2. \quad (1)$$

To actually obtain ϕ from the LWF image, we select for each N a homogeneous and defect-free area, record $d\ln I$, and then select the peak position from the Gaussian-type energy distribution on its histogram. By applying Eq. (1), the value for ϕ can be easily obtained. Figure 2(a) shows the LWF for N in the range from 11 to 34 ML above the wetting layer. Changes in LWF reflect subtle changes in the local DOS near the E_F, as only electrons near the Fermi level can effectively contribute to the measured ϕ.

Note, however, that ϕ measured by the STS depends somewhat on the applied voltage[22] and other parameters related to the distance between tip and sample surface, so the absolute values in Fig. 2(a) may be off from the exact ones. To see this effect, we compare the results at two different modulation distances, 0.7 and 0.1 Å, respectively, in Fig. 2(b). It can be understood that the deviation is larger for larger modulation distance, because in a given time $d\ln I$ may not respond fully to the larger increment in ds. However, the relative change of the LWF from layer to layer,

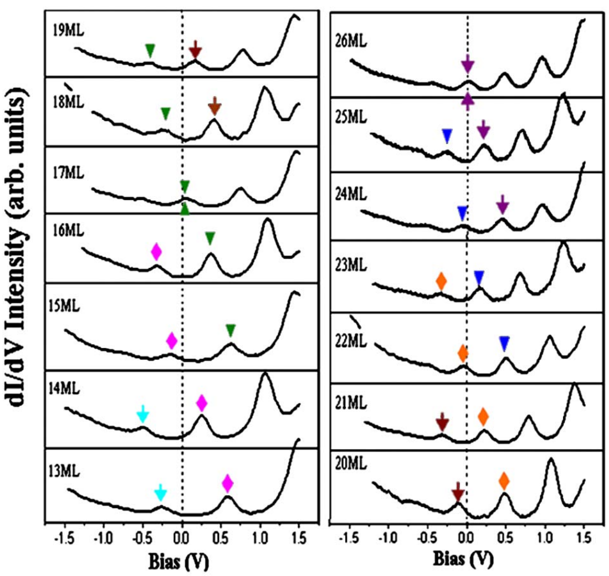

FIG. 3. (Color online) dI/dV curve of Pb films between $N=13$ and 26 ML (without counting the wetting layer). The measurement was done at $T=77$ K with sample bias ramp from −1.5 to 1.5 V. Same shape triangles are used here to indicate the shifts of the peak positions as a function of N, whereas upward triangles indicate the QWS peaks near the Fermi level.

which is the most relevant quantity in this study, does not seem to depend on the choice of either the modulation bias or the distance.

Figure 2(a) shows larger LWF for even layers than for odd layers for N between 11 and 17 ML, whereas larger LWF for odd layers for N between 19 and 26 ML. The trend reverses again at 27 ML. Overall, the bilayer oscillation of the LWF is concomitant with an envelope function of beating at approximately 9 ML. Although the oscillation in term of the exactly layer is different from the theoretical work in Ref. 19 [inset in Fig. 2(a)], as freestanding film was considered in the calculation, the measured oscillatory periodicity and beating behavior show quite reasonable agreement with theory. The same trend has also been observed recently in the surface energy.[23] Such an observation can be reasonably well described by a Friedel-like function of $\lambda_F/2$ and $2d$ along the [111] direction.[24]

We resort to the DOS at E_F revealed by the dI/dV measurement, to explain the oscillatory behavior of the LWF. Figure 3 shows the dI/dV spectra for $N=13-26$ ML above the wetting layer. The dotted line at 0 V is the Fermi level. When N increases, the number of occupied quantum states also increases, accompanied by a decrease in the separation between the quantum states. According to the standing wave theory, every $\lambda_F/2$ increase in the layer thickness will introduce one more occupied QWS. So with every 2 ML increase, the lowest unoccupied QWS will move across the E_F to become occupied, as displayed by the triangles of same shape in Fig. 3. The change in the DOS at E_F, which modulates the probability of electrons for emission, causes the bilayer oscillation in the LWF. The two traversal states at 17 and 26 ML are noticeable too, as their respective peaks are very close to (but slightly above) the E_F: we note that not only 17 and 26, but also 35 and 44 ML are such critical points. They form a sequence of 9 ML interval, which coincides with the nodes in the envelope function of LWF.

By comparing the energy positions of the HOQWS with LWFs, we observe that not only an oscillation pattern and a set of beating nodes exist in both, but they are also in perfect agreement: the closer the HOQWS to the Fermi level, the lower the LWF. This can be qualitatively understood as follows: the higher the local density of states near the E_F, the higher probability for the electrons to tunnel through the potential barrier, and hence the lower the effective local work function. Within the limitation of our STM measurement, our observation is valid without any exception.

In summary, using atomic layer resolved STM we have investigated the LWF dependence on local film thickness N of Pb islands. The LWF images reveal different work functions between even and odd layers and, on top of them, a 9 ML envelope beating pattern over a wide range of N. STS study was also performed to track the evolution of the QWSs as a function of the N. For every two-layer change in N, the lowest unoccupied QWS becomes the highest occupied QWS. At certain layer thicknesses, the peak of the QWS coincides with E_F, resulting in beating in the QWS position δ and the LWF. A smaller LWF always corresponds to a HOQWS closer to the E_F. A relationship between the oscillatory LWF and HOQWS is thus established.

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