Field-Induced Expansion Deformation in Pb Islands on Cu(111): Evidence from Energy Shift of Empty Quantum-Well States

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We use scanning tunneling microscopy and spectroscopy to measure the energy shift of empty quantum-well (QW) states in Pb islands on the Cu(111) surface. It is found that, with an increase of the electric field, the behavior of the energy shift can be grouped into two different modes for most QW states. In the first mode, the state energy moves toward high energy monotonically. In the second mode, the state energy shifts to a lower energy initially and then turns around to a higher energy. Moreover, we have observed that the QW states of higher energy behave in preference to the first mode, but they gradually change to the second mode as the Pb island becomes thicker. This thickness-dependent behavior reflects the existence of local expansion in the Pb islands, due to the electric field, and that the expansion is larger for a thicker island. QW states can thus be used for studying the localized lattice deformation in the nanometer scale.

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The electric field is one of the key factors in the working mechanism for scanning tunneling microscopy (STM) and spectroscopy [1], because there will be no net tunneling current without an electric field. For this reason, the electric field in the tip-sample gap is usually considered ''intrusive'' in the detection of electronic properties using spectroscopy. For example, the discrepancy between the surface state energies measured by photoemission spectroscopy and STM is attributed to the influence of the electric field effect [2]. Limot *et al.* demonstrated that the surface state energy can be shifted away from the Fermi level with an increase of the electric field by raising the tunneling current [2]. Su *et al.* used STM to observe the quantum phenomenon of the transmission resonance in Ag films [3], and it was found that the transmission resonance energy can be moved, owing to the phase contribution of the electric field [4]. Furthermore, with the aid of the electric field, one can use the STM tip to manipulate the surface atoms [5–7] or to create artificial nanostructures on the surface [8,9].

Electrons in metallic films with atomic-scale flatness and nanometer thickness can lead to the quantization of electronic wave vectors along the surface normal to form the quantum-well (QW) states [10–19]. Recently, Ogawa *et al.* have shown that QW state energies are also inevitably affected by the electric field [20]. In the work of Ogawa *et al.*, the energy of a QW state in the two-monolayer Au film on Fe(100) shifted to a higher energy, but those in the 11- and 16-monolayer films shifted to a lower energy for the same current variation. Their results allude to a correlation between the direction of the energy shift and the film thickness, which remains to be verified.

It is well known that the electronic structures of flat Pb islands, grown on the Cu(111) surface, display characteristics of the QW states [21]. Our previous work also exhibited the QW states in a wide energy range from the Fermi level to the vacuum level, for various islands differing in thickness [22]. This Pb/Cu(111) system can thus be used to systematically study the energy shift of each QW state in the Pb island containing 2–16 atomic layers (AL). In this work, we find that, with an increase of the electric field, the energy shift behavior of most of the empty QW states exhibits two different modes. In the first mode, the energy of a QW state shifts toward a higher energy monotonically. On the contrary, in the second, the state energy moves to a lower energy at the beginning and then shifts toward a higher energy. By using the phase accumulation model [23,24], including the phase contributed from the potential in the tunneling gap, only the first mode can be explained. We thus suggest here that there exists the local expansion in Pb islands, resulting from the electric field in the STM gap. The geometric deformation causes a wider quantum well with lower QW state energies, which thus induces an additional phase. This new phase along with the phase from the potential can hence interpret the unique characteristics of the energy shift in the second mode. Furthermore, we observed that a QW state of higher energy normally takes the first mode as it shifts, but it gradually changes to the second mode with the increase of the island thickness. This phenomenon reflects that the expansion is larger for a thicker island and can be explained with the simple concept of a spring in series.

In our experiment, the QW states were observed at 4.3 K by using Z-V spectroscopy. Differentiation of the Z-V

spectrum was performed by a numerical method. The tunneling current varied from 0.1 to 50 nA for tuning the electric field in the tip-sample gap. Figure 1(a) displays average dZ/dV-V spectra acquired on the island with a thickness of 2 AL under set tunneling currents of 0.1, 1, 10, 30, and 50 nA. The energy range of spectra is 0.5–5 eV above the Fermi level, and peaks in each spectrum represent the empty QW states. The quantum numbers n are marked near peaks [22], and the dashed lines indicate the energies of QW states at 0.1 nA. It can be seen in Fig. 1(a) that the energies of both peaks move toward a higher energy with the increase of the current, as quantified in Fig. 1(b). The movement (110 meV) of the $n = 6$ peak is more evident than the movement (60 meV) of $n = 5$. This kind of energy shift behavior is named the first mode in this study. However, the situation is obviously different for some QW states in 9-AL islands for the same current variation, as shown in Fig. 2(a). It is clear to see that only QW state peaks of $n = 18$ and 19 reveal the first mode. For peaks of $n = 15$, 16, and 17, the QW state energies at 0.1 nA are nearly the same as those at 50 nA. The quantified results depicted in Fig. 2(b) show that, with the increase of current, these three peaks move downward initially and then upward, exhibiting a different behavior from the monotonic movement in the first mode, which is thus named the second mode. This mode was not observed by Ogawa *et al.* [20], likely due to the limited current variation in their experiment. In addition, the energy shift of the $n = 19$ peak is larger than that of $n = 18$, implying that the movement of the higher energy peak would be greater, which coincides with the situation seen in Fig. 1.

With further examination, although the peak energy of $n = 5$ in Fig. 1(a) is very close to that of $n = 16$ in Fig. 2(a) at 0.1 nA, these two QW states manifest entirely different behaviors, indicating that the energy shift of the QW state is thickness-dependent. This motivated us to

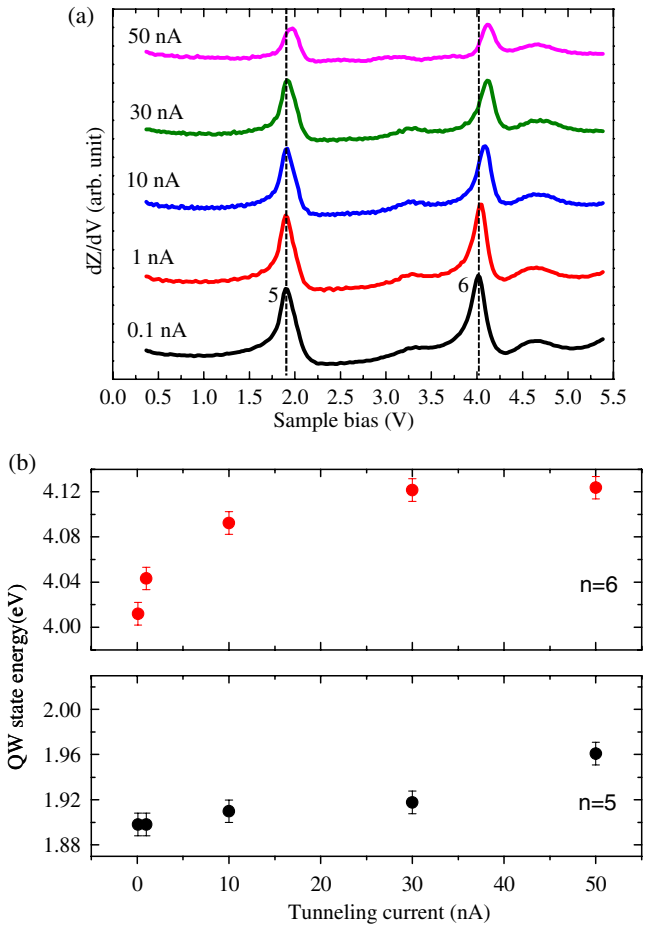

FIG. 1 (color online). (a) dZ/dV-V spectra acquired on the island with a thickness of two atomic layers under set tunneling currents of 0.1, 1, 10, 30, and 50 nA. The peaks of quantum-well states in the spectrum are marked by quantum numbers 5 and 6. Dashed lines mark the peak energies at 0.1 nA. (b) The energies of two peaks as a function of tunneling current, showing a monotonically positive energy shift.

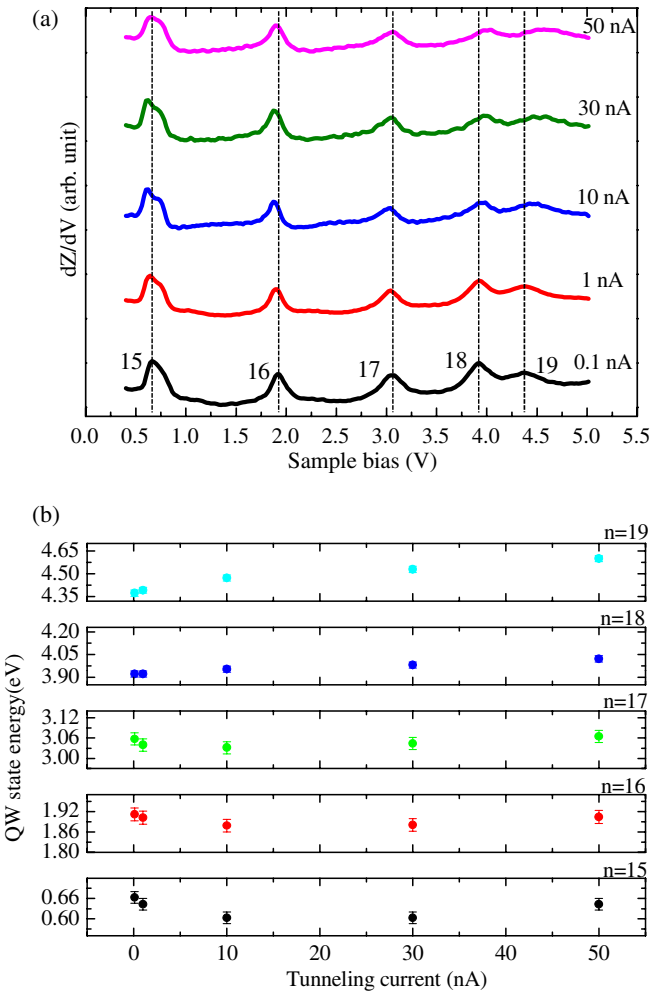

FIG. 2 (color online). (a) dZ/dV-V spectra acquired on the island with a thickness of nine atomic layers at currents of 0.1, 1, 10, 30, and 50 nA. The peaks of quantum-well states in the spectrum are marked by quantum numbers. Dashed lines mark the peak energies at 0.1 nA.

investigate the energy shift of QW states of other thicknesses for the same current variation. Figure 3 displays energies of QW states at 0.1 nA versus island thickness, and those QW states behaving like the first (second) mode are marked by circles (squares). As a result, Fig. 3 reveals a distribution with a clear division between these two modes. For one particular thickness, the QW states with higher energies prefer the first mode, and the second mode can gradually appear in a higher energy with increasing the thickness.

The energy shift of the QW state is due to the electric field, similar to the influence of the electric field on the energies of the surface state [2] and the transmission resonance [4]. Although the electric field can evidently affect the QW states, Su *et al.* recently demonstrated that the image potential is still the dominant factor for determining the energies of empty QW states [25]. Hence, to explain the energy shift behaviors shown above, the situation without the electric field can be considered first, followed by treating the electric field as a perturbation.

The wave vector k of a QW state with an energy E in a Pb island follows the quantized condition

$$2k(N+1)d + \phi_B = 2n\pi, \tag{1}$$

and

$$\phi_B/\pi = [3.4\ \mathrm{eV}/(E_V - E)]^{1/2} - 1, \tag{2}$$

where N is the number of ALs, d is the interlayer spacing, ϕ_B is the phase due to the image potential, and E_V is the vacuum level. On the other hand, the image potential is formulated by

$$E_V - E = e^2/16\pi\epsilon_0 z, \tag{3}$$

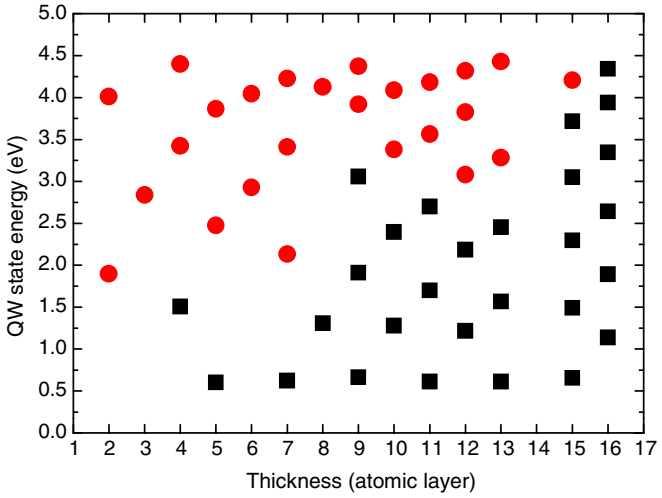

FIG. 3 (color online). Energies of quantum-well states at 0.1 nA versus island thickness. The energy shifts of quantum-well states behaving like the first (second) mode are marked by circles (squares).

where e is the electronic charge, ϵ_0 is the permittivity of free space, and z is the distance between the metallic surface and classical turning point. When $E = E_V$, z becomes infinite. It is found in Eq. (3) that ϕ_B is also infinite as $E = E_V$. In addition, ϕ_B increases as z increases if substituting Eq. (3) into Eq. (2). The relationship between ϕ_B and z can then be established, because a larger phase of the electronic wave is accumulated when the electron is at a larger distance.

When the electric field F is applied, the potential in the tip-sample gap is the superposition of the image potential and external potential eFz. Equations (1) and (3) would become

$$2k'(N+1)d + \phi'_B = 2n\pi, \tag{4}$$

and

$$E_V - E = e^2/16\pi\epsilon_0 z' - eFz', \tag{5}$$

where k', ϕ'_B, and z' are the modified wave vector, phase, and distance due to the electric field, respectively. Since ϕ_B is proportional to $(z)^{1/2}$, it is plausible to assume that ϕ'_B is also proportional to $(z')^{1/2}$. It is known from Eqs. (3) and (5) that $z' < z$ for the same E, and thus $\phi'_B < \phi_B$ for the same n. We can therefore conclude from Eqs. (1) and (4) that $k < k'$ for the same QW state. Previous studies have demonstrated that the energy of an empty QW state is linearly proportional to its wave vector [18,26]. Consequently, under the application of an electric field, a positive energy shift is the only choice for all QW states. Therefore, the existing model offers no explanation for the negative energy shift in the second mode. It is thus suggested that there should be an additional phase $\alpha > 0$ in the quantized condition, and Eq. (4) has to be modified as

$$2k'(N+1)d + \phi'_B + \alpha = 2n\pi. \tag{6}$$

By using Eqs. (1) and (6), it can be known that $k < k'$ when $\alpha < \phi_B - \phi'_B$, and $k > k'$ when $\alpha > \phi_B - \phi'_B$, corresponding to a positive and negative energy shift, respectively.

Using Eqs. (3) and (5), one can calculate $(z)^{1/2} - (z')^{1/2}$ as a function of F and E, as depicted in Figs. 4(a) and 4(b). Since $\phi_B - \phi'_B$ is proportional to $(z)^{1/2} - (z')^{1/2}$, Figs. 4(a) and 4(b) reveal that $\phi_B - \phi'_B$ would also increase with the increment of the electric field and energy, respectively. Therefore, the emergence of the second mode implies that α should have the following properties: (i) α can increase with enhancing the electric field, since the energy shift can be more negative, and (ii) α is thickness-dependent; otherwise, it is not possible to produce the distribution seen Fig. 3. With these two properties, we suggest that α originates from the local expansion of Pb islands along the surface normal, and the expansion is induced by the electric field. Owing to this expansion, the width of the quantum well in a Pb island would become wider, and the energies of its QW states becomes lower.

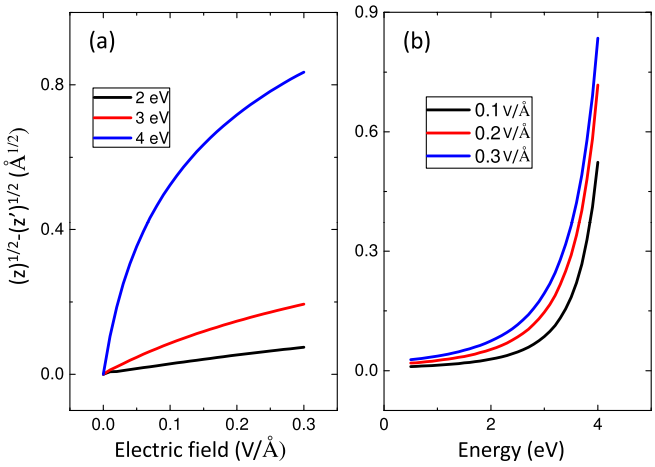

FIG. 4 (color online). (a) $(z)^{1/2} - (z')^{1/2}$ as a function of the electric field at different energies. (b) $(z)^{1/2} - (z')^{1/2}$ as a function of energy at different electric fields.

As a result, the competition between α created from the expansion and $\phi_B - \phi'_B$ due to the potential change determines that the energy shift is positive or negative. When α is always smaller than $\phi_B - \phi'_B$, Fig. 4(a) can explain the monotonically positive energy shift in the first mode. Since the spectra here were taken with the Z-V spectroscopy, it seems plausible to assume that QW states of different energies were probed under the same electric field. With this assumption, Fig. 4(b) can explain why the higher energy QW state reveals a larger positive energy shift, such as the results seen in Fig. 1(b). As evident in Figs. 4(a) and 4(b), α can be greater than $\phi_B - \phi'_B$ at a weaker electric field and a lower energy, and, therefore, QW states of lower energy appear to prefer the second mode.

Figure 3 shows that the second mode can gradually extend to a higher energy with the increase of the thickness, and the QW states of 16-AL islands all behave like the second mode. This implies that α can also increase with the increment of thickness to overcome a larger $\phi_B - \phi'_B$ at a higher energy. Hence, Fig. 3 simply reflects that the thicker island can have a larger expansion under the same electric field. We thus assume $\alpha = k' N \Delta d$, where Δd is the expansion of interlayer spacing. Since the total expansion $N\Delta d$ of an island is proportional to the number of ALs of its thickness, the situation is similar to the spring in series, where the total extension of springs is proportional to the number of springs subjected to an external force. In solid state physics, it is assumed that the potential between atoms in the crystal is a quadratic function. This is equivalent to treating a chain of atoms connected with springs. The distribution in Fig. 3 is essentially consistent with this assumption.

Since the peak energy of $n = 5$ in Fig. 1(a) is very close to that of $n = 16$ in Fig. 2(a), it is reasonable that ϕ'_B is the same for these two peaks. We can thus use Eq. (6) and $\alpha = k' N \Delta d$ to calculate the variation of Δd when the change of k' is known, which can be obtained by measuring the energy shifts of both peaks and utilizing the linear dispersion of energy versus wave vector [26]. When the current is changed from 0.1 to 10 nA, the variation of Δd is calculated to be about 0.01 Å, which is a minute expansion in comparison with $d = 2.86$ Å, the interlayer spacing of Pb crystal.

In the growth of Pb islands on a Cu(111) surface, about one monolayer of Pb is consumed in wetting the Cu substrate before the island's formation. This indicates that the bonding between Pb and Cu atoms is stronger than that between Pb atoms in the surface normal. Consequently, the expansion deformation can sustain in Pb islands under the electric field.

Ogawa *et al.* used the image potential, induced dipole potential, and external potential to explain the energy shift [20]. These potentials essentially have no thickness-dependent properties, and therefore it is not possible to explain the distribution shown in Fig. 3 if only these potentials are considered. In particular, these potentials would be also included in a recent density function theory calculation of Pb/Cu(111) [27]. The calculations have demonstrated that a positive energy shift is the only choice for QW states in Pb islands, which is inconsistent with the observation of the second mode in our work.

In this work, we display experimental evidence to verify that the Pb atoms on and below the surface can be lifted up to establish a local expansion in Pb islands under the STM measurement. The expansion would be directly related to the Young's modulus of the material. We suggest that it is possible to measure the Young's modulus of the thin film in the nanometer scale by using STM combined with atomic force microscopy. The former is used to detect the deformation utilizing the energy shifts of QW states, and the latter is used to measure the force of creating the deformation.

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