Electron relaxation in empty quantum-well states of a Pb island on Cu(111) studied by Z-V (distance-voltage) spectroscopy in scanning tunneling microscopy

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We use the Z-V (distance-voltage) spectroscopy in scanning tunneling microscopy to detect the linewidths of empty quantum-well (QW) states acquired from a Pb island grown on the Cu(111) substrate. It is found that the continual broadening of the linewidth can extend to the electronic states near the vacuum level. We apply the Fermi-liquid theory with the Fabry–Pérot mode to analyze the linewidths of the QW states, and obtain the electron-phonon coupling constant, the electron-electron coupling factor, and the product of the electron reflectivities at the surface and interface of the Pb island. © *2010 American Institute of Physics*. [doi:10.1063/1.3483241]

I. INTRODUCTION

Excitation and relaxation of electrons in a metal system play a key role in many of its physical and chemical behaviors, such as adsorption and desorption of molecules at the surface,[1,2] photochemical reactions,[3] optical processing of surfaces,[4] magneto-optical recording,[5] electrical charge and heat transport,[6,7] and so on. Near metal surfaces, an excited electron can relax, depending on energy, through the bulk electron states, surface state,[8,9] or the image potential states.[10–15] When this occurs in a thin metal film, the quantum-well (QW) states,[16–26] originating from the quantization of the wave vector of electrons in the surface normal, will get into play. Experimentally, the lifetime of excited electrons in a QW state can be detected by the spectral linewidth of that state, as often practiced in the photoemission spectroscopic measurements[20,27–31] for a filled state. The similar properties of empty states are usually acquired by the two-photon photoemission spectroscopy[32,33] and scanning tunneling spectroscopy (STS).[34,35] It is well recognized that the energy dependence of a linewidth involves two main relaxation mechanisms, i.e., the electron–electron and electron–phonon interactions. One can thus quantitatively obtain the electron-phonon coupling (EPC) constant and electron-electron coupling (EEC) factor from the linewidth analysis.

Using I-V (current-voltage) spectroscopy in STS, previous studies have demonstrated the properties of the electron relaxation in empty QW states on the systems of Yb/W(110) (Ref. 34) and Pb/Si(111).[35] Both studies show that the linewidth of the QW states increases with energy above the Fermi level. However, this increasing tendency has been observed in a limited extent of 2 eV from Fermi level because this is the bias range normally set by using I-V spectroscopy. It is natural to ask if the increasing tendency can extend to the vacuum level but it remains to be answered. Moreover, the linewidth widening of the QW states was revealed in previous studies[34,35] by collecting the linewidths from spectra of different thicknesses, which entailed the sporadic feature in the demonstration of linewidth versus energy. It can be expected that the sporadic feature would be eliminated as long as the linewidths of QW states are collected from the spectrum of the same thickness. In this work, we use scanning tunneling microscopy (STM) operated in the Z-V (distance-voltage) mode to detect the empty QW states from near the Fermi level to vacuum level for the Pb islands on Cu(111) surfaces. It is found that the linewidth can widen constantly up to near the vacuum level. Using the Z-V spectroscopy, we have observed nine QW states on the Pb island with a single thickness of 27 atomic layers, and demonstrated the smooth characteristics of the change in linewidth as function of energy. The extracted linewidths are further analyzed by the Fermi-liquid theory combined with the Fabry–Pérot modes.[27] The EPC constant, the EEC factor and the energy dependence of the product of electron reflectivities at the Pb surface and Pb/Cu interface are also acquired.

II. EXPERIMENT

Previous studies have demonstrated that Pb can be grown into flat islands with (111) orientation on Cu(111) surface at room temperature and their electronic structures display characteristics of the QW states.[36] In our experiment, the Cu(111) surface was treated with cycles of ion beam sputtering and annealing at 600 °C. For creating Pb islands, Pb was evaporated onto the Cu surface at room temperature with a flux of 0.03 monolayer (ML) per minute. The sample was then transferred to a homebuilt STM operating at 4.3 K. In contrast to the conventional I-V spectroscopy, we use the Z-V spectroscopy to probe higher energy QW states. For a Z-V measurement, the tip trajectory was recorded with an active feedback, while the sample bias was ramped from 0.5 to 5 V. Differentiation of the Z-V spectrum was performed by a numerical method.

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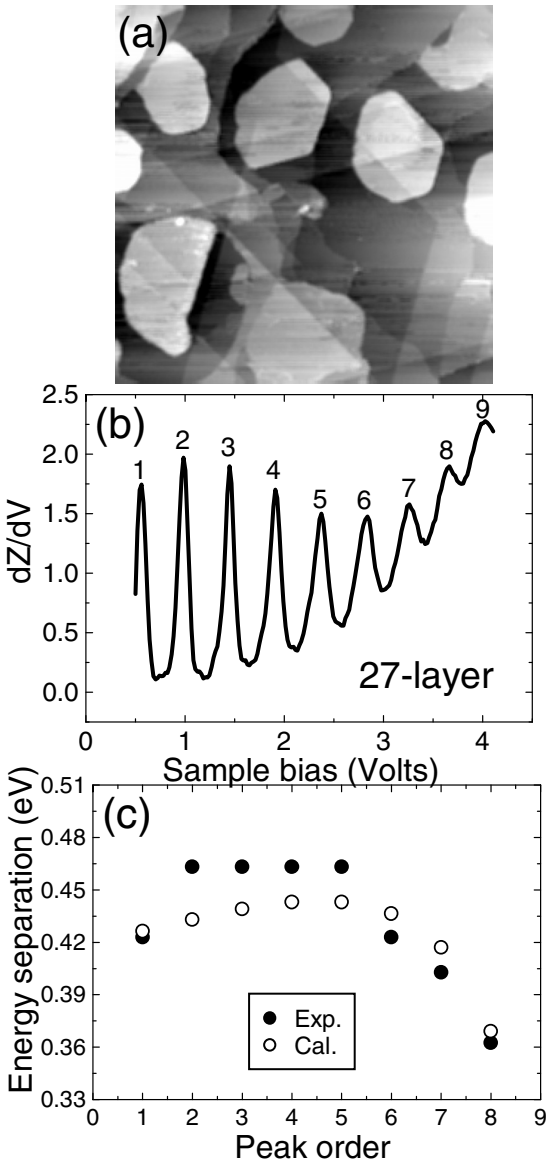

FIG. 1. (a) The growth of Pb islands on Cu(111) surface at room temperature at the coverage of 2.1 ML. The image size is 100×100 nm^2. (b) dZ/dV-V spectrum acquired on the island of 27-layer thickness. The numbers marked close to the peaks denote the order of a QW state. (c) Energy separation of adjacent peaks as function of the order.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a typical topographic image of the Pb film grown on Cu(111) surface with a coverage of 2.1 ML. Before the formation of islands, about 1 ML Pb was consumed in wetting the Cu(111) substrate and the rest grew into islands above the wetting layer. Islands of various thicknesses were observed because the growth is not layer by layer, and the thickness was measured against the exposed wetting layer. When the wetting layer is covered by the film completely, the thickness can be distinguished by the QW states because they are sensitive to the thickness. Figure 1(b) displays dZ/dV-V spectrum acquired on the Pb island with a thickness of 27 atomic layers in the energy range of 0.5–4.2 eV above the Fermi level. It can be seen that there are nine peaks in the spectrum, which are the well-known QW states. The numbers marked close to the peaks denote the order of a QW state. Figure 1(c) depicts the energy separation (solid circles) of the adjacent peaks as a function of the order corresponding to the low-energy one of the adjacent peaks. According to the finite square well model in quantum mechanics, the energy separation should widen with the order. However, Fig. 1(c) reveals that the widening feature only appears at order two. The energy separation is a constant from order two to order five and even shrinks from order five to order eight. Therefore, it is obvious that these QW states cannot be described by the square well model. This is due to the fact that the potential form in the island near the vacuum level is not a simple square shape but should include the contribution of the image potential. Our previous study[26] has demonstrated that the shrinking behavior of the energy separation can be reasonably explained with the phase accumulation model formulated by

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

where k is the wave vector and N is the number of atomic layer of island and d is interlayer spacing of 2.86 Å. ϕ_B is a phase factor for counting the effect of the image potential, and

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

where E_V is the vacuum level which is 4.6 eV above the Fermi level and E is the energy of the QW state and $\hbar^2k^2/2m^*=E+E_F$. Using Eqs. (1) and (2), the energy separations of the adjacent states are calculated for N=27, as shown in Fig. 1(c) (open circles). It is evident that calculated results are in agreement with the experimental measurements, implying that it is necessary to take the image potential into account for understanding the energy levels of empty QW states in the real system.

The spectrum in Fig. 1(b) is further analyzed by using the fitting of a series of Lorentzian peaks for understanding the electron relaxation in QW states of different energies, as shown in Fig. 2(a). The linewidth of each QW state is thus extracted from the fitting. Figure 2(b) shows the linewidth as a function of energy of QW state. It can be seen that the linewidth widens as the energy increases, indicating that the lifetime of the excited electron in QW states is shorter at higher energy. This result is basically consistent with the one observed by using I-V spectroscopy,[34] manifesting that the Z-V spectroscopy is appropriate to study the electron relaxation as well. However, the advantage of using Z-V spectroscopy is that the relaxation of the excited electron at an energy near the vacuum level can be detected, which is not readily available for using I-V spectroscopy.

When the film thickness is not thick enough, the number of QW states is few. In previous studies,[34,35] for revealing the energy dependence with a sufficient energy resolution, the linewidths of QW states acquired on the metal films of different thicknesses had to be collected. Nevertheless, the linewidths extracted from the film of different thicknesses are liable to suffer from a more scattered result, which also appears in our work. For example, Fig. 3(a) shows the dZ/dV-V spectra of thickness range from five to eight atomic layers. It can be seen that there are only three or four QW states in each spectrum. Using the Lorentzian fitting to

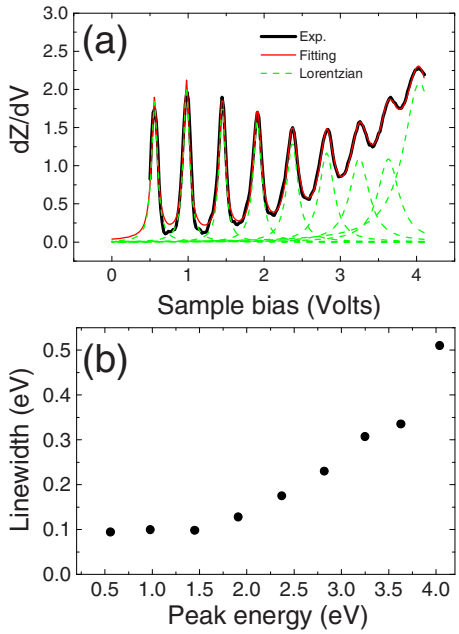

FIG. 2. (Color online) (a) The spectrum in Fig. 1(a) is analyzed by using the fitting of a series of Lorentzian peaks for extracting the linewidth of each peak of QW state. (b) The extracted linewidth as function of peak energy.

extract the linewidths of QW states for all spectra in Fig. 3(a), the extracted linewidth versus the energy of QW state are collected in Fig. 3(b), revealing a sporadic feature similar to previous studies. Recently, the linewidth of the QW states in Pb films on Ag(111) has been studied using the Z-V mode combining with the lock-in technique,[37] again showing that sporadic feature is inevitable. In comparison with Fig. 2(b), it is obvious that the linewidths extracted from the single spectrum of a Pb island reflect a smoother energy dependence.

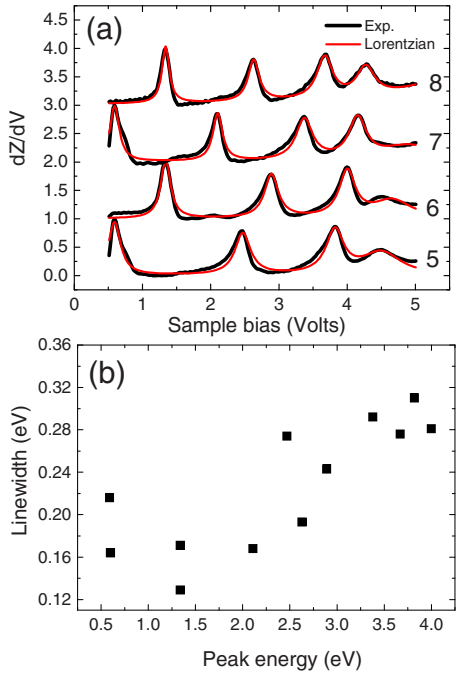

FIG. 3. (Color online) (a) dZ/dV-V spectra of thickness range from five to eight atomic layers and Lorentzian fittings. (b) Extracted linewidths of peaks of all spectra in (a) vs peak energy.

When an electron tunnels into an empty QW state, it can relax to the ground state through inelastic scattering with electrons and phonons. In terms of Fermi-liquid theory,[38] the electron-electron and electron-phonon scattering can be formulated by

$$\Gamma = \Gamma_0 + 2\beta(\mathrm{E} - \mathrm{E_F})^2, \tag{3}$$

where Γ is the inverse lifetime, i.e., the intrinsic linewidth and Γ_0 is related to the electron-phonon scattering and β is the EEC factor. Qualitatively, Eq. (3) can explain why the linewidth may increase with increasing the energy because of the quadratic dependence of energy. However, owing to the electron excitation is through the empty QW state originating from that the electron wave bounces between the Pb/Cu interface and surface, the measured linewidth should include the influence of the reflectivities at the interface and surface. Paggel *et al.*[27] are the first to utilize the Fabry–Pérot modes in the optics to realize the linewidth broadening due to the reflectivity. Here we also use the same formalism to analyze the extracted linewidth δE that follows:

$$\delta E = \Gamma \eta \frac{1 - R\exp(-1/\eta)}{R^{1/2}\exp[-1/(2\eta)]}, \tag{4}$$

where R is the product of the reflectivities at the surface and interface, and $\eta = L/(Md)$ where L is mean free path, M is equal to N+1 (Ref. 26), and d is interlayer spacing. R is assumed to have a quadratic dependence of sample bias similar to previous study,[27] i.e., $R = \mathrm{a} \times \mathrm{E_S^2} + \mathrm{b} \times \mathrm{E_S} + \mathrm{c}$, where $\mathrm{E_S}$ is sample bias voltage and a, b, and c are constants. L is equal to electron velocity v times h/Γ. The electron velocity v (Ref. 39) is obtained from the dispersion relation fitted in the experiment (not shown) and h/Γ is the electron lifetime due to uncertainty principle. Substituting Γ in Eq. (3) into Eq. (4), the extracted linewidth δE can be fitted by adjusting unknown constants: Γ_0, β, a, b, and c. Hence, based on this formalism, it is possible to obtain the five constants from a spectrum of single thickness as long as it has at least six QW states for the fitting. Here this method is named single thickness analysis (STA). Since Fig. 2(b) displays nine extracted δEs, the first six ones is chosen for performing the optimum fitting [circles in Fig. 4(a)] to determine the constants using STA. The determination of the constants leads to acquire the intrinsic linewidth as marked by triangles in Fig. 4(a) and the energy dependence of R shown in Fig. 4(b), which is represented by $R = -0.074 \times \mathrm{E_S^2} + 0.222 \times \mathrm{E_S} + 0.6535$. Moreover, owing to the thickness dependence of η, the extracted linewidth should be also dependent on thickness, which may be a factor resulting in the sporadic feature in Fig. 3(b).

However, if Γ and R are not the quadratic dependence on energy, the STA might not be valid. This can be examined by another method[27,40,41] which is termed multiple thickness analysis (MTA) here. In the MTA, Eq. (4) is still used but there is no assumption of the energy dependence for Γ and R. For acquiring Γ and R at some energy, one needs to find QW states with the same energy from spectra of two different thicknesses and measure their individual δE. Then Γ and R can be calculated from two measured δEs with Eq. (4). By inspecting spectra of thicknesses from 10 to 17 layers,[26] we can find out QW states whose energies coincide with the first

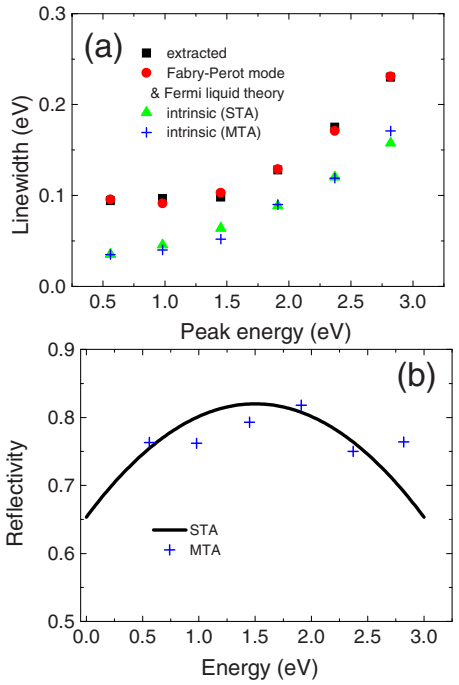

FIG. 4. (Color online) (a) The extracted linewidths in Fig. 2(b) are fitted by the Fermi-liquid theory combining with the Fabry–Pérot modes to obtain the intrinsic linewidths as marked by triangles (STA method). The crosses mark the intrinsic linewidths obtained by the MTA method. (b) The energy dependences of the product of electron reflectivities at the interface and surface obtained by the STA and MTA.

six peaks in the 27-layer spectrum in Fig. 1(b) to calculate Γ and R of different energy. It can be seen that Γ and R obtained with MTA, marked by crosses in Figs. 4(a) and 4(b), are close to the ones with STA. This implies that the assumption of quadratic dependence of Γ and R is valid in STA.

Using STA, Γ_0 and β obtained from the intrinsic linewidth are 30.2 meV and 0.008 V^{-1}, respectively. Γ_0 is related to the electron-phonon scattering, which is expected to depend slightly on energy and can be assumed as $\Gamma_0 = 2\pi\lambda k\theta_D/3$,[42] where θ_D is the Debye temperature and λ is the EPC constant. It is known that θ_D is 105 K for Pb,[43] and thus $\lambda = 1.59$ is acquired from the known Γ_0. This value is consistent with the prediction of calculations[44–47] and the ones acquired from experiments for thin Pb islands.[35,48] The quadratic term in Eq. (3) is related to the electron-electron scattering and $2\beta = 0.0025 r_s^{5/2}$ V^{-1}, where r_s is the electron dimensionless radius parameter. For the Pb bulk crystal, $r_s = 2.30$ (Ref. 43) one obtains $2\beta = 0.020$ V^{-1}. Here, the EEC factor $\beta = 0.008$ V^{-1} obtained from 27-layer Pb island is slightly smaller than $\beta = 0.01$ V^{-1} for bulk crystal. The EPC constant and EEC factor derived from the spectra taken by the Z-V spectroscopy here are comparable to the values in the previous studies.[35,48]

We tested our analytical model again on the spectrum [referring to Fig. 5(a)] acquired on the 21-layer island, involving seven QW states. The first six peaks are used for STA and MTA. As shown in Fig. 5(b), the linewidths of QW states extracted from the spectrum reveals the familiar smooth energy dependence. The intrinsic linewidths are obtained by using both STA and MTA, as marked by triangles and crosses in Fig. 5(b), respectively. However, it can be

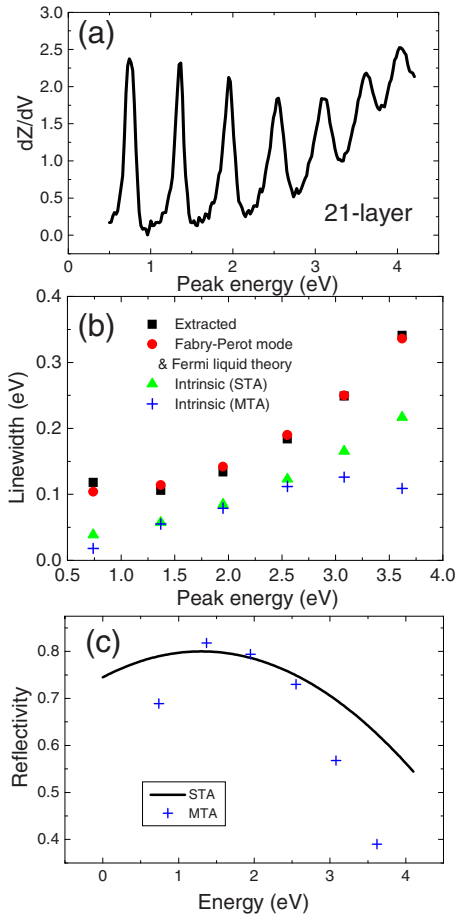

FIG. 5. (Color online) (a) dZ/dV-V spectrum acquired on the island of 21-layer thickness. (b) The extracted linewidths in (a) are fit to obtain the intrinsic linewidths (STA). The crosses mark the intrinsic linewidths obtained by the MTA method. (c) The energy dependences of the product of electron reflectivities obtained by the STA and MTA.

seen that the results of STA and MTA are not consistent for the energy beyond 3 eV from the Fermi level, i.e., one shows increasing tendency with the energy but the other reveals opposite trend. Figure 5(c) also shows that the products of electron reflectivities obtained by STA deviate from the ones by MTA as the energy is above 3 eV. Note that the energy of the sixth peak in the 27-layer spectrum is 2.82 eV and that of the fifth peak in the 21-layer spectrum is 3.1 eV, and thus it seems that there is a boundary around 3 eV beyond which the formalism is not valid. This boundary appears in the analysis of the 27-layer spectrum as well (not shown). Although the STA is valid in a range of 3 eV, it can be used to obtain the reasonable EPC constant and EEC factor with sufficient QW states, indicating that it is useful to understand the electron relaxation. Hence, a criterion is suggested here for performing the STA based on Eq. (4) that the spectrum should involve at least six QW states within 3 eV from the Fermi level.

IV. CONCLUSIONS

In summary, we have demonstrated that the QW states observed by the Z-V spectroscopy exhibit the increasing trend of the linewidth broadening with energy, similar to those observed by the I-V spectroscopy in previous studies.

However, it is found that the linewidth can widen constantly up to near the vacuum level, which was not observed before. Moreover, it is shown that the linewidths extracted from the spectrum of single thickness possess much smoother feature in comparison with the ones collected from the spectra of different thicknesses. The EPC constant and EEC factor can thus be consistently acquired from the analysis of a single spectrum with sufficient numbers of the QW states, which can be achieved by employing the Z-V spectroscopy.

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