Stark shift of transmission resonance in scanning tunneling spectroscopy

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(Received 26 July 2006; published 31 October 2006)

It is known that free electrons scattered by the quantum well in the metal film may manifest the transmission resonance and it can be probed by scanning tunneling spectroscopy (STS). We use STS to observe the transmission resonance on Ag films grown on the Si(111)7×7 surface. In addition to revealing the signal of the transmission resonance in the tunneling spectrum, there also appears that its energy level can be shifted by tuning the tunneling current, i.e., the electric field in the tunneling gap. Our results demonstrate that the transmission resonance is shifted to higher energies with increasing the electric field, but beyond a critical field it may drop to lower energy discontinuously. This field-dependent behavior can be qualitatively explained by a field-induced phase variation in the quantization rule.

DOI: 10.1103/PhysRevB.74.155330 PACS number(s): 73.21.Fg, 68.37.Ef, 68.55.Ac

Transmission resonance is a quantum phenomenon of the free electron scattered by a one-dimensional potential well in the metal film. It originates from the interference of the electron waves, which are reflected from the film surface and the film-substrate interface. Electrons with energy-matching levels of the transmission resonance can, in principle, transmit the well without suffering any reflection loss.[1] In the real systems, transmission resonance can be observed by the low-energy electron transmission spectroscopy[2] (LEETS) for some free-electron-like metal films such as Ag and Cu films.[3] Chung *et al.* have demonstrated that the thickness of Ag films grown W(110) can be discriminated by probing the transmission resonance using low-energy electron microscopy.[4] These previous studies clearly demonstrate a common feature, i.e., when the film thickness increases, the energy levels of transmission resonance prominently shift toward the vacuum level and the separation between them reduces subsequently. This thickness-dependent trend agrees with the prediction of the quantum theory.

The first observation of transmission resonance by the scanning tunneling spectroscopy (STS) was reported by Kubby *et al.* on the $\sqrt{3}\times\sqrt{3}$ Sn/Si(111) surface.[5] However, one cannot unambiguously conclude that their observation is of transmission resonance because there was no report of thickness-dependent behavior. Recently, we used STS to probe the electronic structure, above the vacuum level, of Ag film grown on Si(111)7×7 surface.[6,7] We also observe the signal, which is similar to that observed by Kubby *et al.* The energy level of this signal significantly moves toward the vacuum level with increasing film thickness. When the film is thick enough, the signal can occur twice in the biasing voltage range and the energy separation between them decreases with increasing thickness. This thickness-dependent behavior is consistent with previous studies using LEETS.[3] We thus confirm that the transmission resonance can be probed by STS.

Recently, Limot *et al.* presented STS measurements on surface-state binding energy E_0 and concluded that the surface state[8–10] can be shifted by the electric field between the tip and the sample.[11] This observation motivates us to infer that the electric field may, likewise, shift the levels of transmission resonance. Our experimental results demonstrate that the transmission resonance indeed can be displaced to higher energy with increasing electric field. To explain this phenomenon, we introduce a field-induced phase variation in the quantization rule, and the calculated results show that the shifting of the transmission resonance agrees qualitatively with experimental observation. In addition, the calculation also predicts that beyond a critical field, the transmission resonance may drop discontinuously to lower energy. This abrupt change has been observed in our system as well.

In our experiment, flat silver films with the (111) face were grown by depositing silver on Si(111)7×7 at room temperature[12] with a flux of 0.26 ML per minute. Vacuum during the deposition was kept below 2×10^{-10} torr. After deposition, the sample was transferred to a homebuilt STM in which the sample was cooled to 109 K. The electronic structures of Ag films were measured by the *Z-V* spectroscopy. In a *Z-V* measurement, the tip trajectory was recorded with an active feedback at a set tunneling current, while the sample bias was ramped from 2 to 9 V. A dither voltage of 30 mV at a frequency of 5 kHz was added to the sample bias. The amplitude of modulated tunneling current was extracted by a lock-in amplifier. During the acquisition of a *Z-V* spectrum, the signal from the lock-in amplifier is recorded simultaneously to obtain a spectrum similar to the dZ/dV-V curve.

Figure 1(a) shows *Z-V* spectra acquired on the five-layer film under various set tunneling currents. It is clear that spectra begin to split up when the sample bias V exceeds 3.5 V, indicating that the electron tunneling starts to enter the field-emission regime after this bias. The splitting of the spectra is due to the fact that the feedback system has to control a smaller tip-sample distance to establish a stronger electric field for emitting a larger field-emission current from tip, and vice versa. Therefore the withdrawn distance ΔZ of the tip decreases with increasing current at the same bias, as shown in Fig. 1(a). Figure 1(b) displays the spectra obtained by the lock-in technique, and each spectrum, depending on colors, is acquired simultaneously with each *Z-V* spectrum in Fig. 1(a). In each spectrum, we can observe four peaks of well-known standing-wave states in the tunneling gap,[13,14] marked

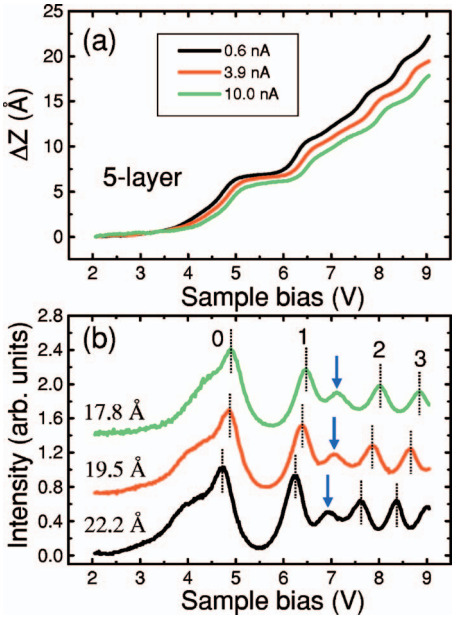

FIG. 1. (Color) (a) *Z-V* spectra acquired on the five-layer film at a different current. (b) Spectra obtained by the lock-in technique, and each spectrum, depending on color, is acquired simultaneously with each *Z-V* spectrum in (a). Arrows and dashed lines mark the energy levels of the transmission resonance and standing-wave states, respectively.

by numbers and one transmission resonance indicated by an arrow. In our observation, the spectral intensity of the standing-wave state is usually larger than that of the transmission resonance, allowing us to distinguish one from the other. Since the electric field is directly related to $1/\Delta Z$, here we use ΔZ of *Z-V* spectra at 9 V to indicate the tunneling condition, as written at the left-hand side of each spectrum. The electric field is thus strongest while the green spectrum was acquired. Consequently, the energy levels of standing-wave states, as indicated by dashed lines, are higher than those in the red or black spectrum. This observation can be interpreted with the model of quantized states formed in a potential well in the tip-sample gap.[13] However, we also observe that the energy level of the transmission resonance moves toward higher energy with decreasing ΔZ, as indicated by the arrows. Figure 2 shows the energy level of the transmission resonance as a function of $1/\Delta Z$. Since the

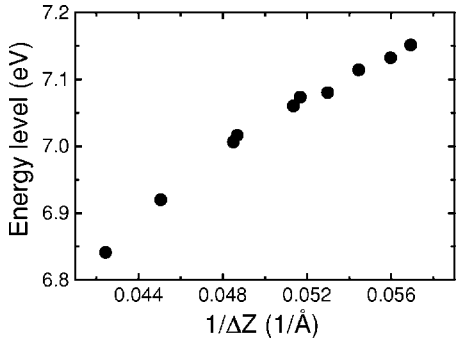

FIG. 2. Energy levels of the transmission resonance of the five-layer film as a function of $1/\Delta Z$.

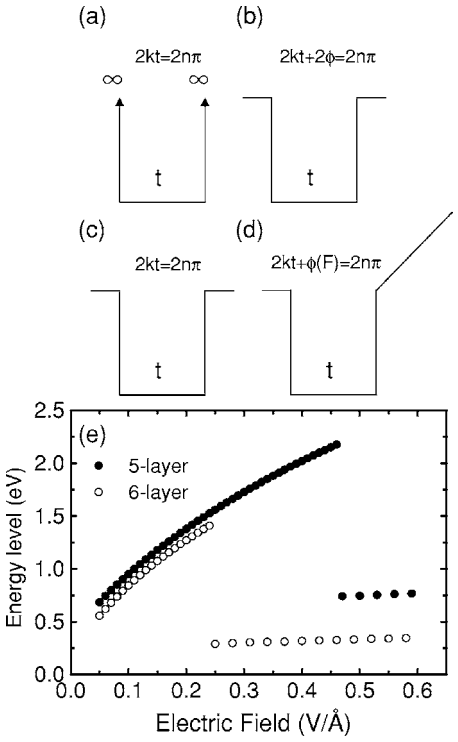

FIG. 3. Quantization rules for quantized states in (a) infinite square well and (b) finite square well and for transmission resonance in (c) square well and (d) square well combined with an accelerating field. (e) Calculated energy level of the transmission resonance as a function of the electric field for the five-layer and the six-layer film.

electric field is approximately proportional to $1/\Delta Z$, Fig. 2 implies that the transmission resonance can be monotonically shifted to a high energy with increasing the electric field. This was not noticed even in another work of Kubby *et al.*[15] The shifting is about 290 meV as the set current is adjusted from 0.6 to 10 nA, which is much larger than the shifting of the surface state, i.e., only 1–2 meV, under a similar condition.[11]

According to quantum mechanics, the condition for the transmission resonance to occur is[1]

$$2kt = 2n\pi, \tag{1}$$

where n is an integer, k is a wave vector of electrons in the square potential well, and t is the width of the well. In addition,

$$\hbar^2 k^2/2m = E + V, \tag{2}$$

where E is the energy of free-electron matching the transmission resonance and V is the depth of the well. It is interesting to note that Eq. (1) is exactly the quantization rule of the quantized states in the infinite square well[1] as shown in Fig. 3(a). For a finite square well as shown in Fig. 3(b), the quantization rule should include a phase because the electron in the well can penetrate into the potential barrier,[15] and it becomes

$$2kt + 2\phi = 2n\pi. \quad (3)$$

It is known that ϕ can be obtained by the following equation:[16]

$$\phi = 2\tan^{-1}(\psi'/k\psi), \quad (4)$$

where ψ and ψ' is the wave function and its differentiation on the barrier side. Since the transmission resonance of the free electron scattered by a square well, as shown in Fig. 3(c), follows the same quantization rule of quantized states in an infinite square well, it is plausible to analogously introduce an extra phase in the quantization rule when the electron is in an accelerating field instead of in a free space, as shown in Fig. 3(d). This phase is field dependent and we assume that it also obeys Eq. (3). As the accelerating field F is applied to the vacuum side, the phase only appears at vacuum/Ag interface and the quantization rule becomes

$$2kt + \phi(F) = 2n\pi. \quad (5)$$

Based on the above argument, we can calculate the energy level of the transmission resonance at a different electric field. In the calculation, we use the potential form in Fig. 3(d) to approximate those in the tip-sample gap (triangular potential) and in the Ag film (square potential). It is known that the wave function in a triangular potential well[15,17] is the Airy function A_i.[18] At the vacuum/Ag interface

$$\psi'/\psi = (2meF/\hbar^2)^{1/3}A_i'(g)/A_i(g), \quad (6)$$

$$g = -(2m)^{1/3}E/(\hbar eF)^{2/3}, \quad (7)$$

where E is the total energy of electron in the triangular potential and F is the electric field. Since the transmission resonance is shifted toward higher energies, according to Eq. (5), $\phi(F)$ should be negative. In addition, V is 8 eV^3 and t is equal to layer number $\times 2.5$ Å for a Ag film in the calculation. Using Eq. (2) and Eqs. (4)–(7) as well as $n=6$ and 7 for five-layer and six-layer films, respectively, the variations of the transmission resonance with the electric field for these films are calculated. Figure 3(e) shows that the calculated transmission resonance of the five-layer film is monotonically shifted to high energy with the electric field, qualitatively agreeing with our observation. However, the calculation also predicts that beyond a critical field, the transmission resonance should drop to lower energy discontinuously. This abrupt change comes from the fact that the phase ϕ is limited to the range of 0 to $-\pi$ for Eq. (4) and it is negative. Before the appearance of the discontinuous drop, the phase negatively increases with increasing electric field, resulting in the monotonic shift of the transmission resonance. When the critical electric field is applied, the phase is equal to $-\pi$. The phase should return to 0 for preserving a given n in Eq. (5) as the electric field exceeds the critical strength, causing a discontinuous drop of the transmission resonance. The calculation also reveals that the shifting after a discontinuous drop becomes much slower. This result is due to the fact that with increasing the electric field, the changing rate of the Airy function is close to that of its differentiation after the discontinuous drop of the transmission resonance, causing the negative increment of the phase to be slow as the electric field increases. These characteristics of calculated field-dependent transmission resonance are similar in the calculation for the six-layer film. However, it is obvious that the critical field of the six-layer film is much lower than that of the five-layer film. This indicates that the phenomenon of the discontinuous drop, which is not observed on the five-layer film because of the requirement of a stronger electric field, may be observable for the six-layer film.

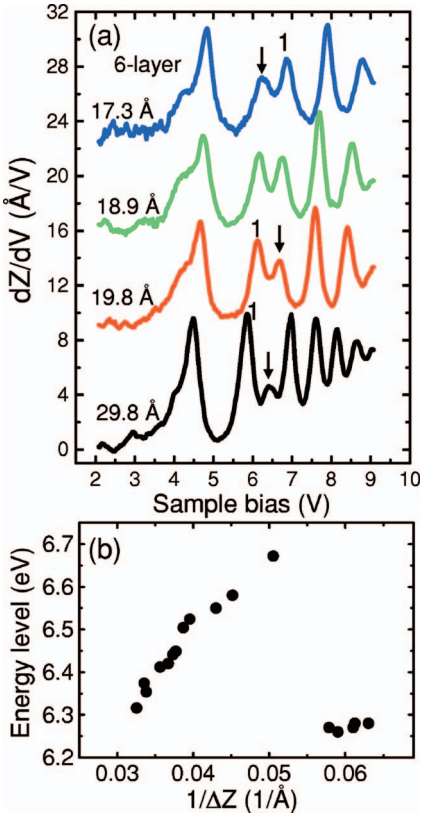

FIG. 4. (Color) (a) dZ/dV-V spectra acquired on the six-layer film at different ΔZ (electric field). (b) Energy levels of the transmission resonance of the five-layer film as a function of $1/\Delta Z$. There appears a discontinuous drop of the transmission resonance in an energy level.

Figure 4(a) shows dZ/dV-V spectra acquired on the six-layer film at a different electric field. From the withdrawn distance ΔZ indicated at the left-hand side of each spectrum, we can know that the electric field of the blue curve is stronger than that of the red curve. Both red and blue curves reveal signals of the transmission resonance as marked by arrows. However, it is obvious to see that the energy level of the transmission resonance in the blue curve is lower than that in the red curve by about 0.4 eV. In addition, we did not observe that the transmission resonance is lowered with decreased ΔZ gradually. The only intermediate situation for a medium electric field, as shown in the green curve, is that the spectral intensity of the transmission resonance is comparable to that of a standing-wave state, in which the transmission resonance is hard to be identified. Therefore, the lowering of the transmission resonance is discontinuous as the electric field is beyond a critical field. This is qualitatively consistent with the prediction of the calculation. The black

curve in Fig. 4(a) shows a case of weaker electric field, in which the energy level of the transmission resonance, marked by an arrow, is lower than that in the red curve. Figure 4(b) shows the energy level of the transmission resonance of the six-layer film as a function of $1/\Delta Z$, in which a discontinuous drop is observed. When the electric field is below the critical field, the transmission resonance is shifted to high energy with increasing the electric field, the same as the case on the five-layer film. After the occurrence of the discontinuous drop, it is obvious that the transmission resonance becomes hardly able to be shifted by the electric field, in agreement with the calculation. Furthermore, the critical field corresponds to $1/\Delta Z$ about 0.05 in Fig. 4(b). This value is in the range of $1/\Delta Z$ of Fig. 2 but in which there is no observation of the discontinuous drop. It indicates that the critical field of the six-layer film is indeed weaker than that of the five-layer film. In Fig. 4(a), the energy level of the standing-wave state marked by 1 in the red and black curves is lower than that of the transmission resonance whereas their energy levels are exchanged in the blue curve. This phenomenon is due to the fact that the appearance of the transmission resonance can push its following standing-wave states to higher energies, which has been observed by Kubby *et al.*[5] and also our recent study.[6] Therefore, the transmission resonance may drop to an energy level low enough to push the standing-wave state 1 to higher energy, appearing that both of the energy levels are exchanged.

The phenomenon of the discontinuous drop of the transmission resonance actually appeared in the work of Kubby *et al.*[15] In Fig. 6 of their report, the authors show the spectra acquired on the $\sqrt{3}\times\sqrt{3}$Sn/Si(111) surface at the different electric field, which can be judged from the amount of standing-wave states, i.e., fewer ones indicate a stronger electric field. By carefully identifying the transmission resonance in their spectra, one can find that its energy level at the strongest electric field is lower than that at the weakest electric field. This indicates that the transmission resonance in this system may also experience a discontinuous drop with increasing electric field. In addition, the spectrum acquired at the medium electric field also exhibits the phenomenon of being unable to distinguish the transmission resonance and the nearby standing-wave state, similar to our observation.

In summary, we have observed that the transmission resonance probed by STS on Ag thin films can be shifted by the electric field in the tunneling gap. A monotonic upward shifting with increasing the electric field is observed on the five-layer film. Although it also appears on the six-layer film, the transmission resonance can drop to lower energy discontinuously as the electric field is beyond a critical strength. These field-dependent phenomena can be qualitatively explained by introducing a field-induced phase variation in the quantization rule. Due to the influence of the electric field, the measurement of the surface-state binding energy E_0 by STS is lower than that by photoemission spectroscopy.[11] Our observation of the field-dependent behavior thus suggests that a discrepancy between STS and LEETS measurements for the energy level of the transmission resonance may also exist.

The authors would like to acknowledge C. S. Kuo, C. Y. Lin, and C. H. Hsieh for assisting in the constructing of the STM. This work was supported by the National Science Council, Academia Sinica, and the project of Academic Excellence of the Ministry of Education of Taiwan.

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