Japanese Journal of Applied Physics **50** (2011) 08LB01 **REGULAR PAPER**
DOI: 10.1143/JJAP.50.08LB01

Disappearance of Lowest-Order Transmission Resonance in Ag Film of Critical Thickness

Shin-Ming Lu[1,2], Hsu-Hsing Huang[2,3,4], Wei-Bin Su[1,2], Pei-Hong Chu[1,2], Chia-Seng Chang[2], Hsi-Lien Hsiao[1], and Tien Tzou Tsong[2]

[1]*Department of Physics, Tunghai University, Taichung 407, Taiwan, R.O.C.*
[2]*Institute of Physics, Academia Sinica, Taipei 115, Taiwan, R.O.C.*
[3]*Taiwan International Graduate Program, Academia Sinica, Taipei 115, Taiwan, R.O.C.*
[4]*Department of Physics, National Taiwan University, Taipei 106, Taiwan, R.O.C.*

Received January 14, 2011; accepted March 24, 2011; published online August 22, 2011

The quantum phenomenon of the transmission resonance can be observed in Ag films grown on a Si(111)7×7 surface using scanning tunneling spectroscopy. It is found that the energy of the transmission resonance moves toward lower energy with increasing film thickness. The formula used is derived from quantum mechanics to demonstrate that this lowering in the transmission resonance energy is proportional to $(w+1)^2/w^2$, where w is the number of atomic layers of film thickness. This relation is justified by experimental results, but only holds for thinner films. The formula also predicts that the lowest-order transmission resonance should disappear when the Ag film reaches its critical thickness. This disappearance of the transmission resonance has also been experimentally confirmed in the dI/dV spectrum.

1. Introduction

In quantum mechanics, the transmission resonance indicates a situation where particles, e.g., electrons penetrate a one-dimensional square well without reflection.[1)] The condition for this situation is $kt = n\pi$, where k is the wave vector of electrons in the square well with a width t and n is the quantum number. Although a similar condition is also applied to the formation of quantum-well states,[2–14)] the transmission resonance is related to the scattering of electrons, which is different from the quantum-well states originating from the confinement of an electron in a square well. In reality, one can observe the transmission resonance in metal films by using low-energy electron transmission spectroscopy,[15,16)] and scanning tunneling microscopy and spectroscopy (STM and STS, respectively).[17,18)] Previous studies of Ag films have shown that the energy of the transmission resonance shifts toward lower energy when the film thickness is increased.[16,18)] Since the transmission resonance originates from electrons scattered by metal films, its energy level should be higher than the vacuum level of the metal film. Hence, the lowering tendency should be terminated at a certain thickness; however, this has neither been experimentally observed nor studied.

In this work, the formula is derived from the emergent condition of the transmission resonance. The derived formula reveals that the energy–thickness relation depends on the inner potential, interlayer spacing, and effective mass of electrons in the film. For Ag films, the energy of the transmission resonance is proportional to $(w+1)^2/w^2$, where w is the number of atomic layers of film thickness. It is found that the experimental data of the transmission resonance fits this relation very well, confirming the validity of the formula. However, the formula derivation also reveals that it holds only for thinner films. The transmission resonance will experience a discontinuous jump when the film is thick enough, which is due to the disappearance of the transmission resonance of the lowest order. We use STS to study Ag films grown on the Si(111)7×7 surface and have observed that the lowest order transmission resonance indeed vanishes at a critical thickness of 27 atomic layers.

2. Experimental Procedure

In this experiment, flat silver films with the (111) face were grown by depositing silver on Si(111)7×7 at room temperature.[19)] The Si(111)7×7 surface was obtained by annealing the sample at 1400 K and then slowly cooling it to room temperature. After silver deposition, the sample was transferred to a laboratory-built STM in which the sample was cooled to 120 K. The transmission resonance of the Ag films is observed by Z–V spectroscopy combined with the lock-in technique. In the Z–V measurement, the tip trajectory is recorded with an active feedback at a set tunneling current, while the sample bias is ramped from 2 to 9 V. A dither voltage of 30 mV at a frequency of 5 kHz is added to the sample bias. The amplitude of modulated tunneling current is 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 dI/dV–V spectrum in which the transmission resonance appears.

3. Results and Discussion

The wave vector k under the emergent condition of transmission resonance

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

follows

$$\frac{\hbar^2 k^2}{2m} = E + U, \tag{2}$$

where E is the energy of the incident electron and U is the depth of the square well. Since the transmission resonance can be experimentally observed, it is plausible to assume that there exists a one-dimensional square well in the metal film in the normal direction and that the width of the square well is equal to the film thickness. The width t is discretely increased by increasing the atomic layer of film thickness, and thus

$$t = wd, \tag{3}$$

where d is the interlayer spacing. Substituting eqs. (1) and (3) into eq. (2), it becomes

$$\frac{\hbar^2 n^2 \pi^2}{2mw^2 d^2} - U = E. \quad (4)$$

Since E is the kinetic energy of the electron outside the square well, it should be larger than zero. Therefore, the inequality $(n/w) > \alpha$ can be obtained from eq. (4) and

$$\alpha = \left(\frac{2md^2 U}{\hbar^2 \pi^2}\right)^{1/2}. \quad (5)$$

Equation (5) involves the interlayer spacing and the depth of the square well which is the inner potential of the metal film; thus α depends on the film properties. It can be determined from the inequality that for a thickness w, there is a minimum quantum number $n_{\min}$ depending on the width and depth of the square well and the interlayer spacing. This differs from the case of the quantum well states in which $n_{\min}$ is always 1. Using eq. (5), eq. (4) becomes

$$E = g\left[\left(\frac{n}{w}\right)^2 - \alpha^2\right], \quad (6)$$

where

$$g = \frac{\hbar^2 \pi^2}{2md^2}. \quad (7)$$

Therefore, as long as α is known, $n_{\min}$ can be determined using the inequality, then the energy of the lowest transmission resonance (LTR) for a thickness w can be calculated using eq. (6).

Figure 1 shows the calculated LTR as a function of film thickness for four α values in the unit of g. It can be seen that the behavior of the LTR significantly changes with α. For instance, Fig. 1(a) shows the case of $\alpha = 0.19$, which shows that the LTR moves toward lower energy, but it may experience a discontinuous jump whenever the thickness increases by five layers, as shown by dashed lines. The discontinuous jump occurs because $n_{\min}$ (indicated by number) has to increase by one every five layers in order to satisfy the inequality. In the continuously lowering region, $n_{\min}$ is the same and the energy level of the LTR is proportional to $1/w^2$. Figure 1(b) shows the case of $\alpha = 0.81$, completely different from what is evidenced in Fig. 1(a). In the first five layers, the LTR remains the same and $n_{\min}$ is equal to w. At a thickness of six layers, the LTR drops discontinuously because $n_{\min}$ becomes equal to $w - 1$; therefore, it may increase with the relation $(w-1)^2/w^2$ in the next five layers. With increasing thickness, discontinuous drop and ascending behaviors appear repeatedly every five layers. Figure 1(c) shows the case of $\alpha = 1.04$, in which $n_{\min}$ is equal to $w + 1$ and the LTR here, specifically named the lowest-order transmission resonance (LOTR), descends following with the relation of $(w+1)^2/w^2$. This relation can hold for w up to 24. When w exceeds 25, the inequality demands $n_{\min}$ to be equal to $w + 2$, the LTR will thus have a discontinuous jump, as shown in the inset in Fig. 1(c). Thus, this LTR belongs to the second-order transmission resonance and the LOTR vanishes at a thickness of $w = 25$. As α is further increased, the thickness range maintaining the relation $(w+1)^2/w^2$ for the LOTR is decreased. For example, in the case of $\alpha = 1.18$, as shown in Fig. 1(d), this relation only holds for the first five layers and the discontinuous jump (or disappearance of LOTR) appears at a thickness of six layers. On the basis of a previous analysis, one could, in principle, observe various relations between the energy level of LTR and the film thickness in real systems.

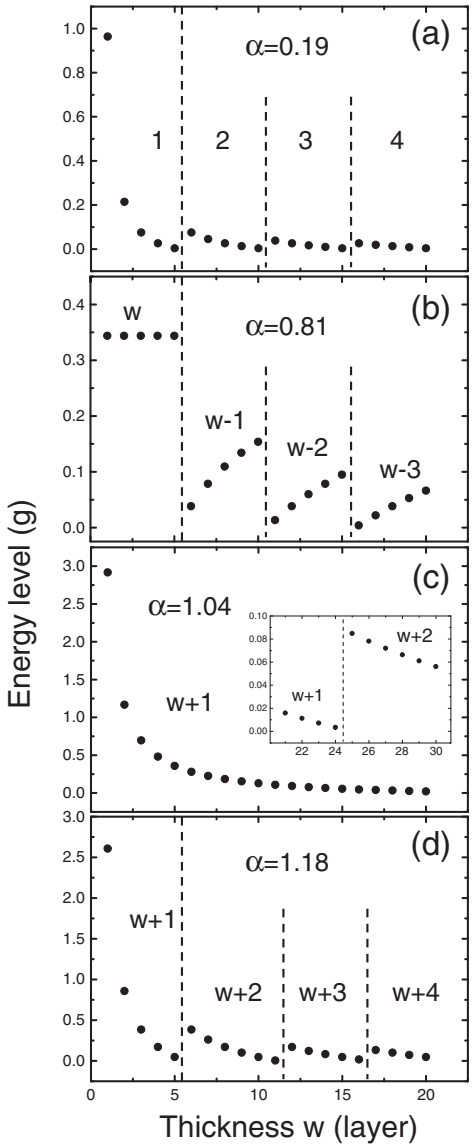

Fig. 1. Calculated energy level of the lowest transmission resonance (LTR) as function of film thickness w (atomic layers) for α values in the unit of g. (a), (b), (c), and (d) correspond to $\alpha = 0.19$, 0.81, 1.04, and 1.18, respectively. The behavior of the LTR significantly changes with α.

In our previous study, the transmission resonance is observed in Ag films using STS.[18] However, owing to the existence of an electric field in the tip–sample gap, it is also found that the energy of transmission resonance can be shifted by changing the electric field.[20,21] Since the emergent condition of transmission resonance in eq. (1) is for a free electron, one may ask whether various relations in Fig. 1 can be observed by STS. Since the use of the electric field is inevitable in STS, the only thing one can do is to maintain the same electric field when the transmission resonances of different thicknesses are observed, which is actually possible. Previous studies of Gundlach oscillations have demonstrated that the electric field can be preserved as long as the tip condition is not changed.[22,23] Figure 2(a)

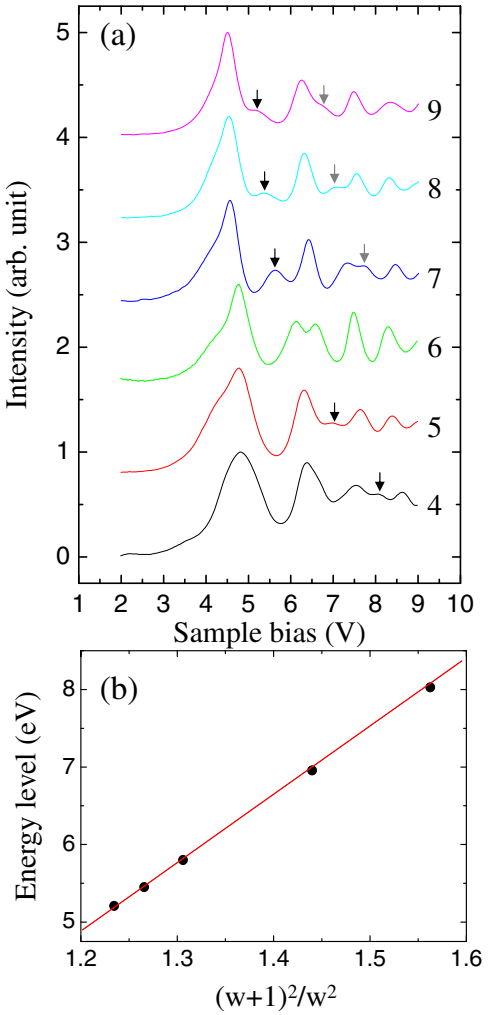

Fig. 2. (Color online) (a) Differential spectra acquired in Ag films with thicknesses from four to nine layers. The number at the right end of each spectrum denotes the film thickness. In each spectrum, the peak feature marked by the black arrow is the lowest-order transmission resonance (LOTR). The second-order transmission resonance (gray arrow) can be observed for thicknesses beyond 7 layers. Other peaks in each spectrum are the well-known standing-wave states in the tunneling gap. (b) The measured positions of the LOTRs in (a) vs $(w+1)^2/w^2$, revealing a good linear relationship, where w is the film thickness (atomic layers).

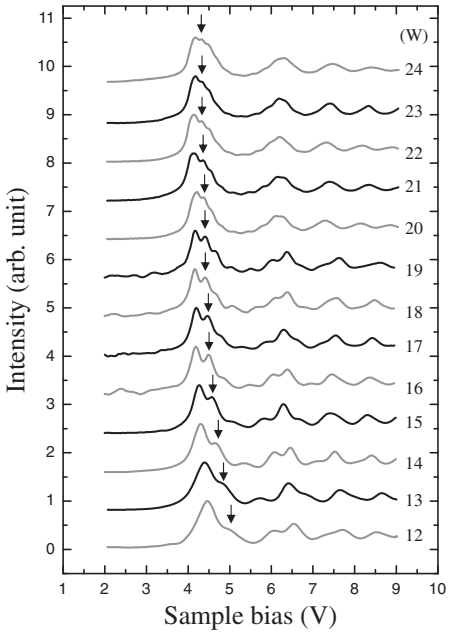

Fig. 3. Differential spectra acquired in Ag films with thicknesses from 12 to 24 layers, showing that LOTR (marked by an arrow) keeps moving toward lower energy as the thickness is increased.

shows the dI/dV spectra of Ag films with thicknesses from four to nine layers at the same electric field. The number at the right end of each spectrum denotes the film thickness. In each spectrum, the peak feature (marked by the black arrow) is the LOTR. The second-order transmission resonance (indicated by the gray arrow) can be observed for thicknesses beyond seven layers. Other peaks in the spectrum correspond to the well-known standing-wave states (or Gundlach oscillations) in tunneling gap.[24–27] It can be seen that the energy of LOTR shifts toward lower energy with increasing thickness except for the LOTR in the six-layer spectrum. Our previous study has explained that this LOTR cannot be distinguished from the nearby standing-wave state because of the effect of the electric field,[20] and thus it is not taken into account. Since there is no observation of a discontinuous jump or a drop for the LOTR, as in the case shown in Figs. 1(a), 1(b), and 1(d), it is plausible to infer that the behavior of the LOTR in Ag films can be described using the case in Fig. 1(c). That is, the quantum number of the LOTR in the Ag film with thickness w is equal to $w+1$ and the energy level is proportional to $(w+1)^2/w^2$. Figure 2(b) shows the measured energies of the LOTRs with respect to the Fermi level (zero sample bias) in Fig. 2(a) versus $(w+1)^2/w^2$. It reveals a good linear relationship, indicating the case in Fig. 1(c) satisfactorily explains the phenomenon of the transmission resonance in Ag films. This also implies that the derived formula can be exploited in the STM with the electric field. In terms of eq. (6), the g-value (8.592 eV) can be obtained from the slope in Fig. 2(b), and the effective mass m of the electron of the LOTR can be calculated using eq. (7) with an STM measured interlayer spacing d of 2.5 Å, which is 0.7 m_0. This is the first time, to our knowledge, that the electron effective mass in Ag films has been obtained from the transmission resonance.

As shown in Figs. 1(c) and 1(d), the lowering in the LOTR with the relation of $(w+1)^2/w^2$ only holds for thinner Ag films. When the film has a critical thickness w_c, the quantum number of transmission resonance would become w_c+2, implying that the LOTR with w_c+1 would disappear at the critical thickness, and thus the energy level of the transmission resonance has a discontinuous jump. Figure 3 shows the LOTR (marked by an arrow) observed in the film with thicknesses ranging from 12 to 24 layers. These signals of the LOTRs are weak, yet reproducibly appear in the dI/dV spectra. It can be seen that the LOTR keeps moving toward lower energy as the thickness is increased, indicating that the disappearance of the LOTR occurs at a larger thickness. However, it can also be determined from the inequality $(n/w) > \alpha$ that n can always be equal to $w+1$ as α is 1. The discontinuous jump may not happen in this situation. Therefore, it is necessary to observe the behavior of transmission resonance on thicker films to determine which case would be manifested. Figure 4

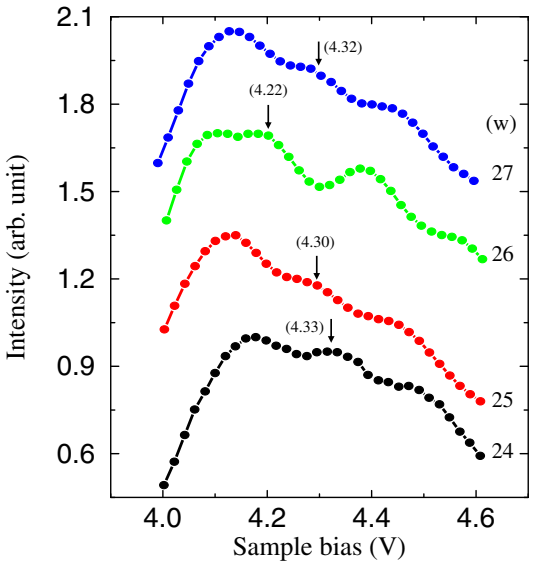

Fig. 4. (Color online) Focusing on the LTR (marked by arrow) in the spectra with film thicknesses ranging from 24 to 27 layers. The values in parentheses are the energies of the LTRs, indicating that the discontinuous jump indeed appears in the 27-layer film.

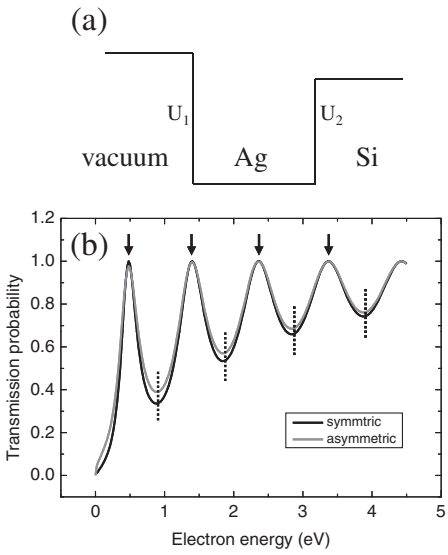

Fig. 5. (a) Schematic illustration of the asymmetric potential well. U_1 and U_2 are the depths of the well at the vacuum/Ag and Ag/Si interfaces, respectively. (b) Calculated spectra of transmission probability as a function of kinetic energy for both symmetric and asymmetric wells. In the calculation, $U_1 = 8\,\text{eV}$ and $U_2 = 7.6\,\text{eV}$ for the asymmetric well, and $U = 8\,\text{eV}$ for the symmetric well. The width of both wells is 40 Å.

demonstrates the LTRs (marked by arrows) in the spectra of film thicknesses from 24 to 27 layers. The values in parentheses are the energies of the LTRs, indicating that the discontinuous jump indeed appears in the 27-layer film because the energy level of the LTR is higher than that in the 26-layer film, but very close to that in the 25-layer film. This implies that the LOTR vanishes at a critical thickness of 27 layers and the observed LTR belongs to the next order. Since the transmission resonance should appear above the vacuum level and its lowest energy we can observe is 4.22 eV, it is plausible to assume that the work function of the Ag film is 4.22 eV.

However, it is known from photoemission studies that the work function of a Ag film with a 27-layer thickness should be equal to the bulk value of 4.6 eV,[28,29] and the assumed value is obviously smaller. In order to explain this inconsistency, an assumption is suggested here that the depth of the potential well at the Ag/Si interface (U_2) is smaller than that at the vacuum/Ag interface (U_1), as shown in Fig. 5(a). According to quantum mechanics, the transmission resonance can still appear in the region between the U_1 and U_2 as long as the electron wavevector k satisfies eq. (1).[30] Therefore, although the energy of the transmission resonance is lower than the vacuum level of 4.6 eV, it can still be observed because its energy is higher than another level named substrate level here at the Ag/Si interface, whose energy is 4.22 eV above the Fermi level. Moreover, the edge of the band gap in the projected bulk band structure of the Ag(111) surface is 3.9 eV above the Fermi level,[31] which is lower than the substrate level. Thus, it is confirmed that the disappearance of the transmission resonance is due to its energy being lower than the substrate level rather than the meeting of the band gap.

The potential well in Fig. 5(a) is not symmetric but the formula derivation is based on the symmetric well. This implies that the emergent condition in eq. (1) is still valid for the transmission resonance in the asymmetric well. In order to prove this point, the spectra of the transmission probability T as a function of kinetic energy are calculated using

$$\frac{1}{T} = \frac{1 + U^2 \sin^2(kt)}{4E(E+U)} \tag{8}$$

for the symmetric well[1] and

$$\frac{1}{T} = \frac{A\cos^2(kt) + B\sin^2(kt)}{4E_a E^{1/2} {E_b}^{1/2}} \tag{9}$$

for the asymmetric well,[31] where

$$E_a = E + U_1, \tag{10}$$

$$E_b = E + U_1 - U_2, \tag{11}$$

$$A = E_a(E^{1/2} + {E_b}^{1/2})^2, \tag{12}$$

$$B = (E_a + E^{1/2}{E_b}^{1/2})^2, \tag{13}$$

as shown in Fig. 5(b). In the calculation, U_1 is 8 eV as cited from previous study,[15] and U_2 is 7.6 eV because the energy difference between the vacuum level and the substrate level is about 0.4 eV here. Figure 5(b) shows that the energies of the transmission resonances as marked by arrows are the same in both cases, indicating that the derived formula is still valid in describing the transmission resonance of the asymmetric well. The distinct difference between these two cases is that the transmission probability of each local minimum (marked by dashed line) is higher for the asymmetric well.

4. Conclusions

In summary, a formula has been derived to relate the energy of the transmission resonance with the thickness of thin metal films. The energy–thickness relation can vary with the physical properties of the metal films, such as the interlayer spacing, derived inner potential, and effective mass of electrons. We apply the formula derived to the lowest

order transmission resonance in Ag films grown on the Si(111)7×7 surface. It is found that the behavior of shifting toward lower energy with increasing thickness w can be well represented by $(w+1)^2/w^2$. This indicates that the formula holds in the case in the free space but still is applicable to the STM using an electric field. The formula also predicts that the transmission resonance of the lowest order will disappear when a Ag film reaches its critical thickness, which has been observed to be 27 atomic layers.

Acknowledgements

The authors are grateful to C. S. Kuo, C. Y. Lin, and C. H. Hsieh for their assistance in the construction of low-temperature STM, and H. L. Hsiao, and A. B. Yang for their help in establishing the laboratory in Tunghai University. This work is supported by the National Science Council and Academia Sinica of Taiwan.

1) R. L. Liboff: *Introductory Quantum Mechanics* (Addison-Wesley, Reading, MA, 1980).
2) D. A. Evans, M. Alonso, R. Cimino, and K. Horn: Phys. Rev. Lett. **70** (1993) 3483.
3) N. V. Smith, N. B. Brookes, Y. Chang, and P. D. Johnson: Phys. Rev. B **49** (1994) 332.
4) J. J. Paggel, T. Miller, and T.-C. Chiang: Science **283** (1999) 1709.
5) R. K. Kawakami, E. Rotenberg, H. J. Choi, E. J. Escorcia-Aparico, M. O. Bowen, J. H. Wolfe, E. Arenholz, Z. D. Zhang, N. V. Smith, and Z. Q. Qiu: Nature **398** (1999) 132.
6) A. Mans, J. H. Dil, A. R. H. F. Ettema, and H. H. Weitering: Phys. Rev. B **66** (2002) 195410.
7) Y. F. Zhang, J. F. Jia, T. Z. Han, Z. Tang, Q. T. Shen, Y. Guo, Z. Q. Qiu, and Q. K. Xue: Phys. Rev. Lett. **95** (2005) 096802.
8) I. B. Altfeder, K. A. Matveev, and D. M. Chen: Phys. Rev. Lett. **78** (1997) 2815.
9) I. B. Altfeder, V. Narayanamurti, and D. M. Chen: Phys. Rev. Lett. **88** (2002) 206801.
10) W. B. Su, S. H. Chang, W. B. Jian, C. S. Chang, L. J. Chen, and T. T. Tsong: Phys. Rev. Lett. **86** (2001) 5116.
11) R. Otero, A. L. Vázquez de Parga, and R. Miranda: Phys. Rev. B **66** (2002) 115401.
12) D. Wegner, A. Bauer, and G. Kaindl: Phys. Rev. Lett. **94** (2005) 126804.
13) S. M. Lu, M. C. Yang, W. B. Su, C. L. Jiang, T. Hsu, C. S. Chang, and T. T. Tsong: Phys. Rev. B **75** (2007) 113402.
14) M. C. Yang, C. L. Lin, W. B. Su, S. P. Lin, S. M. Lu, H. Y. Lin, C. S. Chang, W. K. Hsu, and T. T. Tsong: Phys. Rev. Lett. **102** (2009) 196102.
15) B. T. Jonker, N. C. Bartelt, and R. L. Park: Surf. Sci. **127** (1983) 183.
16) W. F. Chung, Y. J. Feng, H. C. Poon, C. T. Chan, S. Y. Tong, and M. S. Altman: Phys. Rev. Lett. **90** (2003) 216105.
17) J. A. Kubby, Y. R. Wang, and W. J. Greene: Phys. Rev. Lett. **65** (1990) 2165.
18) W. B. Su, S. M. Lu, H. T. Shih, C. L. Jiang, C. S. Chang, and T. T. Tsong: J. Phys.: Condens. Matter **18** (2006) 6299.
19) P. Sobotík, I. Ošt'ádal, J. Mysliveček, T. Jarolímek, and F. Lavický: Surf. Sci. **482–485** (2001) 797.
20) W. B. Su, S. M. Lu, C. L. Jiang, H. T. Shih, C. S. Chang, and T. T. Tsong: Phys. Rev. B **74** (2006) 155330.
21) W. B. Su, C. S. Chang, and T. T. Tsong: J. Phys. D **43** (2010) 013001.
22) C. L. Lin, S. M. Lu, W. B. Su, H. T. Shih, B. F. Wu, Y. D. Yao, C. S. Chang, and T. T. Tsong: Phys. Rev. Lett. **99** (2007) 216103.
23) C. L. Lin, M. C. Yang, W. B. Su, S. P. Lin, S. M. Lu, H. Y. Lin, C. S. Chang, T. Y. Fu, and T. T. Tsong: Chin. J. Phys. **48** (2010) 855.
24) G. Binnig, K. H. Frank, H. Fuchs, N. Garcia, B. Reihl, H. Rohrer, F. Salvan, and A. R. Williams: Phys. Rev. Lett. **55** (1985) 991.
25) R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber: Phys. Rev. Lett. **55** (1985) 987.
26) W. B. Su, S. M. Lu, C. L. Lin, H. T. Shih, C. L. Jiang, C. S. Chang, and T. T. Tsong: Phys. Rev. B **75** (2007) 195406.
27) H. Liu, J. Yan, H. W. Zhao, S. W. Gao, and D. M. Chen: Phys. Rev. B **76** (2007) 113403.
28) R. Fischer, S. Schuppler, N. Fischer, Th. Fauster, and W. Steinmann: Phys. Rev. Lett. **70** (1993) 654.
29) W. Wallauer and Th. Fauster: Surf. Sci. **331** (1995) 731.
30) A. Messiah: *Quantum Mechanics* (Dover, New York, 1984).
31) S. Schuppler, N. Fischer, Th. Fauster, and W. Steinmann: Phys. Rev. B **46** (1992) 13539.