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Tip-induced energy shift in Au/Fe(100) quantum wells

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The quantum well (QW) states in Au/Fe(100) and their energy dependence on tip-sample distance are observed using scanning tunneling spectroscopy. When the tip-sample distance is decreased by 0.2 nm, the QW states shift by as large as 40 meV, which is approximately 20 times larger than the Stark shift observed in the surface state in noble metals. The observed shifts may be caused by the phase shift of the QW wave functions in the Au film as well as at the vacuum/Au interface.

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I. INTRODUCTION

Quantum well (QW) states formed in a noble metal (NM) film on a ferromagnetic metal (FM) substrate have attracted much interest in terms of their fundamental and technological importance in magnetic sensors and memories.[1–5] The QW energies depend on the confinement conditions such as the film thickness and the phase shift at the boundaries and have been studied extensively using various techniques such as photoemission,[2,3] inverse photoemission,[4] and two-photon photoemission.[5] Furthermore, the confinement conditions of the QW states in a (FM/NM/FM) multilayer are believed to play a key role in magnetic exchange interaction between FM films,[6] and the exchange bias has been shown to depend on the film thickness of the FM layer as well as of the NM layer.[7,8] Consequently, the modulation of the confinement condition is related to the magnetic control in a (FM/NM/FM) multilayer.[6]

Quantum electrons in a (vacuum/NM/FM) film are reflected back and forth both by the image potential at the vacuum/NM interface and by the hybridization gap at the NM/FM interface, and the confinement conditions have been described well by the phase accumulation model.[9–11] Because the image potential varies with separation z from the surface as $1/[4(z-z_{\mathrm{im}})]$, where z_{im} is the position of the image plane, the phase shift at the vacuum interface (Φ_B) can be modulated by the presence of a tip of a scanning tunneling microscope (STM)[12] and by adsorbate-induced shifts of the work function.[5] The tip-induced energy shifts, called the Stark shift, have been observed in image potential states,[12,13] surface states in Ag(111), Au(111), and Cu(111),[14,15] and QW states in Na/Cu(111).[16,17] Usually, the shift is in the range of a few meV (Refs. 14 and 15) for the occupied surface states, although it is much larger (approximately 0.15 eV) for image potential states that extend far from the surface.[12,13,16,17]

By contrast to our knowledge in the tip-induced effect on the surface states, little is known for the effect on states in a metallic film or a bulk due to their continuous electronic structure. In this paper, we report the tip-induced effect on the electrons in the Au film by measuring the QW states in Au/Fe(100). We observed energy shifts as large as 40 meV for the occupied and unoccupied QW states, when the tip-surface distance was decreased only by 0.2 nm. The observed shifts are about 20 times larger than the shifts observed in surface states,[14,15] which cannot be explained only by the phase shift induced by the image potential modulation, but suggests the tip-induced modulation of QW wavefunctions in the proximity of the Au surface layer.

II. EXPERIMENT

Single crystal Fe(100) substrates were cleaned by a cyclic procedure of sputtering and annealing from room temperature to 800 K in an UHV chamber. The surface of the Fe(100) is characterized by a strong surface state, which appears at 0.2 eV below the Fermi level in the photoemission spectra. A K cell was used to deposit Au films onto the Fe(100) substrates at 40 K, and after being evaporated they were annealed at 600 K. The low-temperature deposition and post anneal is necessary to achieve homogeneous Au film thickness on a stepped Fe(100) surface. The Au film thickness was calibrated in monolayer resolution by QW energies in the one-photon photoemission spectra, which were obtained with 4ω (6 eV) of a Ti:sapphire laser and Scienta SES100 electron energy analyzer.[5] The Au/Fe(100) sample was exposed to air for approximately 5 min. and then transferred to the STM UHV chamber where the sample was carefully annealed again at approximately 500 K in order to remove the adsorbed water. STM/STS measurements were made at room temperature and at 120 K. The STM tip was prepared from a W wire with a 0.25 mm diameter using electrochemical etching and a field-ion microscope in the UHV chamber. Figure 1(a) shows the STM image of the Au/Fe(100), where $5\times\sim20$ reconstructed structure similar to Au(100) appears, and the contaminated area is clearly distinguished. The ideal vacuum junction between the tip and a sample to avoid contamination can be checked using the tip displacement as a function of tunneling current as explained below. An STS spectrum was obtained by averaging approximately 4000 spectra taken in a clean 1.5×1.5 nm^2 area with a $>50\times50$ nm^2 terrace to enhance the signal to noise ratio, where the position dependence in the area was not clearly observed, which may be due to the 2D character of the QW states. During the STS measurements the drift was less than 0.1 nm, and the tip condition were checked to be unchanged by the spectra.

III. RESULTS AND DISCUSSION

The QW energies in the Au/Fe(100) estimated from one-photon photoemission spectra and STS are shown in Fig.

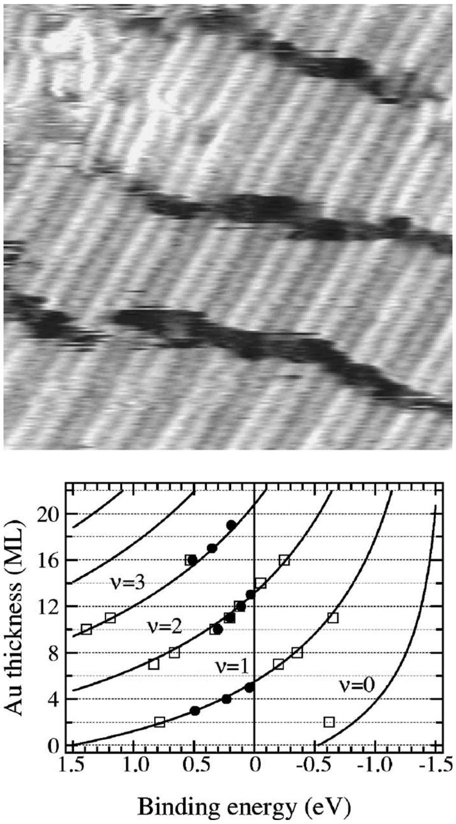

FIG. 1. (a) STM image (10×10 nm^2) of Au/Fe(100) taken at +1 V (tip bias) and 0.1 nA (tunnel current) at 300 K. Irregular structure (upper left) is due to contamination on surface. (b) QW energies of Au/Fe(100) observed by photoemission (closed circle) and STS (open square). QW energies based on the phase accumulation model (solid line) are also shown.

1(b) with the phase accumulation model calculation using two-band nearly-free-electron (TBNFE) treatment.[10,11] The phase accumulation of the QW electrons can be expressed as

$$\Phi^*(E) + 2k(E)Nd = 2n\pi, \tag{1}$$

where $\Phi^*(E)=\Phi_B^*(E)+\Phi_C^*(E)$ is a total phase shift induced by reflection at the vacuum $[\Phi_B^*(E)]$ and the substrate $[\Phi_C^*(E)]$ interface, $k(E)$ is the wave number of the QW electrons, Nd is the Au film thickness (d=0.204 nm), and N and n are integers. The QW series in Fig. 1(b) are represented by $\nu=n-N$, and we obtained $\Phi^*(E)=2\pi(-0.28101-0.5184E+0.02892E^2)$ by fitting the observed QW energies. Since $\Phi_B^*(E)$ is evaluated by WKB approximation at the vacuum image potential barrier,[5,10,11] $\Phi_C^*(E)$, which is fixed in the following calculations, can be estimated.

The modulation of the image potential can also be induced by an STM tip located just above the surface. The dependence of the dI/dV spectra on the tunnel current, which were measured at room temperature, is shown in Fig. 2(a). The tip height was controlled by a constant current mode at a tip bias of 1 V, and the tip-sample distance was decreased by approximately 0.2 nm as the tunnel current (I) was increased from 0.02 to 1 nA. The change of the tip height by 0.2 nm for almost two-order increase of the tunnel current indicates that the sample-tip junction is ideally a vacuum and that the surface is free from contamination because an anomalously large shift in the tip height were observed in the case of the contaminated surface due to sample deformation.[18,19] In Fig. 2(a), the dI/dV spectrum for Au (100) is also shown for reference, and it has an almost flat density of states around the Fermi level (E_F) and does not depend on the tunnel current.

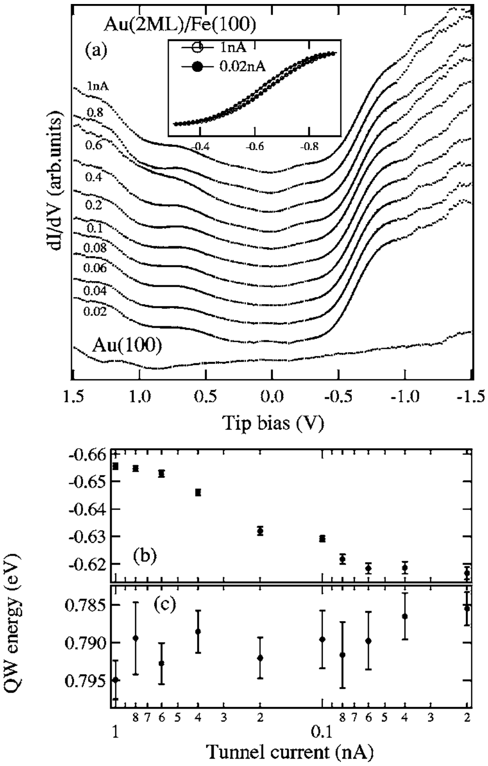

FIG. 2. (a) Dependence of dI/dV spectra on tunnel current for 2 ML Au/Fe(100). Tip height is varied by tunnel current at +1 V tip bias voltage. At bottom dI/dV spectrum for Au(100) is shown. (b) Dependence of QW state energies on tunnel current for $\nu=0$ QW state at −0.64 eV and (c) for $\nu=0$ QW state at 0.79 eV.

As have been observed in surface states in noble metals,[13–17] a two-dimensional state appears as a steplike structure in a dI/dV spectrum. In Fig. 2(a), two steplike structures, which are absent in Au(100), are observed. The steps observed at around +0.79 and −0.64 eV are close to the $\nu=1$ and $\nu=0$ QW states in Au(2 ML)/Fe(100) in Fig. 1(b). Though the steps at around −0.64 eV are slightly lower than the calculated value in Fig. 1(b), the unoccupied $\nu=0$ states for a 2 to 10 ML noble metal film are usually 0.2 to 0.3 eV lower than the phase accumulation model predicts.[1,4,10,11] Considering the film thicknesses estimated from a quartz thickness monitor and comparing the observed step positions with the structure plots in Fig. 1(b), the two peaks are attributed to the two-dimensional QW states in Au(2 ML)/Fe(100). While the structure around +1.1 to 1.5 V, which does not show a tunnel current dependence and is also seen in the Au(100) spectrum, may be originated in Au 4d bands. As the tunnel current increases from 0.02 to 1 nA, the $\nu=1$ state energy slightly decreases, while the $\nu=0$ state shifts upward by as large as 40±5 meV as shown in Figs. 2(b) and

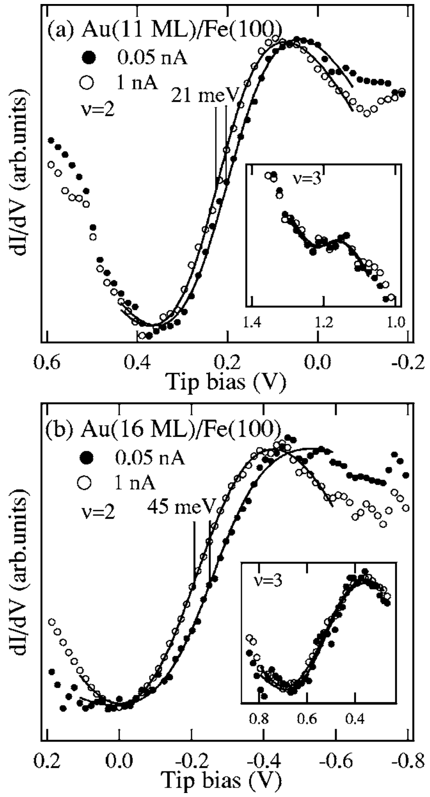

FIG. 3. Dependence of dI/dV spectra measured at 120 K on tunnel current for the $\nu=2$ QW state of (a) Au(11 ML)/Fe(100) and (b) Au(16 ML)/Fe(100) with the least square fits(line). Insets show the $\nu=3$ QW energy region.

2(c). Here, the step positions were estimated by a least square fitting of the dI/dV spectra by a convolution of a step function with a Voigt function and a linear background, which are shown by thick lines in Fig. 2(a). The Gaussian FWHM of the Voigt function was assumed to be 25 meV, which was obtained by fitting a step function broadened by the dI/dV data acquisition procedure in the experiment. The Lorentzian FWHM's are 0.37 ± 0.02 eV for the $\nu=0$ states and 0.30 ± 0.04 eV for the $\nu=1$ states, which are comparable with the width of 0.25 eV for the $\nu=1$ states of Ag(2 ML)/Fe(100) measured by photoemission at 100 K.[2]

The dependence of the dI/dV spectra on the tunnel current, which were measured at 120 K in different Au/Fe(100) samples with different tips, is also shown in Fig. 3. In the insets of Figs. 3(a) and 3(b), different energy regions in the same dI/dV spectra are presented. The steps are observed at around 0.22 and 1.19 eV below E_F in Fig. 3(a) and 3(b) and at around -0.25 eV (above E_F) and 0.53 eV in Fig. 3(b). Comparing the observed step positions with the structure plots and using the nominal film thicknesses estimated from a quartz thickness monitor, the dI/dV steps in Figs. 3(a) and 3(b) are attributed to $\nu=2$ and $\nu=3$ QW states of 11 and 16 ML Au/Fe(100), respectively. The lorentzian FWHM's are 0.24 ± 0.02 eV and 0.34 ± 0.05 eV for the $\nu=2$ states in Au(11 ML)/Fe(100) and Au(16 ML)/Fe(100), which become smaller than the case in Au(2 ML)/Fe(100) because of the temperature, binding energies, and film thicknesses.[2,5] With decreasing the tip height, the $\nu=2$ QW states shift downward by as large as 45 ± 4 meV for Au(16 ML)/Fe(100) and 21 ± 3 meV for Au(11 ML)/Fe(100), while the shift of the $\nu=3$ QW states can not be estimated because of the small S/N ratio. These observed shifts of $\nu=0$ states in Fig. 2(b) and of $\nu=2$ states in Fig. 3 with decreasing of the tunnel resistance are approximately 20 times larger than the observed Stark-shifts of surface states in the same tunnel resistance region, where shifts of a few meV have been reported.[14,15]

The observed tip-induced QW energy shifts may be caused by tip or surface deformation,[14,18] adsorbate polarization,[20] and tip-surface potential modulation.[12–17] When the tip and/or the Au film thickness (Nd) deform, we should expect shifts in the same direction for every QW states as is predicted by Eq. (1), and the tip displacement should be larger than the observed value of 0.2 nm. Furthermore, the tip is expected to deform at $I \geqslant 2\ \mu A$ or less than 0.45 nm of the tip height,[14] which is much closer to the surface than the present condition ($0.02 \leqslant I \leqslant 1 nA$). Second field-induced polarization of adsorbates may influence $\Phi_B^*(E)$. Since we carried out the STS measurement at contamination free areas and observed the tip displacement for an ideal vacuum tunneling barrier, we may exclude this possibility. The third possibility which is caused by the image potential modulation[12–17] is considered under the one-dimensional potential model. As in the Stark effect in the surface state,[14,15] such tip-surface potential modulation can change the $\Phi_B^*(E)$ of the QW wave function, and then the QW energy through Eq. (1). The model potential is based on the Ref. 21:

$$V_1 = A_{10} + A_1 \cos\left(\frac{2\pi}{d}z\right), \quad z \leqslant 0,$$

$$V_2 = B_{10} + A_4 \cos(\beta z), \quad 0 \leqslant z \leqslant z_1,$$

$$V_3 = b(z - z_1) + V_5 \exp[-\alpha(z - z_1)], \quad z_1 \leqslant z \leqslant z_{\mathrm{im}},$$

$$V_4 = b(z - z_1) + V_{\mathrm{im}}(z), \quad z_{\mathrm{im}} \leqslant z \leqslant z_{\mathrm{tip}},$$

where

$$b = (E_v^s - E_v^{\mathrm{tip}} + eV_{\mathrm{bias}})/(z_{\mathrm{tip}} - z_1),$$

$$V_{\mathrm{im}}(z) = -(1 - e^{-\lambda(z - z_{\mathrm{im}})})\left(\frac{1}{4(z - z_{\mathrm{im}})} + \frac{1}{2}\sum_{n=1}^{10}\left(\frac{nD}{(nD)^2 - (z - z_{\mathrm{im}})^2} - \frac{1}{nD}\right)\right).$$

Here, d is the Au monolayer film thickness, E_v^s and E_v^{tip} are the sample and tip work functions, V_{bias} is the sample bias voltage, $D = z_{\mathrm{tip}} - z_{\mathrm{im}}$, and $V_{\mathrm{im}}(z)$ represents the multiple image potential between the sample and the tip.[22,23] The parameters $A_{10} = -10.81$ eV, $A_1 = 4.2$ eV, $A_4 = 6.069$ eV, $\beta = 3.3626$ (a.u.), $z_1 = 5\pi/(4\beta)$, and $z_{\mathrm{im}} = 1.62$ (a.u.), are the same as in Ref. 21, while the remaining parameters are fixed by requiring V and dV/dz to be continuous. The Schrödinger equation was numerically solved under the one-dimensional potentials, and the factors of $k(E)Nd$ and $\Phi_B^*(E)$ in Eq. (1)

are estimated from the logarithmic derivatives at both the substrate and the vacuum interfaces.[5,10,11] Assuming $E_v^s=5.0$ eV and $E_v^{\text{tip}}=5.5$ eV, the estimated shifts of the $\nu=0$ state and the $\nu=1$ state of Au(2 ML)/Fe(100) are −10.7 and +2.6 meV, respectively, when the tip comes 0.2 nm closer to the sample from $D=1$ nm, which is the typical tip height for a tunnel current around 0.1 nA.[24] Here, $\Phi_C^*(E)$ is assumed to be the same as in Fig. 1(b), and QW energies are obtained by Eq. (1). The calculated shifts are relatively larger than those of the surface states, which may in part result from the different phase accumulation condition in Eq. (1). However, the −10.7 meV shift is still smaller than the observed shifts in Fig. 2.[25]

The QW wave function may depend on a charge modulation in the proximity of the Au surface layer. A biased tip induces a positive or negative charge modulation near the first atomic layer at $z=0$.[26] A local potential induced by the tip was assumed as

$$V_{\text{dipole}}(z) = \frac{\alpha}{4\pi\varepsilon_0}\left(\frac{-\Delta\rho}{|z+d/2|} + \frac{\Delta\rho}{|z-d/2|}\right),$$

where ε_0 is the dielectric constant, $\Delta\rho$ is a calculated charge difference between with and without the tip for $z_{\text{im}}\leqslant z$, and α is a coefficient between a potential modulation and an induced charge which is determined numerically under the V_1 model potential. The induced dipole potential around $z=0$ produces the extra phase shift $\Delta\Phi(E)$, for the QW wave function. The phase accumulation relation of QW then becomes

$$\Phi_B^*(E) + \Phi_C^*(E) + 2[k(E)Nd + \Delta\Phi(E)] = 2n\pi. \qquad (2)$$

The QW energies as functions of the tip height obtained under the modulated potential are shown for $N=2$ in Fig. 4. Here $E_v^s=5.0$ eV and $E_v^{\text{tip}}=5.5$ eV, where the tip may be coated by Au, were assumed. As the tip height is decreased by 0.2 nm from $D=1$ nm, the occupied and unoccupied QW energies shift by −40 meV and +7.6 meV which agrees well with the observed shifts in Fig. 2. When $E_v^s=5.0$ eV and $E_v^{\text{tip}}=4.5$ eV were assumed, since the work function of W may vary between 4.47 eV in W(111) and 5.25 eV in W(110),[27] the decrease of $\nu=2$ QW states by +20 and +40 meV in $N=11$ and 16 were reproduced respectively. Further first principle calculation may be needed to understand quantitatively the electronic structure in the vicinity of the surface, however, the model taking account of the dipole induced by the tip explains well the observed large QW energy shifts.

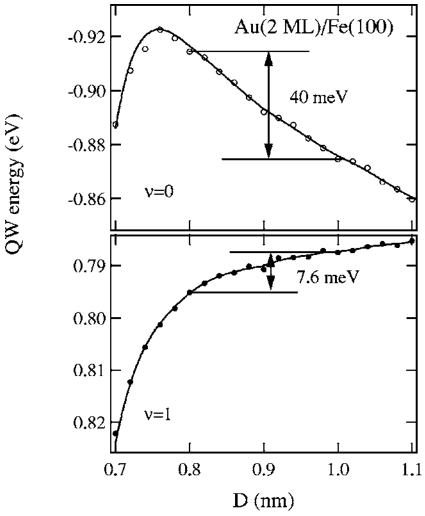

FIG. 4. Calculated tip height dependence of the $\nu=0$ and $\nu=1$ QW energies of Au(2 ML)/Fe(100) based on the model including the surface dipole (V_{dipole}).

IV. SUMMARY

In summary, the QW states in Au/Fe(100) and their energy dependence on tip-sample distance are observed at various Au thicknesses and temperatures. The tip-induced shifts of the QW states in the Au film can be approximately 20 times larger than the Stark shift observed in the surface states of noble metals. The simple one-dimensional pseudopotential model with tip-induced charge modulation may explain the observed large shifts. This work opens the way for direct measurement of the tip-induced effect in a metallic film.

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