Quantum-Well Wave-Function Localization and the Electron-Phonon Interaction in Thin Ag Nanofilms

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(Received 11 July 2006; revised manuscript received 20 October 2006; published 8 December 2006)

The electron-phonon interaction in thin Ag nanofilms epitaxially grown on Cu(111) is investigated by temperature-dependent and angle-resolved photoemission from silver quantum-well states. Clear oscillations in the electron-phonon coupling parameter as a function of the silver film thickness are observed. Different from other thin film systems where quantum oscillations are related to the Fermi-level crossing of quantum-well states, we can identify a new mechanism behind these oscillations, based on the wave-function localization of the quantum-well states in the film.

DOI: 10.1103/PhysRevLett.97.236809 PACS numbers: 73.50.Gr, 71.18.+y, 73.21.−b, 79.60.Dp

Quantum oscillations of various physical properties in thin film quantum-well systems, which are controlled by the thickness of the overlayer film, have generated constant interest in recent years. A very prominent example is quantum oscillations in the superconducting transition temperature of thin Pb films with varying thicknesses [1–4]. In the same context, quantum oscillations in the electron-phonon coupling have been observed in, for example, Ag and Pb [5,6]. Additional examples include oscillations in the magnetic coupling [7], the stability of thin films [8], work function [9], and electronic growth [10]. All these systems are characterized by the existence of discrete electronic quantum-well states (QW) and, up till now, any observed oscillatory behavior has been related to a Fermi-level crossing of a QW state at distinct film thicknesses. In this Letter, we give first evidence for a different mechanism in thin film systems capable of promoting quantum oscillations. We show that quantum oscillations in the electron-phonon coupling of ultrathin Ag-films on Cu(111) are driven by transitions of a QW state into a QW resonance at distinct film thicknesses. This localization process enhances the probability of electron momentum transfer processes and, therefore, promotes electron-phonon scattering. In analogy to the relevance of Fermi-level crossing of QW states we also expect this kind of wave-function localization to alter a variety of relevant material properties in a similar quantum oscillatory way.

Our photoemission data were recorded at normal emission using a hemispherical energy analyzer for parallel energy and momentum detection ($\Delta E < 20$ meV, $\Delta\phi < 0.15°$). Frequency-quadrupled UV light ($h\nu = 6$ eV) of the output of a small bandwidth ($h\nu = 1.5$ eV) pulsed Ti:sapphire laser system was focused onto the surface to a spotsize of approximately 150 μm. Silver films were grown at room temperature followed by a short flash of the sample to 600 K [11]. Figure 1(a) displays a $E(k_\parallel)$ photoemission map of a 36 ML thick silver film recorded at a sample temperature of 211 K (intensity in gray scale as a function of energy and parallel momentum). The spectrum shows an intense signal from the Shockley surface state just below the Fermi level at a binding energy of about 40 meV. The spectral features at binding energies of 390, 600, and 840 meV are due to the $\nu = 1$, $\nu = 2$, and $\nu = 3$ QW states localized within the silver film overlayer [12,13]. The appearance of these states is possible due to the presence of the sp band gap of the Cu(111) substrate, which extends from -4.25 to 0.85 eV binding energy at $k_\parallel = 0$ Å^{-1}. Figure 1(b) shows a set of three photoemission spectra at normal emission for 16, 21, and 28 ML of Ag on Cu(111). In agreement with previous reports

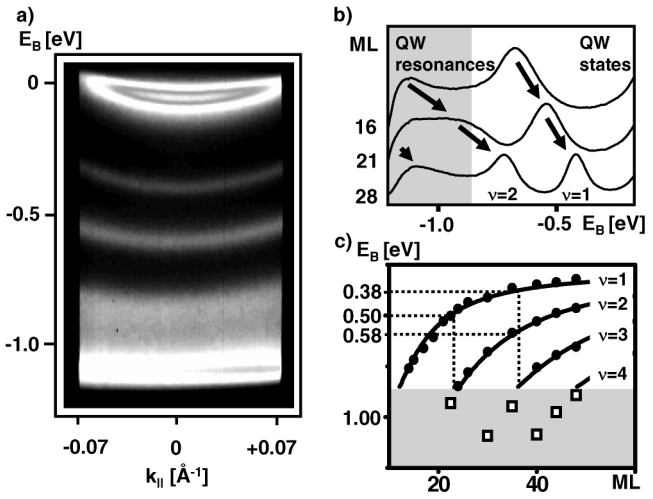

FIG. 1. (a) Typical 2D photoemission map for 36 ML Ag/Cu(111), $T = 211$ K, $h\nu = 6$ eV. (b) Transition of a QW resonance into a QW state with increasing Ag thickness. The shaded area indicates the projected Cu bulk bands to the surface. (c) Energies of the $\nu = 1$ to $\nu = 4$ QW states (dots) and QW resonances (squares) as a function of nominal film thickness [11]. The solid curves are calculations using the phase accumulation model with $m^*/m = 0.65$, in agreement with data published before in [12]. The dotted lines link the QW state QW resonance transitions occurring at 23 and 35 ML to the binding-energy scale.

[12,13], we observe a shift of the QW states to lower binding energies with increasing silver coverage asymptotically approaching the energy of the upper band edge of the silver sp band (300 meV). Furthermore, additional spectral features significantly below the lower edge of the sp band gap (850 meV) are visible (gray shaded area). These are due to photoemission from QW resonances in the silver film. These types of states are supported by a finite electron reflectivity at the silver-copper interface, which is due to wave-function mismatch between the two materials and, in the present system, is enhanced by a lattice mismatch of about 13% between silver and copper [14]. In contrast to pure QW states, these states are obviously in resonance with the copper sp band and couple to real electron states within the copper substrate. The coupling gives rise to extended penetration (delocalization) of these states into the copper going along with a reduction of the wave-function amplitude within the silver film [15,16]. Figure 1(c) shows results from a quantitative analysis of photoemission maps recorded at varying film thicknesses. Monotonous transitions of the $\nu = 2$, $\nu = 3$, and $\nu = 4$ QW resonances (open squares) into QW states occur at film thicknesses of about 23, 35, and 47 ML. Additional evidence for the change in the character of these states at these film thicknesses is a narrowing of their linewidths right at these critical thicknesses in agreement with Ref. [16]. The discrimination between localized QW states and delocalized QW resonances will be an important issue in the interpretation of our experimental data presented below.

A calculation of the binding energy of the $\nu = 1$ to $\nu = 4$ QW states was performed using the phase accumulation model following the details described in Refs. [17,18] (see solid lines in Fig. 1). The model reproduces our experimental data perfectly for $m^*/m = 0.65$, using an interfacial phase contribution given by [17,19]

$$\Phi_C(E) = 2\arcsin\sqrt{(E - E_L)/(E_U - E_L)}, \qquad (1)$$

where $E_L = -0.85$ eV and $E_U = 4.25$ eV are the lower and upper edge of the Cu(111) band gap [20], respectively. The linewidth ΔE of the QW state peaks is related to the lifetime of the photohole via the uncertainty principle and is governed to a considerable extent by electron-phonon interactions. An increased phonon population at elevated temperatures leads to an enhanced phonon scattering rate, and hence a shorter lifetime and an increase in the QW state linewidth. Figure 2(a) shows photoemission spectra of the $\nu = 1$ and $\nu = 2$ QW states for a 36 ML thick silver film at temperatures of 211 and 336 K (open squares). The two Lorentzians result from fits of the QW states while the solid lines represents the total fit of the spectra. Figure 2(b) summarizes for this film the linewidths of the $\nu = 1$ and $\nu = 2$ QW state and the Shockley surface state as a function of temperature between 200 and 350 K. An important parameter that can be directly deduced from these data is the electron-phonon coupling parameter λ [21], which is

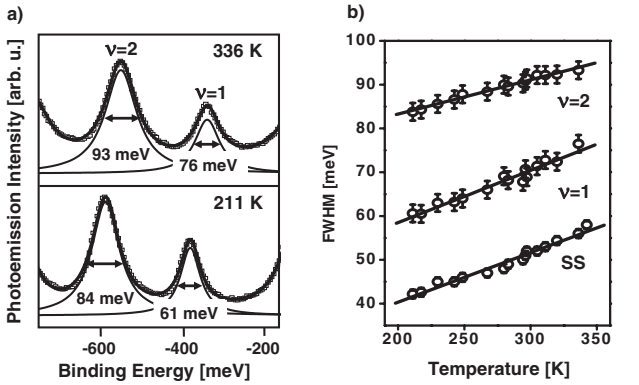

FIG. 2. (a) Temperature-dependent photoemission spectra of 36 ML Ag/Cu(111) for 336 and 211 K. The $\nu = 1$ and $\nu = 2$ peaks shift in binding energy and the linewidth increases with increasing temperature. (b) Linewidths (dots) and linear fit (solid line) of the QW states and the Shockley surface state as a function of temperature for this film.

given by

$$\lambda = \frac{1}{2\pi k_B}\frac{d(\Delta E)}{dT}. \qquad (2)$$

$d(\Delta E)/dT$ is the slope of the observed linear temperature dependence. The electron-phonon coupling parameter clearly depends on the quantum number ν of the QW states.

Next, Fig. 3 shows electron-phonon coupling data obtained from QW state linewidth measurements for silver

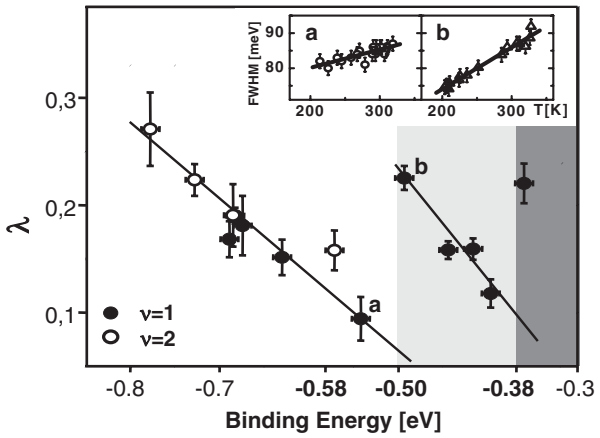

FIG. 3. Electron-phonon coupling parameters for the QW states $\nu = 1$ (closed circles) and $\nu = 2$ (open circles) as a function of binding energy, deduced from T-dependent linewidth measurements as shown in the inset and Fig. 2(b). Oscillations in λ occur at binding energies (bold printed) at which a QW resonance to QW state transition occurs, as can be seen in Fig. 1(c). For reference, the gray shaded areas mark the binding-energy regimes of increased electron-phonon scattering due the $\nu = 1$ to $\nu = 2$ QW state interaction (light gray) and due to the $\nu = 1$ to $\nu = 3$ QW state interaction (dark gray). The inset shows the temperature dependence of the linewidth of the $\nu = 1$ QW state right before (a) and after (b) the λ-step at 0.5 eV binding energy.

films of 15 to 36 ML thickness. The data are displayed here as a function of the QW state binding energy. Closed and open circles correspond to the values obtained for the $\nu = 1$ and $\nu = 2$ QW states, respectively. The general trend observed is an overall decrease of λ with decreasing binding energy (solid lines). This trend is, however, interrupted by steps which are most pronounced at QW state binding energies of about 0.50 and 0.38 eV for the $\nu = 1$ state, but are also visible at a binding energy of 0.58 eV for the $\nu = 2$ state.

The linear decrease is consistent with a simple model previously used to quantitatively describe results for the Ag/Fe(100) system [5]. This model allows us to assign the binding-energy dependence of λ to the phase shift variation of π across the confinement gap at the silver-copper interface [17] [see Eq. (1)]. This phase shift $\Phi_C(E)$ modulates the amplitude of the QW state's wave function at the interface and, therefore, affects the coupling efficiency of the QW states to interfacial phonons. Since this modulation is only dependent on the binding energy of the QW states, the behavior within our film thicknesses is independent of the quantum number ν.

However, the experimentally observed deviations from this linear trend at 0.50 and 0.38 eV binding energy ($\nu = 1$) and at 0.58 eV binding energy ($\nu = 2$) cannot be reproduced by this model. The observed steplike behavior requires a corresponding change in the interfacial phase contribution, which is not existent for the investigated Ag/Cu system.

Oscillations in the electron-phonon coupling parameter as a function of quantum-well thickness have been observed for other quantum-well systems before [1–3,5–10]. In all these cases, the origin of the oscillations was related to a Fermi-level crossing of a QW state. The driving force for this effect is the strong modulation of the occupied density of states near E_F as the QW states cross the Fermi level with increasing film thickness. However, for the Ag/Cu(111) system, this scenario can be excluded. At $k_{\|} = 0$ Å^{-1} the QW states asymptotically converge at the lower edge of the silver sp band gap at 300 meV binding energy, which is well below the Fermi edge (see Fig. 1). Therefore, a Fermi-level crossing is not possible at all film thicknesses and consequently cannot cause the observed oscillations in λ.

We found instead a direct correlation between the appearance of these oscillations and the critical film thicknesses where the transitions from the $\nu = 2$ and $\nu = 3$ QW resonances into the associated QW states occur. For instance, the discontinuity in the $\nu = 1$ QW state at 0.5 eV binding energy is seen at a silver film thickness of 23 ML, exactly where we observe the transition of the $\nu = 2$ QW resonance into the $\nu = 2$ QW state [see dotted lines in Fig. 1(c)]. In addition, both the second step of the $\nu = 1$ QW state at 0.38 eV binding energy and the step seen in the $\nu = 2$ QW state at 0.58 eV binding energy correlate with the $\nu = 3$ QW resonance transition into the $\nu = 3$ QW state at 35 ML. We therefore conclude that the origin of the oscillations in the electron-phonon coupling parameter λ for the Ag/Cu(111) system are directly related to these changes in the electronic structure, which occur at specific film thicknesses as a QW resonance undergoes the transition into a QW state.

The electron-phonon interaction in the silver film is governed by the available decay channels, the available phase space for each decay channel, and the matrix elements for the scattering processes [21–23]. The electron-phonon scattering process responsible for the phonon-mediated hole relaxation probed in the photoemission experiment requires, in particular, a source of electron momentum to compensate for the momentum of the absorbed or created phonon. Highly efficient in this means are QW states interband scattering processes between two QW states of different quantum number ν [see Fig. 4(b)]. This has been previously shown, for example, in the case of d-band QW states' relaxation [23] and, in a similar manner, in connection with the decay of image potential states at Cu(100) surfaces [24]. An important contribution to the matrix element of such a process is the wave-function overlap between the two involved QW states.

In this context, we now consider in more detail the potential decay channels available for the $\nu = 1$ hole created by the photoemission process (see Fig. 4). Three different phonon-mediated scattering processes can be discriminated: the interaction of the $\nu = 1$ QW state hole with (i) the Cu bulk bands and, depending on the silver film thickness, the interaction with (ii) the QW resonance [S/R process, see Fig. 4(a)] and the interaction with (iii) the $\nu = 2$ QW state [S/S process, see Fig. 4(b)]. Because of the negligible wave-function overlap between the $\nu = 1$ QW state confined in the silver film and the bulk states of the copper substrate, the contribution of process (i) to the electron-phonon cross section is of negligible importance. However, for processes (ii) and (iii), both the initial hole state ($\nu = 1$ QW state) and final hole state ($\nu = 2$ QW resonance and QW state, respectively) exhibit a consider-

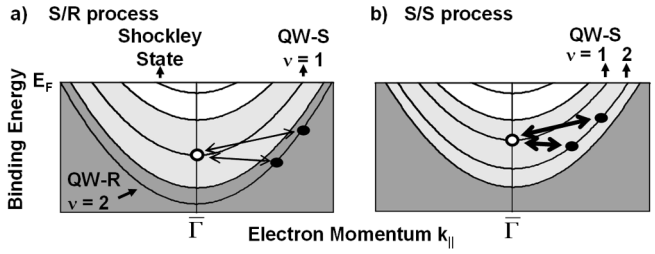

FIG. 4. Schematic illustration of the QW state hole relaxation paths. Hole states are indicated by open circles, while electrons are indicated by solid circles. The dark shaded area is the projected bulk band of the Cu(111)-substrate to the surface. (a) Phonon-mediated scattering into the delocalized $\nu = 2$ QW resonance; (b) enhanced electron-phonon coupling due to phonon-mediated interband scattering into the localized $\nu = 2$ QW state. The energy differences are highly exaggerated.

able wave-function amplitude within the silver film that promotes the electron-phonon interaction. However, the leakage of the QW resonance into resonant Cu bulk states notably reduces its wave-function amplitude in the silver film in comparison to the $\nu = 2$ QW state. Indicative of this leakage are the low intensity and the large linewidth ΔE of the $\nu = 2$ QW resonance above a value of 400 meV at 300 K [Fig. 1(b)]. From this point of view, the phonon-mediated S/R scattering process must be less efficient than the S/S process and this enables us to understand the microscopic mechanism behind the steplike increase in λ at the critical film thickness of 23 ML. For a silver film just below this thickness, the electron-phonon coupling is governed by a phonon-mediated S/R scattering process. As the film thickness increases, the $\nu = 2$ QW resonance is transformed into the $\nu = 2$ QW state corresponding to a wave-function localization and an increase in the wave-function amplitude. Right above the critical film thickness, the electron-phonon coupling is therefore mediated by the S/S scattering process, which is characterized by an enhanced interaction probability as observed in the experiment. The oscillatory behavior in λ is therefore expected at a periodicity given by the rate at which a QW resonance into QW state transition takes place, in perfect agreement with our observations at 23 and 35 ML film thickness. This argument is also valid for the discontinuity of the $\nu = 2$ QW state at 580 meV binding energy corresponding to the $\nu = 3$ QW resonance QW state transition at 35 ML thickness.

The ratio of the efficiency between the S/R scattering process and the S/S process can be quantified by an estimate of the wave-function amplitude of the $\nu = 2$ QW resonance relative to the $\nu = 2$ QW state in the silver film. For a finite reflection coefficient R_{QWR} ($R_{\mathrm{QWR}} < 1$) of the QW resonance at the silver-copper interface, the ratio of the wave-function amplitude between the QW resonance and QW state ($R_{\mathrm{QWS}} \approx 1$) is given by $R_{\mathrm{QWR}}/R_{\mathrm{QWS}} \approx R_{\mathrm{QWR}}$. R_{QWR} can be deduced from the measured linewidth ΔE of the QW resonance. According to Ref. [25], ΔE depends on the number of monolayers N of the silver film, R_{QWR} and the mean free path L of the electrons,

$$\Delta E = \Gamma \eta \frac{1 - R_{\mathrm{QWR}} \exp(-1/\eta)}{R_{\mathrm{QWR}}^{1/2} \exp[-1/(2\eta)]} \qquad (3)$$

with $\eta = L/(Nt)$, t is the monolayer thickness and Γ is the intrinsic linewidth of the QW resonance. For $L \approx Nt/2$ [26] and $\Gamma = 90$ meV as deduced from an extrapolation of the intrinsic linewidth data of the QW state into the QW resonance regime, we obtain a value of the reflectivity $R_{\mathrm{QWR}} < 1/4$. This means that the wave-function amplitude of the QW resonance is reduced in comparison to the wave-function amplitude of the QW state by a factor of about 4. Also of the same order of magnitude is the ratio of the wave-function overlap between the S/R and S/S scattering processes and, consequently, the expected ratio in the electron-phonon coupling constant. In this experiment, we find the ratio for the $\nu = 1$ QW state is equal to a value of about 3.5(1). Taking into account that the above estimation exclusively focuses on the effect of the wave-function amplitude, the experimental and calculated values are in reasonable agreement.

In conclusion, we have observed oscillations in the electron-phonon coupling parameter in thin Ag overlayer films on Cu(111). We have shown that these oscillations correlate with the transition of a QW resonance into a QW state in the silver film. Furthermore, we attribute the microscopic mechanism for these changes to the localization of the QW state wave function within the silver film, which is going along with such a transition. In addition to quantum oscillations in the electron-phonon coupling parameter, we propose that this mechanism is of more general relevance for other thin film properties similar to the effect of the QW state Fermi-level crossing. For example, one property for that oscillatory behavior has been shown in systems with oscillating λ is superconductivity [1–4,27].

Special thanks go to M. Wessendorf. This work was supported by the DFG through SPP 1093 and the Stiftung Innovation RLP.

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