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Temperature-dependent angle-resolved photoemission study for quantum-well states in Ag nanofilms

Kazutoshi Takahashi, Akinori Tanaka, Hiroyuki Sasaki, Wakako Gondo, Shoji Suzuki, and Shigeru Sato
Department of Physics, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

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We have performed a temperature-dependent photoemission study for quantum-well states in Ag(111) nanofilms grown on Cu(111) substrate. It is found that the linewidths of both quantum-well state and surface state broaden and their intensities decrease with increasing a temperature from 40 to 350 K. The linear temperature dependence of the linewidths of both states are explained as the temperature dependence of the phonon contribution to the photohole lifetime width, expressed as $2\pi\lambda k_B T$. It is found that the electron-phonon mass-enhancement parameter λ for quantum-well states is almost the same with that for surface state and an average over the bulk Fermi surface. The temperature dependence of the intensities have been discussed using the standard Debye-Waller factors. It is found that the effective Debye temperature derived from the quantum-well state is higher than that from the surface state, suggesting different properties of phonon states coupled to each electronic state. [S0163-1829(99)13435-0]

I. INTRODUCTION

Metallic nanostructures have attracted considerable interest, since the multilayers composed of alternating ferromagnetic and nonmagnetic metals show the intriguing physical properties such as an oscillatory magnetic coupling and a giant magnetoresistance.[1–3] Connected with these physical properties, the quantum-well (QW) states have been studied in various metallic nanofilms grown on metallic substrates. Especially, angle-resolved photoemission spectroscopy and angle-resolved inverse photoemission spectroscopy have been used as the powerful tools to observe the QW states in metallic nanofilms. From these spectroscopic measurements, it has been found that the QW state shows two-dimensional electronic structure with no dispersion along surface normal direction, and its eigenvalue depends on the film thickness and the electronic structure of the substrate.[4–10] The QW state originates from the quantum confinement effect on the itinerant valence electrons due to the electronic band-structure mismatch between the nanofilm and the substrate. The binding energies of QW states in many systems are found to be well characterized by the calculation based on the phase accumulation model,[11,12] which takes into account the phase shifts upon reflections of electron at both interfaces of nanofilm. However, in order to elucidate the intriguing properties of metallic nanostructures in detail, it is indispensable to understand entirely their electronic structures, phonon properties, and electron-phonon interactions.

Up to now, most of the electron spectroscopic studies for metallic nanofilms are limited to the eigenvalues of the QW states, but to our knowledge, there is no report that highlights the dynamical properties such as the electron-phonon interaction. In this paper, we have carried out a temperature-dependent photoemission study for QW states in Ag nanofilms grown on Cu(111) substrate so as to elucidate the electron-phonon interaction in Ag nanofilms. The photoemission linewidths of the QW states broaden with increasing temperature and their dependence is linear. This is explained as the phonon contribution to the photohole lifetime width. From this dependence, we have derived the electron-phonon mass enhancement parameter. It is also found that the QW states exhibit losses in peak intensities with increasing temperature. We analyzed the temperature dependence of the intensities using the standard Debye-Waller factor. We observed similar dependence for photoemission of the surface state. From these results, we discuss the electron-phonon interaction in Ag nanofilms.

II. EXPERIMENTAL DETAILS

We prepared Ag nanofilms by molecular-beam epitaxial (MBE) method using the JPS-100 (ANELVA Co.) MBE system which is connected directly to the ARUPS-10 (VG. Scientific Co.) photoelectron spectrometer. Ag nanofilms were prepared on Cu(111) single-crystalline films with a thickness of 30 nm grown on a Si(111)-7×7 surface. In the present system, the Cu(111) film acts as the substrate supporting the Ag nanofilms. Firstly, the initial Si(111) single-crystalline substrate was chemically treated using Shiraki's method before loading into the ultrahigh-vacuum (UHV) system. Under the UHV in the MBE chamber a Si(111) single crystal was annealed at 1150 K to remove the oxide layer, and then we obtained the clean Si(111)-7×7 surface. Secondly, a Cu(111) single-crystalline film with a thickness of 30 nm was grown onto a Si(111)-7×7 clean surface at room temperature. The thus-deposited Cu(111) film was subsequently annealed at 420 K to enhance the film uniformity. Finally, a Ag nanofilm was grown onto this Cu(111) film at room temperature and subsequently annealed at 420 K. Both Cu and Ag were evaporated from 3-kW electron-gun evaporators. Both deposition rate were 0.01-0.005 nm/sec monitored by calibrated quartz thickness monitor. The pressure during the deposition was kept in the 10^{-9} Pa range. The surface cleanliness and the structure of the initial Si(111)-7×7 substrate, Cu(111) film and the Ag(111) nanofilm were checked by Auger electron spectroscopy and low-energy electron diffraction (LEED) measurements. Both the Cu film and Ag

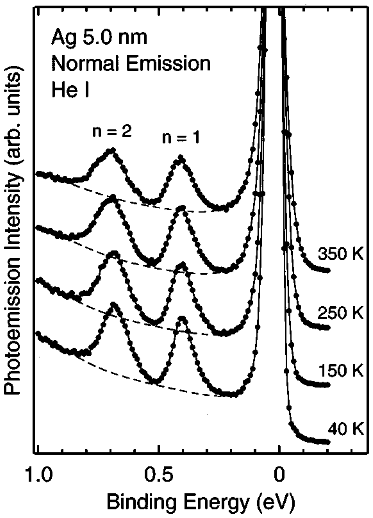

FIG. 1. Temperature dependence of angle-resolved photoemission spectra at normal emission for Ag nanofilm with a thickness of 5.0 nm measured with the He I resonance line ($h\nu = 21.2$ eV). The temperature is indicated on each spectrum.

nanofilm exhibit sharp 1×1 LEED patterns, indicating epitaxial growth along the [111] direction and excellent surface quality.

The thus-prepared samples were transferred into the photoelectron spectrometer through the UHV chamber without exposure to air. The angle-resolved photoemission measurements were performed with the He I resonance line ($h\nu = 21.2$ eV) as the excitation source. The base pressure of the photoelectron spectrometer was also in the 10^{-9} Pa range. The sample temperature was varied between 40 and 350 K using a closed-cycle He refrigerator equipped with a cartridge heater. The total instrumental energy resolution was 50 meV. The acceptance angle of the hemispherical analyzer was ±2°. The angle-resolved photoemission spectra showed no change in the course of the measurements. The Fermi level of the sample was determined by comparison with a gold reference.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of angle-resolved photoemission spectra at normal emission geometry measured for Ag nanofilm with a thickness of 5.0 nm. The intense peak just below the Fermi level originates from the Shockley-type surface state on Ag(111) and its binding energy agrees well with the previous results of photoemission studies for bulk Ag(111) clean surface.[13] The sharpness of this peak, as well as the sharp LEED pattern, reflects the good crystallinity of the present system. In addition, fine structures are observed at 0.40 and 0.67 eV in binding energy. From the detailed thickness-dependent study,[5,6] the energy positions and energy intervals of these fine structures change systematically with nanofilm thickness. Therefore, these fine structures originate from the QW states due to the quantum confinement effect on Ag *sp* valence electrons. In the present system, the potential well confining the Ag *sp* valence electrons is formed by the band gap along Γ-L direction of Cu(111) substrate and a potential barrier associated with the image potential at the vacuum side. As reported previously,[5] the binding energy and quantum number n of each QW state are well characterized by the phase accumulation method,[11,12] which takes into account the phase shifts of the electron wave function on the reflection at both interfaces of Ag nanofilm. In this model, the total phase change during a round trip within the Ag nanofilm should be equal to an integer times 2π. From the calculation based on the phase accumulation model, the observed peaks at 0.40 and 0.67 eV in Fig. 1 correspond to the QW states with the quantum number of $n=1$ and 2, respectively. As shown in Fig. 1, the linewidths of both QW states broaden and their intensities decrease with increasing a temperature. The surface state also exhibits a similar temperature dependence to QW states. This observation for the surface state on Ag nanofilm confirms again the previous results of temperature-dependent photoemission study for bulk Ag(111).[13] Moreover, it is also found that the angle-resolved photoemission spectra for the Ag nanofilms with 3.0 and 6.0 nm show a similar temperature dependence.

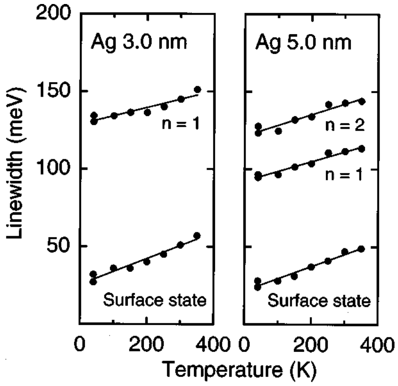

FIG. 2. Temperature dependence of linewidths for QW states and surface state on Ag nanofilms with the thickness of 3.0 and 5.0 nm. Solid lines show the linear fits to the experimental data (see text).

In order to see more clearly the temperature dependence of the linewidth for each sample, we plot the observed linewidth of the QW states (with $n=1$ and 2) and surface state as a function of temperature in Fig. 2. As shown in Fig. 2, it seems that the linewidths of QW states and surface state increase linearly with increasing temperature. In general, the photoemission linewidth can be expressed as a linear combination of the lifetime widths for the photoelectron and photohole. Smith, Thiry, and Petroff[14] have reported the theoretical expression of photoemission linewidths for different data acquisition modes; energy-distribution curve (EDC), constant initial-state spectrum, and constant final-state spectrum. The theoretical linewidth for EDC mode in normal emission geometry indicates that the measured linewidth is identified with the lifetime width for the photohole left after photoemission when the initial-state group velocity component normal to surface is zero (that is, the two-dimensional electronic state with no dispersion along surface normal direction). As reported previously,[4,6] the QW state and the surface state show no dispersion along the surface normal direction and are two-dimensional electronic states. Therefore, the observed linewidths of both QW state and surface state directly reflect the lifetime widths for the photoholes left after photoemission.

The valence photohole mainly decays through the Auger process, phonon scattering and defect and/or impurity scattering. According to the Landau theory of Fermi liquids, the photohole lifetime width due to the Auger process is predicted to be a quadratic dependence on energy, $(E\text{-}E_F)^2$, where E_F is the Fermi level. At finite temperature, the additional temperature dependent term must be taken into account, so this Auger decay contribution to the lifetime width is expressed as $\Gamma_{e\text{-}e} = 2\beta[(\pi k_B T)^2 + (E - E_F)^2]$.[15] However, the theoretical temperature dependence of Auger decay for Ag is less than 1 meV in the relevant temperature region between 40 and 350 K. The defect and/or impurity scattering contribution is proportional to their concentration but independent of temperature. Therefore, we considered that the dominant temperature-dependent contribution to the lifetime width is associated with the phonon scattering as described below. The lifetime width due to phonon scattering can be expressed as

$$\Gamma_{e\text{-}p} = 2\pi\hbar \int_0^{\omega_{\max}} d\omega' \alpha^2 F(\omega')[1 - f(\omega - \omega') + 2n(\omega) + f(\omega + \omega')], \tag{1}$$

where ω is the phonon frequency, $\alpha^2 F(\omega)$ is the Eliashberg coupling function, $f(\omega)$ is the Fermi-distribution function, and $n(\omega)$ is the Bose-Einstein distribution function.[16] In the high-temperature limit, Eq. (1) reduces to

$$\Gamma_{e\text{-}p} = 2\pi\lambda k_B T \tag{2}$$

with the electron-phonon mass-enhancement parameter λ.[16] Therefore, the linear temperature dependence of the observed linewidth originates from the phonon scattering contribution to the photohole lifetime, expressed by Eq. (2).

In addition to the above intrinsic lifetime width, the extrinsic width due to the inhomogeneity of nanofilm thickness should be considered for the observed linewidths of the present QW states, since the binding energies of QW states depend on the nanofilm thickness.[5] Moreover, it should be considered that the energy position of QW state relative to the substrate band gap influence the observed linewidth. The QW state with a binding energy close to the band-gap edge of the substrate has long decay length into the substrate as an evanescent state, and then exhibits bulklike electronic structure. For bulklike transitions, the photoemission linewidth is mostly generated by the momentum broadening along surface normal direction. Of course, the observed linewidth also includes the instrumental width due to the finite energy and angular resolutions. The total observed linewidth can be explained by the combination of the intrinsic lifetime contribution and extrinsic contributions discussed above. It is quite complicated to discuss these contributions independently. However, the above extrinsic contributions to linewidth are independent of the temperature and only the intrinsic lifetime contribution depends on the temperature. Therefore, the temperature-dependent change of the observed linewidth originates from that of the intrinsic photohole lifetime width. We focus here the temperature dependence of the phonon scattering contribution and discuss the electron-phonon mass-enhancement parameter through the experimental temperature coefficient of the linewidth.

In order to estimate the electron-phonon mass enhancement parameter λ for each state, we have carried out a linear fit to the experimental data by the least-squares method. The fitting lines to the experimental data are shown in Fig. 2. The fitting lines reproduce the experimental dependence fairly well. For a Ag nanofilm with a thickness of 3.0 nm, the parameters λ obtained from the fits are 0.10±0.02 and 0.15 ±0.01 for the QW state with $n=1$ and the surface state, respectively. For a thickness of 5.0 nm, the obtained parameters λ are 0.12±0.01, 0.13±0.02, and 0.15±0.01 for the QW state with $n=1$, with $n=2$, and the surface state, respectively. For a thickness of 6.0 nm (not shown in Fig. 2), the obtained parameters λ are 0.13±0.02, 0.10±0.02, and 0.12 ±0.01 for QW state with $n=1$, with $n=2$, and surface state, respectively. These results indicate that the electron-phonon mass-enhancement parameters are almost same for each QW state and surface state. Moreover, it is found that these values are almost the same as that given by Grimvall,[16] which is an average over the Fermi surface of λ=0.13 from completely different methods.

Recently, Matzdorf, Meister and Goldmann[17] have reported a linear temperature dependence of the photoemission linewidths for surface states on Cu(111) and Cu(100) and have discussed the electron-phonon coupling of the *s,p*-like Shockley state and *d*-like Tamm state. According to this paper, the experimental electron-phonon mass-enhancement parameters for the Shockley state and Tamm state are λ=0.14±0.01 and 0.09±0.02, respectively. As is well known, the Shockley state extends its wave function several atomic layers deep below the surface but the Tamm state essentially localizes within the outermost layer. Matzdorf, Meister, and Goldmann have concluded that the difference of the electron-phonon mass-enhancement parameter for each state originates from the different spatial extent of each state. In an analogy with the previous discussion, it is conjectured that the QW state in the present system couples more weakly to phonons than the bulk state and shows a smaller electron-phonon mass-enhancement parameter than the bulk state. In addition, the surface state localizes in the surface region and is consequently expected to show a smaller electron-phonon mass-enhancement parameter than that for QW state. However, the present electron-phonon mass-enhancement parameters for the QW state and surface state show no significant difference, and agree well with an average over the bulk Ag Fermi surface. Therefore, we believe that the electronic states with their spatial extent more than several atomic layers show almost the same electron-phonon mass-enhancement parameter as the bulk state. This suggests that the lateral extent of the wave function may dominate the electron-phonon interaction, because the wave functions of bulk states, QW states, and surface states extend to a same spatial extent in directions parallel to surface.

The QW state originates from the quantization of the parental bulk *sp* valence band $E(k_\perp)$ along the Γ-L direction in reciprocal lattice space and each QW state specifies the corresponding $(E, k_\perp)$.[5] This indicates that we can discuss the binding energy and wave-vector dependence of the electron-phonon mass-enhancement parameter of each QW state. In general, λ depends on binding energy E and wave vector $\mathbf{k}$. In the present study, no significant dependence on the QW state eigenvalue is observed. In other words, no significant

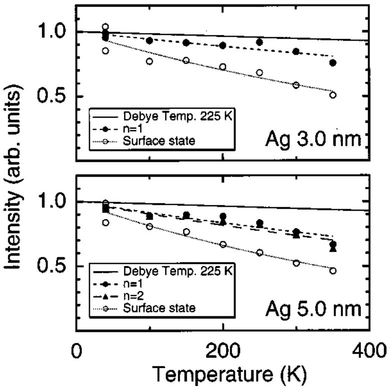

FIG. 3. Temperature dependence of the intensities (amplitudes at peak position) for QW states and surface state on Ag nanofilms with the thickness of 3.0 and 5.0 nm. The short-dashed, long-dashed, and dotted lines show the fits the experimental data by Debye-Waller theory. Temperature dependence predicted by Debye-Waller factor with the bulk Debye temperature of 225 K is also shown by solid line.

dependence on E and $k_\perp$ is observed. The QW states in the present system originate from the *sp* valence band of Ag within the small region of whole Brillouin zone (about 10% of Γ-L wave vector around L point).[5] Therefore, no significant dependence of electron-phonon mass-enhancement parameter on E and $k_\perp$ is observed.

Finally, we discuss the temperature dependence of the photoemission intensity for each state. The temperature dependence of the intensities are shown in Fig. 3. As shown in Fig. 3, the peak intensities for both QW state and surface state decrease with increasing temperature. It is considered that this decrease of peak intensities is due to the increase of transition involving electron-phonon scattering (phonon-assisted indirect transition). In this indirect transition process, the wave vector is changed through emission or absorption of acoustic phonons, resulting in the decrease of direct transition intensity. The probability of the phonon-assisted indirect transition is determined by the occupation of phonon states. This causes a decrease of direct transition-peak intensities with increasing temperature. The decrease of the direct transition can be described by the Debye-Waller factor and the photoemission intensity can be expressed as

$$I = I_0 \exp(-bT) \quad \text{with} \quad b = \frac{3\hbar^2 |\Delta k|^2}{M k_B \Theta_D^2}, \tag{3}$$

in the high-temperature limit, where M is the mass of an atom, Θ_D is a Debye temperature, and Δk is difference in the wave vector which here is equal to a reciprocal lattice vector. The fitted curves to the experimental data using Eq. (3) are shown in Fig. 3. The short-dashed, long-dashed, and dotted lines correspond to QW state with $n=1$, with $n=2$, and surface state, respectively. The calculated curves by using the fit-parameter Θ_D (the ''effective'' Debye temperature) seem to reproduce the experimental data well. In Fig. 3, an important point to note is that the intensities of QW states decrease more slowly with increasing a temperature than the surface state. This indicates that the effective Debye temperature of the phonon states coupled to QW states are higher than those coupled to surface state. The properties of the phonon states coupled to QW states might be characterized by the bulk phonon states, since the QW states extend their wave function whole layer of Ag nanofilm. On the other hand, the surface state localizes in the surface region and consequently couples dominantly to the phonon state at the surface region. In the surface region, the lattice property is modified due to surface phonons and enhanced lattice vibrations. This surface lattice property is expressed by a surface Debye temperature, which is smaller than that of the bulk phonon. Therefore, it is considered that the different damping rate with temperature of the QW and surface state are qualitatively explained as the different ''effective'' Debye temperatures of bulk phonon state and surface phonon state. For a Ag nanofilm with a thickness of 3.0 nm, the effective Debye temperatures Θ_D obtained from the fits using Eq. (3) are 126 ± 12 and 74 ± 7 K for the QW state with $n=1$ and surface state, respectively. For the thickness of 5.0 nm, the obtained Θ_D are 103 ± 10, 97 ± 8, and 68 ± 4 K for the QW state with $n=1$, with $n=2$, and surface state, respectively. The present effective Debye temperature derived from the surface state agree well with the previous report by Paniago *et al.*[13] In Fig. 3, the temperature dependence predicted by Debye-Waller factor with the bulk Ag Debye temperature of 225 K (Ref. 18) is also shown. The effective Debye temperatures for the QW states in both samples are much smaller than the bulk Ag Debye temperature. In addition, the effective Debye temperatures for the surface states on both samples are also much smaller than the typical surface Debye temperature of 150 K determined by previous LEED study.[19] This suggests that the standard Debye-Waller factor does not quantitatively explain the present temperature dependence and it is necessary to consider additional contributions in the photoemission process. In order to fully discuss the experimental temperature dependence of the photoemission intensity, a quantitative interpretation that pays attention to the overall electron-phonon coupling, such as k-dependent Debye-Waller factor, different thermal lattice properties in the bulk and surface regions, and the modification of the initial and final states by electron-phonon coupling (and resulting photoemission matrix element), etc., would be necessary.

IV. SUMMARY

We have performed a temperature-dependent photoemission study for quantum-well states in Ag(111) nanofilms. The linewidths of both the quantum-well and surface state broaden and their intensities decrease with increasing temperature from 40 to 350 K. The linear temperature dependence of the linewidth is explained as the temperature dependence of the phonon contribution to the photohole lifetime width, allowing the discussion about the electron-phonon mass-enhancement parameter λ in Ag nanofilms. The experimental electron-phonon mass-enhancement parameters for quantum-well states are $\lambda = 0.10$–0.15 with no considerable dependence on the film thickness and the binding energy. These are almost the same as that for Shockley-type surface state and also agree well to an average over the bulk Ag Fermi surface. The temperature dependence of the intensity has been discussed using the standard Debye-Waller factor.

The different damping rate with temperature of QW and surface state are qualitatively explained as the different properties of the phonon states coupled to each state. However, the effective Debye temperatures for both states are much smaller than bulk values, suggesting that quantitative interpretation, which consider the overall electron-phonon coupling is necessary.

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