Atomic-layer-resolved bound states in quantum wells analyzed using a pseudopotential approach

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We observed atomic-layer-resolved surface states and quantum-well states using angle-resolved photoelectron spectroscopy on atomically flat Ag/Au(111) thin films grown with a two-step method. The layer dependence of binding energies of the bound states was determined unequivocally for a Ag coverage up to 17 monolayers. We analyzed both the surface states and the quantum-well states using a one-dimensional pseudopotential approach. Our results show a fruitful combination of growth techniques and theoretical analysis for thin-film systems.

Electronic confinement attracts great interest in relation to both a fundamental understanding of quantum mechanics and practical applications. The quantum size effect (QSE) becomes important when the size of a device is comparable with the de Broglie wavelength of charge carriers.[1] Properties of a system such as thermal stability,[2] superconductivity,[3] and surface reactivity[4] alter markedly as the size of the system increases from that of one atom. Manipulating that size with atomic precision becomes a critical issue in tuning the properties of nanoscale devices. For heterostructures of a metal on another metal or semiconductor, the film thickness can be determined on studying the quantized binding energies of their bound states, but an atomic resolution has been typically hindered by the film quality and the thermal broadening of the energy levels. Here we demonstrate that, with the combination of advanced growth techniques, signal detection, and modeling, the uncertainty in the thickness of atomically flat metallic films, such as Ag on Au(111), becomes completely eliminated on analyzing the layer-resolved bound states. Several techniques have been utilized to analyze the quantized energy levels in a metallic thin film, such as the Green's-function matching method,[5,6] the calculations within density-functional theory,[7] and the phenomenological phase accumulation model (PAM).[8,9] Among them, the PAM is employed the most because of its simplicity, but it fails to account for the layer dependence of the binding energies of the bound states that attenuate in the film, such as the surface state of Ag/Au(111) measured in this work. In this study, we adapt a one-dimensional pseudopotential (1DPP) model and in a coherent fashion succeed in analyzing all bound states, including the surface states and the quantum-well states (QWS), in Ag/Au(111).

At the National Synchrotron Radiation Research Center in Hsinchu, Taiwan, we recorded photoemission spectra with an electron energy analyzer, which allows spectra at various emission angles to be collected simultaneously with an angular resolution 0.125°. The sample temperature was kept at 50 K during measurements. Photoelectrons were excited with photons of energy 21 eV; the resolution of the experimental setup was better than 10 meV in kinetic energy and 0.01 Å^{-1} in wave vector in the in-plane direction of the surface. All spectra are shifted to have zero binding energy at the Fermi level. The atomically flat Ag/Au(111) thin films of various Ag coverage were prepared with the two-step

method[9–11] as follows. Silver was evaporated onto a clean Au(111) surface or an atomically flat Ag/Au(111) film, of which the temperature was kept at 50 K. The deposited Ag films were disordered but became crystalline on annealing near 300 K.[11] The sample temperature was kept below 300 K to avoid intermixing between Ag and Au.[12–14] A previous study demonstrated that it is feasible to construct atomically flat Ag/Au(111) films and to perform layer-resolved analysis on them.[11] With an initially clean Au(111) surface, Ag at 1.4 monolayers (ML) was deposited during each deposition cycle; 1 ML denotes one layer of Ag on Ag(111), ~1.39 $\times 10^{15}$ atoms/cm^2. As a result, Ag/Au(111) thin films in a series with an increment 1.4 ML in the Ag coverage became available for photoemission measurements. The amount of deposited Ag was calibrated with the layer-resolved surface state.[11,15] Deposition conditions were controlled with particular care to ensure that the same amount of Ag was deposited each time.

Figure 1 shows typical results from photoemission measurements near the center of the surface Brillouin zone of Ag/Au(111). The sharp surface state near the Fermi level in Figs. 1(a) and 1(b) indicates that each film is well ordered with a Ag(111) surface. The weaker parabolic features with larger binding energies are the QWS. Our results agree with those from previous work[16] apart from one significant distinction: the signals of the QWS are split instead of being single broad lines. For atomically flat films, the two components in a split QWS correspond to signals from Ag/Au(111) films with the film thickness differing by one atomic layer. The binding energies of the two components in a split signal are determined through an analysis of line shape: each split signal is fitted to two Voigt line shapes, of which two typical results appear in Fig. 1(c).

With increasing coverage of Ag, the binding energies of bound states in Ag/Au(111) shift toward the Fermi level,[11,14,16] as seen in Fig. 2. The difference between the binding energies of the two components of each split signal decreases as the Ag film thickness increases. As a result, the spectra of thick Ag films are not layer resolvable even when the films are atomically flat. The binding energies of bound states in Ag/Au(111) are shown as circles in Fig. 3. The surface states with Ag coverage up to 7 ML and the QWS with Ag coverage from 7 to 17 ML were resolvable with atomic resolution, and each resolved component was fitted to
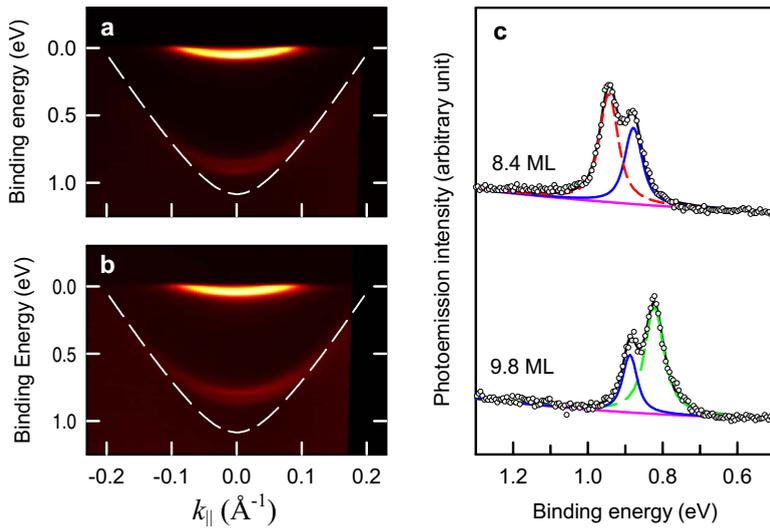
FIG. 1. (Color online) Typical results from photoemission measurements. (a) and (b) both are photoemission intensity plotted against the binding energy and the component of the wave vector of photoelectrons parallel to the surface ($k_\parallel$) measured from Ag of 8.4 ML and of 9.8 ML on Au(111), respectively. Dashed white lines depict the projected band edge of bulk Au. (c) Layer-resolved energy distribution curves. Open circles on the upper and lower curves denote the energy distribution of normal emission ($k_\parallel=0$) in (a) and (b), respectively. The nominal Ag coverages are indicated at the left of the curves. From the analysis of line shape, the 8, 9, and 10 ML peaks are shown as short-dashed red, solid blue, and long-dashed green lines, respectively.
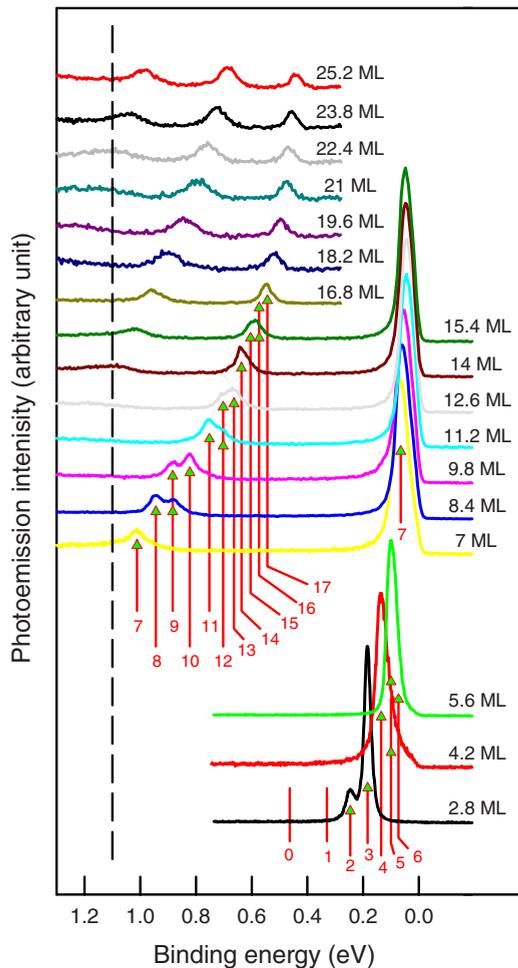

FIG. 2. (Color online) Curves of energy distribution of normal emission from Ag/Au(111). The nominal Ag coverage is shown at the right of the curves. Green triangles indicate binding energies of the layer-resolved bound states determined through the analysis of line shape. The numbers with red leads to green triangles label the Ag coverage to which the layer-resolved signals correspond. The vertical dashed line indicates the binding energy of the band edge of bulk Au.

one Voigt function. The binding energies of the surface states agree with reported results.[11,14] Each bound state that was not layer resolvable was fitted to one Voigt function, and its film coverage was set to the nominal value. To investigate the relation between the binding energy of the bound states and the corresponding film thickness, we first performed an analysis based on the PAM. A bound state exists when the round-trip phase shift of its wave function satisfies the phase relation.[8,9,16] The band dispersion is approximated with the nearly free-electron two-band model, in which the band edge below the Fermi energy (E_{Ag}) and the band gap ($2V_G$) at the L point of Ag and the effective electron mass along the surface normal (m_e^*) are free parameters.[8,9,16,17] A least-squares fit to the binding energies of the QWS yields $E_{Ag}=-0.33$ eV, $V_G=2.17$ eV, and $m_e^*=0.76m_e$; m_e is the free electron mass. These parameters of the band dispersion agree with reported values,[17] and the calculated binding energy of the QWS, plotted as green lines in Fig. 3, agrees satisfactorily with the experimental data.

The assumption of a standing wave in the film in the PAM fails for the surface states that attenuate in the film. To investigate both the surface state and the QWS of Ag/Au(111) simultaneously, we conducted an analysis based on a 1DPP, which has been used to analyze the surface state of a metallic thin film.[14,18] Figure 4(a) shows an example of the 1DPP for Ag/Au(111). Periodic potentials are constructed to produce the correct band edges and band gaps at the L point of Ag and Au. A linear combination of Ag and Au potentials is used to generate a smooth transition of the potential at the interface between the Ag film and the Au bulk. The surface potential, suggested by Chulkov *et al.*,[19] is adapted with two modifications: the potential is referred to the Fermi level, instead of the vacuum level, for correct alignment of potentials at the boundaries, and the free-electron mass is replaced with an effective electron mass to include the multiband effect.[8] Ignoring the small layer-dependent fluctuation,[14,20] we set the work function to the nominal value, 4.74 eV, for Ag(111).[21] Requiring the pseudopotential and its first derivative to be continuous leaves only three free parameters in this analysis: two serve to adjust the strength of the surface potential and the position of its image plane and the third is the effective electron mass for both Ag and Au.
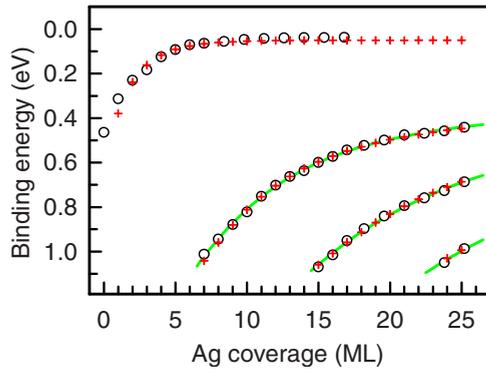
FIG. 3. (Color online) Binding energies of bound states of Ag/Au(111) plotted against Ag coverage. The circles denote the data from experiments. The Ag coverage is set to either integral numbers from counting layer by layer for layer-resolved signals or the nominal values for the signals that are not layer resolvable. The green lines and the red crosses are results from the analyses according to the PAM and the 1DPP approaches, respectively.

With that 1DPP available, we solved the Schrödinger equation numerically to calculate the binding energies and the wave functions (Ψ) of the bound states. Selected probability densities of the bound states ($|\Psi|^2$) are plotted in Fig. 4. The probability densities of the surface states on 4 and 13 ML Ag/Au(111), shown in Figs. 4(b) and 4(c), respectively, are similar, with slightly varied distributions of their probability densities. The binding energies of the two states are within the Ag band gap, and their wave functions both attenuate in the Ag film. Figure 4(d) shows the probability density of the QWS in 13 ML Ag/Au(111), which is a typical QWS of which the binding energy is distant from the Au band edge. Much of the wave function of the QWS resides within the Ag film, with little penetration into the vacuum and the substrate. The penetration of the wave function of a QWS into the Au bulk depends greatly on its binding energy. When the binding energy of a QWS is near the Au band edge, e.g., in the case of the 7 ML Ag/Au(111), the wave function of the QWS can extend far into the Au bulk.

The free parameters were evaluated with a least-squares fit. Because the 1DPP approach treats the case with the coverage of integral atomic layers, only data points associated with integral atomic layers were included in the fits. The effective electron mass, $0.79m_e$, from the fit agrees satisfactorily with the reported value.[17] The parameters from the best fit were used to calculate the binding energies of the bound states of Ag/Au(111) with a Ag coverage up to 25 ML, plotted as red crosses in Fig. 3. With only three free parameters, the experimental data and the calculated results agree well.

Removing uncertainty in a structural dimension is a major challenge in utilizing the QSE. For research on thin films, layer-resolved signals allow removal of the uncertainty in the film thickness. An uncertainty in the absolute coverage remains, however, for systems such as Ag/Au(111) for which the QWS are absent at small coverage. For example, the relative error of a quartz-crystal microbalance (QCM) is 15%–20%, and the error in the film coverage determined with the QCM is thus more than 1 ML for a film thicker than 7 ML. In our work, the deposition conditions were carefully
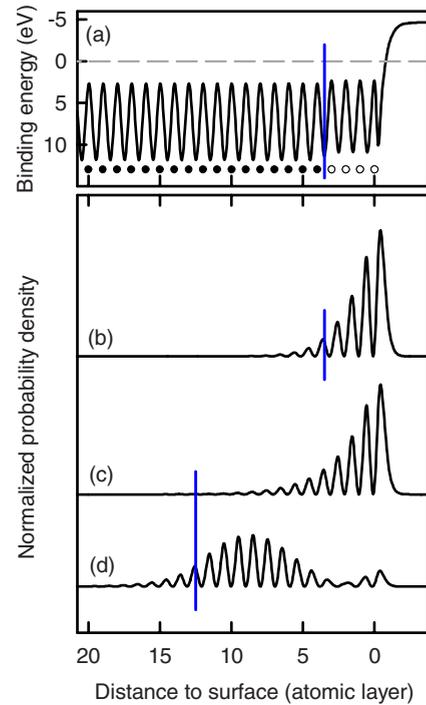

FIG. 4. (Color online) Typical results from the analysis with the 1DPP approach. The origin is set at the position of the Ag atom on the surface. The vertical blue lines mark the interface between the Ag film and the Au substrate. (a) Potential for Au(111) covered by Ag at 4 ML. The positions of Ag and Au atoms are labeled with open and filled circles, respectively. The binding energy is referred to the Fermi level (dashed line). (b) Normalized probability density of the surface state of 4 ML Ag on Au(111); (c) surface state of 13 ML Ag on Au(111); (d) QWS of 13 ML Ag on Au(111).

controlled to maintain constant the amount of Ag deposited during each deposition. The amount of deposited Ag was precisely determined on analyzing the layer-resolved surface state at a small Ag coverage.[11,15] Through counting layer by layer, we determined unequivocally the absolute thickness to which the QWS corresponds.

Several approaches have been employed to treat the bound states in a metallic thin film. As mentioned above, based on a simple phase relation, the PAM is popular for analysis of a QWS in thin films, but an assumption of a standing wave in the film used in the PAM fails for the surface states that attenuate in the film. The calculations within density-functional theory[7] provide a qualitative description of all bound states, but it is difficult for its result to agree quantitatively with experimental data. The Green's-function matching method[5,6] provides a way to solve the one-dimensional Schrödinger equation and, in principle, is equivalent to the 1DPP approach; its main advantage arises from the fewer calculations performed when there are only a few boundaries of potentials of simple form at which the wave functions are matched, but its advantage erodes when treating a system with complicated potentials. The 1DPP approach in this work takes a straightforward approach to treat simultaneously all bound states (such as the surface state and the QWS), with the ability to study systems with complex pseudopotentials. Solving the Schrödinger equation yields

also the wave functions in the film, the substrate, and the vacuum; these wave functions enable further analysis of other physical quantities.

In summary, we have reinvestigated the Ag/Au(111) quantum-well system with the two-step growth method. Angle-resolved photoemission spectra were recorded with atomic-layer resolution on atomically flat Ag/Au(111) thin films. The layer dependence of the binding energies of both the surface states and the QWS in Ag/Au(111) was determined precisely experimentally up to 17 ML and analyzed on the same footing using the 1DPP approaches.

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