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Characterizing the wetting of metallic thin films with angle-resolved photoelectron spectroscopy

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The wetting of thin Ag films on Cu(111) is characterized in detail with angle-resolved photoelectron spectroscopy. After constructing disordered Ag films on Cu(111), we monitored the evolution of their layer-resolved Shockley states during wetting. Our results provide the first observation of a transitional state, which implies a coexistence of clean Cu(111), 1 ML of Ag on Cu(111), and 2 ML of Ag on Cu(111). The evolution of these Shockley states indicates a two-process model of wetting.

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The heteroepitaxial growth of thin films has drawn great interest because of its major role in device construction. The growth of a film involves complicated dynamic processes, and the mode of film growth varies significantly with growth parameters such as film material, rate of deposition, and substrate temperature.[1] The ability to characterize and to control these dynamic processes during film growth is crucial for the success in constructing nanodevices of specific structures. Among many dynamic processes, we are most interested in *wetting*. The importance of wetting is obvious during the growth of flat metallic thin films that serve as a well-defined foundation for constructing advanced nanostructures. Once the conditions for film material wetting a flat substrate are found, an atomic flatness of the film is ensured. Nevertheless, wetting is poorly characterized mainly because of its dynamic nature. Most tools with sufficient surface sensitivity and atomic resolution, such as a scanning probe microscope, are excellent when applied to a static surface, but are inadequate to characterize dynamic processes on a surface because of their slow acquisition of data.

One alternative to characterize the morphology of a metallic thin film is to measure its confined electronic states. Such a film is generally considered to constitute a quantum well; the dispersions of its electronic states are directly linked to the film properties, e.g., thickness, lateral size, roughness.[2–6] In this report, we demonstrate that the wetting of a metallic thin film, a complicated dynamic process, becomes explored on monitoring the evolution of the confined electronic states in that film; for this purpose we apply thin Ag films on Cu(111). Ag/Cu(111) is extensively utilized as a model system for the study of heteroepitaxial growth with a great lattice mismatch. Previous studies showed that Ag in one monolayer (ML) on Cu(111) forms a (9×9) superstructure.[7–10] Furthermore, the growth of Ag on Cu(111) near 300 K conforms to the Stranski-Krastanov mode: layer-by-layer growth up to 2 ML and three-dimensional island growth at greater coverage,[7,8] although the layer-by-layer growth near 300 K might be imperfect.[9] To investigate the wetting of thin Ag films in a controlled manner, we constructed disordered Ag films through depositing Ag onto various ordered surfaces at low temperature, which became subsequently ordered on annealing. This evolution of the film morphology during wetting was characterized through measuring the layer-resolved Shockley states of Ag/Cu(111)[8] with angle-resolved photoelectron spectroscopy (ARPES). Our results reveal that there exist transitional states comprising ordered domains of Cu(111) covered with 0, 1, and 2 ML of Ag before the wetting is completed. A two-process model of wetting is proposed to explain the experimental observations. Our work provides insight into the dynamic process of wetting, and demonstrates the power of real-time ARPES in investigating dynamic processes on the surfaces of thin films.

Our experiments were performed at an ultra-high-vacuum end station installed at beamline 21B1 in Taiwan's National Synchrotron Radiation Research Center (NSRRC). Photoemission measurements were performed with photons of energy 21 eV. The energy distribution of photoelectrons was recorded with an electron-energy analyzer (Scienta SES200) with angular resolution 0.125°. All spectra are shifted to have zero binding energy at the Fermi level. A single crystal of Cu(111) was mounted on a manipulator, of which the temperature was variable from 37 to 1000 K. The sample temperature was measured with a thermocouple junction (type E) mounted right beside the sample. The sample was cleaned with cycles of Ar-ion sputtering and annealing. Silver was evaporated from a Knudsen crucible; its rate of deposition was calibrated with the evolution of the Shockley states on Ag/Cu(111).[8,11,12] To monitor the evolution of the sample surface, we recorded photoemission spectra during sample annealing.

Figure 1 shows typical results from well ordered thin films of Ag on Cu(111). Silver (0.5 and 1.6 ML) was deposited on Cu(111) at 300 K and annealed to 450 K. Although layer-by-layer growth was expected, we found that the uniformity of Ag films (less than 2 ML) deposited near 300 K was substantially improved with brief annealing, in agreement with previous work with thicker Ag films on Cu(111).[13,14] The photoemission spectra measured at 300 K are shown in Figs. 1(a) and 1(b), in which the photoemission intensities are plotted against the binding energy and the in-plane component of the wave vector, $k_{\parallel}$; the corresponding energy distribution curves (EDC) of normal emission ($k_{\parallel}=0$) appear in Fig. 1(c). The Shockley states of different origins are well resolved; S_{Cu}, S_1, and S_2 label the Shockley states on Cu(111), 1-ML Ag/Cu(111), and 2-ML Ag/Cu(111), respectively; "n-ML Ag/Cu(111)" denotes Cu(111) covered with n ML of Ag. The binding energies of these three states agree with reported values,[8] but these energies vary with temperature; they move away from the Fermi level as the

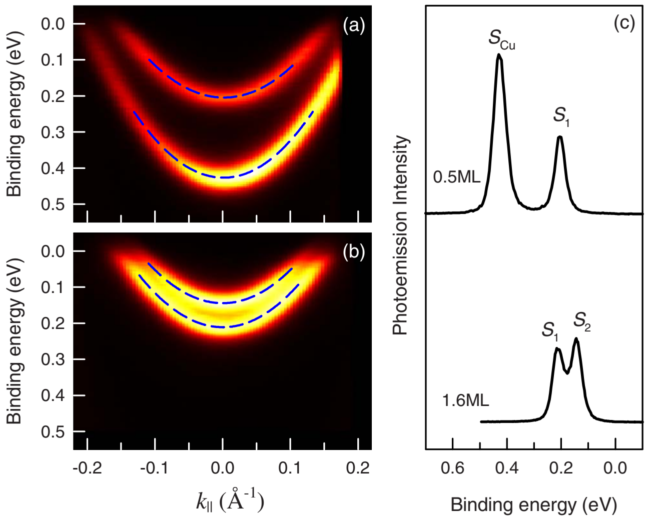

FIG. 1. (Color online) (a) and (b) are the photoemission intensities measured on Cu(111) covered with 0.5 and 1.6 ML of Ag at 300 K, respectively. (c) The energy distributions of normal emission ($k_{\parallel}=0$) in (a) and (b). The Shockley states on Cu(111) covered with 0, 1, and 2 ML of Ag are labeled as S_{Cu}, S_1, and S_2 in (c), respectively, and their dispersions are drawn as blue dashed lines in (a) and (b).

temperature decreases.[15] The observation of only two Shockley states in each spectrum indicates that the Ag films are atomically flat with two distinct film thicknesses under the given growth conditions. The in-plane dispersion of the Shockley states in Figs. 1(a) and 1(b) is sharp and parabolic, which indicates that the lateral dimension of the ordered domains is large and the associated Shockley states are nearly free-electron-like in the in-plane direction. The in-plane effective masses of the Shockley states, $m_{\parallel}^{*}$, were determined through fitting their dispersions to second-order polynomials, yielding $m_{\parallel}^{*}/m_e=0.36$, 0.40, and 0.42 for S_{Cu}, S_1, and S_2, respectively; m_e is the mass of a free electron. The fit, indicated with blue dashed lines in Figs. 1(a) and 1(b), is satisfactory; the values of $m_{\parallel}^{*}$ conform to those reported for Cu(111) and thicker Ag films.[13,16]

The main interest of this work is to investigate the wetting of Ag on Cu(111). Three specially crafted, disordered Ag films, denoted as Samples A, B, and C, became ordered on annealing; the evolutions of their Shockley states were measured as summarized in Fig. 2. In Fig. 2(a), 1 ML of Ag was deposited on Cu(111) at 98 K and annealed to 450 K (Sample A). In Fig. 2(b), 0.5 ML of Ag was deposited on Cu(111) at 66 K and annealed to 392 K (Sample B). After completing the measurement in Fig. 2(b), the sample was cooled to 57 K, and additional 0.5 ML of Ag was deposited (Sample C). The sample was then annealed, and the result is shown in Fig. 2(c). As the Shockley state of Cu(111) (S_{Cu}) was severely suppressed at low temperature because of photon-stimulated surface deterioration,[17] the sample was moved to a new location for measurement at temperatures 234, 191, and 220 K in Figs. 2(a)–2(c), respectively. The spectra measured on a new location show the existence of S_{Cu}, which indicates that S_{Cu} has developed at a lower temperature.

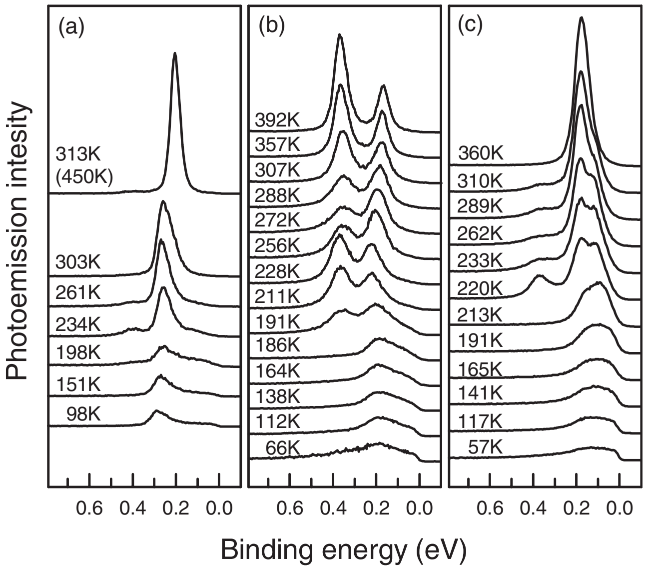

FIG. 2. Three stack plots show the evolution of the Shockley states during annealing. The temperatures of measurements are labeled with the spectra. (a) 1ML of Ag was deposited on Cu(111) and annealed (Sample A); the sample was annealed to 450 K before the spectrum was measured at 313 K. (b) 0.5 ML of Ag was deposited on Cu(111) and annealed (Sample B). (c) 0.5 ML of Ag was deposited on Sample B and annealed (Sample C).

For Sample A [Fig. 2(a)], the spectrum at 234 K comprises a dominant S_1, a small S_{Cu}, and other weak features with binding energy between 0.1 and 0.2 eV; only S_1 is left after the sample was annealed to 450 K, consistent with Ag wetting Cu(111) at an elevated temperature. One thing worth mentioning is the noticeable change in the lineshape of the surface state when the sample was annealed from room temperature to 450 K. This change is associated with a transition of the surface structure from the moiré to the triangular structure.[8] In Fig. 2(b), each spectrum measured on Sample B from 191 K to 392 K comprises two resolved features. The features at the left and right are assigned to S_{Cu} and S_1, respectively.[8] S_{Cu} degrades between 256 and 288 K and recovers on annealing above 288 K. This evolution of S_{Cu} during annealing results from impurity or defect scattering, agreeing with a previous observation.[17] The sharp S_{Cu} and S_1 in the spectrum at 392 K indicate the coexistence of well ordered Cu(111) and 1-ML Ag/Cu(111). In Fig. 2(c), the spectrum measured for Sample C at 57 K shows no noticeable feature, indicating that the surface is disordered after the deposition of Ag at low temperature. The total Ag coverage of Sample C is 1 ML, and, after annealing is completed, 1-ML Ag/Cu(111) is expected on the resulting surface, consistent again with the fact that Ag wets Cu(111) at an elevated temperature. This expectation is verified with the spectrum at 360 K in which only S_1 is observed. Although the total Ag coverage on both Samples A and C is 1 ML, the evolution of their electronic states shows a remarkable dissimilarity. Instead of one dominant S_1 during annealing in Fig. 2(a), disparate traditional states are observed in Fig. 2(c). The spectrum at 220 K in Fig. 2(c) comprises three resolved features, of which the binding energies resemble

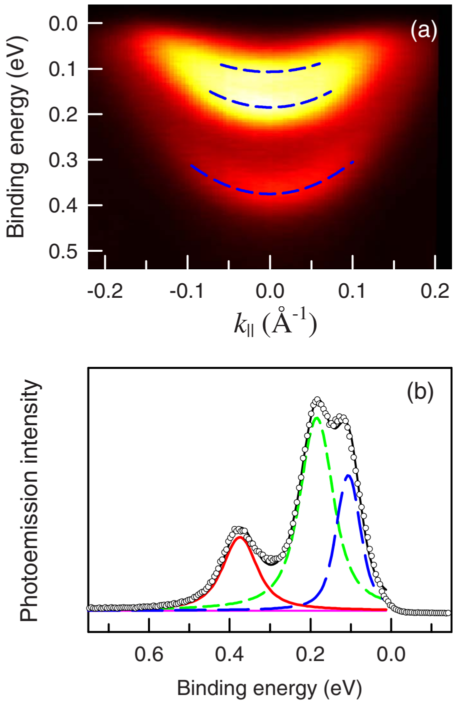

FIG. 3. (Color online) Result of the photoemission measurement on Sample C at 220 K. (a) shows the two-dimensional (2D) photoemission intensity. (b) is the EDC of normal emission in (a). From an analysis of lineshape, S_{Cu}, S_1, and S_2 are plotted as red solid, green short-dashed, and blue long-dashed lines in (b), respectively, and their dispersions are drawn as blue dashed lines in (a).

those of S_{Cu}, S_1, and S_2. The transitional surface implies hence a coexistence of three surfaces—Cu(111), 1-ML Ag/Cu(111), and 2-ML Ag/Cu(111). As the annealing temperature is increased above 220 K, S_{Cu} and S_2 fade gradually and disappear completely at 360 K. Remarkably, the three surfaces coexist until 310 K while the wetting of Cu(111) by Ag is in progress. This result indicates that the wetting of Cu(111) by Ag is not an abrupt process near 300 K; likely for this reason brief annealing greatly improves the quality of thin Ag films deposited on Cu(111) near 300 K.

The nature of the transitional state is better understood with further analyses of its photoemission spectra. Figure 3(a) is a two-dimensional plot of photoemission intensity measured on Sample C at 220 K, and Fig. 3(b) is its EDC of normal emission, which is the same as that at 220 K in Fig. 2(c). The binding energies and the intensities of the three components in each EDC are determined with fitting; the results are plotted in Fig. 3. In Fig. 3(a), the dispersions of the three Shockley states are parabolic, with effective masses $m_{\parallel}^{*}/m_e$=0.55, 0.59, and 0.84 for S_{Cu}, S_1, and S_2, respectively. Relative to the well ordered films in Fig. 1, the dispersions of the Shockley states of the transitional state are broadened, their effective masses are larger, and their binding energies move slightly toward to the Fermi level. All these observations imply that there exists random lateral confinement of these states;[3–5] the Ag film consists of flat ordered patches with substantial variation of their lateral size and shape.

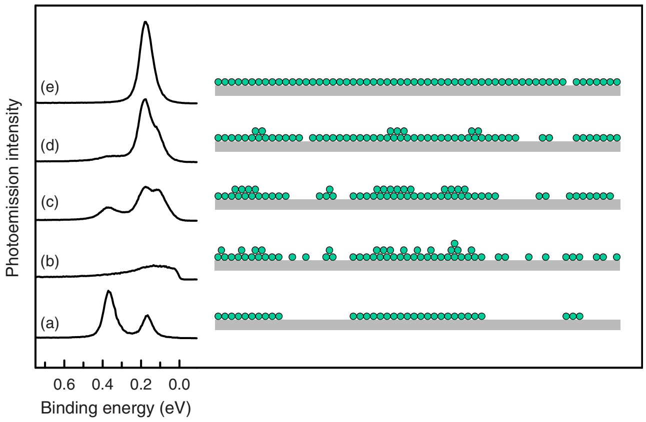

FIG. 4. (Color online) Sketches illustrating the wetting of the Ag film on Sample C. The spectra on the left were measured at various stages of wetting; their corresponding surface morphologies are sketched on the right. (a) Sample B at 392 K (b) Sample C at 57 K. (c) Sample C at 220 K (d) Sample C at 310 K (e) Sample C at 360 K. The strips and circles symbolize the Cu substrate and Ag atoms, respectively.

Additional information about the wetting process is retrieved from analysis of the intensity ratio between components of the spectrum in Fig. 3(b). As mentioned earlier, S_{Cu} is susceptible to photon-induced deterioration,[17] and a quantitative analysis of its intensity is non-trivial. The intensity ratio between S_1 and S_2 is S_1/S_2=2.1, which is explicable with a two-process model of wetting as follows. For fully annealed 0.5 ML Ag/Cu(111), the surface area of Cu(111) and 1-ML Ag/Cu(111) is the same. When additional 0.5 ML of Ag is randomly deposited onto the surface, Ag in an equal proportion (0.25 ML) is expected to be deposited onto both Cu(111) and 1-ML of Ag/Cu(111). Assuming that, at 220 K, Ag diffuses and nucleates into ordered patches on both Cu(111) and 1-ML Ag/Cu(111), and that no 2-ML Ag/Cu(111) is converted into 1-ML Ag/Cu(111), the area of 1-ML Ag/Cu(111) should be twice that of 2-ML Ag/Cu(111). If the photoemission intensity of the Shockley states is proportional to the area of their associated domains, the measurement on the Shockley states should yield S_1/S_2=2, in satisfactory agreement with the experimental result. This agreement between the experimental result and a prediction according to the proposed model indicates that the wetting of Ag/Cu(111) comprises two processes: a more energetically favored process in which Ag atoms diffuse and nucleate into ordered 1-ML domains on both Cu(111) and 1-ML Ag/Cu(111) rapidly even at 220 K, and a less energetically favored process in which the conversion of 2-ML Ag/Cu(111) into 1-ML Ag/Cu(111) proceeds gradually and is incomplete until the temperature attains 360 K.

With this two-process model of wetting, we inspect the stages of Ag wetting Sample C, illustrated in simplified sketches in Fig. 4. Figure 4(a) shows the surface of Sample B [0.5 ML Ag/Cu(111)] after completion of the measurement in Fig. 2(b); the surface comprises Cu(111) and 1-ML Ag/Cu(111). After deposition of 0.5 ML of Ag at 57 K, no well defined Shockley state is observed because of the roughness of the surface [Fig. 4(b)]. As the temperature increases, Ag atoms become mobile and diffuse to form flat 1-ML islands on Cu(111) and on 1-ML Ag/Cu(111); this more energetically favored process of wetting is completed before the temperature reaches 220 K, resulting in a transitional state that constitutes a coexistence of the domains of Cu(111), 1-ML Ag/Cu(111), and 2-ML Ag/Cu(111) with substantial variation of the domain size [Fig. 4(c)]. With further increased temperature, the less energetically favored process of wetting becomes activated, in which 2-ML Ag/Cu(111) is gradually converted into 1-ML Ag/Cu(111) [Fig. 4(d)]; the conversion continues until the wetting is complete at 360 K [Fig. 4(e)].

Dynamic processes on a surface of a thin film generally involve rapid evolution of the surface morphology on an atomic scale. The ability to characterize the surface with an atomic-layer resolution within a sufficiently small period is essential to examine properly the dynamic processes. Techniques utilizing scanning probes achieve great spatial resolution, and are extensively employed in determining surface morphology. However, their slow acquisition of data limit severely their capability in investigating dynamic processes on a surface. Similar to other spectral techniques, the ARPES employed in this work explores surfaces over a macroscopic area; it provides spectral results, typically with poor or no spatial resolution. Nevertheless, with great resolution of energy and wave vector associated with ARPES we discern subtle differences in the dispersion of the confined electronic states resulting from varied film thickness, with a resolution as small as one atomic layer. With the help of high photon flux from a third-generation storage ring and the greatly improved efficiency of detection of electron energy with an analyzer equipped with a channel plate, the measurement of photoemission spectra is completed within a brief period, and investigations of dynamic processes, such as wetting, on a surface become feasible.

The results from our work provide the first detailed investigation of the transitional states during wetting and conform to a two-process model of wetting for Ag/Cu(111), but our experiments lack the capability to answer several interesting questions posed with this model. Why is one process much more rapid than the other? How does 2-ML Ag/Cu(111) convert into 1-ML Ag/Cu(111)? Does the (9×9) surface reconstruction of 1-ML Ag/Cu(111) play a role during wetting? Further investigations with other experimental techniques and theoretical approaches are required to clarify these issues.

In summary, we have investigated the wetting of Ag thin films on Cu(111) in detail with ARPES. The surface morphology is characterized through monitoring the evolution of Shockley states during wetting. For tailored thin Ag films on Cu(111), we report the first observation of transitional states during wetting. Analyses of the evolution of Shockley states during annealing indicate that wetting consists of two distinct processes. The less energetically favored process of wetting is incomplete until the temperature is well above 300 K, which might cause the growth of thin Ag films on Cu(111) near 300 K to deviate from the Stranski-Krastanov mode.

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