Transition from Disorder to Order in Thin Metallic Films Studied with Angle-resolved Photoelectron Spectroscopy

The transition from disorder to order in a Ag film grown on Au(111) was investigated by monitoring the quantum-well states using angle-resolved photoelectron spectroscopy. Silver films were grown on Au(111) with a two-step method, and the in-plane dispersion of the quantum-well states in the Ag films were monitored in real time during the film crystallization. Our results show that the binding energies of the quantum-well states do not alter, but their in-plane dispersion alters from flat to parabolic when the film is annealed. We suggest that there are isolated and ordered patches scattered across the film at an early stage of the transition and that atoms inside the patches are fully ordered along the surface normal. These ordered patches grow and merge together as the annealing temperature increases. Our experiment demonstrates the power of the real-time monitoring of electronic states in studying the crystallization process in metallic thin films.

Flat thin films continue to attract great interest because they provide not only a well defined foundation on which to construct nanodevices but also a platform with which to manipulate physical properties through the quantum size effect. Much effort has been devoted to finding recipes to grow layer by layer, but in many heteroepitaxial systems that mode of growth does not exist. To address this issue, a two-step growth method for flat metallic films was proposed and is gaining popularity. A disordered film can be grown in a quasi-layer-by-layer mode on depositing materials at a low temperature. Such a disordered film can transform into a highly ordered and atomically flat film through annealing at an appropriate temperature. Although the two-step method has thus yielded many beautiful results, how a disordered film transforms into an ordered film remains a question that is seldom asked. In this work, using Ag/Au(111) as a test system, we demonstrate that the transition from disorder to order in a thin metallic film becomes explored on monitoring the dispersion of its quantized electronic states.

Angle-resolved photoemission measurements were conducted on Ag/Au(111) thin films with varied Ag coverage. Figure 1 displays typical photoemission data showing the variation in the electronic states when a Ag/Au(111) thin film is grown with the two-step method. Figures 1(a), 1(c) and 1(e) show the photoemission intensity plotted against the binding energy and $k_{||}$. The in-plane dispersion of the electronic states in the thin film is readily identified in these two-dimensional intensity plots. The energy distribution curves (EDC) of normal emission in Figs. 1(a), 1(c) and 1(e) are plotted in Figs. 1(b), 1(d) and 1(f), respectively. Figures 1(a) and 1(b) are photoemission data from a clean Au(111) surface at 37 K. Figures 1(c) and 1(d) display photoemission data measured after Ag (22 ML) was deposited on a clean Au(111) surface at 37 K. The data show a flat and featureless background with the...
Fermi edge, which indicates the disordered nature of the Ag film; this property is expected because Ag atoms have slight mobility on Au(111) at low temperature. Growth of this type is considered to be a quasi-layer-by-layer mode, which yields a flat film with no macroscopic structure. Figures 1(e) and 1(f) show photoemission data from an Ag film (22 ML) on Au(111) annealed and measured at 258 K. A sharp and intense feature appears near the Fermi edge, and three parabolic bands with greater binding energies are clearly observable: these are the Ag surface state and QWS in the Ag film. The sharp Ag surface state demonstrates unequivocally that the Ag film is crystallized and that the surface is Ag(111). The parabolic dispersion indicates that the QWS are nearly free-electron-like in the in-plane direction.

To explore how the in-plane dispersion evolves from being featureless to nearly free-electron-like, we monitored the in-plane dispersion during sample annealing. Figure 2 shows a stacking plot of the EDC of normal emission from Ag (22 ML) on Au(111) annealed at the indicated temperatures. The spectra evidently vary as the annealing temperature increases. At a temperature less than 165 K, the spectra display the Fermi edge without other noticeable feature. From 165 to 176 K, a surface state and QWS begin to appear. The weak and broad states indicate that a small part of the Ag film becomes ordered. The surface state and the QWS become clear in the spectrum at 180 K. The great variation of the spectra indicates that a transition from disorder to order in the film structure dependent on temperature occurs between 176 and 180 K. At a temperature greater than 180 K, these normal-emission spectra vary little except that the surface state and the QWS continue to enlarge, and become fully developed at 258 K.

Beyond the determination of the transition temperature, an interesting feature observable in Fig. 2 is
that the binding energies of QWS remain constant as they appear at 176 K, as indicated with dashed lines. The fact that the binding energies of QWS remain constant indicates that, even at an initial stage of film crystallization when only a small part of the film has become ordered, the thickness of the ordered part of the film and its interface between the film and the substrate are similar to, if not the same as, those in a fully ordered film.

Further features are observable on comparison of the in-plane dispersions of QWS at various stages of annealing. Figure 3 shows three two-dimensional maps of photoemission intensity measured at various temperatures. The variation of the in-plane dispersion during annealing is remarkable. When the sample is annealed at 180 K, the QWS have flat in-plane dispersion, as shown in Fig. 3(a). When the sample is annealed at 258 K, the QWS have parabolic dispersion, as shown in Fig. 3(c). Figure 3(b) is somewhat complicated: the dispersion spreads as $|k|$ increases, likely as an overlap of flat and parabolic dispersions. To determine the in-plane effective masses of the QWS, $m^*$, in Fig. 3(c), we fitted second-order polynomials to the dispersion; the results are drawn as dashed lines in the figure. Values of $m^*/m_e$ from the fitting are 0.36, 0.35 and 0.39 for the three QWS with binding energies 0.47, 0.73 and 1.01 eV, respectively; $m_e$ is the free electron mass. For a similar analysis applied on Fig. 3(a), the flat dispersions yield large effective masses (> 3 $m_e$), as expected. The fitted results from both Figs. 3(a) and 3(c) are plotted in Fig. 3(b); their satisfactory match with the dispersion strengthens the idea that the dispersion in Fig. 3(b) is an overlap of flat and parabolic dispersions.

The in-plane dispersions are related closely to the characteristic length scale of the electron wave functions along the in-plane directions. In Fig. 3(a), the flat dispersion is an indication that the QWS lack translational symmetry in the in-plane direction; these states are thus localized, as expected because only a small part of the film shows order when the sample is annealed at 180 K. The parabolic dispersion in Fig. 3(c) implies that QWS are nearly free-electron-like, as likewise expected because the entire film is well ordered at 258 K; translational symmetry exists in the in-plane direction. The overlapped dispersion in Fig. 3(b) shows that small and isolated ordered domains coexist with larger ordered domains in the film during the transition from disorder to order.

A summary of discussion on Figs. 2 and 3 provides a clear picture how a disordered Ag film transforms into a well ordered film through annealing. When Ag is deposited on Au(111) at a low temperature, the film grows in a quasi-layer-by-layer mode. Although the film is disordered, its thickness is similar across the entire film. The film initially orders on annealing about the transition temperature. The flat dispersion in Fig. 3(a) indicates that...
the ordered part of the film comprises small and isolated ordered patches scattered across the film. That binding energies of QWS remain constant during annealing in Fig. 2 indicates that the film is completely ordered throughout, along the surface normal inside these isolated ordered patches, even at an initial stage of the transition. As the annealing temperature increases, the isolated ordered patches expand and likely merge. Some patches are still small and isolated, but others are large enough to have $k_i$ defined. During the transition from disorder to order, patches of both kinds coexist in the film, as the overlapped dispersion in Fig. 3(b) implies. After annealing is complete, the dispersion is parabolic and has well defined binding energies along the surface normal, as shown in Fig. 3(c). The entire film is thus crystallized and flat with little variation of thickness.

In this work, we demonstrated that studying QWS during annealing characterizes the process of film crystallization. With real-time monitoring of electronic states, we have identified the transition from disordered states to localized states to free-electron-like states in a metallic thin film for the first time. In addition, we were able to draw a conclusion that the small and isolated ordered patches on a partially ordered film are fully crystallized along the direction normal to the film surface. The structure of ordered patches on a partially ordered film had never before been investigated and documented in such great detail.