Precise determination of absolute coverage of thin films by layer-resolved surface states

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We report a technique to determine the coverage of metallic thin films by analyzing layer-resolved surface states with photoemission by using atomically flat Ag/Au(111) thin films as a test system. We analyzed the surface state on Au(111) covered with Ag up to 4 ML with atomic resolution, and precisely determined the total Ag coverage of Ag/Au(111) through a line-shape analysis. With precise measurements of the absolute coverage of thin films becoming possible, one can calibrate the tooling factor of evaporators with unprecedented accuracy. © 2008 American Institute of Physics. [DOI: 10.1063/1.2916820]

An important application of nanotechnology is the construction of nanodevices for specific problems. Size is typically the parameter that engineers vary while adjusting the physical properties of nanodevices. Because of electronic confinement from the boundary, the properties of a nanostructure strongly depend on its size; this effect is called the quantum size effect (QSE). The QSE on various physical properties has been reported, including magnetic coupling,1,2 electron reflectivity,2 thermal stability,3 surface reactivity,4 electron-phonon coupling,5,6 superconductivity,7 etc. To precisely determine the size of nanostructures with an atomic resolution, Failure to do so not only makes an analysis of the QSE less confident, but also makes the process of manufacturing nanostructures unreliable.

To precisely determine the size of nanostructures remains a major challenge. Few measurements can provide dimensional information with an atomic resolution. According to a report, analysis of the evolution of quantum-well states can yield the absolute coverage of a Pb thin film on Si(111).8 Although the technique there proposed works, its major disadvantage is that the Pb coverage is determined only after spectra of many and varied Pb coverages are measured, assuming a constant deposition rate of Pb.8

To address this issue, we report a novel technique to precisely determine the film coverage by analyzing the thickness-dependent signals in one photoemission spectrum. The signals under study are (Shockley) surface states existing on the (111) surface of noble metals due to the band gap near the Fermi edge at the Γ point.9 The binding energy of the surface state is modifiable by depositing a thin metallic film; its dependence on film coverage has been reported in previous photoemission studies.10–15 In this letter, we demonstrate, by using atomically flat Ag/Au(111) thin films as a test system, that the coverage of a metallic thin film on the (111) surface of noble metals is precisely determined by analyzing its layer-resolved surface state measured with angle-resolved photoelectron spectra. In our work, a surface state on Au(111) covered with up to 4 ML (monolayers) of Ag was analyzed with atomic resolution. Through analysis of the line shape with tabulated binding energies, we precisely determined the absolute Ag coverage of a Ag/Au(111) film by analyzing a single spectrum. With precise measurement of the absolute coverage of thin films becoming possible, evaporators can be calibrated with great accuracy.

The experiments were performed in an ultrahigh vacuum system with a base pressure better than $1 \times 10^{-10}$ torr. The Au(111) surface was cleaned by sputtering and annealing until photoemission spectra showed a sharp Au(111) surface state in normal emission.13 The silver thin films on Au(111) were prepared with the two-step method.14,15 Highly pure Ag was evaporated onto a clean Au(111) surface with the substrate temperature below 50 K. The sample was subsequently annealed up to 250 K, yielding the sharpest features. The Ag deposition rate was $\sim 0.3$ ML/min measured with a quartz crystal microbalance (QCM); 1 ML denotes one layer of Ag on Ag(111), $\sim 1.39 \times 10^{13}$ atoms/cm$^2$. Photoemission spectra were recorded with an electron energy analyzer (Scienta SES-200) with angular resolution 0.25°. The photons of energy 21.218 eV from a He discharge lamp through a monochromator were used in all photoemission measurements. Measurements were carried out at 37 K; energy resolution was better than 10 meV. All spectra have been shifted to have zero binding energy at the Fermi edge.

Figure 1 shows the energy distribution curves of normal emission measured for Ag/Au(111) thin films of various coverages. Figure 1(a) was measured for a clean Au(111) surface. The sharp surface state indicates a satisfactory quality of the Au(111) surface.13 Figures 1(b)–1(e) were measured after Ag films of various coverages were grown on Au(111). A few features in these spectra are noteworthy. First, the binding energy and the shape of surface states vary with Ag coverage. Variation of the binding energy is due to the modification of the confinement of surface electrons, and depends on the coverage of the Ag overlayer.11 Second, each spectrum comprises either one or two peaks. The peaks with varied binding energies are signals from the Ag thin film of various thicknesses.11 The fact that a spectrum comprises only one or two peaks indicates that there are two-dimensional islands of no more than two distinct thicknesses coexisting in the film; the film is considered “atomically flat.” It has been previously reported that the two-step method can produce atomically flat metallic films.8,15 Finally, the binding energies of the peaks in Fig. 1 remain constant.

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Although the peak intensities vary with Ag coverage. Compared to the results from earlier studies, the origins of peaks about 0.47, 0.33, 0.25, and 0.19 eV are assigned to the surface covered with Ag to the extent of 0, 1, 2, and 3 ML, respectively. In our measurements, the signal from the surface covered with Ag to the extent of 0, 1, 2, and 3 ML, peaks about 0.47, 0.33, 0.25, and 0.19 eV are assigned to the surface covered with Ag of 0, 1, 2, and 3 ML, respectively. For convenience of discussion, the peak corresponding to the surface covered with Ag of 0 ML is called “the n-ML peak.”

The Ag coverage on an atomically flat Ag/Au(111) thin film can be roughly estimated directly. For instance, the spectrum in Fig. 1(b) contains 1 and 2-ML peaks, its total Ag coverage is between 1 and 2 ML. Furthermore, the much larger 1-ML peak indicates that the total Ag coverage is near 1 ML. A similar rough estimate is practicable for other spectra in Fig. 1.

To precisely determine the total Ag coverage, we performed a line-shape analysis as follows. We first assumed the peak intensity is proportional to the area of the surface with the corresponding Ag coverage. The intensities of peaks are evaluated by fitting two Voigt functions to a spectrum. The total Ag coverage is calculated from the ratio of intensity between the two peaks. The spectrum in Fig. 1(e) serves as an example to demonstrate the analysis. The binding energies of the two peaks in the spectrum indicate that the peaks correspond to 2 and 3 ML; the total Ag coverage is (2+x) ML, in which x is a fraction between 0 and 1. With a coverage (2+x) ML, the intensity ratio between the two peaks is \(I_2/I_3 = (1-x)/x\); \(I_2\) and \(I_3\) are the intensities of the 2-ML peak, the 3-ML peak, and the intensity ratio between the two peaks is 0.65; the estimated total Ag coverage is 2.61 ML.

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One might query whether it is reasonable to assume that the peak intensity is directly related to the surface area of the corresponding coverage. This assumption was tested by verifying the coverage from the line-shape analysis with the relative coverage determined by using the QCM in the system.

To justify the assumption, we consider two aspects. First, the finite domain size and the boundary between domains of distinct Ag thicknesses alter the peak width but not the peak intensity. Second, previous workers reported that the photoemission from Ag

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\Theta (\text{ML}) \quad \text{Au(111)} \quad 1 \quad 2 \quad 3 \quad 4 \\
E_i (\text{meV}) \quad 469 \quad 333 \quad 253 \quad 188 \quad 139
\]
ionization cross section of the confined states in a Ag film shows a strong dependence on photon energy: the cross section is greatly enhanced for photon energy in the range of 12–16 eV, called the resonant photon energy in the following for convenience of discussion, and the modulation rapidly diminished as the photon energy moves away from the resonant value. The resonant photon energy for the surface states of Ag/Au(111), with binding energy less than 0.5 eV, is about 12 eV. This value is about 10 eV away from the photon energy used in our work (21.218 eV), and a strong modulation of the cross section of a surface state is unexpected. In addition, the modulation of the cross section is further decreased because of the small difference of binding energies of the surface states corresponding to adjacent thicknesses (<0.1 eV). Our photon energy dependent measurements show that the absolute error in the line-shape analysis resulting from assuming the same cross section for the two peaks is within 0.1 ML when the photon energy varies over the range of 15–32 eV.

Upton et al. suggested that layer-resolved quantum-well states on Pb/Si(111) could be analyzed to determine the absolute film thickness. Although the goal of their work is somewhat similar to ours, our technique reported here has several advantages. For Pb/Si(111) in their study, the Pb coverage is retrospectively determined after the spectra of many Pb coverages are measured, with the assumption of a constant deposition rate of Pb. For the Ag/Au(111) in our work, the absolute coverage of an atomically flat film is precisely determined from a single spectrum after Table I is available, with or without a constant deposition rate of Ag during the growth of a film. The film coverage is roughly estimated by comparing the binding energies of the surface states with the values listed in Table I, and precisely determined through the line-shape analysis described above.

As the Ag coverage increases, the difference in binding energies of the surface states of Ag/Au(111) corresponding to two neighboring thicknesses monotonically decreases, and the surface states converge to the surface state of Ag(111). The surface states corresponding to two neighboring thicknesses might not be resolvable when their binding energies become too similar. In our work, the signal from the Ag film of thickness up to 4 ML was resolved. With an energy resolution less than 10 meV in our photoemission measurements, the signal from a Ag film of thickness up to 6 ML should be resolvable. This value serves as a limitation in utilizing a line-shape analysis to determine the Ag coverage of Ag/Au(111) thin films.

A popular tool to measure the deposition rate of evaporators is the QCM. Large errors commonly exist in the rate of deposition measured with QCM because of improperly calibrated tooling factors. The accuracy of measuring the thickness of test films is a major factor in deciding the accuracy of the tooling factor. The ability to determine the film coverage with atomic resolution with our tested technique allows one to calibrate the tooling factor with great accuracy. Research involving deposition of thin films will greatly benefit from well-calibrated QCM and evaporators.

In summary, we report a technique to determine the absolute coverage of metallic thin films by analyzing their layer-resolved surface states with photoemission. The atomically flat Ag/Au(111) thin films grown with the two-step method were studied as a test system. Our results demonstrate that it is possible to analyze the surface state on an Au(111) surface covered with Ag up to 4 ML with atomic resolution; the coverage of Ag/Au(111) is precisely determined through a line-shape analysis of a single photoemission spectrum. With precise measurement of the absolute coverage of metallic thin films becoming possible, one can calibrate the tooling factor of evaporators with unprecedented accuracy.

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