Probing UPD-Induced Surface Atomic Rearrangement of Polycrystalline Gold Nanofilms with Surface Plasmon Resonance Spectroscopy and Cyclic Voltammetry

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Silver underpotential deposition (UPD)-induced surface atomic rearrangement of polycrystalline gold nanofilms was probed with use of surface plasmon resonance spectroscopy (SPRs) as a novel probe tool in combination with cyclic voltammetry. Interestingly, upon repetitive electrochemical UPD and stripping of Ag, the surface structure of the resulting bare Au film is rearranged due to strong adatom–substrate interactions, which causes a large angle shift of SPR R–θ curves, in a good linear relationship with the number of UPDs, to a lower SPR angle. The *n*, *K* values of the surfacial Au monolayers before and after the repetitive Ag UPD and stripping for 27 times are found to be 0.133, 3.60 and 0.565, 9.39, respectively, corresponding to the huge shift of 1.61° to the left of the SPR minima. Cyclic voltammetry experiments in 0.10 M H_2SO_4 are carried out before and after the UPD treatment to examine the quality of the whole electrode surface and confirmed this change. To correlate the angle change in SPRs with the profile change in the cyclic voltammogram, the UPD treatment was also performed on a Au(111) textured thin film. It was therefore confirmed that the resonance position of the SPR spectrum is very sensitive to the surface crystallographic orientation of the bare Au substrates. Some surface atomic rearrangement can cause a pronounced SPR angle shift.

Introduction

An understanding of structural transitions in nanocrystal systems has sparked technological and fundamental interest recently due to the ability to interrogate the structure–property correlation and that the study of phase transitions can be greatly simplified in these systems.[1–3] For example, Hess et al.[4] revealed that apparently small changes in surface structure of CdSe nanocrystals can have a dramatic effect on the coupling of photoexcitations to surface states. Although surface effects are prominent in nanosystems, few details are known about the surface itself, to a great extent because of the lack of a suitable model system and addressable in situ surface analysis tool, which allows for a direct correlation of the structural characteristics of the system with property measurements.

Surface plasmon resonance (SPR) spectroscopy is a powerful surface-sensitive technique. SPR, as a probe of film dielectric properties, film thickness, and morphology, has been used to probe the film nanostructure. On the other hand, the Ag underpotential deposition (UPD) system to date has been probed with use of a wide variety of analytical techniques including low-energy electron diffraction (LEED),[5] atomic force microscopy (AFM),[6–8] scanning tunneling microscopy (STM),[7,9–11] and X-ray photoelectron spectroscopy (XPS).[12] However, to the best of our knowledge, no study by SPR spectroscopy has been used for probing the UPD process to date.

In the present work, we use SPR as a novel probe tool in combination with electrochemistry to study in situ the effect of Ag UPD on the SPR response of the electroless plated gold thin-film electrode. The transition of electronic information on the surface is photonically transduced by using in situ SPR spectroscopy and the surface atomic rearrangement is electro-

chemically evidenced by cyclic voltammetry. The *n*, *K* values of the surfacial Au monolayers before and after the repetitive Ag UPD and stripping for 27 times are found to be 0.133, 3.60 and 0.565, 9.39, respectively, corresponding to the huge shift of 1.61° to the left of the SPR minima. It was therefore found that the resonance position of the SPR spectrum is more sensitive than cyclic voltammograms (CVs) of Ag UPD to the surface crystallographic orientation of the bare Au substrates. Some surface atomic rearrangement can cause a pronounced SPR angle shift.

Experimental Section

Chemicals. All aqueous solutions were made with deionized water, which was further purified with a Milli-Q system (Millipore). The following materials were obtained from Aldrich: H_2O_2, $HAuCl_4 \cdot 3H_2O$, trisodium citrate dihydrate, (3-aminopropyl)trimethoxysilane (APTMS), hydroxylamine hydrochloride, and $NaBH_4$. CH_3OH (spectrophotometric grade) was obtained from EM Sciences. $K_2Cr_2O_7$, H_2SO_4 (double distilled, 98%), Ag_2SO_4 ($c(Cl^-) < 0.02\%$), and glass microscope slides (~1.8 × 1.8 cm²) were obtained from China. All of the chemicals, unless mentioned otherwise, were of analytical grade and were used as received.

Preparation of SPR Substrates. The SPR-active substrates were prepared according to our newly developed method,[13] which is completely solution-based and vacuum-free. In brief, carefully cleaned glass microscope slides were placed in a dilute solution of (3-aminopropyl)trimethoxysilane (APTMS) (0.3 mL of APTMS in 3 mL of CH_3OH) for 12 h and rinsed with copious amounts of CH_3OH upon removal. The APTMS-modified glass slides were subsequently immersed in colloidal Au solution (2.5 nm in diameter) for ca. 12 h for Au nanoparticle assembling. Then the colloidal Au monolayers were rinsed with water and

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13970 *J. Phys. Chem. B, Vol. 107, No. 50, 2003*

Jin and Dong

immediately immersed in 6 mL of aqueous 0.4 mM hydroxylamine hydrochloride and 0.1% $HAuCl_4 \cdot 3H_2O$. The solution was agitated for 10 ± 0.5 min. After plating, the substrates were rinsed thoroughly with copious amounts of water to completely remove weakly adsorbed Chloride. After being immersed in freshly prepared piranha solution (4:1 H_2SO_4:30% H_2O_2) for ca. 2 min to remove any organic impurities, the as-prepared gold films were rinsed again thoroughly with copious amounts of water and dried under a nitrogen stream, then they were ready for Ag UPD and SPR experiments. All the experiments were performed at room temperature.

In Situ SPR Measurements. In situ scanning SPR experiments were performed to assess the effect of the repetitive UPD and stripping of Ag on gold substrates. For these experiments, the piranha solution cleaned SPR-active substrate was pressed onto the base of a half-cylindrical lens (BaK_4, $n = 1.566$) via an index-matching oil. Linearly p-polarized light having a wavelength of 650 nm from a diode laser was directed through the prism onto the gold film in the Kretschmann configuration. The intensity of the reflected light was measured as a function of the angle of incidence, θ, using a photodiode with a chopper/lock-in amplifier technique. The small, single-compartment, three-electrode Teflon cell was mounted against the gold surface of the substrate with use of a Kalrez O-ring, which provided a liquid-tight seal and an electrolyte contact. The Teflon cell allowed for the simultaneous recording of SPR and electrochemical data and the application of a voltage to the sample. The electroless plated gold film on the glass slide was used for the excitation of surface plasmon modes and also served as the working electrode. A series of SPR $R-\theta$ curves were obtained in situ before, during, and after the repetitive UPD and stripping of Ag on the gold film substrate.

Electrochemistry Experiments. Electrochemistry experiments were carried out with a PAR 370 electrochemical system (EG&G, PAR; USA) and an X−Y recorder in a small, single-compartment, three-electrode Teflon cell. The as-prepared SPR-active gold thin-film substrate acted as a working electrode and was pressed at the opening of the carefully cleaned Teflon cell with a Kalrez O-ring (the apparent electrode area was 0.38 cm^2). A Pt wire counter electrode and a KCl-saturated Ag/AgCl reference electrode were used. Electrochemical measurements were all recorded and reported vs the KCl-saturated Ag/AgCl reference electrode. In all experiments, solutions were purged and blanketed with pure N_2. A solution of 0.6 mM Ag_2SO_4 and 0.1 M H_2SO_4 in deionized water (Millipore, 18.2 MΩ) was used to deposit the Ag adlayer on gold by the UPD method. The repetitive electrochemical UPD and stripping of Ag on electroless plated polycrystalline gold was performed by cycling the potential between 0 and +0.70 V at a scan rate of 20 mV/s for ca. 30 min. The Ag adlayer was then removed by scanning unilaterally from 0 to +0.70 V, and holding at +0.70 V for ca. 5 s.

Before and after the repetitively electrochemical UPD and stripping of Ag, electrochemical measurements at various basal Au film electrodes in aqueous 0.10 M H_2SO_4 were carried out to examine the quality of the whole surface. The potential was cycled at the gold electrode between −0.2 and +1.6 V at 100 mV/s.

AFM Characterization. Surface images of gold film substrates were acquired in the tapping mode under ambient conditions (Nanoscope a; Digital Instruments, Inc.) Si_3N_4 cantilevers having integral tips (spring contant, 20−100 N/m) were used. Images were obtained by oscillating the cantilever
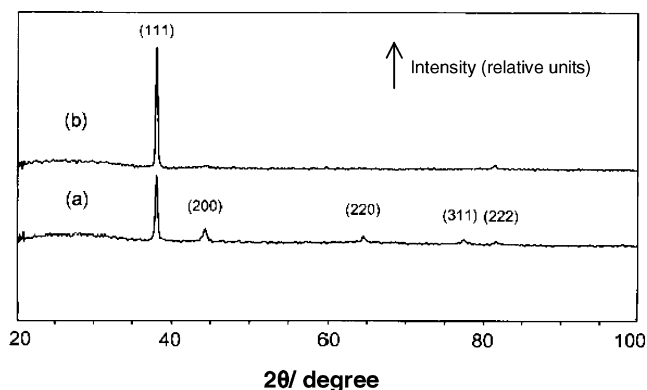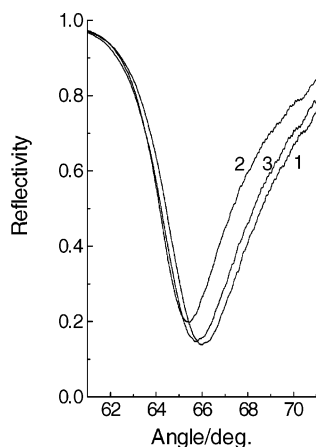

Figure 1. XRD pattern of (a) a typical electroless plated SPR-active Au nanofilm (ca. 50 nm) and (b) a Au(111) textured Au thin film prepared by thermal vaccum evaporation on a glass slide.

slightly below its resonance frequency (typically, 200−300 kHz) and raster scanning across the surface.

Results and Discussion

A gold film of about 50-nm thickness prepared on a glass slide by the wet-chemical method[13a] is used both as the working electrode and for the excitation of surface plasmon modes in the common Kretschman configuration. The as-prepared gold surfaces are polycrystalline in nature[13b] and reproducible, which was confirmed by X-ray diffraction characterization (Figure 1a). In all experiments, solutions were purged and blanketed with pure N_2. A solution of 0.6 mM Ag_2SO_4 and 0.1 M H_2SO_4 in deionized water (Millipore, 18.2 MΩ) was used to deposit the Ag adlayer on gold by the UPD method. The repetitive Ag UPD and stripping on a polycrystalline gold substrate was performed at ambient temperature by cycling the potential between 0 and +0.70 V (vs the KCl-saturated Ag/AgCl reference electrode) at a scan rate of 20 mV/s for the desired time. The Ag adlayers were removed before each SPR characterization by scanning unilaterally from 0 to +0.70 V, and held at +0.70 V for ca. 5 s. All SPR experiments were performed at open circuit.

Upon UPD of Ag monolayers on the substrate, a decrease (ca. 6.4%) in percent reflectivity, a 0.65° shift (to a lower angle) in plasmon minimum, and an overall narrowness of the curve are observed. Upon stripping of Ag adlayers from the Au surface, the shape of the SPR curve is almost recovered. However, the dip of the SPR curve still left-shifts pronouncedly from 66.05° to a lower angle, 65.77°, after the UPD treatment, as shown in Figure 2. Although more information, such as reflectance oscillations during potential cycling, would be recorded in the SPR $R-t$ form when performed at a fixed angle, our main concern herein is the influence of Ag UPD treatment on the SPR response of the bare Au substrates, and thereby all SPR signals were collected at open circuit potential to avoid electrical interference and recorded in the $R-\theta$ form to simplify the SPR data analysis. Interestingly, the dip left-shifts continuously to a lower angle with the increasment of the Ag UPD cycles, as shown in Figure 3A. The dip of the SPR curves left-shifts as much as 1.61° after the repetitive Ag UPD and stripping for 27 times. The inset in Figure 3A shows the effect of repetitive Ag UPD and stripping on the SPR responses of the resulting bare Au films. In this case, the angle shift of the SPR curves shows a good linear relationship ($R = 0.993$, $N = 7$) with the number of UPD treatments. The results were reproducible. Importantly, because the Au film electrodes were cleaned by piranha solution before SPR measurements and all aqueous solutions were prepared with deionized water, and no detectable

Atomic Rearrangement of Polycrystalline Gold Nanofilms

J. Phys. Chem. B, Vol. 107, No. 50, 2003 **13971**

Figure 2. In situ SPR spectra of the polycrystalline Au film recorded in 0.6 mM Ag_2SO_4/0.1 M H_2SO_4 (aq) before (1) and after the UPD (2) and stripping (3) of Ag one time.
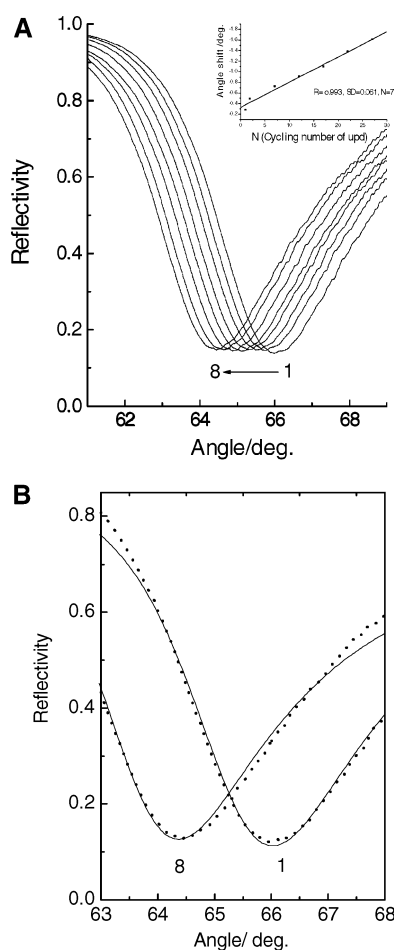
Figure 3. (A) In situ SPR spectra recorded in 0.6 mM Ag_2SO_4/0.1 M H_2SO_4 (aq) after stripping of Ag adlayers: (1) 0, (2) 1, (3) 2, (4) 7, (5) 12, (6) 17, (7) 22, (8) 27 times. The inset shows the linear relationship between the cycling number of UPD and the resulting SPR angle shift. (B) Experimental angular scan curves (dotted lines) and corresponding Frensel fitting results (solid lines) of the polycrystalline Au film recorded in 0.6 mM Ag_2SO_4/0.1 M H_2SO_4 aqueous solution before (curve 1) and after the UPD and stripping of Ag 27 times (curve 8). The parameters used for Frensel fitting are listed in Table 1.

SPR angle shift occurred after incubation of the UPD-treated Au electrode in the reaction solution for ~30 min, the huge shift of 1.61° to the left of the SPR minima cannot be the result of the washing away of organic material and chlorine from the Au film during UPD. Otherwise the SPR angle would shift
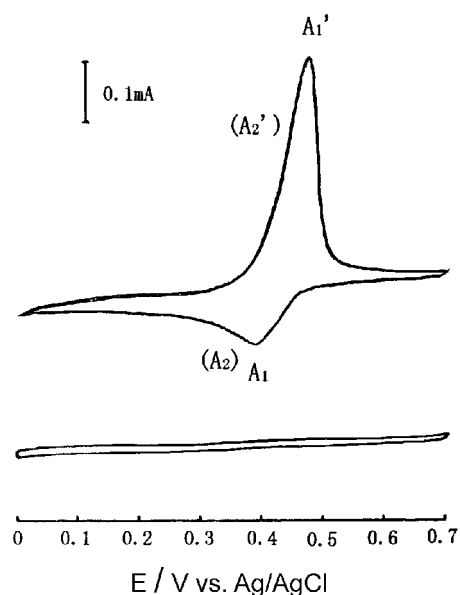
Figure 4. CVs for the Ag UPD and stripping on polycrystalline Au over a period of five successive scans. The scan rate is 20 mV/s. After removing the Ag adlayers, CV running in Ag-free solutions exhibited only a double-layer charging current (bottom).

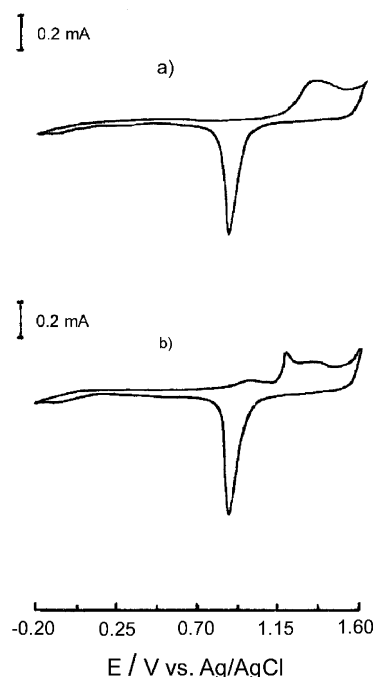gradually back to the right due to readsorption of organic impurities and Cl⁻.

Cyclic voltammograms for Ag UPD on polycrystalline Au film in 0.10 M H_2SO_4 over a period of 5 successive scans are shown in Figure 4. It shows one set of adsorption (labeled A_1) and desorption (labeled A_1') peaks. The cyclic voltammogram (CV) curve differs significantly from that of UPD on the Au-(111) electrode and is somewhat similar to that of UPD on polycrystalline Au both reported by Laibins.[14] The difference in the number and sharpness of CV peaks may be due to the use of polycrystalline electroless Au film here and the purity of chemicals. On the other hand, Laibins et al. found that trace amounts of chloride in the electrolyte have a dramatic effect on the repetitive UPD of Ag onto Au substrates. The increase of Cl⁻ ions due to accumulate on the electrode surface induces a quantitative and reversible shift of the initial Ag UPD layer to a more noble state by roughly 80 mV. In our case the deposition peak (A_1) at 0.395 V and the stripping peak (A_1') at 0.475 V almost persisted during the continuous cycling, except for a fractional decrease in peak current due to some surface smoothing caused by electrochemical annealing. This might suggest that the cleanliness of the Au surface and the cell used here and the influence of chloride is negligible.[14] Although silver UPDs on Au(111) terraces of a well-ordered electrode show almost no defects nor surface alloy, as characterized by the presence of a sharp intense UPD peak, Buess-Herman et al.[15] recently reported that defects such as steps, kinks, and grain boundaries can play a critical role in the initial stages of metal deposition and tend to form a Ag–Au surface alloy via place exchange processes between silver adatoms and gold atoms at defect sites. The some broadness and asymmetry of peak may reflect this process, and stem from the influence of the grain feature (such as size distribution and edges) of the nanofilms on the electrochemical behaviors and be due to overlapping of another couple of peaks (labeled A_2 and A_2'), similar to the case of Gewirth.[16] As a control, CVs running over the entire potential range in Ag-free electrolytes exhibit only double-layer charging currents and no similar SPR angle shift was observed after successively cycling for 27 times. The modification in shape of SPR curves, as is representatively shown in Figure 5,
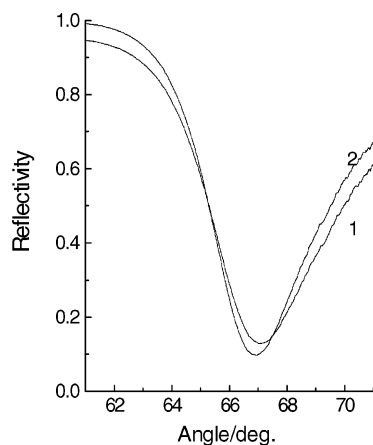
Figure 5. Control SPR spectra recorded before (1) and after (2) successive cycling in 0.1 M H_2SO_4 blank solution (Ag-free) for 27 times.

Figure 6. CVs of polycrystalline Au film in 0.1 M H_2SO_4: (a) before and (b) after the repetitive Ag UPD and stripping for 27 times. The scan rate is 100 mV/s.

TABLE 1: The Parameters Used for Frensel Fitting of SPR Angular Scan Curves

layer ($\lambda = 650$ nm)	before UPD treatment			after UPD treatment for 27 times		
	thickness/ nm	n	K	thickness/ nm	n	K
BaK$_4$ prism		1.566	0		1.566	0
bulk Au film	41.5	0.133	3.60	39.0	0.133	3.60
surface Au monolayer	0.4	0.133	3.60	0.4	0.565	9.39
water		1.33	0		1.33	0

is ascribed to some morphological improvement of the gold film resulting from an electrochemical annealing during the repetitive cycling process.[14] We found that the electrochemical annealing-induced modification of SPR curves occurred mostly within the first several potential cyclings and no further pronounced variation of the SPR response was observed. Such a change would not result from the cleaning of the Au surface because both the Au surface and cell were carefully cleaned just before use and no impurity was introduced during the process. Indeed, similar chemical annealing-induced variation of SPR responses has been reported previously.[17]

Note that UPD is a surface-limited process and the Ag UPD adlayer does not alloy with the underlying bulk gold. In addition, as all SPR spectra were recorded under open circuit, the potential dependence of the optical properties for bare gold SPR substrates is negligible. No pronounced change in width and depth of the spectra (Figure 3A), which are mostly a function of the refractive index, n, and the thickness of the metal film, t, respectively,[18] indicates that both the value of the refraction index and the effective thickness of the gold film were hardly affected by the repetitive Ag UPD treatment. It is noteworthy to mention that Ag–Au surface alloying takes place, although mainly at defective sites (such as grain edges)[15,19] due to the polycrystalline and granular surface nature of the Au films. Indeed, some broadness of the UPD peaks in Figure 4 may be indicative of Au–Ag surface alloying at defective sites.[19] However, all SPR curves were recorded after complete removal of Ag adlayers (confirmed by XPS characterization). Thus the Ag contamination is negligible. There is therefore no doubt that, after the repetitive UPD treatment, the physical properties, especially the extinction coefficient, K, of the resulting bare Au film are changed, thus causing the distinct position shift of the SPR angle.[18] This in turn implies that the extinction coefficient, K, is largely dominated by the surface state of the substrate, since there is no alternation in bulk properties during the UPD treatment.[20] We also give a comparison of SPR experimental data calculated with use of Fresnel equations. The fitted optical parameters n and K of the metal films will be the best indicators of the metal layer quality in terms of homogeneity and packing density. The optical constants can be extracted by nonlinear least-squares fitting to a four-layer (prism/bulk Au film/surface Au monolayer/water) Frensel optical mode. It is reasonable to fit and set the refractive index, n, and the extinction coefficient, K, of the bulk Au films to be -0.133 and 3.60, respectively, and as constants during further fitting because UPD is a surface-limited process and the changes in the n-value not only cause a shift of the

minimum position of the SPR resonance, but also produce an alteration in the shape of the spectrum.[18] The n, K values of the surfacial Au monolayers before and after the repetitive Ag UPD and stripping for 27 times are found to be 0.133, 3.60 and 0.565, 9.39, respectively, corresponding to the huge shift of 1.61° to the left of the SPR minima. The other parameters used for Frensel fitting are listed in Table 1. Figure 3B shows experimental angular scan curves and corresponding Frensel fitting results of the polycrystalline Au film recorded in 0.6 mM Ag_2SO_4/0.1 M H_2SO_4 aqueous solution before (curve 1) and after the UPD and stripping of Ag for 27 times (curve 8). Although the origins of changes in the extinction coefficient and then the SPR angle shift during the rearrangement are not yet clear, qualitatively we confirmed that some surface atom rearrangement alters the surface physical properties (electron distribution, orientation, packing density), and therefore alters the optical properties of the metal nanofilms as revealed by the optically sensitive SPR technique.

Direct evidence of some surface atomic rearrangement comes from electrochemical characterizations. Electrochemical studies of gold single crystals of various surface orientation have shown that the shape of CVs is very sensitive to the surface structure of the electrode,[21,22] and proved to be a good method to examine the quality of the whole gold film surface. Figure 6 shows CVs of the polycrystalline bare Au film before and after 27 times of successive Ag UPDs and stripping measured in 0.10 M H_2SO_4. In all cases, the reduction wave at ca. +0.89 V is observed.

Atomic Rearrangement of Polycrystalline Gold Nanofilms

*J. Phys. Chem. B, Vol. 107, No. 50, 2003* **13973**
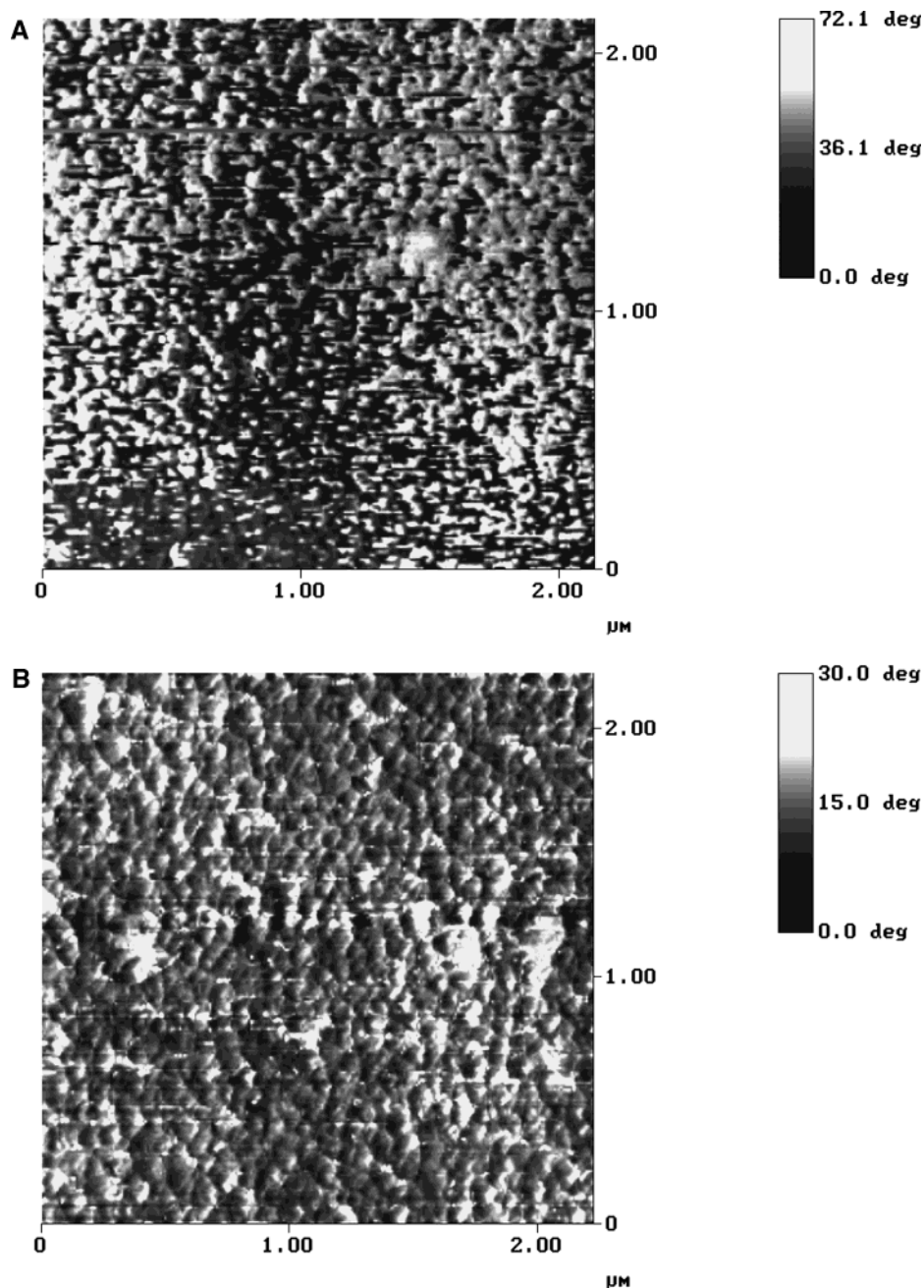
Figure 7. AFM phase images of the same polycrystalline Au film before (A) and after (B) the repetitive UPD and stripping of Ag 27 times.

The freshly prepared Au film exhibits only one broad oxidation wave centered at ca. +1.36 V. In the control experiment, there is no observable change in the shape after continuous cycling in blank solution (Ag-free) for 0.5 h. Thus, it is reasonable to assume that the influence of anions on the voltammetric change is negligible. But, after the repetitive Ag UPD and stripping for 27 times (ca. 0.5 h), the resulting basal Au film shows a pronounced change in the anodic branch of the shape. The main oxidation peak appears at +1.22 V, accompanied by a small prewave as a shoulder at +0.99 V and a postwave centered at ca. +1.35 V, which are quite similar to the CVs of the Au-(111) single-crystal electrode. The first oxidation peak may be a measure of the defect density of the Au(111) surface,[22] and the peaks at 0.99 and 1.22 V are completely consistent with the formation of straight $(100)\times(111)$ edges. Although atomic force microscopy (AFM) images with atomic resolution (such as Au(111) terraces) were difficult to obtain due to the granular morphology features of the film, the AFM phase images (Figure 7) show evidence of some surface smoothing and well-arranged mound arrangement after the treatment. The rms roughness of the same Au film before and after the UPD treatments is 4.3 and 4.0 nm, respectively. It was proposed previously[15] that two competitive processes are involved during the repetitive UPD treatment: the Ag−Au surface alloying (a consequence of the place exchange mechanism) and the self-annealing of the gold surface (surface smoothing). From the electrochemistry point of view, the voltammetric change provides evidence that the repetitive UPD treatment does induce the surface atom crystalline rearrangement and thus results in changing SPR angles.

To correlate the angle change in SPRs with the profile change in CV, we also performed the experiments using an evaporation-prepared and anneal-treated Au(111) textured thin film instead of electroless plated polycrystalline Au thin films. The nearly Au(111) single-crystal nature of the textured thin film was confirmed by X-ray diffraction characterization (Figure 1b). The CV of the Ag UPD on the textured Au film shows a similar
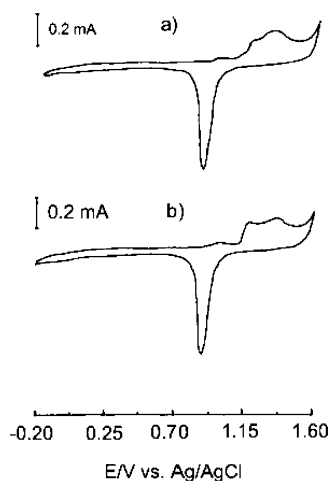
Figure 8. CVs of evaporation-prepared Au(111) textured Au thin film in 0.1 M H_2SO_4: (a) before and (b) after the repetitive Ag UPD and stripping for ca. 0.5 h. The scan rate is 100 mV/s.
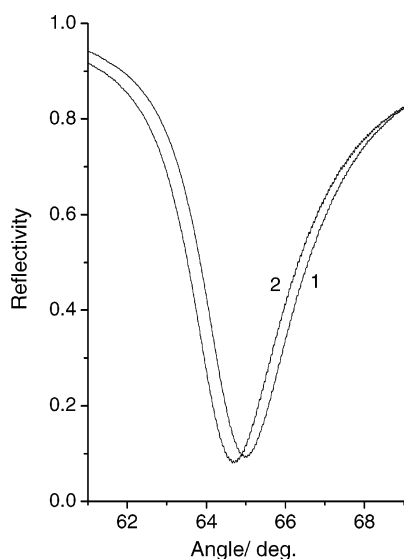
Figure 9. In situ SPR spectra of a evaporation-prepared Au(111) textured Au thin film recorded in 0.6 mM Ag_2SO_4/0.1 M H_2SO_4 (aq) (1) before and (2) after repetitive UPD and stripping of Ag for ca. 0.5 h.

profile as Figure 4 (figure not shown). Figure 8 shows CVs of the Au(111) textured Au film before and after successive Ag UPD and stripping for ca. 0.5 h measured in 0.10 M H_2SO_4. In this case, the freshly evaporation-prepared Au(111) textured Au film exhibits three oxidation peaks centered at ca. 0.99, 1.22, and 1.35 V, respectively, which is very similar to that of electroless plated Au thin films after repetitive UPD treatment for ca. 0.5 h. After the repetitive Ag UPD and stripping for ca. 0.5 h, the resulting basal Au film shows no pronounced change in peak positions, except for some evolution in peak profile caused mainly by morphology modification after the treatment. At the same time, the dip of the SPR curves left-shifts only ~0.30° after the repetitive Ag UPD and stripping for ca. 0.5 h, as shown in Figure 9, which is much smaller than that of electroless plated polycrystalline Au films. The results further confirm that the repetitive UPD treatment does induce some surface atom crystalline rearrangement and thus results in the pronounced variation of SPR angles.

Although it has been known for many years that some surface reconstruction and structural transformations occur as a consequence of repetitive potential cycling in the UPD region of Ag

on Au,[15,23,24] surface atomic rearragement induced by UPD treatment has not been probed by the electrochemical SPR (ESPR) technique to date. In this study, we found that the resonance position is very sensitive to the surface crystallographic orientation of the bare Au substrates. Some surface atomic rearrangement can cause a pronounced signal change. At the same time, there are no significant changes in CV curve recorded in the UPD system while cycling, although it is well-known that CV of UPD Ag on Au single crystal terraces is extremely sensitive to the surface structure of the metal. We repeated the experiments and the results were similar. The CVs of UPD Ag on electroless plated polycrystalline Au films show no pronounced change whereas the SPRs do show an effect, indicating that the surface atomic rearrangement herein is not sensitive to discrimination by the CV curve of UPD and that SPR is a more sensitive tool for probing surface atomic rearrangement. Although SPR probes both bulk and surface layers of gold nanofilms, the changes of SPRs herein mainly reflect the variation of the superficial state of the substrate due to the fact that UPD is a surface-limited process. In this case, the transition of electronic information of the UPD-treated gold surface is photonically transduced by using more sensitive SPRs.

The repetitive Ag UPD and stripping here act as "collective atom tapping", which can tap the surfaces of the polycrystalline gold nanofilms gradually pulling out high-quality ones with partially rearranged crystallographic surface and well-arranged grain edges. This process is slow and varies from electrode to electrode. After about 0.5−1 h of cycling, the SPR angle shift terminated and no further rearrangements were observed by SPR measurements, indicating the formation of a stable film in the end. Although the detailed mechanism is not clear yet, from the electrochemistry point of view, we assume that the strong adatom−substrate (Ag−Au) interactions, such as defect-mediated Ag−Au surface alloying and self-annealing of the Au surface,[15] during the repetitive Ag UPD treatment facilitate mobility, and then surface atomic rearrangement of the superficial Au atoms, and finally obtain a more energetic stable (111) crystal orientation[25] on the nanofilm surface. Detailed examinations of the influence factors, such as scan rate and anions, on the rearrangement behavior need further experiments.

Conclusion

We have investigated the effect of the repetitive UPD and stripping of Ag on the electroless plated SPR-active polycrystalline Au thin-film electrode, using SPRs as a novel probe, and found that the repetitively electrochemical UPD and stripping of Ag have a dramatic effect on both the optical and electrochemical properties of Au nanofilms, as evaluated by using both in-situ SPR and electrochemical measurements. The work reported herein is important for two reasons. First, the Ag UPD-induced *surface* atomic rearrangement of polycrystalline Au nanofilms was reassessed in situ by using the novel technique of SPR spectroscopy and cyclic voltammetry. Second, we found for the first time that the resonance position of the SPR spectroscopy is very sensitive to the *surface* crystallographic orientation of the bare Au substrates. Some *surface* atomic rearrangement can cause a pronounced signal change, a phenomenon not observed before, to our knowledge. The n, K values of the surfacial Au monolayers before and after the repetitive Ag UPD and stripping for 27 times are found to be 0.133, 3.60 and 0.565, 9.39, respectively, corresponding to the huge shift of 1.61° to the left of the SPR minima. The ability of the method to process surface and to examine surface reconstruction at unprecedented levels of detail is interesting

Atomic Rearrangement of Polycrystalline Gold Nanofilms

J. Phys. Chem. B, Vol. 107, No. 50, 2003 **13975**

from a fundamental point of view and can find applications in electrochemistry and nanofilm community.

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