Mechanism of Film Growth of Tellurium by Electrochemical Deposition in the Presence and Absence of Cadmium Ions

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The growth morphology and the kinetics of a thin film of Te on Au during electrochemical deposition at -62mV (vs Ag/AgCl/3 M NaCl) have been studied. The deposition conditions are similar to those used previously by us to grow nanowires inside Au nanotubes by electrochemical deposition in the presence of Cd ions (Cd^{2+}) . By using electrochemical deposition on a planar Au electrode, we explored the growth of the Te film for two conditions: in the presence of Cd^{2+} (0.1 mM $TeO_2 + 1$ mM $CdSO_4 + 50$ mM H_2SO_4 solution) and in the absence of Cd^{2+} (0.1 mM TeO₂ + 50 mM H₂SO₄ solution). We used several surface investigation techniques to study the growth such as: in situ electrochemical atomic force microscopy (EC-AFM), in situ electrochemical surface plasmon resonance (EC-SPR), electrochemical methods, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). In the presence of Cd²⁺, in situ electrochemical atomic microscopy showed that Cd^{2+} acted as a mediator at the early deposition stage and caused smoothing of the Te deposit obtained. In the absence of Cd^{2+} , Te had an island growth. The electrochemical surface plasmon resonance showed that the deposit was characterized by a slower deposition rate in the presence of Cd^{2+} than in the absence of Cd²⁺. Additionally, the thickness of the film was evaluated using EC-AFM measurements, electrochemical stripping analysis, and EC-SPR. The results obtained from all three measurements agree well with the Te film obtained in the presence of Cd²⁺, where a continuous and uniform film was formed. In the presence of Cd²⁺, a Te film with a thickness of 1.04 nm and atomically flat surface was deposited on an ultraflat Au surface. The XPS spectrum showed no significant amount of Cd in the deposit, indicating that the Cd ion acted as a mediator and not as a co-deposition element.

1. Introduction

The study of growth mechanism and kinetics of ultrathin film with ultraflat surface in the early stage of formation is of great importance not only for understanding the growth of thin films but also for the progress of advanced technologies to nanodevice fabrication.¹ For example, Au-Te nanocables have been fabricated in our group using nanotechnology, and Te nanowires have been grown inside Au nanotubes by a well-controlled electrochemical deposition technique.² This method allows us to deposit a smooth and continuous layer of Te on Au surface and results in a sturdy Te nanowire inside a Au nanotube. However, there are exciting scientific challenges associated with the electrochemical deposition process inside metallic nanotubes. Much of these challenges arise from the fact that the existing theories and models are for metal electrodeposition on planar electrodes and not on low-dimension structures. In the case of axially uniform nanocables, there are still unknown effects on the electrochemical deposition. For instance, if the deposited metal or semiconductor layer is discontinuous, the nanowire formed inside the metallic nanotube will be loosely attached to the wall of the nanotube and can be easily torn apart into small pieces after the nanotube template is dissolved. Additionally, a fast growth rate is not desired for forming axially uniform nanocables inside nanotubes or nanopores.^{2,3} Other methods for growing ultraflat thin films have been developed as well. One of them, electrochemical atomic layer epitaxy (ECALE), has been extensively studied by Stickney.⁴ ECALE was reported to grow nanostructured thin film on planar surfaces by alternating atomically layers.⁵ This technique has the potential to form smooth thin films.

Therefore, thin film deposition with atomically smooth morphology for use in nanodevice fabrication represents a foremost goal in surface science investigations. However, an atomically flat surface is not always thermodynamically favorable.⁶ In most deposition cases, atoms deposited during growth are much easier to be moved away from the steps than to cross the steps, the surface diffusion is higher than the interlayer diffusion, and as a result, interlayer mass transport is severely reduced. This is the main reason that causes a significant increase in surface roughness.⁷

To overcome these problems, surface agents that promote layer-by-layer growth have been sought.^{8,9} Surfactants, one type of mediators, have been successfully employed in ultrahigh vacuum (UHV) deposition to promote layer-by-layer (LbL) growth (i.e., two-dimensional or Fran van der Merwe growth), suppress island growth (i.e., three-dimensional (3D), Volmer–Webber, or Stransk–Krastanov growth), and produce a smooth morphology and a better crystalline quality in homoepitaxial^{7,10–14} and heteroexpitaxial^{8,9,15–18} systems. For instance, thick Cu film (1 μ m) can be deposited with excellent surface smoothness by surfactant-assisted chemical vapor deposition.¹⁹ In the case of a nonvacuum deposition of Ag on Au(111) has been reported.²⁰

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These results have been achieved by adding Pb²⁺ in AgClO₄ + HClO₄ electrolyte and by controlling the deposition potential to form a layer of underpotential deposition (UPD) of Pb on top of Ag. Using the layer of Pb UPD as surfactant to induce LbL deposition has resulted in atomically flat film of Ag of 200 monolayers in thickness.²⁰ Taking advantage of the UPD layer as mediator to promote LbL deposition and suppress island growth has also been reported.^{21,22} When the atoms of interest are deposited on the surface, on the top of the UPD layer (mediator or surfactant), the site exchange between topmost layer and UPD layer occurs spontaneously.20 This kind of site exchange process induced by the presence of the surfactant is thought to be the key parameter to lower the Ehrlich-Schwoebel (ES) barrier, to increase the interlayer mass transport, and thus to promote the layer-by-layer deposition, resulting in a smooth surface morphology.^{6,7,10,12,14,17,23–25}

The strategy used in this work aims to explore the use of Cd UPD as a mediator to smooth the deposited layer of Te and to slow the rate of the electrochemical deposition at -62 mV (vs Ag/AgCl). Unlike Te, Cd is highly reversible in its UPD state.²⁶ For the electrolyte containing Te and Cd elements, Cd can be deposited and stripped off from the Te surface around -150 mV (vs Ag/AgCl).²⁶ The deposition potential used in this work is -62 mV (vs Ag/AgCl), which is slightly more positive than the Cd UPD.

Using planar conditions to study the deposition, which are appropriated for surface characterization techniques, the growth of Te film in two conditions, in the presence of Cd^{2+} (0.1 mM TeO₂ + 1 mM CdSO₄ + 50 mM H₂SO₄ solution) and the absence of Cd^{2+} (0.1 mM TeO₂ + 50 mM H₂SO₄ solution), have been explored. We used several surface investigation techniques such as: in situ electrochemical atomic force microscopy (EC-AFM), in situ electrochemical surface plasmon resonance (EC-SPR), electrochemical methods, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS).

Atomic force microscopy (AFM) has been used to investigate surface morphology of thin films.^{19,27–43} High-resolution AFM has been used to reveal the atomic structure of the topmost surface of the deposit.^{27–31,44} For example, the atomic structure of UPD of Te and Cd have been studies by AFM and provides information on surface atomic structure under controlled potentials.^{27,28,42} Additionally, real time investigation of the electrochemical deposition has been performed by in situ electrochemical AFM (EC-AFM).^{27–29,33,44,37,43,44} In this paper, we used the in situ EC-AFM to study the changes in surface morphology during electrochemical deposition in order to understand the effect of the mediator (Cd) on the deposition mechanism of Te thin film.

Surface plasma resonance (SPR) is another surface technique that offers additional information for studying the film thickness and surface roughness.⁴⁵ The SPR method can detect small amounts deposited on the surface, as little as one monolayer of UPD, and surface reconstruction.⁴⁶ However, in situ electrochemical SPR has not been used to date for probing the in situ deposition of inorganic thin films. We present in this work a new approach to the surface investigation of the electrochemical deposition that uses a combination of in situ EC-AFM, which is local in character, and in situ EC-SPR, which averages a large electrode area. Additionally, we demonstrate that the in situ EC-SPR can be used to provide qualitative and quantitative information on growth mechanism of electrochemical deposition of Te at an early stage. These results obtained from an elaborated EC-SPR study on the kinetics and growth mechanism of the electrodeposition can be corroborated with the results obtained

from other surface characterization techniques, such as EC-AFM observation and electrochemical investigations.

Stripping analysis can be additionally used to measure the amount of metal deposited at a certain potential.⁴⁷ Using linearscan anodic stripping voltammetry, the concentration of the deposit on the electrode surface can be determined,^{48,49} and if the deposit is uniform, the thickness of the deposit can be calculated.^{50,51} In this work, we use anodic stripping analysis to estimate the thickness of Te thin film and to compare the results with the values obtained by other techniques. In addition to these surface characterization techniques, we use the XPS to characterize the composition of the deposit formed by electrochemical deposition in the presence and the absence of Cd²⁺.

2. Experimental Procedure

2.1. Materials. Ultraflat Au(111) on mica (for electrochemical atomic force microscopy observations) and thin Au film on glass (for electrochemical surface plasmon resonance) were used. The ultraflat Au(111) surfaces were prepared by a template-stripped method by following the procedure presented in the literature.⁵² First, an Au film of 5 nm in thickness was vapor deposited on mica at 300 °C, followed by annealing for 6 h at 300 °C. Then, the deposition of Au was continued to reach a total thickness of ~ 200 nm. The typical deposition rate is 0.1 nm/s. Second, the gold surfaces on mica/Au were glued on glass cover slips by epoxy (Epo-tek 377, Polyscience) to form the structures of mica/Au/epoxy/glass, and then curing mica/Au/epoxy/glass at 80 °C for 3 h. Right before experiments, the mica was mechanically stripped from mica/Au/epoxy/glass, leaving a fresh Au surface on Au/epoxy/glass. The Au(111) surfaces are atomically flat (typically, mean roughness is 0.2-0.5 nm in a $25 \,\mu\text{m}^2$ area),⁵² which are ideal for the EC-AFM investigation of the surface morphology changes during deposition. Typical triangular facets characterize the gold surfaces, and occasionally, holes of less than 200 nm in diameter are visible during AFM observation.

In the electrochemical surface plasmon resonance experiments, we used Au films on LaSFN9 glass slides as working electrodes. Au films (thickness of 40–50 nm) were vapor deposited on LaSFN9 slides at a deposition rate of 0.02 nm/s. The Au(111) is textured normal to the surface.^{53,54} The optical constants of Au are n = 0.17 and k = 3.58 for wavelength $\lambda = 633$ nm.⁵⁵ The LaSFN9 slides are high-index glasses (n = 1.85 at $\lambda = 633$ nm, Schott, Germany) suited for SPR measurement. ^{56–61}

The electrolyte was prepared by dissolving TeO₂ (99.9995%, Aldrich) and CdSO₄ (99.999%, Aldrich) with 50 mM H₂SO₄ in ultrapure water. The electrolyte was purged with pure nitrogen for at least 15 min right before each experiment. All chemicals were used as received without further purification. Ultrapure water (18 MW·cm) was obtained from the NanoPure Diamond system (Barnstead).

2.2. In situ Electrochemical Atomic Microscopy. A schematic drawing of the setup used for in situ electrochemical atomic microscopy is shown in Figure 1a. The electrode Ag/AgCl/3M NaCl was used as the reference electrode, gold wire was used as the counter electrode, and the ultraflat Au(111) substrate was used as the working electrode. All potentials reported here are relative to the reference electrode of Ag/AgCl/3M NaCl. The Au/epoxy/glass substrate was placed on the XYZ piezotranslator of the AFM instrument. The electrolytes were injected through a tube inlet and secured by an O-ring inside the AFM liquid cell (Figure 1a). Changes in surface morphology of the ultraflat Au(111) surface during the controlled electro-



Figure 1. Illustration of the experimental setup of in situ EC-AFM (a) and in situ EC-SPR (b).

chemical deposition process were investigated in real time by in situ EC-AFM. The potential was kept constant at -62 mVin all in situ EC-AFM experiments, controlled by a bipotentiostat (Model AFCBP1, Pine Instrument Co.) with a computer interface. The electrochemical atomic force microscope was a multimode AFM (NanoScope IIIA, Digital Instruments). Commercially available triangular gold-coated cantilevers with pyramidal tips of 0.5 N/m force constant were used. To correct for tilt and bow, the AFM images were image processed by using the software provided with the instrument.

2.3. Surface Plasmon Resonance and Cyclic Voltammetry Measurements. An illustration of the setup for surface plasmon resonance (SPR) and cyclic voltammetry (CV) measurement is shown in Figure 1b. The setup was according to the Kretschmann configuration.⁶² This setup has been used by us previously^{56,57} and consists of a Teflon cell that is sealed with an O-ring and mounted against the gold surface of the glass substrate. The electrochemical assembly for the SPR (EC-SPR) was similar to that used in the EC-AFM experiments, i.e., the reference electrode was the Ag/AgCl/3 M NaCl electrode, and gold wire was used as a counter electrode. In the EC-SPR experiments, we used Au films on LaSFN9 slides as working electrodes. The reflectivity vs angle (R vs θ) curves measured by SPR in the electrolytes and pure water are identical. The electrochemical SPR cell made of Teflon was filled by 15 mL of electrolyte, and an area of 2.83 cm² of Au surface was exposed to the electrolyte through a circular opening. A prism was mounted on the LaSFN9 slide with matching fluid (sulfur in 1-iodonaphthalene, Cargille Laboratories, Inc.) in between, which kept constant the refractive index through the prism, matching fluid, and LaSFN9 slide.⁵⁶⁻⁶¹ The applied potential was controlled by a bipotentiostat with a computer interface. All potentials reported here are relative to the reference electrode of Ag/AgCl/3 M NaCl. Prior to the EC-SPR measurement, the Au surfaces were electrochemically cleaned in 50 mM H₂SO₄ by cycling the potential between -200 and 1000 mV until we obtained steady voltammograms.^{63,64} The SPR reflectivities vs angle curves were obtained at open circuit before and after deposition. Details on the SPR measurements and calculations are given elsewhere.46,56,65 The thickness of the deposits was calculated using the simulation software WINSPALL (Max-Planck Institute for Polymer Research, Mainz, Germany) by curve-fitting the R vs θ curves, which is based on the Fresnel theory.^{57,66,67}

2.4. X-ray Photoelectron Spectroscopy (XPS). XPS measurement was performed by using a Perkin-Elmer PHI 5300 ESCA system. The XPS includes an X-ray source of fixed-energy radiation, an electron energy analyzer, and a high-vacuum environment. The sample was mounted on a standard puck by using a Ted Pella carbon paper backing. The starting base pressure is usually about 9.0×10^{-9} Torr. The X-ray source was set at: Aluminum Source, 15 kV, 300 W.

2.5. Hazardous Information. Exposure to material containing Cd ions can cause lung and kidney disease and cancer.

3. Results and Discussions

3.1. In Situ Electrochemical Atomic Force Microscopy (EC-AFM). Figure 2 shows a time sequence of the EC-AFM images recorded in situ during Te deposition on an Au substrate in the presence of Cd^{2+} . We use the marker "A" as a trace to locate the initial scanning area. Figure 2a is the original ultraflat Au(111) surface, which is characterized by atomically flat terraces having triangle patterns. Figure 2b clearly shows that, at -62 mV for 346 s, the nucleation process starts and islands are formed on the Au terraces. Figure 2c shows larger islands because the small islands start to coalescence. After 531 s, the features of the original Au surface, i.e., the Au-patterned terraces, fade away. This kind of the coalescence is a typical process that results in smooth surfaces.^{41,68} Figure 2d shows that, after 706 s, the coalescence process continues and the islands merge together and form larger, leveled areas. The smoothing process that occurs during the electrochemical deposition results in a complete disappearance of the original Au terraces. After 877 s, an almost leveled surface with new, larger terraces with a few holes are observed in Figure 2e. For longer deposition time, after 1050 s, some of the holes disappear and a smoother surface is obtained (Figure 2f).

Figure 3 shows time sequences of the EC-AFM images obtained in situ during Te deposition on Au substrate at -62 mV in the absence of Cd²⁺. Figure 3a is the original ultraflat Au(111) surface. Figure 3b shows that the nucleation process has already started after 315 s and Te islands develop. Figure 3c-f show that the density of the islands increases as the deposition progresses and that the original ultraflat Au surface cannot be distinguished anymore. No smoothing process occurs in this case. The EC-AFM observation of the Te layer on ultraflat Au at -62 mV in a solution that does not contain Cd²⁺



Figure 2. Time sequence of AFM images recorded in situ during Te deposition on Au substrate at -62 mV in the presence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 1 mM CdSO₄ + 50 mM H₂SO₄ solution). Point A is a common blemish for all images.

shows that the Te film has an island growth mode. By comparing the surface plots in the two deposits, i.e., in the presence (Figure 4a) and in the absence of Cd^{2+} (Figure 4b), for 40 min, the surface morphology of the film obtained in the presence of Cd^{2+} is smoother than that of the deposit obtained in the absence of Cd^{2+} (in Figure 4b, higher elevations are brighter). Additionally, the mean square roughness (rms) of the surface shown in Figure 4a is 0.376 nm, which is about 70% smaller than that obtained in the absence of Cd^{2+} (Figure 4b, rms = 0.545 nm). These EC-AFM observations demonstrate that Cd acts as a smoothing agent for Te deposition.

3.2. Thickness. The thickness of the Te film (deposited at -62 mV for 40 min in the presence of Cd²⁺) was determined by AFM measurement and electrochemical stripping analysis.

3.2.1. Atomic Force Microscopy Measurements. The thickness of the Te film deposited at -62 mV for 40 min in the presence



Figure 3. Time sequence of AFM images recorded in situ during Te deposition on Au substrate at -62 mV in the absence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 50 mM H₂SO₄ solution).

of Cd^{2+} was estimated from the AFM observations. We measured the section across the areas with and without electrolyte (the electrolyte was confined by the O-ring). Figure 5 shows the AFM image of the regions covered (right and down corner) and uncovered (left and up corner) with Te film. The Te film has a solid and clear edge over 4 μ m in length, which

indicates a fully and evenly developed film. From AFM measurements, the thickness of the Te film measured across the two regions is about 0.60 nm.

3.2.2. Electrochemical Stripping Analysis of the Film. The electrochemical stripping analysis of Te films was performed by scanning the potential from -62 to 700 mV after the Te



Figure 4. Surface plots of films deposited for 40 min at -62 mV in (a) the presence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 1 mM CdSO₄ + 50 mM H₂SO₄ solution) and (b) in the absence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 50 mM H₂SO₄ solution).



Figure 5. AFM image of the regions covered with Te film (right and lower portion) and without Te film (left and upper portion). The step analysis of the crossover region between the Te film and bare surface is 0.60 nm. The deposition was performed in the presence of Cd^{2+} (i.e., 0.1 mM TeO₂ + 1 mM CdSO₄ + 50 mM H₂SO₄ solution) for 40 minutes at -62 mV.

film was deposited at -62 mV for 40 min. The estimation of the film thickness is based on the Faraday's law:⁵⁰

$$\int_{t_0}^t I \mathrm{d}t = \int_{V_0}^V \frac{I}{\nu} \mathrm{d}V = Q = nFM \tag{1}$$

where *I* is the current density recorded at a stripping potential, *V*, from -62 to 700 mV, *t* is time, ν is the potential sweep rate of stripping ($\nu = 5 \text{ mV/sec}$), *Q* is the total charge per 1 cm² surface area of the electrode, *n* is the number of electrons



Figure 6. Stripping voltammograms of film deposited for 40 min at -62 mV in (a) the presence of Cd^{2+} (i.e., 0.1 mM $TeO_2 + 1 \text{ mM}$ $CdSO_4 + 50 \text{ mM}$ H₂SO₄ solution) and (b) in the absence of Cd^{2+} (i.e., 0.1 mM $TeO_2 + 50 \text{ mM}$ H₂SO₄ solution).



Figure 7. (a) Four-layer model with continuous Te layer; (b) Fourlayer model with discontinuous Te layer.

involved in the reaction (n = 4), F is the Faraday constant, and *M* is amount of the deposit stripped off from 1 cm^2 area of the electrode surface. The amount (per cm²) of the deposit stripped off from the electrode surface, M, equals the thickness times the concentration (assuming that the concentration is uniform in the deposit). Figure 6 shows stripping voltammograms of the deposits, which were used for thickness calculations. A smaller amount of Te was deposited in the presence of Cd²⁺ than in the absence of Cd^{2+} . To make sure that all the deposit was stripped off from the Au surface, the R vs θ curves were recorded under in situ EC-SPR before deposition and after stripping. Figure 8 shows the SPR *R* vs θ curves of the surface obtained at -62 mV for 40 min in the presence of Cd²⁺ and in the absence of Cd²⁺. Figure 8 shows that the *R* vs θ curve after stripping is restored back to the initial condition (i.e., before deposition), which indicates that the charge obtained from the stripping experiment reflects the total amount of material deposited on the surface. The total charge calculated for the film deposited in the presence and in the absence of Cd²⁺ was $Q = 1.04 \text{ mC/cm}^2$ and $Q = 1.81 \text{ mC/cm}^2$, respectively. The total charge associated with the film deposited in the presence of Cd²⁺ is 42% smaller than that obtained in the absence of Cd²⁺. These results suggest that Cd slows down the deposition of Te at the deposition potential of -62 mV. The slower rate observed for the deposition of Te in the presence of Cd might be due to the competition between Te and Cd ions during electrochemical deposition at the deposition potential of -62 mV.

Assuming that the Te film has uniform concentration (the density of Te film is assumed to be identical to bulk density of Te, 6.25 g/cm³),⁶⁹ a thickness of 0.58 nm was calculated from the total charge after stripping the deposit obtained in the presence of Cd²⁺ at -62 mV for 40 min. This thickness value (0.58 nm) obtained from stripping analysis agrees well with the



Figure 8. SPR $R-\theta$ curves of the surface obtained at -62 mV for 40 min in (a) the presence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 1 mM CdSO₄ + 50 mM H₂SO₄ solution) and (b) in the absence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 50 mM H₂SO₄ solution).

thickness value of 0.60 nm that was obtained from the AFM measurements for the same deposition condition. Therefore, we assume that a uniform and continuous Te layer was deposited in the presence of Cd^{2+} on Au substrate.

3.2.3. Electrochemical Surface Plasmon Resonance Measurements. The thickness of ultrathin film deposited on Au can be determined by simulation of the SPR R vs θ curves, using the Fresnel equation, if the refractive index of the ultrathin film is known.⁵⁵ We employed a four-layer model (Figure 7a) for simulation. When the film is not continuous (Figure 7b), the simulation can be used to estimate an effective thickness and refractive index by using the Bruggeman formula, which assumes that the ultrathin layer consists of a mixture of the deposit and the electrolyte.⁴⁵ The Bruggeman formula is represented in eq 2.^{70,71}

$$(1-f)\frac{n_{\rm solu}^2 - n_{\rm eff}^2}{n_{\rm solu}^2 + 2n_{\rm eff}^2} + f\frac{n_{\rm Te}^2 - n_{\rm eff}^2}{n_{\rm Te}^2 + 2n_{\rm eff}^2} = 0$$
(2)

where n_{eff} is the effective refractive index of the mixture layer, n_{solu} is the refractive index of the electrolyte, n_{Te} is refractive index of the Te bulk, and *f* is the volume fraction of Te in the mixture layer.

The SPR R vs θ curves used for the study of the surface obtained at -62 mV for 40 min in the presence and in the absence of Cd²⁺ is given in Figure 8. In Figure 8a, the initial state of the bare Au layer on a LaSFN9 glass substrate is referred to as "before deposition" on the SPR R vs θ curve. Simulation of this curve gives a thickness value of 40.48 nm for the Au layer, taking into consideration the known values of the optical constants of the LaSFN9 glass substrate, Au, and the electrolyte. The simulation curve fits well with the experimental data points. After the deposition performed at -62 mV for 40 min ("after deposition" in Figure 8a), the experimental SPR $R-\theta$ data are shifted from "before deposition", suggesting that a new deposit on top of the Au surface was formed. Similarly, the simulation curve for the "after deposition" data shown in Figure 8a fits well, giving a thickness of 0.55 nm and optical constants of the deposit of n = 4.64 and k = 4.64. The thickness value of the deposit agrees with the values obtained from the AFM measurement and stripping analysis. Additionally, the optical constants are close to the optical constants for Te (n = 4.67 and k = 4.67at a photoelectron energy = 2.0 eV).⁷² The results suggest that the deposit obtained at -62 mV for 40 min is a continuous Te layer on top of Au, which is also consistent with the AFM measurement. Repeated experiments on several different Au/ LaSFN9 samples gives an average thickness of 0.58 \pm 0.03 nm, and $(n, k) = (4.68 \pm 0.03, 4.68 \pm 0.03)$. We have attempted



Figure 9. SEM images of the film deposited in the presence (a, c) and the absence (b, d) of Cd^{2+} . Scale for (a) and (b) is 2 μ m and for (c) and (d) 200 nm.

to simulate the SPR $R-\theta$ data with a Cd layer or a CdTe layer, but the fitting was not possible, indirectly indicating there is no Cd in the deposit. Actually, the XPS spectrum shows no Cd in the deposit (see later section).

In the case of the deposition performed in the absence of Cd^{2+} , we were unable to fit the curve of "after deposition" (Figure 8b) using the optical constant values obtained before, i.e., (n, k) = 4.68, 4.68. The best fitting gives an effective thickness of 1.82 nm and (n, k) = (1.88, 2.92). The optical constants in this case are different from those of bulk Te, which suggests that the deposit is not a continuous layer on the Au surface. In this case, it is difficult to evaluate the thickness from the SPR results. By application of eq 2, we estimate the volume fraction of Te in a discontinuous film on the surface to be f = 24% in the absence of Cd^{2+} .

The scanning electron microscopy (SEM) images show a continuous film (Figure 9a,c) for the deposition performed in the presence of Cd²⁺ and a discontinuous film (Figure 9b,d) for the deposition performed in the absence of Cd²⁺. The SPR measurement can be used to accurately estimate the thickness of the Te deposit if the deposit is a continuous film. Additionally, if the deposit is a continuous film, we can further investigate the growth rate of the Te film in the presence of Cd²⁺. Figure 10 shows the SPR *R* vs θ curves scanned at 0, 40, 80, and 120 min. The curves have good fitting with n = 4.64 and k = 4.64. We were able to monitor the growth of a continuous Te film up to 1.04 nm in thickness. Figure 11 represents the thickness vs time for Te electrochemical deposited film in the presence (a) and the absence (b) of Cd²⁺. In the presence of Cd²⁺, the



Figure 10. SPR $R-\theta$ curves scanned at 0, 40, 80, and 120 min of the film deposited for 40 min at -62 mV in the presence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 1 mM CdSO₄ + 50 mM H₂SO₄ solution).



Figure 11. Thickness vs time for the film deposited for -62 mV in (a) the presence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 1 mM CdSO₄ + 50 mM H₂SO₄ solution) and (b) in the absence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 50 mM H₂SO₄ solution).

thickness vs time curve was obtained from the growth rate data presented in Figure 10. In the absence of Cd^{2+} , the estimated thickness is the effective thickness, because the Te deposit does not develop a continuous film in this case. Figure 11 shows that the growth rate decreases as the deposition time increases, the growth of the deposit being faster in the absence of Cd^{2+} . These results suggest that the rate of Te deposition is slowed by the presence of Cd^{2+} in the electrolyte. The slower growth rate is the reason Te nanowires can be grown inside Au nanotubes.²

3.3. X-ray Photoelectron Spectroscopy. We used XPS to identify the composition of the deposit formed in the presence of Cd^{2+} . The deposition was performed at the potential of -62 mV for 80 min in the presence of Cd^{2+} on an ultraflat Au surface. Figure 12 shows the XPS spectrum of the elements and the chemical structure near the outmost surface. The deposit contains elemental tellurium and no tellurium oxide⁷³ because the Te 3D spectrum shows a peak at 573 eV and no peak at 576 eV. Additionally, there is no peak around 405 eV in Figure 12, indicating the absence of Cd in the deposit. The oxygen and carbon peaks in Figure 12 are from air contamination. From these XPS results, we confirm that Cd is not co-deposited along with Te at the deposition potential of -62 mV. When the applied potential is removed, the weak absorbed Cd atoms are removed from the surface. Thus, XPS shows no Cd in the deposit.

Elemental Cd is less noble than Te, and this makes Cd a good candidate as a mediator.²¹ Unlike Te, Cd is highly



Figure 12. XPS spectrum of the film obtained by electrochemical deposition at -62 mV film for 80 min in the presence of Cd²⁺ (i.e., 0.1 mM TeO₂ + 1 mM CdSO₄ + 50 mM H₂SO₄ solution).

reversible in its UPD state.²⁶ For the electrolyte containing Te and Cd elements, Cd can be adsorbed and desorbed from the Te surface around -150 mV (vs Ag/AgCl).²⁶ The mobility of the specifically adsorbed Cd²⁺ is high at the deposition potential used in this work, which is around Cd UPD on Au. A similar fast mobility of the mediator during deposition has been associated with a smoothing mechanism in the case of the Ag-Pb system.^{20–22} In our work, the smoothing effect induced by Cd has been identified by in situ EC-AFM (Figure 2). Because Cd could not be detected in the Te deposit obtained in the presence of Cd²⁺, we assume that Cd acts only as a mediator in the electrochemical deposition of Te.

If the effective bond strengths satisfy the inequalities $V_{A-A} > V_{A-M} \gg V_{M-M}$, then a submonolayer of mediator (M) efficiently acts as a surfactant and promotes layered A-on-A growth.¹⁰ In the case of the Cd–Te system discussed in this paper, V_{Te-Te} (259.8 kJ/mol)⁷² > V_{Te-Cd} (100 kJ/mol)⁷² \gg V_{Cd-Cd} (7.36 kJ/mol),⁷² meets the inequalities above for using Cd as a mediator for LbL deposition of Te. Cd acts a mediator to lower the Ehrlich–Schwoebel (ES) barrier and to increase the interlayer mass transport and, thus, to promote the layer-by-layer deposition, resulting in a smooth surface morphology.

It worth mentioning that the SPR results obtained in this work shows that the optical constant of a continuous layer of Te in the presence of Cd²⁺ is n = 4.64 and k = 4.64, which agrees with the values parallel to the *c*-direction of Te crystal. ⁷² These results suggest that the *c*-axis is oriented perpendicular to the Au surface, and therefore, the Te(0001) plane is parallel to the Au(111) surface. The distance measured between the Te atoms on the (0001) plane is 0.445 nm, which agrees with the AFM observation of (3 × 3) Te structure on Au(111) at the initial Te bulk deposition.⁴²

4. Conclusion

The morphology and film formation of the Te deposit has been studied in the presence and in the absence of Cd^{2+} using various surface characterization techniques. The Te layer on ultraflat Au shows different growth mechanisms depending on the presence or the absence of Cd^{2+} in the solution. The surface morphology of the film obtained in the presence of Cd^{2+} is smoother than that of the deposit obtained in the absence of Cd^{2+} . The roughness analysis from AFM images shows that the roughness of the film obtained in the presence of Cd^{2+} is 70% smaller than that obtained in the absence of Cd^{2+} . The smoothing role played by Cd was also verified by SEM observation. Additionally, the thickness of the film was evaluated using AFM measurements, electrochemical stripping analysis, and SPR. The results obtained from all three measurements agree well for the Te film obtained in the presence of Cd^{2+} , where a continuous and uniform film was formed. In the presence of Cd^{2+} , a Te film with a thickness of 1.04 nm and an atomically flat surface is deposited on the ultraflat Au surface. However, in the absence of Cd^{2+} , the Te film is not uniformly deposited, the thickness obtained from the stripping analysis, and that obtained from SPR do not agree. In situ EC-SPR provides additional information on the kinetics and growth mechanism of the Te film, which explains the smoothing effect induced by Cd during Te deposition. Although Cd^{2+} is present in the electrolyte, its role is only to mediate the layer-by-layer deposition process of the Te film. The XPS analysis supports the smoothing mechanism induced by Cd and shows no trace of Cd in the Te deposit.

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