An approach to producing films of nanometer-sized copper oxide particulates, based on polyelectrolyte-mediated assembly of the precursor, copper(II)phthalocyanine tetrasulfonate (CPTS), is described. Multilayered CPTS and polydiallyldimethylammonium chloride (PDADMAC) were alternately assembled on different planar substrates via the layer-by-layer (LbL) procedure. The growth of CPTS multilayers was monitored by UV-visible spectrometry and quartz crystal microbalance (QCM) measurements. Both the UV-visible spectra and the QCM data showed that a fixed amount of CPTS could be attached to the substrate surface for a given adsorption cycle. Cyclic voltammograms at the CPTS/PDADMAC-covered gold electrode exhibited a decrease in peak currents with the layer number, indicating that the permeability of CPTS multilayers on the electrodes had diminished. When these CPTS multilayered films were calcined at elevated temperatures, uniform thin films composed of nanoparticulate copper oxide could be produced. Ellipsometry showed that the thickness of copper oxide nanoparticulate films could be precisely tailored by varying the thickness of CPTS multilayer films. The morphology and roughness of CPTS multilayer and copper oxide thin films were characterized by atomic force microscopy. X-ray diffraction (XRD) measurements indicated that these thin films contained both CuO and Cu2O nanoparticles. The preparation of such copper oxide thin films with the use of metal complex precursors represents a new route for the synthesis of inorganic oxide films with a controlled thickness.

**Keywords:** Layer-by-Layer, Nanoparticulate Thin Films, Polyelectrolyte.

1. INTRODUCTION

Construction of ordered and functional metal oxide films with nanometer-sized grains and thickness has attracted interest in the field of materials research, because these films may find desirable applications in heterogeneous catalysis, electronic and photonic device fabrication, and sensor development. Films containing copper oxide have been noted for their unique properties, such as high temperature superconductivity, magnetic properties, improved radiation cooling, and unique optical and electrical characteristics. Numerous methods have been developed for the preparation of thin copper oxide films, including, but not limited to, molecular beam epitaxy, spin coating, metal-organic chemical vapor deposition, and sol-gel chemistry. However, production of thin metal oxide films with a controllable thickness has been challenging. Recently, sequential deposition and reaction at a substrate surface has been purported as a remedy. The Ferguson, Kunitake, and Mallouk groups reported a sol-gel-based technique, which permits tuning of titania film thickness down to the nanometer range. Keszler and co-workers developed a method involving adsorption of the ionic layer for a subsequent reaction to prepare crystalline metal oxide thin films with a variable thickness.

An alternative and versatile strategy for fabricating functional films with nanometer thickness is the layer-by-layer (LbL) self-assembly technique. The LbL method, originally developed to form films of oppositely charged polyelectrolytes at a planar substrate or on a colloidal particle, has been extended to prepare metal, semiconductor, and metal oxide nanoparticulate thin films. The advantage of the LbL approach is that control of the film thickness can be realized by varying the layer deposition cycles, and the film composition can be varied by the selection of the precursors.

**Keywords:** Layer-by-Layer, Nanoparticulate Thin Films, Polyelectrolyte.
of different charged precursors and calcination conditions. Moreover, the method is straightforward and does not require a sophisticated apparatus. Thus it is highly complementary to bulk syntheses of metal or metal oxide nanoparticles for cases that are challenging and cost-ineffective. For instance, Caruso and co-workers\textsuperscript{45, 46} and Ferguson and co-workers\textsuperscript{47} fabricated thin titania films with a finite and controllable thickness by employing titanium(IV)bis(ammonium lactato)dihydroxide as the precursor. However, the preparation of nanometer-sized metal oxide films or other nanostructures with water-soluble and charged metal complexes as precursors has not been widely reported.

In the present study, a copper phthalocyanine tetratsulfonate (CPTS) (molecular structure shown in Scheme I) was used as a precursor and sequentially adsorbed with polydiallyldimethylamonium chloride (PDADMAC) to a solid substrate to prepare thin copper oxide nanoparticulate films. These two oppositely charged constituents could be LbL assembled. The multilayer buildup was confirmed by UV-visible spectrophotometer, quartz crystal microbalance (QCM), and electrochemical measurements. After calcination at an elevated temperature, nanoparticulate copper oxide thin films were formed. The thickness and morphology of these films were characterized by ellipsometry and atomic force microscopy (AFM), and the composition of the copper oxide nanoparticles formed in the films was determined by X-ray diffraction (XRD). Because the LbL approach allows nanometer-scale control of film thickness by variation of the adsorption cycles of CPTS and PDADMAC, fine-tuning of the copper oxide film thickness becomes feasible. This approach may be extended to prepare a variety of metal oxide thin films.

2. EXPERIMENTAL DETAILS

2.1. Materials

CPTS and PDADMAC (MW < 200,000) were obtained from Aldrich. NaCl was purchased from Fisher. Hexamethylenetetramine(III)chloride (Aldrich) was used as received. Water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system.

2.2. Preparation of CPTS Multilayer Films

2.2.1. Quartz Substrates

Thin, alternating PDADMAC/CPTS films were LbL-assembled on quartz substrates (Hellma, Germany), cleaned by soaking in a 5:1:1 (vol%) H\textsubscript{2}O/H\textsubscript{2}O\textsubscript{2}/NH\textsubscript{3} mixture at 70 °C for 10 min (RCA protocol),\textsuperscript{48, 49} and rinsed with a copious amount of water. The first layer of PDADMAC was adsorbed to the negatively charged quartz surface by immersion of the quartz substrate in a 1 mg/ml PDADMAC solution (containing 0.5 M NaCl) for 15 min. The PDADMAC-covered substrates were rinsed with water three times, followed by drying under a gentle stream of N\textsubscript{2}. CPTS was then attached to the PDADMAC layer by immersion of the PDADMAC-modified quartz substrate in a CPTS solution of different concentrations. These processes were repeated to produce the multilayered films. The LbL growth of CPTS multilayers was monitored by a UV-visible spectrophotometer (SLM-AMINCO, model 3000).

2.2.2. Silicon Wafers and Gold Surfaces

Silicon wafers (111) were treated by the RCA protocol described above. Thin films containing PDADMAC/CPTS multilayers were assembled on the silicon wafers. Gold-coated glass slides were also used for the multilayer deposition. The gold substrates were prepared by sputtering 30 nm of gold with a 0.5-nm-thick chromium underlayer onto thin glass slides (Fisher Scientific), with a Kurt J. Lesker coater (model 108; Clairton, PA). The gold surface was treated with a piranha solution (30% H\textsubscript{2}O\textsubscript{2} and 70% concentrated H\textsubscript{2}SO\textsubscript{4}) and rinsed thoroughly with water before PDADMAC and CPTS adsorption. **CAUTION:** Piranha solution reacts violently with organic solvents and is a skin irritant. Extreme caution should be exercised when handling piranha solution.

2.2.3. QCM Electrodes

AT-cut 9.995-MHz crystals (ICM Technologies, Oklahoma City, OK) with both sides coated with gold films were employed for PDADMAC/CPTS multilayer formation. The crystal surface could again be cleaned with a piranha solution. Frequency measurements were carried out with an ICM oscillator and a PM6680B counter/timer (Fluke Corp., Everett, WA).
The total mass deposited at the QCM crystal surface can be calculated from the cumulative frequency change with the Sauerbrey equation. For a 9.995-MHz QCM crystal with an electrode area of 0.196 cm², the relationship between the adsorbed mass \((\Delta m)\) of each PDADMAC and CPTS layer and the change in the resonant frequency \((\Delta F)\) is given by

\[
\Delta m(\text{ng}) = -0.86 \times \Delta F(\text{Hz})
\]

### 2.3. Formation of Copper Oxide Films

PDADMAC/CPTS multilayer films coated onto silicon wafers were calcined at 500 °C under N₂ for 4 h and O₂ for 8 h. We selected 500 °C to calcine the CPTS multilayer films to produce the copper oxide nanoparticulate films (mixtures of Cu₂O and CuO, vide infra). To completely form CuO, a higher temperature (e.g., 900 °C) must be used. The outermost layer of these films was kept as PDADMAC to avoid the adsorption of sodium ions from the solution (which could lead to sodium oxide formation during the calcination step). The resultant films were subsequently characterized by contact angle, AFM, ellipsometry, and XRD measurements.

### 2.4. Electrochemical Measurements

A CHI 440 electrochemical workstation (CH Instruments; Austin, TX) was used for the voltammetric experiments. Gold films covered with PDADMAC/CPTS films served as the working electrode, and a Pt flag and a Ag/AgCl electrode were employed as the auxiliary and reference electrodes, respectively. A phosphate buffer (pH 7.8) solution with 1 mM Ru(NH₃)₆⁴⁺ was purged with nitrogen for 3 min before the voltammetric measurement.

### 2.5. Contact Angle

Contact angles at multilayered PDADMAC/CPTS films before and after calcination were measured with a contact angle meter (KSV Instruments, Monroe, CT). Measurements were performed on several portions of each silicon wafer. Values reported here are the averages of at least nine measurements.

### 2.6. Atomic Force Microscopy

AFM measurements were conducted with an AFM equipped with a magnetic alternating current (MAC) mode (Molecular Imaging, Phoenix, AZ). Both contact and MAC modes were used for the characterization of PDADMAC/CPTS films before and after calcinations. Images of multilayer films of PDADMAC/CPTS on silicon wafers were obtained with an oscillating frequency of 25 kHz and a driver current of 30 ± 5 A.

### 2.7. Ellipsometry

Ellipsometric measurements were carried out on a picometer (Beaglehole Instruments, Wellington, New Zealand). The measuring wavelength was selected to be 550 nm by filtration of the light from a halogen lamp. The angle of incidence was set at 75°, which is near the Brewster angle of the silicon substrate. The thickness is statistically averaged over an 8 × 8 mm area. Calculations of the film thickness were based on a film model consisting of silicon (refractive index \(n = 3.865\), absorption coefficient \(k = 0.020\)), polymer \((n = 1.68, k = 0)\), and air \((n = 1, k = 0)\).

### 2.8. X-Ray Diffraction

XRD measurements were performed with a θ–2θ diffractometer (Crystal Logic) with Cu-Kα radiation. Scans were taken in the range of 2θ, 10–100°, at 0.10° or 0.05° intervals, and with 3-s count times.

### 3. RESULTS AND DISCUSSION

#### 3.1. Formation of PDADMAC/CPTS Multilayer Films

The LbL assembly of PDADMAC and CPTS thin films was performed on quartz substrates. The absorption spectra (Fig. 1) are characteristic of the phthalocyanine ligand complexed to copper and agree well with previously reported absorption spectra. Hence the plot of absorbance at 226 nm vs. the layer number (inset of Fig. 1) shows the stepwise increase only at the even number. CPTS also absorbs in the visible range with peaks at 611 nm and 691 nm (data not shown), and, in principle, one can use either of the two peaks to monitor the growth of the multilayer thin films. We envision that the use of the peaks at 611 nm and 691 nm would produce similar plots.
ever, these peaks are weaker and less sensitive for monitoring the film growth. PDADMAC does not show any appreciable absorption within the wavelength range. Note that after each PDADMAC layer deposition, the absorbance at 226 nm decreased, suggesting that CPTS was partially dissolved from the surface. Such behavior has been reported for LbL-assembled composite films in which one component is a low-molecular-weight compound (e.g., a dye molecule).48, 54–56 The partial loss is due both to the relatively weak electrostatic force between small charged species and the polyelectrolytes and to the higher mobility of small species. This partial loss can be compensated for by the incorporation of more CPTS through a few additional adsorption cycles.

We also investigated the relationship between the CPTS loading and the CPTS concentration used for the film preparation. Figure 2 plots the absorbance values at 226 nm of the PDADMAC/CPTS multilayers assembled, with different CPTS concentrations as a function of layer number. As can be seen, all of the PDADMAC/CPTS multilayers showed a gradual increase in absorbance (at 226 nm) for all of the concentrations studied. Partial loss of the CPTS precursor was also observed for all cases. With the increase in CPTS concentration, greater amounts of CPTS can be loaded. We found that 0.1 M CPTS was an optimal concentration for constructing quality films without large consumption of the CPTS precursor.

The growth of PDADMAC/CPTS multilayer thin films was also monitored by QCM. Figure 3 shows the frequency decrease ($\Delta F$) at the QCM electrode caused by the attachment of PDADMAC and CPTS. The QCM frequency decreases incrementally with the layer number, demonstrating the possibility of fine control over the extent of precursor loading. The average frequency decreases for each PDADMAC and CPTS layer are 47 ± 21 Hz and 76 ± 6 Hz, respectively. The former corresponds to a mass increase of 40 ± 18 ng and the latter to 65 ± 5 ng. Inasmuch as the mass increase of CPTS after each consecutive PDADMAC adsorption cycle was quite steady, the small decline in the CPTS absorbance implies that the partial loss of the precursor is insignificant and the remaining CPTS precursor still results in the deposition of additional PDADMAC layers.

To understand the influence of the layer number on the compactness of the multilayered films, voltammetric experiments were carried out to assess the permeability of a small charged redox ion, Ru(NH$_3$)$_6$$_3$$^{3+}$. Figure 4 shows an overlay of four voltammograms at gold electrodes coated with 0, 4, 8, and 12 bilayers of PDADMAC/CPTS. The voltammograms at the unmodified electrode exhibited the typical diffusion-controlled reversible waves of Ru(NH$_3$)$_6$$_3$$^{3+}$. When four layers were deposited on the gold electrode, the peak currents decreased only slightly, suggesting that there were
still abundant pores present in the films. The overall voltammetric behavior is similar to what would be observable at the ensemble of many small conductive sites.\textsuperscript{57} However, when the layer number increased to 8 and 12 layers, the shapes of the voltammograms became significantly different, showing responses resembling those at microelectrodes. Such a change is clearly indicative of the transition from an electrode modified with a porous film to that covered with much more compact films. As a result, only a small number of pores allow the Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+} to permeate the films and to approach the underlying electrode. The voltammetric waves of Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+} eventually become indiscernible when layers higher than 14 were deposited on the electrode (data not shown). The decrease in permeability of PDADMAC/CPTS multilayers with the layer number is similar to that of poly(allylamine hydrochloride)/poly(styrene sulfonate) multilayers investigated by Bruening et al.\textsuperscript{58, 59} We also found that there was an abrupt decline in the peak currents when the layer number exceeded 6. Such nonlinearity could be attributed to the different structure in the first two bilayers compared with the rest of the film, a behavior noted in previous reports.\textsuperscript{58–61}

3.2. Structural Characterization of PDADMAC/CPTS Multilayers and Subsequent Copper Oxide Films

In a previous study, copper phthalocyanine was used as a precursor to prepare copper oxide thin films by chemical beam epitaxy. In this study, we chose CPTS as the precursor because of its multiple charges and water solubility. Both of these factors make the LbL procedure for assembling the multilayered films straightforward. The PDADMAC/CPTS multilayer films were characterized by contact angle, ellipsometry, and AFM measurements before and after calcination, and the composition of the final films was examined by XRD.

We measured the contact angles of PDADMAC/CPTS multilayer films (the outermost layer being PDADMAC) before calcination to be 30 ± 1°. After calcination, the contact angle increased to 42 ± 3°. Such an increase is indicative of the change in the film composition, suggesting the conversion from a more hydrophilic surface (PDADMAC) to a more hydrophobic surface (copper oxide, as shown by the XRD spectrum presented below).

Calcination should also cause a change in the thickness of the multilayered PDADMAC/CPTS films because of the combustion of the PDADMAC polymer and the organic ligands of CPTS at a high temperature (500 °C). Such a thickness change can be conveniently measured by ellipsometry. Table I lists the change in the PDADMAC/CPTS film thickness with the layer number before and after calcination. Films with layer numbers of 11, 21, and 41 have thicknesses of 11, 27, and 45 nm, respectively. These data correlate well with the cumulative values of the total number of PDADMAC (each layer \( \approx 1.4 \pm 0.2 \) nm) and CPTS (each layer \( \approx 0.8 \pm 0.1 \) nm) layers. After calcination, the thickness of PDADMAC/CPTS multilayer films decreased and the extent of the decrease was found to be dependent on the layer number. A PDADMAC/CPTS film of 11 layers decreased to 9.1 nm, and the 41-layer counterpart diminished to 29.8 nm. We believe that the formation of nanocrystalline copper oxide granules in the final film might result from the calcination of the CPTS when a polyelectrolyte layer serves as the interlayer. PDADMAC may somehow reduce the rate of copper oxide particle formation. The layer dependence of the thickness change implies that fewer PDADMAC layers would not significantly hinder the copper oxide particle formation, whereas more layers could limit the particle growth. However, the latter effect is partially offset by the fact that more layers of PDADMAC would also incorporate a larger amount of CPTS complex. As a consequence, a thicker copper oxide film can be produced. It thus becomes clear that, by judicious optimization of the layer number and the amount of precursor loading, thin metal oxide films with controlled thickness can be prepared with this methodology.

The morphologies of the multilayered PDADMAC/CPTS films before and after calcination were examined by AFM. Figure 5 shows AFM images of three PDADMAC/CPTS multilayer films with layer numbers of 11 (a), 21 (c), and 41 (e). Images (b), (d), and (f) represent the thin copper oxide films formed after calcination of the PDADMAC/CPTS films with the corresponding layer number.

### Table I. Thickness and root-mean-square roughness of PDADMAC/CPTS multilayer films before and after calcination.

<table>
<thead>
<tr>
<th>Layer number</th>
<th>Before calcination</th>
<th>After calcination</th>
<th>Before calcination</th>
<th>After calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>1.62</td>
<td>0.76</td>
<td>11.4</td>
<td>9.1</td>
</tr>
<tr>
<td>21</td>
<td>6.96</td>
<td>1.85</td>
<td>27.4</td>
<td>21.4</td>
</tr>
<tr>
<td>41</td>
<td>10.10</td>
<td>2.26</td>
<td>45.0</td>
<td>29.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ellipsometric measurements.

\textsuperscript{b}AFM measurements over a 3 \( \mu \text{m} \times 3 \mu \text{m} \) area of each sample.

Fig. 5. AFM images of PDADMAC/CPTS multilayer films with layer numbers of 11 (a), 21 (c), and 41 (e). Images (b), (d), and (f) represent the thin copper oxide films formed after calcination of the PDADMAC/CPTS films with the corresponding layer number.
CPTS multilayer films deposited on Si(111) single crystal wafers and the corresponding copper oxide films. In general, both the grain sizes and the roughness of the films calcined from a smaller number of PDADMAC/CPTS layers were found to be less than those from a larger number of layers. The root mean square (RMS) roughnesses of these films with layer numbers 11 (Fig. 5a), 21 (Fig. 5b), and 41 (Fig. 5c) were 1.62 nm, 6.96 nm, and 10.1 nm, respectively. Compared with films containing multilayers of PDADMAC and PSS (polystyrene sulfonate sodium salt), these PDADMAC/CPTS multilayers appear to be smoother.\textsuperscript{60, 61} Such a difference in the film morphologies could be ascribed to the difference in charges between CPTS and PSS (many more charges reside on the long PSS backbone). Caruso and co-workers have also investigated the influence of charge density of PDADMAC-NMVA (N-methyl-N-vinylacetamide) copolymer on the multilayer film morphology\textsuperscript{86} and found that when the PDADMAC-NMVA copolymer charge density is above a critical value, multilayered films with a greater roughness are produced.

After calcination, nanoparticulate copper oxide films were prepared. The RMS roughness in the AFM images of nanoparticulate films derived from 11, 21, and 41 layers of PDADMAC/CPTS films decreased drastically, indicating the removal of the organic constituents during the calcination (Table I). It can be seen that the morphology of copper oxide films is quite uniform and the uniformity of the nanometer-sized particles depends on the number of PDADMAC/CPTS multilayers (Fig. 5b, d, and f). Films derived from 11 layers are composed of particles with a diameter of 116 ± 13 nm with a RMS roughness of 0.76 nm, whereas films produced from 21 and 41 layers of PDADMAC/CPTS contain grain particles with diameters of 169 ± 12 nm and 237 ± 32 nm with RMS roughnesses of 1.85 and 2.26 nm, respectively. The increase in the particle diameters may have originated from the incorporation of greater amounts of the CPTS precursor with more layer numbers.

XRD measurements were performed to determine the composition of films produced from calcination of the multilayered PDADMAC/CPTS films. In a typical XRD pattern (Fig. 6), both CuO and Cu$_2$O phases can be found. Peaks at 33.1°, 61.3°, and 82.5° are associated with the reflection of CuO (JCPDS file no. 44-0706), whereas peaks at 52.5° and 69.6° can be attributed to the reflection of Cu$_2$O (JCPDS file no. 05-0667). Note that the reflection peak at 69.6° is overlapped with the Si signal from the underlying silicon wafer (69.2°, 400 reflection). Hence the calcination of the multilayered PDADMAC/CPTS films produced nanoparticulate films composed of CuO and Cu$_2$O phases. We have also carried out a UV-visible measurement of the calcined thin films and found no absorption peaks characteristic of the CPTS precursor (data not shown), suggesting that the calcination of the multilayer films has converted the as-prepared films to copper oxide nanoparticulate thin films. The formation of Cu$_2$O could result from incomplete oxidation during the calcination step.

4. CONCLUSIONS

This work demonstrates that CPTS can be assembled on a planar substrate with the sequential adsorption of a poly-electrolyte (i.e., PDADMAC) as the interlayer and can serve as a precursor to form nanocrystalline copper oxide thin films. PDADMAC and CPTS can be adsorbed to quartz, silicon, or gold surfaces via the LbL procedure, and the formation of the multilayered films was verified by UV-visible spectrometric, quartz crystal microbalance, and electrochemical measurements. The results show that the LbL procedure can precisely control the amount of precursor loading in the multilayered film structure, and the compactness becomes greater with a thicker multilayer. XRD spectra show that calcination of these multilayered films at an elevated temperature leads to the formation of thin films containing both CuO and Cu$_2$O. Both ellipsometric and AFM measurements were employed for characterizing multilayered PDADMAC/CPTS and copper oxide films. The film thickness and surface roughness were found to be dependent on the PDADMAC/CPTS layer number. Smaller copper oxide grains with a smoother morphology were obtained with a smaller number of PDADMAC/CPTS layers, illustrating that fine control of both the copper oxide film thickness and morphology can be accomplished by variation of the PDADMAC/CPTS layer number before the calcination step. The approach described here may provide an alternative route for the preparation of nanocrystalline metal oxide thin films; it is relatively straightforward and does not require stringent synthetic procedures involving a sophisticated apparatus and expensive precursors.

Acknowledgments: Valuable discussions with Matthew C. Traub (California Institute of Technology) are appre-
References and Notes


Received: . Revised/Accepted: .