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## Stepwise Formation of Ultrathin Films of a Titanium (Hydr)Oxide by Polyelectrolyte-Assisted Adsorption\*\*

By Jason H. Rouse and Gregory S. Ferguson\*

The ability to form ultrathin films of metal oxides with nanometer control over thickness is an area of intense study, as these films have desirable electronic, optical, and magnetic properties.<sup>[1]</sup> Titanium-oxide films, in particular, have attracted both industrial and academic attention for such potential uses as the gate dielectric in (metal oxide) semiconductor field-effect transistors (MOSFETs),<sup>[2]</sup> and as a surface for solar energy conversion<sup>[3]</sup> and photocatalysis.<sup>[4]</sup> These films are usually formed using gas-phase processes, such as chemical vapor deposition or atomic layer epitaxy, which require costly high-vacuum equipment.<sup>[5,6]</sup> The development of alternative approaches that do not require such equipment is of great interest.

A widely studied wet-chemical method for the formation of metal oxide films involves the spin-coating of hydrolyzed metal alkoxide solutions, i.e., sol-gel chemistry.<sup>[7]</sup> Although this technique allows the formation of uniform films, the ability to control film deposition at the nanometer scale of length has proven difficult.<sup>[8]</sup> Recently, we<sup>[9]</sup> and others,<sup>[10–12]</sup> have developed a modified sol-gel technique to allow the controlled de-

position of metal oxide films via the sequential reaction of metal alkoxides on hydroxyl-containing surfaces, a method closely related to the gas-phase formation of films using reactive intermediates (metal halides, etc.).<sup>[6]</sup> Such precursors have also been allowed to hydrolyze and condense at the air/water interface, followed by Langmuir-Blodgett transfer onto the desired substrate to deposit thin films.<sup>[13,14]</sup> In this communication, we describe the development of a method for the formation of ultrathin films of titanium (hydr)oxide by the alternate adsorption of a poly(diallyldimethyl ammonium chloride) (PDDA) and titanium(IV) bis(ammonium lactato)dihydroxide (TiL<sub>n</sub>), followed by calcination at elevated temperature. This polyelectrolyte-assisted adsorption of a molecular coordination compound complements previous methods that employ exfoliated silicate<sup>[15–17]</sup> and titania (or titanonibate)<sup>[18]</sup> sheets or colloidal particles.<sup>[17,19–24]</sup>

Films were prepared by dripping a 0.25 wt.-% aqueous solution of PDDA onto the surface of a silicon wafer, and after ~10 s, rinsing the surface with deionized water. After the surface was blown dry with nitrogen, the rinsing and drying steps were repeated. Subsequently, the surface was treated, again by dripping, with a 0.01 M aqueous solution of TiL<sub>n</sub> for ~10 s, and then rinsed and dried twice. A linear increase in ellipsometric thickness was observed for separate films each prepared with a different number of adsorption cycles on silicon wafers (Fig. 1a, open symbols),<sup>[25]</sup> indicating both the regularity of the growth from cycle to cycle as well as the reproducibility of the adsorption process from sample to sample. A linear fit to the growth data gave an average growth per cycle of ~1.5 nm. Stepwise adsorption on a single sample showed an average of ~0.3 nm for PDDA and ~1.2 nm for TiL<sub>n</sub> added in each adsorption step. The average refractive index determined ellipsometrically for films greater than 60 nm in thickness was 1.80, a value considerably higher than that of PDDA (~1.53) and consistent with the incorporation of the titanium oxide species. Uniform film growth was also observed during the formation of a 40 cycle film on a quartz slide, as monitored by ultraviolet-visible spectrophotometry, and the spectra of this film were similar to that obtained for a dilute solution of the titanium precursor (Fig. 1b).<sup>[26]</sup>

The elemental composition of the top ~9 nm of a 22 nm thick film was determined by high-resolution X-ray photoelectron spectroscopy (XPS) prior to calcination (Table 1).<sup>[27,28]</sup> Surprisingly, the amount of carbon incorporated into the film was substantially lower than that expected theoretically, assuming an exact electrostatic balance in the film, that is, one TiL<sub>n</sub> dianion for every two PDDA repeat units. These measurements indicated a Ti/C/O/N ratio for the as-adsorbed film of 1:2.9:2.9:0.1 compared to the expected theoretical ratio of 1:24:8:2. After accounting for the amount carbon and nitrogen associated with the PDDA, the elemental ratio associated with the adsorbed titanium species was 1:2.3:2.9:<0.1. The relatively small amount of photoemission associated with the polyelectrolyte is in agreement with the ellipsometric measurements which indicated that the majority of film growth took place during the titanium adsorption step.

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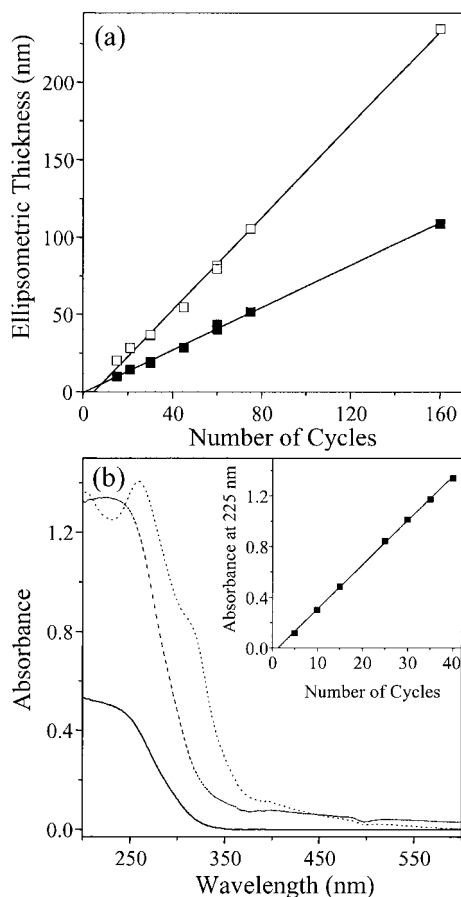


Fig. 1. a) Ellipsometric thickness of thin films prepared by the sequential adsorption of PDDA and  $TiL_n$  before (open symbols) and after calcination at  $500\text{ }^\circ\text{C}$  in air for 10 h (closed symbols). The lines are linear least-square fits to the data. b) UV-vis spectra of a dilute aqueous solution of  $TiL_n$  (solid line); a 40 cycle film, as-adsorbed (dashed line), and the 40 cycle film after calcination at  $500\text{ }^\circ\text{C}$  in air for 10 h (dotted line). The figure inset shows the absorbance of a film at 225 nm as a function of the number of adsorption cycles on a quartz slide.

With the  $TiL_n$  dianion itself having a Ti/C/O ratio of 1:8:8, the amounts of carbon and oxygen present in the film indicate that upon adsorption the lactato ligands were lost or that the adsorbing species was not  $TiL_n$ , but was perhaps rather an oligomer derived from it. A peak consistent with an acidic carbonyl functionality (288.6 eV) was present in the C 1s region of the XPS spectrum, but at a relative abundance of only 10 % of that expected for the  $TiL_n$  species. Analysis of the  $TiL_n$  solution by molar conductance and cyroscopic measurements indicated that the species is primarily monomeric,<sup>[29]</sup> but this result does not rule out the possibility that the solution may contain a small amount of oligomeric material that is actually the absorbing species.

To verify that our adsorption process was in fact depositing a thin uniform layer of a titanium species in each cycle, and not a submonolayer of larger colloidal particles, a cross-sectional scanning electron micrograph of a fractured film on silicon was obtained (Fig. 2a).<sup>[30]</sup> The micrograph shows that the film is uniform in thickness, a result confirmed by the uniform interference color associated with each thickness.<sup>[31]</sup> While it

was not possible to obtain higher-resolution images of the cross-section because of charging, the film does not appear to be made up of particles any larger than a few nanometers in size, consistent with the adsorption of small titanium species. The absence of ordered structure within the film was indicated by the absence of Bragg peaks in an X-ray diffractogram of a 75 cycle film.

To reduce the amount of carbon present and to convert these films into a titanium oxide, samples were heated at  $500\text{ }^\circ\text{C}$  in air for 10 h.<sup>[32]</sup> Calcination resulted in a 53 % reduction in film thickness and an increase in refractive index from  $\sim 1.8$  to  $\sim 2.1$ . This index is consistent with that measured for sol-gel films<sup>[33]</sup> but lower than that seen for either vacuum deposited<sup>[34]</sup> or crystalline forms of  $TiO_2$  (anatase, 2.49; rutile, 2.90).<sup>[35]</sup> The thicknesses of the calcined films remained linearly related to the number of adsorption cycles used to prepare them (Fig. 1a, filled symbols). Upon heating, the Ti:C ratio from XPS at a  $90^\circ$  takeoff angle increased to 1:1 from 1:2.9 (Table 1). Comparison of these results to scans taken at a lower takeoff angle ( $15^\circ$ ) indicated that the carbon is homogeneously distributed throughout the top  $\sim 9$  nm of the film and is not due to adventitious surface contamination. High-resolution spectra of the C 1s region taken at  $90^\circ$  and  $15^\circ$  take off angles indicated the presence of oxidized and unoxidized carbon, as well as the absence of carbide species. Although these results are consistent with formation of a titanium oxide, the absence of crystalline  $TiO_2$  by X-ray diffraction suggests that the films should be described as an amorphous titanium (hydr)oxide.

In addition to its effect on the real part of the refractive index, calcination also affected the optical absorption of these films. Heating at  $500\text{ }^\circ\text{C}$  in air for 10 h (Fig. 1b) caused a noticeable red-shift in absorption relative to that of the as-adsorbed film, with a new peak centered at approximately 259 nm and a new shoulder at about 317 nm. This red-shift is consistent with formation of titanium oxide aggregates and closely resembles that seen for nanometer-sized particles<sup>[36]</sup> and films formed from such particles.<sup>[20]</sup> In bulk titanium oxide, for comparison, absorption extends to  $\sim 425$  nm.<sup>[37]</sup> Further heating of samples to  $900\text{ }^\circ\text{C}$  in air for 10 h (spectrum not shown) resulted in only a slightly further red-shift of both the main peak and the shoulder, to 261 nm and 321 nm, respectively. The small difference between these two treatments on the optical absorbance of these films indicates that sintering, and not coalescence, of the titanium (hydr)oxide probably occurs upon further heating at the higher temperature.

Cross-sectional scanning electron microscopy (SEM) images of a film heated at  $500\text{ }^\circ\text{C}$  in air for 10 h (Fig. 2b and c) show that film uniformity is retained upon calcination, but that a fused nodular microstructure of  $\sim 20$ – $30$  nm particles are formed within the film during this process. An image of the surface of the same film (Fig. 2d) also appeared to have a nodular morphology of particles  $\sim 20$  nm in size. We suspect that the carbon contained within the film may act as a passivating layer that could inhibit particle coalescence during calcination.

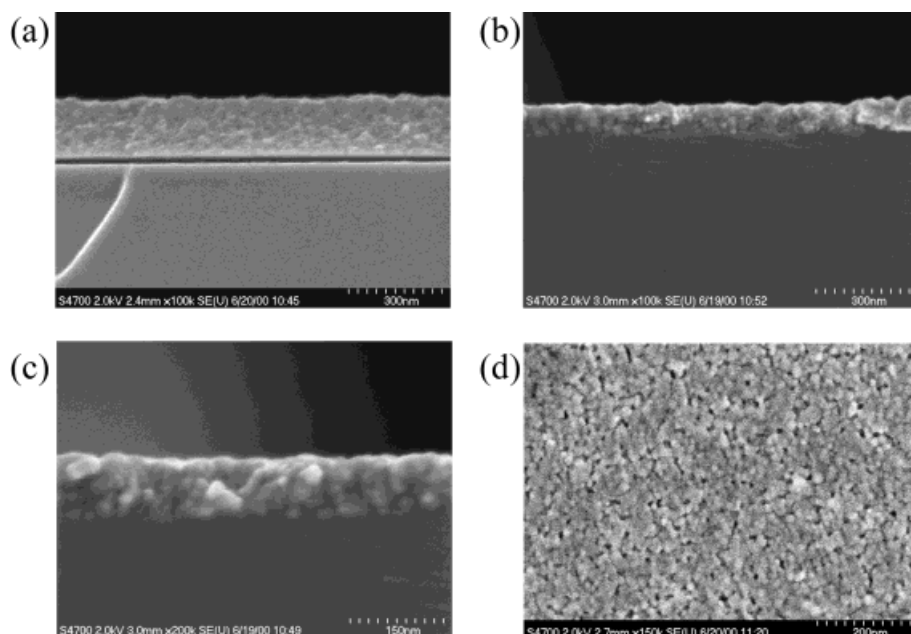


Fig. 2. Cross-sectional SEM images of a titanium (hydr)oxide film on a silicon substrate a) before and b,c) after calcination at 500 °C in air for 10 h. d) SEM image of the same calcined film from above its surface.

Table 1. Film composition [at.-%] as determined by XPS.

Element	As-Adsorbed	Calcined @ 500 °C	
	90° Takeoff	90° Takeoff	15° Takeoff
Oxygen	41.4	56.3	52.7
Carbon	42.3	21.1	25.8
Titanium	14.5	21.5	19.8
Nitrogen	1.8	0.6	0.8
Silicon [a]	0.0	0.5	0.9

[a] The binding energy and angular dependence of the silicon photoemission were consistent with surface contamination by siloxane.

In summary, we have demonstrated a method of forming ultrathin films of titanium (hydr)oxide with precise control over thickness via the alternate adsorption of an organic polyelectrolyte and a titanium coordination compound, followed by calcination at elevated temperature. Films were uniform in thickness both before and after calcination, as evidenced by their uniform interference color and cross-sectional SEM analysis. Film thickness was linearly related to the number of adsorption cycles used to assemble the structure. The optical absorbance of the calcined films resembled that reported for nanometer-size particles and is consistent with the fused nodular morphology of ~20–30 nm particles observed by SEM. The presence of such optical and morphological properties suggests that this method may be suitable for the formation of coatings for use in photoelectrochemical applications.<sup>[3,4]</sup>

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- [27] The approximate escape depth of photoemission,  $d$ , is given by  $3\lambda(\sin\theta)$ , where  $\lambda$  is the inelastic mean free path of the photoelectron in the film and  $\theta$  is the takeoff angle. We approximate  $\lambda$  as 3 nm, a value between that of TiO<sub>2</sub> and organic polymers, from: M. P. Seah, W. A. Dench, *Surf. Interface Anal.* **1979**, *1*, 2.
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## Patterning Mesoscale Gradient Structures with Self-Assembled Monolayers and Scanning Tunneling Microscopy Based Replacement Lithography\*\*

By Ryan R. Fuieler, R. Lloyd Carroll, Daniel L. Feldheim,\* and Christopher B. Gorman\*

Chemical gradients transport materials in a directional manner, and are responsible for driving many important biological and physical processes. The growth of axons from ganglions to target tissues and the directed movement of certain bacteria toward nutrients occur in response to concentration gradients of molecules emanating from axon target or food source (chemotaxis).<sup>[1]</sup> Concentration gradients of molecules in fluids or on surfaces also affect phenomena such as osmotic swelling, surface pressure, and surface wettability. By learning to establish and manipulate these parameters, new methods of transporting fluids in microchannels are emerging, which offer new transport paradigms for the fabrication of chip-based chemical devices.<sup>[2]</sup>

Surface-bound chemical gradients have previously been produced on millimeter to micrometer length scales.<sup>[1–9]</sup> In some cases, these gradients have been used in directional transport. For example, Whitesides and Chaudhury, fabricated self-assembled monolayer (SAM) gradients composed of decyltrichlorosilane on silicon substrates using a diffusion controlled vapor deposition technique. Water droplets were observed to travel uphill under the influence of the resulting spatial gradient in the surface free energy.<sup>[3]</sup> Liedberg and co-workers prepared millimeter scale SAM gradients on gold surfaces by cross diffusing two different alkanethiols from opposite ends of a polysaccharide matrix.<sup>[5,6,8]</sup> Efimenko and Genzer recently demonstrated the ability to tailor surface-bound gradients by fine tuning the molecular grafting density of mechanically assembled monolayers on hydroxyl terminated silicon based substrates. Systematic control over the wettability of the resulting surfaces was demonstrated.<sup>[7]</sup>

Scanning probe lithography techniques can be employed to pattern SAMs at the sub-micrometer length scale.<sup>[10–20]</sup> For example, Crooks and co-workers produced patterns in SAMs on gold by selectively removing the alkanethiolates with a scanning tunneling microscope (STM).<sup>[10–12]</sup> More recently, other SAM patterning techniques such as nanografting,<sup>[13,14]</sup> and dip pen nanolithography<sup>[15,16]</sup> have been described. Recently, we reported a STM based replacement lithography technique in which SAM thiolates are selectively desorbed from the gold substrate and replaced with a second alkanethiol in solution.<sup>[17]</sup>

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