Metal–organic coordinated multilayer film formation: Quantitative analysis of composition and structure

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ABSTRACT

Metal–organic coordinated multilayers are self-assembled thin films fabricated by alternating solution–phase deposition of bifunctional organic molecules and metal ions. The multilayer film composed of α,ω-mercaptoalkanoic acid and Cu (II) has been the focus of fundamental and applied research with its robust reproducibility and seemingly simple hierarchical architecture. However, internal structure and composition have not been unambiguously established. The composition of films up to thirty layers thick was investigated using Rutherford backscattering spectrometry and particle induced X-ray emission. Findings show these films are copper enriched, elucidating a 2:1 ratio for the ion to molecule complexation at the metal–organic interface. Results also reveal that these films have an average layer density similar to literature values established for a self-assembled monolayer, indicating a robust and stable structure. The surface structures of multilayer films have been characterized by contact angle goniometry, ellipsometry, and scanning probe microscopy. A morphological transition is observed as film thickness increases from the first few foundational layers to films containing five or more layers. Surface roughness analysis quantifies this evolution as the film initially increases in roughness before obtaining a lower roughness comparable to the underlying gold substrate. Quantitative analysis of topographical structure and internal composition for metal–organic coordinated multilayers as a function of number of deposited layers has implications for their incorporation in the fields of photonics and nanolithography.

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1. Introduction

A multilayer architecture of either organic (soft) or inorganic (hard) materials is a common structure for a variety of technological applications, from capacitors to photonic devices. Within the realm of organic multilayers, some common synthetic methods include polyelectrolyte assembly, dendrimeric growth, surface-initiated ring-opening metathesis polymerization, and chemical vapor deposition [1–7]. These systems have been integrated in a wide range of applications such as anti-fouling coatings or for drug delivery [8–10]. Inorganic examples of alternating layers for device architectures (i.e., capacitors and multilevel flash memory) are formed by traditional processing methods such as metal evaporation, ion beam sputtering, and molecular beam epitaxy as well as by nontraditional solution-phase layer-by-layer methods [11–14]. Metal–organic coordinated multilayers are a hybrid inorganic–organic system characterized by the ability to tailor and tune thickness in the sub-nanometer scale with chemically selective deposition [15–26]. These metal–organic coordinated multilayers are simple to fabricate as they do not require high energy or vacuum systems, and they have been

studied for applications in lithography, electronics, and photonics [27–40].

The metal–organic coordinated multilayer system that has been systematically characterized here is α,ω-mercaptoalkanoic acid complexed with copper (II) ions. This system was first studied by ellipsometry, followed by X-ray photoelectron spectroscopy investigations that revealed a mixture of oxidation states of the copper ions within the compositional structure [15,41]. Other key studies investigated the protonation of the terminal carboxylic acid and its impact on coordinating the copper ions [42,43]. These multilayers have application as "molecular rulers" to measure out or build up precise nanoscale lithographic resists, which can define spacings between metal features [29–32,34]. These films are often represented by a figure showing a 1:1 ratio for metal:molecule and an equal density of the additional layers relative to the base layer (Fig. 1), but the structure for this seemingly simple system has not been established unambiguously. In an effort to understand the film formation, research in the past decade has looked at this multilayer film structure and composition by scanning probe microscopy, ellipsometry, contact angle goniometry, and infrared reflection spectroscopy [44–46]. These previous studies, which focused on examining the initial few layers of the film, found a composition that was copper deficient and a topographic structure with islands formed atop underlying layers due to incomplete layer formation. Research described here
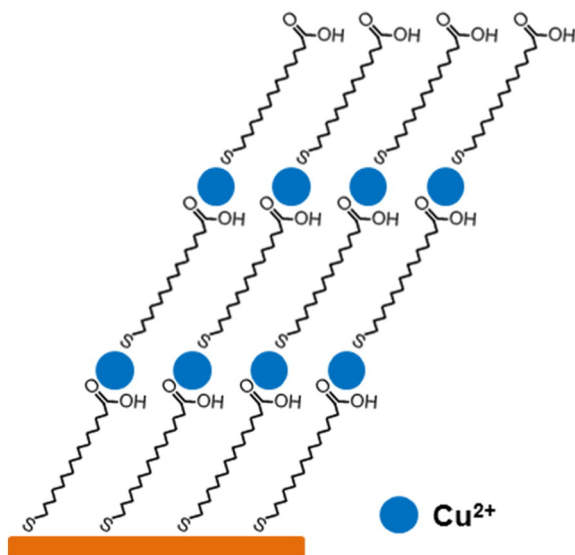
Fig. 1. Schematic representing three layers of a metal–organic coordinated multilayer thin film, composed of α,ω-mercaptoalkanoic acid and Cu^{2+} ions (blue spheres). This is the commonly accepted structure with a 1:1 ratio of metal ion to organic component [15]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

systematically investigated foundational layers as well as thicker films to understand the physical phenomenon that underpins film growth, describing the transition from foundational layers to thicker films when the film takes on its own unique stable morphology.

In the studies presented herein, the topographical structure and the internal composition of these metal–organic coordinated multilayers have been investigated quantitatively as a function of the number of layers deposited to understand their film formation. Topographic structure has been examined by scanning probe microscopy (SPM) with a quantitative investigation of surface roughness and a qualitative observation of film morphology. This comprehensive study of layers 1–30 has allowed for the visualization of how the film morphology changes from a conformal coating mimicking the underlying substrate to a material with its own distinct structure. Films up to 30 layers in thickness have had their composition investigated by Rutherford backscattering spectrometry (RBS) and particle induced X-ray emission (PIXE). These are techniques commonly used to look at inorganic films, but are here shown to be effective for determining molecule-to-metal ion ratios and molecular film density for this hybrid inorganic–organic multilayer system [47,48].

2. Experimental details

2.1. Materials

Copper (II) perchlorate hexahydrate (98%) and 16-mercaptohexadecanoic acid [MHDA] (90%) were used as received from Aldrich (Saint Louis, MO). Absolute, anhydrous ethanol (200 proof, ACS/USP Grade) was obtained from Phamco-Aaper (Shelbyville, KY). Silicon wafers were received from Silicon Quest International (San Jose, CA) and the deposited metals of chromium and gold were purchased from Kurt J. Lesker (Jefferson Hills, PA).

2.2. Sample preparation

The multilayers were formed through bottom-up assembly by alternating solution–phase deposition between 1 mM ethanolic solutions containing MHDA or Cu (II) ions [15]. The multilayers were deposited on a gold film prepared by metal evaporation. The substrate was a silicon wafer substrate with 100 nm of thermally grown oxide and the

metal film was composed of a 10 nm Cr adhesion layer followed by 100 nm Au. The first self-assembled monolayer (SAM) was grown on the gold substrate by submersion in the MHDA solution. After 1 h, the sample was removed, rinsed with ethanol, and gently dried with lab air. The sample was then submerged in the copper ion solution for 15 min, and similarly rinsed and dried. Submersion in a fresh solution of MHDA for 1 h followed by rinsing and drying completed the second layer, and this process was continued to deposit the desired number of layers. To obtain a sample set (set of 0, 1, 5, 10, *etc.* layers), the substrate was cleaved into separate samples after completion of the desired layer, and the remaining substrate was used for continued growth. In this manner, sample sets were prepared from the same gold substrate for consistency within the sample. In all cases, the terminal layer was the organic component.

2.3. Ellipsometry

To investigate linear film growth, film height was characterized *via* ellipsometry. Measurements were obtained using a variable angle discreet wavelength ellipsometer (PHE-101 VADE, Angstrom Advanced, Braintree, MA). A wavelength of 632.8 nm and a fixed angle of 70° were used to collect multiple points per substrate (for each sample, a minimum of three spots were measured). Using the PHE-102 analysis software, the film height was calculated based on refractive index values of $n = 1.5$ and $k = 0$ [15].

2.4. Contact angle goniometry (CAG)

To examine film growth by studying film hydrophobicity and surface roughness, static contact angles were obtained using an Easy Drop contact angle goniometer (Krüss, Matthews, NC). At ambient conditions, a 10 μL water droplet was delivered *via* a 500 μL syringe and flat-tipped needle. Then an image was collected to measure the angle between the droplet and the sample surface. The Kruss Drop Shape Analysis program was used to determine the contact angle. A minimum of three drops per sample were collected.

2.5. Scanning probe microscopy (SPM)

Images were obtained using a Dimension Icon Atomic Force Microscope (Bruker, Santa Barbara, CA) operating in peak force tapping mode (ScanAsyst) using etched silicon tips, and SCANASYST-AIR (Bruker, Santa Barbara, CA), with a spring constant range of 0.2–0.8 N/m and a resonant frequency range of 45–95 kHz. A minimum of three images (512 × 512 pixels) were collected for each sample and scan parameters were as follows: 1 Hz scan rate, 13.8 μm z-range, 205 mV amplitude setpoint, and 155 mV drive amplitude. Image analysis was routinely undertaken using the Nanoscope Analysis software (Bruker, Santa Barbara, CA). Matlab (MathWorks) and Image J (NIH online resource) software were also used for advanced image analysis to determine surface roughness and surface coverage, respectively.

2.6. Particle induced X-ray emission (PIXE)

To study the elemental concentration of the samples, PIXE spectrometry was performed using the Ion Beam Analysis Lab at Hope College. An ion beam of protons (H^+) accelerated to 3.4 MeV was used to irradiate each sample *in vacuo*, and the resultant X-rays were detected at 135° relative to the incident beam by a lithium-drifted silicon detector. Each sample was irradiated by several nA of beam for ~5 min per sample. A minimum of three locations across each sample were measured and the X-rays were quantified by thick-target analysis with the program GUPIXWin to determine elemental composition (in ppm) [49]. NIST-SRM calibration standards (614 and 2586) provided absolute normalization of elemental concentrations.