

SYNTHESIS AND CHARACTERIZATION OF HYBRID ORGANIC-INORGANIC THIN FILMS VIA ATOMIC LAYER DEPOSITION FOR MEMS/NEMS

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ABSTRACT

We report a hybrid atomic layer deposition (ALD) / molecular layer deposition (MLD) approach that produces a new class of hybrid organic-inorganic films. These novel films have very low densities, yet display typical ALD characteristics: controllable linear growth, conformality, low roughness, and uniform composition. The etch behavior of these materials indicates that they are completely removed in acidic solutions. Due to their low density and high carbon content the new hybrid materials are promising as protective coatings and sacrificial layers in MEMS/NEMS devices.

INTRODUCTION

Atomic layer deposition (ALD) is a thin film deposition technique that produces accurately controlled, dense inorganic films at low processing temperatures. Al₂O₃ ALD has been used previously as micro-/ nano-scale structural material [1-3] (Fig. 1), protective, and wear resistant coating in MEMS devices [4, 5].

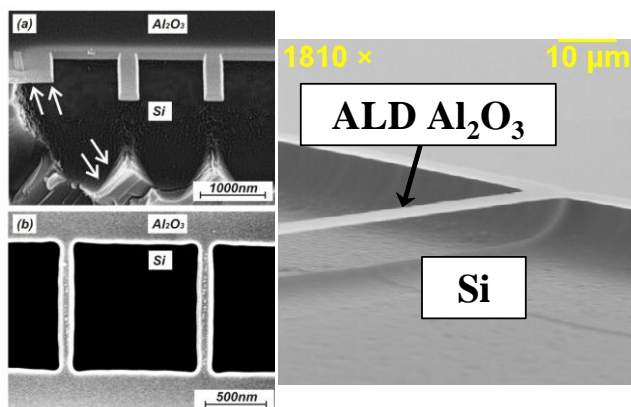


Figure 1. ALD Al₂O₃ structures grown at either 177°C or 120°C.

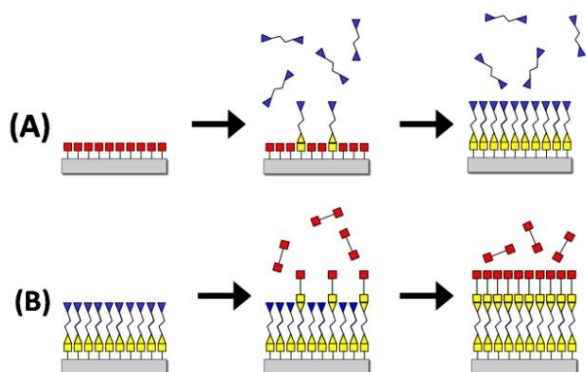


Figure 2. Schematic of the most general binary ALD or MLD system. For ALD the precursors are small inorganic molecules, while in MLD they are larger bifunctional organic species.

Molecular layer deposition (MLD) is a sequential self-limiting surface chemistry process similar to atomic layer deposition (ALD) [6]. As shown in Fig. 2, during MLD growth two bifunctional organic precursors are used to produce a purely organic film [7, 8]. The ability to perform ALD for inorganic materials and MLD for organic materials suggests the extension of a hybrid MLD/ALD approach using organic and inorganic precursors for hybrid organic-inorganic film growth.

Two general classes of hybrid ALD/MLD materials are reported. First is a binary system, where two precursors are used: an inorganic reactant, trimethylaluminum (TMA) and an organic reactant, ethyleneglycol (EG). This hybrid system produces polymeric aluminum alcoxides, or alucones [9].

The second class of hybrid systems uses three reactants: an inorganic molecule, TMA, a heterobifunctional organic molecule, ethanolamine (EA), and a cyclic molecule, maleic anhydride (MA) [10]. This new approach will therefore require three steps, and the obtained hybrid organic / inorganic films will be referred to as “ABC”. The extension to three-step ABC MLD processes expands the variety of reactants and compositional diversity that can be achieved with MLD.

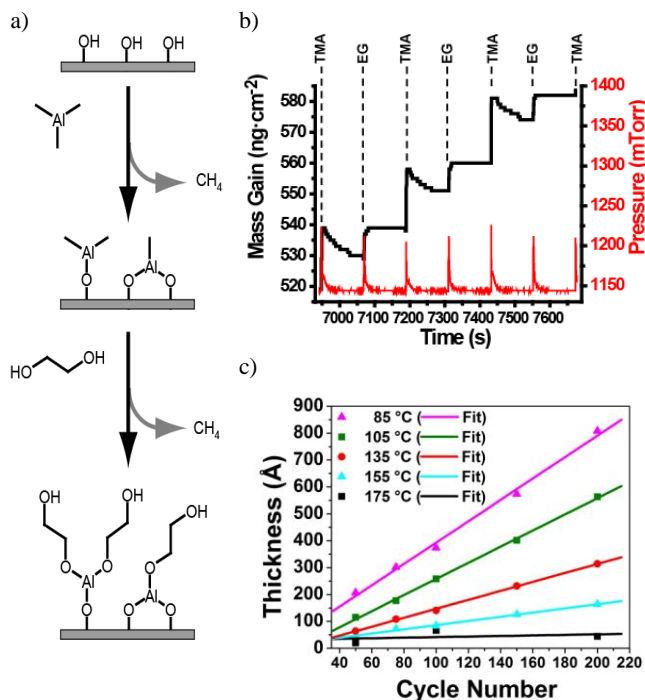


Figure 3. Surface chemistry and growth characteristics for the AB alucone: (a) schematic of the reaction mechanism, (b) quartz crystal microbalance mass gains during TMA and EG exposures, and (c) linear growth vs. number of cycles for various growth temperatures, as measured by x-ray reflectivity

RESULTS AND DISCUSSION

Alucone growth

As illustrated in Figure 3a, the alucone growth is a binary self-limiting process. The initial exposure of the surface to trimethylaluminum leads to a reaction with the hydroxylated surface. At the end of this reaction, when all the hydroxyls are consumed, the surface functionality is changed entirely from hydroxyl to methyl. After a purge of the extra reactants and biproducts, the surface is exposed to ethyleneglycol. One hydroxyl end of this molecule reacts with the methylated surface, producing and aluminum alcoxyde on the surface. The other end of the molecule regenerates the hydroxyl terminated surface. After all the methyls have reacted, a purge step removes the extra reactants and products. Since the newly formed surface has the same hydroxyl functionality as the initial surface, the process can be repeated in a cyclic fashion.

Figure 3b displays the mass gains during TMA and EG exposures for steady state growth recorded by the *in situ* quartz crystal microbalance (QCM) at 135 °C. Details about our experimental setup have been given elsewhere [11]. The decrease in mass gain during TMA exposure occurred over a period of 60-90s. This long progressive decrease is much longer than the time required for the TMA to return back to the baseline pressure in other ALD systems. Mass gains with decreases of this type have been observed previously during Al₂O₃ ALD on polymers [12].

Ex situ x-ray reflectivity (XRR) scans confirmed the linear growth of alucone films versus number of cycles over a wide range of temperatures. As shown in Figure 3c, the alucone growth rates were inversely proportional to the growth temperature. Growth rates varied between 4 Å per cycle at 85°C and 1.7 Å per cycle at 135°C. The growth rates measured with XRR agreed very well with *in situ* results from the QCM. Although the growth rates varied inversely proportional to temperature, the density of the films remained relatively constant at 1.5 g/cm³ [9].

ABC growth

The surface chemistries involved in the growth of the new ABC films is schematically shown in Figure 4a. Similar to alucone, TMA is the inorganic species used in the first step to react with the hydroxylated surface and produce a reactive methylated surface. In the second step, ethanolamine, a hetero-bifunctional molecule is used to change the functionality from methyl to amine. In the third step maleic anhydride is dosed to react with the amine groups in a ring-opening reaction to produce carboxyl groups on the surface. The resulting carboxyls are identical in functionality to the hydroxyls in the first step and allow the three step process to be repeated in a cyclic fashion. The resulting polymeric film is composed of monomer units that contain one Al atom, six C atoms, four O atoms and one N atom.

In situ QCM studies showed that the ABC hybrid material grows linearly versus number of cycles, as indicated in Figure 4b. Similar to the alucone mass gain profile, the slow decrease in mass after the TMA dose suggests the low density, and hence polymeric character of the grown ABC film. As measured *ex situ* by XRR, the average growth rate for the ABC film was 23 Å/cycle at 90°C and 11 Å/cycle at 110°C (Figure 4c) [10].

Physical properties

XRR scans revealed that the obtained ABC films had very low roughness and very uniform composition. As shown in Figure 5, Bragg peaks are sharp even past 8000 arcseconds. Such high reflectivity at large angles in an XRR experiment suggests minimum scattering at the interfaces. This is obtained for very smooth films which have a roughness correlated with the

underlying layer. For the film in Figure 5 the 560 Å thick film had a roughness of 5 Å, which is similar to the typical roughness of the Si substrates used in the experiment. The good agreement between the experimental scan and the theoretical fit confirms the uniform composition of the obtained ABC film.

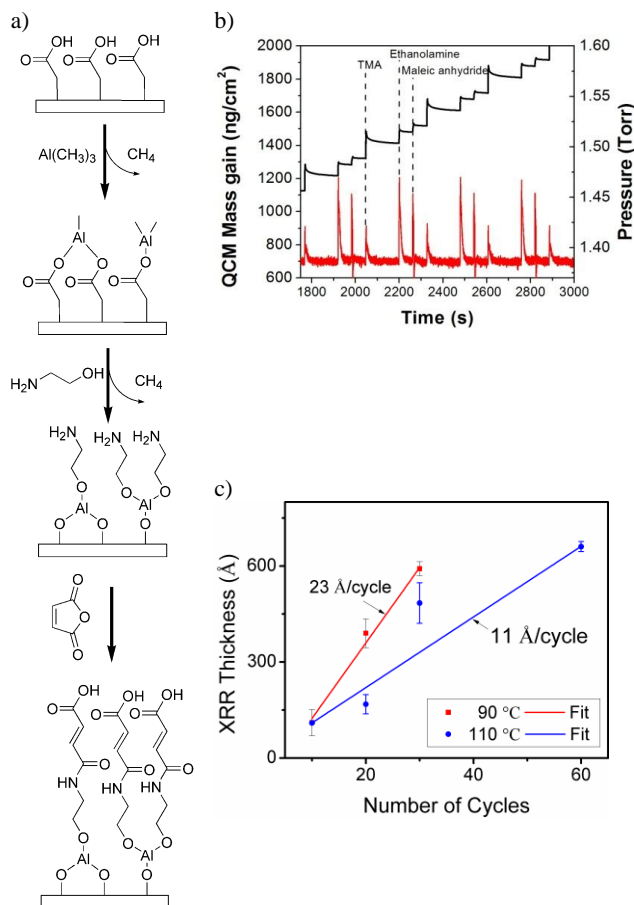


Figure 4. Surface chemistry and growth characteristics for the ABC films: (a) reaction mechanism, (b) QCM mass profile for four cycles, and (c) linear growth vs. number of cycles for different growth temperatures, as measured by XRR

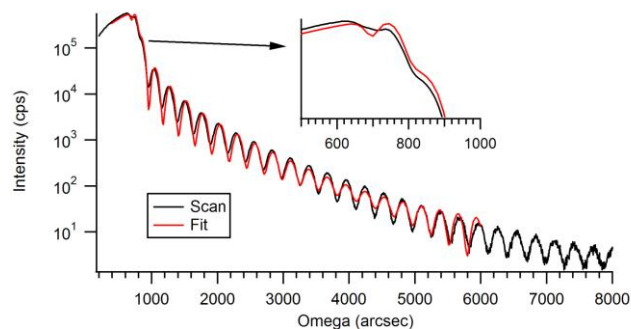


Figure 5. XRR scan of a typical ABC film grown at 90°C. The critical angle (inset) provides the density of the material, 1.6g/cm³, while the periodicity of the Bragg peaks confirms the low roughness and uniformity of the ABC films.

Nanoindentation of alucone films measured an average Young's modulus of 18.8 GPa and an average Berkovitch hardness of 1.46GPa. These values are higher than those of typical polymers (~10GPa and ~0.5GPa) but lower than values typical for metals or ceramics (~100GPa and ~10GPa).

Etch behavior

Both dry-etching and wet-etching behaviors of the ABC film were investigated. Reactive ion etch (RIE) with oxygen was performed on the ABC films. The smooth initial ABC film was transformed into two layers. The bottom layer had the same density as the initial ABC film, while the top layer was denser. The plasma process leads to the formation of a passivation layer that prevent further etch, as shown in Table 1.

Table 1. Film structure before and after reactive ion etching with oxygen, as measured by XRR

Material	Thickness (Å)	Density ₃ (g/cm ³)	Roughness (Å)
Initial			
ABC	591.5	1.59	6.2
After O₂ plasma			
ABC	223.0	1.59	50.0
unknown	289.7	2.08	6.6

As for wet-etching behavior, the ABC film was immersed into different solutions. As shown in Table 2, aprotic solvents did not interact with the ABC material. This result confirmed that the ABC film contains covalently bonded organic molecules. If the organic precursors were simply condensed on the surface, or if the amide linkage would not have been achieved, the aprotic solvents were expected to solvate the hydrophobic organic backbone of the molecule. Consequently, some of the ABC film would have been etched.

Table 2. Wet etch behavior of the ABC films in various solutions

Solvent	Solvent type	Observations after 90 min	Film structure by XRR after 90 min
Toluene	non-polar	no visible change	no change
Acetone	polar aprotic	no visible change	no change
Isopropanol	polar protic	color change formation of spots	thickness decrease film roughening two films formed
Water	polar protic	color change formation of spots	thickness decrease film roughening two films formed
1M NaOH	basic	formation of a spotted white film	too rough to measure
1M HCl	acidic	complete removal of polymer film	bare Si substrate

Both protic solvents had similar effects on the ABC film. The resulting two layers structure with the formation of a denser layer at the top is similar to the result obtained after the dry etch process. The interaction with the proton containing solutions is in agreement with the observation that the alucone MLD films were susceptible to degradation upon exposure to water. The exact mechanism of this proton mediated process is not yet understood.

While the 1M basic solution led to the formation of a white precipitate on the sample, the 1M acidic solution was successful in etching the ABC film. This contrasting behavior can be explained by the chemical composition of the ABC film. The existing amide linkage could react with the base solution with the formation of carboxylic acid salts that are insoluble. In contrast, the ammonium chloride salt formed in the reaction with the acid solution is soluble, leading to a complete etch of the ABC film. The acid solution is therefore a promising solution to using the ABC layer as a sacrificial material in MEMS/NEMS structures.

Potential applications

Multilayers that combine alternate soft flexible layers with hard brittle layers have extraordinary mechanical properties. These multilayer structures are exploited in one of the strongest structures in nature, the nacreous layer of the mollusk shell [13, 14]. The unique organic-inorganic structure of nacre produces approximately two times the mechanical strength and approximately one thousand times the fracture toughness of its inorganic material [15]. Given the contrast between Young's modulus values of the alucone and ABC films and other typical ALD systems (alumina, tungsten) alternating multilayer structures could be fabricated to imitate the nacreous shell structure (Figure 6). Such high toughness structures could be used to coat conformally MEMS devices and improve their wear resistance.

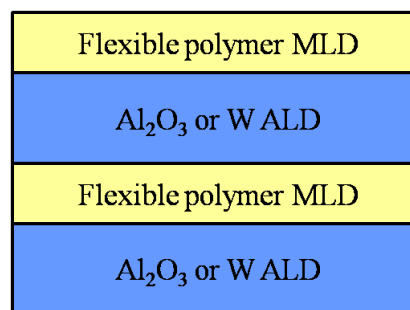


Figure 6. High toughness hard/soft multilayer to be used as wear resistant coating for MEMS/NEMS devices.

Ultra-thin film micro-/nano-scale resonators are another promising application of the novel hybrid materials. Nano-resonators have been used for precise mass detection [16] or high frequency applications [17]. The availability of ALD materials with contrasting mechanical properties allows for the design of composite materials with desired mechanical properties for MEMS/NEMS devices. The composite mechanical properties of a multilayer structure could be tuned by varying the ratio of organic to inorganic material. This control over the mechanical properties could be used to create a resonator with a tunable resonant frequency.

Alucone and ABC films can also be used as sacrificial spacer layers for MEMS/NEMS structures. Very thin hybrid organic/inorganic film can be grown at low temperatures with high conformity and low roughness. Embedding these films as sacrificial layers in the manufacturing process can produce MEMS devices with angstrom-level precision vertical gaps after release.

A layer of 80nm thick MLD alucone was first deposited on silicon substrates at 80°C. 2nm Al₂O₃ and 20nm W were deposited on top of the alucone layer at 120°C. After patterning AZP photoresist on the ALD W layer, tungsten etchant and 0.05% HF were used to etch the ALD W and ALD alumina, respectively. The patterned AZP photoresist was then removed by acetone. Diluted NaOH was used to remove the MLD alucone under ALD W

structure. The sample was then immersed in methanol and dried in a CO₂ critical point dryer. The released structure is shown in Figure 7. The upright ALD W structure is due to the mechanical stress within the ALD W thin film. This residual stress can be further tuned by varying the growth temperature and film thickness of the W ALD layer.

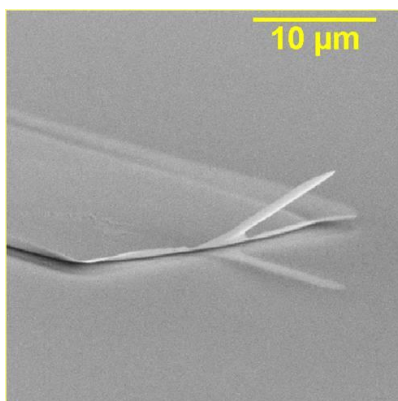


Figure 7. ALD W cantilever released via wet-etch from 80nm ALD/MLD alucone layer.

CONCLUSIONS

We demonstrated the growth of novel hybrid organic-inorganic films using ALD/MLD techniques. In situ characterization showed the self-limiting and linear growth behaviors typical to ALD systems. The physical properties of these materials suggest a polymeric character. Due to their high carbon content and since they etch in acidic solutions, these new materials are suitable as sacrificial layers in MEMS devices. In addition, the reported films could be used as protective layers for MEMS applications when embedded in periodic organic/inorganic structures with exceptional mechanical properties.

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