

Hybrid Organic-Inorganic Films Grown Using Molecular Layer Deposition

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1. Introduction

There has been a dramatic growth in the field of atomic layer deposition (ALD) over the past 10 years [1]. Some of this ALD development has been driven by the needs of the semiconductor industry. Other developments have resulted from the application of ALD to non-semiconductor arenas. The atomic layer control and conformality of the ALD film thickness have proved useful for a diverse array of applications such as the fabrication of photonic bandgap materials [2] and gas diffusion barriers [3]. In addition to the new technological developments, there also has been an expansion of the types of films that can be grown using ALD-inspired processes. The introduction of organic precursors using molecular layer deposition (MLD) has greatly extended the compositional identity of the deposited film. MLD is distinguished from ALD because a molecular fragment can be added during one self-limiting sequential surface reaction [4]. An illustration of the sequential, self-limiting growth in MLD is displayed in Figure 1 [5].

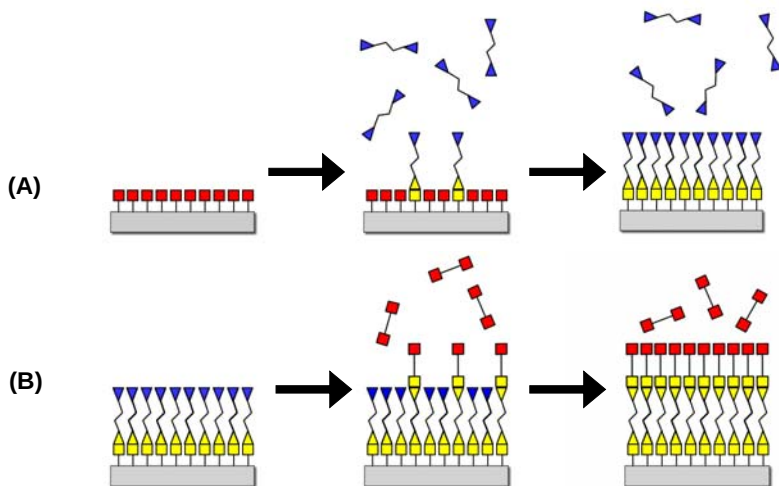


Figure 1 Schematic illustrating ideal sequential, self-limiting reactions for MLD growth using two homobifunctional reactants.

The original definition of MLD described the sequential, self-limiting chemistry used for the growth of an organic polymer. The first MLD system was based on condensation polymerization reactions and deposited a polyimide [6]. More recently, the MLD of a variety of organic polymers has been demonstrated including polyimide [7], polyamide [5, 8], polyurea [9], polyurethane [10], polythiourea [11] and polythiolene [12]. The organic precursors used for all-organic MLD can also be mixed with the inorganic ALD precursors to define new hybrid organic-inorganic materials [13, 14]. The expanded basis set introduced by these hybrid materials has greatly enlarged the possible materials that can be grown using ALD and MLD. The large quantity of organic precursors available from

Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE MAR 2011		2. REPORT TYPE		3. DATES COVERED 00-00-2011 to 00-00-2011	
4. TITLE AND SUBTITLE Hybrid Organic-Inorganic Films Grown Using Molecular Layer Deposition				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Departments of Chemistry and Chemical Engineering, University of Colorado, ,Boulder, CO,80309				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES This research was funded by the National Science Foundation (NSF), the Air Force Office of Scientific Research (AFOSR), the Defense Advanced Research Program Agency (DARPA) and DuPont Central Research and Development.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Public Release	18. NUMBER OF PAGES 14	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

organic chemistry leads to a huge variety of possibilities for hybrid organic-inorganic films using MLD.

Several hybrid organic-inorganic materials have been developed recently using MLD techniques [4, 13-20]. These systems have begun to define the wide range of materials that can be deposited using MLD. The possibility to mix and match organic and inorganic precursors and their relative fraction in the film will lead to a wide spectrum of film properties. In particular, the mechanical properties can be tuned by controlling the organic and inorganic proportions. This short report will first review several MLD systems that have been demonstrated to illustrate the current state-of-the-art. Some new systems will then be introduced to show the diversity of chemistries that can be employed to grow various hybrid organic-inorganic films. Lastly, speculations will be offered on the future prospects for the MLD of hybrid organic-inorganic materials.

2. Previously Demonstrated Hybrid Organic-Inorganic MLD Films

One of the first hybrid organic-inorganic materials grown using MLD was an “alucone” [21] based on the reaction between trimethylaluminum (TMA) and ethylene glycol (EG) [13]. The EG molecule, $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$, contains two hydroxyl groups and is very analogous to H_2O as a reactant in the well-studied Al_2O_3 ALD process [22, 23]. The difference is that a $-\text{CH}_2-\text{CH}_2-$ molecular fragment is introduced into the hybrid organic-inorganic film. A schematic showing the growth of the alucone based on TMA and EG is displayed in Figure 2 [13].

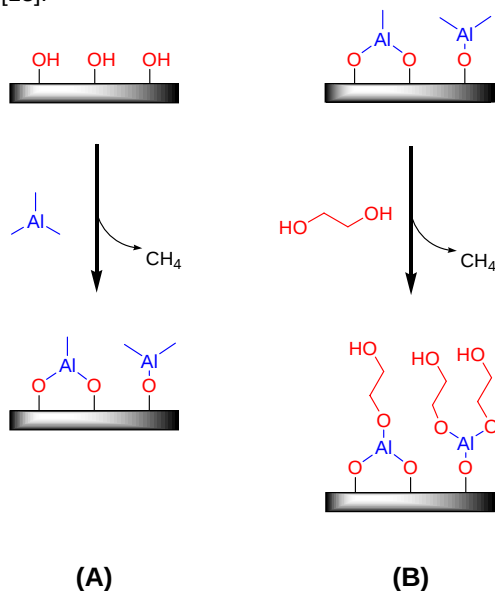
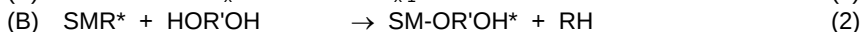
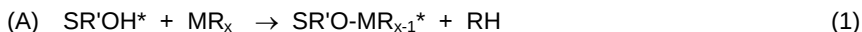


Figure 2 Schematic depicting two-step AB alucone MLD growth using trimethylaluminum (TMA) and ethylene glycol (EG). TMA is exposed to a hydroxylated surface and produces a surface covered with $-\text{AlCH}_3$ species. The subsequent EG exposure produces a surface covered with $-\text{OCH}_2\text{CH}_2\text{OH}$ species.

In general, a two-step MLD reaction between a metal alkyl, such as TMA, and a diol, such as EG, can be written as follows [4, 13]:



The asterisks indicate the surface species and S denotes the substrate with the reaction products from the previous reactions. In the A reaction, the reaction stops when all the $\text{SR}'\text{OH}^*$ species have completely reacted to produce $\text{SR}'\text{O-MR}_{x-1}^*$ species. In the B reaction, the reaction stops when all the SMR^* species have completely reacted to produce $\text{SM-OR}'\text{OH}^*$ species. The sequential and self-limiting reactions of TMA and EG ideally yield a polymeric film described by $\text{Al}(\text{O-CH}_2\text{-CH}_2\text{-O-})$ linkages.

Previous studies have demonstrated that alucone MLD using TMA and EG is very efficient [13]. X-ray reflectivity (XRR) investigations showed that the MLD growth rate was linear versus the number of TMA/EG cycles. In addition, the MLD growth rate was temperature dependent and decreased from 4.0 Å per TMA/EG cycle at 85°C to 0.4 Å per TMA/EG cycle at 175°C [13]. Quartz crystal microbalance (QCM) measurements also revealed the linearity of alucone MLD growth versus TMA and EG exposures [13]. The QCM results also showed a large mass increase during the TMA exposures that subsequently decayed immediately after the TMA exposure. This mass transient was consistent with TMA diffusion into and out of the AB alucone MLD film [24]. The TMA diffusion also helped explain the temperature dependence of the MLD growth.

The surface reactions during MLD with TMA and EG displayed self-limiting behavior [13]. The AB alucone MLD films also displayed a contraction of ~22% over the first 3 days that the films were exposed to air. After this contraction, the films were extremely stable. The AB alucone films were extremely smooth and conformal when deposited on nanoparticles. Figure 3 shows the TEM image of a BaTiO_3 particle that was coated with 40 AB cycles of Al_2O_3 ALD and then 50 AB cycles of AB alucone MLD at 135°C [13]. The quality of the overlying MLD film is comparable with the underlying ALD film.

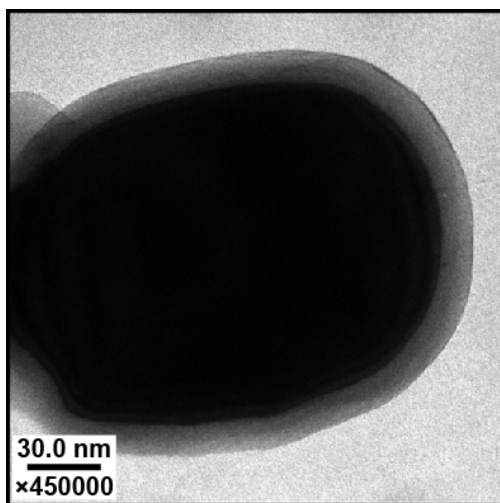
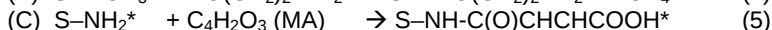
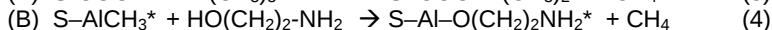
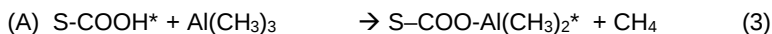


Figure 3 TEM image of a BaTiO_3 particle coated at 135 °C with 40 AB cycles of Al_2O_3 ALD and then 50 AB cycles of AB alucone MLD using TMA and EG.

EG is one of many organic diols that can be used together with TMA for alucone film growth. One difficulty with diols is that they are homobifunctional precursors and can react twice with the AlCH_3^* surface species [4, 8]. These “double reactions” lead to a loss of reactive surface sites and could produce a decreasing growth per cycle during MLD. The problem of double reactions may be minimized using polyols to assure that a hydroxyl group will be available for the subsequent TMA exposure. This strategy will be discussed below for the MLD of the alucone based on TMA and glycerol.

Alternatively, a heterobifunctional precursor, such as ethanolamine, $\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ (EA) can be employed that shows preferential reactivity between its hydroxyl group and the AlCH_3^* surface species [20]. This preference leaves an amine ($-\text{NH}_2$) group available for the subsequent surface reaction. Likewise, ring-opening reactions can be employed that will react and then express a new functional group when the ring is opened [4, 20]. The ring-opening reaction also has the advantage of containing the functional group in a hidden form. The hidden functionality leads to higher vapor pressures and shorter purge times compared with precursors that have the same exposed functionality.

One three-step ABC MLD process that can be accomplished without using homobifunctional precursors is based on: (1) TMA, a homomultifunctional inorganic precursor; (2) ethanolamine (EA), a heterobifunctional organic reactant and (3) maleic anhydride (MA) a ring-opening organic reactant [20]. The proposed surface reactions during the ABC growth are [20]:



This surface reaction mechanism is illustrated in Figure 4 [20].

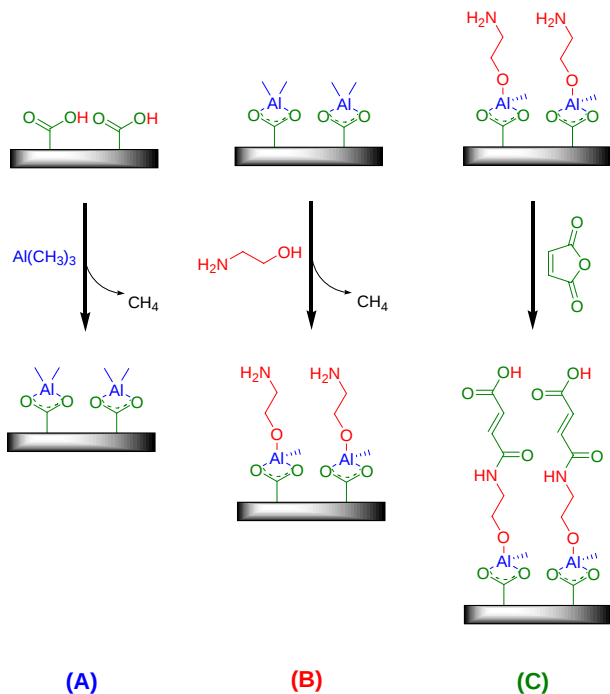


Figure 4 Schematic showing the three-step reaction sequence for ABC MLD growth using (A) trimethylaluminum (TMA), (B) ethanolamine (EA), and (C) maleic anhydride (MA).

In this ABC reaction sequence, TMA reacts with carboxylic groups in reaction A given by Eqn. 3 to form AlCH_3^* species. Subsequently, the AlCH_3^* species react preferentially with the hydroxyl end of the EA reactant to form $\text{Al-OCH}_2\text{CH}_2\text{NH}_2^*$ surface species in reaction B given by Eqn. 4. MA then reacts with amine-terminated surface functional groups to reform carboxylic groups through a ring-opening reaction in reaction C given by Eqn. 5. The three-step reaction sequence is repeated by exposure to TMA, EA and MA to grow the ABC MLD film.

A variety of studies have characterized the ABC MLD process [18, 20]. FTIR difference spectra were consistent with the reaction mechanism shown in Figure 4. The ABC MLD displayed linear growth as evidenced by the QCM measurements. However, large mass gains of $\sim 2500 \text{ ng/cm}^2$ per ABC cycle were observed at 90°C [18]. This large mass gain may indicate the diffusion of a substantial quantity of TMA into the ABC MLD film. After the TMA exposure, there was also a subsequent mass loss that was consistent with the diffusion of TMA out of the ABC MLD film. The diffusion of TMA in and out of the ABC film was measured experimentally and then fit using a numerical model based on Fick's Law [18]. The importance of TMA diffusion into and out of the ABC film was verified by observing that the mass gain per cycle was dependent on the TMA purge time.

In addition to TMA, other inorganic ALD precursors can be matched with various organic precursors to define other classes of hybrid organic-inorganic materials. For example, diethylzinc (DEZ) can react with diols to produce "zincone" MLD films [17, 19]. Zincone MLD has been demonstrated using DEZ and EG [17, 19]. The growth and film characteristics of zincone MLD were similar to alucone MLD. Linear growth rates were observed for zincone MLD versus number of MLD cycles [19]. However, the growth rates were lower for higher growth temperatures and the EG precursor was observed to react twice almost exclusively at the highest growth temperatures [19].

3. New Hybrid Organic-Inorganic MLD Films

A. Use of Homotrifunctional Precursor to Promote Cross-linking

The AB alucone MLD system using TMA and EG displayed efficient reactions [13]. However, this MLD system suffered from double reactions because EG is a homobifunctional precursor. This MLD system also displayed some film contraction over the first several days after this film was exposed to air [13]. In addition, tensile strain measurements of MLD films grown using TMA and EG with a thickness of 100 nm had a low critical tensile strain of 0.69% [25]. This low critical tensile strain may result from the small amount of cross-linking in the MLD film. These problems with the TMA + EG MLD system led to the recent exploration of the TMA + glycerol system. Glycerol provides an additional hydroxyl group for reaction and should increase the cross-linking between the chains in the deposited film. The proposed reaction sequence TMA and glycerol (GL) is displayed in Figure 5 [26].

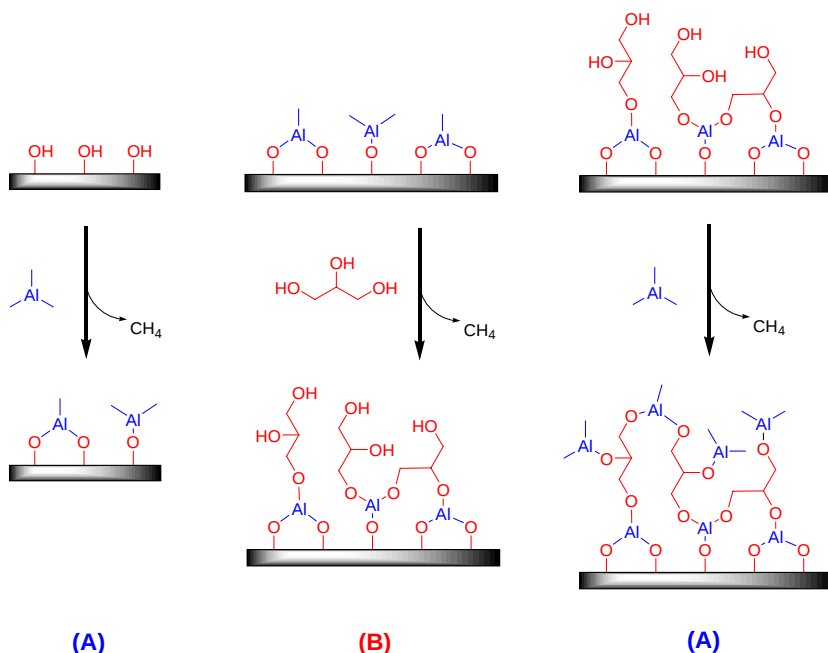


Figure 5 Schematic depicting two-step AB alucone MLD growth using trimethylaluminum (TMA) and glycerol (GL).

Studies of the surface species using Fourier transform infrared (FTIR) difference spectra after the TMA and GL exposures revealed that the surface reactions are efficient and proceed to near completion [26]. Figure 6 shows the FTIR difference spectra for Glycerol – TMA and TMA – Glycerol [26]. The spectra are displaced for clarity in presentation. The added surface species appear as positive absorbance features and the removed surface species appear as negative absorbance features. The FTIR spectra show the “flipping” of the O-H stretching vibrations at higher frequencies with each TMA and GL exposure. This flipping between positive absorbance for one reactant and then a mirror image negative absorbance for the second reactant is consistent with repetitive self-limiting reactions. There is also a flipping of the strong AlCH_3 deformation mode at lower frequencies that is consistent with the addition and subtraction of the AlCH_3^* surface species.

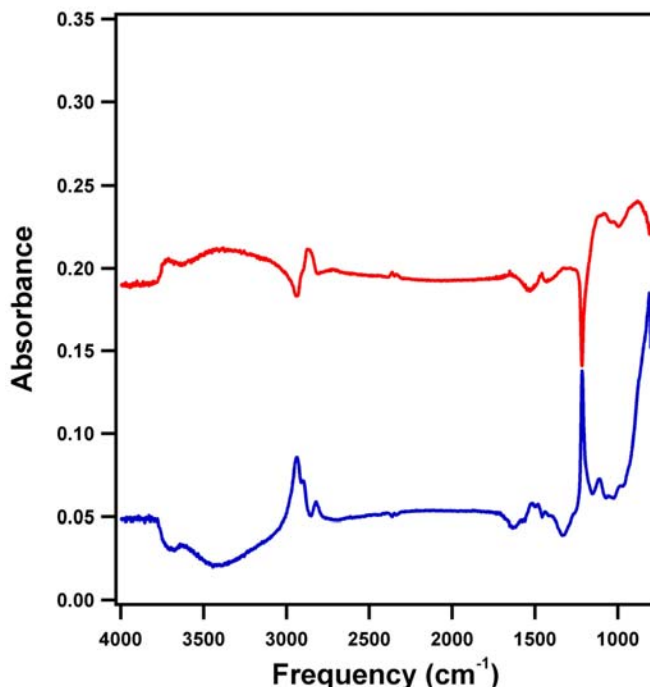


Figure 6 FTIR difference spectra after TMA and GL exposures during AB alucone MLD at 150 °C. The FTIR difference spectra are referenced with respect to the previous reactant exposure.

The TMA + GL reaction can also be characterized using QCM studies. The QCM analysis revealed linear MLD growth with an average mass gain of 41.5 ng/cm²/cycle at 150°C. This mass gain of 41.5 ng/cm²/cycle is equivalent to a growth rate of 2.5 Å/cycle. Figure 7 displays QCM results for two TMA + GL cycles at 150°C [26]. The QCM shows that a mass gain is observed during the TMA exposure. Likewise, a small mass loss is observed after the TMA exposure. This behavior suggests that some TMA may be diffusing out of the MLD film after the TMA exposure. A similar mass gain is observed during the GL exposure. The slight mass loss after the GL exposure may also indicate that some GL diffuses out of the MLD film.

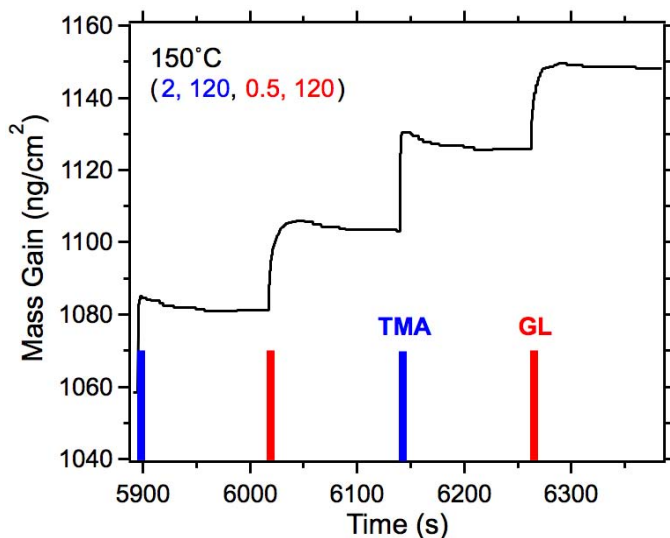


Figure 7 Mass gain from QCM measurements for two cycles of AB alucone MLD film growth with TMA and GL in the linear growth region at 150 °C. The pulse sequence was TMA 2 s, N₂ purge 120 s, GL 0.5 s and N₂ purge 120 s.

The TMA + GL system also shows a growth rate that is much less dependent on temperature than the growth rate for TMA + EG [13]. XRR analysis was employed to study the film thickness after various numbers of MLD cycles at temperatures of 150, 170 and 190°C. These XRR results are shown in Figure 8 [26]. The film thicknesses are similar for all three temperatures and are consistent with a growth rate of 2.0-2.3 Å per cycle. The growth rate of 2.3 Å per cycle at 150°C is in reasonable agreement with the QCM measurement of 2.5 Å/cycle at 150°C under similar reaction conditions. These more constant growth rates versus temperature compared with TMA + EG suggests that TMA diffusion may be less of a factor because of the more extensive cross-linking between the growing chains.

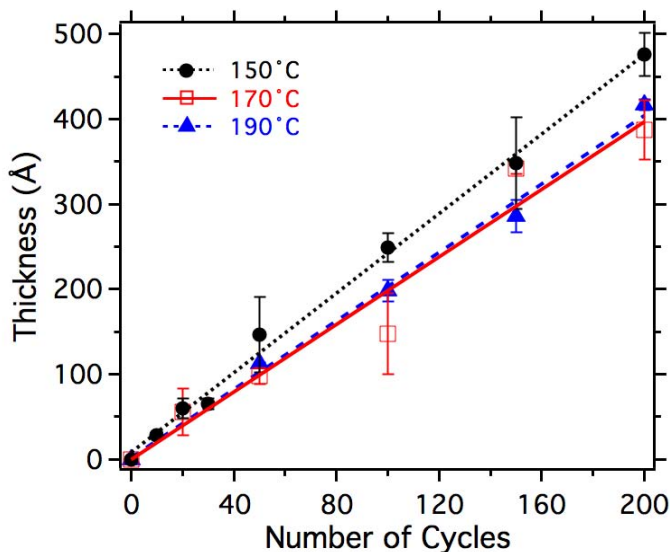


Figure 8 Thickness of AB alucone MLD films grown using TMA and GL measured using XRR analysis versus number of AB reaction cycles. Results are shown for growth temperatures of 150, 170 and 190 °C.

The XRR analysis of the TMA + GL MLD films indicated that the film thickness was nearly constant versus time after exposure to ambient [26]. The MLD films grown using TMA + GL were not observed to contract like the MLD films grown using TMA + EG [13]. This higher film stability may indicate that there is more cross-linking that increases the MLD film stability. Recent mechanical testing has also revealed that the MLD films grown using TMA + GL have a higher critical tensile strain for cracking than the MLD films grown using TMA + EG [26].

B. MLD of Hybrid Alumina-Siloxane Films Using an ABCD Process

Polydimethylsiloxane (PDMS) is one of the most important organic-inorganic polymers and contains $[-\text{Si}(\text{CH}_3)_2\text{O}]_n$ chains. The strength and flexibility of the Si-O bonds and bond angles give PDMS desirable thermal and mechanical properties [27, 28]. PDMS MLD would be extremely useful for the growth of flexible and compliant thin films. However, initial attempts at PDMS MLD revealed that the growth rate became negligible after approximately 15 MLD cycles. These attempts were made using the sequential dosing of water with homobifunctional silane molecules such as bis(dimethylamino)dimethylsilane and 1,3-dichlorotetramethyldisiloxane or hetrobifunctional silane molecules such as dimethylmethoxychlorosilane (DMMCS). The lack of growth after approximately 15 MLD cycles was attributed to the competing desorption of cyclic siloxanes such as hexamethylcyclotrisiloxane (D3) or decamethylcyclopentasiloxane (D5) from the PDMS film [29, 30].

To prevent the desorption of cyclic siloxanes, a new approach was pursued where DMMCS and H_2O were used together with TMA in an ABCD process defined by TMA/ H_2O /DMMCS/ H_2O [31]. A schematic of this reaction sequence is given in Figure 9 [31]. This reaction sequence introduces the $-\text{Si}(\text{CH}_3)_2\text{O}-$ linkage into the growing film. The addition of TMA adds $-\text{Al-O}-$ subunits into the growing chain and prevents the

competing desorption of cyclic siloxanes. The TMA can be introduced during every reaction cycle. The TMA can also be introduced less frequently to grow longer $[-\text{Si}(\text{CH}_3)_2-\text{O}-]_n$ chains before inserting the $-\text{Al}-\text{O}-$ subunit.

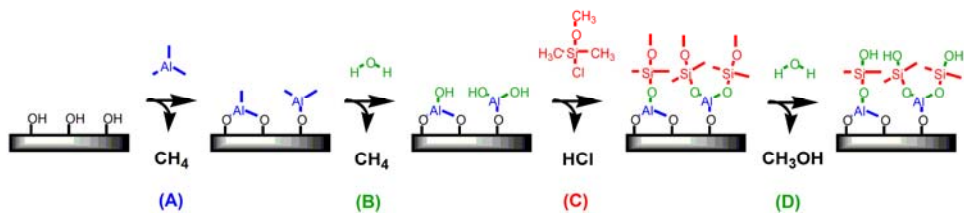


Figure 9 Schematic showing the four-step reaction sequence for ABCD MLD growth of an alumina-siloxane film using trimethylaluminum (TMA), H₂O, dimethylmethoxychlorosilane (DMMCS) and H₂O.

Initial work has explored the ABCD process to demonstrate the growth of alumina-siloxane hybrid organic-inorganic films [31]. QCM experiments revealed that the MLD growth was linear with a mass gain of $\sim 21 \text{ ng/cm}^2/\text{cycle}$ at 200°C . The film growth at 200°C was also examined using XRR analysis. The XRR measurements confirmed linear growth at 200°C with a growth rate of $0.9 \text{ \AA}/\text{cycle}$ [31]. Using the density of 2.3 g/cm^3 for the alumina-siloxane MLD films, the mass gain of $\sim 21 \text{ ng/cm}^2/\text{cycle}$ yields a growth rate of $0.9 \text{ \AA}/\text{cycle}$. FTIR analysis of the surface reactions was also consistent with the reaction mechanism shown in Figure 9. However, a low atomic concentration of silicon in the MLD film measured by x-ray photoelectron spectroscopy indicated that the chlorosilane reaction with the hydroxylated surface was not very efficient.

8. Future Prospects for MLD of Hybrid Organic-Inorganic Films

The use of various organic and inorganic precursors offers a nearly limitless set of combinations for the MLD of hybrid organic-inorganic films. Many of these combinations can be used to fabricate films with specific functional properties. One example of a functional hybrid organic-inorganic film is an MLD film grown using TMA and triethylenediamine (TED). TMA is a Lewis acid and TED is a Lewis base. An exposure sequence of TMA and TED can be used to grow an MLD film with unreacted AlCH_3 species remaining in the film [32]. A schematic of this reaction sequence is given in Figure 10 [32]. These AlCH_3 species can react with H_2O and serve as a H_2O getter. The H_2O getters may be useful as interlayers in multilayer gas diffusion barrier films.

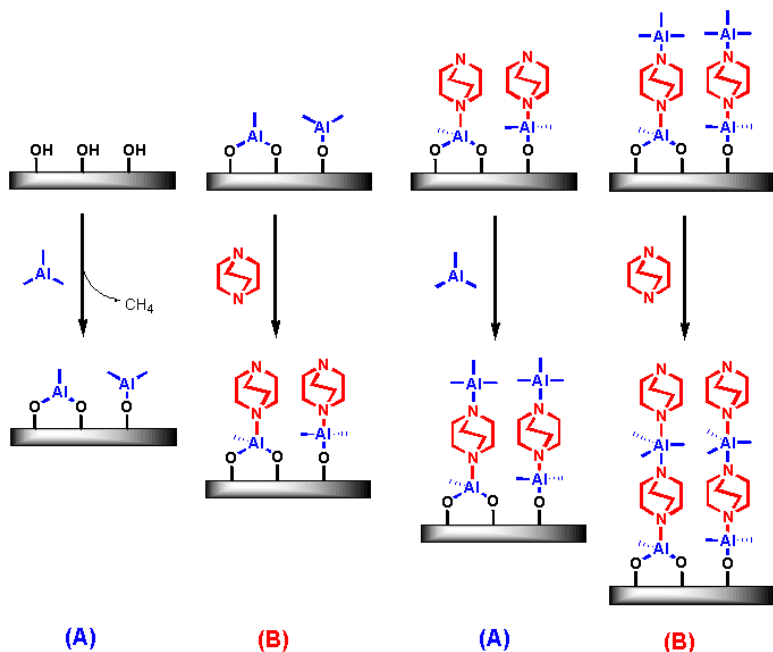


Figure 10 Schematic depicting the two-step reaction sequence for AB MLD growth of a Lewis acid-Lewis base film using trimethylaluminum (TMA) and triethylenediamine (TED).

Conductive hybrid organic-inorganic films may also be useful for flexible displays. ZnO ALD films are known to have a low resistivity of $\sim 1 \times 10^{-2} \Omega \text{ cm}$ [33]. ZnO ALD films are grown using diethylzinc (DEZ) and H_2O [34]. Hybrid organic-inorganic MLD films can be grown using DEZ and EG as mentioned earlier and are called “zincones” [17, 19]. Although the zincone MLD film based on DEZ and EG does not display any conductivity, recent results have shown that zincone films based on DEZ and hydroquinone (HQ) have displayed some conductivity when alloyed with ZnO ALD films [35]. The schematic showing the surface chemistry for zincone MLD using DEZ and HQ is given in Figure 11 [35]. If these conducting MLD alloy films display sufficient toughness because of their organic constituents, then they may be useful for flexible displays and may be candidates to replace indium tin oxide (ITO).

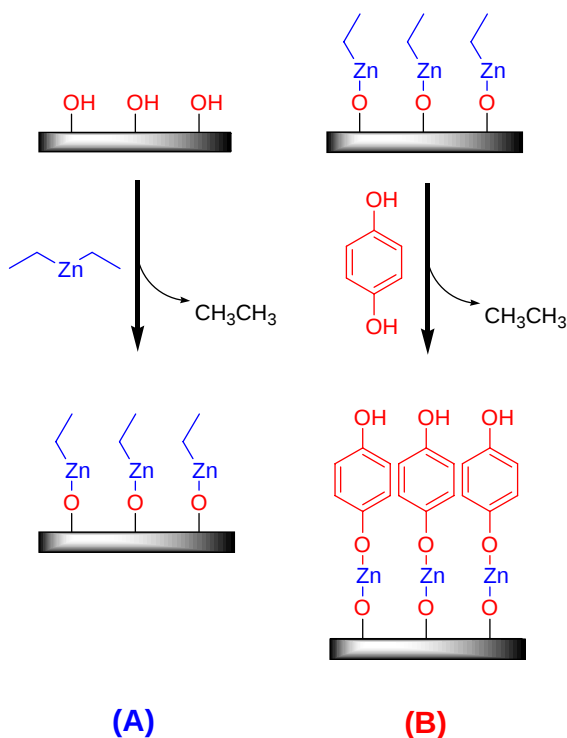


Figure 11 Schematic showing the two-step reaction sequence for AB zincone MLD growth using diethylzinc (DEZ) and hydroquinone (HQ).

The hybrid organic-inorganic MLD films have a low density that approaches the low densities of organic polymers. In contrast, inorganic ALD films have a much higher density. Mixtures of hybrid organic-inorganic MLD layers with ALD layers can be used to obtain films with a density that varies from the low density of the pure MLD film to the high density for the inorganic ALD film [36]. As an example, the density of hybrid Al_2O_3 ALD: AB Alucone MLD films are shown in Figure 12 [36]. Al_2O_3 ALD was grown using TMA and H_2O [22, 23]. AB Alucone MLD was grown using TMA and EG [13]. The density was varied by changing the relative number of ALD and MLD cycles during the alloy growth.

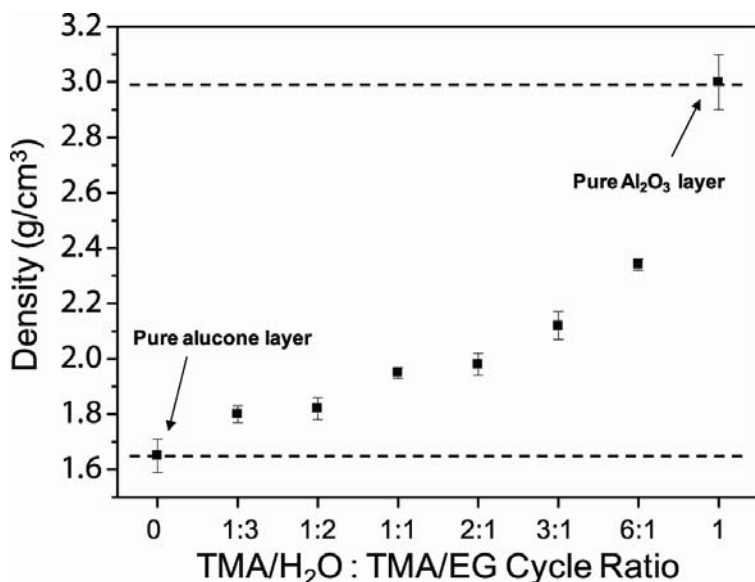


Figure 12

Density of alloys of Al_2O_3 and AB alucone using TMA and EG from XRR analysis. The alloys were prepared using different numbers of TMA/ H_2O and TMA/EG cycles. For example, the 3:1 ratio sample was prepared using repetitive sequences of 3 cycles of TMA/ H_2O and then 1 cycle of TMA/EG.

Figure 12 indicates that the density can be varied widely with changing organic-inorganic film composition. Other properties that are dependent on density will also change accordingly. For example, mechanical properties such as the elastic modulus and stiffness should be tunable [37]. Optical and electrical properties such as refractive index and dielectric constant should also vary with the composition of the alloy film [38]. In general, films with a variety of tunable properties should be possible by changing the ratio of ALD and MLD cycles used to grow the alloy film.

Most of the MLD systems reviewed in this chapter have been based on AB, ABC or ABCD processes using TMA. Other organometallic and organic precursors are also possible. As mentioned earlier, hybrid organic-inorganic films based on zinc are possible using DEZ [17, 19]. Other hybrid organic-inorganic systems based on zirconium and titanium are possible using $\text{Zr}(\text{O}-t\text{-Bu})_4$ and TiCl_4 , respectively [36, 39]. Many other organometallic precursors can also be used to define other hybrid organic-inorganic MLD polymers. For example, metal alkyls based on magnesium (Mg) and manganese (Mn) are available as $\text{Mg}(\text{EtCp})_2$ and $\text{Mn}(\text{EtCp})_2$. These metal alkyls are expected to react with diols or carboxylic acids to define new MLD systems [40, 41].

The possibilities for the MLD of hybrid organic-inorganic films are virtually unlimited given all the metals on the periodic table and organic compounds available from organic chemistry. The challenge over the next few years will be to determine the hybrid organic-inorganic films that may be grown easily and that may display useful properties. The tunable mechanical, optical, dielectric, conductive and chemical properties of the hybrid organic-inorganic films should be valuable for a wide range of applications.

Acknowledgements

This research was funded by the National Science Foundation (NSF), the Air Force Office of Scientific Research (AFOSR), the Defense Advanced Research Program Agency (DARPA) and DuPont Central Research and Development. The author also thanks B. Yoon, R.A. Hall, A.I. Abdulagatov, Y. Lee, and B.H. Lee. These members of his research group were responsible for the recent MLD and ALD results presented in this report.

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