

HYBRID ORGANIC-INORGANIC FILMS FABRICATED USING ATOMIC AND MOLECULAR LAYER DEPOSITION

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ABSTRACT

Atomic layer deposition (ALD) and molecular layer deposition (MLD) are based on sequential, self-limiting surface reactions that produce atomic layer controlled and conformal thin film growth. ALD can deposit inorganic films and MLD can deposit films containing organics. ALD and MLD can be used together to fabricate a wide range of flexible hybrid organic-inorganic films. The tunable mechanical properties of alucone alloys grown using Al₂O₃ ALD and alucone MLD may be useful as flexible barrier films. The tunable electrical conductivity of zincone alloys grown using ZnO ALD and zincone MLD may be useful as flexible transparent conducting films. These hybrid organic-inorganic films could have many applications for flexible sensors and actuators.

KEYWORDS

Hybrid organic-inorganic materials, atomic layer deposition, molecular layer deposition, flexible films.

INTRODUCTION

Flexibility is needed for many applications of sensors and actuators. Examples include flexible pressure sensors, chemiresistor sensors, biological sensors and photosensors [1,2]. Flexible sensors and actuators require the flexibility of the various materials used to fabricate the sensor and actuator. A flexible thin film device would utilize flexible conducting layers, insulating layers, functional layers and barrier and packaging layers. Unfortunately, most of the materials currently employed to make thin film devices, such as the metal oxides used as insulators, are usually quite brittle.

Flexibility is generally associated with organic polymeric materials that have minimal crosslinking and weak dispersion interactions between the polymer chains. A key challenge for flexible sensors and actuators is to develop devices based on flexible conducting, insulating, functional and barrier materials. One solution to obtain flexible materials is to make alloys by combining a flexible organic polymer with the more brittle inorganic material used for conduction, insulation, functionality or packaging.

Atomic layer deposition (ALD) and molecular layer deposition (MLD) are thin film deposition techniques based on sequential, self-limiting surface reactions that produce atomic layer controlled and conformal thin film growth [3]. ALD is generally restricted to the deposition of inorganic films [3]. MLD can deposit organic or hybrid organic-inorganic films [4]. A schematic showing the sequential nature of the surface reactions during the MLD of a hybrid organic-inorganic material is shown in Figure 1. In addition, ALD and MLD can be used together to fabricate a wide range of hybrid organic-

inorganic alloy films [5,6]. These ALD:MLD alloys can have properties that vary from the all-inorganic film to the all-organic or hybrid organic-inorganic film.

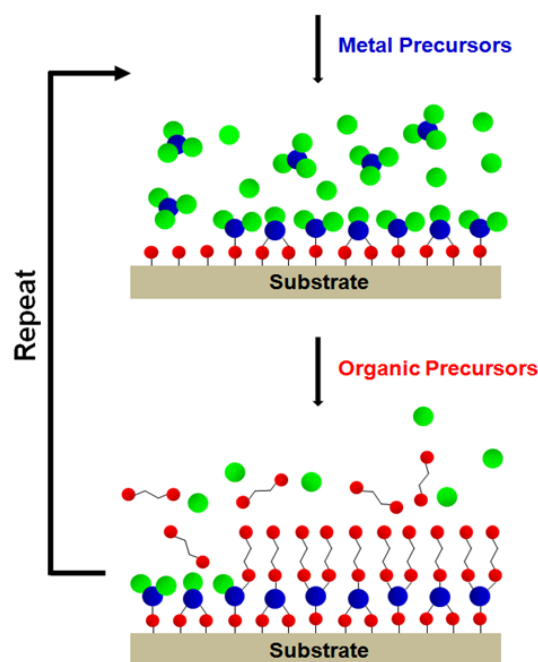


Figure 1. Schematic of the sequential surface reactions used in the deposition of hybrid organic-inorganic MLD films using a metal precursor and an organic precursor.

This paper will discuss the growth and properties of alloys grown using ALD and MLD. Al₂O₃ ALD and alucone MLD will first be employed to deposit ALD:MLD alloys that may be useful as flexible barrier films. ZnO ALD and zincone MLD will then be used to deposit ALD:MLD alloys that may be useful as flexible transparent conducting films. These hybrid organic-inorganic films could have many applications for flexible sensors and actuators.

GROWTH AND PROPERTIES OF ALD:MLD ALLOYS BASED ON Al₂O₃ ALD AND ALUCONE MLD

Al₂O₃ ALD is one of the best studied and useful ALD systems based on the reaction of trimethylaluminum (TMA) and H₂O [3]. Alucone MLD was the first reported aluminum alkoxide polymer MLD system based on TMA and ethylene glycol (EG) [7]. ALD:MLD alloys can also be deposited by varying the number of ALD and MLD reaction cycles used to fabricate the film. These ALD:MLD alloys may serve as flexible insulating and protecting barrier layers for flexible sensors and actuators.

The ALD:MLD alloy is expected to be more flexible at higher organic compositions. The organic content of the film will increase with higher ratios of MLD cycles to ALD cycles in the reaction sequence used to fabricate the ALD:MLD alloy. For example, a 1:1 ALD:MLD alloy is defined by one reaction cycle of TMA/H₂O and then one reaction cycle of TMA/EG. A schematic showing the surface reactions during the growth of a 1:1 ALD:MLD alloy is shown in Figure 2.

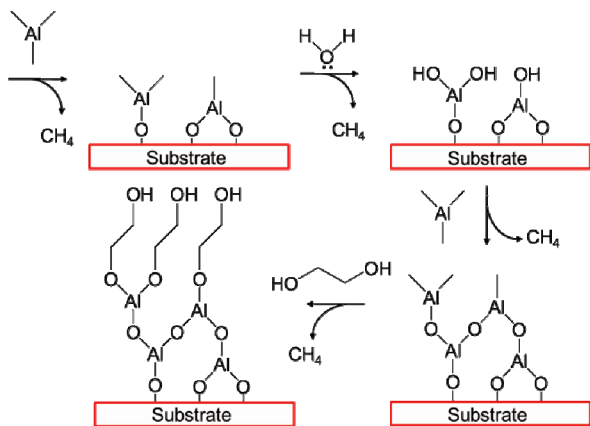


Figure 2. Schematic of the growth of the 1:1 ALD:MLD alloy using Al₂O₃ ALD and alucone MLD. The repeating reaction sequence is TMA/H₂O/TMA/EG.

The growth of the ALD:MLD alloys can be monitored using quartz crystal microbalance (QCM) measurements. The QCM is very sensitive to the mass changes during each surface reaction in the sequence. QCM results for the growth of the 1:1 ALD:MLD alloy are displayed in Figure 3 [5]. These results display the very digital and reproducible nature of the ALD and MLD film growth. The growth rate for the sequence of 1 ALD reaction cycle and 1 MLD reaction cycle at 135°C is 30 ng/cm² or 3.1 Å/sequence [5].

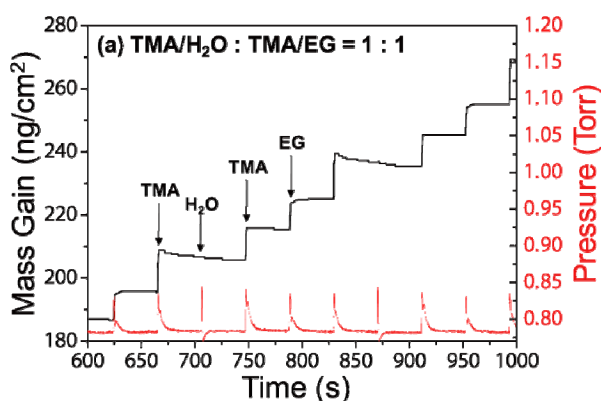


Figure 3. QCM results for the growth of the 1:1 ALD:MLD alloy grown using Al₂O₃ ALD and alucone MLD at 135°C.

The composition of the ALD:MLD alloys can be varied by changing the relative number of ALD and MLD reaction cycles in the sequence. The changing composition of the ALD:MLD alloys can be used to tune the properties of ALD:MLD alloy film. Previous studies

have shown that the density, refractive index, elastic modulus and hardness can all be varied by changing the number of ALD and MLD cycles in the sequence [5]. For example, the results for the elastic modulus and hardness of the ALD:MLD alloys of Al₂O₃ ALD and alucone MLD are shown in Figure 4 [5]. The upper and lower bounds are the predictions from the “rule of mixtures”. The elastic modulus and hardness both increase at larger fractions of ALD cycles in the sequence.

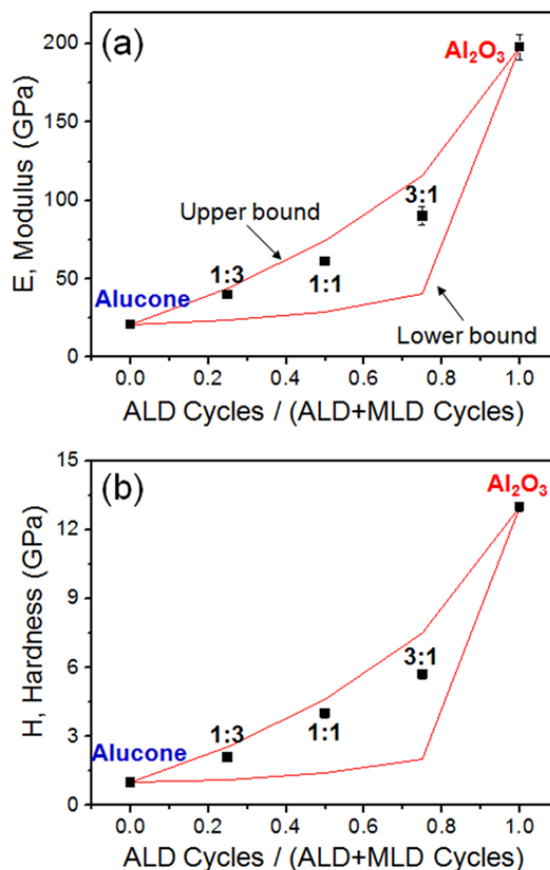


Figure 4. Elastic modulus and hardness for the ALD:MLD alloys grown using Al₂O₃ ALD and alucone MLD.

The Al₂O₃ ALD films are excellent gas diffusion barriers on polymers [8]. Al₂O₃ ALD may serve as barrier and encapsulation layer to protect sensors and actuators. For flexible barriers, the ALD:MLD alloys may offer advantages of improved flexibility if the addition of the organic MLD component does not degrade the barrier performance. The critical tensile strain was measured to determine the flexibility of the ALD:MLD alloys [9]. The water vapor transmission rate (WVTR) was measured to determine the gas diffusion barrier properties of the ALD:MLD alloys [9]. The results from these measurements are shown in Figure 5.

The 1:1 and 3:1 ALD:MLD alloys have higher critical tensile strains than either the pure alucone MLD or pure Al₂O₃ ALD films. The organic component in the ALD:MLD alloy films does increase the flexibility of the film. The pure alucone MLD film is believed to have a lower critical tensile strain because this film is easily torn

by tensile strain. The explanation is that most of the bonding in the alkoxide polymer chains is in the growth direction [10]. There is little cross-linking between the alkoxide polymer chains in the plane of the surface [10].

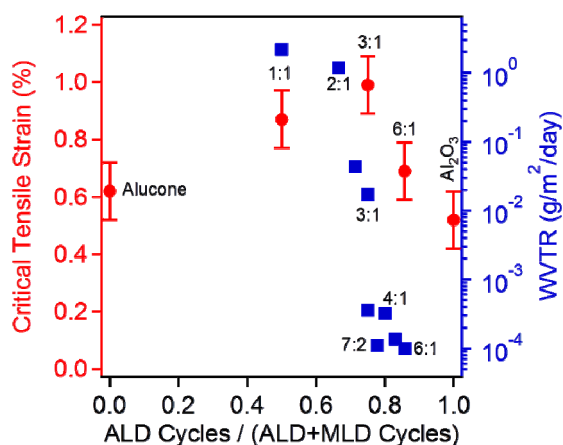


Figure 5. Critical tensile strain and water vapor transmission rate (WVTR) for various ALD:MLD alloy films grown using Al_2O_3 ALD and alucone MLD.

The ALD:MLD alloys are also very good barriers when the ALD:MLD ratio is $> 3:1$. Figure 5 shows that the 1:1 and 2:1 ALD:MLD alloys have a high WVTR of $\sim 1 \text{ g}/(\text{m}^2 \text{ day})$ [9]. In contrast, the ALD:MLD alloys with a higher ALD:MLD ratio of $> 4:1$ have a much lower WVTR of $1 \times 10^{-4} \text{ g}/(\text{m}^2 \text{ day})$. This low WVTR is the same as the glass lid control and the Al_2O_3 ALD films. These low WVTR values are at the limit of the Ca test measurement technique. The results in Figure 5 indicate that flexible barrier films with excellent gas diffusion barrier properties can be fabricated using ALD:MLD alloy films. These flexible barrier films should be useful for the fabrication of flexible sensors and actuators.

GROWTH AND PROPERTIES OF ALD:MLD ALLOYS BASED ON ZnO ALD AND ZINCONE MLD

ZnO is a well known transparent, conducting oxide material. Aromatic organic entities can also display high electrical conductivity. To obtain flexible transparent conducting films, ZnO ALD can be used together with zincone MLD. Zincone MLD deposits a zinc alkoxide polymer using diethylzinc (DEZ) and various diols [11]. If the diol is an aromatic molecule, such as hydroquinone (HQ), then the zincone MLD film may display electrical conductivity. ALD:MLD alloys can also be deposited using ZnO ALD and zincone MLD to obtain flexible conducting films.

Recent studies have observed that the zincone MLD film grown using DEZ and HQ does not display high electrical conductivity [12]. However, ALD:MLD alloys of ZnO ALD and zincone MLD can have electrical conductivity much higher than ZnO ALD by itself [12]. A schematic showing the surface reactions during the growth of a 1:1 ALD:MLD alloy using ZnO ALD and zincone MLD with DEZ and HQ is shown in Figure 6.

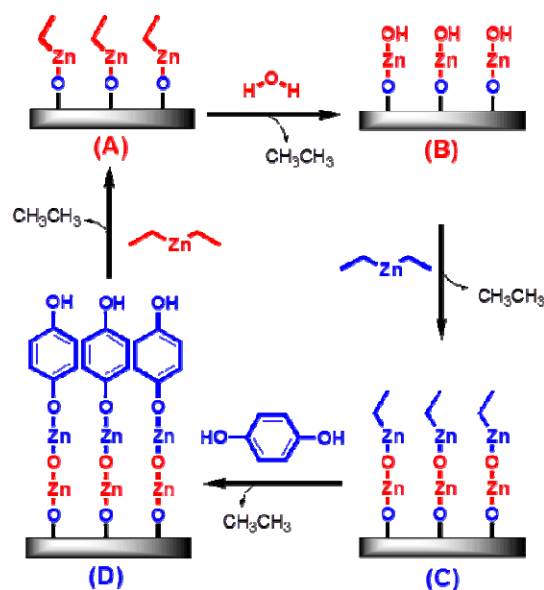


Figure 6. Schematic of the growth of the 1:1 ALD:MLD alloy using ZnO ALD and zincone MLD. The repeating reaction sequence is DEZ/ H_2O /DEZ/HQ.

The growth of the 1:1 ALD:MLD alloy can be monitored using QCM measurements. QCM results for the growth of the 1:1 ALD:MLD alloy are displayed in Figure 7 [12]. Like the results shown in Figure 3, these results also display the very digital and reproducible nature of the ALD and MLD film growth. The growth rate for the sequence of 1 ALD reaction cycle and 1 MLD reaction cycle at 150°C is $76 \text{ ng}/\text{cm}^2$ or $1.5 \text{ \AA}/\text{sequence}$ [12].

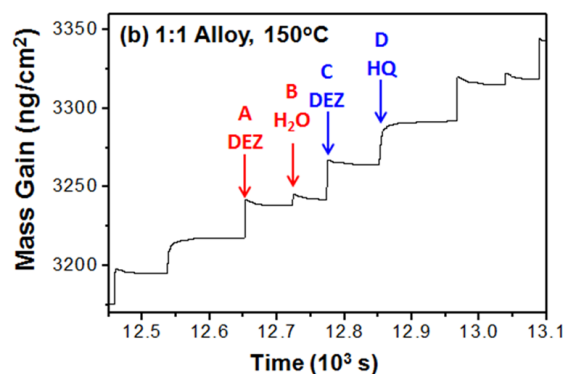


Figure 7. QCM results for the growth of the 1:1 ALD:MLD alloy grown using ZnO ALD and zincone MLD at 150°C .

The electrical conductivity of the ALD:MLD alloys may vary as the composition of the ALD:MLD alloy is changed from pure ZnO ALD to pure zincone MLD. The electrical conductance was measured for ALD:MLD alloy films versus the relative number of ZnO ALD and zincone MLD reaction cycles in the sequence. Figure 8 shows the electrical current versus the applied voltage for films having film thicknesses of $\sim 140\text{-}250 \text{ nm}$ [12].

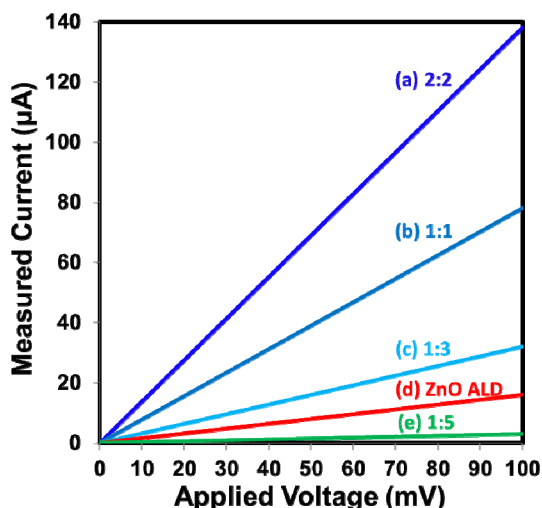


Figure 8. Measured current versus applied voltage for ZnO ALD and various ALD:MLD alloys grown using ZnO ALD and zincone MLD at 150°C.

The highest current versus voltage was consistently obtained from the 2:2 ALD:MLD alloys. The 1:1 ALD:MLD alloys and the 1:3 ALD:MLD alloys also displayed electrical conductance much higher than the ZnO ALD films for films with comparable thicknesses. These results are very promising and indicate that flexible high electrical conductivity films can be grown using ALD:MLD alloys. A summary of the conductivities of the various ALD:MLD alloys, zincone MLD and ZnO ALD films is given in Table 1 [12]. Results are presented for conductivities in ambient light, in the dark and after UV illumination.

Films	Thickness (nm)	Conductivity (S/cm)		
		In Ambient Light	In Dark	After UV
ZnO ALD	166	14	14	20
1:1 Alloy	139	116	116	118
2:2 Alloy	184	170	170	200
1:3 Alloy	237	40	40	83
1:5 Alloy	252	6	6	10
5:5 Alloy	186	13	13	26
DEZ/HQ MLD	166	Non-Conductive		
DEZ/EG MLD	120	Non-Conductive		

Table 1. Conductivities for ZnO ALD and various ALD:MLD alloys grown using ZnO ALD and zincone MLD at 150°C.

CONCLUSIONS

Atomic layer deposition (ALD) and molecular layer deposition (MLD) can be employed to deposit hybrid organic-inorganic films. Because MLD allows organics to be incorporated in the film, the films are much more flexible than pure inorganic films. ALD:MLD alloys allow the composition of the film to be varied from the all

inorganic ALD film to the all organic or hybrid organic-inorganic MLD film. The mechanical, electrical and chemical properties of the ALD:MLD alloys can be tuned by changing the relative number of ALD and MLD cycles in the reaction sequence.

This paper has focused on ALD:MLD alloys grown using Al₂O₃ ALD and alucone MLD. The tunable mechanical properties of alucone alloys grown using Al₂O₃ ALD and alucone MLD may be useful as flexible barrier films. This paper has also focused on ALD:MLD alloys grown using ZnO ALD and zincone MLD. The tunable electrical conductivity of zincone alloys grown using ZnO ALD and zincone MLD may be useful as flexible transparent conducting films. These hybrid organic-inorganic films and many additional films that can be deposited using other metal and organic precursors could have many applications for flexible sensors and actuators.

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