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14. ABSTRACT

This AFOSR grant concentrated on the fabrication and properties of thin films grown using atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques. The goal was to produce a flexible gas diffusion barrier for polymers. The work examined the flexibility of Al2O3 ALD films on polymer substrates versus film thickness. Thinner thicknesses yielded higher critical tensile strain and critical compressive strain. The research also examined alloys grown using Al2O3 ALD and alucone MLD. These alloys displayed higher critical tensile strain than either the Al2O3 ALD films or alucone MLD films. In addition, the water vapor transmission rate (WVTR) was also excellent for the alloys with high Al2O3 ALD content. The results illustrate that more flexible gas diffusion barriers can be fabricated using ALD:MLD alloys. The alucone MLD film was also employed as a compliant interlayer between films with a mismatch of thermal expansion coefficients. The alucone MLD interlayer was able to reduce the thermal stress between Teflon substrates and Al2O3 ALD films. The Ca test was also developed to the measure the WVTR of gas diffusion barrier films.

15. SUBJECT TERMS

Thin films, atomic layer deposition, molecular layer deposition, gas diffusion barriers, water vapor transmission rate, flexible films, alloy films, critical tensile strain, critical compressive strain, mechanical properties of thin films

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Final Technical Report

February 2012

Fabrication and Properties of Organic-Inorganic Nanolaminates Using Molecular and Atomic Layer Deposition Techniques

AFOSR Grant No. FA9550-09-1-0053

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I. Overview/Objectives

Over the last three years, our AFOSR grant focused on issues related to gas diffusion barriers on flexible polymers. We focused on the fabrication of nanolaminates and alloys using atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques. The goal was to produce gas diffusion barriers on polymers that were flexible and could function as ultrabarriers to prevent H_2O permeation. We focused on three key issues: the critical strains for cracking of Al_2O_3 ALD films; the improvement of flexibility by fabricating ALD/MLD alloys; and the use of MLD films as compliant interlayers.

We initially focused on careful measurements of the critical tensile and compressive strains for Al_2O_3 ALD films on polymers. We measured film cracking versus film thickness to establish the ability of Al_2O_3 ALD films to serve as flexible barrier films. These studies are also important for understanding the mechanical properties of Al_2O_3 ALD films. These measurements revealed that thinner films are more flexible. We also verified that mechanical models work well to describe critical tensile strains at the nanoscale.

We also grew ALD/MLD alloys to incorporate more organic into the gas diffusion barrier. The idea was that a higher organic composition would be more flexible. For these studies, we measured the critical tensile strain and water vapor transmission rate (WVTR) to determine if adding more organic into the barriers could both improve flexibility and retain excellent barrier properties. These studies were performed using Al_2O_3 ALD and alucone MLD to grow the ALD/MLD alloys.

We also explored MLD films as interlayers between films that have a mismatch in their coefficients of thermal expansion. The MLD films are more flexible and may be able to relieve the strain between the films with dissimilar thermal expansion coefficients. One example of such a mismatch is a low thermal expansion coefficient Al_2O_3 ALD film on a high thermal expansion coefficient Teflon substrate. We examined the cracking thresholds for Al_2O_3 ALD films on Teflon versus alucone MLD layer thickness to evaluate the MLD films as compliant interlayers.

II. Research Topics

Over the three years, our AFOSR effort has concentrated on the following main topics:

- Growth of ALD gas diffusion barriers on polymers and testing of the barrier properties using the Ca test.
- Measurements of the critical tensile strain and critical compressive strain for Al_2O_3 ALD films on polymers.
- Growth of Al_2O_3 ALD and alucone MLD alloys by varying the number of ALD and MLD cycles during film deposition.
- Measurements of the critical tensile strain for the Al_2O_3 ALD and alucone MLD alloys.
- Measurements of the water vapor transmission rate for the Al_2O_3 ALD and alucone MLD alloys.
- Exploration of alucone MLD as a compliant interlayer to relieve thermal stress between films with dissimilar thermal expansion coefficients.

We have made excellent progress over the last three years on these research topics. The majority of our research effort was conducted by Dr. Shih-Hui Jen, a postdoctoral research associate, and Jacob Bertrand, a graduate student. Shi-Hui did the majority of the work on the mechanical properties of the films and performed all the critical tensile and compressive strain measurements. Jake Bertrand used our Ca test apparatus to measure gas diffusion barrier properties. In addition, Byoung Hoon Lee, worked on the Al_2O_3 ALD and alucone MLD alloys primarily with support from DuPont.

We also completed earlier work from our previous AFOSR grant during the last three years. Dragos Seghete, a graduate student, finished up some studies related to graded multilayers and nanolaminates. Rickard Wind, a postdoctoral associate, finished up some studies on nucleation and growth during the fabrication of W/Al_2O_3 nanolaminates.

III. Accomplishments/ New Findings

A. Al_2O_3 ALD Gas Diffusion Barriers on Polymers

Over the last three years, we have concentrated on ALD and MLD films and ALD/MLD multilayers as flexible barriers and protective coatings on polymer substrates. These flexible films have important applications as gas diffusion barriers for H_2O and O_2 sensitive flexible organic light emitting diodes (OLEDs) and thin film solar devices. In collaboration with DuPont, our work has demonstrated that Al_2O_3 ALD films are excellent gas diffusion barriers on polymers. DuPont provided the Ca testing to measure the water vapor transmission rate (WVTR).

Figure 1 shows the measured WVTR for Al_2O_3 ALD films on polyethylene naphthalate (PEN) substrates. The Al_2O_3 ALD barrier films are as good as the glass lid control and have WVTRs < 1 x 10^{-4} g/m^2/day. These results are the best that have been ever measured for a single inorganic film on a polymer substrate. The Al_2O_3 ALD coatings

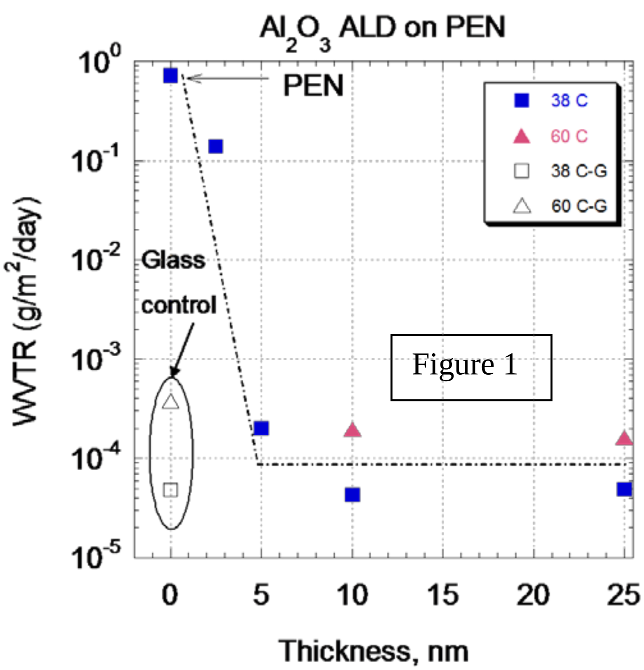


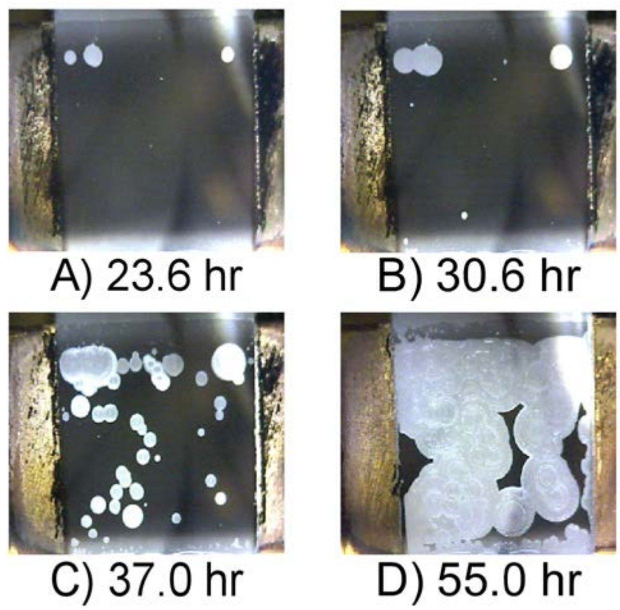
Figure 1

are currently being commercialized by DuPont for gas diffusion barriers on polymer substrates for thin film solar devices.

B. Testing of Al_2O_3 ALD Gas Diffusion Barriers Using the Ca Test

Using our new Ca test apparatus at the University of Colorado, Al_2O_3 gas diffusion barriers were grown directly on Ca films using atomic layer deposition (ALD) techniques. These barriers were then evaluated using several methods based on Ca oxidation. The oxidation of the Ca films was monitored versus time at 70°C and ~28% relative humidity either by measuring the electrical conductance of the Ca film or by recording the photographic image of the Ca film.

Figure 2



In the photographic images, the Ca films revealed that the Al_2O_3 ALD films have a small number of pinhole defects that lead to Ca film oxidation areas that grow radially around the pinhole defect versus time. A burst of new oxidation areas also appeared suddenly at later times and grew radially versus time. This rapid "blooming" may be related to another type of defect caused by water corrosion of the Al_2O_3 ALD films. A picture of the oxidation areas versus time is shown in Figure 2.

The photographic images of the Ca film were also analyzed to obtain a WVTR value assuming radial oxidation of the Ca film around defects. The WVTR values obtained from the electrical conductance and the photographic images were in approximate agreement and increased versus Ca film oxidation until the rapid "blooming" of new circular oxidation areas. The WVTR value was also estimated from the time required for the electrical conductance to be reduced to nearly zero. These estimated WVTR values were comparable with the largest WVTR values obtained from the electrical conductance and the photographic images after the onset of the "blooming".

C. Measurements of Critical Tensile Strain and Critical Compressive Strain for Al_2O_3 ALD Films on Polymers

To understand the flexibility of Al_2O_3 ALD films on polymers, the critical strains at which the Al_2O_3 ALD films will crack were determined for both tensile and compressive strains. The tensile strain measurements were obtained using a fluorescent tagging technique to image the cracks. The results showed that the critical tensile strain is higher for thinner thicknesses of the Al_2O_3 ALD film on heat-stabilized polyethylene naphthalate (HSPEN) substrates. The critical tensile strains versus film thickness are shown in Figure 3.

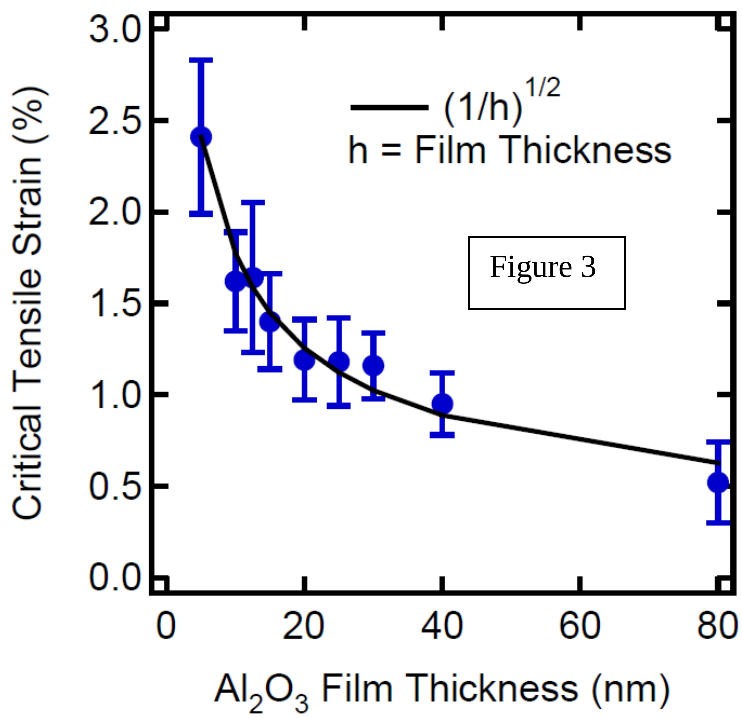
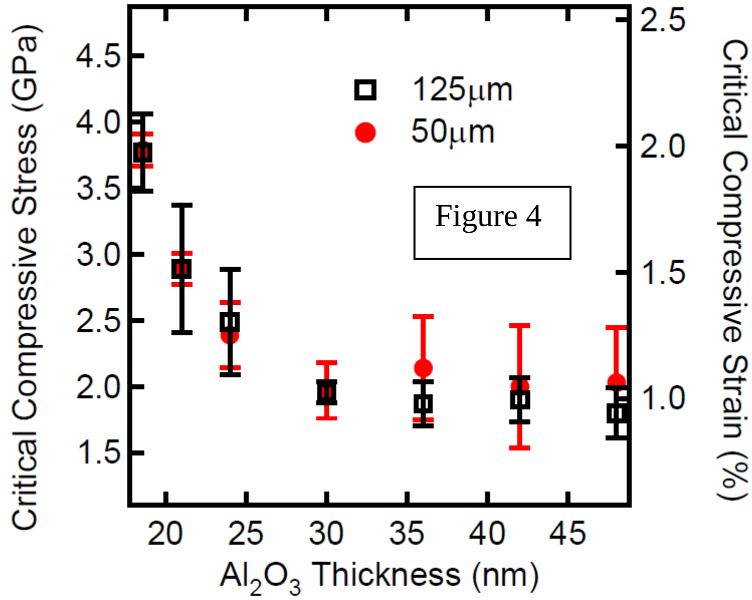


Figure 3

A low critical tensile strain of 0.52% was measured for a film thickness of 80 nm. The critical tensile strain increased to 2.4% at a film thickness of 5 nm. In accordance with fracture mechanics modeling studies, the critical tensile strains and the saturation crack densities scaled as $(1/h)^{1/2}$ where h is the Al_2O_3 ALD film thickness.

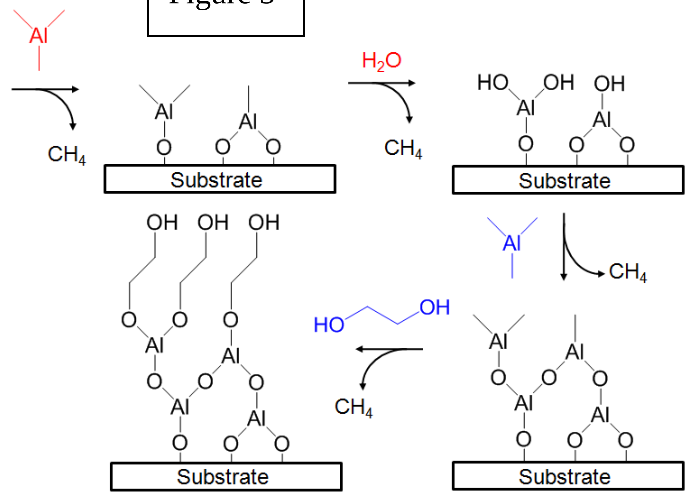
Thinner Al_2O_3 ALD film thicknesses also had higher critical strains for cracking from compressive strains. Field-emission scanning electron microscopy (FE-SEM) images of Al_2O_3 ALD films with thicknesses of 30-50 nm on Teflon fluorinated ethylene propylene (FEP) substrates were observed to crack at a critical compressive strain of ~1.0%. The critical compressive strain increased to ~2.0% at a film thicknesses of ~20 nm. The critical compressive strains versus Al_2O_3 ALD film thickness is shown in Figure 4. Similar critical compressive stresses and strains are observed on both 50 μm and 125 μm Teflon substrates. The high critical tensile and compressive strains for thin Al_2O_3 ALD films should be very useful for flexible gas diffusion barriers on polymers.



D. Growth of Al_2O_3 ALD and Alucone MLD Alloys

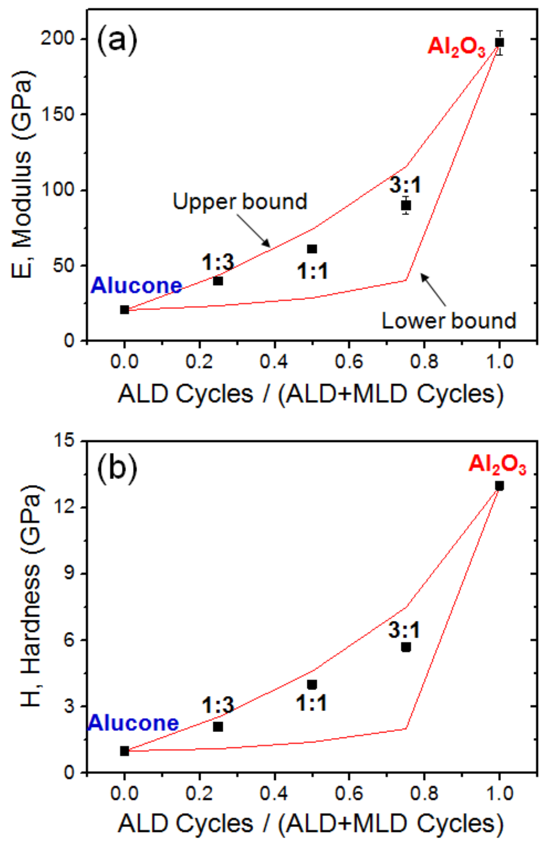
By combining the hybrid organic-inorganic MLD process with an inorganic atomic layer deposition (ALD) process, ALD/MLD alloy films can be deposited that have an adjustable organic-inorganic composition. These alloys have tunable properties that may be useful for designing various functional films. Alucone MLD using trimethylaluminum (TMA) and ethylene glycol (EG) was employed together with Al_2O_3 ALD using TMA and H_2O to deposit alucone alloys at 135°C. The composition of the alucone alloy was varied by adjusting the relative number of ALD and MLD cycles in the reaction sequence. A schematic showing the reaction sequence for the 1:1 ALD:MLD alloy is shown in Figure 5.

Figure 5



Alucone alloys were grown using relative numbers of ALD and MLD cycles varying from 1:3 to 6:1 (TMA/H_2O:TMA/EG). These alucone alloys displayed varying density, refractive index, elastic modulus and hardness. The density and refractive index changed from 1.6 g/cm^3 and n = 1.45 for pure alucone to 3.0 g/cm^3 and n = 1.64 for pure Al_2O_3, respectively. The elastic modulus and hardness varied from 21 ± 8 GPa and 1.0 ± 0.1 GPa for pure alucone to 198 ± 8 GPa and 13.0 ± 0.2 GPa for pure Al_2O_3, respectively, as shown in Figure 6. These results demonstrate the potential of ALD/MLD alloy films to provide tunable properties for many functional film applications.

Figure 6



E. Measurements of Critical Tensile Stain and Water Vapor Transmission Rate for Al_2O_3 ALD and Alucone MLD Alloys

Critical tensile strains (CTSs) and water vapor transmission rates (WVTRs) were measured for alloy films grown on polyimide substrates using Al_2O_3 atomic layer deposition (ALD) and alucone molecular layer deposition (MLD). Alloy composition was controlled by varying the ratio of ALD: MLD cycles during film growth. For ~100 nm film thicknesses, the CTS obtained its highest value of ~1.0 % for the 3:1 alloy as displayed in Figure 7. The WVTR decreased dramatically versus alloy composition and reached the measurement sensitivity limit at WVTR~1×10^{-4} $g/m^2/day$ for the 7:2, 5:1 and 6:1 alloys as shown in Figure 8. These results demonstrate that the ALD:MLD alloys may be useful as flexible gas diffusion barriers on polymers.

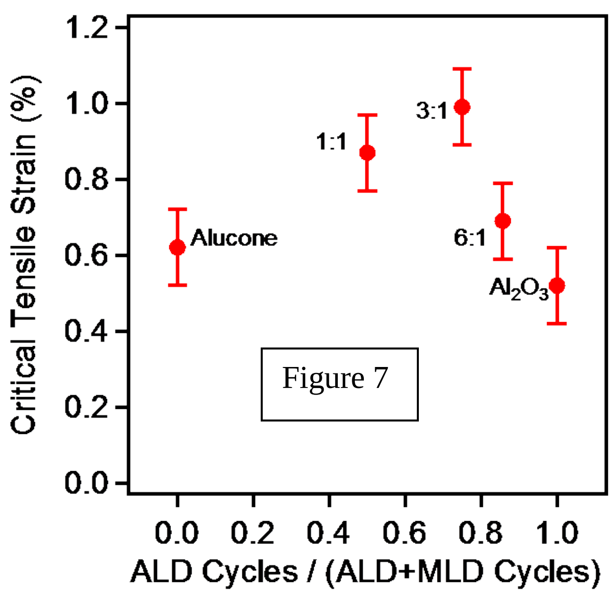


Figure 7

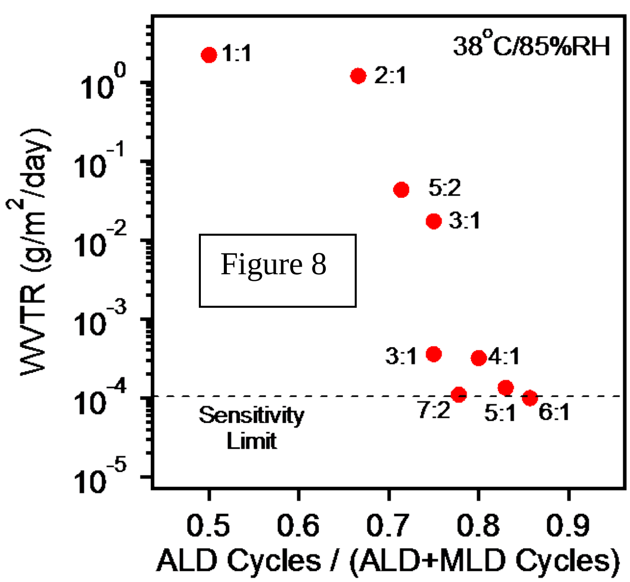
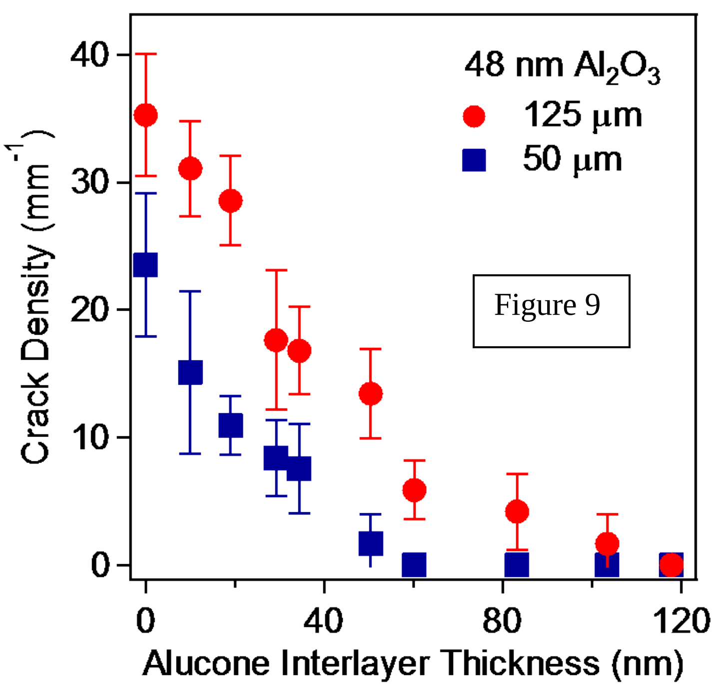


Figure 8

F. Alucone MLD as a Compliant Interlayer to Relieve Thermal Stress

Alucone films were employed as interlayers to minimize stress caused by thermal expansion mismatch between Al_2O_3 films grown by atomic layer deposition (ALD) and Teflon fluorinated ethylene propylene (FEP) substrates. The alucone films were grown by molecular layer deposition (MLD) using trimethylaluminum (TMA), ethylene glycol (EG) and H_2O. Without the alucone interlayer, the Al_2O_3 films were susceptible to cracking resulting from the high coefficient of thermal expansion (CTE) mismatch between the Al_2O_3 film and the Teflon FEP substrate. Cracking was observed by field emission scanning electron microscopy (FE-SEM) images of Al_2O_3 films grown directly on Teflon FEP substrates at temperatures from 100ºC to 160°C and then cooled to room temperature.

With an alucone interlayer, the Al_2O_3 film had a crack density that was reduced progressively versus alucone interlayer thickness. For Al_2O_3 film thicknesses of 48 nm deposited at 135ºC, no cracks were observed for alucone interlayer thicknesses >60 nm on 50 µm thick Teflon FEP substrates. The results for crack density versus alucone interlayer thickness are shown in Figure 9. For thinner Al_2O_3 film thicknesses of 21 nm deposited at 135°C, no cracks were observed for alucone interlayer thicknesses >40 nm on 50 µm thick Teflon FEP substrates. Slightly higher alucone interlayer thicknesses were required to prevent cracking on thicker Teflon FEP substrates with a thickness of 125 µm.



The alucone interlayer linearly reduced the compressive stress on the Al_2O_3 film caused by the thermal expansion mismatch between the Al_2O_3 coating and the Teflon FEP substrate. The average compressive stress reduction per thickness of the alucone interlayer was determined to be 8.5±2.3 MPa/nm. Comparison of critical tensile strains for alucone films on Teflon FEP and HSPEN substrates revealed that residual compressive stress in the alucone film on Teflon FEP could help offset applied tensile stress and lead to the attainment of much higher critical tensile strains.

G. Other Collaborations

We have also collaborated with various outside groups on ALD applications over the three years of this grant. We have continued to work on applications of ALD for enhanced properties of nano and microelectromechanical systems (N/MEMS). This work has drawn heavily from our AFOSR research. We are also working on ALD on the electrodes of Li ion batteries in our work in the iMINT DARPA Center centered at the University of Colorado. This DARPA Center is focused on *Nanoscale Science and Technology for Integrated Micro/Nano-Electromechanical Transducers*. This work has utilized many of the instruments that have been obtained from DURIP funding.

IV. Personnel Supported

Faculty

1. Prof. Steven M. George (One Month Summer Salary)

Postdoctoral Research Associates

1. Dr. Shih-Hui Jen (2009-2011)
2. Dr. Byoung Hoon Lee (2010-2011-partial) (primarily supported by DuPont)
3. Dr. Rikard Wind (2009-partial)

Graduate Students

1. Jacob Bertrand (2009-2011)
2. Dragos Seghete (2009)

V. Publications

Many manuscripts describing our AFOSR-supported research and collaborations involving our AFOSR-supported research have been published during the last three years. This list includes publications from our parent AFOSR grant (***), publications resulting from AFOSR support through STTR funding (**) and publications using equipment (AFM, XRR and XPS instruments) obtained from AFOSR support through DURIP grants (*).

1. X. Liang, P. Li, S.M. George and A.W. Weimer, "Nanocoating Hybrid Polymer Films on Large Quantities of Cohesive Nanoparticles by Molecular Layer Deposition", *AIChE J.* **55**, 1030-1039 (2009).*

2. B.B. Burton, D.N. Goldstein and S.M. George, "Atomic Layer Deposition of MgO Using Bis(ethylcyclopentadienyl)magnesium and H_2O", *J. Phys. Chem. C* **113**, 1939-1946 (2009).*

3. J.R. Scheffe, A. Francés, D.M. King, X. Liang, B.A. Branch, A.S. Cavanagh, S.M. George and A.W. Weimer, "Atomic layer deposition of iron(III) oxide on zirconia nanoparticles in a fluidized bed reactor using ferrocene and oxygen", *Thin Solid Films* **517**, 1874–1879 (2009).*

4. B. B. Burton, S. W. Kang, S.W. Rhee and S.M. George, "SiO_2 Atomic Layer Deposition Using Tris(dimethylamino)silane and Hydrogen Peroxide Studied by in situ Transmission FTIR Spectroscopy", *J. Phys. Chem. C* **113**, 8249 (2009).*

5. S.M. George, B. Yoon and A.A. Dameron, "Surface Chemistry for Molecular Layer Deposition of Polymers", *Acc. Chem. Res.* **42**, 498-508 (2009).***

6. R.K. Wind, F.H. Fabreguette, Z.A. Sechrist and S.M. George, "Nucleation Period, Surface Roughness and Oscillations in Mass Gain per Cycle during W Atomic Layer Deposition on Al_2O_3", *J. Appl. Phys.* **105**, 074309 (2009).***

7. A.S. Cavanagh, C.A. Wilson, A.W. Weimer and S.M. George, "Atomic Layer Deposition on Gram Quantities of Multiwalled Carbon Nanotubes", *Nanotechnology* **20**, 255602 (2009).*

8. B. B. Burton, S. W. Kang, S.W. Rhee and S.M. George, "SiO_2 Atomic Layer Deposition Using Tris(dimethylamino)silane and Hydrogen Peroxide Studied by in situ Transmission FTIR Spectroscopy", *J. Phys. Chem. C* **113**, 8249-8257 (2009).*

9. B.B. Burton, F.H. Fabreguette and S.M. George, "Atomic Layer Deposition of MnO Using Bis(ethylcyclopentadienyl)manganese and H_2O", *Thin Solid Films* **517**, 5658-5665 (2009).*

10. P. F. Carcia, R.S. McLean, M. D. Groner, A. A. Dameron and S. M. George, Al_2O_3 ALD and SiN PECVD Films as Gas Diffusion Ultra-barrier on Polymer Substrates, *J. Appl. Phys.* **106**, 023533 (2009).***

11. Y. Zhang, J.A. Bertrand, R. Yang, S.M. George and Y. C. Lee, "Electroplating to Visualize Defects in Al_2O_3 Thin Films Grown Using Atomic Layer Deposition", *Thin Solid Films* **517**, 3269-3272 (2009).*

12. Y. Zhang, Y.Z. Zhang, D.C. Miller, J.A. Bertrand, S.H. Jen, R. Yang, M.L. Dunn, S.M. George and Y. C. Lee, "Fluorescent Tags to Visualize Defects in Al_2O_3 Thin Films Grown Using Atomic Layer Deposition", *Thin Solid Films* **517**, 6794-6797 (2009).*

13. B. Yoon, D. Seghete, A.S. Cavanagh and S.M. George, "Molecular Layer Deposition of Hybrid Organic-Inorganic Alucone Polymer Films Using a Three-Step ABC Reaction Sequence", *Chem. Mater.* **21**, 5365-5374 (2009).*

14. S.M. George, B. Yoon and A.A. Dameron, "Surface Chemistry for Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers", *Acc. Chem. Res.* **42**, 498-508 (2009).***

15. R.A. Wind, F.H. Fabreguette, Z.A. Sechrist and S.M. George, "Nucleation Period, Surface Roughness and Oscillations in Mass Gain per Cycle during W Atomic Layer Deposition on Al_2O_3", *J. Appl. Phys.* **105**, 074309 (2009).***

16. B. Yoon, J.L. O'Patchen, D. Seghete, A.S. Cavanagh and S.M. George, "Molecular Layer Deposition of Hybrid Organic-Inorganic Polymer Films Using Diethylzinc and Ethylene Glycol", *Chem. Vap. Deposition* **15**, 112-121 (2009).*

17. G.B. Rayner, Jr. and S.M. George, "Nucleation and Growth of Tantalum Nitride Atomic Layer Deposition on Al_2O_3 Using TBTDET and Hydrogen Radicals", *J. Vac. Sci. Technol. A* **27**, 716-724 (2009).*

18. D.C. Miller, R.R. Foster, Y. Zhang, S.H. Jen, J.A. Bertrand, Z. Lu, D. Seghete, J.L. O'Patchen, R. Yang, Y.C. Lee, S.M. George and M.L. Dunn, "The Mechanical Robustness of Atomic Layer- and Molecular Layer-Deposited Coatings on Polymer Substrates", *J. Appl. Phys.* **105**, 093527 (2009).*

19. D.C. Miller, R.R. Foster, S.H. Jen, J.A. Bertrand, D. Seghete, B. Yoon, Y.C. Lee, S.M. George and M.L. Dunn, "Thermo-Mechanical Properties of Aluminum Alkoxide (Alucone) Films Created Using Molecular Layer Deposition", *Acta Mater.* **57**, 5083-5092 (2009).*

20. R.A. Wind and S.M. George, "Quartz Crystal Microbalance Studies of Al_2O_3 Atomic Layer Deposition Using Trimethylaluminum and Water at 125°C", *J. Phys. Chem. A* **114**, 1281-1289 (2010).***

21. Y.S. Jung, A.S. Cavanagh, A.C. Dillon, M.D. Groner, S.M. George and S.H. Lee, "Enhanced Stability of $LiCoO_2$ Cathodes in Lithium-ion Batteries Using Surface Modification by Atomic Layer Deposition", *J. Electrochem. Soc.* **157**, A75-A81 (2010).*

22. S.M. George, "Atomic Layer Deposition: An Overview", *Chem. Rev.* **110**, 111-131 (2010).***

23. Y.S. Jung, A.S. Cavanagh, A.C. Dillon, M.D. Groner, S.M. George and S.H. Lee, "Ultrathin Direct Atomic Layer Deposition on Composite Electrodes is Critical for Highly Durable and Safe Li-Ion Batteries ", *Adv. Mater.* **22**, 2172-2176 (2010).*

24. D. Seghete, R.A. Hall, B. Yoon and S.M. George, "Importance of Trimethylaluminum Diffusion in Three-Step ABC Molecular Layer Deposition Using Trimethylaluminum, Ethanolamine and Maleic Anhydride", *Langmuir* **26**, 19045-19051 (2010).*

25. T.K. Minton, B. Wu, J. Zhang, N.F. Lindholm, A.I. Abdulagatov, J.L. O'Patchen, S.M. George and M.D. Groner, "Protecting Polymers in Space with Atomic Layer Deposition Coatings", *ACS Appl. Mater. Interfaces* **2**, 2515-2520 (2010).**

26. S.K. Sarkar, J.Y. Kim, D.N. Goldstein, N.R. Neale, K. Zhu, C.M. Elliott, A.J. Frank and S.M. George, "In_2S_3 Atomic Layer Deposition and Its Application as a Sensitizer on TiO_2 Nanotube Arrays for Solar Energy Conversion", *J. Phys. Chem. C* **114**, 8032-8039 (2010).*

27. J.Y. Kim and S.M. George, "Tin Monosulfide Thin Films Grown by Atomic Layer Deposition Using Tin 2,4-Pentanedionate and Hydrogen Sulfide, *J. Phys. Chem. C* **114**, 17597-17603 (2010).*

28. L.A. Riley, A.S. Cavanagh, S.M. George, Y.S. Jung, Y. Yan, S.H. Lee and A.C. Dillon, "Conformal Surface Coatings to Enable High Volume Expansion Li-ion Anode Materials", *ChemPhysChem*. **11**, 2124-2130 (2010).*

29. D.C. Miller, R.R. Foster, S.H. Jen, J.A. Bertrand, S.J. Cunningham, A.S. Morris, Y.C. Lee, S.M. George and M.L. Dunn, "Thermo-mechanical Properties of Alumina Films Created Using the Atomic Layer Deposition Technique", *Sensors and Actuators A* **164**, 58-67 (2010).*

30. I.D. Scott, Y.S. Jung, A.S. Cavanagh, Y. Yan, A.C. Dillon, S.M. George, S.H. Lee, "Ultrathin Coatings on Nano-$LiCoO_2$ for Li-Ion Vehicular Applications", *Nano Letters* **11**, 414-418 (2011).*

31. L.A. Riley, A.S. Cavanagh, S.M. George, S.H. Lee and A.C. Dillon, "Improved Mechanical Integrity of ALD-Coated Composite Electrodes for Li-Ion Batteries", *Electrochem. Solid-State Lett.* **14**, A29-A31 (2011).*

32. D. Seghete, G.B. Rayner, Jr., A.S. Cavanagh, V.R. Anderson and S.M. George, "Molybdenum Atomic Layer Deposition Using MoF_6 and Si_2H_6 as Reactants", *Chem. Mater.* **23**, 1668-1678 (2011).*

33. D. Seghete, F.H. Fabreguette and S.M. George, "Using a Slit Doser to Probe Gas Dynamics during Al_2O_3 Atomic Layer Deposition and to Fabricate Laterally Graded Al_2O_3 Layers", *Thin Solid Films* **519**, 3612-3618 (2011).***

34. B. Yoon, Y. Lee, A. Derk, C.B. Musgrave and S.M. George, "Molecular Layer Deposition of Conductive Hybrid Organic-Inorganic Thin Films Using Diethylzinc and Hydroquinone", *ECS Transactions* **33** (27) 191-195 (2011).*

35. L. Baker, A.S. Cavanagh, D. Seghete, S.M. George, A.J.M. Mackus, W.M.M. Kessels, Z.Y. Liu and F.T. Wagner, "Nucleation and Growth of Pt Atomic Layer Deposition on Al_2O_3 Substrates Using (Methylcyclopentadienyl)-Trimethyl Platinum and O_2 Plasma", *J. Appl. Phys.* **109**, 084333 (2011).*

36. S.H. Jen, J.A. Bertrand and S.M. George, "Critical Tensile and Compressive Strains for Cracking of Al_2O_3 Films Grown by Atomic Layer Deposition", *J. Appl. Phys.* **109**, 084305 (2011).***

37. S.M. George, "Hybrid Organic-Inorganic Films Grown Using Molecular Layer Deposition", *The Strem Chemiker*, Vol. XXV, No. 1, March 2011 (Strem Chemicals, Inc., Newburyport, Massachusetts) pp. 13-26.***

38. L.A. Riley, S.V. Atta, A.S. Cavanagh, Y. Yan, S.M. George, P. Liu, A.C. Dillon and S.H. Lee, "Electrochemical Effects of ALD Surface Modification on Combustion Synthesized $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ as a Layered Cathode Material", *J. Power Sources* **196**, 3317-3324 (2011).*

39. B.D. Davidson, D. Seghete, S.M. George and V.M. Bright, "ALD Tungsten NEMS Switches and Tunneling Devices", *Sensors & Actuators A* **166**, 269-276 (2011).*

40. J.A. Bertrand and S.M. George, "Atomic Layer Deposition on Polymers for Ultralow Water Vapor Transmission Rates: The Ca Test", *54th Technical Conference Proceedings of the Society of Vacuum Coaters (SVC)*, 492-496 (2011).***

41. S.M. George, P.R. Fitzpatrick and Z.M. Gibbs, "Atomic Layer Deposition for Continuous Roll-to-Roll Processing", *54th Technical Conference Proceedings of the Society of Vacuum Coaters (SVC)*, 76-81 (2011).*

42. S.M. George, P.R. Fitzpatrick and Z.M. Gibbs, "Atomic Layer Deposition for Continuous Roll-to-Roll Processing", *Summer Bulletin of the Society of Vacuum Coaters (SVC)*, pages 50-54 (2011).*

43. S.M. George, B.H. Lee, B. Yoon, A.I. Abdulagatov and R.A. Hall, "Metalcones: Hybrid Organic-Inorganic Films Fabricated Using Atomic & Molecular Layer Deposition Techniques", *J. Nanoscience & Nanotechnology* **11**, 7948-7955 (2011).***

44. Y. Lee, B. Yoon, A.S. Cavanagh and S.M. George, "Molecular Layer Deposition of Aluminum Alkoxide Polymer Films Using Trimethylaluminum and Glycidol", *Langmuir* **27**, 15155-15164 (2011).*

45. B. Yoon, B. H. Lee and S. M. George, "Molecular Layer Deposition of Flexible, Transparent and Conductive Hybrid Organic-Inorganic Thin Films", *ECS Transactions* **41** (2) 271-277 (2011).*

46. B. H. Lee, V. R. Anderson and S. M. George, "Metalcone and Metalcone/Metal Oxide Alloys Grown Using Atomic & Molecular Layer Deposition", *ECS Transactions* **41** (2) 131-138 (2011).*

47. Y. Zhang, R.G. Yang, S.M. George and Y.C. Lee, "In-Situ Inspection of Cracking in Atomic-Layer-Deposited Barrier Films on Surface and in Buried Structures", *Thin Solid Films* **520**, 251-257 (2011).*

48. A.I. Abdulagatov, Y. Yan, J.R Cooper, Y. Zhang, Z.M. Gibbs, A.S. Cavanagh, R.G. Yang, Y.C. Lee and S.M. George, "Al_2O_3 and TiO_2 Atomic Layer Deposition on Copper for Water Corrosion Resistance", *ACS Appl. Mater. Interfaces* **3**, 4593-4601 (2011).*

VI. Interactions/ Transitions

Over the last three years (February 2009-November 2011), the PI has been invited to discuss our AFOSR-supported research or research supported by equipment obtained through AFOSR at many invited talks:

1. "Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers", Materials Science and Engineering Department, University of Texas at Dallas, Richardson, Texas, April 23, 2009.

2. "Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers", Department of Chemistry, University of Helsinki, Helsinki, Finland, June 12, 2009.

3. "Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers", Department of Chemistry, University of Oslo, Oslo, Norway, June 18, 2009.

4. "Atomic Layer Deposition for Flexible Coatings", 9th International Conference on Atomic Layer Deposition (ALD2009), Monterey, California, July 19, 2009.

5. "Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers", Dept. of Chemical & Biological Engineering, University of Colorado, Boulder, Colorado, October 20, 2009.

6. "Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers", Dept. of Chemistry and Biochemistry, Brigham Young University, Provo, Utah, April 13, 2010.

7. "ALD for Engineering Materials Properties", Workshop on *ALD: The Next Ten Years*, 10^{th} International Conference on Atomic Layer Deposition (ALD2010), Seoul, Korea, June 20, 2010.

8. “Flexibility of Al_2O_3 ALD Films”, 10th International Conference on Atomic Layer Deposition (ALD2010), Seoul, Korea, June 22, 2010.

9. “Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers”, Sanyo Chemical Industries, Kyoto, Japan, June 25, 2010.

10. “Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers”, Israel Vacuum Society Workshop on *Atomic Layer Deposition*, Bar-Ilan University, Ramut Gan, Israel, July 8, 2010.

11. “Surface Chemistry of Molecular Layer Deposition”, Telluride Summer Science Workshop on *Semiconductor Surface Chemistry*, Telluride, Colorado, Monday, July 26, 2010.

12. “Metalcones: Hybrid Organic-Inorganic Films Fabricated Using Atomic & Molecular Layer Deposition Techniques”, EuroCVD 18, Kinsale, Ireland, Sept. 5, 2011.

13. “Flexibility of Al_2O_3 ALD Films & Scaleup Using Spatial ALD”, Rocky Mountain Materials Research Society Meeting, September 28, 2011.

14. “Molecular Layer Deposition of Flexible, Transparent and Conductive Hybrid Organic-Inorganic Thin Films”, B.Yoon, B.H. Lee and S.M. George, 220th Electrochemical Society Meeting, Boston, Massachusetts, October 12, 2011.

The PI and other members of the research group have also presented the results of our work as contributed talks or posters at various meetings and conferences. This work includes AFOSR-supported studies, research supported by equipment obtained through AFOSR and various AFOSR-collaborations:

Contributed Talks:

1. "Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD) for Barrier Coatings on Polymers" Dragos Seghete, Shih-Hui Jen, Jacob A. Bertrand, Steven M. George, IMAPS/ACerS 2009 International Conference and Exhibition on *Ceramic Interconnect and Ceramic Microsystems Technologies* (CICMT), Denver, Colorado, April 21, 2009.
2. "Defect Inspection of ALD/MLD-Based Barrier Coatings", Yadong Zhang, Yu-Zhong Zhang, David C. Miller, Jacob A. Bertrand, Shih-Hui Jen, Ronggui Yang, Martin L. Dunn, Steven M. George and Y. C. Lee, IMAPS/ACerS 2009 International Conference

and Exhibition on *Ceramic Interconnect and Ceramic Microsystems Technologies* (CICMT), Denver, Colorado, April 21, 2009.

3. "Mechanical Robustness of ALD/MLD-Based Barreir Coatings", David C. Miller, Ross R. Foster, Yadong Zhang, Shih-Hui Jen, Jacob A. Bertrand, Zhixing Lu, Dragos Seghete, Jennifer L. O'Patchen, Ronggui Yang, Yung-Cheng Lee, Steven M. George and Martin L. Dunn, IMAPS/ACerS 2009 International Conference and Exhibition on *Ceramic Interconnect and Ceramic Microsystems Technologies* (CICMT), Denver, Colorado, April 21, 2009.

4. "Molecular Layer Deposition of Hybrid Organic-Inorganic Films Formed from Lewis Acids and Lewis Bases", B. Yoon, Z.M. Gibbs and S.M. George, 9th International Conference on Atomic Layer Deposition (ALD2009), Monterey, California, July 22, 2009.

5. "Evaluation of Al_2O_3 ALD Gas Diffusion Barriers and Visualization of Barrier Defects Using the Ca Test", J.A. Bertrand, S.H. Jen, D. Seghete and S.M. George, American Vacuum Society (AVS) International Symposium, San Jose, California, November 10, 2009.

6. "Critical Compressive Stress for Cracking of Al_2O_3 ALD Films", S.H. Jen, J.A. Bertrand and S.M. George, American Vacuum Society (AVS) International Symposium, San Jose, California, November 11, 2009.

7. "Molecular Layer Deposition (MLD) of Hybrid Alumina/Siloxane Films", A.I. Abdulagatov, B. Yoon, D.N. Goldstein & S.M. George, NanoForum Workshop, NanoSurfaces Session, University of Helsinki, Helsinki, Finland, May 25, 2010.

8. "Molecular Layer Deposition of Hybrid Organic-Inorganic Films Using Trimethylaluminum and Sugar Alcohols", R.B. Hall, B. Yoon and S.M. George, 10th International Conference on Atomic Layer Deposition (ALD2010), Seoul, Korea, June 23, 2010.

9. "Molecular Layer Deposition (MLD) of Hybrid Alumina/Siloxane Films", A.I. Abdulagatov and S.M. George, Nanotechnologies of Functional Materials (NFM 2010); St. Petersburg State Polytechnical University, Saint Petersburg, Russia, September, 23, 2010.

10. "Molecular Layer Deposition of Hybrid Siloxane/Alumina Polymer Films", A.I. Abdulagatov, B. Yoon, V.R. Anderson, Z.M. Gibbs, A.S. Cavanagh and S.M. George, AVS 57th International Symposium & Exhibition, Albuquerque Convention Center, Albuquerque, New Mexico, October 18, 2010.

11. "Molecular Layer Deposition of Alucones Using Trimethylaluminum and Glycerol or Glycidol", R.B. Hall, B. Yoon, Y. Lee and S.M. George, AVS 57th International Symposium & Exhibition, Albuquerque Convention Center, Albuquerque, New Mexico, October 18, 2010.

12. "Atomic Layer Deposition on Polymers for Ultralow Water Vapor Transmission Rates", J.A. Bertrand and S.M. George, Society for Vacuum Coaters Technical Conference, Chicago, Illinois, April 19, 2011.

13. “Zircone and Tunable Zircone:ZrO_2 Alloy Films Using Molecular Layer Deposition Techniques”, B.H. Lee, V.R. Anderson and S.M. George, 11th International Conference on Atomic Layer Deposition (ALD2011), Cambridge, Massachusetts, June 29, 2011.

14. “Titanicone Molecular Layer Deposition Using $TiCl_4$ and Ethylene Glycol or Glycerol and Porous TiO2 Films Produced by Annealing”, A.I. Abdulagatov, R.A. Hall and S.M. George, 11th International Conference on Atomic Layer Deposition (ALD2011), Cambridge, Massachusetts, June 29, 2011.

15. “Molecular Layer Deposition of Flexible, Transparent and Conductive Hybrid Organic-Inorganic Thin Films”, B.Yoon, B.H. Lee and S.M. George, 11th International Conference on Atomic Layer Deposition (ALD2011), Cambridge, Massachusetts, June 29, 2011.

16. “Metalcone and Metalcone/Metal Oxide Alloys Grown Using Atomic & Molecular Layer Deposition Techniques”, B.H. Lee, V.R. Anderson and S.M. George, Session on ALD/MLD Hybrid Films, AVS 58th International Symposium & Exhibition, Nashville, Tennessee, November 2, 2011.

17. “Titanicone Molecular Layer Deposition Using $TiCl_4$ and Sugar Alcohols and Porous TiO_2 Films Produced by Annealing”, R.A. Hall, A.I. Abdulagatov and S.M. George, Session on ALD/MLD Hybrid Films, AVS 58th International Symposium & Exhibition, Nashville, Tennessee, November 2, 2011.

18. “Metalcone and Metalcone/Metal Oxide Alloys Grown Using Atomic & Molecular Layer Deposition Techniques”, B.H. Lee, V.R. Anderson and S.M. George, 220th Electrochemical Society Meeting, Boston, Massachusetts, October 10, 2011.

Posters:

1. "Critical Compressive Stress for Cracking of Al_2O_3 ALD Films", S.H. Jen, J.A. Bertrand and S.M. George, 9th International Conference on Atomic Layer Deposition (ALD2009), Monterey, California, July 20-21, 2009.

2. "Evolution of Al_2O_3 ALD Gas Diffusion Barriers and Visualization of Barrier Defects Using the Ca Test", J.A. Bertrand, S.H. Jen, D. Seghete and S.M. George, 9th International Conference on Atomic Layer Deposition (ALD2009), Monterey, California, July 20, 2009.

3. "Molecular Layer Deposition of Organic-Inorganic Films using Bifunctional Silanes", Aziz Abdulagatov, Byunghoon Yoon, Virginia Anderson, Zachary Gibbs and Steven George, 2009 Annual Symposium of the Rocky Mountain Chapter of the American Vacuum Society, Westminster, Colorado, September 17, 2009.

4. "Evaluation of Al_2O_3 ALD Gas Diffusion Barriers and Visualization of Barrier Using the Ca Test", Jacob A. Bertrand, Shih-Hui Jen, Dragos Seghete and Steven M. George, 2009 Annual Symposium of the Rocky Mountain Chapter of the American Vacuum Society, Westminster, Colorado, September 17, 2009.

5. "Molecular Layer Deposition of Hybrid Organic-Inorganic Thin Films Using Heterobifunctional Precursors", Zach Gibbs, Alan Derk, Andrew Cavanagh, Paul

Zimmerman, Charles Musgrave and Steven George, 2009 Annual Symposium of the Rocky Mountain Chapter of the American Vacuum Society, Westminster, Colorado, September 17, 2009.

6. "Molecular Layer Deposition (MLD) Incorporated with Atomic Layer Deposition (ALD)", Byunghoon Yoon, Shih-Hui Jen, Zachary M. Gibbs and Steven M. George, 2009 Annual Symposium of the Rocky Mountain Chapter of the American Vacuum Society, Westminster, Colorado, September 17, 2009.

7. "Protecting Polymers from the Natural Space Environment with Films Grown Using Atomic Layer Deposition", M.D. Groner, A.I. Abdulagatov, R.P. Fitzpatrick and S.M. George, AVS 57th International Symposium & Exhibition, Albuquerque Convention Center, Albuquerque, New Mexico, October 19, 2010.

VII. New Discoveries, Inventions or Patent Disclosures

The University of Colorado has received and applied for a variety of patents based on the research in Prof. Steven George's research group that has been supported by AFOSR. Previous awarded patents based on AFOSR support include:

1. J.W. Klaus, O.Sneh and S.M. George, "Method of Growing Films on Substrates at Room Temperature Using Catalyzed Binary Reaction Sequence Chemistry", U.S. Patent 6,090,442, July 18, 2000.

2. J.W. Klaus and S.M. George, "Method for Forming SiO_2 by Chemical Vapor Deposition at Room Temperature", U.S. Patent Number 6,818,250, November 16, 2004.

3. J.W. Klaus and S.M. George, "A Solid Material Comprising a Thin Metal Film on its Surface and Methods for Producing the Same", U.S. Patent 6,958,174, October 2005.

4. V.M. Bright, J.W. Elam, F. Fabreguette, S.M. George, N. Hoivik, Y.C. Lee, R. Linderman and M. Tripp, "Atomic Layer Deposition on Micro-Mechanical Devices", U.S. Patent 7,426,067, September 16, 2008.

5. S.M. George and C.R. Herrmann, "Al_2O_3 Atomic Layer Deposition to Enhance the Deposition of Hydrophobic or Hydrophyllic Coatings on Microelectromechanical Devices", U.S. Patent 7,553,686, June 30, 2009.

Patent applications based on AFOSR support currently under review include:

1. S.M. George, J.D. Ferguson, A.W. Weimer and C.A. Wilson, "Method for the Deposition of an Inorganic Film on an Organic Polymer, U.S. Patent Application Number

20040194691, PCT International Publication Number WO 03/008110 A1.

2. S.M. George, A.A. Dameron and N.M. Adamczyk, "Molecular Layer Deposition Process for Making Organic or Organic-Inorganic Polymers", University of Colorado Docket Number UTC 014. Full Patent Filed Fall 2007).

3. A.A. Dameron and S.M. George, "Protective Coatings for Organic Electronic Devices Made Using Atomic Layer Deposition and Molecular Layer Deposition Techniques", University of Colorado Docket Number UTC 016, app. No. 60/939,818. (Full Patent Filed Spring 2008).

VIII. Honors/Awards

Prof. George is very active in the American Vacuum Society (AVS). He was elected by the AVS membership to serve as an AVS Trustee (January 2007-December 2009). He also served as Chair of the AVS Trustees (January 2009-December 2009). He was then elected to the AVS Board of Directors (January 2010-December 2012). He is currently finishing his third year on the Board of Directors and is a candidate for President-elect of AVS for 2013.

Prof. George has been previously elected a Fellow in the American Vacuum Society (2000) and a Fellow in the American Physical Society (1997).