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Nanolaminates with Novel Properties Fabricated Using Atomic Layer Deposition Techniques

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Prof. Steven M. George, PI
Dept. of Chemistry and Biochemistry
Dept. of Chemical and Biological Engineering
University of Colorado
Boulder, CO 80309

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**Report Title:** Nanolaminates with Novel Properties Fabricated Using Atomic Layer Deposition Techniques

**Abstract:** This AFOSR grant worked on the development, understanding and applications of atomic layer deposition (ALD) for nanolaminates. ALD can be used to fabricate unique nanolaminates with novel properties. Nanolaminates are multilayered thin film structures with nanometer dimensions and very high interfacial density. These multilayer structures can display novel properties that are not simply a “rule of mixtures”. These special properties can be optimized by manipulating the thickness and composition of the individual nanolayers. The optimized nanolaminates may have important applications as better protective thermal barrier coatings and enhanced superlattice Bragg reflectors in the x-ray region. During the course of this research, the growth and characterization of W/Al2O3 nanolaminates was examined as a model system. The W/Al2O3 nanolaminate has revealed many fascinating thermal and optical properties. Very low thermal conductivity W/Al2O3 nanolaminates were demonstrated that displayed thermal conductivities less than yttria-stabilized ZrO2. Extremely high x-ray reflectivities were also observed for W/Al2O3 nanolaminates. In particular, world record x-ray reflectivities were observed in the hard x-ray region. The quality of the W/Al2O3 nanolaminate is dependent on the nucleation and growth of the W and Al2O3 nanolayers. Consequently, detailed experimental measurements and theoretical simulations have explored W ALD surface chemistry and the nucleation of W ALD on Al2O3. The project has aimed to establish correlations between thermal and optical properties and nanolaminate structure, interfacial density and composition.
I. Overview

This AFOSR grant has worked on the development, understanding and applications of atomic layer deposition (ALD) for nanolaminates. Atomic layer deposition can be used to fabricate unique nanolaminates with novel properties. Nanolaminates are multilayered thin film structures with nanometer dimensions and very high interfacial density. These multilayer structures can display novel properties that are not simply a "rule of mixtures". These special properties can be optimized by manipulating the thickness and composition of the individual nanolayers. Atomic layer deposition offers exquisite control for this optimization. The optimized nanolaminates may have important applications as better protective thermal barrier coatings and enhanced superlattice Bragg reflectors in the x-ray region.

We have studied the growth and characterization of W/Al₂O₃ nanolaminates as a model system. The quality of the W/Al₂O₃ nanolaminate is dependent on the nucleation and growth of the W and Al₂O₃ nanolayers. Consequently, we have explored the surface chemistry of W ALD and have performed detailed experimental measurements and theoretical simulations of W ALD nucleation on Al₂O₃. Our objective has been a thorough understanding of the nanolaminate ALD growth to be able to fabricate precise nanostructures that display desired properties.

The precisely fabricated W/Al₂O₃ nanolaminates by ALD have then been employed to understand structure/property relationships. Over the last three years, our work has concentrated on thermal and optical properties that are important for designing better thermal barrier protective coatings and enhanced x-ray mirrors. We aim to establish correlations between thermal and optical properties and nanolaminate structure, interfacial density and composition. We have fully characterized the ultralow thermal conductivity and ultrahigh x-ray reflectivity of W/Al₂O₃ nanolaminates. These investigations are important for a basic understanding of nanolaminates and for many future applications of nanolaminate films.

II. Research Topics

Our AFOSR effort has concentrated on a number of important topics during the course of this research. These topics include:

- Understanding the ultrahigh x-ray reflectivity from W/Al₂O₃ nanolaminates. We have performed additional characterization of 16-bilayer W/Al₂O₃ nanolaminates using transmission electron microscopy (TEM) and x-ray rocking curves.
- Examination of the nucleation and growth during W ALD on Al₂O₃ using high resolution quartz crystal microbalance (QCM) studies. These QCM studies were complemented by atomic force microscope (AFM) studies following the nucleation and growth of the surface roughness of the W ALD films.
• Development of a model for W ALD on Al₂O₃ that is consistent with the nucleation of W islands that then the coalescence of these W islands into a continuous W film.

• Theoretical simulations of nucleation and growth during W ALD on Al₂O₃ to understand the relationship between the W ALD growth per cycle and the change in surface roughness of the W ALD film.

• Optimization of the growth of W/Al₂O₃ nanolaminates. The quality of the W/Al₂O₃ nanolaminates depends on a thorough knowledge of the nucleation of W ALD on Al₂O₃ and Al₂O₃ ALD on W during W/Al₂O₃ nanolaminate growth. These studies were performed using in situ quartz crystal microbalance (QCM) measurements.

• X-ray reflectivity of W/Al₂O₃ nanolaminates. We varied the W/Al₂O₃ nanolaminate properties (number of bilayers, thickness of bilayers, relative thickness of two materials in the bilayer) to optimize the x-ray reflectivity. These studies made extensive use of our x-ray diffractometer obtained from the DURIP program.

• Examination of the nucleation and growth during W ALD on Al₂O₃ using atomic force microscopy (AFM). We measured the surface roughness during the nucleation region. These measurements revealed a surface roughness that was consistent with the nucleation of islands that then coalesce into a continuous smooth film.

• Improvement of treatment of excess reactant and products during W ALD and Al₂O₃ ALD. Pumping of these reactants and products seriously degrades vacuum pump performance. We evaluated a new burn box design that can chemically degrade the reactants and products before they reach the vacuum pumps.

• Thermal conductivity of the W/Al₂O₃ nanolaminates. We have evaluated the thermal conductivity of W/Al₂O₃ nanolaminates versus bilayer thickness in conjunction with Prof. David Cahill at the University of Illinois at Urbana.

• X-ray reflectivity of W/Al₂O₃ nanolaminates. We examined the effect of the various W/Al₂O₃ nanolaminate properties (number of bilayers, thickness of bilayers, relative thickness of two materials in the bilayer) to optimize the x-ray reflectivity.

In addition to these core topics, we also explored a number of additional topics including:

• New ALD surface chemistry for the growth of AlN and WN. These materials will be interesting in combination with Al₂O₃ or W in nanolaminate structures.

• Transitions of ALD techniques to industry for various technological applications. We have worked with several collaborators to transition ALD techniques to various applications including microelectromechanical systems (MEMS).

• Development of new methods to use ALD to deposit laterally-graded multilayers for x-ray optical applications.
• Exploration of ALD on carbon nanotubes to insulate the carbon nanotubes and to define a carbon nanotube coaxial cable.

• Investigation of W and Al$_2$O$_3$ ALD on polymers for possible applications such as flexible x-ray mirrors.

Our progress in studying these research topics over the last three years has been excellent. Our research effort has been headed by postdoctoral research associate Dr. Francois Fabreguette. He has been in charge of the W/Al$_2$O$_3$ nanolaminates for x-ray mirrors and has been responsible for the characterization of the W/Al$_2$O$_3$ nanolaminates using x-ray reflectivity (XRR) and TEM and the work on laterally graded multilayers. Francois has worked closely with a graduate student, Zachary Sechrist. Francois and Zach have worked together on the optimization of the W/Al$_2$O$_3$ nanolaminates for x-ray mirrors. Francois has also worked closely with Dr. Rikard Wind. Dr. Wind is a postdoctoral research associate who is working on the QCM studies of W/Al$_2$O$_3$ nanolaminate growth and also performing the theoretical simulations of W ALD on Al$_2$O$_3$.

We have also explored some additional topics outside of our core research on W/Al$_2$O$_3$ nanolaminates. Some of this work was performed by graduate student, Chris Wilson. Chris has examined Al$_2$O$_3$ ALD and W ALD on various polymers. Additional work was performed by another postdoctoral research associate, Cari Herrmann. Cari was largely responsible for various fruitful applications of ALD with our many collaborations. Many of these collaborations have focused on ALD on MEMS and ALD on carbon nanotubes.

III. Accomplishments/ New Findings

One key accomplishment of this research was our growth of W/Al$_2$O$_3$ nanolaminates with various bilayer thicknesses and the measurement of their thermal conductivity by Prof. David Cahill at the University of Illinois at Urbana. A number of films with a thickness of 400 Å were grown with different number of bilayers (BL) as shown in Figure 1.

The thermal conductivity was then measured to determine the effect of interfacial density on thermal conductivity. The results
of the thermal conductivity measurements are shown in Figure 2. The thermal conductivity was reduced dramatically versus number of bilayers. These results were very significant because they illustrated the importance of interfacial density for thermal conductivity. In addition, the magnitude of the thermal conductivity was very low. ZrO$_2$ has the lowest known thermal conductivity for a refractory inorganic material of ~0.01 Wcm$^{-1}$K$^{-1}$. The lowest thermal conductivity for the W/Al$_2$O$_3$ nanolaminate is almost a factor of 3 lower. This low thermal conductivity could be important for future thermal barrier coatings.

Another key accomplishment from this research was our optimization of the x-ray reflectivity from W/Al$_2$O$_3$ nanolaminates. We knew from our previous work that high x-ray reflectivities could be obtained from W/Al$_2$O$_3$ nanolaminates deposited at 177°C. We initially measured a reflectivity of 67% for $\lambda$=1.54 Å from the CuKα transition. Since this result was obtained without any knowledge of the optimum parameters for an x-ray mirror, we were confident that we could improve on this reflectivity after we understood the factors that dictate x-ray reflectivity.

One of important parameters for x-ray reflectivity is the interfacial roughness in the superlattice structure. To minimize the interfacial roughness to maximize the reflectivity, we examined the surface roughness of W ALD films versus growth temperature. We determined that lower growth temperatures yield much lower surface roughnesses. A summary of surface roughness versus growth temperature
during W ALD is shown in Figure 3. Based on these results, we determined that the W ALD nanolayers in the W/Al₂O₃ nanolaminates needed to be grown at 125°C.

The change of W ALD growth temperature from 177°C to 125°C also led to interesting changes in the W crystal structure. The W ALD films grown at higher temperatures ≥ 200°C displayed three diffraction peaks consistent with lower density, β-tungsten (14.6 g/cm³). In contrast, W ALD films grown at lower temperatures ≤ 150°C displayed a single diffraction peak consistent with higher density α-tungsten (19.3 g/cm³). This change in crystal structure is displayed in Figure 4. This discovery was relevant to the optimization of the x-ray mirror reflectivity because the x-ray reflectivity is dependent on the density difference between the two layers in the superlattice. The larger the density difference, the higher the x-ray reflectivity. Consequently, we determined that the lower temperatures < 150°C were important both for lower surface roughness and higher density W ALD films.

After determining that the W/Al₂O₃ nanolaminates needed to be grown at 125°C, we reoptimized the nucleation and growth during W ALD on Al₂O₃ and Al₂O₃ ALD on W using in situ quartz crystal microbalance (QCM) experiments. The nucleation was optimized by studying the effect of the parameters for the WF₆ and Si₂H₆ reactant exposures (pressure and time) during W ALD on the nucleation behavior. Optimization of these parameters led the best nucleation of W ALD shown in Figure 5. Even under the best conditions, 4-5 WF₆/Si₂H₆ cycles are required to nucleate the W ALD and obtain linear growth.

The mass gain during each WF₆/Si₂H₆ cycle reveals interesting detail about the W ALD nucleation. Figure 6 shows the W mass gain per WF₆/Si₂H₆ cycle. Notice that the mass gain per cycle increases dramatically after 3 WF₆/Si₂H₆ cycles. The mass gain per cycle then overshoots and “rings” down after 15-20 WF₆/Si₂H₆ cycles. This interesting oscillatory behavior is very reproducible.
We believe that these data can be used to model the nucleation and growth of W ALD on Al₂O₃. This topic is extremely important for a basic understanding of ALD.

The W mass gain per cycle suggests that W ALD nucleates as islands after ~3 WF₆/Si₂H₆ cycles. The islands then progressively grow during cycles 4-8. By cycle 8, the W mass gain per cycle reaches a peak and then decreases. This puzzling behavior can be explained in terms of surface roughness. The islands are rough and will display the highest W mass gain per cycle at the moment where the islands have grown together with each other to create a continuous film. Further W ALD will then smooth the surface roughness and lead to a reduced W mass gain per cycle.

To test this idea about the existence of W islands and surface roughness, the W ALD layer on Al₂O₃ was examined with atomic force microscopy (AFM) after different numbers of WF₆/Si₂H₆ cycles. If the islands exist during the initial stages of W ALD growth on Al₂O₃, then these islands should lead to increased surface roughness. The AFM measurements confirmed that the roughest surface was obtained during the region of rapid increase of W mass gain per cycle. This correlation is shown in Figure 7. We also have modeled this data to further develop our understanding of W ALD on Al₂O₃. We note that these are the most detailed measurements of nucleation and growth during ALD for any system to date.

Based on these QCM and AFM studies, we realized that the smoothest W ALD films will be obtained after 11 WF₆/Si₂H₆ cycles. The requirement to utilize 11 WF₆/Si₂H₆ cycles places some restrictions on the minimum W ALD layer thickness that can be employed for the Bragg reflector based on the W/Al₂O₃ nanolaminate. We then set out to optimize the reflectivity of the W/Al₂O₃ superlattice as an x-ray mirror for hard x-rays at 1.54 Å.

The reflectivity of a Bragg mirror reflector is dependent on a superlattice structure of absorber and spacer layers. A bilayer is one absorber/spacer layer characterized by D, the bilayer thickness and γ, the spacer fraction defined by the spacer thickness divided by D. Figure 8 shows these various parameters that define the Bragg reflector.
These results from both the reflectivity measurements versus spacer fraction at constant bilayer thickness and versus bilayer thickness at constant spacer fraction allowed us to confirm the expected behavior of the x-ray reflectivity on these two key parameters. After confirming this expected behavior, a much larger superlattice was grown to obtain the highest possible x-ray reflectivity. This larger superlattice was composed of 16 bilayers.

The optimized 16-bilayer superlattice displayed very high reflectivity. The logarithm of the reflected intensity versus incident angle is shown in Figure 9. The reflectivity for the $n=1$ Bragg peak is nearly equal to the total beam intensity. The total beam intensity is obtained at the critical angle. The critical angle occurs just before the x-rays begin to penetrate into the underlying substrate. At angles less than the critical angle, the x-rays undergo complete external reflection. This superlattice was grown to obtain $\gamma=0.72$ and $D=122\text{Å}$. The x-ray reflectivity measurements yielded $\gamma=0.76$, $D=142\text{Å}$.

The high reflectivity of this 16-bilayer superlattice is most dramatically revealed by a plot of the linear reflected intensity versus the incident angle. This plot is shown in Figure 10. The reflectivity of the $n=1$ Bragg peak is 96%. This reflectivity of 96% is the highest reflectivity ever reported for Bragg reflectors at 1.54 Å. The reflectivity for the $n=2$ and $n=3$ Bragg peaks is also exceptional. These high reflectivities for higher order Bragg peaks are only observed from exceptional superlattice structures.

The x-ray reflectivity for the CuKα line at 1.54 Å is important because hard x-rays are used for a variety of analytical purposes to characterize crystal structure and to determine the characteristics of thin films using x-ray reflectivity measurements. The CuKα line is one of the dominant x-ray wavelengths used for x-ray analysis. The Lawrence Berkeley Laboratory keeps
multilayer where the dark thin layers are the W ALD absorber layers and the thick lighter layers are the Al2O3 ALD spacer layers. The first eight bilayers are perfectly conformal to the underlying Si(100) substrate. The top bilayers show some roughness that replicates the roughness in the underlying bilayers.

The roughness on the top of the W/Al2O3 multilayer is believed to result primarily from the W crystallinity. This roughness is correlated and propagates through the whole W/Al2O3 multilayer. This correlated roughness should not seriously affect the specular reflectivity at the Bragg peak. The inset in Figure 11 shows a high resolution TEM image of the W/Al2O3 multilayer. This TEM image illustrates the sharp interfaces between the W and Al2O3 layers and confirms the thicknesses for the spacer layer and W absorber layer.

An off-specular transverse scan at the first-order Bragg peak is shown in Figure 12. This rocking curve is obtained by stopping the θ,2θ scan at the maximum reflectivity. The incident angle, θ, is then "rocked" while keeping the detector fixed at the initial Bragg condition. Figure 3 displays a sharp specular component when the incident angle, θ, reaches the Bragg condition. The peak occurs at an incident angle of approximately 0.42°. The specular component is on top of a diffuse background that is caused by both the correlated and uncorrelated interfacial roughnesses. For the W/Al2O3 multilayers, the ratio is ~10,000. This ratio is comparable or
higher than the ratio of ~5,000 reported for the best multilayer x-ray mirrors with low interfacial roughness.

The high x-ray reflectivity obtained by ALD techniques is attributed to the precise bilayer thicknesses and ultra-smooth interfaces obtained by ALD. The atomic level control of growth during ALD produces precise bilayer thicknesses. The self-limiting surface chemistry during ALD ensures that every surface reaction goes to completion. This ALD growth mechanism prevents randomness in the deposition process that can produce interfacial roughness. In contrast, the stochastic nature of the deposition process during PVD can lead to more interfacial roughness depending on the growth mechanism.

Some interfacial roughness may result during ALD from nucleation difficulties or film crystallinity. However, the nucleation can be optimized by tuning the reaction conditions and the film crystallinity can be reduced by lowering the growth temperature. Because of the excellent conformality of the ALD process, any roughness in the multilayer will occur as correlated roughness. Correlated roughness is much less detrimental to specular reflectivity at the Bragg peak than uncorrelated roughness.

The growth of the W/Al₂O₃ nanolaminates is critically dependent on the nucleation and growth of the individual W and Al₂O₃ layers. Al₂O₃ ALD nucleates readily on the W nanolayer. However, W ALD has nucleation difficulties on the Al₂O₃ nanolayer. To understand the growth of the W/Al₂O₃ nanolaminate, we have explored the details of the W ALD nucleation on Al₂O₃ using QCM studies.
Figure 13 shows the W ALD mass gain per cycle (MGPC). This W ALD MGPC shows a distinct "ringing" behavior that reveals information about the underlying nucleation and growth mechanism. The "ringing" is always observed but can be shifted depending on the reaction conditions. The WF$_6$ exposures have little effect on this "ringing" as shown in Figure 13a. However, the Si$_2$H$_6$ exposures will shift the position of the "ringing" as shown in Figure 13b.

The low Si$_2$H$_6$ exposures require more cycles for nucleation.

These QCM results are in agreement with three-dimensional W island growth that produces a maximum in the W ALD MGPC. This maximum corresponds to the largest W surface area prior to the coalescence of the W islands. The growth of W islands is also revealed by atomic force microscope measurements of RMS roughness in Figure 14. The maximum roughness at low Si$_2$H$_6$ exposure is observed after 9 cycles as the W islands are reaching their largest surface area prior to coalescence.

We have explored the effect of the various reaction parameters on the W ALD MGPC and the surface roughness. We find that the smoothest W ALD films are fabricated using the high Si$_2$H$_6$ reactant exposures. The lower RMS surface roughness obtained with the higher Si$_2$H$_6$ exposures is shown in Figure 15. The best x-ray mirrors are obtained using these higher Si$_2$H$_6$ exposures.

We have excellent QCM data to use to test various models for the nucleation and growth of W ALD on Al$_2$O$_3$. The initial peak in the W ALD MGPC is attributed to the higher surface area of the W ALD film just prior to the coalescence of the W islands. One-dimensional and two-dimensional modeling has been performed to simulate the W ALD nucleation and growth. The increasing roughness with number of AB cycles can be understood in terms of initial
expansion of circles or spheres. One of these simulations is shown in Figure 16. Colors indicate the time evolution from red to blue and then the repetition of this same progression. Four islands are nucleated randomly in time. After the initial peak in surface roughness, the film progressively smooths as the islands grow together.

Many applications of the W/Al₂O₃ nanolaminates for x-ray optics, such as x-ray lasers and x-ray microscopes, may require a laterally-graded multilayer. Laterally graded multilayers have a bilayer spacing that continuously changes versus spatial position. These graded multilayer structures are important for x-ray collimation and x-ray focusing. To obtain laterally graded W/Al₂O₃ multilayers, the normal conformality of ALD must be circumvented by preventing ALD on the entire substrate.

Laterally graded multilayers can be fabricated using a slit doser to localize reactant delivery in a viscous flow gas stream. The substrate is then translated relative to the slit doser with a magnetic linear translator as displayed in Figure 17. Since the viscous flow entrains the reactants and moves them downstream, substrate translation upstream of the slit doser prevents ALD on the entire substrate.
A laterally graded $\text{Al}_2\text{O}_3$ ALD film was initially demonstrated by translating the substrate relative to the slit doser during $\text{Al}_2\text{O}_3$ ALD reaction cycles. The variable angle ellipsometry and XRR results in Figure 18 quantified a varying $\text{Al}_2\text{O}_3$ film thickness grown on a Si(100) wafer with a length of 6 inches. Changes in leakage current density and capacitance confirmed the $\text{Al}_2\text{O}_3$ thickness gradient. In addition, a laterally graded ZnO/$\text{Al}_2\text{O}_3$ multilayer was grown and characterized using XRR. The angle of the first Bragg peak revealed a bilayer spacing that changed as expected versus spatial position. This work on laterally-graded multilayers is just beginning and will be developed further in the continuation of our AFOSR research.

In addition to our core research on W/$\text{Al}_2\text{O}_3$ nanolaminates, nucleation and growth during ALD and fabrication of designer multilayers for various technological applications, we have also worked on a variety of other ALD applications. We have started a new project on ALD on polymers. We have demonstrated $\text{Al}_2\text{O}_3$ ALD on various polymer films and polymer particles. We have also collaborated with a number of outside groups on ALD applications. We have continued to work on applications of ALD for microelectromechanical systems (MEMS). We have also demonstrated ALD on carbon nanotubes. Both of these collaborations have been very fruitful and have led to interesting results and publications.

The application of ALD on carbon nanotubes is especially interesting since carbon nanotubes are being proposed for a variety of technological applications. In most cases, the applications require that the carbon nanotube be functionalized to obtain a particular property. We have demonstrated that multi-walled carbon nanotubes can easily be coated with $\text{Al}_2\text{O}_3$ ALD. The $\text{Al}_2\text{O}_3$ ALD can then act as a starting layer for important
multilayer structures. For example, W ALD can be deposited on the Al₂O₃ ALD layer to form a conducting layer. Subsequently, an additional Al₂O₃ ALD layer can be deposited on the W ALD layer to form an additional insulating layer. This Al₂O₃/W/Al₂O₃ layer on the carbon nanotube would create a "carbon nanotube coaxial cable". A transmission electron micrograph (TEM) of a multi-walled carbon nanotube coated with an Al₂O₃/W/Al₂O₃ layer is shown in Figure 19. This TEM image was obtained by our collaborators at NIST-Boulder.

IV. Personnel Supported

Faculty

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

Postdoctoral Research Associates

1. Dr. Francois Fabreguette
2. Dr. Rikard Wind

Graduate Students

1. Zachary Sechrist
2. Chris Wilson

V. Publications

Many manuscripts describing our AFOSR-supported research and collaborations involving our AFOSR-supported research have been published during the last three years.


VI. Interactions/ Transitions

The results from our AFOSR-sponsored research on ALD and nanolaminates grown using ALD are technologically relevant. Atomic layer deposition (ALD) techniques have many useful industrial applications. In the past, our results have been implemented by the semiconductor industry. The most prominent example is W ALD. We initially developed W ALD to fabricate Al₂O₃/W ceramic/metal nanolaminates for superior thermal barrier coatings. Our W ALD process is now being used for contact hole filling. The self-limiting surface chemistry that we developed for W ALD is used by Applied Materials (Sunnyvale, Calif.) and Novellus (San Jose, Calif.) as a W seed in contact holes for W chemical vapor deposition (CVD). W CVD is used to fill the contact holes in the first level of backend interconnects.

Our ALD-supported by AFOSR has also found many applications for MEMS. We have collaborations with several groups in the Mechanical Engineering Department and CAMPmode at the University of Colorado. This work has been very productive. Over the first two years of this AFOSR grant, CAMPmode supported a postdoctoral research associate, Dr. Cari Herrmann,
who was dedicated to ALD for MEMS applications. Part of Cari’s research focused on a collaborative MEMS project with the Air Force Research Laboratory in Dayton, Ohio. In addition, we had a two year collaboration with Sandia National Laboratory in Albuquerque, New Mexico. Sandia funded a part time (2/3) postdoctoral research associate, Dr. Rikard Wind, to investigate the mechanical properties of ALD films for potential MEMS applications.

Over the last three years, we also have deposited a variety of ALD films on different devices and substrates for various industries. A list of our collaborations is given below. Some of these collaborations have led to direct industrial funding and others have led to Phase I or Phase II SBIR funding or in-kind support including equipment donations.

A. **Intel Corporation (through the NSF-sponsored Ceramic and Composite Materials Center at the University of New Mexico).** Intel Corporation is interested in diffusion barriers for copper interconnects and copper seeds for copper electrodeposition for multilevel interconnects. This collaboration has been funded by Intel membership in the NSF-sponsored Ceramic and Composite Materials Center at the University of New Mexico. This research utilizes one of the viscous flow ALD reactors that we developed during our support from AFOSR.

B. **Advanced Energy.** Advanced Energy in Fort Collins, Colorado, is a maker of power supplies and plasmas sources for the semiconductor industry. Advanced Energy is very interested in plasma ALD. They have provided plasma sources to facilitate our exploration of plasma ALD over the past several years. One of these plasma sources was used on a project that focused on ALD coatings on energetic organic materials. This project has been sponsored by Eglin Air Force Base and more recently by Phase II STTR funding.

C. **Synkera.** Synkera is a startup in Longmont, Colorado, that is focused on various nanotechnologies. We worked with them on an Phase I SBIR program. This project focused depositing nanorods in anodic alumina membranes for infrared dome applications. The ALD surface chemistry for the target material for the nanorods, AIN, was developed during our previous support from AFOSR. This project began Phase II funding in September 2005.

D. **Genus, Inc.** Genus, Inc. in Sunnyvale, California, is a provider of equipment for semiconductor fabrication. In the last several years, Genus has concentrated on equipment for ALD. We have worked with Genus on the development of new ALD surface chemistries for the deposition of nitrides, such as AIN. This work utilizes the ALD viscous flow reactors that we have built for our AFOSR-supported research.

E. **ALD NanoSolutions.** ALD NanoSolutions is a startup founded by the PI and Prof. Al Weimer in the Dept. of Chemical and Biological Engineering at the University of Colorado. Earlier, we received support from ALD NanoSolutions through an Phase I STTR program entitled "ALD of Oxidizer Coatings on Aluminum Nanoparticles to Fabricate SuperThermite Explosives". This earlier research initiated our work on organic energetic materials that is now
partially supported by Eglin Air Force Base. In addition, a subcontract on the Phase II STTR contract to ALD NanoSolutions for the continuation of this work began in January 2005.

We also received support from ALD NanoSolutions over the last year to demonstrate W ALD on Co nanoparticles and polycarbonate particles. The W ALD on Co nanoparticles is needed to protect small Co nanoparticles from oxidation. These Co nanoparticles are used to make WC/Co hard coatings. W ALD on polycarbonate particles may be useful to make conducting polymers that are effective for reduction of electromagnetic interference (EMI). ALD NanoSolutions has a strategic partnership with the OM Group in Cleveland, Ohio, that is supporting this research. The W ALD was developed during our earlier support from AFOSR.

**F. Hewlett Packard.** We have continued to collaborate with Hewlett Packard in Corvallis, Oregon to deposit tungsten on various MEMS structures using W ALD. These MEMS structures are for inkjet printers. The W ALD was developed during our earlier support from AFOSR.

**G. DuPont Research & Development.** Over the last two years, we received support from DuPont for two exploratory ALD projects. The first DuPont contract is funding a postdoctoral research associate to study the deposition of Al2O3 ALD on two DuPont polymers, Kapton and polyethylene naphthalate (PEN). Both of these polymers are important for organic electronics and organic light emitting diodes (OLEDs). This project has demonstrated that the Al2O3 ALD gas diffusion barrier helps to prevent H2O and O2 gases from diffusing through the polymer substrate and reacting with the oxygen-sensitive parts of organic electronic devices. This project utilizes an ALD flow reactor whose design was developed in our earlier research supported by AFOSR.

The second DuPont contract funded a postdoctoral research associate to study Cu ALD using some new precursors developed by DuPont. This project was very exploratory and used an ALD flow reactor design that was developed in our earlier research supported by AFOSR. This project was conducted from January 2004 through January 2005.

**H. Ferro Electronic Material Systems.** We have received support from Ferro for studies of ALD on BaTiO3 particles for application in multilayer capacitors. This work utilized surface chemistries for ZnO and SiO2 ALD that were developed during our earlier AFOSR support.

The PI has been invited to discuss our AFOSR-supported research at many invited talks:


42. "Atomic Layer Deposition on Polymers", Analytical Chemistry Division Seminar, Department of Chemistry and Biochemistry, University of Colorado, September 19, 2005.

43. "Al₂O₃ ALD as a Model ALD System", Division of Materials Science and Engineering, Hanyang University, Seoul, Korea, October 4, 2005.

45. "Atomic Layer Deposition on Polymers", Korea Research Institute of Chemical Technology (KRICT), Daejeon, Korea, October 5, 2005.


49. "Atomic Layer Deposition on Polymers", College of Natural Sciences, Kookmin University, Seoul, Korea, October 8, 2005.

50. "ALD of W/Al$_2$O$_3$ Nanolaminates: Applications and Challenges", 208th Meeting of the Electrochemistry Society (ECS), Symposium on ALD Applications: Challenges and Opportunities, Westin Bonaventure, Los Angeles, California, October 18, 2005.

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:


Patent applications based on AFOSR support currently under review include:


VIII. Honors/Awards

Over the last three years, Prof. Steven M. George received a number of honors and awards. These were: the University of Colorado Boulder Faculty Assembly Award for Excellence in Research, Scholarly and Creative Work (2006), the American Chemical Society Colorado Section Award (2004), the R&D 100 Award for Particle-ALD™ (2004) and the Inventor of the Year, University of Colorado at Boulder (2004). Prof. George also has received a National Science Foundation Creativity Award, 2002-2004.

Prof. George has also been elected a Fellow in the American Vacuum Society (2000) and a Fellow in the American Physical Society (1997). Prof. George has also received the Presidential Young Investigator Award (1988-1993) and the Alfred P. Sloan Foundation Award (1988). Prof. George is also very active in the American Vacuum Society (AVS). He was Program Chair for the AVS International Symposium in Boston from Oct. 30-Nov. 4, 2005. He also teaches the AVS one-day short course on Atomic Layer Deposition and has been on the Conference Committee for the AVS Topical Conference on Atomic Layer Deposition from 2001-2006.