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Use of Plasma Enhanced ALD to Construct Efficient Interference Filters for Astronomy in the FUV

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ABSTRACT

Over the past few years the advent of atomic layer deposition (ALD) technology has opened new capabilities to the field of coatings deposition for use in optical elements. At the same time, there have been major advances in both optical designs and detector technologies that can provide orders of magnitude improvement in throughput in the far ultraviolet (FUV) and near ultraviolet (NUV) passbands. Recent review work has shown that a veritable revolution is about to happen in astronomical diagnostic work for targets ranging from protostellar and protoplanetary systems, to the intergalactic medium that feeds gas supplies for galactic star formation, and supernovae and hot gas from star forming regions that determine galaxy formation feedback. These diagnostics are rooted in access to a forest of emission and absorption lines in the ultraviolet (UV)[1], and all that prevents this advance is the lack of throughput in such systems, even in space-based conditions. We outline an approach to use a range of materials to implement stable optical layers suitable for protective overcoats with high UV reflectivity and unprecedented uniformity, and use that capability to leverage innovative ultraviolet/optical filter construction to enable astronomical science. These materials will be deposited in a multilayer format over a metal base to produce a stable construct. Specifically, we will employ the use of PEALD (plasma-enhanced atomic layer deposition) methods for the deposition and construction of reflective layers that can be used to construct unprecedented filter designs for use in the ultraviolet.

Keywords: Plasma Enhanced, Atomic Layer Deposition, Far Ultraviolet, Reflective Coatings, Interference Filters, Optical Construction

1. INTRODUCTION

NASA is interested in fostering the development of innovative low-TRL techniques that support the maturation of key technologies to the point at which they are feasible for implementation in space flight missions. The case for this need in the UV has been made by Scowen et al [2] where, as part of a COPAG (Cosmic Origins Program Analysis Group) RFI to the astronomical community, next generation science cases were submitted to NASA for what new UV capabilities would be necessary to address pivotal science in the next decade. While no specific UV space mission has been identified by the Decadal Survey on Astronomy and Astrophysics, the need for the development of this technology has been made clear in the NASA Space Techology Roadmap (2012), and places priority on the improvement of coating technologies for FUV reflectivity and associated filter design and manufacture in the same passband. It is this need that our work seeks to address.

Our work seeks to demonstrate several things:

- That films of material can be deposited as a demonstration of the approach using PEALD (plasma-enhanced atomic layer deposition) techniques to produce low-loss oxide films of materials such as Si, Hf and Al. The resulting coatings will be of a thickness and a purity far higher than can be delivered by current techniques that involve sputtering deposition.

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- That using the same deposition techniques, PEALD can be used to deposit thin (10s of nm) low-loss films of fluoride materials such as MgF_2, LiF, AlF_3, LaF_3, CaF_2, BaF_2 that will be used as protective overcoats for materials that can easily be oxidized by exposure to air.
- That Al deposition, protective layer deposition and characterization can be completed *in-situ*. Such a controlled environment will minimize the oxidation forming undesirable compounds, to improve the reflectivity of the resulting films and their interfaces by reducing scattering and adsorption.
- That deposition of such protective overcoats over aluminum metal can be achieved with PEALD to provide a sufficiently crystalline, uniform and stable structure that extend the range of diagnostic emission and absorption lines available for science.
- To apply multiple alternating layers of metals and dielectrics using our PEALD approach to produce multi-cavity structures exhibiting very high performance. This goal is currently limited by the inability to deposit very thin layers with great accuracy, while demonstrating film toughness and 'bulk' thin film material losses.
- To apply the PEALD approach to the construction of multi-layer dielectric layers to act as reflection filters or high reflectors in narrow band systems.
- To similarly construct multi-layer broadband reflective surfaces which are thought to exhibit higher performance than metal-based mirrors (using a short wave extension to prototype dichroics our group is already developing for space).

The deposition techniques listed above have been observed in several independent test cases, and the technology approach has been designed and formulated using computer modeling. As such we can assign a TRL of 3 to the use of ALD materials in this manner, in accordance with the typical definitions used by NASA. This program will demonstrate the ALD approach to deliver low-loss oxide films, and then merge that approach with deposition over metal to produce multilayer filters that can isolate specific emission lines for scientific use in space (where one has to observe the FUV due to atmospheric absorption). Our goal is to demonstrate the approach as a proof of concept to raise the technology to a TRL of 4 by the end of the program.

The improvement in performance in surface reflectivity, combined with the advances in FUV filter design and construction using the same deposition techniques, provide the promise of a dramatic increase in performance and reliability in space-based FUV mission design. We will be investigating whether the application of fluoride-based coatings using our approach can provide better coating techniques that will allow better, more controlled and higher throughput coatings. We believe the use of ALD to construct both reflective layers and multilayer Fabry-Perot cavities using heretofor untested fluoride-based materials will provide the desired performance improvement which NASA seeks because it will deliver thicker, more stable, more uniform ALD coatings using fluorides that can produce high UV reflectivity.

To be clear, the techniques we will be using have already been demonstrated to work individually – the goal of this work is to combine these techniques in a single working environment to produce the proposed end products: thicker, more stable, more uniform ALD coatings using fluorides that can produce high UV reflectivity, and to use that capability to build alternate metal / dielectric filter assemblies that provide high efficiency narrowband filters for use in the FUV. Our goal is to demonstrate the ability to provide production reliability for our processes so they can be used for instrument development for future space missions.

1.1 Filter Coatings and Design

Reflective coatings in the UV have typically employed aluminum with a magnesium fluoride protective overcoat to prevent a highly absorbing oxide layer from building up on the aluminum surface. Magnesium fluoride is highly transmitting throughout the UV but cuts off sharply below 120 nm. Aside from the short wavelength cut-off, magnesium fluoride layers can be tuned to optimize reflectance near a single wavelength, reflectance maxima peak near 90% though more typically reflectance between 85-90% is achieved. Such performance gains, when applied to larger astronomical optics and multiple surfaces, can enhance performance by 20-50%. Broadband transmissive coatings are mainly used as an anti-reflection coating and/or a protective coating for hygroscopic window/lens materials. As with broadband reflective coatings, these provide gains of a few percent per surface, with an impact that grows when additional optical components are added.

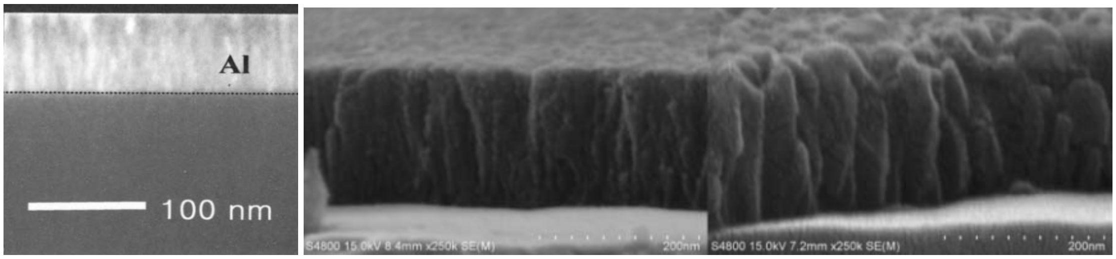

Figure 1. At Left: Cross-section SEM images of Al/Si, At Center and Right: MgF2/SiO2/Si. Varied deposition temperatures achieved different film morphologies. These coatings are not optimized for minimal thickness as we will do in this project.

Past approaches applied to coating bare aluminum surfaces have suffered from a number of issues and have not met theoretical expectations[3]. One of the primary degradation mechanisms is related to the oxidation of the Al surface. Even a 5nm oxide results in a 3% reflectivity reduction at 193 nm wavelength and a > 30% reduction at wavelengths less than 140 nm. *In situ* deposition of a protective coating layer is required, but even here there are restrictions that have limited past approaches based on physical deposition. The morphology of deposited Al reflective surfaces substantially degrades at elevated temperatures (maintaining a temperature less than 100C is recommended). Sputtered or evaporated protective layers at these low temperatures typically exhibit columnar structure and oxidation can proceed through grain boundary diffusion leading to Al surface oxidation (see Figure 1). The low deposition temperatures and uniform coverage of plasma enhanced ALD holds the potential to overcome these limitations. Based on our models, PEALD oxide protective layers (SiO_2 or Al_2O_3) can extend the cutoff to less than 190nm and PEALD fluoride coatings (MgF_2, AlF_3, LaF_3, etc.) hold the potential to extend the cutoff to less than 120 nm. In addition, a thin oxide could be used to protect the fluoride layers for some applications. The fact that pinhole free PEALD layers can routinely be obtained at thicknesses less than 5nm is another significant advantage when designing the coating thickness for a specific application.

Unlike the broadband filters, conventional UV bandpass filters require dielectric multilayer coatings. High index layers are highly absorbing, limiting their use in transmission filters. A lack of options for a mix of high and low index materials complicate the design of filters and dichroics. In addition, the preservation of wavefront error becomes more difficult as the number of layers increases, which will be critical for future diffraction limited system in space to produce filters that do not contribute to the overall wavefront error. Narrower high index layers improve performance at the cost of increased requirements for deposition thickness control and uniformity. Reflective bandpass and blocking filters can achieve good performance, although it is hard to incorporate these into compact optical designs. Bandpass filter requirements are application specific (e.g. centered on key astrophysical emission lines or bands, line-free regions or absorption features). Reflective narrowband and dichroic/red-rejection filters have been designed and implemented using standard deposition techniques (electron beam with and without ion-assist, thermal evaporation). In general, these filters have never achieved theoretical performance because maintaining layer thickness control and uniformity of film optical constants is challenging using these deposition techniques. With the availability of atomic layer deposition, the empirical limits of coating performance can be re-evaluated, and new designs incorporating single atom nano-layers can now be implemented.

1.2 Plasma-Enhanced Atomic Layer Deposition

Research suggests ALD will have favorable implications for optical coatings. In particular, ALD not only produces conformal and uniform films with precision control of the thickness to a fraction of a monolayer but also allows for the tuning of films properties. For example, a recent study by Yang *et al*.[4] has shown the index of refraction of Al_2O_3 varies from 1.61 to 1.68 as the deposition temperature ranges from 110 to 300 °C. Moreover, there is evidence that ALD deposited coatings show extraordinary resistance towards concentrated alkali solutions, various chemical etchants, and solvents as shown by Du *et al.*[5]; this research demonstrate ALD films were able to protect aluminum mirrors from dissolution for 30 times longer than those with e-beam sputtered films.

Plasma-enhanced ALD (PEALD) is an energy-enhanced ALD technique that utilizes the reactivity of plasma radicals to drive the surface reaction rather than thermal energy like traditional ALD (see Figure 2). Consequently, this system has several key advantages over traditional thermal ALD and other vapor-phase deposition techniques:

Lower impurity content. In comparison to thermal ALD, PEALD reduces the impurity content in the film. This advantage is a consequence of the reactivity of the plasma radicals, which more effectively remove the ligands—generally consisting of carbon and hydrogen[6-11]. For example, Muschoot *et al.*[12] showed that while ALD V_2O_5 films contained ~7% carbon, incorporating a plasma-process reduced the carbon contamination below the XPS detection limit.

Increased growth rate. In some cases, plasma-enhanced ALD has been shown to generate more reactive surface sites than thermal ALD. This enables a higher growth rate in cases where the growth per cycle (GPC) is reactive-site limited. For example, Ru is a particular difficult metal to nucleate with thermal ALD, which may take up to 40 cycles; however, with PEALD, this nucleates within the very early stages[13]. Furthermore, since plasma-enhanced is more reactive than thermal ALD, the second reactant step is often shorter, decreasing cycle time. Consequently, PEALD can increase ALD throughput capabilities, a desirable trait for industrial applications.

Improved stoichiometry. The non-equilibrium aspects associated with ALD plasma can be tuned to control the surface reaction and ultimately the stoichiometry of the material. In particular, additional operating variables such as operating pressure, plasma power, exposure time, biasing voltage, and admixing additional gasses into the plasma can tune the surface reaction. For example, in some cases, N_2 gas may be introduced during the O_2 plasma reactant step, resulting in N-doped films. This is not possible with thermal ALD.

Lower deposition temperature. Since the high reactivity of the radicals and kinetic energy of the ions supply energy to drive the reaction, significant thermal energy is not required. Consequently, PEALD can deposit high-quality films at much lower substrate temperatures. This feature accommodates a wider variety of substrates, which may be temperature sensitive. Moreover, films deposited at lower-temperature may have properties, such as film density or reflectivity, which are not achievable at higher temperatures.

Greater range of materials. The higher reactivity of the plasma radicals also allows for the use of precursors with relatively high chemical and thermal stabilities; e.g. metal oxides from β-diketonates. These precursors exhibit little or no reactivity in thermal processes but demonstrate high-quality oxides with O_2 plasma. In other words, PEALD allows for the incorporation of less reactive precursors, which often reduces the safety hazards associated with the precursors as well.

Versatility. The energy brought to the surface may also be tuned with greater versatility using parameters such as plasma power, operating pressure, exposure time, admixing of additional gases, and sample biasing to induce ion bombardment at the sample surface; this enables a greater range of control in the tuning of film properties.

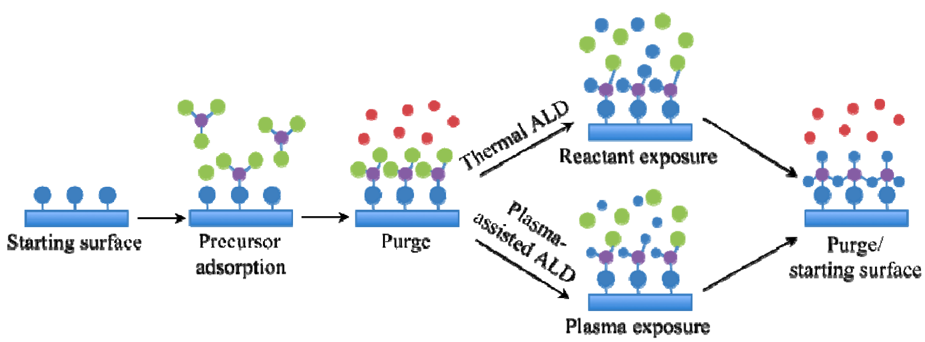

Figure 2. Schematic representation of the layer-by-layer deposition process of the thermal and plasma-enhanced ALD. During the reactant or plasma exposure, the surface is exposed to a reactant gas or plasma.

In other words, PEALD results in films with improved materials properties with greater versatility and tunability. Films deposited by PEALD may thus have distinct properties from those deposited by thermal ALD, where PEALD presents a unique approach with gainful capabilities. In particular, both the reduction of impurities and the additional energy provided by the plasma, which increases the local temperature of the films, improve crystallization. The extent of crystallization is, therefore, often critically dependent on the plasma properties, or conversely, tuning the plasma characteristics can regulate the crystallinity, density, and thus reflectivity[14].

1.3 The Promise of Narrowband FUV Data

It has been recognized that at mid- and near-ultraviolet wavelengths ($90 < \lambda < 300$ nm), it is possible to detect and measure important astrophysical processes, which can shed light into the physical conditions of many environments of interest. For example, in the local interstellar medium (LISM) all but two (Ca II H and K lines) of the key diagnostic of resonance lines are in the UV[15], which is depicted in Figure 3. In addition to the fruitful science areas that UV spectroscopy has contributed since the early 1970s, France et al[17] have emphasized the role of UV photons in the photodissociation and photochemistry of H_2O and CO_2 in terrestrial planet atmospheres, which can influence their atmospheric chemistry, and subsequently the habitability of Earth-like planets. However, only limited spectroscopic data are available for extrasolar planets and their host stars, especially in the case of M-type stars. Similarly, new areas of scientific interest are the detection and characterization of the hot gas between galaxies and the role of the intergalactic medium (IGM) in galaxy evolution[1].

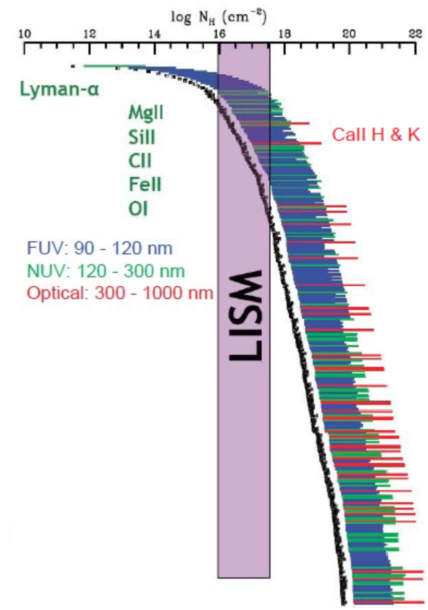

Figure 3. All but two of the key diagnostics lines are in the UV for the local interstellar medium (LISM) (taken from [16]). The top scale indicates the typical column densities these diagnostic transitions probe.

NASA has invested substantial resources in advancing UV imaging and spectroscopy in space missions, most recently, in the Small Explorer Galaxy Evolution Explorer (GALEX[18]) and the Hubble Space Telescope (HST) instruments Cosmic Origins Spectrograph (COS) and the Space Telescope Imaging Spectrograph (STIS). Legacy NASA missions include Copernicus, IUE, Astro I/II (UIT, WUPPE, HUT), ORFEUS (SPAS I & II; IMAPS, BEFS, TUES), EUVE, FUSE, HST instruments (FOC, WPFC2, FOS, GHRS, ACS) and some limited imaging capabilities in SWIFT. Other substantial investments include technology development and maturation in devices such as detectors, optics, coatings, and other supporting technologies like spectral calibrators, coronagraphs, and occulters. Similarly, NASA has an active technology program in the area of suborbital platforms, including stratospheric balloons and sounding rockets and several of these payload experiments include UV imaging and spectroscopy capabilities (e.g., FIREBALL, FORTIS, FIRE, IMAGE, PICTURE, etc). This work would directly improve all of these missions by improve the quality and control over the construction of optical filters in the ultraviolet.

The Habitable Zone around Low-Mass Stars

The ultimate goal for exoplanetary science in the next two decades is the detection and characterization of habitable, Earth-like worlds. Stellar characterization is critical to interpreting these observations. An investment in stellar characterization is particularly important for low-mass stars (M- and K-dwarfs), which are perhaps the most promising targets for the detection of habitable planets[19,20]. A spectroscopic survey of low-mass exoplanet host stars from 91.2 – 400 nm would be able to characterize the spectral and temporal behavior of these systems, an essential input for atmospheric models of habitable zone planets. A candidate future UV mission employing narrowband moderate resolution (~10 km s^{-1}), low-background equivalent flux levels ($\leq 10^{-18}$ erg cm^{-2} s^{-1} $Å^{-1}$ in 10^4 sec), and photon-counting detectors ($\Delta t \leq 1$ sec) would enable such a survey of the known M-dwarf exoplanetary host stars within 50 pc (and K-dwarfs to > 200 pc), which would include all of the systems that can be studied in detail by *JWST*. The UV bandpass offers the best set of chromospheric, transition region, and coronal activity diagnostics in low-mass stars (the HI Lyman series, FeXVIII λ97.4, CIII λ97.7, OVI λ103.2, SiIII λ120.6, OI λ130.4, CII λ133.5, FeXXI λ135.4, CIV λ155.0, HeII λ164.0, and MgII λ280.0) that are critical to the characterization of the energetic radiation environment.

Transiting Planets

Short period planets are exposed to strong UV radiation fields from their host stars, and this energy deposition can inflate the planetary atmosphere. UV observations can probe the extended upper atmospheres of the planets, providing unique access to the strong resonant transitions of the most abundant atomic constituents that can be observed in absorption during transit (e.g., H, O, C^+, Si^{2+}, and Mg^+ have been detected so far[21,22,23,24]). In order to probe the details of atmospheric escape from "hot Jupiters", and eventually terrestrial mass planets, a new observational capability would be required. Observations of Rayleigh scattering are the most direct means of determining the atmospheric scale height for both Jovian and terrestrial planets[25,26], an essential parameter for the interpretation of near- and mid-IR molecular transmission spectra from future (or proposed) NASA missions such as *FINESSE* and *JWST*. High-sensitivity, moderate spectral resolution near-UV (170 – 400 nm) narrowband observations would allow us to observe Rayleigh scattering of H_2, haze, and possibly CO_2 and N_2 atmospheres at the wavelengths where this mechanism has the largest observable signature[27].

Measuring the Radial Structures and Elemental Abundances of Gas Disks

At the distances of typical star-forming regions (e.g., Taurus-Auriga or the Orion Nebula Cluster), 1 AU corresponds to an angular scale of < 0.01′′. ALMA is carrying out high-resolution molecular spectroscopy of protoplanetary disks, but is less sensitive to warm/hot gas at terrestrial planet-forming radii. Therefore, if one wishes to probe molecules in the region of terrestrial and giant planet-formation, UV and IR spectroscopy will be the technique of choice for the foreseeable future. UV narrowband observations are a unique tool for observing the inner molecular disk as the strongest electronic band systems of H_2 and CO reside in the 100 – 170 nm bandpass[17,28]. The composition and physical state (e.g., temperature, turbulent velocity, ionization state) of a cross-section of the circumstellar environment can be probed using high-resolution absorption line spectroscopy of high-inclination (i > 60□) disks. Spectral coverage in the 91.2 – 115 nm bandpass is particularly important for this work as the bulk of the warm/cold H_2 gas is only observable at λ < 112 nm (via the Lyman and Werner (v' - 0) band systems).

2. TECHNICAL DETAILS AND METHODS

The Nano Science Laboratory (NSL) at Arizona State University (ASU) maintains a multi-chamber UHV system, and is managed by Nemanich. The system, pictured in Figure 4, includes a linear UHV sample transfer and chambers for surface processing, film growth, and electronic structure analysis. Currently, the chambers consist of the following: remote plasma processing for surface treatment, remote plasma enhanced atomic layer deposition, reactive molecular electron beam deposition, electron beam metal deposition, electron-cyclotron resonance (ECR) deposition of boron nitride, UV photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), and auger electron spectroscopy (AES). *Ex-situ* characterization via atomic force and related probe microscopy techniques is also available at this facility. This integrated system has unique capabilities for coating freshly deposited metal layers, where maintaining a clean surface and interface is crucial.

Oxide PEALD. This chamber is used to grow metal oxides or alloys with precise thickness control, including HfO_2, Al_2O_3 and SiO_2, ZnO, and Ga_2O_3.

Proposed fluoride PEALD (Plasma-Enhanced Atomic Layer Deposition). PEALD is used to grow metal fluorides or alloys with precise thickness control. This will include the proposed materials i.e., MgF_2, LiF, AlF_3, LaF, CaF_2, and BaF_2 as described by the deposition process below.

Proposed Metal PEALD. N_2, H_2, and NH_3 can also be used as reducing agents to grow metals in ALD as discussed below. This system is also used for surface preparation or post-deposition processing using the remote plasma reducing agents. This system will be modified to enable Al deposition using trimethylaluminum (TMA) and hydrogen. The modification will include an exhausted cabinet to hold the pyrophoric TMA, a system level upgrade to enable computer control of gas delivery and plasma, and a modified pumping system (upgraded dry pumping).

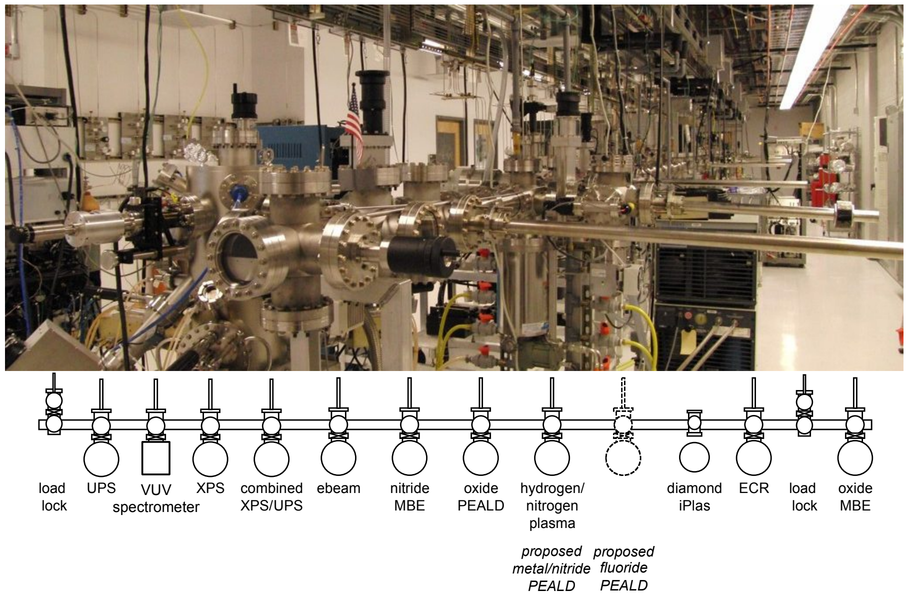

Figure 4. Photograph and schematic of the integrated processing, growth, and characterization system of the Nanoscience Laboratory. The new ALD chambers are indicated in the schematic. The other chambers are all used in the research outlined in section 2.

E-beam. This deposition system is equipped to deposit five metals, including Al, Au, Cu, Ti, and Ta. The Al source will be employed prior to availability of the PEALD Al deposition.

XPS (X-ray Photoelectron Spectroscopy). XPS can be used to characterize the electronic state, chemical state, elemental composition, and empirical formula of the elements in the measured material. This technique will be used to monitor interface contamination and dielectric film properties and thickness. The in situ capability is crucial for optimizing the ALD growth processes.

UPS (Ultraviolet Photoemission Spectroscopy). UPS is used to characterize the electron affinity, work function, or valence band maximum of materials. This UV discharge lamp can accommodate He, Ar, and Kr which will enable a number of lines to explore optically induced electron transitions at the metal-dielectric interface.

UV-reflectivity. An existing UHV chamber will be modified to obtain UV reflectivity and/or transmission measurements to ~125nm in year 1 and to ~90nm. The system will initially include a deuterium source with a VUV double monochromator (McPherson 234/302D double monochromator). The monochromator will be pumped for these measurements. The sample chamber is fitted with a MgF_2 window to allow light into the system. The reflected light intensity will be measured with a calibrated photodiode. The system will be upgraded to include a windowless hydrogen discharge lamp. The sample chamber will be modified to include a gate valve between the chamber and the monochromator which will provide windowless access to the PEALD samples. This system is connected to the UHV transfer line which means that samples can be measured immediately after preparation, and then as a function of time to assess degradation mechanisms.

AES (Auger Electron Spectroscopy). AES can specify the composition of the surface layer of a sample.

AFM (Atomic Force Microscopy). *Ex situ* AFM can characterize the morphology, physical, chemical, and magnetic properties of the sample surface.

2.1 Atomic Layer Deposition

Our implementation of the atomic layer deposition (ALD) process uses a chemical vapor deposition technique, which we use to synthesize the ultra-thin films. This process uses a cyclic self-limiting gas-phase chemical process, where each cycle of ALD growth consists of four steps, shown above in Figure 2. First, there is a self-limiting reaction between the substrate and precursor; second, a purge step to remove non- reacted precursor and gaseous by-products of the reaction; third, a self-limiting reaction between the reactant and the surface, which typically replaces the ligands of the precursor; and last, another purge step. This gives a growth rate in terms of growth per cycle (GPC), typically 0.5-1.5 Å[29]. Consequently, the thickness of the film can be precisely controlled to a fraction of a monolayer. Furthermore, the self-limiting process generates uniform conformal films[30,31].

At NSL, the ALD is a remote oxygen plasma-enhanced ALD (PEALD) system. This system is a subset of ALD that uses oxygen plasma as the oxidizer rather than H_2O as traditional in thermal ALD. Use of a plasma oxidizer has several advantages over traditional thermal ALD and other vapor-phase deposition techniques. Since plasma species are highly reactive, PEALD allows for more freedom in processing conditions and for a wider range of material properties. More specifically, the increased reactivity of the plasma species enables deposition at lower substrate temperatures, which reduces the thermal damage to the substrate; permits the use of less reactive precursors, which increases the choice of precursors; allows for better control of stoichiometry and film composition; and accelerates the growth. The results are films with improved materials properties, such as film density[32-38], impurity content[39-47], and optical properties[35,38,39,41-43]. Furthermore, the oxygen plasma allows for better processing versatility.

2.2 PEALD Metal Oxides

Background: The deposition of Al_2O_3, HfO_2, and SiO_2 via PEALD has been developed in the NSL and described in recent papers[48-50]. These studies have provided the opportunity to optimize and characterize the growth of these oxides with the specifics of the system at NSL. Results demonstrate the PEALD system reduces residual carbon contamination in the dielectrics below the detection limit of XPS, which shows fewer impurities than thermal ALD or other conventional thin film deposition method. (See Figure 5) Furthermore, the optimization process ensures each ALD cycle is indeed self-limiting. This process is summarized in Figure 6 for PEALD Al_2O_3 using DMAI (dimethylaluminum isopropoxide, $(CH_3)_2AlOCH(CH_3)_2$). In this case, Al_2O_3 was grown on Si with a native oxide. The thickness of the films was determined with an *in-situ* quartz crystal microbalance and XPS and further confirmed with Rutherford Backscattering (RBS) and x-ray reflectivity (XRR). The self-limited growth rate of Al_2O_3 is ~1.5 Å/cycle within the growth window of 130-220 ºC. This process gives a film density of ~2.96 g/cm^3 as measured by XRR, which is about 10-20% higher than thermal ALD[41]. Similar studies for HfO_2 and SiO_2 have determined the respective growth rates of ~1.4 Å/cycle and 0.7 Å/cycle at ~220 ºC and 300 ºC. It is worth noting that these growth rates are slightly higher than expected, which is likely related to the presence of active oxygen at the surface after oxidation[42-54].

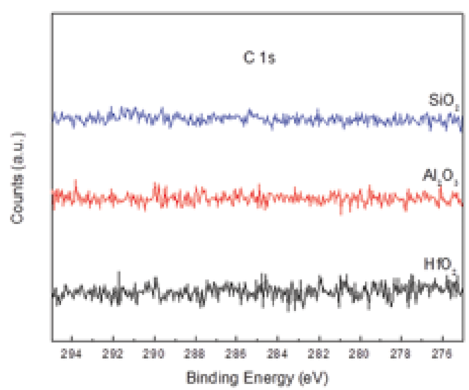

Figure 5. XPS C 1s peak of PEALD SiO_2, Al_2O_3, and HfO_2.

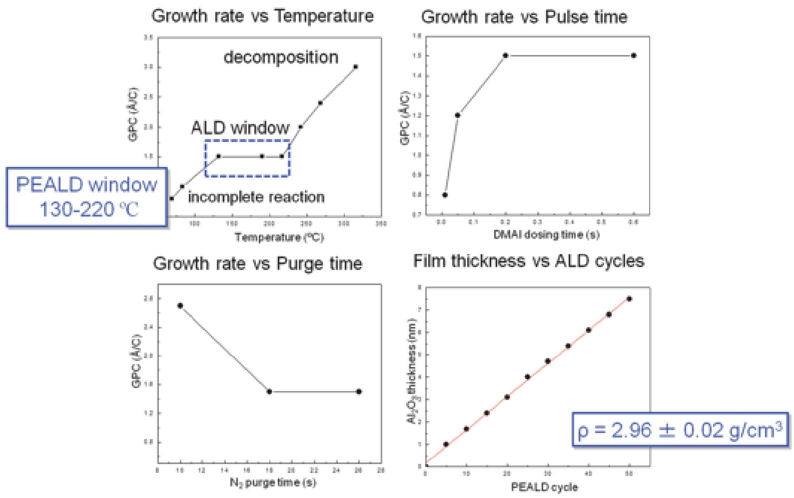

Figure 6. Growth rate dependence of PEALD Al_2O_3 using DMAI on substrate temperature and pulse time. This process optimizes deposition to ensure self-limiting, uniform, and conformal deposition.

Research Goals: The goal of this task will be to deposit oxide layers directly on freshly deposited Al surfaces – it is regarded as a necessary intermediary step in the development of the approach and is not intended to be part of the production recipe as we know that the UV reflectivity of oxides is very low – this is the very problem we are looking to solve by moving to the use of fluorides in the next step. The fresh Al surfaces will be prepared in the metals PEALD system or by e-beam evaporation. Both chambers are part of the UHV system and the Al surfaces will be transferred in ultra high vacuum to the oxide PEALD system. In this project, we intend to further adapt PEALD to examine the optical properties of these materials for UV applications. This will include determining relevant properties such as the index of refraction, adsorption coefficient, band gap…etc. We will also continue characterizing and optimizing the deposition process to ensure that the films are of the highest quality possible. In addition to optimizing the PEALD process, we plan to include a He plasma pulse after the oxygen plasma step. This additional step will add only a few seconds to each cycle, and will provide UV light to assist in ligand removal. We anticipate that this step will result in substantially reduced optical absorption.

A sidebar here is that while oxide deposition would seem to be counter-productive to our stated goals, since Al_2O_3 has terrible UV reflectivity, it should be pointed out that use of the oxide can be made to develop, for instance, a narrowband 190.9nm transmission filter, as evidenced by the model shown in Figure 7. The point to be made here is that while the oxide stage is a necessary step in our development path, there is an actual application that the material could be used for. The specific matching of material to bandpass selection and width is something that our approach will open up and provide a level of flexibility that is quite marketable.

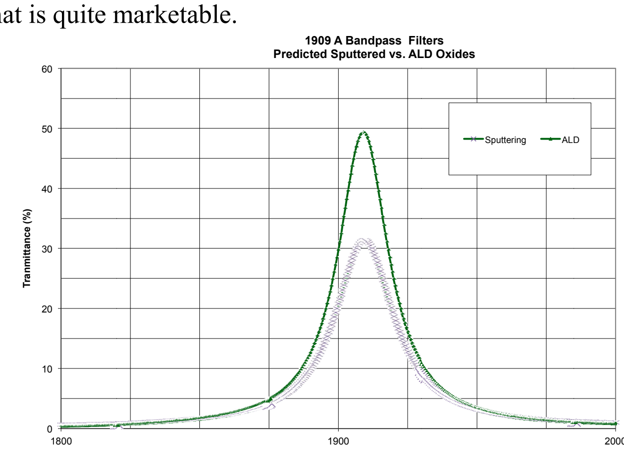

Figure 7: Comparison of Bandpass Filter performance with layers deposited via sputtering as compared with the performance expected from ALD deposited layers. This is for aluminum oxide layers providing a bandpass transmission at 1909 Angstroms. Notice the 66% improvement in throughput, which in the UV, is a large difference due to low reflectivity problems with most coatings.

2.3 PEALD Metal Fluorides

Background: In light of the traditional ALD chemistry mentioned, which utilizes the chemisorption of a precursor and subsequent oxidation to grow metal oxide, it is reasonable to assume a similar process could be adopted to grow metal fluorides, which possess the desired high reflectivity in the UV. However, a simple fluorination step has proven difficult. The selection of non-metal reactive precursors that contain fluoride is limited, and the few reactants that are available, namely HF, are highly corrosive[55]. More recent work has thus focused on alternative fluorination sources. Research by Pilvi *et al.*[56,57] used metal β-diketonates as metal precursors and metal fluorides, such as TiF_4 and TaF_5, as a fluoride source to successfully deposit MgF_2, CaF_2, and LaF_2. The reactive ligand exchange that occurs between these two precursors results in the deposition of oxygen-free films; however, the process also introduces small amounts of titanium and tantalum contamination. Another approach to deposit metal fluorides has been demonstrated using oxide chemistry by Putkonen *et al.*[58]. This study took two approaches. The first used a fluorinated Ca β-diketonate and O_3 to successfully deposit CaF_2. The low concentration of oxygen in the CaF_2 films (<5%) implies that the strong oxidation of ozone is not so reactive as to convert metal fluoride into metal oxide. The second approach introduced additional steps to the ALD cycle, using non-fluorinated β-diketonates and ozone to generate a metal oxide followed by hexafluoroacetylacetone dehydrate (Hhfac) and ozone to fluorinate the oxide. The results were polycrystalline MgF_2, CaF_2, and LaF_2 films with less <2% oxygen content at a growth rate of ~0.4-0.5 Å/cycle. It was noted that the ALD fluoride films were characterized by an increase roughness as measured by AFM, TEM, and ellipsometry regardless of the deposition chemistry[56,58,59]. More specifically, films around 50 nm had a roughness of ~5 nm and the ellipsometrically deduced surface layer thickness ranged from 2 to 8 nm suggesting post processing surface reactions.

Research Goals: The successful deposition of metal fluorides through oxide chemistry suggests that oxygen plasma may also be used to successfully grow metal fluoride films. We, therefore, suggest a similar approach to deposit MgF_2, LiF, AlF_3, LaF_3, CaF_2, and/or BaF_2. Properties are summarized in Table 1.

Table 1: Physical and Atomic Properties of Metal Fluorides

Material	Band Gap	Refractive Index		Refs.
MgF_2	10.8 eV	1.36	1.43*	[60,61]
LiF	~14.0 eV	1.39	1.47*	[61-63]
AlF_3	10.8 eV		1.43*	[64,65]
LaF_3	10.3 eV		1.69*	[61,66]
CaF_2	~12.1 eV	1.80		[67,68]
BaF_2	11.3 eV	1.54		[69]

*Refractive index of films deposited by ALD. Please note that there are variations in these values as dependent on the deposition and/or measurement techniques.

A new PEALD system will be developed for the fluoride materials. Sources for MgF_2, CaF_2 and LaF_3 or AlF_3 will be incorporated into the system. The system will be designed to use an oxygen plasma source following the process developed by Putkonen *et al.*[58]. While that process employed ozone, we anticipate that the oxygen plasma will provide more flexibility and enable lower deposition temperatures. The three materials are chosen to provide layers with different dielectric constants to enable multi-layer interference structures. With the precise thickness control obtainable with PEALD and the computer controlled system we anticipate being able to demonstrate highly reflective VUV structures.

We will continue our investigations to optimize the process and determine related surface chemistry. The optical properties of the subsequent films will be characterized by spectroscopic ellipsometry for UV applications. We will also explore specific surface terminations that will improve the stability of the fluorides.

2.4 PEALD Metals

Background: Unlike the deposition of oxides or fluorides, the deposition of metals via PEALD cannot be achieved with oxide chemistry. This is particularly true of Al, which readily oxidizes. Instead, metals must be deposited with a reducing reactant such as H_2, N_2/H_2 or NH_3 plasma. There are several studies[70-79] that have successfully deposited Al. In the studies by Lee *et al*.[70,71], deposition was achieved using trimethylaluminum (TMA) and H_2 plasma. The growth rate was saturated at 1.5 Å/cycle. AFM showed the subsequent Al films to be smooth surface, and cross-sectional FESEM revealed excellent step coverage and conformality. As noted above a low deposition temperature is required and would be readily obtained with PEALD[29]. With the multi chamber system available in the NSL, these surfaces will be transferred to the oxide or fluoride PEALD systems for layer growth or to the XPS system to characterize the Al surface oxide.

Research Goals: We will be upgrading our current $H_2/N_2/NH_3$ plasma chamber to a PEALD system, which will allow for the deposition of metals. This conversion has previously been achieved, when a similar remote O_2 plasma chamber deposition was converted into what is now the oxygen PEALD system. The chamber will have computer controlled precursor delivery as well as purge and plasma cycles. The deposited layers will be characterized in situ by XPS and reflectivity measurements. These surfaces will serve as substrates for the oxide or fluoride layers or multilayers.

3. OUTCOMES

The work we are engaged in will demonstrate for the first time whether loss-free oxides of materials such as Al, Hf and Si can be deposited using ALD to lower cutoff reflectivities in the UV. We will also demonstrate the success of using ALD to deposit low-loss thin films of fluoride-based materials, and aluminum metal. Using these techniques we will then demonstrate our proof of concept of using these techniques together to construct thin-film multilayer metal-dielectric cavities that can be tuned to isolate specific emission lines of astronomical importance, when combined with a reflective surface as the foundation. The resulting optical technologies will advance the performance of thin-films in the FUV to match the UV detector advances that have been made to deliver the improvement in coating stability, thickness and performance that NASA seeks. Such improvement will enable next generation space-based FUV missions, opening access to the wealth of diagnostic information the FUV offers for exoplanet science, star formation science and cosmological/IGM science.

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