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Submitted to: DOE OFFICE OF SCIENTIFIC AND TECHNICAL INFORMATION (OSTI)

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New Deposition Processes for the Growth of Oxide and Nitride Thin Films

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The goal of this effort is to study the use of homoleptic metal amido compounds as precursors for chemical vapor deposition (CVD). The amides offer potential for the deposition of a variety of important materials at low temperatures. The establishment of these precursor compounds will enhance the ability to exploit the properties of advanced materials in numerous coatings applications. Experiments were performed to study the reactivity of $Sn[NMe_2]_4$ with oxygen. The data demonstrated that gas-phase insertion of oxygen into the Sn-N bond, leading to a reactive intermediate, plays an important role in tin oxide deposition. Several CVD processes for technologically important materials were developed using the amido precursor complexes. These included the plasma enhanced CVD of TiN and Zr_3N_4, and the thermal CVD of GaN and AlN. Quality films were obtained in each case, demonstrating the potential of the amido compounds as CVD precursors.

Background and Research Objectives

Thin-film coatings provide the basis for many current and emerging technologies. They are becoming ever more diverse in their applications, with increasing demands on their performance. Our conception of coatings has expanded far beyond simple passive barriers to more sophisticated and demanding applications such as electronics, gas turbines, solar energy, and other modern technologies [1]. Historically, most metallic and some ceramic coatings were produced by melt solidification technology. Since the advent of deposition technologies, i.e. production of solid materials from the vapor phase, the diversity and quality of available coatings materials has increased dramatically [2].

Chemical vapor deposition (CVD) is the deposition of a thin film by the chemical reaction of gas-phase precursor compounds at a (generally) heated surface [2-4]. The

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deposit can be a metal, semiconductor, alloy, or ceramic. Applications of CVD coatings include protective layers that are chemically inert, wear resistant, or resistant to extremes in temperature; thermally/electrically conducting or insulating layers; diffusion barriers; and coatings that facilitate the joining of dissimilar materials. CVD coatings technologies are used in the fields of optoelectronics, advanced microelectronics, energy applications, aerospace technologies, and transportation systems [4-7].

CVD provides some significant advantages over other deposition methods. For example, it is a non-line-of-sight process that allows the uniform coating of complex shaped parts. Very high purities can be obtained through appropriate choice of precursor compounds and processing conditions. Furthermore, materials with a wide-range of stoichiometries and structures, difficult or impossible to prepare by other techniques, can be deposited with relative ease.

Conventional CVD processes use metal halide precursor compounds. While functional, there are problems associated with these methods. The high thermal stability of most metal halides requires the use of very high temperatures (i.e., >800°C) to initiate the chemical reactions that lead to film growth. These reactions also produce corrosive gases (i.e., HCl and HF) that can be deleterious to film growth, deposition system integrity, and worker safety.

The limitations associated with halide-based CVD have led to increasing use of organometallic compounds as CVD precursors [9-10]. Many organometallic compounds have relatively low decomposition temperatures, in the range of 200 to 500°C. The lower temperatures make it possible to coat thermally sensitive materials such as polymers and conducting glasses. Also, low-temperature depositions can yield metastable materials that cannot be formed at higher temperatures. These new materials can exhibit enhanced properties, such as corrosion and wear resistance, not achievable by conventional means. Lowering the deposition temperature also reduces the undesirable side effects of interlayer atomic diffusion, residual stress resulting from thermal expansion mismatches, or temperature induced changes in the shape or crystallinity of the substrate.

Organometallic CVD (OMCVD) has been slow in gaining acceptance in coatings applications despite the possibilities for significant advantages over metal-halide based processes. Many organometallic compounds attractive for CVD are either not available from commercial sources, or are only available in small research quantities. Many OMCVD processes suffer from low growth rates, and the thermal decomposition of most organometallic compounds can lead to undesirable amounts of residual carbon in product films. While these secondary limitations to OMCVD do exist, the major underlying limitation is the lack of understanding of the chemistry important to the deposition process.

The conversion of an organometallic compound to a useful thin film involves stripping off most of the coordinated ligands from the precursor molecules, often with concomitant fragmentation reactions that leave behind residual H, C, N, or O atoms. Understanding the details of the thermal decomposition mechanism will help determine what factors dictate if the precursor undergoes desirable chemical reactions that lead to a pure product. The efficiency of the CVD process depends critically on the proper choice of precursor molecule that will allow deposition reactions to occur by way of chemically productive pathways with low activation barriers. Control of the fundamental chemistry of the deposition process is the key to the advancement of the OMCVD method.

Recently, the efficient transammination of homoleptic metal amides, $M(NR_2)_x$, with ammonia has been used to develop low-temperature, high growth rate processes for the deposition of high-purity metal nitrides [11-16]. The generality of this approach is illustrated by the large number of monometallic nitride materials that have been prepared from their corresponding homoleptic amido metal complexes. The technological significance of this result, specifically for the growth of TiN, is illustrated by the large effort undertaken by the microelectronics industry to apply this technology near term. The significant advance is the understanding and control of the fundamental chemistry enabling the design of an almost ideal deposition process.

We have recently extended this work to the low-temperature (200 to 400°C) deposition of high-purity metal oxides [17-18]. SnO_2 and SiO_2 have been deposited from the corresponding homoleptic amido complexes and O_2. We find little or no carbon or nitrogen in the deposited materials, indicating that all of the amido ligands are cleanly removed from the precursor molecules. We have proposed that the key step in the reaction pathway is insertion of oxygen into the metal-nitrogen bond, forming a reactive intermediate that thermalizes at low temperature to yield a high-purity monometallic oxide. The key to the deposition process appears to be a reactive metal-nitrogen bond.

The extension of homoleptic amido metal precursors to oxide deposition represents a significant advance. From the precursor perspective, the amido complexes may be as versatile a precursor set as the metal halides, as homoleptic amides are known for almost every element in the periodic table [19]. The amido complexes are volatile, easily synthesized, and relatively safe to handle. From the materials viewpoint, a tremendous wealth of materials systems of technological importance are available from a single set of precursors via low temperature, high growth rate deposition processes. Low deposition temperatures (< 500°C) and high growth rates (> 1 μm/hr) are critical requirements for many of the applications that use thin film deposition processes.

In spite of their technological importance, relatively few research groups have pursued extensive studies of the fundamentals of OMCVD processes. Although the interest in these types of studies has increased recently, most of the research groups are restricted by the low commercial availability of precursor complexes. Also, these efforts lack a connection to process development and do not incorporate molecular design of new precursors using the knowledge gained from fundamental studies. This project is a unique combination of precursor design, the elucidation of precursor reactivity, and process development.

The development of homoleptic-metal, amide-based deposition processes for oxide and nitride thin films will impact a large number of areas that are presently limited by the high deposition temperatures required for currently used precursors. It will also facilitate the deposition of bimetallic materials, such as $SrTiO_3$, where the current processes are greatly complicated by the widely different chemical or physical properties of the required precursors. Specific areas impacted by this development will include conducting oxides, dielectrics, ferroelectrics, wide band gap materials for optoelectronics, and display materials.

Importance to LANL's Science and Technology Base and National R&D Needs

This project makes a significant contribution to the Laboratory's competency in the area of advanced materials and also impacts national R&D needs. Thin-film coatings provide the basis for many current and emerging technologies. Their use has expanded far beyond simple passive barriers to more sophisticated and demanding applications such as electronics, optoelectronics, gas turbines, solar energy, and other modern technologies. Because of its unique capabilities, CVD is in principle often the method of choice for thin film applications. However, its use in practice is still limited by the high deposition temperatures often required. The use of metal amide complexes as CVD precursor compounds offers potential for the deposition of a wide variety of high quality, technologically important materials at very low substrate temperatures. The establishment of this diverse set of precursor compounds will push Los Alamos to the forefront of CVD research, and enhance the Laboratory's and the nation's ability to exploit the properties of advanced materials in numerous modern coatings applications.

An example of direct relevance to DOE is the use of large-band-gap materials, such as AlN, as electron sources for high-fluence electron beams. The ability to produce high-fluence electron beams is important to the success of the Los Alamos DAHRT project, and hence has a significant impact upon stockpile stewardship activities. An example for the commercial sector is the potential use of GaN-based phosphors in full-color electroluminescent display panels. By increasing the efficiency of blue phosphors much closer to acceptable values, they offer the potential for a significant advance in a multi-billion dollar per year industry.

Scientific Approach and Accomplishments

The overall goal of the project was to investigate new low-temperature OMCVD routes for oxide and nitride thin film growth. The focus was on the use of homoleptic amido complexes as precursor compounds, and the work built upon our previous results for the deposition of tin and silicon oxides [17-18]. The project involved two interrelated thrusts. The first was the study of the chemical reactivity of selected metal amido complexes to better understand the reaction mechanisms relevant to the CVD of thin films. The second thrust consisted of process development for the deposition of nitride and oxide films from metal amido complexes. The materials focus was on specific applications requiring a low-temperature deposition process.

A. Chemical Reactivity of Metal Amido Complexes

To study the reactivity of the amido precursor compounds, a high-pressure gas mixing chamber was constructed. The chamber provided for mixing of the reactant gases in an ultra-clean environment, and at a pressure somewhat higher than that used for conventional CVD processes. A small pinhole in one wall of the mixing chamber allowed the reactants and their gas-phase products to diffuse into an adjoining ultra-high vacuum (UHV) chamber equipped with a quadrupole mass spectrometer (QMS). The QMS allowed identification of the reaction products, which were monitored as a function of time, temperature, pressure, and reactant composition. Complementary experiments were performed in which precursor in the vapor phase was adsorbed onto a silicon substrate placed within the UHV chamber. The sample was heated according to a prescribed temperature versus time profile, and the desorption products monitored as a function of time by the QMS. From this compilation of data, information on reaction pathways and intermediates important to film growth could be extracted.

Experiments were performed to study the reaction of tetrakis(dimethylamido) tin, or $Sn[NMe_2]_4$ (where Me = CH_3), with oxygen. This is the reactant combination previously used for the deposition of tin oxide films. The mixing experiments demonstrated that gas-phase reactions, leading to reactive intermediates, play an important role in the deposition of oxide films from metal amido complexes. The data are consistent with the insertion mechanism shown below:

$$Sn[NMe_2]_4 + O_2 \text{ ---> } (Me_2N)_3Sn(O\text{-}O\text{-}NMe_2).$$

For this mechanism, the oxygen molecule is inserted into the Sn-N bond, forming a reactive intermediate that pyrolizes at low temperature to yield SnO. This is theorized to be a general mechanism for the reaction of metal amides with oxygen.

The desorption experiments furthermore showed that β-hydride elimination is not an important thermal decomposition pathway for the Sn amido complex. This means that the volatile methyl groups within the molecule are desorbed intact, without the loss of individual H atoms. This may account in part for the high purity of the deposited Sn and Si oxide films.

Although the reactivity experiments showed initial promise for understanding the reaction pathways important to amide-based CVD processes, they were discontinued as the result of personnel changes.

B. Process Development

Experiments relating to process development for amide-based CVD fell into two categories. The first of these was plasma enhanced CVD, and focused on the materials Zr_3N_4 and TiN. The second category was conventional, low-pressure CVD. These experiments focused on the materials GaN and AlN.

Plasma Enhanced CVD

TiN is an important industrial material. It is stable at high temperatures, highly resistant to corrosion, and has excellent hardness and wear resistance [12]. Its applications include cosmetic plating (because of its gold color), window tinting for heat control, diffusion barriers in microelectronics, and protective wear-resistant coatings for cutting tools and firearms components. On the other hand, the compound Zr_3N_4 is relatively little studied. It is metastable with respect to ZrN and, in contrast to the mononitride, is a transparent, highly insulating material [12]. It also has potential microelectronics applications, but low-temperature deposition routes must be more firmly established.

Thin films of Ti and Zr nitride were deposited by plasma enhanced CVD (PECVD) [20]. The use of a high-frequency plasma discharge creates a highly non-thermodynamic equilibrium environment within the reactor volume. The plasma environment is populated by very reactive species such as ions and free radicals, and allows the chemical reactions required for film deposition to occur at lower temperatures than would be possible in an equilibrium system. This further reduces residual stress resulting from thermal expansion mismatches between film and substrate, and reduces the degradation of temperature-sensitive substrates. It also facilitates the deposition of metastable phases, such as Zr_3N_4, that often have desirable properties not achievable by other means.

The reactor vessel was a stainless steel six-way cross. The substrates were Si wafers, secured to a stainless steel sample stage that was heated from behind by a quartz lamp. For the deposition of Zr_3N_4 the precursor compound was $Zr(NEt_2)_4$, where Et = CH_3CH_2, prepared by a literature method [21]. The precursor was placed within a stainless steel vessel that was warmed with a heating tape to increase the vapor pressure of the Zn amide complex. The precursor vapor was flushed into the reactor volume by the flow of ultra-high purity Ar carrier gas. The second reactant, semiconductor grade ammonia, was introduced through a separate gas line. All of the gas flows were regulated by mass flow controllers, and the chamber pressure was kept at 0.3 Torr. The plasma discharge within the reactor volume was maintained by a microwave cavity operating at a frequency of 2.45 GHz. Films were deposited for the substrate temperature range of 200 to 400°C. They were then characterized by ion beam analysis for composition, x-ray diffraction (XRD) and scanning electron microscopy (SEM) for structure, and light transmission versus wavelength for bandgap.

Ion beam analysis showed that the films have the desired Zr_3N_4 stoichiometry, within experimental uncertainty, over the entire substrate temperature range. Impurity levels for the films are fairly low, with 5 at.% C and 9 at.% H being typical. No correlation was observed between impurity level and substrate temperature. No oxygen was detected within the films, although a small amount of surface oxidation was observed.

The films are polycrystalline, with an x-ray diffraction pattern consistent with the metastable phase Zr_3N_4. The crystallite orientation is random, except at the highest deposition temperatures where a slight degree of preferential orientation is observed. SEM shows that the films are smooth and pinhole free, with uniform coverage of the substrates.

The transmission of light through the film was measured as a function of wavelength. From these data, the width of the bandgap was determined to be 3.1 eV. This is somewhat higher than a previously reported value of 2.2 eV [22]. Film resistivities were in the range of several MΩ-cm, as expected from a highly insulating phase.

The experiments demonstrate that the use of the amide precursor, especially in conjunction with a plasma environment, allows the very low-temperature processing required for the preparation of metastable phases such as Zr_3N_4. This result helps to establish a viable deposition route for Zr_3N_4, facilitating its study.

The precursor compound $Ti(NMe_2)_4$, prepared by literature methods [21], was used for the plasma deposition of TiN films. Deposition conditions were generally similar to those for Zr_3N_4, and films of comparable quality were obtained on Si substrates.

One application investigated for TiN films, for which a patent application has been filed, was that of protective coatings on Kevlar® fibers. Kevlar® is a lightweight, flexible, thread-like material. Despite their light weight, the fibers and fiber bundles offer extreme strength and durability. Current applications for Kevlar® include use in bullet-proof vests, aircraft components, and sporting goods such as skis. A limitation of Kevlar®, however, is that the fibers easily buckle when subjected to compressive stress. One way of improving the compressive properties of Kevlar® is to coat the fibers with a thin film of high modulus material such as TiN. The cylindrical TiN shell would essentially act as a protective girdle around the fiber, inhibiting compressive failure. A potential problem with this approach is that Kevlar® begins to break down at temperatures above 400°C. A low-temperature deposition process, such as that made possible by the use of amide precursors, is therefore required.

Depositions were performed in the plasma system described above, at temperatures of 150 to 250°C. Typical coating thicknesses were 0.5 to 1.0 µm (the uncoated fibers are 10.8 µm in diameter), which required 10 to 20 minutes of deposition time. The mechanical properties of coated and uncoated fibers were measured by a three-point bend test. A Nanoinstruments nanoindentor was used with a modified tip and sample fixture that allowed load versus displacement measurements to be made for the bending of individual fibers. The nanoindentor allows continuous monitoring of the fiber displacement as a function of applied load, so that failure loads and displacements can easily be determined. Furthermore, the shape of the loading and (if failure does not occur) unloading curves can be used to calculate the modulus of the fiber [23].

The TiN coatings significantly improved the failure load and displacement of the fibers. Loads at failure increased on average from 3.8 to 4.8 mN. The corresponding displacements increased from 2.2 to 3.6 µm. These values, of course, are highly dependent upon the test geometry. However, the relative changes indicate a significant improvement in compressive properties. A more fundamental number is the elastic modulus. The modulus value for the fiber/coating composite was found to be 31 ± 3 GPa. This value is consistent with the expected behavior of a hollow TiN cylinder of the relevant dimensions [23]. The mechanical behavior of the coated fiber is therefore being dominated by the protective TiN girdle, as desired.

Additional work is required to fully determine the utility of this approach. However, it is clear that the low-temperature amide CVD process may provide a means of enhancing the mechanical properties of Kevlar® fibers with little sacrifice in weight gain.

Conventional Thermal CVD

In addition to plasma processing, conventional thermal CVD methods were also investigated. The materials focus for these experiments was GaN and AlN, both very important technological materials.

GaN has potential application in optoelectronic devices such as light emitting diodes and diode lasers, ultraviolet detectors, and high power, high frequency devices [14]. Actual CVD applications have been limited to date because most processes produce conductive n-type GaN. The conductivity has been attributed to the presence of nitrogen vacancies resulting from the high temperatures required for deposition [14]. AlN has potential application as dielectric and passivation layers in microelectronic devices, in optoelectronic devices, and in surface acoustic wave devices [24]. Again, many of these applications require low-temperature deposition processes to be fully realized.

The reactor for these experiments was a glass, cold-wall system. Substrates are glued to a stainless steel holder by thermally conductive silver paint and heated from behind by resistive heating elements. The substrate holder is placed in the reactor with the substrate face down. This orientation is desirable to prevent particulates from dropping onto the substrate surface.

The precursor compound for GaN deposition was hexakis (dimethylamido) digallium, or $Ga_2(NMe_2)_6$. The corresponding compound for AlN deposition was $Al_2(NMe_2)_6$. Both were prepared by literature methods [25]. The precursors were placed in stainless steel vessels that were warmed by heating tapes to increase the vapor pressures of the compounds. Precursor vapor was transported to the reactor volume by ultra-high-purity He carrier gas. As was the case for the plasma system, the second reactant was semiconductor grade ammonia delivered by a separate gas line. Gas flows were regulated by mass flow controllers, and the chamber pressure was maintained at 1.0 Torr. Depositions were performed for substrate temperatures of 200 to 550°C.

Ion beam analysis showed that the stoichiometry of the GaN films was close to the desired value, with ratios of N/Ga in the range of 0.9 to 1.1. Carbon and oxygen impurity levels were found to be quite low, <2 at.%. Hydrogen levels were somewhat higher, at 13 to 30 at.%, with the lower values obtained for higher deposition temperatures. Infrared absorption spectroscopy showed that at least some of the H impurity was present in the form of N-H bonds.

Several samples were deposited with deuterated ammonia, ND_3, to determine the source of H in the films. Isotopic determination by ion beam analysis showed that the films contained 94% H and 6% D. The results imply that nearly all of the H comes from fragmentation of the amide precursor molecules. This is not consistent with the desorption measurements described above, which implied that the CH_3 groups were desorbed without fragmentation. The difference may be the result of reaction with ammonia rather than oxygen, and merits further study.

X-ray diffraction showed that the films deposited at the higher substrate temperatures were polycrystalline, while those deposited at lower temperatures were essentially amorphous. As desired, the films have excellent, very high resistivities, in the range of 100 MΩ-cm. This shows that the low-temperature amide process is indeed capable of depositing insulating GaN material with the desired dielectric properties.

Results for the AlN films were generally similar. However, the deposition in this case seemed to be cleaner, with H impurity levels in the films of <10 at.%. Resistivity values are comparable or higher than those of GaN, and these films are now under evaluation as photoelectron sources for high-fluence electron beams.

C. Conclusions

The above examples illustrate that amide-based CVD processes are capable of providing low-temperature deposition of a wide variety of materials of technological importance. As proposed in the background section, metal-amide complexes may indeed turn out to be an extremely useful, versatile family of compounds for use as CVD precursors.

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