AN ABSTRACT OF THE THESIS OF

Sharon A. Betterton for the degree of Master of Science in Chemistry presented on September 6, 2011.

Title: Deposition and Characterization of Transition Metal Oxides from Aqueous Solution.

Abstract approved:

________________________________
Douglas A. Keszler

The aqueous chemistries of two transition metal cations, Zr$^{4+}$ and Nb$^{5+}$, are examined and then used to develop inorganic precursor solutions. The oxides of these cations (ZrO$_2$ and Nb$_2$O$_5$) are deposited and characterized, and their morphological and optical properties discussed. Due to the obstacles created by niobium's aqueous chemistry, an alternative to the straightforward hydrolysis-condensation chemistry utilized to deposit ZrO$_2$ is identified, making use of Nb$_{10}$O$_{28}$ clusters.
Master of Science thesis of Sharon A. Betterton presented on September 6, 2011.

APPROVED:

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request

Sharon A. Betterton, Author
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Hidekel A. Moreno Luna assisted with much of the deposition and characterization in Chapter 2. Dr. William Casey, Dr. C. André Ohlin, and Dr. Eric Villa provided much of the \([\text{N(CH}_3\text{)}_4\text{]}_6[\text{Nb}_{10}\text{O}_{28}]\cdot6\text{H}_2\text{O}\) used in Chapter 3, as well as the hydrous niobium oxide used in our own synthesis of the \(\text{Nb}_{10}\) cluster. Dr. Casey and Rene Johnson provided invaluable insight into the aqueous \(\text{Nb}^{5+}\) chemistries discussed in Chapter 3. Wei Wang assisted in some thin film deposition in Chapter 3. Sujing Xie collected TEM images of films in Chapter 3. Theeranun Siritanon assisted with TGA data collection in Chapter 3. Dennis Thayer at the Analytical and Development Laboratory at Hewlett Packard, Corvallis collected SEM images of films in Chapter 3. Hidekel A. Moreno Luna collected X-ray reflectivity data in Chapters 2 and 3, as well as ellipsometry data in Chapter 3. Dr. Doug Keszler was, of course, the guiding force behind all the research herein, and provided the vital opportunities for collaboration that made this work possible.
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2.1  Model fitting results for ZrO\textsubscript{2} thickness, Cauchy parameters A, B, and C, and mean square error (MSE)
To Mom, whom I love,
Jean-Raymond, who inspires me,
and Patrick, my patronus.
Deposition and Characterization of Transition Metal Oxides from Aqueous Solution

CHAPTER 1: INTRODUCTION
1.1 Preamble and Scope

If inorganic chemistry were a film genre and we were to concern ourselves with indexing its various 'motifs,' surely one of the most common tropes would be the study of metal oxides. From those metal oxides most common in our lives (rust or sand, perhaps) to the more exotic and luminescent lanthanide oxides, humans have studied and put these materials to use for well over a thousand years\(^1\) – so much so that it is easy to take them for granted. Despite years of intrigue and purpose, there is still much to do and discover in this area: synthesizing those metal oxides that, due to thermodynamic restraints, are not yet able to be synthesized; finding applications, new and old, to which metal oxides might be usefully put; and the age-old desire to truly understand the chemistry of oxide formation and interaction. Each presents a challenging task to the scientist or the engineer, but it is in the fuzzy realm both share – materials science – that all three purposes can come together and to fruition. The goal of this work is to serve as an example of progress being made towards such lofty goals.

Before we begin, however, a considerable amount of narrowing down must be done, lest this become a work of unmanageable proportions, expanding uselessly into myriad chapters in the hopes of covering so broad a scope as 'metal oxides.'
First, we cull from the theme of metal oxides the very precise topic of aqueous solution-based thin-film deposition. Thin-film deposition presents unique challenges, in the realms of both chemistry and engineering, and thus provides ample opportunity for exploration. From the perspective of chemistry, a field concerned largely with how-things-work, we have motive to understand the chemical mechanics of solution precursors so that we may exploit those mechanics for a particular end: thin-film deposition. For the materials scientist, an engineering perspective is also useful – and that domain, with its emphasis on making-things-practical, can be used to take interesting chemistries and put them towards practical application. The varying applications for thin films provide goals towards which the chemist may work.

It is important to note that though this work has been completed with an eye towards practicality, it is still primarily a study in chemistry, and, as such, the scope of this work is not geared to application. Beyond what is necessary to frame our goals, and to confirm that this work is practical in nature, we will not be delving deeply into the mechanics of metal oxide thin film applications.

In order to thoroughly define our scope, we lastly limit ourselves to discussing two specific transition metal oxides: zirconium (IV) oxide \([\text{ZrO}_2]\) and niobium (V) oxide \([\text{Nb}_2\text{O}_5]\) – the former having a
straightforward enough precursor chemistry as to illustrate the elegance of solution-processed thin-film deposition at its best, and the latter involving problematic aqueous interactions that will allow us to explore how inorganic chemistry can provide detours around thermodynamic obstacles.

1.2 Metal Oxide Thin Films

While the potential and established applications for metal oxide thin films are many, of particular note is the impact to be made on the electronics industry through the integration of high-κ metal oxides as dielectrics, either as replacements for or in conjunction with traditional SiO₂ dielectrics. A 2007 press release² from industry leader Intel conveys the important role high-κ materials are already having in shaping the future of microelectronics:

Transistor gate leakage associated with the ever-thinning silicon dioxide gate dielectric is recognized by the industry as one of the most formidable technical challenges facing Moore’s Law. To solve this critical issue, Intel replaced the silicon dioxide with a thicker hafnium-based high-k material in the gate dielectric, reducing leakage by more than 10 times compared to the silicon dioxide used for more than four decades.

Though it is not the purpose of this work to expound upon the specifics of function, a clarification on the limitations of silicon-based dielectrics may help to place this research into the context of one particular
application.

Figure 1.1a represents a simple capacitor – an insulating dielectric layer between two conductive layers (or plates) connected to a voltage source. When a voltage is applied across the plates, illustrated in Figure 1.1b, electrons cannot pass through the insulating dielectric layer and so build up along the interface between the bottom plate and the dielectric layer. This build-up of negative charge causes a polarization of the electrons in the dielectric material, which results in a positive charge on the top conductive plate, as electrons move away from the polarized dielectric and into the connecting lead. The potential difference created between the conductive plates is referred to as charging the capacitor. Capacitance \( C \) describes how much the capacitor can be charged, and is defined by the following equation:

\[
C = \frac{\kappa \varepsilon_0 A}{d}
\]

where \( \kappa \) is the dielectric constant of the dielectric material, \( \varepsilon_0 \) is the permittivity of free space, \( A \) is the area of the plates, and \( d \) is the distance between the plates (or thickness of the dielectric).

This frame of reference provides a straightforward, if simplistic, understanding of the limitations of using SiO\(_2\) as a dielectric layer. As the demand for smaller and smaller transistors continues, \( A \) must
necessarily decrease. Since $\kappa$ remains constant for a SiO$_2$ dielectric material, in order to increase or maintain $C$ for a smaller transistor, the thickness of the dielectric layer, $d$, must decrease – as it has done in electronics over the last few decades. However, there is ultimately a point at which the thickness of the dielectric material can no longer decrease, from both a physical (atom size) and electronic (leakage) standpoint. Because it is the purpose of the dielectric layer to keep charge separated, the loss of electrons through that layer is undesirable, and, due to electron tunneling, it is no longer sufficient or possible to simply make that layer thinner.

The answer, then, is to find a material with a higher dielectric constant. Dubbed 'high-$\kappa$' dielectrics, many materials have been considered, including silicates, lanthanide oxides,$^{12}$ and, pertinent to this research, transition metal oxides. In the context of this work, the application of dielectric layer, while not an exclusive use for the oxides to be discussed, is a model by which goals might be set. For integration into electronics, it is invaluable that metal oxide thin films be smooth, dense, amorphous (to prevent leakage of electrons through grain boundaries), and homogenous, properties that are important to bear in mind when considering deposition methods of those thin films.$^{11}$
1.3 Traditional Methodology

The deposition of metal oxides is not a new pursuit and is not limited to the purpose of depositing dielectrics, or even to the use of metal oxides in electronics, but presented here is an overview of methods frequently used to produce thin films for that latter purpose, so that an appropriate comparison and contrast can be drawn to the methods described in this work.

Physical vapor deposition (PVD) is commonly used in the deposition of thin films, including metal oxides. Described simply, a bulk preparation of the desired substance is vaporized in a low pressure environment (frequently a vacuum) and transported to the surface of a substrate. Because the vaporization process can result in a change in stoichiometry at the final surface, sometimes ambient gases are used to offset the loss (e.g. oxygen gas can be used to replace oxygen lost during oxide deposition). For insulating materials, like the metal oxides discussed in this work, sputter deposition (vaporization via high-energy plasma) is the preferred method, specifically radio-frequency sputtering, which prevents the detrimental charge build-up common in direct-current sputter methods.

While PVD methods have been a long-standing means of depositing uniform, highly dense films, and have the advantage of allowing for a
wide variety of substrates (due to low surface temperatures), they also present limitations. Controlling the deposition of very thin films is difficult, and for tasks in which conformal coverage of substrates with three-dimensional features is needed, PVD is typically unsuitable.

In contrast to PVD methods, wherein species are, in effect, transported to the surface identity intact, chemical vapor deposition (CVD) comprises a variety of methods in which gaseous precursors react in a vacuum chamber and on the substrate surface to form a final product. With such a broad range of methods that fall under the umbrella 'CVD' (metal-organic CVD, plasma-enhanced CVD, photo-assisted CVD, chemical beam epitaxy, and atomic layer deposition (ALD)), it would be impractical to review each individually. Thus, one particular method, ALD, is singled out for consideration, and a general description of the advantages and disadvantages of CVD will follow.

ALD is a form of CVD which involves 'pulses' of segregated gases to allow for the build up of oxides at an atomic level. It is especially useful in the formation of very thin, smooth, and dense films – which have been required for the capacitance needs of increasingly smaller transistors, as touched upon in the previous section – and is considered one of the highest quality methods available. As with all seemingly ideal methods, however, this high quality comes with drawbacks,
primarily that of time. Because of the methodology – alternating pulses of water vapor (to provide OH groups) and metal complexes (which adsorb onto each previous layer of OH) interspersed with purges to prevent vapor reactions – and the steric hindrances created by ligands and OH groups, the process is extremely time consuming. Other difficulties with depositing oxides via ALD are largely substrate and precursor dependent; the possibility that metal precursor molecules will decompose into undesired species, for example, must be taken into account, as they can have a detrimental impact on both growth rate and the integrity of the film itself.\textsuperscript{7}

Overall, CVD processes provide a suitable means to deposit high quality films, with good coverage and conformity regardless of substrate shape,\textsuperscript{4} good composition control,\textsuperscript{5} and, depending on method, high deposition rates.\textsuperscript{4} The variety afforded by CVD (in temperature, pressure, precursor gases, and substrate material) also allows for a great deal of flexibility, making it a fit choice of deposition for a wide range of applications. However, there are difficulties inherent in the use of CVD. As with any vacuum-system based method, there is a natural limitation to the size of substrates onto which material may be deposited. While not limited, in theory, to small coverage areas, the practical cost-limitations of providing a vacuum system capable of
depositing over meters, desirable in new generations of macro-electronics, is prohibitive. Also limiting is the fundamental requisite that precursors must be in vapor phase at room temperature, a drawback improved (but not eliminated) by the use of metal-organics, which can be, themselves, toxic to humans or detrimental to the environment. Byproduct gases from the deposition process may also prove prohibitively dangerous, requiring expensive cleaning processes.

In an attempt to find alternative methods of metal oxide thin film deposition, in particular those that reduce the costs and limitations associated with high power, vacuum-based vapor deposition, chemists began making use of less technologically intense methods of deposition. In the realm of solution depositing, sol-gel methods dominate the literature. Developed initially to form high quality glasses and ceramics, the sol-gel process is based on the principles of metal cation hydrolysis and condensation, which are limited through the use of organic ligands and solvents and careful control of water content.\textsuperscript{13}

The archetypal sol-gel process involves a solution of metal alkoxides ($\text{M(OR)}_n$) in alcohol.\textsuperscript{14} Upon exposure to water, the alkoxides begin to hydrolyze and condense (forming a sol), and then polymerize, forming a massive network across the solution (a gel). The gel can then be dried and annealed to form a metal oxide. For transition metal oxides, this
method has been especially useful, as those metal species tend to be considerably less stable than typical sol-gel metals, and can hydrolyze and condense rapidly if not carefully controlled.\(^\text{16}\)

When applied to thin films, often via dip-coating, sol-gel methods can produce thicknesses up to 1 µm in a single coat, dependent on withdrawal speed. As there are no vacuum chambers, the only limitations on substrate coverage are the size of available substrates and, ultimately, that of the furnace used to anneal. Dip-coating allows for uniformity across large substrates, regardless of shape, and spin-coating may also used for two dimensional coverage.\(^\text{13}\)

Though a testament to the creativity of chemists, a sacrifice is made in using these methods, particularly in the realm of electronically useful thin films. Bulky organic ligands, which serve an important function in precursors, are necessarily incorporated into the thin films,\(^\text{15}\) and often require high decomposition temperatures to remove them from the final films. This decomposition leaves the films with a much lower density than the more traditional vapor deposition methods, and also leaves them much rougher.

1.4 Summary

Is it possible, then, to get dense, smooth films without resorting to
the power intensive and costly methods used in industry? Is it possible to have a functional metal oxide thin film without making use of vacuum technology? Yes! Aqueous solution chemistry is certainly not perfect, but it provides an elegant middle ground to the cost-effective, less-functional sol-gel methods and the cost-intensive, high-quality vapor methods.

While the more traditional wet method of sol-gel chemistry attempts to hinder hydrolysis and condensation through the use of organic chelation, aqueous methods control hydrolysis and condensation by creating meta-stable intermediates that are simultaneously stable enough to prevent the aqueous oxide species from precipitating out of the solution precursor, yet unstable enough to hydrolyze and condense where the metal oxide is needed: on the substrate.

In this work, the deposition of two distinct transition metal oxides is discussed. In Chapter 2, a nitrate-based aqueous solution precursor is developed for the deposition of high quality, smooth, and dense ZrO$_2$ thin films. In Chapter 3, an examination is made of the difficulties typical of Nb$^{5+}$ solution chemistry and of the use of niobate clusters in a novel approach to depositing smooth, moderately dense, amorphous Nb$_2$O$_5$ thin films.
References


Figures

**Figure 1.1** Representation of a simple capacitor. a) 'Switched off' – no applied voltage and b) 'Switched on' – voltage applied across the plates.
CHAPTER 2: AQUEOUS SOLUTION CHEMISTRIES FOR SOLUTION-DEPOSITED ZIRCONIUM (IV) OXIDE

Sharon A. Betterton, Hidekel A. Moreno Luna, Douglas Keszler

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2.1 Abstract

An aqueous peroxozirconium precursor has been developed for the deposition of amorphous and crystalline ZrO$_2$ via spin-coating. Deposition using an 0.2 M [Zr$^{4+}$] precursor yields thin films at 6-7 nm per coat after a modest anneal temperature of 150 °C. Films annealed between 150 °C and 800 °C demonstrate low roughness (0.2-1.7 nm RMS) when analyzed by AFM, confirmed by XRR analysis. Densities as high as 5.11 g/cm$^3$ (88% bulk) and refractive indices of n (λ = 550 nm) = 1.97 were determined for films annealed at 300 °C. Furthermore, ultra-thin films <10 nm have been deposited by diluting a standard solution, demonstrating an easily tunable means of depositing ZrO$_2$ at a desired thickness.
2.2 Introduction

High-permittivity metal oxides such as ZrO\textsubscript{2}, HfO\textsubscript{2}, and Ta\textsubscript{2}O\textsubscript{5} are attractive candidates for use as gate dielectrics across a wide range of high-performance thin-film transistor platforms.\textsuperscript{1} These materials are under consideration as potential replacements for SiO\textsubscript{2}, with which high current leakage is observed at low thicknesses. Hafnium and zirconium oxides have received considerable attention for their high dielectric constants and electrical performance.\textsuperscript{1-4} ZrO\textsubscript{2} and HfO\textsubscript{2} films deposited by using atomic layer deposition (ALD) methods exhibit dielectric constants ranging from 20-29 and 16.3-18.5, respectively,\textsuperscript{5} more than four times that exhibited by SiO\textsubscript{2}. Zirconia, both amorphous and crystalline, has traditionally been deposited using many methods: sputtering,\textsuperscript{6} pulse layer deposition,\textsuperscript{2} CVD,\textsuperscript{7} liquid-phase deposition,\textsuperscript{8} successive ionic layer absorption and reaction,\textsuperscript{9} and ALD.\textsuperscript{4,10}

Though the development of high-\(\kappa\) dielectrics has gained a great deal of attention, deposition of high-\(\kappa\) metal oxides by solution-based methods is often neglected, in part due to concerns about moisture incorporation, which can result in sharp increases in conductivity,\textsuperscript{10} and because of difficulties in obtaining appropriate film morphologies. For thin-film dielectrics to be considered appropriate for use in electrical applications, films must be smooth, dense, and free of major defects.\textsuperscript{1}
While organic solution deposition methods typically seek to resolve moisture issues by replacing water with organics (such as metal amides\textsuperscript{5}), this resolution is problematic due to the higher temperatures required to anneal films and remove residual organics, which can result in inhomogeneous, rough, and low-density films.

We shift our attentions away from the pitfalls of organic solution deposition by utilizing aqueous, inorganic solution deposition – which combats both moisture incorporation (through a dehydration step) and density issues (by making use of small, inorganic ligands that do not require high annealing temperatures). Deposition of oxide thin films from aqueous precursors, specifically via spin-coating, is a technique that has yielded promising results with regard to the incorporation of metal oxides (e.g. HfO\textsubscript{2},\textsuperscript{11} ZnO,\textsuperscript{12} Al\textsubscript{2}O\textsubscript{3-3x}(PO\textsubscript{4})\textsubscript{2x},\textsuperscript{13} and (InGaZn)\textsubscript{x}O\textsubscript{y}\textsuperscript{14}) into electronic applications.

The deposition and characterization of HfO\textsubscript{2} and ZrO\textsubscript{2} is often a dual investigation due to their similar chemistries. This work seeks to expand upon others’ research\textsuperscript{11} on the deposition of HfO\textsubscript{2} by focusing on the aqueous, inorganic deposition, and subsequent characterization, of ZrO\textsubscript{2}. A similar study was done by Jiang and Anderson, in which they used a peroxohafnium complex precursor solution to deposit high quality HfO\textsubscript{2} thin films via spin-coating.\textsuperscript{11} Gao and Masuda likewise
attempted a similar study: using a peroxozirconium solution, based on the ZrO(NO$_3$)$_2$ complex, they were able to deposit ZrO$_2$ on p-type Si wafers using a chemical bath method. However, their resulting solutions were unstable at room temperature and had a stability window that restricted deposition. Notable advantages of our precursor synthesis are the reasonable stability of the precursor, as well as the elimination of ammonia, which can raise the dehydration temperature of the deposited films.

2.3 Experimental Details

2.3.1 Preparation of Precursor Solution and Thin Film Deposition. ZrOCl$_2$•8H$_2$O (Alfa Aesar, 99+) was dissolved in 18-MΩ Millipore H$_2$O to a concentration of 0.5 M. This stock solution was further diluted to desired concentrations with 18-MΩ H$_2$O. As a representative solution, 0.5 M ZrOCl$_2$(aq) was diluted to 20 mL [0.12 M]. To this 20 mL solution, 6.7 mL of 1 M NH$_3$(aq) (Mallinckrodt, ACS) was added and vigorously stirred. The resultant precipitate was centrifuged and then washed with H$_2$O a total of 5 times to remove Cl$^-$ and NH$_3$. After the final decant, 1.4 mL 2 M HNO$_3$ (EDS, ACS) and 2.5 mL 30% H$_2$O$_2$(aq) (Mallinckrodt, ACS) were added. This final solution was stirred for 12 h until clear and chilled prior to deposition.
2.3.2 Thin Film Deposition. Thin films were deposited via spin-coating. Precursors were filtered through a 0.45µm PTFE syringe filter onto a substrate and then spun at 3000 rpm for 30 s, followed by a 150 °C cure for 60 s and a 20 s cooling step. This process was repeated until the desired thickness was achieved. For a 0.2 M [Zr⁴⁺] solution, the deposition cycle produced a 6-7 nm layer, dependent on synthesis yield; for an 85% [Zr⁴⁺] yield, the layer thickness per deposition cycle was 6.6 nm. Films were annealed in air for 1 h at temperatures ranging from 200°C to 800 °C. Substrates (200 nm SiO₂ thermally grown on Si) were prepared by sonicating for 60 min in a 5% Contrad solution at 45 °C and then thoroughly rinsing with 18-MΩ Millipore H₂O.

2.3.3 Structural Characterization. Diffraction data of deposited thin films were collected on a Rigaku RAPID diffractometer from 0-60 ° (2θ). Thin-film-surface-morphology was analyzed by using a Digital Instruments NanoScope III Multimode atomic force microscope (AFM) in contact mode operation with a Veeco NP-20 SiNx probe and a scan rate of 1.5 Hz. X-ray reflectivity (XRR) measurements were collected with Cu Ka radiation by using a Rigaku Ultima IV X-Ray diffractometer. Reflectivity was measured from 0-10 ° (2θ) and roughness, thickness, and density analyses were performed using the GlobalFit Reflectivity Program. Critical angles were useful for
calculating densities.

2.3.4 Optical Characterization. Film thicknesses and indices of refraction of ZrO\textsubscript{2} thin films were measured by using a J.A. Woollam HS-190 ellipsometer. Incident angles used were 65-75 ° with 5 ° steps from 300 nm to 800 nm. VASE software was used to model measured data. Data were fit using the Cauchy model for a ZrO\textsubscript{2} layer. Table 1 shows the parameters: anneal temperature (°C), precursor concentration (M), film thickness (nm), Cauchy parameters $A$, $B$, and $C$ for dispersion ($n(\lambda) = A + B/\lambda^2 + C/\lambda^4$) in the ZrO\textsubscript{2} layer, and mean square error ($MSE$).

2.4 Results and Discussion

2.4.1 Thin Film Deposition and Characterization. Root-mean-square (RMS) roughness values were calculated via contact-mode AFM in order to determine the roughness of thin films with respect to temperature. At lower anneal temperatures, ZrO\textsubscript{2} thin films demonstrate low roughness, which increases at higher annealing temperatures. RMS roughness values from AFM scans ranged from 0.2 nm to 1.7 nm, with values <0.4 nm for anneal temperatures 500 °C and below. Reflectivity measurements of the film at low incident angles are provided in Figure 2.1. The modeled data show low roughness values at
both non-crystalline and crystalline phases with values between 0.01 nm and 0.02 nm for films that were 41.96 nm, 41.42 nm, and 42.53 nm thick and annealed at 300 °C, 500 °C, and 700 °C, respectively. Shown is the experimental log(I) of the annealed films as a function of incident X-ray angle.

Densities of the annealed films, also determined by using XRR, decrease with annealing temperatures: At 300 °C, a film with a thickness of ~41 nm and a roughness value of 0.015 nm had a density of 5.11 g/cm$^3$ – reasonably close to the maximum bulk density calculated by Adam and Rogers for monoclinic ZrO$_2$ (5.836 g/cm$^3$). This confirms that high densities of deposited ZrO$_2$ thin films can be realized by modest annealing temperatures.

The refractive indices of crystalline films were found to be lower than those of amorphous films (see Figure 2.2 for representative films). At 550 nm, the refractive index for a 300 °C annealed film is 1.97, while at 700 °C it is 1.95. These n values at $\lambda = 550$ nm are close to that of monoclinic ZrO$_2$ (n = 2.1). The refractive index can also be used to estimate the density of the films, allowing for comparison with XRR results. This relationship is described by:
\[ \frac{\rho_f}{\rho_m} = \left( \frac{n_f^2 - 1}{n_f^2 + 2} \right) \left( \frac{n_m^2 + 2}{n_m^2 - 1} \right) \]

where \( n_f \) is the refractive index of the film, \( n_m \) is the refractive index of the bulk material, \( \rho_f \) is the density of the film, and \( \rho_m \) is the density of the bulk material. Using this equation, estimated densities were calculated to be between 93% and 94% of bulk for films annealed between 300 °C and 700 °C, a value of 5.49 g/cm\(^3\) at 300 °C. At this temperature, a value of 5.11 g/cm\(^3\) was measured by XRR.

Ultra-thin films <10nm were also made by diluting the standard concentration and depositing diluted precursor solutions. Average thicknesses per deposition cycle were found for 0.035–0.200 M [Zr\(^{4+}\)] by depositing 5 layers of ZrO\(_2\) and dividing measured thicknesses by 5 (see Figure 2.3); a relationship is clear, demonstrating the ability to control most layer thicknesses precisely. The minimum thickness per cycle experimentally achieved was 1.02 nm per deposition cycle, at 0.035 M [Zr\(^{4+}\)].

Thinner films demonstrated typical refractive properties compared with those for thicker films, as shown in Figure 2.4. A thinner film (6 nm) annealed at 150 °C exhibited \( n (\lambda = 300 \text{ nm}) = 2.6 \), whereas a thicker film (22.5 nm) annealed at 150 °C had \( n (\lambda = 300 \text{ nm}) = 2.1 \). This behavior suggests a higher density of the film at lower thicknesses,
which is reasonable, as a thinner film is more apt to densify at lower temperatures than one four times as thick.

2.4.2 Precursor Chemistry. The overall reaction and products have been shown in Scheme 1 as a flow chart of the precursor synthesis. Upon dissolution of ZrOCl$_2$•8H$_2$O (an ionic cluster containing [Zr$_4$(µ-OH)$_8$(H$_2$O)$_{16}$]$^{8+}$]$^{18}$ in water, the tetrameric cation has been determined by others$^{19}$ to be preserved, though subsequent polymerization is dependent on pH (changes in pH can often lead to different conformations around Zr$^{4+}$), aging temperature, and concentration of the solution.$^{20}$

In Step 2, ammonia is added, raising the pH considerably. This leads to the formation of a hydrous zirconia precipitate through olation and oxolation of the previously described tetramers. The nature of this hydrous zirconia is described by Clearfield$^{21}$ as an anhydrous ZrO$_2$ core, with each metal cation coordinated to eight oxygens (themselves coordinated to four Zr$^{4+}$ cations), terminated by protonated oxygens. These terminal surface oxygens, in the form of hydroxide anions and water molecules, are due to incomplete oxolation and prevent the precipitation of insoluble ZrO$_2$ in solution.

Washing steps, designed to remove ammonia and chloride, are necessary for film quality. In order to assure that the unwanted ionic
species were fully washed from the precipitate, decanted supernatants from wash steps were tested with AgNO₃ (aq) and checked for any resultant precipitate.

The addition of HNO₃ to the final, washed precipitate allows the dissolution of the precipitate without the destruction of polymeric species (Step 3). Because of the weak bonding of NO₃⁻ to the Zr complex, film dehydration is then possible with low-temperature curing steps.

The addition of H₂O₂ in Step 4 improves the dissolution time of the precipitate in HNO₃ and has other benefits, as well. The presence of peroxo ligands in the solution prevent premature condensation by replacing hydroxo bridges and ultimately lower the film curing temperature because they are easily decomposed.

2.5 Conclusions

Thin, dense, and smooth ZrO₂ films that are free of major defects have been deposited by using a peroxozirconium precursor via spin-coating deposition. Deposited films show densities as high as 90% of the bulk density. Films further demonstrate high refractive properties at annealing temperatures as low as 150 °C. Ultra-thin films were prepared by diluting standard solutions, demonstrating one of the unique advantages over traditional methods: precise control of metal
oxide thickness without the need for expensive vacuum systems.

Because of the high density and smoothness of the films, and control over deposition thickness, the next stage of research should certainly be the incorporation of these thin films into test devices for electrical characterization.
References


Figures

**Figure 2.1** X-Ray Reflectivity measurements at low incident angles for ZrO\textsubscript{2} thin films annealed 1 h at varying temperatures

**Figure 2.2:** Refractive index vs. wavelength for ZrO\textsubscript{2} thin films deposited from 0.2 M precursor at two representative anneals.
Figure 2.3 ZrO$_2$ thin film thickness vs. precursor concentration. Points calculated by depositing 5 layers at 150 °C for 1 h and then dividing by 5.

\[ y = 67.143x^2 + 18.432x + 0.2306 \]
\[ R^2 = 0.9994 \]

Figure 2.4 Refractive index vs. $\lambda$ for ZrO$_2$ thin films deposited from lower concentration precursors and annealed at 150 °C.
Figure 2.5 Flow diagram for the preparation of ZrO\(_2\) precursor.

Table 2.1 Model fitting results for ZrO\(_2\) thickness, Cauchy parameters A, B, and C, and mean square error (MSE).

<table>
<thead>
<tr>
<th>Anneal (°C)</th>
<th>[Zr(^{4+})] (M)</th>
<th>(t) (ZrO(_2)) (nm)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>MSE</th>
</tr>
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<tr>
<td>300</td>
<td>0.20</td>
<td>231.7(4)</td>
<td>1.932(2)</td>
<td>(8.79(65) \times 10^{-3})</td>
<td>(8.26(5) \times 10^{-4})</td>
<td>15.43</td>
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<tr>
<td>700</td>
<td>0.20</td>
<td>210.9(5)</td>
<td>1.919(4)</td>
<td>(7.25(10) \times 10^{-3})</td>
<td>(9.10(10) \times 10^{-4})</td>
<td>11.94</td>
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<tr>
<td>150</td>
<td>0.15</td>
<td>22.51(25)</td>
<td>2.019(29)</td>
<td>(-71.60(10) \times 10^{-3})</td>
<td>(6.48(97) \times 10^{-3})</td>
<td>14.37</td>
</tr>
<tr>
<td>150</td>
<td>0.10</td>
<td>13.90(18)</td>
<td>2.015(76)</td>
<td>(-113(22) \times 10^{-3})</td>
<td>(10.5(1) \times 10^{-3})</td>
<td>8.99</td>
</tr>
<tr>
<td>150</td>
<td>0.05</td>
<td>6.15(24)</td>
<td>2.278(33)</td>
<td>(-68.60(97) \times 10^{-3})</td>
<td>(7.90(9) \times 10^{-3})</td>
<td>3.92</td>
</tr>
<tr>
<td>150</td>
<td>0.035</td>
<td>5.10(42)</td>
<td>2.20(11)</td>
<td>(124(47) \times 10^{-1})</td>
<td>(11.3(4) \times 10^{-1})</td>
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CHAPTER 3: AQUEOUS CLUSTER CHEMISTRIES
FOR SOLUTION-DEPOSITED NIOBIUM (V) OXIDE

Sharon A. Betterton, Wei Wang, William Casey, Douglas Keszler

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3.1 Abstract

A novel method to deposit Nb₂O₅ has been realized by making use of the discrete [N(CH₃)₄]₆[Nb₁₀O₂₈] cluster in an aqueous, inorganic solution precursor. Due to the inclusion of the tetramethylammonium ligand, anneal temperatures of 350 °C are required to build thickness, and nano-cavities have been discovered in deposited films. Despite these cavities, densities of up to 90% bulk are observed. AFM analysis demonstrates very smooth films (RMS roughness values <0.5 nm), which are amorphous below 550 °C.
3.2 Introduction

Nb$_2$O$_5$ thin films have garnered attention for use in a variety of applications (electrochromic devices,$^{1,2}$ second harmonic oscillators,$^2$ optical waveguides,$^{2,3}$ UV protective materials,$^2$ interference filters,$^3$ anti-reflective coatings for solar cells,$^4$ and high permittivity dielectrics$^4$) due to niobium oxide's high index of refraction, transparency in the visible range, insolubility, stability, and non-reactivity,$^5$ and the methods of depositing Nb$_2$O$_5$ films have been equally diverse. Efforts into thin film deposition include physical vapor deposition (PVD),$^{2,3,5}$ chemical vapor deposition (CVD),$^4$ thermal oxidation,$^6$ spray pyrolysis,$^{7,8}$ electrodeposition,$^9,10$ and sol-gel solution precursors,$^{1,11-19}$ each method with its own advantages and limitations contingent on the film's intended purpose.

Vapor deposition is often the go-to method for oxide deposition in electronics,$^{20}$ and has been used frequently to deposit Nb$_2$O$_5$ thin films.$^{2-5}$ As can be the case with vapor deposition of oxides, proper stoichiometry of the final films can present an obstacle.$^5$ Solution processing, nearly all of it focused on sol-gel methods, has attracted interest in the past 20 years as an alternative to conventional techniques because of its potential to provide larger area coverage without the need for an unwieldy vacuum system (thus reducing costs),
and in attempts to standardize film quality and stoichiometry.\textsuperscript{11-13}

The first reported use of sol-gel for the deposition of Nb\textsubscript{2}O\textsubscript{5} was by Lee and Crayston in 1991,\textsuperscript{13} and though their novel approach was to have a significant impact on the solution processing efforts to follow, initial results demonstrated numerous difficulties typical of early sol-gel methods. The deposited films showed inconsistent thicknesses across the substrate, and though they found that the organics used to deposit the film were completely removed by only 150 °C, the Nb\textsubscript{2}O\textsubscript{5} began to crack and delaminate as the film dried.\textsuperscript{13} Subsequent sol-gel methods have utilized similar approaches – namely chloroalkoxides in organic media with acidic catalysts (typically acetic or citric acid) – with varying results.\textsuperscript{1,11,12,14-18} Characteristic of the sol-gel method are the presence of large colloid particles (20 nm to 100 nm),\textsuperscript{14,16,18,19} resulting in high surface roughness, low densities compared to vapor deposited films,\textsuperscript{3,5,11,15,18} and high annealing temperatures.\textsuperscript{12,14,18} As a recurring goal of those using the sol-gel method has been the use of Nb\textsubscript{2}O\textsubscript{5} films for electrochromic purposes, in which cation diffusion is directly correlated to device functionality, porosity is considered a favorable quality.\textsuperscript{11,13} However, for use in electronic devices, porosity and large grain size (occasionally an obstacle in sputtering\textsuperscript{3}) are detrimental to device performance.
An alternative to current sol-gel technologies, then, seems necessary in order to deposit low-cost and environmentally 'green' Nb$_2$O$_5$ films that are dense, smooth, and of high enough quality for use in electronic devices. Whereas in sol-based chemistry, large organic ligands are necessary to stabilize solutions, frequently requiring high temperatures to decompose said organics, aqueous precursors frequently reduce or eliminate the need for such organics, lowering annealing temperatures and improving film quality and smoothness. A particular difficulty arises with regard to niobium-based aqueous precursors, however, as niobium species are highly pH sensitive and especially prone to polymerizing and precipitating out niobium oxides.$^{21,22}$

Our goal in this work is to employ a novel approach to depositing Nb$_2$O$_5$ from an aqueous precursor, while minimizing the need for organics. Recently, Ohlin, Villa, and Casey$^{23}$ developed a simple method to synthesize a decaniobate cluster of the formula [N(CH$_3$)$_4$]$_6$[Nb$_{10}$O$_{28}$], which we have used in the development of an aqueous precursor for the deposition of dense, smooth, solution-processed Nb$_2$O$_5$ thin films.

3.3 Experimental

3.3.1 Precursor solutions. Aqueous niobate precursor solutions were prepared by dissolving crystallized decaniobate clusters (synthesis
described elsewhere\textsuperscript{23} in 18-MΩ Millipore water to a final metal concentration of 0.2 M. Solution pH was controlled by adding 0.1 M NH\textsubscript{3}(aq) (Alfa Aesar, 99.99%) drop-wise to a final value of 7 to 11.

3.3.2 Thin-film deposition. Precursor solutions were filtered through a 0.45-μm PTFE syringe filter and applied to 200-nm SiO\textsubscript{2}/Si substrates. Prior to spin-coating, substrates were cleaned in an ultrasonic bath by using a 5% solution of Contrad-70 (Decon Labs) for 45 min at 45 °C, rinsed with 18-MΩ H\textsubscript{2}O, and then treated in a Plasma-Therm reactive ion etching system by using a 10 min oxygen plasma ash at 10 mTorr, 5 sccm O\textsubscript{2}, and 0.75 W cm\textsuperscript{−2}. Substrates coated with precursor were spun at 3000 rpm for 30 s and then immediately cured at 350 °C for 2 min on a hotplate. Films deposited from 0.2 M solution were typically 9 nm per coat. These steps were repeated to produce a desired thickness in the range 90–450 nm. Films were then annealed for 1 h at selected temperatures over the range 350–550 °C.

3.3.3 Structural and chemical characterization. Decaniobate crystals (17 mg) were characterized by using a Mettler Toledo thermogravimetric analyzer (TGA 850) with a ramp rate of 2 °C min\textsuperscript{−1} in an alumina crucible under flowing Ar(g). X-ray diffraction (XRD) data on deposited thin films were collected on a Rigaku RAPID diffractometer with Cu Kα radiation. Film-surface-morphology data
were collected on a Digital Instruments NanoScope III Multimode atomic force microscope (AFM) in contact mode by using a Veeco NP-20 SiNx probe and a scan frequency of 1.5 Hz. A first-order flatten was applied to all data to eliminate image bow. Cross-sectional scanning electron microscope (SEM) images were obtained from the Analytical and Development Laboratory at Hewlett Packard, Corvallis. Cross-section transmission electron microscopy (TEM) samples were prepared by using an FEI Helios 600 dual-beam system and then analyzed by scanning transmission electron microscopy annular dark-field images and atomic-resolution TEM imaging using an FEI Titan 80-300 TEM with an image aberration-corrector through the Center for Advanced Materials Characterization at the University of Oregon, Eugene.

3.3.4 Optical characterization. Film thicknesses and refractive indices of Nb$_2$O$_5$ films (10 layers deposited on 200-nm SiO$_2$/Si substrates and annealed at 350 °C, 450 °C, and 550 °C) were determined by using a J.A. Woollam HS-190 Ellipsometer; data were analyzed with the Woollam VASE software package. X-ray reflectivity (XRR) measurements were collected with Cu Kα radiation by using a Rigaku Ultima IV X-Ray diffractometer. Reflectivity was measured from 0-10 ° (2θ) and roughness, thickness, and density analyses were performed using the GlobalFit Reflectivity Program.
3.4 Results and Discussion

3.4.1 Precursor chemistry and analysis. TGA data were collected on decaniobate crystals to allow for predictions about the decomposition chemistry of deposited films. In the TGA results shown in Figure 3.1, two significant mass loss regions are observed near 100 °C and 350 °C. The first region (50–150 °C) corresponds to mass loss from the dehydration of incorporated H$_2$O. Mass loss in the 270–380 °C region can be attributed to the decomposition of tetramethylammonium (TMA) ligands, likely coordinated or bonded to water. As indicated by TGA data, an inter-layer temperature of 350 °C was required to build thickness during spin-coating.

Upon dissolution of decaniobate crystals into H$_2$O, the subsequent solution is transparent and nearly colorless (pale yellow) with a pH = 7. A decrease in pH is observed in basic solutions (pH = 8–11) after a few hours. No precipitate forms in any sealed solution after storage for months at ambient temperature.

3.4.2 Film morphology. Film-surface quality is observed to correlate directly with the pH of the precursor solution. After spin-coating, films deposited from precursor solutions of pH = 7–8 show visible signs of precipitation, whereas film quality improves considerably when the pH
of the precursor solution is raised to 9–10. These results point to the importance of various niobate cluster species in solution, the identities of which rely upon pH. In the regime in which Ohlin et al. report decaniobate to be stable (pH = 5–8), several other niobate species are also present. Above pH = 6.5, the Lindqvist ion (H₃Nb₆O₁₉⁺⁻ [x = 0–3]) predominates, whereas below pH = 6.5, polymerization of hexaniobate species is theorized to form both the Keggin ion (Nb₁₂O₃₆⁴⁻) and hydrated Nb₂O₅ precipitate.

The stability of these species provides valuable insight into the observed results, and was ultimately the deciding factor for which precursor pH range we were able to utilize. Whereas the aqueous hexaniobate species is considered stable, particularly in the basic pH regime, niobate species present in acidic aqueous solutions are far more prone to hydrolysis and polymerization. This instability makes the as-dissolved aqueous decaniobate precursor (pH = ~7) problematic to spin-coat. At the cusp of the acidic regime, a finely balanced equilibrium between Nb₁₀O₂₈⁶⁻ and H₃Nb₆O₁₉⁵⁻ should exist; this equilibrium is disrupted during spin-coating, as rapid evaporation of water results in the polymerization of the hexaniobate species and the generation of protons. As the system becomes more acidic, polymerization occurs more readily, as does a decrease in pH, moving the system into a
regime in which hydrated Nb$_2$O$_5$ precipitates before the film can be properly deposited.

In order to hinder this regime shift, the pH of the precursor solution is adjusted higher, to pH = 8–10. At pH = 8, film quality is somewhat improved, but similar defects due to precipitation are observed. At pH = 9–10, precipitation effects are no longer visible to the naked eye, as the system is shifted into a pH range in which the decaniobate-hexaniobate equilibrium provides considerable stability.

Root-mean-square roughness values calculated via contact-mode AFM surface analysis over a 1.0 × 1.0 μm area were 0.2 nm, 0.3 nm, and 0.5 nm for films annealed at 350 °C, 450 °C, and 550 °C, respectively. These values indicate very smooth films that do not roughen significantly with higher annealing temperatures or film crystallization.

XRD patterns for deposited Nb$_2$O$_5$ over a range of temperatures are graphed in Figure 3.2. The lack of diffraction peaks in the non-annealed film, as well as in those films annealed at 350 °C and 450 °C suggest that the films are amorphous at these temperatures. At 550 °C, crystallization is apparent, and Nb$_2$O$_5$ peaks characterize the TT phase ("pseudohexagonal").

SEM cross-section data (see Figure 3.3) reveal a thickness of 9 nm
per deposition layer at both 450 °C (Figure 3.3a) and 550 °C (Figure 3.3b). These values were confirmed by ellipsometry. At 450 °C, the film appears uniform, though this cross-section provides an interesting contrast to the seemingly straightforward crystallization temperature, as determined via XRD. Though the XRD pattern for the Nb$_2$O$_5$ thin films demonstrates an amorphous nature at 450 °C, the SEM cross-section appears to be crystalline in nature, with defined grains on the scale of ~20 nm. Common causes of XRD peak broadening (small crystallite size and micro-strain)$^{26,27}$ are unlikely culprits in this 2θ range, leaving the cause of the discrepancy unclear. At 550 °C, at which temperature crystallization is predicted by the XRD analysis, grain growth is clear, as is the manifestation of voids. The minute change in thickness (~2%) is likely due to the simultaneous shrinkage from the densification of grains and expansion from grain/void growth.

Thin-film cross sections were analyzed by TEM to provide insight into the films' crystallinity and micro-structure. At 350 °C and 450 °C, the films are clearly amorphous, and at 550 °C, the TEM confirms the crystallization temperature suggested by XRD. A stippled contrast in the 450 °C film (Figure 3.4) indicates the presence of inclusions, which may be nano-cavities, as suggested by the presence of similar contrast variations in other oxide films;$^{28}$ it has been suggested that these nano-
cavities are the result of metal-organic decomposition processes, and may be related to the presence of TMA in our film precursor. The presence of these nano-cavities is supported by the considerable voids present in the thin films upon crystallization, and may account for the previously discussed micro-structure observed in the SEM cross-section of the 450 °C film.

3.4.3 Optical properties. Index of refraction as a function of wavelength for Nb$_2$O$_5$ films annealed at 350 °C, 450 °C, and 550 °C is shown in Figure 3.5. Amorphous films (350 °C and 450 °C anneal) showed consistently higher refractive indexes at all wavelengths than the crystallized films (550 °C anneal), and there were no appreciable differences between the measured n values of films annealed at 350 °C versus 450 °C. The difference in refractive indices before and after crystallization are likely due to the network of voids in the crystallized films, as shown earlier in the TEM cross-section.

The relationship between density and the refractive index of a material is described by the equation:

\[
\frac{n_1^2 n_2^2 + 2n_1^2 - n_2^2 - 2}{n_1^2 n_2^2 + 2n_1^2 - n_2^2 - 2} = \frac{\rho_1}{\rho_2}
\]

where \(n_1\) and \(n_2\) are the indices of refraction of a thin film and bulk material, respectively, and \(\rho_1\) and \(\rho_2\) are the materials' respective
densities. Using this method to compare the densities of our thin films to that of the bulk material \( n (\text{Nb}_2\text{O}_5) = 2.4, \lambda = 550 \text{ nm} \), we find that by spin-coating an aqueous precursor we are able to achieve a calculated density of \(~90\%\) bulk at 350 °C. Upon crystallization, the density of our material, like the refractive index, diminishes to \(~86\%\) of that of bulk. XRR analysis revealed that a \( \text{Nb}_2\text{O}_5 \) thin film deposited at 350 °C had a density of 4.14 g/cm\(^3\), or 90% of that of bulk, a good agreement with refractive index calculations. To put these numbers into perspective, a typical sol-gel film deposits at a density of \(~71\%\), and sputtered materials range in the mid 90s compared to bulk.

### 3.5 Conclusions

Though the use of solution processing methods in the deposition of niobium oxide is certainly not a new technique, the great majority of previously reported techniques have employed the sol-gel method, for reasons that are immediately obvious when niobium solution chemistry is considered. Niobium species in aqueous solutions are notoriously unstable and begin precipitating out solid \( \text{Nb}_2\text{O}_5 \) at pHs as low as 7. Historical efforts to circumvent this rapid hydrolysis have been focused primarily around the use of organic media and through the incorporation of large organic ligands to inhibit polymerization and
stabilize precursor solutions. However, the often unfavorable impact these organics have on film quality for electronic purposes spurred our investigations of an aqueous based precursor solution.

In order for an aqueous precursor to be suitable, the niobium species must be stable enough to prevent the formation of a colloid solution, as large particles limit density and increase film roughness, but not so stable that requisite frameworks cannot form on a film during spin-coating. Considerations must also be made with regard to pH stability, as the hydrolysis induced by spin-coating results in a pH drop that can be detrimental to the quality of the film if solid precipitates form before the process is complete.

Of all the niobium based species that form in aqueous solution, those in the neutral to basic range, decaniobate $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ and hexaniobate $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(x-8)}$, were appealing due to their small size and reported stability.$^{21,23,34}$ An answer to the difficulties of spin-coating presented itself in findings by Casey,$^{23,34}$ who reported the discovery of a simple synthesis of the decaniobate salt $[\text{N(CH}_3)_4]^6[\text{Nb}_{10}\text{O}_{28}]\cdot6\text{H}_2\text{O}$. At near neutral pHs [pH 5-8], the decaniobate ion remains intact, and at a pH of 9.3, they propose that an equilibrium state between the decaniobate ion and the hexaniobate ion exists, in which the two species interconvert and the remaining tetramer forms a heptaniobate
ion. This unique relationship provides a particularly stable aqueous pH regime, one which we have been able to exploit for the purposes of deposition.

$\mathrm{Nb}_2\mathrm{O}_5$ thin films have been deposited from an aqueous decaniobate-cluster-based precursor solution. At temperatures of 350 °C and 450 °C, these films are very smooth, amorphous and have refractive indices indicative of high densities (~90% bulk). Upon crystallization, the refractive index and density drop slightly, likely due to extensive void growth. TEM contrast suggests the possibility of nano-cavities in the amorphous films, potentially due to the presence of the organic ligand TMA in the solution precursor.
References


Figures

**Figure 3.1** TGA mass-loss curve of $[\text{N(CH}_3\text{)}_4]_6[\text{Nb}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$ crystals under flowing Ar and its derivative.

**Figure 3.2** X-Ray Diffraction patterns of Nb$_2$O$_5$ films at different anneal temperatures (1 h).
Figure 3.3 Cross-sectional SEM image of ~230 nm Nb$_2$O$_5$ films annealed for 1 h at a) 450 °C and b) 550 °C.
Figure 3.4 TEM cross-section of Nb$_2$O$_5$ film annealed for 1 h at 450 °C; stippling is caused by the presence of nano-cavities.

Figure 3.5 Index of refraction vs. $\lambda$ for Nb$_2$O$_5$ films (90 nm) annealed at varying temperatures.
CHAPTER 4: CONCLUSIONS
With the growing demand for high-\(\kappa\) dielectric materials to replace or complement existing SiO\(_2\) dielectrics, the deposition of transition metal oxides is an increasingly pertinent subject. As micro-electronics grow smaller and macro-electronics bigger, flexible deposition techniques become more appealing, particularly those that remove the need for expensive and impractical vacuum systems.

This work has demonstrated clearly the potential of inorganic aqueous solution-based deposition methods. A nitrate-based precursor solution has been developed for the deposition of amorphous ZrO\(_2\) films without the need for bulky organic ligands so prevalent in other solution-based works. A calculable relationship between concentration and thickness makes clear the thickness-control provided by aqueous precursors, and the density (88\% of bulk) and atomic smoothness suggest ZrO\(_2\) deposited via solution methods is a promising candidate for incorporation into electrical test devices.

A Nb\(_2\)O\(_5\) precursor has also been developed, making use of aqueous cluster chemistries to circumvent the marked instability of Nb\(^{5+}\) in water. By utilizing the discrete, small \([\text{N(CH}_3\text{)}_4]_6[\text{Nb}_{10}\text{O}_{28}]\) cluster, and its metastable equilibrium with hexaniobate at higher pHs, it was possible to deposit smooth, dense (~90\% bulk), amorphous thin films. Due to the inclusion of the N(CH\(_3\))\(_4\) ligand, nano-cavities were observed
in the final films. Though these are undesirable in making use of the thin films for the purposes of dielectric layers, they do provide an avenue for future density studies, in which density may prove to be another 'tunable' quality of thin films deposited by aqueous methods.
BIBLIOGRAPHY


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