AN ABSTRACT OF THE DISSERTATION OF


Title: Reaction Pathways of Oxo-Hydroxo Group 5 Clusters to Metal Oxide Thin Films.

Abstract approved: ________________________________________________________________

Douglas A. Keszler Brady J. Gibbons

Oxo-hydroxo Group 5 metal clusters are an untapped resource to study and advance aqueous solution processing of metal oxide thin films. The tetramethylammonium (TMA) hexatantalate salt (TMA$_6$[H$_2$Ta$_6$O$_{19}$]) yields dense Ta$_2$O$_5$ films (~95% of the bulk $\beta$-Ta$_2$O$_5$ density) with atomically smooth surfaces (<4 Å root mean square surface roughness). This same precursor produces single-digit-nanometer thick films at low solution concentrations. The diprotonated cluster TMA$_6$[H$_2$Ta$_6$O$_{19}$] cluster produces films much different from those of the triprotonated analog TMA$_5$[H$_3$Nb$_6$O$_{19}$]. One additional proton in [H$_3$Nb$_6$O$_{19}$]$^5^-$ yields rougher Nb$_2$O$_5$ films with nanoparticles at the surface. A temperature-programmed desorption study of TMA$_6$[H$_2$Ta$_6$O$_{19}$] elucidates the reaction pathway of precursor to solid oxide. Lastly, the acid-base, ion-exchange chemistry of the basic [H$_2$Ta$_6$O$_{19}$]$^{6^-}$ precursor enables a path to produce amorphous tantalum oxide films at temperatures as low as 200 °C.
Doctor of Philosophy dissertation of Ryan H. Mansergh presented on June 19, 2017

APPROVED:

Major Professor, representing Chemistry

Major Professor, representing Materials Science

Chair of the Department of Chemistry

Head of the School of Mechanical, Industrial, and Manufacturing Engineering

Dean of the Graduate School

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

Ryan H. Mansergh, Author
ACKNOWLEDGEMENTS

I would like to thank my advisor, Prof. Douglas A. Keszler for his guidance, support, and intellectual inspiration. I owe my co-advisor Brady J. Gibbons many thanks, for his support and contribution to my knowledge of Materials Science. I would also like to thank my graduate committee Profs. Paul Ha-Yeon Cheong, David Xiulei Ji, May Nyman, Prasad Tadepalli, and John F. Wager, whose diverse expertise has truly helped me to evaluate my work from a multitude of angles. I have had the opportunity to work with a talented group of individuals as a member of the Keszler group and the Center for Sustainable Materials Chemistry (CSMC). I wish to acknowledge the great work done by the CSMC leadership, especially Dr. Bettye L.S. Maddux. This material is based on work in the Center for Sustainable Materials Chemistry, which is supported by the U.S. National Science Foundation under Grant CHE-1102637.

I would like to sincerely thank Bradley A. Zenger for his mentorship and financial support through Pivotal Investments. I learned a great deal in the Lens of the Market program thanks to Judith C. Giordan of ecosVC, and for that I owe her a debt of gratitude.

I would like to thank the undergraduate researchers that have worked with me throughout the years, including Stefan Lucchini, Joshua Motley, Gabrielle Westerfield, and Eaton Fong. I would also thank the numerous SMaRT Camp students that I have mentored over the years.

Last, but not least, I would like to thank my family, including my mother and two sisters for always sticking together through good times and bad.
CONTRIBUTION OF AUTHORS

This work reflects the fruitful collaboration with the Nyman group, and I am deeply appreciative for the intellectual input Prof. May Nyman has provided throughout the course of this project. Additionally, I wish to give great thanks to Dr. Lauren B. Fullmer for her synthetic work, small- and wide-angle X-ray scattering, Raman spectroscopy studies, and powder characterization, as well as Deok-Hie Park for her assistance with the thermogravimetric analysis-mass spectrometry and temperature-programmed desorption studies. For spectroscopic studies in Chapters 5 and 6, I would like to thank Dr. Cory K. Perkins and Jenn M. Amador. I would like to acknowledge the work of Nicholas P. Landau of the Wager group, for device fabrication and electrical measurements in Chapter 2. Additional electrical characterization was performed by Dr. Juan Carlos Ramos.

I would like to thank Dr. P. Eschbach and T. Sawyer with assistance in scanning electron microscopy (SEM) and transmission electron microscopy imaging in the OSU Electron Microscope Facility. I would also like to acknowledge the assistance of the staff at CAMCOR, including J. Ditto and R. E. Fischer in SEM imaging, and Dr. S. L. Golledge in his assistance during the X-ray photoelectron spectroscopy studies. I also would like to acknowledge the use of the facilities at the Microproducts Breakthrough Institute (MBI), and the assistance of J. Motley and S. Lucchini with collecting atomic force microscopy data. I wish to acknowledge Prof. M. Dolgos for her expertise in X-ray diffraction structural refinements. I would like to thank C. Tasker and R. Presley for their tireless efforts in keeping the cleanroom fully operational.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter 1: INTRODUCTION TO USING POLYOXOMETALATES FOR THE AQUEOUS SOLUTION DEPOSITION AND PROCESSING OF METAL OXIDE THIN FILMS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>2</td>
</tr>
<tr>
<td>Tantalum Oxide Thin-Film Literature Review</td>
<td>3</td>
</tr>
<tr>
<td>The Current Landscape of Tantalum Polyoxyometalates</td>
<td>4</td>
</tr>
<tr>
<td>References</td>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 2: A BASELINE STUDY OF TMA TANTALUM POLYOXOMETALATE SALTS FOR THE AQUEOUS SOLUTION DEPOSITION OF HIGH-DENSITY TANTALUM OXIDE THIN FILMS</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>12</td>
</tr>
<tr>
<td>Experimental Methods</td>
<td>13</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>18</td>
</tr>
<tr>
<td>Conclusion</td>
<td>63</td>
</tr>
<tr>
<td>References</td>
<td>66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 3: Nb$_2$O$_5$ and Ta$_2$O$_5$ THIN FILMS FROM POLYOXOMETALATE PRECURSORS: A SINGLE PROTON MAKES A DIFFERENCE</th>
<th>69</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>70</td>
</tr>
<tr>
<td>Introduction</td>
<td>71</td>
</tr>
<tr>
<td>Experimental Methods</td>
<td>74</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>78</td>
</tr>
<tr>
<td>Conclusions</td>
<td>93</td>
</tr>
<tr>
<td>References</td>
<td>95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 4: REACTION PATHWAY: AQUEOUS HEXATANTALATE CLUSTERS TO HIGH-DENSITY TANTALUM OXIDE NANOFILMS</th>
<th>98</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>99</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>100</td>
</tr>
<tr>
<td>Experimental Methods</td>
<td>101</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>104</td>
</tr>
<tr>
<td>Conclusions</td>
<td>116</td>
</tr>
<tr>
<td>References</td>
<td>118</td>
</tr>
</tbody>
</table>

Chapter 5: ION EXCHANGE FOR LOW-TEMPERATURE PROCESSING AND ENHANCED FUNCTIONALITY OF SOLUTION-PROCESSED TANTALUM OXIDE THIN FILMS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>121</td>
</tr>
<tr>
<td>Experimental Methods</td>
<td>122</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>126</td>
</tr>
<tr>
<td>Conclusions</td>
<td>145</td>
</tr>
<tr>
<td>References</td>
<td>146</td>
</tr>
</tbody>
</table>

Chapter 6: LOW-TEMPERATURE PROCESSING OF AMORPHOUS TANTALUM OXIDE FILMS VIA CHEMICAL CONDENSATION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>148</td>
</tr>
<tr>
<td>Experimental Methods</td>
<td>149</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>154</td>
</tr>
<tr>
<td>Conclusions</td>
<td>166</td>
</tr>
<tr>
<td>References</td>
<td>168</td>
</tr>
</tbody>
</table>

Chapter 7: CONCLUSIONS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bibliography</td>
<td>171</td>
</tr>
</tbody>
</table>

Appendix A: Supporting Information for Chapter 3

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction Pathway: Effect of Additional Proton on Nb₆ Film Formation</td>
<td>194</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy Study on Nb₆-Derived Films</td>
<td>202</td>
</tr>
</tbody>
</table>
## TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Appendix B: Supporting Information for Chapter 4</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effects of Thermal Processing on Ta₆-Derived Films</td>
<td>211</td>
</tr>
<tr>
<td>Electrical Characterization of Ta₆-Based MIS Devices</td>
<td>215</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy Study on Ta₆-Derived Films</td>
<td>223</td>
</tr>
<tr>
<td>References</td>
<td>226</td>
</tr>
<tr>
<td>Appendix C: Supporting Information for Chapter 5</td>
<td>228</td>
</tr>
<tr>
<td>Appendix D: Supporting Information for Chapter 6</td>
<td>229</td>
</tr>
<tr>
<td>Appendix E: Supporting Information for Chapter 6</td>
<td>234</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Fit of the pair distance distribution function analysis determined from SWAXS studies of the 7 wt % precursor solution exhibiting dimerization</td>
<td>19</td>
</tr>
<tr>
<td>2.2</td>
<td>HAADF-STEM image of a TMA-Ta1 agglomeration (left); the associated EDX map of the same agglomerate (right). The tantalum content is indicated in magenta.</td>
<td>20</td>
</tr>
<tr>
<td>2.3</td>
<td>Raman spectra of the tantalate salt solution and powder and a TMAOH solution for comparison.</td>
<td>21</td>
</tr>
<tr>
<td>2.4</td>
<td>Scanning electron microscope image of the TMA-Ta1 powder.</td>
<td>22</td>
</tr>
<tr>
<td>2.5</td>
<td>TGA-DSC data of TMA-Ta1 collected in air</td>
<td>23</td>
</tr>
<tr>
<td>2.6</td>
<td>TGA-MS data collected under air. Fragments showing no appreciable response have been removed for clarity.</td>
<td>24</td>
</tr>
<tr>
<td>2.7</td>
<td>TGA-DSC data of TMA-Ta1 collected with N₂ flow gas.</td>
<td>25</td>
</tr>
<tr>
<td>2.8</td>
<td>TGA-MS data collected under N₂. The molecular fragments ranging from 15 to 59 amu were selected as likely candidates for the decomposition of TMA.</td>
<td>26</td>
</tr>
<tr>
<td>2.9</td>
<td>A 30 wt % solution used for film deposition (left); typical film appearance post-annealing (right).</td>
<td>27</td>
</tr>
<tr>
<td>2.10</td>
<td>GIXRD pattern of an as-deposited film made with 30 wt % TMA-Ta1.</td>
<td>27</td>
</tr>
<tr>
<td>2.11</td>
<td>XRR scans of 400, 600, and 800 °C samples</td>
<td>28</td>
</tr>
<tr>
<td>2.12</td>
<td>AFM images of the 400 °C sample (top), perspective view of the 600 °C sample (middle), and the 800 °C sample (bottom)</td>
<td>29</td>
</tr>
<tr>
<td>2.13</td>
<td>Select XRR models for the 400 and 800 °C samples</td>
<td>30</td>
</tr>
<tr>
<td>2.14</td>
<td>Del-psi plots and dispersion curves for the 400 °C sample (top), the 600 °C sample (middle), and the 800 °C sample (bottom)</td>
<td>31</td>
</tr>
<tr>
<td>2.15</td>
<td>Cross-sectional SEM image of the 400 °C sample; a film thickness of ca. 80.4 nm was measured (top); cross-sectional SEM image of the 800 °C sample with an approximate film thickness of 72 nm and an interfacial oxide of ca. 3.8 nm (bottom).</td>
<td>32</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.16</td>
<td>XRD data from an annealing study on films prepared from 30 wt % TMA-Ta1 solutions. The films remain amorphous until approximately 725 °C. The simulated orthorhombic β-Ta2O5 phase is shown (top pattern) in addition to the Si(100) substrate (bottom pattern)</td>
<td>33</td>
</tr>
<tr>
<td>2.17</td>
<td>XRR for samples annealed at temperatures ranging from 300 to 800 °C for 10 min</td>
<td>34</td>
</tr>
<tr>
<td>2.18</td>
<td>Film thickness as determined via SE and XRR; the refractive indices measured at 550 nm are shown on the same plot</td>
<td>35</td>
</tr>
<tr>
<td>2.19</td>
<td>Film density and RMS roughness as a function of temperature as determined XRR. XRR-derived RMS roughness values are compared to AFM results</td>
<td>36</td>
</tr>
<tr>
<td>2.20</td>
<td>(a) Cross-sectional TEM image of sample annealed at 400 °C for 10 min; interfacial SiO2 layer shown in inset. (b) CBED pattern of amorphous Ta2O5 layer. (c) CBED pattern of the same layer after ~1 min of electron beam exposure. (d, e, f) HAADF image and EDX mapping of tantalum (magenta) and oxygen (blue) content. White scale bars in HAADF and EDX maps represent 40 nm.</td>
<td>38</td>
</tr>
<tr>
<td>2.21</td>
<td>XRR patterns of samples annealed from 5 to 60 minutes at 400 °C</td>
<td>39</td>
</tr>
<tr>
<td>2.22</td>
<td>Film thickness as determined via XRR and SE and refractive indices (also determined by SE) for samples annealed from 5 to 60 min at 400 °C</td>
<td>40</td>
</tr>
<tr>
<td>2.23</td>
<td>Film density and RMS roughness as a function of annealing time as determined by XRR modeling results</td>
<td>41</td>
</tr>
<tr>
<td>2.24</td>
<td>Thickness of the interfacial SiO2 layer as determined by SE and XRR</td>
<td>42</td>
</tr>
<tr>
<td>2.25</td>
<td>HRTEM micrograph of the interfacial SiO2 layer in a sample annealed for 10 min at 400 °C</td>
<td>42</td>
</tr>
<tr>
<td>2.26</td>
<td>XRR data for samples prepared with concentrations ranging from 3.5 to 28 wt %; all samples were annealed at 400 °C for 10 min</td>
<td>43</td>
</tr>
<tr>
<td>2.27</td>
<td>XRR data for samples prepared with concentrations ranging from 0.14 to 1.4 wt %; all samples were annealed at 400 °C for 10 min</td>
<td>44</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.28</td>
<td>Film thicknesses (SE and XRR) and refractive indices (SE); thicknesses range from ~10 nm to 80 nm for this sample set.</td>
<td>45</td>
</tr>
<tr>
<td>2.29</td>
<td>Film density and RMS roughness as a function of solution concentration determined via XRR modeling.</td>
<td>46</td>
</tr>
<tr>
<td>2.30</td>
<td>GIXRD pattern for a film prepared from a 7 wt% solution and annealed at 400 °C for 10 min.</td>
<td>46</td>
</tr>
<tr>
<td>2.31</td>
<td>Graphical summary of the results from the temperature, time, and concentration studies.</td>
<td>49</td>
</tr>
<tr>
<td>2.32</td>
<td>Thin-film stack used in XRR modeling. The dense crust containing lower Ta-oxides is denoted TaO_x.</td>
<td>50</td>
</tr>
<tr>
<td>2.33</td>
<td>XPS data for the Ta4f_{5/2} and Ta4f_{7/2} peaks for the sample annealed at 400 °C.</td>
<td>51</td>
</tr>
<tr>
<td>2.34</td>
<td>XPS data for the O1s peak for the sample annealed at 400 °C.</td>
<td>51</td>
</tr>
<tr>
<td>2.35</td>
<td>XPS data for the Ta4f_{5/2} and Ta4f_{7/2} peaks for the sample annealed at 600 °C.</td>
<td>52</td>
</tr>
<tr>
<td>2.36</td>
<td>XPS data for the O1s peaks for the sample annealed at 600 °C.</td>
<td>52</td>
</tr>
<tr>
<td>2.37</td>
<td>XPS data for the Ta4f_{5/2} and Ta4f_{7/2} peaks for the sample annealed at 800 °C.</td>
<td>53</td>
</tr>
<tr>
<td>2.38</td>
<td>XPS data for the O1s peaks for the sample annealed at 800 °C.</td>
<td>53</td>
</tr>
<tr>
<td>2.39</td>
<td>Typical electronic characteristics for MIS diodes fabricated with a highly-doped n-type silicon bottom electrode, a 99.1-nm Ta_2O_5 insulator, and aluminum top contacts.</td>
<td>55</td>
</tr>
<tr>
<td>2.40</td>
<td>Logarithm of current density versus field. Current density values between ±4 volts are in the picoamp range and within the noise floor of the tool.</td>
<td>56</td>
</tr>
<tr>
<td>2.41</td>
<td>Capacitance measurements for devices with 5 mm, 7 mm, and 12 mm contact diameters. A linear fit yields the following equation: $y = 0.0020778 \pm 0.000216 x + 4.4558e-011 \pm 8.71e-012$.</td>
<td>57</td>
</tr>
<tr>
<td>2.42</td>
<td>Poole-Frenkel linearized current versus voltage (I-V) data showing it to be the dominant conduction mechanism with $R^2 &gt; 0.999$.</td>
<td>58</td>
</tr>
<tr>
<td>2.43</td>
<td>XRR data for a nanofilm prepared using 3.5 wt% TMA-Ta1 solution and annealed at 400 °C for 10 min.</td>
<td>59</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.44</td>
<td>XRR data for a nanofilm prepared using 3.5 wt % TMA-Ta1 solution and annealed at 600 °C for 10 min.</td>
<td>60</td>
</tr>
<tr>
<td>2.45</td>
<td>J-ξ sweeps for nanofilms annealed for 10 min at 400 °C (top) and 600 °C (bottom).</td>
<td>61</td>
</tr>
<tr>
<td>2.46</td>
<td>Plot of the logarithm of current density versus field, log (J)-ξ.</td>
<td>62</td>
</tr>
<tr>
<td>2.47</td>
<td>Poole-Frenkel linearization of current versus voltage (I-V) data showing the dominant conduction mechanism with trendlines and R^2 fitting values.</td>
<td>63</td>
</tr>
<tr>
<td>3.1</td>
<td>Ball and stick model (left) and polyhedral representation (right) of the [M_6O_{19}]^{6-} (M=Nb,Ta) Lindqvist ion. Red spheres are oxygen, blue spheres are Nb or Ta; blue polyhedra are MO_6.</td>
<td>74</td>
</tr>
<tr>
<td>3.2</td>
<td>TGA-DSC analysis of powder Ta_6 (left) and Nb_6 (right). Red lines correspond with heat flow, blue lines correspond with weight percent. Dotted line is experimental data in argon gas while solid line is in air.</td>
<td>79</td>
</tr>
<tr>
<td>3.3</td>
<td>Nb_2O_5-Top, Ta_2O_5-bottom a. AFM and SEM. The white scale bar is 500 nm. b. X-ray reflectivity c. Comparison of XRR derived and AFM roughness values.</td>
<td>80</td>
</tr>
<tr>
<td>3.4</td>
<td>Representation of the hydrogen bonded clusters of Ta_6 (top) and Nb_6 (bottom).</td>
<td>83</td>
</tr>
<tr>
<td>3.5</td>
<td>Rotary evaporated solutions of Ta_6 (left) and Nb_6 (right).</td>
<td>86</td>
</tr>
<tr>
<td>3.6</td>
<td>Representation of Nb_6 clusters linked by H-bonding, along with their TMA counterions.</td>
<td>88</td>
</tr>
<tr>
<td>3.7</td>
<td>Scattering curves of Ta_6 (blue) and Nb_6 (black) in water. Pink box at low q indicates structure factor region.</td>
<td>86</td>
</tr>
<tr>
<td>3.8</td>
<td>Scattering curves of Ta_6 (blue) and Nb_6 (black) in 0.2-M TMAOH. Pink box indicates structure factor region.</td>
<td>90</td>
</tr>
<tr>
<td>3.9</td>
<td>Scattering curves of Ta_6 (blue) and Nb_6 (black) in 0.2-M TMANO_3. Pink box indicates structure factor region.</td>
<td>92</td>
</tr>
<tr>
<td>4.1</td>
<td>Polyhedral representation of the Lindqvist anion [H_2Ta_6O_{19}]^{6-} with [(CH_3)_4N]^+ counterions.</td>
<td>100</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>107</td>
</tr>
<tr>
<td>4.3</td>
<td>109</td>
</tr>
<tr>
<td>4.4</td>
<td>110</td>
</tr>
<tr>
<td>4.5</td>
<td>112</td>
</tr>
<tr>
<td>4.6</td>
<td>116</td>
</tr>
<tr>
<td>5.1</td>
<td>127</td>
</tr>
<tr>
<td>5.2</td>
<td>128</td>
</tr>
</tbody>
</table>

- **4.2**: (a) Temperature programmed desorption results depicting the dehydration behavior of a Ta6-derived thin film deposited on silicon (100). (b) TPD results showing major TMA degradation products in the same film. (c) TPD results showing species lost using the same precursor deposited on 100-nm thermally grown SiO₂.

- **4.3**: (a) X-ray diffraction patterns for films deposited from aqueous 0.22-M Ta₆. Film thicknesses range from 52 to 60 nm. Samples were annealed at the indicated temperatures for 10 min. (b) X-ray diffraction patterns in the temperature range 700 – 725 °C. Substrate peaks are indicated with a star (★).

- **4.4**: (a) Cross-sectional SEM images of films deposited with 0.22-M Ta₆ solutions. Films were annealed at 400, 600, and 800 °C for 10 min, producing thicknesses of 58, 53, and 54 nm, respectively. Scale bars represent 500 nm. (b) Cross-sectional TEM image of a 60-nm Ta₆-derived thin film annealed at 400 °C. Coats of amorphous carbon and chromium were deposited prior to focused ion beam sample preparation.

- **4.5**: (a) XRR data for films annealed at 400, 600, and 800 °C. (b) SE-derived refractive indices (λ = 550 nm) and film thicknesses. The film thicknesses derived via XRR modeling are included for comparison. (c) Results of XRR-derived densities and surface roughness values. The XRR-derived surface roughness values are compared to AFM measurements.

- **4.6**: (a) XRR patterns for films prepared from designated concentrations of Ta₆ used to model film thickness and surface roughness. (b) SE- and XRR-derived film thicknesses as a function of solution concentration (left axis); XRR-derived RMS roughness values (right axis).

- **5.1**: TDP results for a film deposited using a 0.22-M Ta₆ solution and annealed for 10 min at 400 °C.

- **5.2**: Scanning electron micrograph of a film prepared with a 0.22-M Ta₆ solution and annealed for 10 min at 400 °C.
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>XRR data for the 0.22-M Ta₆ control film and films soaked in DI water and 10-mM HNO₃</td>
<td>129</td>
</tr>
<tr>
<td>5.4</td>
<td>TPD results for the 0.22-M Ta₆ control film and samples treated in DI water or 10-mM HNO₃ showing mass fragments related to trimethylamine (m/z = 58, top) and dimethyl ether (m/z = 45, bottom)</td>
<td>130</td>
</tr>
<tr>
<td>5.5</td>
<td>Plan view (left) and cross-sectional (right) scanning electron microscopy images of a 0.22-M Ta₆ film treated in 10-mM HNO₃ and annealed at 400 °C for 10 min</td>
<td>131</td>
</tr>
<tr>
<td>5.6</td>
<td>TPD results for a film prepared using 50-mM Ta₆ and soft baked at 175 °C for 4 min. The results track the signal for trimethylamine (m/z = 58, top) and dimethyl ether (m/z = 45, bottom) for the control film and HNO₃-treated sample</td>
<td>132</td>
</tr>
<tr>
<td>5.7</td>
<td>TPD signals for trimethylamine (m/z = 58, top) and dimethyl ether (m/z = 45, bottom) for the control film and HNO₃-treated sample, both cured at 200 °C for 4 min</td>
<td>133</td>
</tr>
<tr>
<td>5.8</td>
<td>Magnified TPD signals for trimethylamine (m/z = 58) for HNO₃ films cured at 175 and 200 °C</td>
<td>134</td>
</tr>
<tr>
<td>5.9</td>
<td>Raman spectra for the control film (top) and a film treated in 10-mM HNO₃ (bottom). Both films were cured at 175 °C</td>
<td>136</td>
</tr>
<tr>
<td>5.10</td>
<td>FTIR spectra for the control film cured at 175 °C (top) and a film cured at the same temperature and exposed to 10-mM HNO₃ for 30 s (bottom)</td>
<td>137</td>
</tr>
<tr>
<td>5.11</td>
<td>XRR data for the treated and control samples cured at 175 °C (top) and 250 °C (bottom)</td>
<td>139</td>
</tr>
<tr>
<td>5.12</td>
<td>Spectroscopic ellipsometry data for the treated and control samples showing thickness (top, control = black circles; treated = green squares) and refractive indexes (bottom, control = black triangles; treated = green diamonds). Data were collected at λ = 550 nm</td>
<td>141</td>
</tr>
<tr>
<td>5.13</td>
<td>TPD results for a film prepared using 0.22-M Ta₆ solution, soft baked at 200 °C, and then soaked in an aqueous 0.1-molar lithium nitrate solution</td>
<td>143</td>
</tr>
<tr>
<td>5.14</td>
<td>X-ray diffraction data collected from a lithiated Ta₆ film after TPD experiment. The final temperature was 900 °C</td>
<td>144</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
</tbody>
</table>
| 5.15   | Scheme depicting the conversion of TMA hexatantalate to lithium tantalate.
| 6.1    | TPD results depicting the primary mass fragments associated with the thermal decomposition of TMA for the control film and a film treated in FA/EtOH.
| 6.2    | TPD results depicting the dehydration behavior for the control film and a film treated in FA/EtOH.
| 6.3    | Raman spectra for the Ta$_6$-derived control and treated (chemically condensed) films (top); FTIR spectra for the same sample set (bottom).
| 6.4    | Spectroscopic ellipsometry results for thermally condensed (tc) and chemically condensed (cc) films, along with tc and cc films subjected to additional annealing at 200 °C. Results show film thicknesses (top) and refractive indexes (bottom) for the four samples of the study.
| 6.5    | X-ray reflectivity data and model fits (shown in black) for the control film and treated films subjected to a 200 °C thermal dehydration (top); XRR-derived film densities (middle); and film roughness as determined by XRR (bottom).
| 6.6    | AFM image of a 10 μm by 10 μm area from a chemically condensed film annealed at 200 °C for 1 h.
| 6.7    | Cross-sectional TEM micrographs of a thermally condensed (tc) film (top), and a chemically condensed (cc) film (bottom).
| 6.8    | Electron diffraction pattern collected from a chemically condensed (cc) film.
| A1     | Grazing Incidence XRD on thin films of Ta$_2$O$_5$ (left) and Nb$_2$O$_5$ (right).
| A2     | IR spectra of Ta$_6$ (left) and Nb$_6$ (right) show sharp peaks at 1486, 951 cm$^{-1}$ and 1484, 952 cm$^{-1}$ respectively, which is characteristic of TMAOH. The peak at 834 for Ta$_6$ and 842 cm$^{-1}$ for Nb$_6$ can be attributed to the vibration of a terminal M-O bond. The peaks at 703 and 661 for Ta$_6$ and 695 and 645 for Nb$_6$ can be attributed to bridging M-O-M vibrations. The bond between a metal and the central oxygen is represented by peaks at 522 cm$^{-1}$ and 510 cm$^{-1}$ for Ta$_6$ and Nb$_6$ respectively.
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>Simulated XRD pattern from single crystal data of Ta6</td>
<td>199</td>
</tr>
<tr>
<td>A4</td>
<td>Simulated XRD pattern from single crystal data of Nb6</td>
<td>199</td>
</tr>
<tr>
<td>A5</td>
<td>Powder XRD pattern of Nb6</td>
<td>200</td>
</tr>
<tr>
<td>A6</td>
<td>Powder XRD pattern of Ta6</td>
<td>200</td>
</tr>
<tr>
<td>A7</td>
<td>Unit cell representation of tetramethylammonium salt of [M₆O₁₉]⁸⁻</td>
<td>201</td>
</tr>
<tr>
<td>A8</td>
<td>TPD results for film deposited with 0.22-M Nb₆ solutions and cured at 80 °C for less than 1 min</td>
<td>202</td>
</tr>
<tr>
<td>A9</td>
<td>TPD results for film deposited with 0.22-M Nb₆ solutions and cured at 80 °C for less than 1 min</td>
<td>203</td>
</tr>
<tr>
<td>A10</td>
<td>Optical light microscope images for films prepared using 0.22-M Nb₆ solutions and annealed at 400 °C (top), 600 °C (middle), and 800 °C (bottom). The circular pattern at the center of the image represents about 60 µm</td>
<td>204</td>
</tr>
<tr>
<td>A11</td>
<td>SEM micrographs for films prepared using 0.22-M Nb₆ solutions and annealed at 400 °C (top), 600 °C (middle), and 800 °C (bottom)</td>
<td>205</td>
</tr>
<tr>
<td>A12</td>
<td>AFM results for films prepared using 0.22-M Nb₆ solutions and annealed at 400 °C (top), 600 °C (middle), and 800 °C (bottom). Scan areas were 1 µm × 1 µm</td>
<td>206</td>
</tr>
<tr>
<td>A13</td>
<td>XRR modeling results for roughness and density for films prepared using 0.22-M Nb₆ solutions and annealed at 400, 600, and 800 °C. XRR-derived roughnesses are compared to AFM measurements</td>
<td>207</td>
</tr>
<tr>
<td>A14</td>
<td>XRR modeling results for film thickness compared to film thicknesses determined by ellipsometry for films prepared using 0.22-M Nb₆ solutions and annealed at 400, 600, and 800 °C. The refractive indexes reported are at λ = 550 nm</td>
<td>208</td>
</tr>
<tr>
<td>A15</td>
<td>XPS results for a film prepared using 0.22-M Nb₆ solution and annealed at 400 °C for 10 min</td>
<td>209</td>
</tr>
<tr>
<td>A16</td>
<td>XPS results for a film prepared using 0.22-M Nb₆ solution and annealed at 600 °C for 10 min</td>
<td>210</td>
</tr>
<tr>
<td>A17</td>
<td>XPS results for a film prepared using 0.22-M Nb₆ solution and annealed at 800 °C for 10 min</td>
<td>210</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>B1</td>
<td>Grazing incidence X-ray diffraction (GIXRD) data for an as-deposited film spun from 0.22-M Ta₆ solutions (Ta₆ = [(CH₃)₄N][H₂Ta₆O₁₉]•xH₂O). The substrate peak is indicated with a star (★).</td>
<td>211</td>
</tr>
<tr>
<td>B2</td>
<td>GIXRD data for a sample spun from 0.22-M Ta₆ and annealed at 900 °C for 10 min that was used for structural refinements.</td>
<td>211</td>
</tr>
<tr>
<td>B3</td>
<td>(a) Plan-view scanning electron microscopy (SEM) image of a 0.22-M Ta₆ sample annealed at 400 °C for 10 min. Plan-view SEM images of samples annealed at (b) 600 °C and (c) 800 °C for 10 min using the same 0.22-M Ta₆ precursor.</td>
<td>212</td>
</tr>
<tr>
<td>B4</td>
<td>Spectroscopic ellipsometry (SE) data for samples prepared using 0.22-M Ta₆ precursor solution collected at 60° and 65°. SE data for the sample annealed at (a) 400 °C, (b) 600 °C, and (c) 800 °C. All samples were annealed in air for 10 min.</td>
<td>213</td>
</tr>
<tr>
<td>B5</td>
<td>Atomic force microscopy (AFM) images for samples prepared using a 0.22-M Ta₆ precursor solution. Samples annealed for 10 min at (a) 400 °C, (b) 600 °C, and (c) 800 °C.</td>
<td>214</td>
</tr>
<tr>
<td>B6</td>
<td>XRR data for samples annealed at 100, 200, and 300 °C for 10 min.</td>
<td>214</td>
</tr>
<tr>
<td>B7</td>
<td>XRR data for samples prepared using 0.01 and 0.025-M Ta₆ solutions. Films were annealed for 10 min...</td>
<td>215</td>
</tr>
<tr>
<td>B8</td>
<td>Film deposited from 0.22-M Ta₆ solution and annealed at 680 °C for 3 h. Inset is an SEM micrograph of the same film.</td>
<td>216</td>
</tr>
<tr>
<td>B9</td>
<td>Film deposited from 0.22-M Ta₆ solution and annealed at 600 °C for 1 day.</td>
<td>216</td>
</tr>
<tr>
<td>B10</td>
<td>Film deposited from 0.22-M Ta₆ solution and annealed at 500 °C for 1, 2, and 3 days.</td>
<td>217</td>
</tr>
<tr>
<td>B11</td>
<td>Films deposited from 0.22-M Ta₆ solutions and annealed at 550 °C for 1, 2, and 3 days.</td>
<td>218</td>
</tr>
<tr>
<td>B12</td>
<td>Films deposited from 0.22-M Ta₆ solutions and annealed at 500, 550, and 600 °C for 1 day.</td>
<td>219</td>
</tr>
<tr>
<td>B13</td>
<td>Modeling results from an in situ XRR experiment conducted on a film deposited from a 0.22-M Ta₆ solution.</td>
<td>220</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>B14</td>
<td>TEM micrographs of a sample prepared using 0.22-M Ta6 solution heated to 200 °C (a), 300 °C (b), 400 °C (c), 600 °C (d), 700 °C (e), and 800 °C (f)</td>
<td>222</td>
</tr>
<tr>
<td>B15</td>
<td>TEM micrograph of a sample prepared using 0.22-M Ta6 solution heated to 800 °C for 10 min</td>
<td>223</td>
</tr>
<tr>
<td>B16</td>
<td>I-V measurements for Al/Ta2O5/n-Si MIS devices for samples annealed at 400, 600, and 800 °C. All samples were annealed for 10 min prior to device fabrication</td>
<td>225</td>
</tr>
<tr>
<td>B17</td>
<td>XPS results for a film prepared using 0.22-M Ta6 solution and annealed at 400 °C for 10 min</td>
<td>226</td>
</tr>
<tr>
<td>B18</td>
<td>XPS results for a film prepared using 0.22-M Ta6 solution and annealed at 600 °C for 10 min</td>
<td>227</td>
</tr>
<tr>
<td>B19</td>
<td>XPS results for a film prepared using 0.22-M Ta6 solution and annealed at 800 °C for 10 min</td>
<td>227</td>
</tr>
<tr>
<td>C1</td>
<td>X-ray reflectivity data for the control films prepared using 50-mM Ta6 solutions and cured in the temperature interval 100—250 °C</td>
<td>229</td>
</tr>
<tr>
<td>C2</td>
<td>X-ray reflectivity data for films cured in the temperature interval from 175—250 °C and then treated in aqueous 10-mM HNO3 for 30 s. All films were prepared using 50-mM Ta6 solutions</td>
<td>230</td>
</tr>
<tr>
<td>C3</td>
<td>TPD results showing water content (m/z = 18) for the treated and control films that were initially soft baked at 175 °C (top) and 200 °C (bottom)</td>
<td>231</td>
</tr>
<tr>
<td>C4</td>
<td>TPD results showing water content as a function of temperature for a film prepared using a 0.22-M Ta6 solution, soft baked at 200 °C, and then soaked in a LiNO3 solution for 1 min</td>
<td>232</td>
</tr>
<tr>
<td>C5</td>
<td>X-ray diffraction data collected from a Ta6-based film cured at 200 °C for 4 min and treated in 0.1-M LiNO3</td>
<td>232</td>
</tr>
<tr>
<td>C6</td>
<td>X-ray diffraction data collected from a lithiated Ta6 film annealed in air. The final temperature was 1000 °C</td>
<td>233</td>
</tr>
<tr>
<td>D1</td>
<td>Plan-view SEM images of a thermally condensed (top) film compared to the chemically condensed (bottom) film. Both samples were annealed at 200 °C for 1 h</td>
<td>234</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2</td>
<td>Preliminary X-ray reflectivity studies for 50-mM Ta₆ films treated in FA/EtOH (top) and FA/IPA (bottom). Films were soaked for 30 s. The treatment in FA/IPA did not yield apparent thickness changes, which could indicate limited efficacy of TMA removal...</td>
<td>235</td>
</tr>
<tr>
<td>D3</td>
<td>Energy-dispersive X-ray spectroscopy line scan of a film prepared using 50-mM Ta₆ solutions, treated in FA/EtOH for 30 s, then annealed at 200 °C for 1 h....</td>
<td>236</td>
</tr>
<tr>
<td>D4</td>
<td>Grazing incidence X-ray diffraction data collected from a film prepared using 50-mM Ta₆ solutions, treated in FA/EtOH for 30 s, then annealed at 800 °C for 10 min...</td>
<td>237</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>48</td>
</tr>
<tr>
<td>3.1</td>
<td>82</td>
</tr>
<tr>
<td>3.2</td>
<td>84</td>
</tr>
<tr>
<td>3.3</td>
<td>85</td>
</tr>
<tr>
<td>3.4</td>
<td>89</td>
</tr>
<tr>
<td>3.5</td>
<td>91</td>
</tr>
<tr>
<td>4.1</td>
<td>114</td>
</tr>
<tr>
<td>A1</td>
<td>196</td>
</tr>
<tr>
<td>A2</td>
<td>197</td>
</tr>
<tr>
<td>A3</td>
<td>198</td>
</tr>
<tr>
<td>A4</td>
<td>201</td>
</tr>
</tbody>
</table>

- **Table 2.1**: Comparing Results to Bulk $\beta$-Ta$_2$O$_5$ Density and Refractive Index.
- **Table 3.1**: Crystallographic data and structure refinement for Ta6 and Nb6.
- **Table 3.2**: Bond lengths and bond valence sum of oxygens in Ta6 structure.
- **Table 3.3**: Bond lengths and bond valence sum of oxygens in Nb6 structure.
- **Table 3.4**: Radii for simulated and experimental samples in water, along with interparticle interferences.
- **Table 3.5**: Radii and interparticle interactions of samples in 0.2-M TMAOH solutions.
- **Table 4.1**: Tantalum Pentoxide Film Comparison.
- **Table A1**: Crystallographic data and structure refinement for Ta6 and Nb6.
- **Table A2**: Bond lengths and bond valence sum of oxygens in Ta6 structure.
- **Table A3**: Bond lengths and bond valence sum of oxygens in Nb6 structure.
- **Table A4**: Size distribution results from Irena, Ta6 and Nb6 in water (left) and 0.2-M TMAOH solution (right).
Chapter 1

INTRODUCTION TO USING POLYOXOMETLATES FOR THE AQUEOUS SOLUTION DEPOSITION AND PROCESSING OF METAL OXIDE THIN FILMS

Ryan H. Mansergh, Lauren B. Fullmer, May Nyman, and Douglas A. Keszler
Introduction

Nanosized metal oxo-hydroxo clusters represent a compelling new approach for the facile deposition of materials relevant to numerous of applications. More specifically, within this class of metal oxo-hydroxo clusters are polyoxometalates (POMs),\(^1,2\) which are beginning to show great utility for the fabrication of an expanding list of metal oxides. The study of precursors for the solution processing of thin films is a worthwhile target for a more sustainable, energy-efficient way of processing high-quality, dense films. Water-soluble POMs are oxo-hydroxo cluster precursors that can be processed to yield a metal oxide; these clusters provide pre-connectivity between metal and oxygen which decreases the energetic barrier of forming a metal oxide, relative to monomeric precursors. The chemistry of POMs provides a high degree of control to produce films with desired compositions and morphologies as compared to other deposition methods.

In this work, we sought to develop and study tantalum-containing POMs for the deposition of tantalum pentoxide (Ta\(_2\)O\(_5\)) thin films. Ta\(_2\)O\(_5\) has been the subject of considerable research efforts because of its chemical, mechanical, and thermal stability,\(^3\) and also largely because of its potential role as a high-\(\kappa\) dielectric in ultra-large-scale integration (ULSI).\(^4\) Beyond the role of Ta\(_2\)O\(_5\) as dielectric layers in memory capacitors\(^5,6\) and in nanoscale dynamic random access memories\(^7\) (DRAMs), it has shown potential as a diffusion barrier;\(^8\) and more recently, as a robust memristive material.\(^9,10\) In addition to its use in advanced microelectronic applications with micro- and nanoscale feature sizes, Ta\(_2\)O\(_5\) has macroscale uses as
well, including corrosion protection,\textsuperscript{11} as an antireflective coating,\textsuperscript{12} and in electrochromic\textsuperscript{13} smart windows.

Herein, we describe tantalum oxide films deposited with nanosized polyoxotantalates. We synthesize the clusters by a method adapted from the synthesis of alkali hexatantalates first developed by Anderson and co-workers.\textsuperscript{14} The resulting tantalum oxide films are comparable to films formed via vapor-based deposition methods, while utilizing a solution-based deposition method that is inherently scalable, enabling the deposition of $\text{Ta}_2\text{O}_5$ on surface areas scaling to square meters. Using a spin coater under ambient conditions, these polyoxotantalate clusters in aqueous solution provide a new route to greener chemistry and improved atom economy in a manner that is both energy- and cost-efficient, through the use of lower temperatures and greatly simplified processing equipment.

\textbf{Tantalum Oxide Thin-Film Literature Review}

Ta$_2$O$_5$ thin films have been produced using a diverse set of deposition methods including: oxidative methods such as anodization\textsuperscript{15,16} and thermal oxidation;\textsuperscript{17,18} physical methods such as physical vapor deposition\textsuperscript{19,20} (PVD), sputtering,\textsuperscript{21–28} electron beam evaporation,\textsuperscript{29,30} molecular beam epitaxy\textsuperscript{31} (MBE), pulsed-laser deposition\textsuperscript{32} (PLD), ion-assisted deposition\textsuperscript{33–35} (IAD); and chemical methods such as chemical vapor deposition\textsuperscript{36–40} (CVD), low-pressure CVD\textsuperscript{41,42} (LPCVD), plasma-enhanced CVD\textsuperscript{41,43,44} (PECVD), electron cyclotron resonance PECVD\textsuperscript{\textsuperscript{3}} (ECR-PECVD), UV-photo CVD,\textsuperscript{45} metalorganic CVD\textsuperscript{46,47} (MOCVD), and atomic layer deposition\textsuperscript{48–54} (ALD) and its variants such as plasma-enhanced ALD\textsuperscript{55} (PE-ALD) and photo-ALD.\textsuperscript{56} A number of techniques using solution-phase precursors have also
been used for the deposition of Ta₂O₅ including sol-gel¹³,⁵⁷–⁵⁹ techniques and electrospray deposition.⁶⁰

Several of the aforementioned techniques are capable of producing dense⁵⁴–⁵⁵ (~96-98% bulk β-Ta₂O₅), atomically smooth¹⁶,⁲⁴,⁵²,⁵⁴,⁵⁶,⁵⁸,⁶¹ (root mean square roughness (RMS) values of a few ångströms) films with high refractive indices¹⁷,³³,⁴⁸ (~97-99% bulk β-Ta₂O₅). Depending on the process parameters, several of the above techniques can yield amorphous, polycrystalline, or crystalline Ta₂O₅ films which can greatly affect their electrical properties, including the dielectric constant, breakdown field, and leakage current density. Ezhilvalavan and co-workers report dielectric constants for reactive magnetron sputtered films in the range from 30-31 for amorphous Ta₂O₅ films and 45-50 for crystalline Ta₂O₅ films with leakage current densities increasing from 10⁻¹⁰ A·cm⁻² to 10⁻⁷ A·cm⁻² at 0.1 MV·cm⁻¹ with annealing temperature.²² Ta₂O₅ breakdown voltages have been reported as high as 6.5 MV·cm⁻¹ by Huang and colleagues.⁵⁷

The Current Landscape of Tantalum Polyoxometalates
To enable the aqueous solution deposition of Ta₂O₅ thin films, a suitable tantalum-based POM would be advantageous. Tantalum POMs have eluded significant development and exist only as the Lindqvist ion and the decatantalate recently discovered by Matsumoto co-workers.⁶² The applicability of POMs as aqueous precursors may be limited by the large-volume counterions. Common counterions for tantalate salts include alkali cations (Li, Na, K, Rb, and Cs) and tetrabutylammonium hydroxide (TBAOH).¹⁴,⁶³ For solution deposition of thin films, an organic counterion, e.g. TBAOH, which can be driven off upon annealing. The TBA hexatantalate salt,
however, is poorly soluble in water. We have synthesized a water-soluble
tetramethylammonium (TMA) salt of a tantalate POM cluster and studied how the
presence of the TMA counter ion affects Ta$_2$O$_5$ thin-film properties.
References


(7) Atanassova, E.; Paskaleva, V. Challenges of Ta_2O_5 as High-K Dielectric for Nanoscale DRAMs. Microelectron. Reliab. 2007, 47, 913–923.


(13) Ozer, N.; Lampert, C. M. Structural and Optical Properties of Sol-Gel Deposited Proton Conducting Ta_2O_5 Films. J. Sol-Gel Sci. Technol. 1997, 8,


Anghinolfi, L.; Prato, M.; Chtanov, A.; Gross, M.; Chincarini, A.; Neri, M.;


Chapter 2

A BASELINE STUDY OF TMA TANTALUM POLYOXOMETALATE SALTS FOR THE AQUEOUS SOLUTION DEPOSITION OF HIGH-DENSITY TANTALUM OXIDE THIN FILMS

Ryan H. Mansergh, Lauren B. Fullmer, Deok-Hie Park, May Nyman, and Douglas A. Keszler
Introduction

We conducted a baseline study of the recently synthesized tetramethylammonium (TMA) polyoxometalate salt (henceforth referred to as “TMA-Ta1” for brevity) as an aqueous solution precursor for tantalum oxide thin films. While many aspects of polyoxometalate (POM)\textsuperscript{1–4} clusters have been explored, their use as thin-film precursors is still relatively unexplored. We initially anticipated that the large volume change associated with the loss of the TMA counterion during thermal processing would lead to porous tantalum oxide films. By definition of their water solubility, POMs carry a negative or positive charge, and therefore must have counterions. The counterions play extremely important multiple roles which include providing solubility, enhancing gelation upon deposition, and are easily volatilized or ion-exchanged to yield dense, coherent films of the desired composition and phase. Tantalate POMs have eluded significant development, and thus far exist only as the hexatantalate Lindqvist ion [Ta\textsubscript{6}O\textsubscript{19}]\textsuperscript{8–}, and the recently discovered decatanalate [Ta\textsubscript{10}O\textsubscript{28}]\textsuperscript{6–} by Matsumoto and co-workers.\cite{5} Counterions for tantalate POMs thus far include any alkali metal (Li, Na, K, Rb, and Cs)\textsuperscript{6,7} and tetrabutylammonium hydroxide (TBAOH).\textsuperscript{6,8} These counterions are non-ideal in tantalum oxide precursors, as the presence of alkalis promote the formation of alkali tantalate phases such as perovskites, and TBAOH does not provide good aqueous solubility. Thus we strategically targeted hexatantalate with TMA\textsuperscript{+} counterions, where the TMA\textsuperscript{+} both
provides water solubility and can be removed by combustion during the film-annealing process.

Thin films of Ta$_2$O$_5$ are of significant technological relevance owing to its favorable chemical, thermal, and mechanical properties. Additionally, Ta$_2$O$_5$ has a number of potential uses in advanced electronics as a high-$\kappa$ dielectric, diffusion barrier, or more recently, as a robust memristive material. The ability to deposit high-quality films of Ta$_2$O$_5$ over large surface areas is also of value for corrosion resistance, antireflective coatings, and electrochromic smart windows.

At present, the solution processing of tantalum oxide films is achieved via sol-gel methods and the resultant films are often porous or require toxic organic solvents, such as 2-methoxyethanol. Here we deposit Ta$_2$O$_5$ films by a method with a water-soluble TMA hexatantalate cluster. We report its conversion to continuous, atomically flat thin films.

**Experimental Methods**

**Materials**

H$_2$O$_2$ (30%), isopropanol (ACS Grade), and NH$_4$OH (28.0-30.0% as NH$_3$(aq), ACS Grade) were purchased from Macron Fine Chemicals. TaCl$_5$ (99.99%), and (CH$_3$)$_4$NOH (25% w/w aq. solution, 99.999%) were purchased from Alfa Aesar. The $n$-type silicon(100) wafers were sourced from Sumco Oregon Corp.

**Synthesis of (NH$_4$)$_3$Ta(O$_2$)$_4$**

The synthesis for (NH$_4$)$_3$Ta(O$_2$)$_4$ was adapted from previous methods. The reaction is shown in eq 2.1. TaCl$_5$ (2.4 g) was dissolved in 40 mL of 30% H$_2$O$_2$ in an ice water
bath. With moderate stirring throughout the entire reaction, the solution was kept between 5 and 15 °C. A total of 12-mL NH₃(aq) (14.5 M) was added in 1-mL aliquots. The solution became cloudy on initial addition of NH₃(aq), however, once the entire 12 mL is added, the solution became clear. Upon addition of ethanol (approximately 150 mL) the solution yielded a white precipitate. This precipitate was then vacuum-filtered with a Büchner funnel and washed with ethanol. The yield is between 97 and 100%.

$$2\text{TaCl}_5 + 8\text{H}_2\text{O}_2 + 16\text{NH}_4\text{OH} \rightarrow 2(\text{NH}_4)_3\text{Ta(O}_2\text{)}_4 + 10\text{NH}_4\text{Cl} + 16\text{H}_2\text{O}$$  \hspace{1cm} (2.1)

**Synthesis of TMA-Ta1**

The synthesis for TMA-Ta1 was adapted from the synthesis²¹ of alkali hexatantalates. A 125-mL flask was charged with (NH₄)₃Ta(O₂)₄ (1.32 g) and 2.8-M TMAOH(aq) (8.25 mL). The solution was refluxed for 5 h with the condensing column chilled to approximately 5 °C. The resulting solution was filtered with a 0.45-µm nylon syringe filter. The filtered solution was agitated with isopropyl alcohol (~40 mL) and centrifuged to yield a small clear layer, which was decanted. Upon further agitation of the remaining denser layer with isopropyl alcohol (~30 mL) a white precipitate formed. The precipitate was washed with isopropanol and dried under vacuum at ~60 °C. The yield is between 38 and 63%.

**Powder Characterization**

Thermogravimetric analysis-mass spectrometry (TGA-MS) scans were performed in air as well as N₂ from 20 to 1000 °C with a ramp rate of 10 °C·min⁻¹ using a TA Instruments SDT Q600 and a Hiden HPR-20 mass spectrophotometer.
Elemental composition was determined by Galbraith Laboratories, Inc. (Knoxville, TN) through the use of inductively coupled plasma atomic emission spectroscopy (ICP-AES) and a Thermo Finnigan FLASH 2000 Elemental Analyzer.

Solution Characterization

Small- and wide-angle X-ray scattering (SWAXS) were collected on an Anton Paar SAXSess instrument with Cu $K\alpha$ radiation utilizing line collimation. An aqueous solution of the TMA tantalate salt was prepared at 7 wt %. The solution and a water background were measured in a 1.5 mm glass capillary tube for 30 min. Anton Paar SAXSquant$^{22}$ software was used for collecting and processing the scattering data. WaveMetrics Igor Pro$^{23}$ software with Irena$^{24}$ macros was used for analyzing the SWAXS data to determine size and shape with pair distance distribution function. Raman spectra of the tantalate salt solution and powder, along with TMAOH solutions, were collected on a Thermo Scientific DXR Smart Raman spectrometer with a 780-nm filter.

Thin-Film Fabrication and Thermal Processing

The $n$-type silicon(100) wafers were cleaved into approximately 25.4 × 25.4 mm$^2$ substrates. The substrates were then rinsed in Millipore 18.2 MΩ deionized water, dried in Ar, and then ashed in an O$_2$ plasma for 10 min at 200 W and ~175 mTorr. The films were deposited using a CEE Model 100 spin coater at 3000 rpm for 30 s. The films were cured on a hot plate at 200 °C for 1 min and cooled on an aluminum block for approximately 1 min. The samples were then annealed in air using a Neytech Qex furnace with a 20 °C ·min$^{-1}$ ramp rate.
Thin-Film Characterization

X-ray diffraction (XRD) and X-ray reflectivity (XRR) were both performed on a Rigaku Ultima-IV diffractometer with Cu Kα radiation (λ = 1.5409 Å). For XRR data collection the instrument was configured with a 5.0° incident Soller slit, a 10 mm divergent height limiting slit (DHL), and a 5.0° receiving Soller slit; the divergent slit (DS), scattering slit (SS), and receiving slit (RS) were set to 0.2 mm, 0.5 mm, and 0.2 mm, respectively. Grazing incidence X-ray diffraction (GIXRD) scans were performed on this instrument for phase identification and XRR results were used to determine the appropriate ω value for use during GIXRD scans. For GIXRD scans the instrument was configured with a 5.0° incident Soller slit, a 10 mm divergent height limiting slit, and a 0.5° parallel beam slit; the DS was set to 0.2 mm and the SS and RS were left open. The Rigaku software packages PDXL²⁵ and GlobalFit²⁶ were used for the analysis of XRD and XRR data, respectively. Using GlobalFit, the best fits to XRR data were obtained assuming a thin, dense tantalum oxide top layer, a thicker tantalum oxide layer, and a SiO₂ layer on a Si substrate. Structural refinements of XRD data were performed using the TOPAS-Academic²⁷ software package using the Pawley method.

Atomic force microscopy (AFM) measurements were performed on either a Veeco Innova SPM or a Digital Instruments NanoScope III, both in tapping mode with silicon AFM probes (300 kHz, 40 N-m⁻¹). Initial sample scans were performed on 1 × 1 µm² areas and later scans were performed on 20 × 20 µm² areas. Root mean square roughness values were obtained using multiple 2 × 2 µm² sections of the larger 20 × 20 µm² scan areas using Bruker NanoScope Analysis software.²⁸
Spectroscopic ellipsometry (SE) measurements were collected on a J.A. Woollam, Inc. M-2000 spectroscopic ellipsometer. A 9-point recipe was used to automate measurements of each 25.4 × 25.4 mm² sample. Modeling of the acquired data was carried out using the CompleteEASE software package. A Cauchy model was used to extract the index of refraction of the tantalum oxide layer and the thickness of the tantalum oxide and interfacial SiO₂ layers.

Scanning electron microscopy (SEM) images were collected on a FEI QUANTA 600F environmental, FEI QUANTA 3D dual beam SEM/FIB, FEI NOVA NanoSEM 230 high resolution, and FEI Helios Dual Beam FIB SEMs. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were performed on a FEI TITAN 80-200 TEM/STEM with ChemiSTEM Technology at 200 kV. For precursor studies in the TEM, a dilute solution was dried on a holey carbon TEM grid and dried at a temperature slightly above room temperature. Particle and cluster sizes were determined using the ImageJ software package. For thin-film TEM sample preparation, a protective coat of carbon was deposited, followed by platinum, and the TEM sample was removed using a focused ion beam with a gallium ion source. The TEM sample was welded to a TEM grid and thinned to approximately 100 nm using the ion beam.

X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo Fischer Scientific ESCALAB 250 XPS system using an Al Kα anode, hemispherical analyzer, and multi-channel detector under UHV conditions. An electron flood gun was used for charge neutralization, and peak offsets were corrected using the C1s peak associated with adventitious carbon at 284.5 eV. Gaussian-Lorentzian peak fits and
background subtractions were performed using the XPS-vendor supplied Advantage software package.\textsuperscript{31}

Electrical current-voltage measurements were made on a Cascade Microtech Alessi REL-4800 probe station stage using an Agilent B1500A semiconductor device parameter analyzer along with an Agilent E4980A precision LCR meter for capacitance measurements.

**Results and Discussion**

**TMA Tantalum Polyoxometalate Salts Solids and Solutions**

A TMA tantalate POM (or alternatively, polyoxotantalate) salt was synthesized as outlined in the Experimental Methods section. The nanosized tantalate clusters were characterized in aqueous solution using SWAXS to determine the radius of gyration and the maximum extent. The derived pair distance distribution function in Figure 2.1 shows that the cluster has a radius of gyration of 10.402(12) Å and a maximum extent of 36 Å. The two peaks indicate the presence of monomers and dimers in the solution with a higher concentration of monomers.
Figure 2.1: Fit of the pair distance distribution function analysis determined from SWAXS studies of the 7 wt % precursor solution exhibiting dimerization.

The precursors were imaged via high-angle annular dark-field (HAADF) STEM. Energy dispersive X-ray (EDX) spectroscopy was used for elemental mapping. As shown in the HAADF-STEM image (Figure 2.2, left), the clusters tended to form agglomerates. We mapped the elemental composition of the agglomerate through EDX (Figure 2.2, right), and we found the agglomerate to be tantalum rich.
Figure 2.2: HAADF-STEM image of a TMA-Ta1 agglomeration (left); the associated EDX map of the same agglomerate (right). The tantalum content is indicated in magenta.

We used Raman spectroscopy to “fingerprint” the tantalate salt solutions and powders and to confirm the presence of TMAOH; we also collected Raman spectra of an aqueous solution of TMAOH for comparison. The Raman spectra (Figure 2.3) confirm that TMAOH is present in the cluster solution, while there are also peaks unique to the cluster identifying terminal Ta-O bonds (~850 cm\(^{-1}\)) and bridging Ta-O-Ta bonds (~550-600 cm\(^{-1}\)).
Figure 2.3: Raman spectra of the tantalate salt solution and powder and a TMAOH solution for comparison.

We studied the TMA-Ta$_1$ salts (an SEM micrograph is shown Figure 2.4) by TGA-MS in order to determine the temperatures at which the loss of water and TMA content occurred and to optimize annealing conditions.
Figure 2.4: Scanning electron microscope image of the TMA-Ta1 powder.

The TGA curve shown in Figure 2.5 shows the major weight loss of ~20% in the range from 40 – 345 °C. Then, starting from 345 °C we observe a dip in the gravimetric curve with a local minimum at ~500 °C; around this temperature we approach a local maximum in the DSC exothermic scan (Fig. 2.5) before entering into a local minimum, suggesting an initial increase followed by a decrease in atomic ordering. The weight gain continues until ~750 °C, after which we observe an abrupt mass loss concomitant with a sharp exothermic crystallization peak near 770 °C, when the amorphous phase intermediate rapidly converts to Ta₂O₅; the observed mass loss is consistent with the formation of Ta₂O₅. If we stop the experiment prior to the crystallization event (at ~600 °C) we observe a black powder, which indicates elemental carbon from the TMA, the presence of reduced tantalum oxide, carbide or nitride (i.e. Ta(III) or Ta(IV)) (TaO₂ is black³²), or both. If the black color came only from carbon, we would not expect a weight gain in the gravimetric curve, only weight loss. Thus we conclude that a reduced tantalum intermediate is present, and perhaps
an important step in obtaining the extremely dense thin films from these precursors. These data all further support our interpretation that reduced tantalates are a component of the intermediate before Ta$_2$O$_5$ forms and crystallizes takes place.

**Figure 2.5:** TGA-DSC data of TMA-Ta1 collected in air.

From the MS data (shown in Fig. 2.6) associated with the previously shown TGA-DSC data *(cf. Fig. 2.5)*, we observe that the weight loss from 40 to 345 °C corresponds with the loss of water and CO$_2$ (the latter being from the carbon content of TMA). The large quantities of CO$_2$ and water observed starting lower temperatures are likely due to the reaction of trimethylamine and air. As seen in eq 2.2 below, this reaction produces significant quantities of CO$_2$ and H$_2$O in addition to NO (which was detected by MS)

$$4(CH_3)_3N + 23O_2 \rightarrow 12CO_2 + 4NO + 18H_2O \quad (2.2).$$
It is possible that the strong abrupt CO$_2$ and water signals near 345 °C may be attributed to the dimethyl ether (DME) ignition—the ignition temperature for DME is ~350 °C, and DME has been evaluated as an additive to enhance combustion in internal combustion engines and even as a fuel on its own.\textsuperscript{33,34} This reaction produces additional CO$_2$ and water as shown in eq 2.3

$$\text{CH}_3\text{OCH}_3 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \quad (2.3).$$

A final spike of CO$_2$ detected by the mass spectrometer just prior to crystallization suggests the combustion of the remaining carbon content in the sample; the transition from amorphous to crystalline Ta$_2$O$_5$ may allow the CO$_2$—possibly from a Ta-carbonate source—to more readily escape the metal-oxide lattice.

\textbf{Figure 2.6:} MS data collected under air. Fragments showing no appreciable response have been removed for clarity.

When the same TGA experiment is performed under N$_2$ (Figure 2.7) rather than air, the weight gain is not observed, and the change in mass is consistent with the
formation of a reduced tantalum oxide, such as TaO₂. The bluish-black appearance of
the sample at the conclusion of the TGA-DSC experiment further supports this
assertion.

Figure 2.7: TGA-DSC data of TMA-Ta1 collected with N₂ flow gas.

In the associated MS data shown in Figure 2.8 the loss of TMA-related fragments,
such as trimethylamine are readily observed at ~220 °C. This result may have
important implications under inert ambients during thin-film annealing, as this could
lead to changes in film properties due to the reduction of TMA content at lower
annealing temperatures.
Figure 2.8: MS data collected under N\textsubscript{2}. The molecular fragments ranging from 15 to 59 amu were selected as likely candidates for the decomposition of TMA.

To gain further compositional insight as the nature of the TMA-Ta\textsubscript{1} powder product, an independent elemental analysis (Galbraith Laboratories, Knoxville, TN) of the TMA-Ta\textsubscript{1} powder found that it was comprised of 6.90% C, 2.76% H, 2.42% N, and 58.2% Ta.

**Thin-Film Studies**

In Figure 2.9, one of the clear and colorless TMA-Ta\textsubscript{1} solutions used for film deposition is shown in the left, and a film that typifies the prepared samples is shown on the right. We prepared the initial thin-film samples with precursor solutions at the solubility limit of TMA-Ta\textsubscript{1} of 30 wt %; details of solution and thin-film sample preparation are provided in the Experimental Methods section.
Figure 2.9: A 30 wt % solution used for film deposition (left); typical film appearance post-annealing (right).

We used grazing incidence X-ray diffraction (GIXRD) to study as-deposited films (Figure 2.10) and we observed a broad amorphous peak at ~30°, the value of 2θ where the peaks of crystalline tantalum oxide reside.

Figure 2.10: GIXRD pattern of an as-deposited film made with 30 wt % TMA-Ta1.
We annealed the initial sample set at 400, 600, and 800 °C for 10 min in air, and studied these samples using X-ray reflectivity (XRR) and spectroscopic ellipsometry (SE). From the XRR data (Figure 2.11), we observed that the 400, 600, and 800 °C samples had Kiessig fringes which remained relatively strong up until $2\theta \approx 8^\circ$, suggesting smooth film surfaces.

![Figure 2.11: XRR scans of 400, 600, and 800 °C samples.](image)

AFM (Figure 2.12) corroborated this observation—the films possessed near-atomically smooth surfaces, with RMS roughness as low as 0.3 nm.
Figure 2.12: AFM images of the 400 °C sample (top), perspective view of the 600 °C sample (middle), and the 800 °C sample (bottom).
This result is comparable to tantalum oxide films deposited using vacuum-based deposition methods such as sputtering,\textsuperscript{35} atomic layer deposition (ALD),\textsuperscript{36} and chemical vapor deposition (CVD).\textsuperscript{37} The AFM image of a sample annealed at 800 °C shows apparent grains and a crystal-like surface morphology. The results of XRR modeling (see Figure 2.13) on these samples show films with densities relative to that of bulk $\beta$-Ta$_2$O$_5$ (8.2 g·cm$^{-3}$) as high as ~95%, which approaches some of the highest reported densities for ALD-deposited films which can reach ~96-98% bulk $\beta$-Ta$_2$O$_5$.\textsuperscript{36,38}

![Figure 2.13: Select XRR models for the 400 and 800 °C samples.](image)

SE data for this initial sample set are shown in Figure 2.14; from the dispersion curves in this figure, we note that the 600 °C sample shows a higher refractive index at all wavelengths. We used a Cauchy model to determine the film thickness and index of refraction. And we used the resulting indices of refraction with the Clausius-Mossotti relation to calculate film densities, and the resultant densities were found to be in good agreement with those determined by XRR models.
Figure 2.14: Del-psi plots and dispersion curves for the 400 °C sample (top), the 600 °C sample (middle), and the 800 °C sample (bottom).
A disordered morphology with no apparent grains can be observed in the cross-sectional SEM images of the samples annealed at 400 °C (Figure 2.15, top); the cross-sectional SEM image of the sample annealed at 800 °C (Figure 2.15, bottom) appears to have an angular, more grain-like morphology, more suggestive of a crystalline material upon fracture.

**Figure 2.15:** Cross-sectional SEM image of the 400 °C sample; a film thickness of *ca.* 80.4 nm was measured (top); cross-sectional SEM image of the 800 °C sample with an approximate film thickness of 72 nm and an interfacial oxide of *ca.* 3.8 nm (bottom).
The initial study was later expanded to include a wider range of annealing temperatures, ranging from 300 to 800 °C. All of the samples in this study were annealed for 10 min. An X-ray diffraction (XRD) study was performed on the samples ranging from 400 to 800 °C to determine the transition temperature from amorphous to crystalline tantalum pentoxide and to investigate the possible presence of other tantalum oxide phases. As shown in Figure 2.16, samples annealed up to 700 °C remain XRD amorphous. At approximately 725 °C, the films transition to a crystalline phase, which was found to match the orthorhombic $\beta$-Ta$_2$O$_5$ phase (space group: $Pmm2$, No. 25) with the structural parameters $a = 6.226(1)$ Å, $b = 40.20(1)$ Å, and $c = 3.884(9)$ Å with $\alpha = \beta = \gamma = 90^\circ$. These parameters are in good agreement with those found by Roth and coworkers (ICSD Card 43498).

**Figure 2.16:** XRD data from an annealing study on films prepared from 30 wt % TMA-Ta1 solutions. The films remain amorphous until approximately 725 °C. The simulated orthorhombic $\beta$-Ta$_2$O$_5$ phase is shown (top pattern) in addition to the Si(100) substrate (bottom pattern).
The XRR data (Figure 2.17) show a dramatic difference between the 300 °C sample and the 400 °C, where not only does the film undergo densification, but the Kiessig fringes become much more pronounced. SE and XRR data shown in Figure 2.18, both suggest a decrease in thickness with increasing annealing temperatures up until 600 °C; beyond this temperature, samples increased in thickness. The film thicknesses based on XRR were found to range from 90 nm for the 300 °C samples, down to approximately 65 nm after a 600 °C anneal. Recalling the TGA-DSC data (Fig. 2.5), we anticipated a denser film owing to the observed mass increase attributed to reduced tantalum, or possibly the formation of tantalum carbonate.

**Figure 2.17:** XRR for samples annealed at temperatures ranging from 300 to 800 °C for 10 min.
Figure 2.18: Film thickness as determined via SE and XRR; the refractive indices measured at 550 nm are shown on the same plot.

A maximum refractive index of 2.056(3) was measured at 550 nm for the 600 °C sample by SE, which again nearly matches the values achievable through the use of ALD, CVD\textsuperscript{9} or sputtering.\textsuperscript{40} Qualitatively, the shifting of the critical angles in the XRR patterns shown in Figure 2.17 suggest an increase in density with annealing temperature; however, XRR modeling suggests a peak density at 600 °C with a decrease in density beyond this temperature. In regard to RMS surface roughness values, the annealing temperature appears to have limited effects on surface roughness; values determined via AFM are compared to values obtained by XRR modeling as shown in Figure 2.19 and we see good agreement.
Figure 2.19: Film density and RMS roughness as a function of temperature as determined XRR. XRR-derived RMS roughness values are compared to AFM results. There are some notable aspects to the samples prepared at 600 °C that deserve comment. These samples were found to have higher densities (Figure 2.19) and higher indices of refraction (Figure 4.18), while also being the thinnest films (also shown in Figure 2.18). As previously noted from the TGA-DSC powder study (Figure 2.4) there is evidence that the system may be undergoing a transition from a state of higher order at ~600 °C to one of a more disordered, amorphous nature just prior to the crystallization at ~800 °C; a similar phenomenon may be occurring in the film samples around the same temperature, leading to greater densification through the appearance of an amorphous phase.

To further study the structure of the films resulting from the TMA-Ta1 precursor, a sample annealed at 400 °C for 10 minutes was studied using TEM. A cross-sectional TEM image is shown in Figure 2.20a. The film demonstrated sharp interfaces and from the contrast differences, appears very dense. Using convergent beam electron diffraction (CBED), the film was confirmed amorphous as evidenced by the smearing
of the diffraction lines (Figure 2.20b), which agrees with the GIXRD studies (Figure 2.16). The electron beam was left on the same location on the sample for over 1 minute, and some induced crystallinity was noted (Figure 2.20c). A STEM-EDX analysis was performed on a different TEM sample (shown in Figures 2.20d-f). The HAADF image where the EDX scan was performed is shown in Figure 2.20d. Again, sharp interfaces are observed and the oxygen and tantalum appear to be mostly restricted to the tantalum oxide layer, which is expected to contain not only Ta$^{5+}$, but lower oxidation states as well, recalling the TGA-DSC studies (cf. Figure 2.5).
Figure 2.20: (a) Cross-sectional TEM image of sample annealed at 400 °C for 10 min; interfacial SiO$_2$ layer shown in inset. (b) CBED pattern of amorphous Ta$_2$O$_5$ layer. (c) CBED pattern of the same layer after ~1 min of electron beam exposure. (d, e, f) HAADF image and EDX mapping of tantalum (magenta) and oxygen (blue) content. White scale bars in HAADF and EDX maps represent 40 nm.
We also studied the effect of annealing times on films prepared from the 30 wt % TMA tantalate salt solutions (with annealing temperatures held at 400 °C). As can be noted by the raw XRR data (Figure 2.21), the effects of anneal time are subtle; there appears to be minimal differences between the samples.

![XRR pattern graph](image)

**Figure 2.21:** XRR patterns of samples annealed from 5 to 60 minutes at 400 °C.

We modeled film thicknesses from these XRR data and compared to thicknesses determined via ellipsometry (Figure 2.22). We observe a thinning of the film with increasing annealing time. The effect of annealing on the refractive indices of the films (also Figure 2.22) appears minimal; however, the sample annealed for 1 h yielded the highest refractive index.
Figure 4.22: Film thickness as determined via XRR and SE and refractive indices (also determined by SE) for samples annealed from 5 to 60 minutes at 400 °C.

Through modeling the density and RMS roughness of the samples annealed from 5 to 60 minutes, some of the subtle effects of annealing time that were not apparent through the raw XRR data become evident. We note that the sample annealed for 1 h demonstrates the greatest density, which corroborates the SE results (Figure 2.22)—the 1 h sample also demonstrates the highest refractive index. Interestingly, we observe a decrease surface roughness with annealing time; however, these results were not confirmed by direct AFM measurements.
Figure 2.23: Film density and RMS roughness as a function of annealing time as determined by XRR modeling results.

As can be noted in Figure 2.22, there are some discrepancies observed between film thickness values determined via SE and XRR. A similar discrepancy is observed for the interfacial SiO$_2$ layer (Figure 2.24), yet both methods seem to indicate an increase in the interfacial SiO$_2$ layer with time. One might anticipate that at higher anneal temperatures, that interfacial SiO$_2$ growth could be substantial. An approximation of its expected thickness can be modeled using the Deal-Grove model,$^{41}$ assuming a wet oxidation environment at lower temperatures ($<$400 °C cf. Figure 4.6), and a dry oxidation at higher temperatures.
Figure 2.24: Thickness of the interfacial SiO$_2$ layer as determined by SE and XRR.

Through a comparison with the HRTEM image (shown in Figure 2.25) of the interfacial SiO$_2$ layer obtained from a sample annealed at 400 °C for 10 min, which shows a thickness of approximately 2.25 nm, it appears that in this case the XRR model provides superior results with a modeled thickness of ~1.5 nm versus the nearly 5 nm found via SE.

Figure 2.25: HRTEM micrograph of the interfacial SiO$_2$ layer in a sample annealed for 10 min at 400 °C.
To determine the minimal film thickness achievable through the solution-based deposition of the TMA-Ta1 solution, films of varying concentrations ranging from 0.14 wt % to 30 wt % were studied after being annealed at 400 °C for 10 min. These XRR data (Figure 2.26) show that samples prepared from solutions of 3.5 wt % and above demonstrated critical angles indicative of tantalum oxide. For films deposited from solutions at 1.4 wt % and below (Figure 2.27), the critical angles shifted from the samples deposited from the 3.5 wt % solutions, suggesting that either a different phase of tantalum oxide was present, or that a substrate effects were more pronounced. Preliminary XRR modeling results of the data shown in Figure 2.27 suggest the formation of a reduced tantalum oxide, with densities higher than that of Ta2O5.

**Figure 2.26:** XRR data for samples prepared with concentrations ranging from 3.5 to 28 wt %; all samples were annealed at 400 °C for 10 minutes.
**Figure 2.27**: XRR data for samples prepared with concentrations ranging from 0.14 to 1.4 wt%; all samples were annealed at 400 °C for 10 minutes.

These data show that especially at lower concentrations, the number of Kiessig fringes appears to scale with concentration. From XRR modeling and SE results (Figure 2.28), films on the order of 10 nm can be readily achieved, which is notable as this allows for the deposition of thin, dense films which typically require deposition techniques such as thermal or O$_3$ ALD$^{38}$ and CVD.$^{42}$
**Figure 2.28:** Film thicknesses (SE and XRR) and refractive indices (SE); thicknesses range from ~10 nm to 80 nm for this sample set.

As can be seen in Figure 2.28, film thickness trends in a linear manner. Film thicknesses can be approximated with the linear fit given in eq 2.4, where \( t \) is the film thickness in nanometers and \( c \) is the solution concentration in wt %.

\[
t = [2.85c] \text{ nm}
\]  \hspace{1cm} (2.4)

Also in Figure 2.28, we see a gradual decrease in refractive index with increasing solution concentration; these values approach the refractive indices of ALD-grown \( \text{Ta}_2\text{O}_5 \) films reported in the literature.\(^{43}\) In Figure 2.29, via XRR modeling we observe a similar increase in density with decreasing solution concentration.
Figure 2.29: Film density and RMS roughness as a function of solution concentration determined via XRR modeling.

A GIXRD scan (Figure 2.30) was performed on the 7 wt % sample (~15 nm) and it was determined that the film consisted of X-ray amorphous tantalum oxide.

Figure 2.30: GIXRD pattern for a film prepared from a 7 wt % solution and annealed at 400 °C for 10 min.

For all of the samples from the temperature, time, and concentration studies, multiple XRR models were applied, including treating the tantalum oxide layer as a homogenous slab, treating the tantalum oxide layer as a film composed of a thicker
oxide capped with a thin tantalum oxide crust, and assuming a linear density gradient of tantalum oxide in the film. Of these models, the assumption of a thin, dense tantalum oxide crust provided the best fit to the XRR data. The modeling suggested the presence of a tantalum oxide crust above the bulk density of $\text{Ta}_2\text{O}_5$. The results of XRR modeling for all sample sets are shown in Table 1. From the graphical summary of the three studies (Figure 2.31), the film deposited using 3.5 wt % solution annealed at 600 °C for 1 h should yield a film with a density approaching that of bulk $\beta$-$\text{Ta}_2\text{O}_5$. 
Table 2.1. Comparing Results to Bulk $\beta$-Ta$_2$O$_5$ Density and Refractive Index

<table>
<thead>
<tr>
<th>Conc. (wt %)</th>
<th>Anneal temperature ($^\circ$C)</th>
<th>Anneal time (min)</th>
<th>Density (g·cm$^{-3}$)</th>
<th>Density relative to bulk (%)</th>
<th>Refractive index, $n$</th>
<th>Refractive index, $n$ relative to bulk (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>300</td>
<td>10</td>
<td>6.68(8)</td>
<td>81.5</td>
<td>1.922(4)</td>
<td>84.5</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
<td>10</td>
<td>7.24(8)</td>
<td>88.3</td>
<td>2.002(3)</td>
<td>88.0</td>
</tr>
<tr>
<td>30</td>
<td>500</td>
<td>10</td>
<td>7.71(8)</td>
<td>94.0</td>
<td>2.036(3)</td>
<td>89.5</td>
</tr>
<tr>
<td>30</td>
<td>600</td>
<td>10</td>
<td>7.81(11)</td>
<td>95.2</td>
<td>2.056(6)</td>
<td>90.4</td>
</tr>
<tr>
<td>30</td>
<td>700</td>
<td>10</td>
<td>7.49(3)</td>
<td>91.3</td>
<td>2.013(8)</td>
<td>88.5</td>
</tr>
<tr>
<td>30</td>
<td>800</td>
<td>10</td>
<td>7.66(7)</td>
<td>93.4</td>
<td>2.02(2)</td>
<td>88.8</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
<td>5</td>
<td>7.543(7)</td>
<td>92.0</td>
<td>1.965(6)</td>
<td>86.4</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
<td>10</td>
<td>7.24(8)</td>
<td>88.3</td>
<td>2.002(3)</td>
<td>88.0</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
<td>15</td>
<td>7.635(7)</td>
<td>93.1</td>
<td>1.99(3)</td>
<td>87.5</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
<td>30</td>
<td>7.655(7)</td>
<td>93.4</td>
<td>1.995(6)</td>
<td>87.7</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
<td>45</td>
<td>7.579(7)</td>
<td>92.4</td>
<td>1.98(1)</td>
<td>87.0</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
<td>60</td>
<td>7.921(8)</td>
<td>96.6</td>
<td>2.010(2)</td>
<td>88.4</td>
</tr>
<tr>
<td>3.5</td>
<td>400</td>
<td>10</td>
<td>8.18(3)</td>
<td>*</td>
<td>2.0(2)</td>
<td>87.9</td>
</tr>
<tr>
<td>7</td>
<td>400</td>
<td>10</td>
<td>7.78(4)</td>
<td>94.9</td>
<td>2.00(7)</td>
<td>87.9</td>
</tr>
<tr>
<td>14</td>
<td>400</td>
<td>10</td>
<td>7.585(5)</td>
<td>92.5</td>
<td>2.00(1)</td>
<td>87.9</td>
</tr>
<tr>
<td>20</td>
<td>400</td>
<td>10</td>
<td>7.620(6)</td>
<td>92.9</td>
<td>1.974(5)</td>
<td>86.8</td>
</tr>
<tr>
<td>28</td>
<td>400</td>
<td>10</td>
<td>7.49(14)</td>
<td>91.3</td>
<td>1.965(4)</td>
<td>86.4</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
<td>10</td>
<td>7.24(8)</td>
<td>88.3</td>
<td>2.002(3)</td>
<td>88.0</td>
</tr>
</tbody>
</table>

*Evidence suggests some suboxide character in this sample hence it is not compared to bulk Ta$_2$O$_5$. 
The best fits obtained during XRR modeling necessitated the incorporation of a dense crust, typically on the order of a few nanometers (diagramed in Figure 2.32). To validate the model assumptions XPS was used to interrogate the first several nanometers of the thin-film samples.
Three samples were studied, including the 400 °C, 600 °C, and 800 °C samples, which were all annealed for 10 minutes. After deconvoluting the XPS peaks using Gaussian-Lorentzian functions, as can be seen in Figure 2.33, in addition to the peaks at 27.14 and 29.01 eV which are associated with the Ta4f7/2 and Ta4f5/2 peaks, respectively of pure Ta2O5, the 400 °C sample shows evidence of the suboxides or TaO2. This supports the results of previous XRR modeling, which suggested the presence of a sub-10 nm top layer of greater density than that of bulk β-Ta2O5 (8.2 g·cm⁻³). The rutile phase TaO2 has a calculated density of 10.41 g·cm⁻³.
Figure 2.33: XPS data for the Ta4f_{5/2} and Ta4f_{7/2} peaks for the sample annealed at 400 °C.

The O1s peaks of the 400 °C sample at 530.63 and 531.63 eV shown in Figure 2.34 are indicative of the low binding energy (LBE) and high binding energy (HBE) peaks, which may be concomitant with the presence of TaO₂ at the surface.

Figure 2.34: XPS data for the O1s peak for the sample annealed at 400 °C.

As the annealing temperature was increased from 400 °C to 600 °C as shown in the Figures 2.35 and 2.36, we see the emergence of yet another oxidation state of tantalum, likely associated with the cubic rock-salt structure. TaO. The
The aforementioned phase of tantalum oxide has shown calculated densities of approximately 14.96 g·cm⁻³, and the sub-10 nm layers of tantalum oxide in several of the samples converged upon this value.

**Figure 2.35:** XPS data for the Ta₄f₅/₂ and Ta₄f₇/₂ peaks for the sample annealed at 600 °C.

**Figure 2.36:** XPS data for the O₁s peaks for the sample annealed at 600 °C.
At 800 °C (Figure 2.37), the amount of TaO present at the surface exceeds the amount of TaO\(_2\) and a shift in fitted peak intensities is noted in the O1s peaks (Figures 2.36 and 2.38, for the 600 and 800 °C samples, respectively), which suggests a possible relationship to this phenomenon and the increased presence of TaO at the surface.

Figure 2.37: XPS data for the Ta4f\(_{5/2}\) and Ta4f\(_{7/2}\) peaks for the sample annealed at 800 °C.

Figure 2.38: XPS data for the O1s peaks for the sample annealed at 800 °C.
Clearly, from the XRD pattern shown previously in Figure 2.16, the primary tantalum oxide layer is a phase-pure $\beta$-Ta$_2$O$_5$, so a possible explanation of the appearance of these surface suboxides can be related to the entropically-favorable loss of oxygen near the surface as annealing temperatures increase. Yet another explanation is that during air annealing the surface oxides are being reduced by gaseous, carbon-containing species (cf. TGA-MS results in Figure 2.6). It is suspected that this thin suboxide top layer is amorphous, which may mitigate the surface roughening typically associated with grain growth and crystallization—by constraining grain growth in the lateral directions. This phenomenon may explain the low RMS roughnesses measured by AFM (Figure 2.12) for the samples annealed at 800 °C, which appears somewhat crystalline in cross-sectional SEM (Figure 2.15).

Electrical measurements were taken from MIS diodes, constructed for the first time using TMA-Ta1 precursor-derived Ta$_2$O$_5$ thin films. Heavily doped, $n$-type silicon was used as the back contact. Since the silicon is degeneratively doped, it can be treated as a metal. A blanket amorphous Ta$_2$O$_5$ insulating layer 99.1-nm thick, annealed at 400 °C for 10 min formed the insulator, and shadow-masked thermally evaporated aluminum formed the top contacts. Electrical results from these diodes, including current versus field data and Log($J$)-$\xi$ plots are shown in Figures 2.39 and 2.40. Device current versus field measurements (Figure 2.39) showed a small counter-clockwise hysteresis indicative of positively-charged mobile ions in the Ta$_2$O$_5$ film, likely due to protons leftover from incomplete dehydration during
annealing. From the log($J$)-$\xi$ plot (Figure 2.40), we observe leakage current densities in the range typically reported for MIS devices containing amorphous Ta$_2$O$_5$ films produced via vacuum-based deposition$^{47}$ as well as by sol-gel$^{19}$ methods.

**Figure 2.39:** Typical electronic characteristics for MIS diodes fabricated with a highly-doped $n$-type silicon bottom electrode, a 99.1-nm Ta$_2$O$_5$ insulator, and aluminum top contacts.
Figure 2.40: Logarithm of current density versus field. Current density values between ±4 volts are in the picoamp range and within the noise floor of the tool.

The dielectric constants of the amorphous films were calculated using saturated capacitance values measured at 100 kHz for three different circular diode sizes: 5, 7, and 11 mm in diameter (see Figure 2.41). Aluminum contact sizes were measured by optical microscope, and the film thickness was determined via SE. Many diodes were measured and the results presented are representative of typical device behavior with no significant changes in hysteresis, conduction fit, or current response. The extracted dielectric constant for an amorphous Ta$_2$O$_5$ film was found to be 23.3. This was within the values tabulated by Ezhilvalavan and co-workers who report dielectric constants ranging from 18 to 30 for amorphous Ta$_2$O$_5$ films dependent on deposition technique.\textsuperscript{48}
Figure 2.41: Capacitance measurements for devices with 5 mm, 7 mm, and 12 mm contact diameters. A linear fit yields the following equation: 

\[ y = 0.0020778 \pm 0.000216 x + 4.4558e-011 \pm 8.71e-012 \]

Previous reports on both ALD- and sol-gel-deposited Ta₂O₅ thin films have found Poole-Frenkel to be the dominant conduction mechanism. Poole-Frenkel emission is trap-mediated conduction and traps in an insulator cause localized potential barrier lowering. When the energy of an electron is greater than the barrier, it is able to surmount the barrier where it is captured and emitted by traps in order to traverse the insulating barrier. Less energy is required to surmount the barrier due to trap-assisted barrier lowering. This allows an increase in thermal emission when an external electric field is applied increasing overall current response. Poole-Frenkel emission is modeled using the eq 2.5.

\[ I \propto A E \varepsilon_i \exp \left[ \frac{q \sqrt{q V / \pi \varepsilon_i} - \phi_B}{kT} \right] \]  

(2.5)

where \( I \) is current, \( A \) is the area of the device, \( E \) is the applied voltage, \( \varepsilon_i \) is the high-frequency dielectric constant, \( q \) is the elementary electron charge, \( d \) is the insulator
thickness, \( \phi_B \) is the energy barrier height, \( k \) is Boltzmann’s constant, and \( T \) is temperature.\(^{50}\) Linearizing the above equation results in the simplified relation, \( \log \left( \frac{I}{V} \right) \propto \sqrt{V} \). Figure 2.42 shows \( \text{Ta}_2\text{O}_5 \) diodes data plotted using this linearization. A least-squares linear-regression fit has an \( R^2 = 0.999 \) spanning nearly three orders of magnitude, showing a good fit.

**Figure 2.42:** Poole-Frenkel linearized current versus voltage (\( I-V \)) data showing it to be the dominant conduction mechanism with \( R^2 > 0.999 \).

In light of the findings that tantalum oxide films prepared using the 3.5 wt % TMA-Ta1 yielded some of the highest densities, nanofilms and nanolaminates were fabricated using this particular precursor concentration. Additionally, some of these samples were used to construct MIS device structures for electrical characterization.

The first sample prepared (as described in Experimental Methods section) using the 3.5 wt % solution was annealed at 400 °C for 10 min. This sample was studied by
XRR (Figure 2.43) and the film thickness was found to be ~10 nm and the density approximately 95% of the bulk $\beta$-Ta$_2$O$_5$ density.

![XRR data](image)

**Figure 2.43:** XRR data for a nanofilm prepared using 3.5 wt % TMA-Ta1 solution and annealed at 400 °C for 10 min.

A second sample using the same precursor solution was annealed for 600 °C for 10 minutes; this annealing temperature was chosen based on the observation that films annealed at 600 °C yielded the highest film densities found during the temperature study. The XRR pattern obtained for this sample is shown in Figure 2.44. This nanofilm was found to be slightly thinner than 10 nm, with a density in excess of $\beta$-Ta$_2$O$_5$ density. At this annealing temperature and film thickness it is likely that the nanofilm may contain TaO$_2$ and TaO in addition to Ta$_2$O$_5$ (*cf.* previously discussed XPS results).
Both of these samples were incorporated into MIS devices (see the Experimental Methods section for the details of device fabrication) and measured electrically for leakage, breakdown electric field, and conduction mechanisms. $J-\xi$ characteristics of both samples are shown in Figure 2.45; the 600 °C nanofilm demonstrates superior MIS diode performance over that of the 400 °C sample, as evidenced by the lower current density values found during the voltage sweeps.
Figure 2.45: $J-\xi$ sweeps for nanofilms annealed for 10 min at 400 °C (top) and 600 °C (bottom).

As can be seen in Figure 2.46, the diodes annealed at 400 °C show higher leakage at turn on and display negative curvature roll-off at high electric field indicative of electron trapping. By contrast, the diodes annealed at 600 °C show lower overall leakage and display no high-field roll-off suggesting a lower trap density in the Ta$_2$O$_5$ film. However, the sample annealed at 400 °C showed a higher breakdown voltage (5.6 MV•cm$^{-1}$) than that of the 600 °C sample (4.5 MV•cm$^{-1}$).
Figure 2.46: Plot of the logarithm of current density versus field, log \( (J) - \zeta \).

Figure 2.47 shows best-fit lines for mathematical linearizations based on Poole-Frenkel conduction. Again, samples annealed at 600 °C show better electrical performance indicated by a higher R^2 value pertaining to goodness of fit. These results suggest that higher annealing temperatures improve thin-film electrical performance by dehydrating the film, while also reducing the number of trap states due to the presence of reduced tantalum oxide (recalling XPS results).
Figure 2.47: Poole-Frenkel linearization of current versus voltage ($I$-$V$) data showing the dominant conduction mechanism with trendlines and $R^2$ fitting values.

**Conclusion**

We have shown that aqueous TMA tantalate salts can be used for the facile deposition of high-quality, dense $\text{Ta}_2\text{O}_5$ films with thin-film properties that match or exceed many of the existing $\text{Ta}_2\text{O}_5$ depositions methods. TGA-MS data on the powder product show the loss of water and $\text{CO}_2$ (from the combustion of carbon in TMA) between 40 °C and 345 °C and an exothermic crystallization peak at ~800 °C.

The aqueous solution precursor of TMA-Ta1 was used to deposit films on $n$-type Si(100) substrates using a spin coater in air. The films remain amorphous up until the crystallization temperature of approximately 725 °C, after which the films become crystalline in the orthorhombic $\beta$-$\text{Ta}_2\text{O}_5$ phase. The effects of annealing temperatures and times were studied, as well as the effects of varying solution concentrations. Thin-film properties were characterized using SE and XRR, with the former showing
refractive indices as high as 2.056(3) and the latter showing film densities approaching the bulk density of $\beta$-Ta$_2$O$_5$. As far as we know, this is the first report of strong Kiessig fringes being observed past 8°. The effects of concentration were also studied using SE and XRR and found to follow a direct linear trend, with films ranging from about 10 to 100 nm per coat depending on the solution concentration. Tantalum oxide thin film prepared using the dilute precursor (e.g. 3.5 wt %) are notable in that they are not only sub-10 nm films, but they have densities that are up to ~97% of bulk Ta$_2$O$_5$. This result will prove more relevant as device dimensions continue to shrink. The AFM and XRR modeling results both indicate films with near-atomically smooth surfaces, with RMS roughness values on the order of a few Ångströms. Imaging performed via SEM and TEM confirmed the thicknesses obtained via SE and XRR modeling efforts. Both imaging techniques can qualitatively show dense Ta$_2$O$_5$ layers by apparent contrast differences. Cross-sectional SEM shows the presence of a crystalline phase in the 800 °C sample, and CBED confirms the presence of an amorphous phase in the 400 °C sample. The HAADF imaging and STEM-EDX analysis shows limited interdiffusion between layers with sharp interfaces.

XPS studies were conducted to study the film surfaces and to support the models used during XRR modeling. It was found that with increasing annealing temperature, the surface of the films evinced increasing suboxide character, including TaO$_2$ and TaO, which explains the need for a dense crust during XRR modeling. The formation of this reduced-oxide crust can likely be attributed to the entropically favorable loss of oxygen near the film surface.
Electrical characterization was performed on an amorphous ~100 nm thick sample annealed at 400 °C and for this sample a dielectric constant of 23.3 was calculated. The conduction mechanism in the same sample was found to be Poole-Frenkel.

Nanofilms of ~10 nm were annealed at 400 °C and 600 °C for 10 minutes and used to fabricate MIS devices. Annealing the prepared nanofilms at 600 °C improves the electrical performance of the insulator, which is reasonable in light of the other findings of this study, viz. the 600 °C anneal temperature yielded dense tantalum oxide films and the ~10 nm nanofilms were found to approach ~97% of the bulk density of Ta$_2$O$_5$.

Future studies will focus on understanding the speciation, structure, sizing, and aging of the cluster species and how these factors relate to film formation. A study concerning hexatantalate Lindqvist ions and their resultant films was run in parallel to this work; this should provide rich opportunities for the comparison of novel aqueous precursor chemistries and their associated thin films.
References


(15) Ozer, N.; Lampert, C. M. Structural and Optical Properties of Sol-Gel


Chapter 3

Nb$_2$O$_5$ and Ta$_2$O$_5$ THIN FILMS FROM POLYOXOMETALATE PRECURSORS: A SINGLE PROTON MAKES A DIFFERENCE

Lauren B. Fullmer, Ryan H. Mansergh, Lev N. Zakharov, Douglas A. Keszler, and May Nyman

Abstract
Thin-film materials from water-based precursors follow the principals of green chemistry, leading to a more sustainable future in the energy intensive era in which we currently reside. While simple in practice, aqueous metal-oxide chemistry is complex at the molecular level. Here we develop the first water-based formation of Nb_2O_5 and Ta_2O_5 thin films; utilizing tetramethylammonium salts of [H_2Ta_6O_{19}]^{6-} and [H_3Nb_6O_{19}]^{5-} polyoxometalates. Although the clusters are structurally identical group V analogues and differ only by a single proton, this difference has a considerable influence on the quality of the films that are obtained. Through characterization of the solid-state precursor (single-crystal X-ray diffraction), the aqueous precursor solution (X-ray scattering), and the thin films (atomic force and scanning electron microscopies, X-ray diffraction and reflectivity); we rationalize the important roles of cluster protonation that carry through all chemical processes from the precursor to the metal oxide coating.
**Introduction**
Fabricating functional thin films from aqueous metal-oxo cluster precursors embodies several principals of green chemistry. Therefore development of appropriate chemistries for materials broadly used in data storage, energy storage, and energy generation would provide technologies towards a sustainable future. Metal-oxo cluster chemistry that has been most substantially developed is that of the group V/VI polyoxometalates\(^1\) and the group 13 polyoxocations.\(^2\) Clusters of these chemical families can be isolated in discrete forms without the use of organic ligands to prevent irreversible precipitation of the related oxide. Therefore, these clusters are entirely inorganic, with only H\(_2\)O, OH\(^-\), and O\(^{2-}\) for ligands. Water-solubility of metal-oxo clusters arises naturally from the positive or negative charge, which requires charge-balancing counterions. By necessity, counterions are incorporated into a film that is spun-cast from aqueous solution and therefore removal of these counterions must be carried out with enhancement, rather than degradation of the fundamental film characteristics that include density, continuity, compositional and phase purity, interfacial homogeneity, and smoothness. Thus ideal counterions are preferably small and volatile and/or combustible at a low temperature. Suitable counterions for accomplishing this ideal end-product include cations H\(^+\), NH\(_4^+\), and N(CH\(_3\))\(_4^+\); or anions NO\(_3^-\), SO\(_4^{2-}\), or CO\(_3^{2-}\). Less suitable counterions include bulky organics that would leave large voids in the film upon removal, or that cannot be completely removed; or nonvolatile counterions such as alkalis or halides.
Thin films of group V metal oxides (Ta$_2$O$_5$ and Nb$_2$O$_5$) are of significant technological relevance owing to their favorable chemical, thermal, and mechanical properties.\textsuperscript{3} They have a number of potential uses in advanced electronics as high-$\kappa$ dielectric materials\textsuperscript{4} or as diffusion barriers.\textsuperscript{5} More recently, Ta$_2$O$_5$ has been coveted as a robust memristive material.\textsuperscript{6} Prior solution deposition of Ta$_2$O$_5$ and Nb$_2$O$_5$ films was achieved by utilizing non-aqueous alkoxide or halide solutions.\textsuperscript{7–11} These molecular precursors are moisture sensitive and react with exposure to ambient air: the degree of reaction is variable with temperature, humidity, and time. Therefore the speciation of these precursors changes with time, which is not amenable to reproducible and reliable thin film deposition. Also starting with tantalum alkoxide, Sone and coworkers prepared an aqueous acidic-peroxide solution for the deposition of Ta$_2$O$_5$.\textsuperscript{12} However, this solution both requires the decomposition of excess peroxide using platinum and it is not stable, as it continuously precipitates tantalum oxide. Again this leads to irreproducibility of film quality and characteristics. Therefore, reliable aqueous routes to Ta$_2$O$_5$ and Nb$_2$O$_5$ thin films have not yet been realized. The group V Lindqvist-ion polyoxometalates ([H$_x$Ta$_6$O$_{19}$]$^{(8-x)^{-}}$ and [H$_x$Nb$_6$O$_{19}$]$^{(8-x)^{-}}$—hexatantalate and hexaniobate respectively) are robust, highly water-soluble, isostructural clusters featuring a superoctahedron of six mutually edge-sharing octahedra (Fig. 3.1) and are ideal for developing routes to Ta$_2$O$_5$ and Nb$_2$O$_5$ thin film materials that are: 1) entirely water-based and 2) are executed in ambient conditions. Of the potential countercations listed above, only N(CH$_3$)$_4^+$ (TMA or tetramethylammonium) or a mixture of N(CH$_3$)$_4^+$ and H$^+$ are suitable. NH$_4^+$ produces an insoluble salt, and due to the limited pH stability range of these clusters (>11),
only up to three H\(^+\) counterions are possible.\(^{13,14}\) While the TMA salt of hexaniobate has been made and structurally characterized,\(^{17}\) a TMA salt of hexatantalate has not yet been reported. While Matsumoto and coworkers have successfully synthesized tetrabutylammonium salts of hexatantalate and the first decatantalate structure, they were from non-aqueous methods.\(^{16-18}\) Here we report synthesis and structural characterization of both TMA-hexatantalate, and a TMA-hexaniobate (modified from the literature procedure). Thin films produced from these analogous cluster precursors differ notably in quality; while hexatantalate produced Ta\(_2\)O\(_5\) thin films of remarkable density and smoothness, Nb\(_2\)O\(_5\) films produced from hexaniobate were rough. This was surprising, given the similarity of the precursors and the general periodic relationship between Nb and Ta. By small and wide angle X-ray scattering studies (SWAXS) of aqueous solutions of the clusters, and noting the protonation state of the clusters and the influence on crystallization behavior and subsequent thin film characteristics, we hypothesized the dissimilar results to be simply the differing protonated states of the two group V analogues. More broadly, it is noted that a seemingly innocuous difference can strongly influence chemical processes, and ultimately, performance of functional materials.
Figure 3.1. Ball and stick model (left) and polyhedral representation (right) of the $[\text{M}_6\text{O}_{19}]^{8-}$ (M=Nb,Ta) Lindqvist ion. Red spheres are oxygen, blue spheres are Nb or Ta; blue polyhedra are MO$_6$.

**Experimental Methods**

**General Methods and Materials**

H$_2$O$_2$ (30%), isopropanol (ACS Grade), and NH$_4$OH (28.0-30.0% as NH$_3$, ACS Grade) were purchased from Macron Fine Chemicals. TaCl$_5$ (99.99%), and (CH$_3$)$_4$NOH (25% w/w aq. solution, 99.9999%) were purchased from Alfa Aesar. TGA-DSC scans were performed in air as well as argon from 20 to 900 °C with a ramp rate of 10 °C-min$^{-1}$ using a TA Instruments SDT Q600. Infrared spectra (400-3500 cm$^{-1}$) were collected on a Thermo Scientific Nicolet iS10 with a Smart Orbit Diamond ATR accessory. Small and wide angle X-ray scattering was collected at beamline 12-ID-B at the Advanced Photon Source at Argonne National Lab. The samples and appropriate backgrounds were collected with a flow through quartz capillary (1.5 mm) cell for 20 scans using incident energy of 14 keV and a sample to detector distance of 2 meters. WaveMetrics Igor Pro software$^{19}$ with Irena macros was used for analyzing the SWAXS data.$^{20}$ SolX software was used for creating simulated scattering curves.$^{21,22}$ Radius and interparticle interactions were determined
for each sample and the simulated data by using a fitting method of least squares.

Elemental composition was determined by Galbraith Laboratories, Inc. (Knoxville, TN) through the use of inductively coupled plasma atomic emission spectroscopy (ICP-AES; Nb & Ta) and a Thermo Finnigan FLASH 2000 Elemental Analyzer (C, H, N).

Single crystal X-ray diffraction experiments for Nb6 and Ta6 were carried out on a Bruker Smart Apex diffractometer at 173(2) K and 150(2) K, respectively, using MoKα radiation (λ=0.71073 Å). Absorption corrections were applied by SADABS.23 Space groups were determined based on the intensity statistics. The structures were solved using direct methods with calculations of difference Fourier maps and refined with full-matrix least-squares methods based on $F^2$. Non-hydrogen atoms were refined with anisotropic thermal parameters except those in one of the N(CH$_3$)$_4$ cations in Nb6 disordered around an inversion center. The H atoms in both structures were treated in calculated positions and refined in a rigid group model. H atoms in the Nb$_6$O$_{19}$H anion in Nb6 were not found. In the structure of Nb6, there are five N(CH$_3$)$_4$ cations; three of them are located in general positions, and two are disordered over two positions around inversion centers. In Nb6, of the 13 solvent water molecules, 7 of them are disordered and they create a H-bonded network. This framework was modeled by using SQUEEZE$^{24}$ with 201 electrons/cell, which compares with the required value of 130 electrons/cell (10 electrons per water molecule). This suggests there are actually 20 water molecules in the unit cell of Nb6 and this agrees with the thermal analysis. All calculations were performed using the SHELXTL (v. 6.10) package$^{25}$. 

For the film deposition and analysis, $n$-type silicon (100) wafers, purchased from Sumco, OR USA, were used. The substrates were rinsed in Millipore 18.2-MΩ deionized water, dried in argon, and then ashed in an O$_2$ plasma for 10 min at 200 W and ~175 mTorr. The films were spun using a CEE Model 100 spin coater at 3000 RPM for 30 s. The films were soft baked on a hot plate at 200 °C for 1 min. The samples were then annealed in air using Neytech Qex furnaces with a 20 °C·min$^{-1}$ ramp rate.

X-ray diffraction (XRD) and X-ray reflectivity (XRR) were both performed on a Rigaku Ultima-IV diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5409$ Å). For XRR data collection, the instrument was configured with a 5.0° incident Soller slit, a 10-mm divergent height limiting slit, and a 5.0° receiving Soller slit; the divergent slit, scattering slit, and receiving slit were set to 0.2, 0.5, and 0.2 mm, respectively. Out-of-plane scans were performed for phase identification; XRR results were used to determine the appropriate $\omega$ value for out-of-plane scans. For these scans, the instrument was configured with a 5.0°-incident Soller slit, a 10-mm divergent height limiting slit, and a 0.5° parallel beam slit; the divergent slit was set to 0.2 mm and the scattering slit and receiving slit were left open. The Rigaku software packages PDXL$^{26}$ and GlobalFit$^{27}$ were used for the analysis of XRD and XRR data, respectively.

Atomic force microscopy (AFM) measurements were performed on a Veeco Innova SPM and a Digital Instruments NanoScope III in tapping mode with silicon AFM probes (300 kHz, 40 N·m$^{-1}$). Initial sample scans were performed on $1 \times 1 \mu m^2$ areas and later scans were performed on $20 \times 20 \mu m^2$ areas. Root-mean-square roughness
values were obtained by analyzing data from multiple \(2 \times 2 \mu m^2\) sections of the larger \(20 \times 20 \mu m^2\) scan with Bruker NanoScope Analysis software.\(^{28}\) Scanning electron microscopy (SEM) images were collected on an FEI NOVA NanoSEM 230 high resolution microscope.

**Synthesis**

\((NH_4)_3Ta(O_2)_4\)

The synthesis for ammonium peroxtantalate, \((NH_4)_3Ta(O_2)_4\), was adapted from previous methods.\(^{29}\) \(TaCl_5\) (2.4 g) was dissolved in 40 mL of 30% \(H_2O_2\) in an ice water bath. With moderate stirring throughout the entire reaction, the solution was kept between 5-15 °C. A total of 12-mL \(NH_4OH\) (14.5 M) was added in 1 mL aliquots. The solution became cloudy with early additions of \(NH_4OH\); however once the entire 12 mL is added, the solution became clear. Upon addition of ethanol (approximately 150 mL) the solution yielded a white precipitate. This precipitate was then vacuum-filtered with a Büchner funnel and washed with ethanol. The yield is between 97 and 100%.

\[[(CH_3)_4N]_6[H_2Ta_6O_{19}] \cdot 21H_2O \text{ (Ta6)}\]

The synthesis for Ta6 was adapted from the synthesis of alkali hexatantalates.\(^{30}\) A 125-mL flask was charged with \((NH_4)_3Ta(O_2)_4\) (1.32 g) and 1.4 M tetramethylammonium hydroxide (8.25 mL). The solution was refluxed for 5 h with the condensing column chilled to approximately 5 °C. The resulting solution was filtered with a 0.45-µm nylon syringe filter. The filtered solution was agitated with isopropyl alcohol (~40 mL) and centrifuged to yield a small heavier layer containing the product. Further agitation of the bottom layer with isopropyl alcohol (~30 mL)
yielded a white precipitate. The precipitate was washed with isopropyl alcohol and oven dried under vacuum (~60 °C). The yield is between 38 and 63 %. Elemental analysis found C 13.59%, H 4.90%, N 3.62%, Ta 46.9%.

\[ \text{[(CH}_3\text{)}_4\text{N}]_3[\text{H}_3\text{Nb}_6\text{O}_{19}]\cdot20\text{H}_2\text{O} \ (\text{Nb6}) \]

The synthesis for Nb6 was adapted from the synthesis of alkali hexaniobates. A 150-mL beaker was charged with tetramethylammonium hydroxide solution (2.8 M, 100 mL) and heated to 90 °C. Hydrous Nb\(_2\)O\(_5\) (20 g) was added in small aliquots, allowing full dissolution before addition of new aliquots. After addition of all the niobium oxide, the solution was allowed to cool to room temperature. Isopropyl alcohol was added to precipitate the final product. After excessive washing with isopropyl alcohol, a white crystalline powder is obtained through vacuum filtration. The yield is between 94 and 100%. Elemental analysis found C 16.80%, H 6.63%, N 4.74%, Nb 25.9%.

**Results and Discussion**

**Nb\(_2\)O\(_5\)** and **Ta\(_2\)O\(_5\)** thin films. Thin films were prepared from spin coating 0.22-M (with respect to the cluster) aqueous solutions of the TMA hexametalate salts on n-type silicon wafers. The films were annealed at 400, 600, and 800 °C and then characterized using various methods including XRD, XRR, SEM, and AFM. These anneal temperatures were chosen based on TGA-DSC analysis of the powder samples. Thermal analysis revealed that all water and TMA is mostly driven out of the samples by 400 °C and predominantly metal oxide remains. However, Nb\(_2\)O\(_5\) crystallizes at 600 °C, accompanied by a sharp weight-loss event; Ta\(_2\)O\(_5\) crystallizes at 800 °C with a similar weight-loss event (Fig. 3.2). Prior to the sharp weight loss is
a symmetric shallow decrease/increase in weight (in air). This is a result of a complicated decomposition of the TMA cation, which will be published elsewhere. When the samples are heated in an oxygen-free, inert atmosphere such as argon, we do not see this behavior, and a black powder is obtained, as opposed to the white powder from air calcination. The volatilization of water and TMA are associated with endothermic peaks, while crystalization of the oxide is an exothermic reaction. Thermal analysis of the samples revealed 17 water molecules for Ta6 and 18 water molecules for Nb6 which agrees closely with the crystallographic stucture.

**Figure 3.2.** TGA-DSC analysis of powder Ta6 (left) and Nb6 (right). Red lines correspond with heat flow, blue lines correspond with weight percent. Dotted line is experimental data in argon gas while solid line is in air.

Grazing incidence XRD revealed that the Nb2O5 and Ta2O5 films are crystalline at 600 and 800 °C, respectively (Appendix A, Fig. A1)—consistent with exothermic peaks at similar temperatures in the DSC analyses. Both Ta2O5 and Nb2O5 films crystallize in the orthorhombic phase, with space groups Pmm2 (25) and Pbam (55) respectively. These crystallization temperatures are higher than what has been reported for Nb2O5 and Ta2O5 films from other deposition methods. Films deposited
via plasma enhanced chemical vapor deposition crystalize at ~600—700 °C for Ta₂O₅ and ~400—500 °C for Nb₂O₅.³²

The films were imaged using scanning electron microscopy (SEM) in order to visually determine relative thickness and roughness. (Fig. 3.3a) Ta₂O₅ films were shown to have continuous, atomically smooth surfaces regardless of anneal temperature, while Nb₂O₅ film roughness varied with anneal temperature. The 400 °C annealed film for Nb₂O₅ has roughness values comparable with the Ta₂O₅ film despite observable differences by eye. However at higher temperatures the quality of the films degraded and the change in morphology was noticeable. The 600 °C and 800 °C anneals of Nb₂O₅ had a considerable increase in roughness.

**Figure 3.3.** Nb₂O₅-Top, Ta₂O₅-bottom a. AFM and SEM. The white scale bar is 500 nm. b. X-ray reflectivity c. Comparison of XRR derived and AFM roughness values

The qualitative observations from SEM were verified quantitatively with atomic force microscopy (AFM) and X-ray reflectivity (XRR). Through modeling XRR data, values for roughness, density, and thickness are generated. The period of oscillations
of the Kiessig fringes is dependent on film thickness, where the shorter the period the thicker the film. The amplitude of the oscillations depends on the difference between the densities of the film and its substrate. The roughness of a film can be determined by the $2\theta$ angle at which the fringes decay. A decay of the reflected x-rays at lower $2\theta$ means the film has a larger surface roughness. By comparing the XRR for Ta$_2$O$_5$ and Nb$_2$O$_5$ in Fig. 3.3b, it is apparent that the Nb$_2$O$_5$ films are less dense and considerably rougher. The fringes in the Ta$_2$O$_5$ films are distinguishable until $2\theta$ values of 8—9° in some cases. However, in the Nb$_2$O$_5$ films the fringes decay much earlier, around 5—6°. The roughness values obtained from XRR and AFM are compared in Fig. 3.3c. There is some discrepancy between the roughness values, depending on the technique that is used. This is because the XRR values are from modeled data, while AFM is a direct measurement. Nonetheless, both methods quantitatively show greater roughness in the Nb$_2$O$_5$ films.

Ta$_6$ and Nb$_6$ clusters. Both Ta$_6$ and Nb$_6$ are obtained as single crystals by dissolution in water followed by slow evaporation. The experimental powder X-ray diffraction patterns of the bulk samples of Ta$_6$ and Nb$_6$ (Figs. A5 and A6, Appendix A) are consistent with the simulated patterns from the single crystal data (Figs. A3 and A4, Appendix A), indicating the single-crystals that were analyzed are representative of the bulk. The single-crystal structure of Ta$_6$ revealed a diprotonated hexametalate Lindqvist ion, [H$_2$Ta$_6$O$_{19}$]$^{6-}$, which is charge-balanced by six TMA countercations, all identified in the structure. On the other hand, Nb$_6$ consists of a triprotonated Lindqvist ion [H$_3$Nb$_6$O$_{19}$]$^{5-}$, balanced by five TMA counterions. Table 3.1 summarizes the crystallographic data for Nb$_6$ and Ta$_6$. The
central oxygen is bonded to the metal atoms via long M-O bonds of ~2.4 Å. The terminal M-O bonds are all multiply-bonded and therefore shorter (~1.8 Å).

**Table 3.1.** Crystallographic data and structure refinement for **Ta6** and **Nb6**.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ta6</th>
<th>Nb6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical Formula</strong></td>
<td>Ta₆O₄₂.₅C₂₄H₇₄N₆</td>
<td>Nb₆O₂₅C₂₀H₆₃N₅</td>
</tr>
<tr>
<td><strong>Formula Weight (g/mol)</strong></td>
<td>2214.41</td>
<td>1668.15</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>P -1 (2)</td>
<td>P -1 (2)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.7073(7)</td>
<td>13.719(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.0596(7)</td>
<td>14.024(7)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>20.903(1)</td>
<td>16.390(8)</td>
</tr>
<tr>
<td>α (°)</td>
<td>71.310(1)</td>
<td>67.008(8)</td>
</tr>
<tr>
<td>β (°)</td>
<td>76.972(2)</td>
<td>76.671(8)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>72.889(1)</td>
<td>84.904(9)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>3345.40(32)</td>
<td>2825(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>T (K)</td>
<td>150</td>
<td>173</td>
</tr>
<tr>
<td>d (g·cm⁻³)</td>
<td>2.196</td>
<td>1.565</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>9.865</td>
<td>1.263</td>
</tr>
<tr>
<td>Reflections Measured</td>
<td>96486</td>
<td>44542</td>
</tr>
<tr>
<td>Independent</td>
<td>24199</td>
<td>13966</td>
</tr>
<tr>
<td>R_int</td>
<td>0.0514</td>
<td>0.1417</td>
</tr>
<tr>
<td>Independent Parameters</td>
<td>712</td>
<td>525</td>
</tr>
<tr>
<td>R1</td>
<td>0.0317</td>
<td>0.0609</td>
</tr>
<tr>
<td>wR2</td>
<td>0.0666</td>
<td>0.1041</td>
</tr>
</tbody>
</table>
Figure 3.4. Representation of the hydrogen bonded clusters of Ta_6 (top) and Nb_6 (bottom).

Bridging oxos (M-O-M) typically exhibit bond lengths of 2.0 Å, but protonation is identified in both Ta_6 and Nb_6 with bridging M-O-M bond lengths of 2.1—2.2 Å. Ta_6 has two protons which reside on neighboring bridging oxygens. For Nb_6, there are likewise two protons on neighboring bridging oxygens and a third on an oxygen on the face trans to this doubly-protonated face. The location of these protons were determined by both bond length of the bridging oxygens and by bond valence sum (BVS) calculations (Tables 3.2 and 3.3). Protonation of these clusters leads to characteristic dimerization via mutual hydrogen bonding of the protonated faces (Fig. 3.4). Finally, the third proton on the face trans to the doubly-protonated face of Nb_6
results in assembly of the clusters into chains in the lattice. Reflecting this ion-arrangement macroscopically, the crystals of Nb6 grow as long needles.

**Table 3.2.** Bond lengths and bond valence sum of oxygens in Ta6 structure. * indicates protonated oxygens.

<table>
<thead>
<tr>
<th>Bridging Oxygen</th>
<th>Bond Lengths (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta2-O2-Ta1</td>
<td>1.922(2)</td>
<td>1.991(2)</td>
</tr>
<tr>
<td>Ta3-O3-Ta2</td>
<td>2.137(2)</td>
<td>2.157(2)</td>
</tr>
<tr>
<td>Ta4-O4-Ta3</td>
<td>2.031(2)</td>
<td>1.900(2)</td>
</tr>
<tr>
<td>Ta4-O5-Ta1</td>
<td>1.971(2)</td>
<td>1.979(2)</td>
</tr>
<tr>
<td>Ta5-O6-Ta1</td>
<td>1.923(2)</td>
<td>1.992(3)</td>
</tr>
<tr>
<td>Ta2-O7-Ta5</td>
<td>1.987(3)</td>
<td>1.995(2)</td>
</tr>
<tr>
<td>Ta3-O8-Ta5</td>
<td>2.128(3)</td>
<td>2.157(2)</td>
</tr>
<tr>
<td>Ta5-O9-Ta4</td>
<td>1.961(2)</td>
<td>1.992(3)</td>
</tr>
<tr>
<td>Ta6-O10-Ta1</td>
<td>1.973(2)</td>
<td>1.984(3)</td>
</tr>
<tr>
<td>Ta2-O11-Ta6</td>
<td>1.956(3)</td>
<td>2.005(2)</td>
</tr>
<tr>
<td>Ta3-O12-Ta6</td>
<td>1.894(3)</td>
<td>2.030(2)</td>
</tr>
<tr>
<td>Ta6-O13-Ta4</td>
<td>1.963(2)</td>
<td>1.970(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Terminal Oxygen</th>
<th>Bond Length (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta1-O14</td>
<td>1.802(2)</td>
<td>1.420</td>
</tr>
<tr>
<td>Ta2-O15</td>
<td>1.805(2)</td>
<td>1.409</td>
</tr>
<tr>
<td>Ta3-O16</td>
<td>1.818(2)</td>
<td>1.360</td>
</tr>
<tr>
<td>Ta4-O17</td>
<td>1.799(2)</td>
<td>1.432</td>
</tr>
<tr>
<td>Ta5-O18</td>
<td>1.805(3)</td>
<td>1.409</td>
</tr>
<tr>
<td>Ta6-O19</td>
<td>1.801(3)</td>
<td>1.424</td>
</tr>
</tbody>
</table>
Table 3.3. Bond lengths and bond valence sum of oxygens in Nb6 structure. * indicates protonated oxygens.

<table>
<thead>
<tr>
<th>Bridging Oxygen</th>
<th>Bond Length (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb1-O2-Nb2</td>
<td>1.957(6)</td>
<td>1.79</td>
</tr>
<tr>
<td>Nb2-O3-Nb3</td>
<td>1.981(4)</td>
<td>1.717</td>
</tr>
<tr>
<td>Nb3-O4-Nb4</td>
<td>1.938(6)</td>
<td>1.79</td>
</tr>
<tr>
<td>Nb4-O5-Nb1</td>
<td>1.989(5)</td>
<td>1.679</td>
</tr>
<tr>
<td>Nb5-O6-Nb1</td>
<td>1.902(4)</td>
<td>1.932</td>
</tr>
<tr>
<td>Nb2-O7-Nb5</td>
<td>2.158(5)</td>
<td>1.088*</td>
</tr>
<tr>
<td>Nb3-O8-Nb5</td>
<td>2.146(5)</td>
<td>1.111*</td>
</tr>
<tr>
<td>Nb5-O9-Nb4</td>
<td>1.874(4)</td>
<td>1.849</td>
</tr>
<tr>
<td>Nb6-O10-Nb1</td>
<td>2.119(5)</td>
<td>1.19*</td>
</tr>
<tr>
<td>Nb2-O11-Nb6</td>
<td>1.923(4)</td>
<td>1.859</td>
</tr>
<tr>
<td>Nb3-O12-Nb6</td>
<td>1.941(4)</td>
<td>1.939</td>
</tr>
<tr>
<td>Nb6-O13-Nb4</td>
<td>1.949(5)</td>
<td>1.873</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Terminal Oxygen</th>
<th>Bond Length (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb1-O14</td>
<td>1.771(6)</td>
<td>1.513</td>
</tr>
<tr>
<td>Nb2-O15</td>
<td>1.771(6)</td>
<td>1.513</td>
</tr>
<tr>
<td>Nb3-O16</td>
<td>1.774(5)</td>
<td>1.501</td>
</tr>
<tr>
<td>Nb4-O17</td>
<td>1.771(6)</td>
<td>1.516</td>
</tr>
<tr>
<td>Nb5-O18</td>
<td>1.786(5)</td>
<td>1.456</td>
</tr>
<tr>
<td>Nb6-O19</td>
<td>1.772(5)</td>
<td>1.510</td>
</tr>
</tbody>
</table>

This simple difference of diprotonation leading to dimers of Ta6 versus triprotonation resulting in chains of Nb6 may in fact have a significant effect on the film growth from these aqueous precursor solutions. While both solutions yield crystals through slow evaporation, rapid evaporation yields different results. A rotary evaporator was used to simulate the rapid evaporation of the solution upon spin coating films. The Nb6 solution formed crystallites while Ta6 formed a sticky gel (Fig. 3.5). This visual observation can be extended to hypothesize that Ta6 forms a gelled network upon
film deposition, whereas Nb6 crystallizes. We do observe that films deposited from Ta6 retain a continuous appearance long after spin coating, while films deposited from Nb6 must be immediately placed on the hot plate to prevent a breakdown of film continuity (Fig. A8, Appendix A). We propose that the Nb6 films on standing readily reorganize into a crystalline state. We note that multiple syntheses of the clusters lead to this very reproducible result of triprotonation of the hexaniobate and diprotonation of the hexatantalate; likely driven by combined effects of lattice energy and basicity of the clusters.

Figure 3.5. Rotary evaporated solutions of Ta6 (left) and Nb6 (right).

The AFM and XRR results, however, are somewhat inconsistent with this explanation. With an immediate hot-plate treatment, the Nb6 films are found to be quite smooth at low temperatures. The greatest divergence in film roughness between Nb2O5 and Ta2O5 occurs at elevated annealing temperatures, where the original assembly of ions in the coating upon deposition should have lesser impact. At 800 °C, where Nb2O5 exhibits maximum roughness, the counterions have been completely eliminated, and the film has crystallized. At the same temperature, Ta2O5 films derived from Ta6 remain very smooth. Either grains of Nb2O5 grow with a lower
activation energy than those of Ta$_2$O$_5$, or H-bonding of Nb$_6$ into chains (Fig. 3.6) favors low-temperature nucleation, which translates to enhanced grain growth at higher temperatures. Additional studies are required to further evaluate the factors contributing to grain growth in these systems.

**Figure 3.6.** Representation of Nb$_6$ clusters linked by H-bonding, along with their TMA counterions.

Small and wide angle X-ray scattering (SWAXS) was used to investigate aqueous solutions of Nb$_6$ and Ta$_6$, and determine if the structural arrangements of ions observed in the solid-state (that may be influencing film morphology) is translated from solution behavior. The simulated data for a single Lindqvist ion produced a modeled fit with a radius of 3.27 Å. This is smaller than the expected radius of 4.2 Å based on the solid state structure. The size discrepancy is due to the apparent lack of contrast between the oxygens in the water (solvent is included in the simulation) and the oxygens on the outside of the cluster. However, in many other studies, the entire
cluster including external ligands actually is “observed”, and this could be due to a combination of effects, including the solvent/counterion molecules located in the first-coordination sphere of the cluster.\textsuperscript{34}

**Figure 3.7.** Scattering curves of Ta\textsubscript{6} (blue) and Nb\textsubscript{6} (black) in water. Pink box at low q indicates structure factor region.

Analysis of the scattering curves was performed through two modeling techniques which identify size distributions within a system: *Size Distribution* and *Modeling II*. The fit derived from *Modeling II* in Irena can also determine the extent of interactions between clusters. It was found that in water, Nb\textsubscript{6} has more extensive interaction between clusters in water than Ta\textsubscript{6} (Table 3.4). This is evident in the larger structure factor in the scattering curves for the niobium system (Fig. 3.7). The structure factor consists of a decrease in intensity at low q which gives rise to a coulombic peak around 0.1—0.2 Å\textsuperscript{−1}. Particle-particle interactions can lead to short range order where
there is an increased probability to find a neighboring particle at a specific distance.

For the niobium system in water we see consistently larger structure factors indicating that \( \text{Nb}_6 \) is more ordered in solution than \( \text{Ta}_6 \). The structure factor is modeled by two parameters, describing the distance between clusters (smaller distance means more interaction) and the number of nearest neighbor clusters in solution (more neighbors means more interaction). The radii of scatterers were determined from modeled fits (Table 3.4) which indicate that both clusters partially aggregate in water to form a second population of dimeric species, as we expect for protonated Lindqvist ions.

**Table 3.4.** Radii for simulated and experimental samples in water, along with interparticle interferences.

<table>
<thead>
<tr>
<th>Water</th>
<th>Pop. 1 Radius</th>
<th>Pop. 2 Radius</th>
<th>Distance to Nearest Neighbors (Å)*</th>
<th>Number of Nearest Neighbors*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulated Lindqvist</td>
<td>3.27</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>10mM ( \text{Nb}_6 )</td>
<td>3.37</td>
<td>7.66</td>
<td>31.8</td>
<td>2.2</td>
</tr>
<tr>
<td>10mM ( \text{Ta}_6 )</td>
<td>3.27</td>
<td>8.61</td>
<td>42.9</td>
<td>1.2</td>
</tr>
<tr>
<td>25mM ( \text{Nb}_6 )</td>
<td>3.38</td>
<td>7.30</td>
<td>26.0</td>
<td>4.5</td>
</tr>
<tr>
<td>25mM ( \text{Ta}_6 )</td>
<td>3.32</td>
<td>8.14</td>
<td>32.7</td>
<td>1.9</td>
</tr>
<tr>
<td>50mM ( \text{Nb}_6 )</td>
<td>3.41</td>
<td>7.37</td>
<td>30.0</td>
<td>4.1</td>
</tr>
<tr>
<td>50mM ( \text{Ta}_6 )</td>
<td>3.33</td>
<td>8.18</td>
<td>25.1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*these values were averaged for the two populations of scatterers. Values determined using Modeling II in Irena.*

These systems were also studied in dilute tetramethylammonium hydroxide (TMAOH) solutions. The cluster behavior is dependent on the solvent, as we see with a difference in scattering curves for solutions in water and solutions in TMAOH. Neat water provides an environment in which protonation of the clusters is predominant. TMAOH inhibits protonation as seen from the scattering curves (Fig. 3.8) and the resulting size distributions. At 10 and 25 mM both \( \text{Nb}_6 \) and \( \text{Ta}_6 \) exist as monomeric
species with radii ~3.5 Å. This is consistent with deprotonated monomeric clusters. At higher concentrations however there is evidence of dimerization. Another difference between these systems in water versus TMAOH is a smaller structure factor. In the 10-mM solutions, there is almost no evidence of interparticle interactions. When a structure factor emerges at higher concentrations, the degree of interaction is the same for both Ta₆ and Nb₆, as can be seen in Table 3.5.

![Figure 3.8](image.png)

**Figure 3.8.** Scattering curves of Ta₆ (blue) and Nb₆ (black) in 0.2-M TMAOH. Pink box indicates structure factor region.
**Table 3.5.** Radii and interparticle interactions of samples in 0.2-M TMAOH solutions.

<table>
<thead>
<tr>
<th>0.2M TMAOH</th>
<th>Pop. 1 Radius</th>
<th>Pop. 2 Radius</th>
<th>Distance to Nearest Neighbors (Å)</th>
<th>Number of Nearest Neighbors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulated Lindqvist</td>
<td>3.27</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>10mM Nb₆</td>
<td>3.67</td>
<td>--</td>
<td>22.2</td>
<td>0.4</td>
</tr>
<tr>
<td>10mM Ta₆</td>
<td>3.40</td>
<td>--</td>
<td>23.4</td>
<td>0.3</td>
</tr>
<tr>
<td>25mM Nb₆</td>
<td>3.63</td>
<td>--</td>
<td>21.3</td>
<td>0.7</td>
</tr>
<tr>
<td>25mM Ta₆</td>
<td>3.23</td>
<td>--</td>
<td>23.1</td>
<td>0.7</td>
</tr>
<tr>
<td>50mM Nb₆</td>
<td>3.43</td>
<td>6.61</td>
<td>20.4</td>
<td>1.4</td>
</tr>
<tr>
<td>50mM Ta₆</td>
<td>3.36</td>
<td>7.86</td>
<td>21.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*Values determined from Modeling II in Irena.*

Finally, scattering data were also collected for Nb₆ and Ta₆ in TMANO₃ solution, to provide an equivalent electrolyte as the TMAOH solution, but without inhibiting protonation. These data clearly show a structure factor in the Nb₆ solutions, and no structure factor in the Ta₆ solutions, with the exception of the highest concentration solution (Fig. 3.9).
Figure 3.9. Scattering curves of Ta<sub>6</sub> (blue) and Nb<sub>6</sub> (black) in 0.2-M TMANO<sub>3</sub>.

Pink box indicates structure factor region.

The difference in solution behavior between Ta<sub>6</sub> and Nb<sub>6</sub> could lead to the difference in film quality. As seen from rapid evaporation using the rotatory evaporator, Ta<sub>6</sub> gels while Nb<sub>6</sub> mostly crystallizes. This gel state is crucial to the formation of atomically smooth, high quality, dense films. The mechanism of forming the intermediate gel state is not yet known. The SWAXS results could lead to some insight on this matter. Clusters that aggregate into dimers without any further directional ordering could prevent crystallization, and instead the solution evaporates to give an amorphous gel containing cluster dimers, TMA, and water. The disordered aggregation exhibited in the Ta<sub>6</sub> solutions promotes formation of a gel while Nb<sub>6</sub> crystallizes because of the ordering, promoted by chain formation. Finally, these X-ray scattering studies with varying solution electrolyte confirm that cluster-cluster association is driven by H-bonding of protonated faces.
Conclusions

Given the periodic table position of Nb and Ta, next to Zr and Hf that are virtually identical in structure and behavior due to the lanthanide contraction, we expect Nb and Ta to likewise be very similar. Indeed, in solid-state structures, coordination geometries are nearly indistinguishable,\(^{30}\) but in solution important differences have been recognized in prior studies and have also emerged in the current study. Previous DFT calculations and oxygen isotope exchange rates have led to the findings that hexatantalate has a smaller affinity towards protonation than hexaniobate, the terminal \(\eta=O\) is more labile than the bridging \(\mu_2-O\), and less energy is required to move a proton from \(\mu_2-O\) to \(\eta=O\).\(^{13}\) These differences have merely been owed to the relativistic effect of the 4f electrons of Ta, without a thorough understanding. The enthalpy of formation for \(\text{Nb}_2\text{O}_5\) and \(\text{Ta}_2\text{O}_5\) are respectively -1899 and -2046 kJ/mol;\(^{35}\) perhaps reflecting the greater strength of a Ta-O bond, which may result in a weaker O-H bond, upon protonation. The pH-values for solutions of identical concentrations of \(\text{Nb}_6\) (10.36) and \(\text{Ta}_6\) (9.95) indicate that \(\text{Ta}_6\) is indeed less basic than its niobium analogue. Previous studies,\(^{13,34}\) have demonstrated that hexatantalate is also less stable in solution than hexaniobate. Upon decreasing the pH of a hexatantalate solution, the cluster will decompose to a hydrous tantalum oxide before it accommodates a third proton. This partial decomposition could also be a factor of gel formation: while disadvantageous for discrete cluster formation, it may be advantageous for formation of infinite solids of both powder and thin films. This study provides the first aqueous route to both \(\text{Nb}_2\text{O}_5\) and \(\text{Ta}_2\text{O}_5\) thin films. But also important, the fundamental science of this study illustrates 1) the organization of ions in water correlates to similar order in a solid-state lattice, 2) H-bonding between
metal-oxo clusters in water is very important in controlling precipitation behavior, and 3) acid-base behavior of metal-oxo species in water is very sensitive to the identity of the metal. While the latter point cannot always be neatly predicted by periodic trends of the transition metals, studies such as this can bring us closer to a more global understanding of relativistic and other effects on aqueous speciation of metal cations.

**Acknowledgments**

This material is based on work in the Center for Sustainable Materials Chemistry which is funded by the US National Science Foundation under grant CHE-1102637. We would like to thank Dr. Xiaobing Zuo (APS-ANL) for assistance with SWAXS measurements, and Teresa Sawyer and Dr. Peter Eschbach at the electron microscopy facility at OSU.
References


(14) Hou, Y.; Fast, D. B.; Ruther, R. E.; Amador, J. M.; Fullmer, L. B.; Decker, S.


(25) SHELXTL-6.10. *Program for Structure Solution, Refinement and Presentation*; Bruker AXS Inc: Madison, WI.


(35) www.materialsproject.org.
Chapter 4

REACTION PATHWAY: AQUEOUS HEXATANTALATE CLUSTERS TO HIGH-DENSITY TANTALUM OXIDE NANOFILMS

Ryan H. Mansergh, Lauren B. Fullmer, Deok-Hie Park, May Nyman, and Douglas A. Keszler

Published in *Chemistry of Materials* 2016, 28 (5), 1553–1558.
Abstract
The reaction path from aqueous oxohydroxometalate \([\text{[(CH}_3\text{)}_4\text{N}]_6[\text{H}_2\text{Ta}_6\text{O}_{19}]]\cdot x\text{H}_2\text{O}\) to \(\text{Ta}_2\text{O}_5\) thin film explains observed thin-film morphological characteristics – high density, uniform, pore free, and smooth. Film dehydration and tetramethylammonium thermal decomposition were observed via temperature programmed desorption. The morphological, structural, and optical properties of the films were examined by X-ray diffraction, X-ray reflectivity, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, and spectroscopic ellipsometry. Evolution of \((\text{CH}_3)_4\text{N}^+\) reaction products in concert with condensation of the polyoxometalate clusters and structural relaxation led to film densities as high as 95% of single crystal \(\beta\)-\(\text{Ta}_2\text{O}_5\). The process enabled film deposition with single-digit-nanometer thickness.
**Introduction**
We report the deposition of high-quality Ta$_2$O$_5$ thin films from an aqueous solution of the tetramethylammonium salt [(CH$_3$)$_4$N]$_6$[H$_2$Ta$_6$O$_{19}$]$_x$H$_2$O, herein denoted Ta$_6$. Ta$_6$ exhibits a polyoxohydroxotantalate cluster of the Lindqvist type (Fig. 4.1).

![Polyhedral representation of the Lindqvist anion [H$_2$Ta$_6$O$_{19}$]$^{6-}$ with [(CH$_3$)$_4$N]$^+$ counterions.](image)

**Figure 4.1.** Polyhedral representation of the Lindqvist anion [H$_2$Ta$_6$O$_{19}$]$^{6-}$ with [(CH$_3$)$_4$N]$^+$ counterions.

Polyoxohydroxo metal cluster solutions comprise a new precursor platform for the production of functional oxide films and high-resolution nanopatterns.$^{1-5}$ These cluster solutions contain partially condensed forerunners to solid oxides and lower counterion concentrations than corresponding monomeric salt solutions. Consequently, small volume changes occur on cluster conversion to extended solids, thereby producing high-density films with smooth surfaces. The high tetramethylammonium (TMA) content—70% of the cell volume of Ta$_6$—might negate the cluster advantages to film deposition. Surprisingly, the precursor Ta$_6$ produces highly uniform, smooth Ta$_2$O$_5$ thin films with densities near 95% of bulk values. We
explain this result by investigating the reaction process from Ta₆ precursor to dense thin film via several complementary analytical techniques.

Ta₂O₅ films have garnered technological interest as antireflection coatings, electrochromic materials, and corrosion and diffusion barriers. Dense, pore-free, and smooth films are required for these applications. While commercial deposition methods, such as chemical vapor deposition (CVD), sputtering, and atomic layer deposition (ALD) produce high-quality films, they suffer from high equipment costs, low materials use, high operational costs, or scaling difficulties. Solution deposition provides a cost-effective, facile route to large-area deposition. Solution deposition of Ta₂O₅ films, however, has been described in only a few studies, all focused on pyrolysis of Ta-organic systems. Reported films are porous, proving problematic for corrosion protection; the associated surface roughness also compromises deposition of ultra-thin Ta₂O₅ films and production of high-performance multilayer structures. The films described herein address these performance gaps.

**Experimental Methods**

**Materials.** TaCl₅ (Puratronic, 99.99%) and (CH₃)₄NOH (25% w/w aq. solution, Electronic Grade, 99.9999%) were obtained from Alfa Aesar. H₂O₂(aq) (30%) and NH₄OH (aq) (28.0-30.0% as NH₃, ACS Grade) were purchased from Macron Fine Chemicals. Isopropanol (ACS Grade) was purchased from EMD Millipore Corporation, and ethanol (HPLC-UV Reagent Grade ACS) was purchased from Pharmco-AAPER. The n-type Si (100) wafers were sourced from Sumco Oregon
Corporation; SiO$_2$/Si substrates with 100 nm of thermally grown SiO$_2$ on silicon (100) were obtained from Silicon Valley Microelectronics, Inc.

**Synthesis of TMA Hexatantalate Precursor.** A powder of [(CH$_3$)$_4$N]$_6$[H$_2$Ta$_6$O$_{19}$]$\cdot$xH$_2$O was prepared as previously reported.$^{22}$ Ammonium peroxotantalate, (NH$_4$)$_3$Ta(O$_2$)$_4$, was first synthesized by adapting the methods of Selezneva and Nisel’son.$^{23}$ Briefly, 40 mL of 30% H$_2$O$_2$ was cooled in an iced water bath, and 2.4 g of TaCl$_5$ was added with moderate stirring, while keeping the solution temperature between 5 and 15 °C. 12 mL of 14.5-M NH$_3$ (aq) was then added in 1-mL aliquots, converting the cloudy mixture to a clear solution. Approximately 150 mL of ethanol was added, yielding a white precipitate. This precipitate was vacuum-filtered and washed with ethanol. 1.32 g of the resulting (NH$_4$)$_3$Ta(O$_2$)$_4$ product was added to 8.25 mL of 1.4-M (CH$_3$)$_4$NOH (aq). The solution was then refluxed for 5 h with the condensing column chilled to approximately 5 °C. After cooling, the solution was passed through a 0.45-μm nylon syringe filter. The filtrate was shaken vigorously with 40 mL of isopropanol in a centrifuge tube. After centrifugation, a dense bottom layer became apparent in the centrifuge tube. The supernatant was decanted, and ~30 mL of isopropanol was added to the remaining bottom layer with further agitation to produce a white precipitate. After further washing with isopropanol, the precipitate was dried in a vacuum oven at ~60 °C to yield the final precursor, [(CH$_3$)$_4$N]$_6$[H$_2$Ta$_6$O$_{19}$]$\cdot$xH$_2$O. A 0.22-M stock solution with respect to the cluster was prepared by dissolving the powder product in 18.2-MΩ deionized water. This stock solution was diluted with water to study the effects of solution concentration on film deposition.
**Thin-Film Deposition.** Substrates were cleaved into approximately 2.5 × 2.5 cm² squares, rinsed in 18.2-MΩ deionized water, dried in Ar, then ashed in an O₂ plasma (~175-mTorr O₂) for 10 min at 200 W. Films were deposited onto the prepared substrates by using a CEE Model-100 spin coater at a spin rate of 3000 rpm for 30 s. Coated substrates were cured on a hot plate at 200 °C for 1 min, then cooled on an aluminum block for approximately 1 min. The samples were placed in a Neytech Qex furnace, ramped to selected temperatures at 20 °C·min⁻¹, then annealed for 10 min.

**Thin-Film Characterization.** To identify gases evolved from heated thin films, a temperature programmed desorption (TPD) study was performed under ultra-high vacuum by using a Hiden Analytical TPD Workstation equipped with a quadrupole mass analyzer (3F PIC). The base pressure of the system was approximately 10⁻⁹ Torr. The samples (1 × 1 cm²) were heated from room temperature to 1000 °C at a ramp rate of 30 °C·min⁻¹. Mass spectra were collected by using electron impact ionization with 70-eV ionization potential and 20-μA emission current.

Grazing incidence X-ray diffraction (GIXRD) and X-ray reflectivity (XRR) data were obtained on a Rigaku Ultima-IV diffractometer with Cu Kα radiation (λ = 1.5409 Å). For GIXRD scans, the instrument was configured with a 5.0° incident Soller slit, a 10-mm divergent height limiting (DHL) slit, and a 0.5° parallel beam slit; the divergent slit (DS) was set to 0.2 mm and the scattering slit (SS) and receiving slit (RS) were left open. For XRR data collection, the instrument was configured with a 5.0° incident Soller slit, a 10-mm DHL slit, and a 5.0° receiving Soller slit; the DS, SS, and RS were set to 0.2, 0.5, and 0.2 mm, respectively. GIXRD
and XRR data were analyzed with the Rigaku software packages PDXL\textsuperscript{24} and GlobalFit,\textsuperscript{25} respectively.

Atomic force microscopy (AFM) measurements were performed on a Veeco Innova SPM in tapping mode with Si probes (300 kHz, 40 N·m\textsuperscript{-1}). Scans were performed on 10 × 10 µm\textsuperscript{2} areas. Root-mean-square (RMS) surface roughness was determined by analyzing an ordered grid of multiple 1 × 1 µm\textsuperscript{2} sections within the initial 10 × 10 µm\textsuperscript{2} scan areas with the Bruker NanoScope Analysis software package.\textsuperscript{26}

Spectroscopic ellipsometry (SE) data were collected on a J.A. Woollam, Inc. M-2000 instrument. Measurements were taken in an ordered 9-point grid, covering ~90% of the area of each sample and modeled with the CompleteEASE software package.\textsuperscript{27} The index of refraction (λ = 550 nm), film thickness, and SiO\textsubscript{2} interfacial layer thickness layer were extracted by using a Cauchy model.

Scanning electron microscope (SEM) images were obtained on an FEI Nova NanoSEM 230 SEM. Transmission electron microscope (TEM) imaging was performed on an FEI Titan 80-200 TEM operating at 200 kV. The TEM sample was prepared by depositing a bilayer of C and Cr on the film. After depositing a protective Pt pad, a focused ion beam was used to extract a sample lamella for analysis; this procedure was performed with an FEI Quanta 3D dual beam SEM/FIB.

**Results and Discussion**

To examine the cluster-to-film transformation, we first followed the thermal decomposition processes via TPD. With this technique, species evolving from the heated film are monitored with a mass spectrometer. The precursor film is strongly
hydrated–[(CH$_3$)$_4$N]$_6$[H$_2$Ta$_6$O$_{19}$]•xH$_2$O – so constitutional water evolves on heating. As shown in Figure 4.2a, signal I (m/z = 18) indicates substantial water loss at temperatures below 200 °C. Signals II and III at higher temperatures likely derive from protonated states of the cluster and associated dehydroxylation and dehydration.

Eq 4.1 describes a thermal process for transformation of Ta$_6$ to Ta$_2$O$_5$:

\[
[(CH$_3$)$_4$N]_6[H_2Ta_6O_{19}] \xrightarrow{\Delta} 3Ta_2O_5 + 6(CH_3)_3N + 3CH_3OCH_3 + H_2O \quad (4.1)
\]

As shown in Figure 4.2b, desorption signals at m/z = 58 and 45 correspond to evolution of trimethylamine and dimethyl ether, respectively, i.e., two reaction products in eq. 4.1. Together, these molecules evolve over the rather broad temperature range 100 to 400 °C. The trimethylamine signal above 150 °C indicates the presence of tetramethylammonium carbonate (TMAC) in the film. Likewise, coincident CO$_2$ and CO signals are associated with corresponding carbonate decomposition (Figures 4.2b & 4.2c). Alternatively, the m/z = 28 signal could be associated with C$_2$H$_4$. TMAC has been reported previously to decompose at temperatures as low as 180 °C.$^{28}$ Tetramethylammonium hydroxide solutions readily absorb atmospheric CO$_2$, so carbonate in the films is expected. Because the polyoxotantalate cluster is protonated, an additional decomposition pathway is represented by eq. 4.2:

\[
[(CH$_3$)$_4$N]_6[H_2Ta_6O_{19}] \xrightarrow{\Delta} 2(CH_3)_3N + 2CH_3OH + [(CH$_3$)$_4$N]_4[Ta$_6$O$_{17}$] \quad (4.2)
\]

As shown in Figure 4.2b, the methanol signal corresponding to this reaction occurs near 170 °C. While TMA is mostly burned out at temperatures below 400 °C, higher-temperature CH$_4$, H$_2$O, and CO (C$_2$H$_4$) signals (Figures 4.2a & 4.2c) indicate additional TMA cracking and reactions. We note that bulk samples of the precursor
heated under inert atmosphere, corresponding to the vacuum environment of the TPD, are recovered as black powders. In addition to the processes already described, some carbon byproducts likely extract oxygen from the matrix, resulting in reduced Ta oxidation states. Reduced tantalum oxide powders are known to be black or bluish-black in appearance.\textsuperscript{29}
Figure 4.2. (a) Temperature programmed desorption results depicting the dehydration behavior of a Ta$_6$-derived thin film deposited on silicon (100). (b) TPD results showing major TMA degradation products in the same film. (c) TPD results showing species lost using the same precursor deposited on 100-nm thermally grown SiO$_2$. 
Visually uniform, continuous thin films are readily deposited onto Si substrates from 0.22-M $\text{Ta}_6$ solutions. GIXRD patterns of an as-deposited film (Fig. B1, Appendix B) and films annealed at 400 and 600 °C (Figure 4.3a) reveal only broad features indicative of amorphous materials. The film is clearly crystalline after annealing at 800 °C. Additional annealing temperatures were examined to better define the crystallization temperature. As shown in Figure 4.3b, crystalline grains of sufficient size to be readily detected with XRD begin to appear near 705 °C. Comparable crystallization temperatures have been reported for other $\text{Ta}_2\text{O}_5$ deposition methods.$^{30,31}$ A sample annealed at 900 °C for 10 min yields cell parameters, $a = 6.1642(7)$, $b = 39.746(4)$ and, $c = 3.8252(4)$ Å (Fig. B2, Appendix B), which are slightly shorter than those, $a = 6.198$, $b = 40.29$, and $c = 3.888$ Å, reported by Roth and co-workers.$^{32}$
Figure 4.3. (a) X-ray diffraction patterns for films deposited from aqueous 0.22-M Ta$_6$. Film thicknesses range from 52 to 60 nm. Samples were annealed at the indicated temperatures for 10 min. (b) X-ray diffraction patterns in temperature range 700 – 725 °C. Substrate peaks are indicated with a star (★).

As shown by representative SEM images (Figure 4.4a), the films are continuous and free of major defects, such as voids and cracks. A grain structure is readily apparent in the image of the film annealed at 800 °C, which is consistent with the onset of grain growth above 700 °C. Featureless plan-view SEM images (Fig. B3a-c, Appendix B) are consistent with the cross-sectional images, highlighting the continuous and uniform nature of the coatings. The cross-sectional TEM image (Figure 4.4b) also reveals a dense, continuous film, free of pores and voids. These
images emphasize a significant difference between cluster and conventional sol-gel routes for oxide film deposition, as conventional sol-gel methods for \( \text{Ta}_2\text{O}_5 \) deposition have produced films with rough surfaces and considerable porosity.\(^{21}\)

**Figure 4.4.** (a) Cross-sectional SEM images of films deposited with 0.22-M \( \text{Ta}_6 \) solutions. Films were annealed at 400, 600, and 800 °C for 10 min, producing thicknesses of 58, 53, and 54 nm, respectively. Scale bars represent 500 nm. (b) Cross-sectional TEM image of a 60-nm \( \text{Ta}_6 \)-derived thin film annealed at 400 °C. Coats of amorphous carbon and chromium were deposited prior to focused ion beam sample preparation.

Strong Kiessig fringes (Figure 4.5a) are observed to approximately 8° 2\( \theta \) in the XRR data for all samples—an extraordinary result that highlights the extreme surface smoothness of the films. Even the crystalline film annealed at 800 °C retains this quality.

Film thickness (Figure 4.5b), determined by XRR and SE, varies between approximately 60 and 52 nm over the temperature range 400 – 800 °C. The thickness reaches a minimum near 500 °C, then remains constant to approximately 700 °C. The
modest increase above 700 °C is associated with grain growth and film coarsening. The refractive index (λ = 550 nm) behaves in a similar manner, achieving a maximum value, 2.10, near 600 °C, then dropping at higher temperatures as the film crystallizes and grains grow.

As shown in Figure 4.5c, the maximum XRR-derived density, 8.18 g cm⁻³, occurs near 600 °C. This value is approximately 95% of single-crystal β-Ta₂O₅ density. The maximum refractive index, 2.10, is also observed near 600 °C (Figure 4.5b). The decrease in density from 700 to 800 °C is again associated with grain growth and film coarsening, i.e., void formation at grain boundaries. By 800 °C, the surface roughness has approximately doubled, but with a 0.4-nm surface roughness, the film is still extremely smooth. The trend in roughness (Figure 4.5c) derived from AFM data (Fig. B5a-c, Appendix B) is consistent with the XRR measurements.

Table 4.1 compares results for the Ta₆-derived Ta₂O₅ film and those of Ta₂O₅ films prepared by other methods. Densities for the Ta₆ approach, and in some cases exceed, the densities currently accessible by vacuum-based deposition methods such as ALD. Additionally, RMS roughness values are comparable to those produced via ALD, CVD, and sputtering. The refractive indexes of the Ta₆-derived films are comparable to films produced by CVD.

To correlate film densification to dehydration and thermal desorption of TMA decomposition products, XRR data were collected for samples annealed for 10 min at 100, 200, and 300 °C (Fig. B6, Appendix B). Again, referring to Figure 4.5c, starting from 100 °C, a dramatic densification occurs concomitantly with the loss of constitutional water and TMA decomposition products. Notably, TMA evolution
ceases near 400 °C, i.e., where the density of the film is near its upper limit; compare Fig. 4.2.

**Figure 4.5.** (a) XRR data for films annealed at 400, 600, and 800 °C. (b) SE-derived refractive indices (λ = 550 nm) and film thicknesses. The film thicknesses derived via XRR modeling are included for comparison. (c) Results of XRR-derived densities
and surface roughness values. The XRR-derived surface roughness values are compared to AFM measurements.

Why does the TMA tantalate precursor produce such high-quality, dense films relative to other solution-deposition methods? The TMA cations occupy approximately 70% of the dehydrated crystal volume, a large fraction. From the TPD results, we find that TMA evolves over a wide temperature range from 100 to 400 °C. From XRR and SE measurements, film thickness decreases continuously and density increases smoothly as the small molecules associated with TMA thermal decomposition evolve from the film. Abrupt gas evolution is not observed during the heating process. Under these conditions, product gases diffuse and escape from an initially porous film. As the temperature increases, viscous flow in the amorphous film promotes structural relaxation and densification. Hence, thermally driven gas evolution and viscous flow function in a complementary manner to produce and preserve exceptional film qualities.
Table 4.1. Tantalum Pentoxide Film Comparison*  

<table>
<thead>
<tr>
<th>Reference material</th>
<th>Density (g·cm⁻³)</th>
<th>Refractive index, n</th>
<th>RMS roughness (nm)</th>
<th>Deposition/annealing temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Ta₆</td>
<td>7.81</td>
<td>2.1⁰</td>
<td>0.16</td>
<td>25/600</td>
</tr>
<tr>
<td>ALD (ozone, O₃-ALD)</td>
<td>7.85</td>
<td>—</td>
<td>1.30</td>
<td>300⁴</td>
</tr>
<tr>
<td>ALD (ozone, O₃-ALD)</td>
<td>7.90</td>
<td>—</td>
<td>0.14</td>
<td>300⁴</td>
</tr>
<tr>
<td>ALD (thermal, Th-ALD)</td>
<td>7.30</td>
<td>—</td>
<td>1.30</td>
<td>300⁴</td>
</tr>
<tr>
<td>CVD</td>
<td>—</td>
<td>2.1³</td>
<td>0.17</td>
<td>445/800</td>
</tr>
<tr>
<td>RF magnetron sputtering</td>
<td>—</td>
<td>—</td>
<td>0.41</td>
<td>30⁴</td>
</tr>
</tbody>
</table>

*The reported values represent the highest densities and refractive indices and the lowest RMS roughness values from the given references. Values that were not reported in the cited references are indicated with a dash (—). ⁰λ = 550 nm. ³Wavelength not reported. ⁴Reported values for as-deposited films.
The high density and near-atomic smoothness of the films provide an opportunity to explore deposition of ultra-thin films. To this end, the stock solution was diluted to selected concentrations, then cast on substrates to evaluate film thickness via SE and XRR. Each sample was annealed at 400 °C for 10 min. As shown in Figure 4.6a, Kiessig fringes for films derived from dilute solutions extend beyond $8^\circ 2\theta$, again representing the extreme surface smoothness. From XRR modeling, RMS surface roughness does not exceed 0.4 nm (Figure 4.6b). Fringe spacing scales directly with concentration, qualitatively suggesting a near-linear decrease in film thickness with decreasing $\text{Ta}_6$ concentration. A linear fit of the XRR data (Figure 4.6b) yields the relationship (eq 4.3) between film thickness, $t$, and $\text{Ta}_6$ molarity, $c$:

$$t = [211.3c \text{ M}^{-1}] \text{ nm} \quad (4.3).$$

Across the studied concentration range, thickness is readily adjusted from 1.8 to 42 nm by setting the $\text{Ta}_6$ concentration between 0.01 and 0.20 M.
Conclusions
We have discovered a new aqueous precursor for deposition of high-quality Ta$_2$O$_5$ films on the basis of the water solubility of the polyoxohydroxometalate $[(\text{CH}_3)_4\text{N}]_6\text{H}_2\text{Ta}_6\text{O}_{19}$. Volume changes associated with evolution of TMA decomposition products do not hinder densification of the films. Indeed, smooth decomposition between 100 and 400 °C precludes abrupt nanoparticle formation, which would limit uniformity and hinder densification. Accordingly, the reaction path affords continuous Ta$_2$O$_5$ films with densities near 95% of single-crystal values.
The precursor should enable Ta$_2$O$_5$ film deposition via many common liquid and aerosol techniques, applied to substrates ranging in size from standard semiconductor wafers to large glass sheets. Hence, cluster-processed Ta$_2$O$_5$ delivers vapor-deposition performance in a scalable framework. Simultaneously, this performance can be delivered in ultra-thin films. Considering the derived results and unique chemical aspects of the Ta$_6$ precursor, we continue to examine process variables to affect the Ta$_2$O$_5$ amorphous structure, reduce process temperatures, and enhance film properties.

**Acknowledgments**

This material is based on work in the Center for Sustainable Materials Chemistry supported by the U.S. National Science Foundation under Grant CHE-1102637. The authors thank P. Eschbach and T. Sawyer for assistance with SEM and TEM imaging in the OSU Electron Microscope Facility. The TEM was acquired with funds from the M.J. Murdock Charitable Trust, the Oregon Nanoscience and Microtechnologies Institute, and the U.S. National Science Foundation (Grant No. 1040588).
References


(15) Jagadeesh Chandra, S. V.; Choi, C.-J.; Uthanna, S.; Mohan Rao, G. Structural and Electrical Properties of Radio Frequency Magnetron Sputtered Tantalum


Chapter 5

ION EXCHANGE FOR LOW-TEMPERATURE PROCESSING AND ENHANCED FUNCTIONALITY OF SOLUTION-PROCESSED TANTALUM OXIDE THIN FILMS

Ryan H. Mansergh, Deok-Hie Park, Jenn M. Amador, Cory K. Perkins, Eaton C. Fong, Lauren B. Fullmer, May Nyman, and Douglas A. Keszler
Introduction
A requisite to ultimately lower the cost of thin-film transistors\textsuperscript{1,2} is to open up new scalable and energy-efficient routes to their fabrication; a key impediment in this regard is the high processing temperatures needed for metal oxide processing,\textsuperscript{3,4} which gates scalable film deposition methods, such as roll-to-roll processing. To lower processing temperatures—and to enable the deposition of materials on low-melting-point, flexible substrates—we have developed a method to chemically assist the transformation from thin-film precursor to condensed film. The conversion of the $\text{[(CH}_3\text{)₄N]}₆\text{[H}_2\text{Ta}_6\text{O}_{19}]$ cluster to tantalum oxide has been previously shown to require temperatures in excess of 400 °C to transform the precursor to $\text{Ta}_2\text{O}_5$.\textsuperscript{5} Even with the substantial volume change associated with the burnout of TMA, it was found that the resultant films were pore free, continuous, and dense—suitable for macroelectronics and other applications requiring large-area deposition, such as antireflective coatings\textsuperscript{6} and corrosion barriers.\textsuperscript{7} Further, this aqueous precursor may enable spray coating such as aerosol deposition, allowing for non-line-of-sight conformal coatings of 3-dimensional structures—useful for applications such as chemically inert coatings for biomedical implants.\textsuperscript{8} In this work, we advance an “ion-exchange” process which facilitates the removal of the TMA counterion by chemical means, rather than baking. One of the advantages of cluster-based solution processing of thin films over conventional vacuum-based deposition methods is the ability to further exploit the film chemistry after deposition. In the present work, the “living films” aspect of solution-processed thin films are exploited to remove the TMA counterions at temperatures near 200 °C, by treating films in dilute nitric acid after deposition. The efficacy of TMA removal as a function of film thickness is explored, and the effect of
temperature on film solubility is assessed. We also revisit our prior hypotheses concerning the role of TMA decomposition in resulting film morphologies, and whether the absence of TMA during thermal annealing is detrimental. Lastly, we demonstrate a novel method of LiTaO$_3$ formation via exchange of TMA for Li$^+$. These results combine the materials efficient approach of cluster-based thin-film deposition with improved energy efficiency, while providing opportunities to enhance film function through this ion-exchange process.

**Experimental Methods**

**Materials**

TaCl$_5$ (Puratronic, 99.99%), (CH$_3$)$_4$NOH (25% w/w aq. solution, Electronic Grade, 99.9999%), and LiNO$_3$ (anhydrous, 99.999% metals basis) were obtained from Alfa Aesar. H$_2$O$_2$ (30%), NH$_4$OH (aq) (28.0-30.0% as NH$_3$, ACS Grade), and HNO$_3$ (aq) (68.0-70%, ACS Grade) were purchased from Macron Fine Chemicals. Isopropanol (ACS Grade) was purchased from BDH VWR Analytical. Ethanol (HPLC-UV Reagent Grade ACS) was purchased from Pharmco-AAPER. The $p$-type silicon (100) wafers with 1000 Å of thermally grown SiO$_2$ were purchased from Silicon Valley Microelectronics, Inc.

**Synthesis of TMA Hexatantalate Precursor**

The [((CH$_3$)$_4$N)$_6$[H$_2$Ta$_6$O$_{19}$]$\cdot$$x$H$_2$O precursor was prepared as previously reported.$^5$ Stock solutions of the precursor were prepared at the concentrations of 0.22-M and
50-mM (with respect to the cluster) by dissolving the powder product in 18.2-MΩ deionized water.

**Thin-Film Deposition**

Samples were prepared using 2.5 × 2.5 cm² square substrates, that were rinsed in 18.2-MΩ deionized water, dried in Ar, then ashed in an O₂ plasma for 5 min at 50 W. SiO₂/Si substrates used for Raman and FTIR studies were coated with Al by thermal evaporation using a Veeco thermal evaporator. The Al-coated substrates were treated using a Novascan ultraviolet ozone system for 5 min prior to film deposition. Films were deposited using a Laurell Technologies spin coater at a spin rate of 3000 rpm for 30 s. Freshly deposited films were cured on a high-precision Wenesco hot plate at the required curing temperature for 4 min, then cooled on an aluminum block for approximately 1 min. Sample annealing was conducted in a Neytech Qex furnace, typically at ramp rates of 20 °C·min⁻¹ or lower.

**Ion-Exchange Process**

Films were soaked in 10-mM HNO₃ for 30 s right after the 1-min post cure cooldown period. Different HNO₃ concentrations and soak times were tested, but the above treatment conditions were used throughout the course of the study. During the lithiation study, aqueous ~0.1-M LiNO₃ solutions were used, and the soak time was 1 min. All ion-exchanged samples were rinsed in 18.2-MΩ deionized water after treatment, and then thoroughly dried in Ar.
Thin-Film Characterization

Temperature programmed desorption (TPD) experiments were performed using a Hiden Analytical TPD Workstation at a base system pressure approximately $10^{-9}$ Torr. Samples were cleaved to $\sim 1 \times 1 \text{ cm}^2$ dimensions and were heated from room temperature to 900 °C at a ramp rate of 30 °C-min$^{-1}$. An electron impact ionization with a 70-eV ionization potential and 20-µA emission current was used to collect mass spectra.

Thin film Raman spectra were collected using a Horiba LabRAM HR equipped with a 100x objective and 532-nm laser. Fourier transform infrared spectroscopy data were collected on a Thermo Scientific Nicolet 6700 FTIR spectrophotometer.

X-ray reflectivity (XRR) and grazing X-ray diffraction (GIXRD) data and were obtained on a Rigaku Ultima-IV diffractometer with Cu Kα radiation ($\lambda = 1.5409 \text{ Å}$). The Rigaku software packages GlobalFit$^9$ and PDXL$^{10}$ were used for the analysis of XRR and GIXRD data, respectively.

A J.A. Woollam, Inc. M-2000 was used for spectroscopic ellipsometry (SE) measurements. Data were collected from an ordered 9-point grid, which covered ~90% of each 2.5 × 2.5 cm$^2$ sample. The CompleteEASE software package$^{11}$ was used for modeling, and a Cauchy model was used to extract the index of refraction ($\lambda = 550 \text{ nm}$) and film thicknesses.

Scanning electron microscopy (SEM) images were obtained on an FEI Helios NanoLab 650 SEM.
Results and Discussion
From our prior studies,\textsuperscript{5} we determined that during film formation, annealing temperatures in excess of 400 °C are required to burn out the TMA counterions associated with the aqueous $[\text{H}_2\text{Ta}_6\text{O}_{19}]^{6-}$ precursor. We slowly heated (3 °C·min\textsuperscript{-1}) a film up to 400 °C and maintained this temperature for 10 min; we then tracked evolved species from this film during thermal ramp up in a TPD to confirm the complete removal of TMA-related residue. From the TPD results (Fig. 5.1), it is clear that signals related to products of the thermal decomposition of TMA, such as trimethylamine ($m/z = 58$), dimethyl ether ($m/z = 45$), carbon dioxide ($m/z = 44$), and methanol ($m/z = 32$) are at the instrumental baseline. We observe an elevated water signal from film rehydration (Fig. 5.1). Film rehydration continues to be a challenge in aqueous solution-processed thin films, and we have developed strategies to mitigate this phenomenon.\textsuperscript{12,13} The primary focus of this present work will be on the facile removal of TMA at temperatures below 400 °C with the tacit understanding that film dehydration must be addressed as well.
The strategy employed to remove the residual TMA makes use of the basic character (pH ≈ 10) of the Ta₆ precursor (Ta₆ = [H₂Ta₆O₁₉]) to drive the removal of TMA via an acid-base reaction with nitric acid (eq 5.1)

\[
[(\text{CH}_3)_4\text{N}]_6[\text{H}_2\text{Ta}_6\text{O}_{19}] + 6\text{HNO}_3 \rightarrow [\text{H}]_6[\text{H}_2\text{Ta}_6\text{O}_{19}] + 6(\text{CH}_3)_4\text{N}\text{NO}_3 \quad (5.1).
\]

Through this reaction, the intent is to effect a neutralization, or “ion exchange,” of the nascent film—consisting of partially crosslinked metal oxo hydroxo clusters—and to chemically drive additional cluster condensation.

In an effort to establish a reference baseline, we prepared a control film with a 0.22-M Ta₆ precursor and subjected it to thermal treatment only (annealed 400 °C for 10 min). An electron micrograph of the control film is shown in Fig. 5.2; as apparent in the micrograph, the film has a smooth surface and demonstrates good film continuity.
Figure 5.2. Scanning electron micrograph of a film prepared with a 0.22-M Ta₆ solution and annealed for 10 min at 400 °C.

We conducted an initial series of experiments to determine the optimal acid concentration and film curing temperature, and found an acid concentration of no more than 10-mM HNO₃ and a film curing temperature of at least 175 °C (for 4 min) yielded a relatively insoluble film. Films cured at 150 °C remained soluble and were washed away after the acid soak, and films dissolved in acid concentrations much above 10-mM HNO₃. The effect of exposure time was studied as well, but not explored extensively. Initial results suggested a 30-s soak was sufficient to engender cluster crosslinking, so this time was used throughout the remainder of the study. In addition to the untreated control film, films were soaked in deionized water for 30 s to assess the effect of the nitrate anion. XRR data (Fig. 5.3) were collected for a control film and films soaked in deionized water and 10-mM HNO₃. All films were cured for 4 min at 200 °C. Qualitatively, the XRR data suggest that the HNO₃ treatment may have had a densifying effect, owing to the shift of the critical angle to higher values of 2θ and the enhancement of the Kiessig fringes relative to that of the control. The
H₂O treatment appeared to be detrimental rather than beneficial. Ellipsometry data were also collected, and the HNO₃-treated film demonstrated the highest refractive index and the H₂O-treated film the lowest; however, the high water content still present in the films introduced significant error in these measurements. The substantial water content also introduced challenges with respect to XRR modeling, but the qualitative trends observed via XRR, coupled with ellipsometry measurements hinted at the efficacy of the acid treatment.

**Figure 5.3.** XRR data for the 0.22-M Ta₆ control film (baked only) and films soaked in water and 10-mM HNO₃.

We conducted TPD experiments to track TMA removal in the treated film compared to the control and H₂O-treated films. As shown in the TPD signal (Fig. 5.4, top) associated with the TMA decomposition product, trimethylamine (m/z = 58), we see that both the control and H₂O-treated samples display decomposition onset temperatures at ~130 °C; the H₂O treatment appears to remove some of the loosely bound C₃H₈N⁺, as there is a desorption offset between the control and H₂O-treated samples. The treated sample shows little signal intensity related to C₃H₈N⁺ until
~250 °C. The signal for \( \text{C}_3\text{H}_8\text{N}^+ \) reaches a maximum intensity at ~350 °C, but this intensity is about an order of magnitude less than what is observed for the other two samples. The signal for the mass-to-charge ratio associated with dimethyl ether \( (m/z = 45) \) (Fig. 5.4, bottom) is nearly at the instrumental baseline for the HNO\(_3\)-treated sample. The signals for the control and H\(_2\)O-treated films show substantial residual dimethyl ether content, and reach maximum intensity ~350 °C.

**Figure 5.4.** TPD results for the 0.22-M Ta\(_6\) control film and samples treated in DI water or 10-mM HNO\(_3\) showing mass fragments related to trimethylamine \( (m/z = 58, \text{top}) \) and dimethyl ether \( (m/z = 45, \text{bottom}) \).

In our prior studies,\(^5\) we learned that the gradual thermal decomposition of TMA actually led to dense films, rather than porous films as we first hypothesized. We also have observed that the structurally analogous \([\text{H}_3\text{Nb}_6\text{O}_{19}]^5\) often leads to substantially
rougher films than the \([\text{H}_2\text{Ta}_6\text{O}_{19}]^6^-\) precursor, owing to difference of one proton.\(^{15}\)

Would the ion exchange of TMA\(^+\) for H\(^+\) be detrimental? Indeed, there does appear to be a tradeoff, as the surface of the HNO\(_3\)-treated film annealed at 400 °C for 10 min (Fig. 5.5, left) appears to be porous. Furthermore, by cross-sectional SEM (Fig. 5.5, right) we no longer observe a film surface as smooth as we saw in Fig. 5.2 for the control film. The \(~90\) nm film appears continuous, but appears more porous in cross-section than the control.

![Figure 5.5. Plan view (left) and cross-sectional (right) scanning electron microscopy images of a 0.22-M Ta\(_6\) film treated in 10-mM HNO\(_3\) and annealed at 400 °C for 10 min.](image)

Clearly, the treatment is effective at removing the majority of the TMA content; however, as apparent in the C\(_3\)H\(_8\)N\(^+\) signal (Fig. 5.4, top), it is not 100% effective. To that end, and taking into account the possibility of the \(~90\) nm-thick films posing challenges with respect to diffusion lengths—which become increasingly circuitous near the film surface as cluster crosslinking commences—a series of experiments were conducted with films prepared using 50-mM Ta\(_6\) solutions. We initially sought to examine if thinner films would enable the complete removal of TMA, so we ran
TPD experiments on control films and films treated in HNO₃. A film of each type was cured at 175 and 200 °C. The signals for trimethylamine for the treated films—Fig. 5.6, top and Fig. 5.7, top for the 175 and 200 °C samples, respectively—both demonstrate signals for C₃H₈N⁺ just above baseline. Similarly, for dimethyl ether content, the TPD results for the 175 °C sample (Fig. 5.6, bottom) and the 200 °C sample (Fig. 5.7, bottom), both indicate that the HNO₃ treatment is quite effective at removing TMA. From a magnified view of the C₃H₈N⁺ signal (Fig. 5.8), it appears that the films soft baked at 200 °C and treated in HNO₃ have comparable C₃H₈N⁺ residue.
Figure 5.6. TPD results for a film prepared using 50-mM Ta₆ and soft baked at 175 °C for 4 min. The results track the signal for trimethylamine (m/z = 58, top) and dimethyl ether (m/z = 45, bottom) for the control film and HNO₃-treated sample.

Figure 5.7. TPD signals for trimethylamine (m/z = 58, top) and dimethyl ether (m/z = 45, bottom) for the control film and HNO₃-treated sample, both cured at 200 °C for 4 min.
Figure 5.8. Magnified TPD signals for trimethylamine ($m/z = 58$) for HNO$_3$ films cured at 175 and 200 °C.

We further explored the amount of TMA left in the films after treatment and examined the film structure via Raman spectroscopy. Raman spectra for a control sample and a film treated in HNO$_3$ (both cured at 175 °C) are shown in Fig. 5.9. We observe a number of features in the Raman spectra of the control that are associated with TMA (Fig. 5.9, top). The peak A at ~955 cm$^{-1}$ and C at ~760 cm$^{-1}$ are associated with a CN stretch and CN symmetric stretch, respectively. The peaks labeled F and G are assigned to CN and C$_4$N bending deformations, respectively. Peaks at similar wavenumbers are not observed in the treated sample (Fig. 5.9, bottom), providing additional evidence of the efficacy of removing TMA via the ion exchange process. The peak labeled D in the treated sample could be related to TMA residue, but no comparable reference peaks could be found. Peak D in the control and B in the treated samples are assigned to Ta-O stretching in TaO$_6$ octahedral units. Peaks E in the control and peaks A and C in the treated sample are also ascribed to Ta-O stretching. Peaks H and E in the control and treated sample, respectively are attributed to Ta-O-
Ta bending modes. The origin of peak B in the control sample is unknown at this time, but could be due to secondary Raman scattering.\textsuperscript{17} Ta-Ta vibrations may be responsible for peak I in the control and peak F in the treated sample.\textsuperscript{18} Peaks in both samples in the range of \(~130–200\) cm\(^{-1}\) may be due to Ta-O-Ta or O-3Ta bending modes.\textsuperscript{19} The peaks at \(~104\) cm\(^{-1}\) labeled K and J in the control and treated film, respectively, are due to a tilting motion of 5-coordinate pyramidal TaO\(_5\) units, or Ta-O units of lower coordination. Modes below 100 cm\(^{-1}\) have been attributed to interactions between Ta-containing clusters and Ta polyhedra.\textsuperscript{20}
We further studied the same samples by Fourier transform infrared spectroscopy (Fig. 5.10). It is unclear why the treated sample demonstrated diminished signal intensity—the films were of comparable thickness. The peaks associated with TMA are seen in the control (Fig. 5.10, top), and include C-H stretches (B) and -CH₃ (D) and N-C-H
asymmetric deformations (E).\textsuperscript{21,22} These peaks are clearly absent in the FTIR spectra of the treated film, even with the diminished signal intensity. The control film has features associated with H-bonded species (e.g. H\textsubscript{2}O) labeled A, and a rocking mode associated with H\textsubscript{2}O labeled C. The treated film has the same features labeled A (H-bonded species) and B (H\textsubscript{2}O rocking mode). Peak F in the control and peak C in the treated film may be related to Ta-O-Ta modes.\textsuperscript{23} We note that there are no features related to NO\textsubscript{3}\textsuperscript{-} in the treated film observable by FTIR.

Figure 5.10. FTIR spectra for the control film cured at 175 °C (top) and a film cured at the same temperature and exposed to 10-mM HNO\textsubscript{3} for 30 s (bottom).
We collected X-ray reflectivity data for a series of control films in the temperature range of 100—250 °C (see Fig. C1, Appendix C); based on our prior solubility studies, we prepared a set of HNO₃-treated films starting at 175 °C and up to 250 °C (Fig. C2, Appendix C). The treated and control samples cured at 175 °C did not yield XRR data (Fig. 5.11, top) readily amenable to modeling, but qualitatively it is clear that both films possess inhomogeneities, likely due to constitutional water. Curing at 175 versus 200 °C did not have an appreciable effect on water content as determined by TPD (Fig. C3, Appendix C), but the treated samples both contained more constitutional water at both temperatures (likely due to the soaking treatment). It was not until 250 °C (XRR data in Fig. 5.11, bottom) that both the control and treated films reached a level of parity (which happens to be the temperature at which the water TPD signals reaches baseline). We completed XRR modeling for the samples cured at 250 °C. The control had a modeled density of 4.93 g·cm⁻³, while the treated sample was only slightly denser at 4.99 g·cm⁻³. Film thicknesses were similar, with the control having a thickness of 22.8 nm and the treated sample being slightly thicker at 24.3 nm. The detrimental effects of the treatment on film roughness we found in thicker films (cf. Fig. 5.5) was not observed through XRR modeling in these thinner films. By XRR, both the control and treated samples remained atomically smooth, with the control film having a root mean squared roughness ($R_q$) of 0.27 nm and the treated having an $R_q = 0.25$ nm.
**Figure 5.11.** XRR data for the treated and control samples cured at 175 °C (top) and 250 °C (bottom).

From these XRR results, it appeared that soft bake temperatures at 200 °C and above were required to achieve comparable film qualities between the control and treated films. By ellipsometry (Fig. 5.12), we compared treated films soft baked in the temperature range of 200—250 °C, to the control films in the range 100—250 °C. As the soft bake temperature is increased, we witness a substantial loss in thickness (Fig. 5.12, top) in the control, as we lose constitutional water and begin to burn out some of the TMA. The treated samples had similar thicknesses to the control (Fig. 5.12, top), and at 250 °C were within nanometers (22.8 nm versus 24.8 nm for the control and treated sample, respectively). The refractive indexes (Fig. 5.12, bottom) trend in a
similar way between the control and treated sample in the temperature interval of 200—250 °C. Both the treated and control sample eventually reach similar refractive indexes of ~1.75, which is about 80% of the refractive index for bulk Ta₂O₅. Recalling the modeled XRR densities—which are only ~60% of the bulk Ta₂O₅ density—it is clear that additional thermal processing is required to drive out constitutional water and to ultimately achieve dense films.
**Figure 5.12.** Spectroscopic ellipsometry data for the treated and control samples showing thickness (top, control = black circles; treated = green squares) and refractive indexes (bottom, control = black triangles; treated = green diamonds). Data were collected at $\lambda = 550$ nm.
With these relatively low densities and refractive indexes in mind, and recalling the Raman data that suggested Ta coordination numbers of 5 or lower, we explored the possibility of intercalating cationic species into the film, in exchange for the TMA counterions. Also recalling the plan-view and cross-sectional SEM images (Fig. 5.5), it appeared that the thicker films may have a porous structure that could facilitate ionic transport. There has been growing interest in using tantalum oxide as an ionic conductor for lithium. Initial trials were conducted to attempt a lithiation of the TaO₅ films by this ion-exchange process. Films prepared using 0.22-M Ta₆ solutions were deposited and soft baked at 200 °C, and then these films were soaked in aqueous ~0.1-M LiNO₃ solutions for 1 min. I suspected that the lithium content would volatize upon further annealing of the films. We performed a TPD experiment to track lithium and other species that evolved during a thermal ramp. The TPD results are shown in Figure 5.13. We did not detect an $m/z = 7$ signal associated with Li⁺. Interestingly, the signals associated with TMA decomposition (e.g. $m/z = 58$ and $m/z = 45$) were absent as well. This suggested that perhaps the Li⁺ may have fully replaced the TMA⁺ cations. Further, the water signal (Fig. C4, Appendix C) reaches a maximum at ~70 °C and no prominent water peaks related to TMA decomposition products are observed at higher temperatures.
Figure 5.13. TPD results for a film prepared using 0.22-M Ta₆ solution, soft baked at 200 °C, and then soaked in an aqueous 0.1-molar lithium nitrate solution. Since it appeared that the film retained lithium, GIXRD diffraction data were collected to identify the resultant phase; the data are shown in Fig. 5.14. From a Rietveld refinement, we determined the predominant phase to be LiTaO₃. X-ray data were also collected for a film just after lithiation (Fig. C5, Appendix C), and a separate sample was annealed in air outside of the TPD for comparison (Fig. C6, Appendix C). The air-annealed sample was also determined to consist primarily of LiTaO₃. A schematic representation of the conversion of TMA₆[H₂Ta₆O₁₉] to LiTaO₃ by ion exchange is shown in Figure 5.15.
Figure 5.14. X-ray diffraction data collected from a lithiated Ta$_6$ film after TPD experiment. The final temperature was 900 °C.

Figure 5.15. Scheme depicting the conversion of TMA hexatantalate to lithium tantalate.
Conclusions
By utilizing acid-base chemistry, we have demonstrated a method to remove the bulky tetramethylammonium cation at temperatures as low as 175 °C. The resultant films, while still of low density, offer the opportunity for further optimization. Additional thermal treatments (possibly for longer anneal times) are likely needed to further dehydrate the films and reach densities approaching that of bulk Ta₂O₅. We have shown that through the ion exchange process, we can convert Ta₆-derived films into films of new functionalities, such as LiTaO₃, which has myriad applications, including nonlinear optics and pyroelectricity.²⁶⁻²⁹ Lastly, in the case of building up multilayer, nanolaminate thin-film structures, this ion exchange process introduces the opportunity to exploit the interesting chemistry that may happen between film interfaces, as the ions from one film may be exchanged into the next, offering a new pathway to enhanced film functionality.
References


(15) Fullmer, L. B.; Mansergh, R. H.; Zakharov, L. N.; Keszler, D. A.; Nyman, M. Nb$_2$O$_5$ and Ta$_2$O$_5$ Thin Films from Polyoxometalate Precursors: A Single


Chapter 6

LOW-TEMPERATURE PROCESSING OF AMORPHOUS TANTALUM OXIDE FILMS VIA CHEMICAL CONDENSATION

Ryan H. Mansergh, Cory K. Perkins, Deok-Hie Park, Nizan Kenane, Jenn M. Amador, Eaton C. Fong, Lauren B. Fullmer, May Nyman, and Douglas A. Keszler
Introduction
Numerous applications involving thin-film transistors,\textsuperscript{1,2} flexible electronics now call for the ability to process thin-film materials at low temperatures (\(T \leq 200 \, ^\circ\text{C}\)).\textsuperscript{3–5} In this contribution, we report a method to enable the aqueous solution deposition of high-quality amorphous tantalum oxide thin films at 200 °C—a reduction of over 200 °C from our previously reported results.\textsuperscript{6} As this method offers the ability to process materials at scale, in a more environmentally sustainable way, the benefits of solution processing have been enumerated at length.\textsuperscript{7–12} In prior work\textsuperscript{13} we have examined the transition metal polyoxometalates\textsuperscript{14–16} (POMs) as thin-film precursors, as POMs offer unique advantages over monomeric or low-nuclearity precursors, as POM clusters often possess geometric subunits needed to form the target metal oxide, thereby reducing energy inputs. To marry the benefits of POM chemistry to that of aqueous solution processing, charge-balancing countercations are a requisite for aqueous solubility. We previously found that the tetramethylammonium (TMA) hexatantalate salt produces atomically smooth, high-density tantalum oxide films, in spite of the bulky TMA counterions.\textsuperscript{6} While the TMA counterion surprisingly has no adverse effects on film roughness and density, processing temperatures in excess of 400 °C are required to thermally decompose the TMA countercation. Owing to the basic nature of the precursor (henceforth referred to as Ta\textsubscript{6} for shorthand), we have explored the use of a post-deposition acidic treatment to chemically condense\textsuperscript{17} the films via the removal of TMA counterions. Through the exchange of the TMA counterions for H\textsuperscript{+}, we drive the densification chemically, rather than thermally. We remove TMA at room temperature using this method, and anneal the films 200 °C to remove residual water. The resultant films are of comparable quality to those
deposited using vacuum-based deposition methods, such as atomic layer deposition. The ability to not only deposit tantalum oxide films using aqueous processing, but to do so with minimal thermal inputs remains a worthwhile pursuit—the applications of tantalum oxide are numerous, and include antireflective coatings, corrosion protection, medical implants, and memristors. And in this report we offer a new route to deposit high-quality amorphous tantalum oxide films at low temperatures via solution processing, that can be of great benefit to the aforementioned applications by offering a more materials- and energy-efficient approach.

**Experimental Methods**

**Materials**

TaCl$_5$ (Puratronic, 99.99%) and (CH$_3$)$_4$NOH (25% w/w aq. solution, Electronic Grade, 99.9999%) were obtained from Alfa Aesar. H$_2$O$_2$ (30%) and NH$_4$OH (aq) (28.0-30.0% as NH$_3$, ACS Grade) were purchased from Macron Fine Chemicals. Isopropanol (IPA) (ACS Grade) was purchased from BDH VWR Analytical. Ethanol (HPLC-UV Reagent Grade ACS) was purchased from Pharmco-AAPER. Formic acid (88%) was purchased from J.T. Baker Avantor Performance Materials. Triethyl orthoformate (TEOF) (>98%) was purchased from TCI. The $p$-type Si (100) wafers with 100 nm of thermally grown SiO$_2$ were purchased from Silicon Valley Microelectronics, Inc.

**Synthesis of Ta$_6$**

The Ta$_6$ ([(CH$_3$)$_4$N]$_6$[H$_2$Ta$_6$O$_{19}$]$\times$H$_2$O) powder product was synthesized as previously reported. The ammonium peroxotantalate ((NH$_4$)$_3$Ta(O$_2$)$_4$) used as the
starting materials for the two-stage Ta$_6$ synthesis was prepared through methods adapted from Selezneva and Nisel'son.$^{25}$

A 50-mM (with respect to the cluster) stock solution of the precursor was prepared by dissolving the Ta$_6$ product in 18.2-MΩ deionized water.

**Thin-Film Deposition**

The $p$-type Si (100) wafers were cleaved into approximately $2.5 \times 2.5$ cm$^2$ coupons, which were rinsed in 18.2-MΩ deionized water to remove particulates, dried in Ar or N$_2$, and then made hydrophilic through the use of an O$_2$ plasma etcher (Plasma Etch, Inc.) operating at 50 W for 5 min. For Raman and FTIR studies, Al was deposited on Si/SiO$_2$ wafers using a Veeco thermal evaporator; the Al-coated substrates were treated in a Novascan ultraviolet ozone system for 5 min to improve wettability. Ta$_6$ solutions were deposited using a syringe with a 0.45-μm nylon filter and a Laurell Technologies spin coater at a spin rate of 3000 rpm for 30 s. A high-precision Wenesco hotplate was used for post-deposition film curing for ~4 min at 175 °C; films were allowed to cool on an aluminum block for ~1 min. Samples that were further annealed (for dehydration) were heated at a ramp rate of 20 °C·cm$^{-1}$ to 200 °C and held at this temperature for 1 in Neytech Qex furnaces.

**Chemical Condensation Process**

Films were soaked for 30 s in fresh 10% v/v formic acid in ethanol solutions immediately after the 1-min cooldown period after deposition. Organic solvents were dried using molecular sieves. For chemical dehydration, films were soaked in TEOF for ~1 day at 100 °C (a 3 day treatment is prescribed by Milliron et al.$^{17}$ The thermally dehydrated films were annealed for 1 h at 200 °C. All chemically
condensed samples were rinsed in 18.2-MΩ deionized water after treatment and dried in Ar.

**Thin-Film Characterization**

The temperature programmed desorption (TPD) studies were conducted under ultra-high vacuum (~10⁻⁹ Torr) conditions in a Hiden Analytical TPD Workstation with a quadrupole mass analyzer (3F PIC) to identify gas-phase species evolved from the films during heating. Samples were cleaved into 1 × 1 cm² coupons and heated in the TPD sample chamber from room temperature to 900 °C at a ramp rate of 30 °C·min⁻¹. The mass spectra were collected with a 70-eV ionization potential and 20-μA emission current.

The thin-film Raman spectra were collected with a Horiba LabRAM HR a 532-nm laser and a 100x objective. The FTIR spectroscopy data were collected on a Thermo Scientific Nicolet 6700 FTIR spectrophotometer with a diamond attenuated total reflectance accessory.

A Rigaku Ultima-IV diffractometer with Cu Kα radiation (λ = 1.5409 Å) was used for grazing X-ray diffraction (GIXRD) and X-ray reflectivity (XRR) with. During XRR data collection, the instrument was configured with a 5.0° incident Soller slit, a 10-mm divergent height limiting (DHL) slit, and a 5.0° receiving Soller slit; the divergent slit (DS), scattering slit (SS), and receiving slit (RS) were set to 0.2, 0.5, and 0.2 mm, respectively. For GIXRD scans, the instrument was configured with a 5.0° incident Soller slit, a 10-mm slit, and a 0.5° parallel beam slit; and the DS was set to 0.2 mm and the SS and RS were left open. The Rigaku software packages
GlobalFit\textsuperscript{26} and PDXL\textsuperscript{27} were used for the analysis of XRR and GIXRD data, respectively.

A Veeco Innova SPM atomic force microscope in tapping mode with silicon probes (300 kHz, 40 N-m\(^{-1}\)) was used for atomic force microscopy (AFM) measurements. AFM images were collected on 10 \(\times\) 10 \(\mu\)m\(^2\) areas. The Bruker NanoScope Analysis software package\textsuperscript{28} was used to extract, root mean square (RMS) roughness values from an ordered grid of multiple 1 \(\times\) 1 \(\mu\)m\(^2\) sections within the larger 10 \(\times\) 10 \(\mu\)m\(^2\) scan areas.

Spectroscopic ellipsometry (SE) was conducted on a J.A. Woollam, Inc. M-2000. Measurements were taken along an ordered 9-point grid which covered ~90\% of each sample. Using the CompleteEASE software package\textsuperscript{29}, a Cauchy model was used to extract the index of refraction (\(\lambda = 550\) nm) and film thickness of the tantalum oxide layer.

Scanning electron microscopy (SEM) imaging and focused ion beam (FIB) sample preparation were conducted on a Helios NanoLab 650 dual beam FIB/SEM. An amorphous carbon protective coat was deposited on film samples via physical vapor deposition. Additional carbon and platinum protect coats were deposited in situ, using the dual beam tool. The final lamella thicknesses were less than 100 nm as determined by electron energy loss spectroscopy (EELS). The transmission electron microscopy (TEM) images were taken on an FEI Titan 80-200 TEM operating at 200 kV. Energy-dispersive X-ray spectroscopy (EDX) and EELS data were collected via accessories installed on the Titan. Electron diffraction patterns were also collected on the same tool, using nanoprobe electron diffraction.
Results and Discussion
To assess the efficacy of TMA removal via chemical condensation, we performed a series of temperature-programmed desorption (TPD) experiments on control films and those treated with formic acid (FA) in ethanol. From prior studies, as shown in eqs 6.1 and 6.2, we anticipate the presence of mass fragments associated with water, trimethylamine, dimethyl ether, and methanol during the film formation process:

\[
((\text{CH}_3)_4\text{N})_6[\text{H}_2\text{Ta}_6\text{O}_{19}] \xrightarrow{\Delta} 3\text{Ta}_2\text{O}_5 + 6(\text{CH}_3)_3\text{N} + 3\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad (6.1)
\]

\[
((\text{CH}_3)_4\text{N})_6[\text{H}_2\text{Ta}_6\text{O}_{19}] \xrightarrow{\Delta} 2(\text{CH}_3)_3\text{N} + 2\text{CH}_3\text{OH} + [(\text{CH}_3)_4\text{N}]_4[\text{Ta}_6\text{O}_{17}] \quad (6.2).
\]

By treating the films in FA, we intended to effect the idealized metathesis reaction as shown below in eq 6.3.

\[
[(\text{CH}_3)_4\text{N}]_6[\text{H}_2\text{Ta}_6\text{O}_{19}] + 6\text{HCO}_2\text{H} \rightarrow [\text{H}]_6[\text{H}_2\text{Ta}_6\text{O}_{19}] + 6[(\text{CH}_3)_4\text{N}]\text{CO}_2\text{H} \quad (6.3).
\]

If the FA/EtOH treatment successfully exchanged the TMA, we expect to observe reduced signals associated with the attendant TMA decomposition products—namely trimethylamine, dimethyl ether, and methanol. Indeed, for the mass-to-charge ratio of 58 associated with trimethylamine (Fig. 6.1, top), we observe a \( \text{C}_3\text{H}_8\text{N}^+ \) signal nearly at the instrumental detection limit. In the control film, we observe the initial TMA decomposition at \( \sim 130 \) °C, and it is not until \( \sim 500 \) °C that the \( m/z = 58 \) signal approaches zero. As shown in the TPD signal associated with dimethyl ether (Fig. 6.1, middle), we observe the onset of decomposition at \( \sim 230 \) °C; the signal reaches maximum intensity at \( \sim 360 \) °C and continues until nearly 500 °C. The treated sample, however, has an \( m/z = 45 \) signal intensity just barely above baseline. In Fig. 6.1 (bottom), a methoxy-like mass fragment in the control sample is first detected at \( \sim 150 \) °C, reaches maximum signal intensity at \( \sim 260 \) °C, and is seen until nearly 600 °C. An additional local maximum is seen around \( \sim 360 \) °C—likely due to the decomposition
of dimethyl ether; at lower temperatures (e.g. 260 °C), this CH$_3$O$^+$ fragment can be (possibly) attributed to methanol. We note that no mass fragments were observed via TPD that could be attributed to the inclusion of formate as a result of the chemical condensation treatment.

**Figure 6.1.** TPD results depicting the primary mass fragments associated with the thermal decomposition of TMA for the control film and a film treated in FA/EtOH.
Top: $m/z = 58$, associated with trimethylamine; middle $m/z = 45$ associated with dimethyl ether; and bottom $m/z = 31$ associated with methanol.

The starting precursor material $([(CH_3)_4N][H_2Ta_6O_{19}]*21H_2O)$ is heavily hydrated and contributes significant water, plus from the solvent we trap constitutional water during the initial film formation. Fig. 6.2 shows the TPD results for the mass-to-charge ratio associated with water ($m/z = 18$) for the control film and the treated film. Both the control and treated films contain similar amounts of constitutional water, and the associated signals reach a maximum at $\sim 100$ °C. For the control film, beyond $100$ °C, we observe an elevated water signal with respect to that of the control, due to the associated water products produced during the thermal decomposition of the TMA. In a similar vein, we attribute the lower water content at higher temperatures in the FA/EtOH-treated sample to a simplified reaction, with fewer attendant products.

![Figure 6.2. TPD results depicting the dehydration behavior for the control film and a film treated in FA/EtOH.](image)
To further confirm TMA removal, and to gain structural insight regarding the cluster-to-film transformation, we conducted thin-film Raman spectroscopy on the control and FA/EtOH treated films (Fig. 6.3, top). In the control film, peaks labeled A and B are associated with the CN\(^+\) stretch and symmetric stretch, respectively.\(^{30}\) In the treated (chemically condensed) sample, these peaks are not observed. The broad peak (labeled D) seen in the chemically condensed sample can be attributed to the Ta-O stretch in an octahedral TaO\(_6\) unit.\(^{31}\) The control film and treated sample both have peaks near 120 cm\(^{-1}\) (labeled C and E for the control and treated films, respectively) which suggests a tilting motion of corner-shared TaO\(_5\) pyramidal units or polyhedra of lower coordination.\(^{31}\) It is interesting to note the absence of peaks associated with the Ta-O stretch of a TaO\(_7\) pentagonal bipyramidal unit that one might observe in a crystalline \(\beta\)-Ta\(_2\)O\(_5\) film, which consists of alternating vertex-sharing TaO\(_6\) and TaO\(_7\) polyhedra.

We obtained further confirmation of TMA removal through FTIR experiments on the control and treated films (Fig. 6.3, bottom). We first note similar intensities of the broad peaks in both samples relating to the O-H stretch of H\(_2\)O, which indicates similar water content and is in agreement with the TPD signal for water (cf. Fig. 6.1). The peaks in the spectra at \(~2360\) cm\(^{-1}\) (labeled A) are attributed to atmospheric CO\(_2\); however, in some studies\(^{32,33}\) of tantalum oxide films conducted using FTIR instruments purged of atmospheric CO\(_2\), similar peaks have been attributed to a Ta=O stretching mode. The peaks labeled B are associated with the rocking mode of H\(_2\)O. Peaks labeled C and E are only present in the control sample, and are associated with the TMA countercation residue. Peak C is assigned to an NCH asymmetric
deformation,\textsuperscript{34} and peak E may be related to the v(N-C) mode.\textsuperscript{34,35} Both the control and treated samples have Ta-O-Ta vibration modes, labeled D; the peak in the control is \( \sim \) 952 cm\(^{-1}\) and \( \sim \) 939 cm\(^{-1}\) in the treated.\textsuperscript{33} The proximity of these two wavenumbers may suggest a similar level of structural disorder shared between the two samples—recall the Raman results that suggested both samples possess tilted corner-sharing TaO\(_5\) units or polyhedra of lower coordination.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6_3.png}
\caption{Raman spectra for the Ta\(_6\)-derived control and treated (chemically condensed) films (top); FTIR spectra for the same sample set (bottom).}
\end{figure}
From the TDP, Raman, and FTIR results, it is apparent that while the FA/EtOH treatment effectively removes the TMA countercations, the treated films still contain comparable amounts of water to that of the control film. To that end, possible routes to fully dehydrate the films have been evaluated. Previous studies\textsuperscript{17} have made use of water scavengers, such as TEOF to chemically dehydrate polyoxometalate-derived films. Alternatively, an additional thermal treatment can serve to remove the remaining water from the film bulk. Both approaches were taken in this study. The TEOF treatment for the Ta\textsubscript{6} system appeared to be ineffective at fully removing water as confirmed by TPD (data not shown), so we focused solely on thermal dehydration. It should be noted that our films were treated in TEOF for \textasciitilde1 day at 100 °C, rather than 3 days as prescribed by Milliron and coworkers, which may have hindered the effectiveness of this approach.

We used spectroscopic ellipsometry to study the effect of the FA treatment on film thickness and refractive index. We will refer to the control films as thermally condensed (tc) and the FA/EtOH-treated films as being chemically condensed (cc). Also, we subjected a sample of each type (tc and cc) to a thermal dehydration step for 1 h at 200 °C; we selected this temperature based on the TPD results for water (\textit{cf.} Fig. 6.2). The film thickness changes we observe via ellipsometry can serve as an indicator of TMA and H\textsubscript{2}O content. We surmise comparable water levels between the control and treated sample by referring to the FTIR results of Fig. 6.3 (bottom), as both samples have similar intensities for features associated with –OH stretches and \textit{H}_2\textit{O} rocking modes. Therefore, a reduction in thickness can serve as an indicator for
TMA loss. The tc films condenses down to ~6 nm from ~10 nm—a 40% reduction in thickness. The cc film starts with a thickness of ~8.3 nm and the thermal dehydration thins the film to ca. 4.6 nm—about a 45% reduction. After thermal dehydration, the cc film is ~23% thinner than the tc film. The TMA content in the Ta₆ precursor occupies about 70% of the unit cell volume found from single-crystal data, so this sets the upper limit of what we might anticipate in terms of volume change. The change in thickness as a result of chemical condensation and thermal dehydration is ~60%, and assuming equal, 2.5 × 2.5 cm² sample dimensions, is in line with the volume change one might anticipate upon TMA removal. The refractive indexes of the four samples were also determined via spectroscopic ellipsometry (Fig. 6.4, bottom). Recalling the FTIR spectra (Fig. 6.3, bottom), both the tc and cc samples contained similar –OH content. The chemically condensed sample annealed at 200 °C was found to have a refractive index of 1.98—which approaches the highest refractive index found (n = 2.10) in our prior study on the Ta₆ system. In that study, to reach n = 2.10, we annealed films to 600 °C, so the chemical condensation process offers a substantial improvement in energy efficiency.
**Figure 6.4.** Spectroscopic ellipsometry results for thermally condensed (tc) and chemically condensed (cc) films, along with tc and cc films subjected to additional annealing at 200 °C. Results show film thicknesses (top) and refractive indexes (bottom) for the four samples of the study.
From the ellipsometry results, it was clear that the thermal dehydration showed promise in improving film quality. The tc and cc films annealed at 200 °C were further studied by X-ray reflectivity (data and model shown in Fig. 6.5, top). The refractive index of a metal oxide is generally expected to trend with film density by virtue of the Clausius–Mossotti relation, so it was anticipated that the cc sample annealed at 200 °C would also have the highest film density. Indeed, from the XRR modeling results for film density (Fig. 6.5, middle) we find a density of 9.942(19) g·cm⁻³, which exceeds the generally reported value of 8.2 g·cm⁻³ for the single-crystal bulk density of β-Ta₂O₅. This modeled density suggests a more Ta-rich amorphous film, with a density closer to that of TaO₂, which has a calculated density of 10.41 g·cm⁻³. It is possible that formic acid is reducing the Ta. The Raman spectra discussed earlier also suggest oxygen-deficient amorphous tantalum oxide thin films. The untreated film annealed at 200 °C was found to have a bulk film density of 7.704(15) g·cm⁻³, which is still approximately 93% of the bulk density of crystalline β-Ta₂O₅. It is possible that in thinner films, a long, low-temperature may facilitate the removal of TMA. We will further examine this possibility through follow-on TPD studies. It should be noted that both XRR models entailed the addition of a thin ~1 nm tantalum oxide crust to improve the model fits, which both had χ² values of about 0.006. The presence of these denser crusts have been confirmed in other metal oxide films deposited via aqueous solution processing, and we have also confirmed the presence of a crustal layer in our solution-processed tantalum oxide films by X-ray photoelectron spectroscopy in previous studies.
Figure 6.5. X-ray reflectivity data and model fits (shown in black) for the control film and treated films subjected to a 200 °C thermal dehydration (top); XRR-derived film densities (middle); and film roughness as determined by XRR (bottom).
Film roughnesses were also determined via XRR (Fig. 6.5, bottom), and both samples demonstrated comparable surface roughnesses on the order of 3 Å. The film roughness of the tc films were similar to our prior studies, both by XRR and atomic force microscopy. We corroborated the XRR roughness for the cc film with AFM measurements (Fig. 6.6), which confirmed that atomically smooth film surfaces are retained after the chemical densification process. Plan-view scanning electron microscopy images (Fig. D1, Appendix D) of the tc and cc films also depict smooth, featureless films.

**Figure 6.6.** AFM image of a 10 µm by 10 µm area from a chemically condensed film annealed at 200 °C for 1 h.

We used cross-sectional transmission electron microscopy to assess the effect of the chemical condensation process on film continuity. The tc film (Fig. 6.7, top) and the cc film (Fig. 6.7, bottom), both typify dense, continuous films. The film thicknesses observed by TEM are in reasonable agreement with film thickness determined via ellipsometry. There are no apparent crystalline lattice fringes observed in either sample, supporting the notion that both samples are dense, amorphous tantalum.
oxide. We confirmed the thermally dehydrated cc film to be amorphous by the presence of the diffuse halo seen in the nanoprobe electron diffraction pattern (Fig. 6.8).

**Figure 6.7.** Cross-sectional TEM micrographs of a thermally condensed (tc) film (top), and a chemically condensed (cc) film (bottom).
Figure 6.8. Electron diffraction pattern collected from a chemically condensed (cc) film.

Conclusions
We have introduced a low-temperature route to produce atomically smooth, dense amorphous tantalum oxide films, which are of comparable quality to films fabricated using traditional vacuum-based deposition methods. The required processing temperatures have been decreased by over 200 °C compared to our previous report. The new processing temperature of 200 °C opens up the possibility of using flexible polymeric substrates for use in roll-to-roll processing. With the lowered energy inputs and improved atom efficiency of the Ta₆ precursor, we advance a sustainable method of material production that is eminently scalable. Further, this chemical condensation platform offers much room for exploration.
Acknowledgments

The work was performed in the Center for Sustainable Materials Chemistry, which is supported by the U.S. National Science Foundation under Grant CHE-1606982. The authors thank P. Eschbach and T. Sawyer for assistance in SEM and TEM imaging in the OSU Electron Microscope Facility. TEM imaging is based upon work supported by the National Science Foundation via the Major Research Instrumentation (MRI) Program under Grant No. 1040588. We also gratefully acknowledge financial support for acquisition of the TEM instrument at OSU from the Murdock Charitable Trust and the Oregon Nanoscience and Microtechnologies Institute (ONAMI). We also acknowledge the use of the facilities at the Advanced Technology and Manufacturing Institute (ATAMI) for AFM data collection.
References


(32) Ono, H.; Koyanagi, K. Infrared Absorption Peak due to Ta=O Bonds in Ta$_2$O$_5$


(38) Mansergh, R. H. Reaction Pathways of Oxo Hydroxo Group 5 Clusters to Metal Oxide Thin Films, Oregon State University, 2017.
CONCLUSIONS
The overall theme of this thesis has been centered on using oxo hydroxo clusters, or more specifically, group 5 polyoxometalates (POMs) for the aqueous solution processing of metal oxide thin films. This approach offers a more atom efficient and potentially energy efficient way to produce materials used in a whole host of application ranging from advanced electronics to energy.

Chapter 1 offered an introduction to aqueous solution processing using POMs as thin-film precursors and set the scope of the work to explore new thin-film precursors for the aqueous solution deposition of tantalum oxide thin films. The current landscape of Ta$_2$O$_5$ deposition was presented, including vacuum-based methods such as sputtering and atomic layer deposition (ALD), as well as solution-based sol—gel methods.

Chapter 2 represented the initial exploratory work to understand the nature of the tetramethylammonium (TMA) hexatantalate precursor as a thin-film precursor, and to learn how solution concentration and annealing time and temperature affect thin-film properties. The physicochemical properties of the precursor powder product were examined as well.

Chapter 3 compared the TMA hexatantalate (Ta$_6$) to the TMA hexaniobate (Nb$_6$) as thin-film precursors. Single-crystal data of these precursors shows that the Ta$_6$ precursor is diprotonated, while the Nb$_6$ precursor is triprotonated. This difference of one proton leads to markedly different films—the Ta$_6$ systems yields dense, smooth films, while the Nb$_6$ system forms rough films consisting of nanoparticles because of enhanced hydrogen bonding.

Chapter 4 took a deeper look at the reaction pathway of the transformation from Ta$_6$ precursor to thin film, and the decomposition of the TMA counterion was elucidated.
It was anticipated that this bulky counterion would lead to porous films, yet we find that the presence of TMA actually enhances structural relaxation of the nascent metal oxide lattice and dense, smooth films result.

Chapters 5 and 6 both explored way to remove the TMA counterions at lower temperatures by exploiting the basic character of the precursor through an acid-base reaction. The processing temperatures were reduced from over 400 °C to ~200 °C. Further, the ion exchange process was presented as a new platform to enhance film functionality, by strategically choosing dopant counterions to replace TMA.
Bibliography


Anghinolfi, L.; Prato, M.; Chtanov, A.; Gross, M.; Chincarini, A.; Neri, M.; Gemme,
Bibliography (Continued)


Bibliography (Continued)


Chandra, S. V. J.; Choi, C.-J.; Uthanna, S.; Rao, G. M. Structural and Electrical Properties of Radio Frequency Magnetron Sputtered Tantalum Oxide Films:


Bibliography (Continued)


Bibliography (Continued)


Bibliography (Continued)


Kim, M.-G.; Kanatzidis, M. G.; Facchetti, A.; Marks, T. J. Low-Temperature Fabrication of High-Performance Metal Oxide Thin-Film Electronics via Combustion Processing. Nat. Mater. 2011, 10, 382–388.

Kim, M.-K.; Kim, W.-H.; Lee, T.; Kim, H. Growth Characteristics and Electrical


Bibliography (Continued)


Bibliography (Continued)


Mansergh, R. H. Reaction Pathways of Oxo Hydroxo Group 5 Clusters to Metal Oxide Thin Films, Oregon State University, 2017.


Bibliography (Continued)


Matsumoto, M.; Ozawa, Y.; Yagasaki, A.; Zhe, Y. Decatantalate—the Last Member of the Group 5 Decametalate Family. Inorg. Chem. 2013, 52 (14), 7825–7827.


Bibliography (Continued)


Bibliography (Continued)


Sheldrick, G. M. *Bruker/Siemens Area Detector Absorption Correction Program*;


SHELXTL-6.10. *Program for Structure Solution, Refinement and Presentation*;

Bruker AXS Inc: Madison, WI.

Kwong, D. L.; Roberts, D. A.; Vrtis, R. N. Ultrathin Ta₂O₅ Film Growth by Chemical
Vapor Deposition of Ta(N(CH₃)₂)₅ and O₂ on Bare and SiOₓNᵧ-Passivated Si(100) for
Gate Dielectric Applications. J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 1998,
16, 1670.

Stephenson, N. C.; Roth, R. S. Structural Systematics in the Binary System Ta₂O₅-
WO₃. V. The Structure of the Low-Temperature Form of Tantalum Oxide L-Ta₂O₅.


Sun, Y. S.; Chang, J. H.; Huang, H. H. Corrosion Resistance and Biocompatibility of
Titanium Surface Coated with Amorphous Tantalum Pentoxide. Thin Solid Films
2013, 528, 130–135.

Sundqvist, J.; Högberg, H.; Hårsta, A. Atomic Layer Deposition of Ta₂O₅ Using the

Sze, S. M.; Ng, K. K. Physics of Semiconductor Devices; John Wiley & Sons: New

Tanczos, I.; Pokol, G.; Borsa, J.; Tóth, T.; Schmidt, H. The Effect of
Tetramethylammonium Hydroxide in Comparison with the Effect of Sodium

Bibliography (Continued)


www.materialsproject.org.
Bibliography (Continued)


Appendix A: Supporting Information for Chapter 3

This appendix contains the original Supporting Information published with \( \text{Nb}_2\text{O}_5 \) and \( \text{Ta}_2\text{O}_5 \) Thin Films from Polyoxometalate Precursors: A Single Proton Makes a Difference, along with related data that was either excluded from the initial publication or collected at a later date.

**Figure A1.** Grazing Incidence XRD on thin films of \( \text{Ta}_2\text{O}_5 \) (left) and \( \text{Nb}_2\text{O}_5 \) (right).
Figure A2. IR spectra of Ta6 (left) and Nb6 (right) show sharp peaks at 1486, 951 cm\(^{-1}\) and 1484, 952 cm\(^{-1}\) respectively, which is characteristic of TMAOH. The peak at 834 for Ta6 and 842 cm\(^{-1}\) for Nb6 can be attributed to the vibration of a terminal M-O bond. The peaks at 703 and 661 for Ta6 and 695 and 645 for Nb6 can be attributed to bridging M-O-M vibrations. The bond between a metal and the central oxygen is represented by peaks at 522 cm\(^{-1}\) and 510 cm\(^{-1}\) for Ta6 and Nb6 respectively.
Table A1. Crystallographic data and structure refinement for Ta₆ and Nb₆.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ta₆</th>
<th>Nb₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>Ta₉O₄₂.₅C₂₄H₇₄N₆</td>
<td>Nb₆O₃₂C₂₄H₇₇N₅</td>
</tr>
<tr>
<td>Formula Weight (g/mol)</td>
<td>2212.55</td>
<td>1331.21</td>
</tr>
<tr>
<td>Crystal System</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P -1 (2)</td>
<td>P -1 (2)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.7073(7)</td>
<td>13.719(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.0596(7)</td>
<td>14.024(7)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>20.9034(12)</td>
<td>16.390(8)</td>
</tr>
<tr>
<td>α (˚)</td>
<td>71.310(1)</td>
<td>67.008(8)</td>
</tr>
<tr>
<td>β (˚)</td>
<td>76.972(2)</td>
<td>76.671(8)</td>
</tr>
<tr>
<td>γ (˚)</td>
<td>72.889(1)</td>
<td>84.904(9)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>3345.40(32)</td>
<td>2825(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>T (K)</td>
<td>150</td>
<td>173</td>
</tr>
<tr>
<td>d (g·cm⁻³)</td>
<td>2.196</td>
<td>1.565</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>9.865</td>
<td>1.263</td>
</tr>
<tr>
<td>Reflections Measured</td>
<td>96486</td>
<td>44542</td>
</tr>
<tr>
<td>Independent</td>
<td>24199</td>
<td>13966</td>
</tr>
<tr>
<td>R_int</td>
<td>0.0514</td>
<td>0.1417</td>
</tr>
<tr>
<td>Independent Parameters</td>
<td>712</td>
<td>525</td>
</tr>
<tr>
<td>R1</td>
<td>0.0317</td>
<td>0.0609</td>
</tr>
<tr>
<td>wR2</td>
<td>0.0666</td>
<td>0.1041</td>
</tr>
</tbody>
</table>
Table A2. Bond lengths and bond valence sum of oxygens in Ta6 structure. * indicates protonated oxygens.

<table>
<thead>
<tr>
<th>Bridging Oxygen</th>
<th>Bond Lengths (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta2-O2-Ta1</td>
<td>1.922(2)</td>
<td>1.991(2)</td>
</tr>
<tr>
<td>Ta3-O3-Ta2</td>
<td>2.137(2)</td>
<td>2.157(2)</td>
</tr>
<tr>
<td>Ta4-O4-Ta3</td>
<td>2.031(2)</td>
<td>1.900(2)</td>
</tr>
<tr>
<td>Ta4-O5-Ta1</td>
<td>1.971(2)</td>
<td>1.979(2)</td>
</tr>
<tr>
<td>Ta5-O6-Ta1</td>
<td>1.923(2)</td>
<td>1.992(3)</td>
</tr>
<tr>
<td>Ta2-O7-Ta5</td>
<td>1.987(3)</td>
<td>1.995(2)</td>
</tr>
<tr>
<td>Ta3-O8-Ta5</td>
<td>2.128(3)</td>
<td>2.157(2)</td>
</tr>
<tr>
<td>Ta5-O9-Ta4</td>
<td>1.961(2)</td>
<td>1.992(3)</td>
</tr>
<tr>
<td>Ta6-O10-Ta1</td>
<td>1.973(2)</td>
<td>1.984(3)</td>
</tr>
<tr>
<td>Ta2-O11-Ta6</td>
<td>1.956(3)</td>
<td>2.005(2)</td>
</tr>
<tr>
<td>Ta3-O12-Ta6</td>
<td>1.894(3)</td>
<td>2.030(2)</td>
</tr>
<tr>
<td>Ta6-O13-Ta4</td>
<td>1.963(2)</td>
<td>1.970(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Terminal Oxygen</th>
<th>Bond Length (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta1-O14</td>
<td>1.802(2)</td>
<td>1.420</td>
</tr>
<tr>
<td>Ta2-O15</td>
<td>1.805(2)</td>
<td>1.409</td>
</tr>
<tr>
<td>Ta3-O16</td>
<td>1.818(2)</td>
<td>1.360</td>
</tr>
<tr>
<td>Ta4-O17</td>
<td>1.799(2)</td>
<td>1.432</td>
</tr>
<tr>
<td>Ta5-O18</td>
<td>1.805(3)</td>
<td>1.409</td>
</tr>
<tr>
<td>Ta6-O19</td>
<td>1.801(3)</td>
<td>1.424</td>
</tr>
</tbody>
</table>
Table A3. Bond lengths and bond valence sum of oxygens in Nb6 structure.

* indicates protonated oxygens.

<table>
<thead>
<tr>
<th>Bridging Oxygen</th>
<th>Bond Length (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb1-O2-Nb2</td>
<td>1.957(6)</td>
<td>1.79</td>
</tr>
<tr>
<td>Nb2-O3-Nb3</td>
<td>1.981(4)</td>
<td>1.717</td>
</tr>
<tr>
<td>Nb3-O4-Nb4</td>
<td>1.938(6)</td>
<td>1.79</td>
</tr>
<tr>
<td>Nb4-O5-Nb1</td>
<td>1.989(5)</td>
<td>1.679</td>
</tr>
<tr>
<td>Nb5-O6-Nb1</td>
<td>1.902(4)</td>
<td>1.932</td>
</tr>
<tr>
<td>Nb2-O7-Nb5</td>
<td>2.158(5)</td>
<td>1.088*</td>
</tr>
<tr>
<td>Nb3-O8-Nb5</td>
<td>2.146(5)</td>
<td>1.111*</td>
</tr>
<tr>
<td>Nb5-O9-Nb4</td>
<td>1.874(4)</td>
<td>1.849</td>
</tr>
<tr>
<td>Nb6-O10-Nb1</td>
<td>2.119(5)</td>
<td>1.19*</td>
</tr>
<tr>
<td>Nb2-O11-Nb6</td>
<td>1.923(4)</td>
<td>1.859</td>
</tr>
<tr>
<td>Nb3-O12-Nb6</td>
<td>1.941(4)</td>
<td>1.939</td>
</tr>
<tr>
<td>Nb6-O13-Nb4</td>
<td>1.949(5)</td>
<td>1.873</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Terminal Oxygen</th>
<th>Bond Length (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb1-O14</td>
<td>1.771(6)</td>
<td>1.513</td>
</tr>
<tr>
<td>Nb2-O15</td>
<td>1.771(6)</td>
<td>1.513</td>
</tr>
<tr>
<td>Nb3-O16</td>
<td>1.774(5)</td>
<td>1.501</td>
</tr>
<tr>
<td>Nb4-O17</td>
<td>1.771(6)</td>
<td>1.516</td>
</tr>
<tr>
<td>Nb5-O18</td>
<td>1.786(5)</td>
<td>1.456</td>
</tr>
<tr>
<td>Nb6-O19</td>
<td>1.772(5)</td>
<td>1.510</td>
</tr>
</tbody>
</table>
Figure A3. Simulated XRD pattern from single crystal data of Ta6.

Figure A4. Simulated XRD pattern from single crystal data of Nb6.
Figure A5. Powder XRD pattern of Nb6.

Figure A6. Powder XRD pattern of Ta6.
Figure A7. Unit cell representation of tetramethylammonium salt of \([M_6O_{19}]^8\).

Table A4. Size distribution results from Irena, Ta\(_6\) and Nb\(_6\) in water (left) and 0.2-M TMAOH solution (right).

<table>
<thead>
<tr>
<th>Water</th>
<th>Diameter Pop 1(Å)</th>
<th>Diameter Pop 2 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10mM Nb(_6)</td>
<td>6.25</td>
<td>--</td>
</tr>
<tr>
<td>10mM Ta(_6)</td>
<td>6.33</td>
<td>16.91</td>
</tr>
<tr>
<td>25mM Nb(_6)</td>
<td>6.41</td>
<td>--</td>
</tr>
<tr>
<td>25mM Ta(_6)</td>
<td>6.52</td>
<td>17.13</td>
</tr>
<tr>
<td>50mM Nb(_6)</td>
<td>6.77</td>
<td>15.94</td>
</tr>
<tr>
<td>50mM Ta(_6)</td>
<td>6.44</td>
<td>17.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>0.2M TMAOH</th>
<th>Diameter Pop 1(Å)</th>
<th>Diameter Pop 2 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10mM Nb(_6)</td>
<td>6.52</td>
<td>--</td>
</tr>
<tr>
<td>10mM Ta(_6)</td>
<td>6.07</td>
<td>--</td>
</tr>
<tr>
<td>25mM Nb(_6)</td>
<td>6.45</td>
<td>--</td>
</tr>
<tr>
<td>25mM Ta(_6)</td>
<td>6.50</td>
<td>--</td>
</tr>
<tr>
<td>50mM Nb(_6)</td>
<td>6.58</td>
<td>15.33</td>
</tr>
<tr>
<td>50mM Ta(_6)</td>
<td>6.89</td>
<td>16.58</td>
</tr>
</tbody>
</table>
Reaction Pathway: Effect of Additional Proton on Nb₆ Film Formation
We carried out temperature-programmed desorption (TPD) studies on Nb₆-derived films to examine the effect of the additional proton of the triprotonated hexaniobate cluster. The TPD results are shown in Fig. A8. The dehydration behavior of the Nb₆ precursor is similar to the Ta₆ precursor at lower temperature; however, we observe high intensity water peaks beyond 400 °C. These high-temperature water peaks are likely due to the more circuitous route offered by the enhanced hydrogen bonding of the triprotonated Nb₆ cluster.

Figure A8. TPD results for film deposited with 0.22-M Nb₆ solutions and cured at 80 °C for less than 1 min.

In the TPD results seen in Fig. A9, we observe the same TMA thermal decomposition products for Nb₆ films as was found for Ta₆-based films (cf. Chapter 4). A proposed reaction is given below in eq 1:
\[(\text{CH}_3)_4\text{N})_5[\text{H}_3\text{Nb}_6\text{O}_{19}] \rightarrow 3\text{Nb}_2\text{O}_5 + 5(\text{CH}_3)_3\text{N} + 2.5\text{CH}_3\text{OCH}_3 + 1.5\text{H}_2\text{O} \quad (1)\]

We see an intense trimethylamine \((\text{C}_3\text{H}_8\text{N}^+)\) peak ~400 °C—in Ta$_6$-based films the trimethylamine was almost completely removed by this temperature. This again is likely due to enhanced hydrogen bonding, which introduces an additional energetic penalty to the removal of TMA in Nb$_6$-based films, and precludes the gradual film formation observed in the Ta$_6$ system.

**Figure A9.** TPD results for film deposited with 0.22-M Nb$_6$ solutions and cured at 80 °C for less than 1 min.

The rather violent off-gassing at higher temperatures has detrimental consequences on film properties—especially with respect to film roughness, which dramatically increases with increasing temperature. This behavior is clearly depicted by the optical light microscope (Fig. A10), SEM (Fig. A11), and atomic force microscopy (Fig. A12) images.
**Figure A10.** Optical light microscope images for films prepared using 0.22-M Nb$_6$ solutions and annealed at 400 °C (top), 600 °C (middle), and 800 °C (bottom). The circular pattern at the center of the image represents about 60 μm.
Figure A11. SEM micrographs for films prepared using 0.22-M Nb₆ solutions and annealed at 400 °C (top), 600 °C (middle), and 800 °C (bottom).
Figure A12. AFM results for films prepared using 0.22-M Nb$_6$ solutions and annealed at 400 °C (top), 600 °C (middle), and 800 °C (bottom). Scan areas were 1 μm × 1 μm.

The roughness values obtained via AFM were compared to XRR modeling results (Fig. A12), and we see very good agreement. From the modeled densities (Fig. A13), it is not until 800 °C that we reach the bulk density of Nb$_2$O$_5$ (4.6 g·cm$^{-3}$). The densities determined via XRR likely represent the densities of the Nb$_2$O$_5$ nanoparticles at the film surface. It should be noted that the Nb$_6$ films annealed at
400 °C remained atomically smooth, so the Nb₆ system may be worth further at lower temperatures. The XRR-derived film thicknesses are compared to film thicknesses determined via spectroscopic ellipsometry (Fig. A14); the refractive indices determined by ellipsometry are included in the same figure.

**Figure A13.** XRR modeling results for roughness and density for films prepared using 0.22-M Nb₆ solutions and annealed at 400, 600, and 800 °C. XRR-derived roughnesses are compared to AFM measurements.
Figure A14. XRR modeling results for film thickness compared to film thicknesses determined by ellipsometry for films prepared using 0.22-M Nb₆ solutions and annealed at 400, 600, and 800 °C. The refractive indexes reported are at $\lambda = 550$ nm.
X-ray Photoelectron Spectroscopy Study on Nb₆-Derived Films

An X-ray photoelectron spectroscopy study was conducted to assess the film surfaces of samples prepared using 0.22-M Nb₆ solutions; all samples were annealed for 10 min. The sample annealed at 400 °C (Fig. A15) evidenced a mixture of oxidation states, while the samples annealed at 600 °C (Fig. A16) and 800 °C (Fig. A17) both had Nb3d₅/₂ and Nb3d₃/₂ peaks associated with Nb₂O₅ and Nb⁵⁺.

![Figure A15. XPS results for a film prepared using 0.22-M Nb₆ solution and annealed at 400 °C for 10 min.](image-url)
Figure A16. XPS results for a film prepared using 0.22-M Nb₆ solution and annealed at 600 °C for 10 min.

Figure A17. XPS results for a film prepared using 0.22-M Nb₆ solution and annealed at 800 °C for 10 min.
Appendix B: Supporting Information for Chapter 4

This appendix contains the original Supporting Information published with Reaction: Aqueous Hexatantalate Clusters to High-Density Tantalum Oxide Nanofilms, along with related data that was either excluded from the initial publication or collected at a later date.

**Figure B1.** Grazing incidence X-ray diffraction (GIXRD) data for an as-deposited film spun from 0.22-M Ta₆ solutions (Ta₆ = [(CH₃)₄N]₆[H₂Ta₆O₁₉]·xH₂O). The substrate peak is indicated with a star (★).

**Figure B2.** GIXRD data for a sample spun from 0.22-M Ta₆ and annealed at 900 °C for 10 min that was used for structural refinements.
Figure B3. (a) Plan-view scanning electron microscopy (SEM) image of a 0.22-M Ta$_6$ sample annealed at 400 °C for 10 min. Plan-view SEM images of samples annealed at (b) 600 °C and (c) 800 °C for 10 min using the same 0.22-M Ta$_6$ precursor.
Figure B4. Spectroscopic ellipsometry (SE) data for samples prepared using 0.22-M Ta₆ precursor solution collected at 60° and 65°. SE data for the sample annealed at (a) 400 °C, (b) 600 °C, and (c) 800 °C. All samples were annealed in air for 10 min.
Figure B5. Atomic force microscopy (AFM) images for samples prepared using a 0.22-M Ta₆ precursor solution. Samples annealed for 10 min at (a) 400 °C, (b) 600 °C, and (c) 800 °C.

Figure B6. XRR data for samples annealed at 100, 200, and 300 °C for 10 min.
Figure B7. XRR data for samples prepared using 0.01 and 0.025-M Ta₆ solutions. Films were annealed for 10 min.

**Effects of Thermal Processing on Ta₆-Derived Films**
The following data and discussions concerning the effects of thermal processing were not included in the original *Reaction Pathway: Aqueous Hexatantalate Clusters to High-Density Tantalum Oxide Nanofilms* manuscript.

As noted in Figure 4.3b of Chapter 4, films spun from 0.22-M Ta₆ solutions show evidence of grain growth detectable by X-rays when annealed at 705 °C for 10 min. Another sample prepared using 0.22-M Ta₆ solutions was annealed at 680 °C for 3 h. The crystallinity of the film is apparent from the X-ray pattern and the inset SEM image in Fig. B8.
Figure B8. Film deposited from 0.22-M Ta₆ solution and annealed at 680 °C for 3 h. Inset is an SEM micrograph of the same film.

As noted in Figure 4.5c of Chapter 4, we reach a maximum density after annealing films at 600 °C for 10 min. A sample prepared using a 0.22-M Ta₆ solution was annealed for 1 day at 600 °C and showed evidence of grain growth by GIXRD.

Figure B9. Film deposited from 0.22-M Ta₆ solution and annealed at 600 °C for 1 day.
To establish a lower bound for crystallization, a sample was prepared using the same solutions and annealed at 500 °C for 1, 2, and 3 days. The X-ray patterns of Figure B10 all demonstrate that the film is X-ray amorphous after at least 3 days of annealing.

**Figure B10.** Film deposited from 0.22-M Ta₆ solution and annealed at 500 °C for 1, 2, and 3 days.
Another sample set was annealed at 500 °C for 10 min, 1 h, and 1 day. These samples also remained X-ray amorphous as seen in Fig. B11. Broad features are apparent that coincide with the peak locations in Ta$_2$O$_5$.

**Figure B11.** Films deposited from 0.22-M Ta$_6$ solutions and annealed at 550 °C for 1, 2, and 3 days.
From this annealing study we can conclude that given sufficient annealing times, Ta₆-derived films will begin to crystallize at temperatures between 550 and 600 °C. The 1-day anneals at 500, 550, and 600 °C are shown below for comparison in Fig. B12.

**Figure B12.** Films deposited from 0.22-M Ta₆ solutions and annealed at 500, 550, and 600 °C for 1 day.
A series of *in situ* heating experiments were conducted to compare to *ex situ* observations. A sample was prepared using 0.22-M Ta$_6$ solutions and cured at 200 °C for 1 min. We started heating the sample from room temperature, and the sample was ramped up at a rate to simulate typical annealing conditions and held at each temperature under study for 10 min. The change in film thickness and density were modeled from the XRR data. These results (Fig. B13) corroborated the changes in film thickness and density observed in prior annealing studies of Ta$_6$-derived thin films.

**Figure B13.** Modeling results from an *in situ* XRR experiment conducted on a film deposited from a 0.22-M Ta$_6$ solution.
To examine morphological changes during annealing, we conducted an in situ TEM experiment on a thin-film sample prepared using a 0.22-M Ta₆ solution. The resultant TEM micrographs are shown in Fig. B14a-f. The sample lamella began to fold, possibly due to mismatched thermal expansion coefficients, and a shadow was cast over the sample starting at ~600 °C. No significant changes were observed in the tantalum oxide film—no significant crystalline grains are apparent by the conclusion of the experiment, suggesting that anneals in vacuo may be a way to mitigate grain growth. In Fig. B14f, the interfacial SiO₂ layer appears thicker than at the beginning of the experiment, which suggests that the oxidative environment of the aqueous precursor is sufficient for the growth of the SiO₂ layer in the absence of air.
Figure B14. TEM micrographs of a sample prepared using 0.22-M Ta₆ solution heated to 200 °C (a), 300 °C (b), 400 °C (c), 600 °C (d), 700 °C (e), and 800 °C (f).
In the case of a sample annealed ex situ to 800 °C (Fig. B15), grains are readily apparent. Further, the interfacial SiO₂ layer has undergone a significant growth in thickness compared to the starting native oxide of ~1-2 nm.

**Figure B15.** TEM micrograph of a sample prepared using 0.22-M Ta₆ solution heated to 800 °C for 10 min.

**Electrical Characterization of Ta₆-Based MIS Devices**

Electrical measurements were performed on MIS devices which were fabricated using samples annealed at 400, 600, and 800 °C. Current-voltage (I-V) measurements were carried out at room temperature in dark conditions on these Al/Ta₂O₅/n-Si devices, and the I-V data are shown in Figure B16. A reduction in the leakage current is
observed from ~1 x 10^{-7} to ~5.6 x 10^{8} A\cdot cm^{-2} at 0.5 MV\cdot cm^{-1} on samples annealed at 400 and 600 °C, respectively. This behavior was expected considering the TPD results, which indicate that the majority of the TMA has been driven out of the films and that the films have undergone a substantial dehydration. The 800 °C MIS device sample demonstrated an improved leakage current value over that of the other samples (~2 x 10^{8} A\cdot cm^{-2}). The observed behavior, at first glance seems counter to what would be expected due to the grains and apparent defect formation in the 800 °C sample. However, this sample underwent a more complete dehydration (cf. TPD results) and presents a thicker interfacial SiO\textsubscript{2} layer (recall Fig. B15) at the Si/Ta\textsubscript{2}O\textsubscript{5} interface. This thicker SiO\textsubscript{2} layer serves to enhance the apparent dielectric properties of the device. The films under study typically demonstrated a doubling of the interfacial SiO\textsubscript{2} layer, creating a thicker dielectric in series across the electric field. This increase in interfacial SiO\textsubscript{2} thickness has been observed previously by Alers et al.\textsuperscript{1} in Ta\textsubscript{2}O\textsubscript{5} thin films deposited using chemical vapor deposition. The leakage current values obtained in our Ta\textsubscript{2}O\textsubscript{5} system are close to those observed on SiO\textsubscript{2} films grown by vapor-based methods such as plasma-enhanced chemical vapor deposition.\textsuperscript{2}
Figure B16. $I-V$ measurements for Al/Ta$_2$O$_5$/n-Si MIS devices for samples annealed at 400, 600, and 800 °C. All samples were annealed for 10 min prior to device fabrication.
X-ray Photoelectron Spectroscopy Study on Ta₆-Derived Films

The effects of annealing on film surfaces were also studied by X-ray photoelectron spectroscopy (XPS). From these results (Figs. B17—B19), it was determined that the film surfaces contain reduced tantalum at the surface until 800 °C. At 800 °C we observe the Ta4f₅/₂ and Ta4f₇/₂ peaks associated with Ta₂O₅ with tantalum in its group oxidation state.

**Figure B17.** XPS results for a film prepared using 0.22-M Ta₆ solution and annealed at 400 °C for 10 min.
Figure B18. XPS results for a film prepared using 0.22-M Ta$_6$ solution and annealed at 600 °C for 10 min.

Figure B19. XPS results for a film prepared using 0.22-M Ta$_6$ solution and annealed at 800 °C for 10 min.
References


Appendix C: Supporting Information for Chapter 5

This appendix contains Supporting Information for *Ion Exchange for Low-Temperature Processing and Enhanced Functionality in Solution-Processed Tantalum Oxide Thin Films*

![X-ray reflectivity data](image)

**Figure C1.** X-ray reflectivity data for the control films prepared using 50-mM Ta$_6$ solutions and cured in the temperature interval 100—250 °C.
**Figure C2.** X-ray reflectivity data for films cured in the temperature interval from 175—250 °C and then treated in aqueous 10-mM HNO₃ for 30 s. All films were prepared using 50-mM Ta₆ solutions.
Figure C3. TPD results showing water content ($m/z = 18$) for the treated and control films that were initially soft baked at 175 °C (top) and 200 °C (bottom).
Figure C4. TPD results showing water content as a function of temperature for a film prepared using a 0.22-M Ta$_6$ solution, soft baked at 200 °C, and then soaked in a LiNO$_3$ solution for 1 min.

Figure C5. X-ray diffraction data collected from a Ta$_6$-based film cured at 200 °C for 4 min and treated in 0.1-M LiNO$_3$. 
Figure C6. X-ray diffraction data collected from a lithiated Ta₆ film annealed in air. The final temperature was 1000 °C.
Appendix D: Supporting Information for Chapter 6

This appendix contains Supporting Information for *Low-Temperature Processing of Amorphous Tantalum Oxide Films via Chemical Condensation*

**Figure D1.** Plan-view SEM images of a thermally condensed (top) film compared to the chemically condensed (bottom) film. Both samples were annealed at 200 °C for 1 h.
Figure D2. Preliminary X-ray reflectivity studies for 50-mM Ta₆ films treated in FA/EtOH (top) and FA/IPA (bottom). Films were soaked for 30 s. The treatment in FA/IPA did not yield apparent thickness changes, which could indicate limited efficacy of TMA removal.
Figure D3. Energy-dispersive X-ray spectroscopy line scan of a film prepared using 50-mM Ta₆ solutions, treated in FA/EtOH for 30 s, then annealed at 200 °C for 1 h.
Figure D4. Grazing incidence X-ray diffraction data collected from a film prepared using 50-mM Ta₆ solutions, treated in FA/EtOH for 30 s, then annealed at 800 °C for 10 min.