Chemical vapor deposition of TiO$_2$ thin films from a new halogen-free precursor

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TiO$_2$ films are synthesized by chemical vapor deposition using the recently synthesized precursor Ti(H$_3$BNMe$_2$BH$_3$)$_2$ with H$_2$O as the co-reactant. Films grown between 350 and 450 °C are crystalline and consist of a mixture of rutile and anatase phases; the fraction of rutile/anatase is larger at 450 °C. The films are continuous, dense, and pure, with the sum of B, C, and N impurities <1 at. %. The growth rate is ~1.2 nm/min, limited by the precursor feed rate and therefore independent of temperature. The growth rate decreases monotonically with increasing H$_2$O pressure due to the competition between precursor and co-reactant molecules for adsorption sites on the surface. The advantages of this system compared with other available Ti-bearing precursors are the absence of halogen and the synthesis of mixed-phase material at modest temperatures. © 2014 American Vacuum Society. [http://dx.doi.org/10.1116/1.4894454]

I. INTRODUCTION

Titanium dioxide, TiO$_2$, is a useful material owing to its photocatalytic properties and exceptional chemical stability in aqueous environments. When irradiated with ultraviolet light it is able to split water and generate molecular hydrogen, to degrade organic pollutants in water purification processes, to act as a self-cleaning surface, and to perform other useful catalytic reactions. Photocatalytic activity with visible light can be achieved by coating TiO$_2$ with dyes or doping it with various heteroatoms. In addition, the high dielectric constant of the rutile phase, ~80, makes TiO$_2$ an attractive capacitor and gate dielectric material.

TiO$_2$ coatings can be deposited by sol–gel, magnetron sputtering, chemical vapor deposition (CVD), and atomic layer deposition (ALD) processes. We focus on the latter two because they are most amenable to conformal deposition. Interestingly, the catalytic properties of TiO$_2$ are often enhanced if it is prepared as a mixture of the anatase and rutile phases. Various CVD and ALD precursors to afford mixed phase TiO$_2$ have been investigated as a function of film thickness, coreactant pressure, and temperature (Table I). For example, the precursors TiCl$_4$ and TiI$_4$ afford mixed phase films at ~325 °C; for most other precursors, the deposition temperature to obtain mixed phase films (as opposed to amorphous or single-phase material) is typically ~600–700 °C.

We report the deposition of TiO$_2$ films by CVD from a recently synthesized precursor, Ti(DMADB)$_2$, where DMADB = N,N-dimethylaminodiboranate (H$_3$BNMe$_2$BH$_3$). This precursor is a solid with a vapor pressure of 0.01–0.1 Torr at 25 °C (estimated by comparison of the sublimation rate with those of other volatile compounds). The magnesium analog Mg(DMADB)$_2$ reacts cleanly with water under CVD conditions to form MgO with liberation of H$_2$ and volatile N,N-dimethylaminodiboranate (B$_2$H$_5$NMe$_2$). We show that a similar reaction of Ti(DMADB)$_2$ with water affords an attractive, halogen-free route for the growth of high quality TiO$_2$ films at temperatures as low as 150 °C, and mixed phase oxide at 350–450 °C, similar to TiCl$_4$ and TiI$_4$.

II. EXPERIMENT

The Ti(DMADB)$_2$ precursor is synthesized as previously described. Film deposition is carried out in a cold wall high vacuum system with a base pressure of 10$^{-8}$ Torr, most of which is H$_2$. The substrates are single crystalline n-type Si (100) covered with ~2 nm of native oxide and heated directly by passage of a dc current. The precursor and water are stored in separate glass tubes at room temperature and enter the chamber through separate stainless steel tubes that are nearly perpendicular to and 7 cm away from the substrate holder. No carrier gas is used with either molecule. A capacitance manometer measures the average total pressure inside the chamber, which is lower than the effective pressures of reactants that effuse from the tubes and impinge on the substrate surface.

Film thickness is measured in-situ by spectroscopic ellipsometry. The reference dielectric function is determined by ex-situ variable angle spectroscopic ellipsometry on
identically prepared material. Ellipsometry values are within ±5% of those measured by postgrowth SEM. The film phases are determined using XRD in the h-2h geometry. The film stoichiometry is analyzed by RBS and the impurity content by XPS and AES. The XPS spectra are energy calibrated using the C 1s peak at 284.6 eV.

### III. RESULTS AND DISCUSSION

#### A. Composition

The composition of films grown from the Ti(DMADB)_2 precursor depends on the deposition conditions. When no water is used as a coreactant, the precursor decomposes on the growth surface at temperatures > 300°C to afford deposits containing mostly titanium and boron. With sufficient water partial pressure, high purity TiO_2 can be obtained. For representative conditions, e.g., a precursor pressure of 0.01 mTorr, a water pressure of 2.0 mTorr, and a growth temperature of 350°C, the total content of B, C, and N is <1 at. % (Fig. 1, inset).

A strong C 1s peak is seen for the air-exposed surface, but disappears after Ar^+ sputtering, indicating that the bulk is carbon-free. Peaks due to B, C, and N are undetectable on a survey scan. In high resolution spectra, very weak signals for the N 1s and B 1s peaks are observed, accounting for no more than 0.5 at. % each. The O 1s binding energy is 529.9 eV, and the Ti 2p_{1/2} and 2p_{3/2} peaks have binding energies of 464.2 and 458.5 eV, respectively. The XPS data agree very well with the reported values for TiO_2 but not with those for other oxidation states.33 Additional small features in high-resolution scans indicate trace amounts of suboxides or defect states (supplementary materials34).

#### B. Growth kinetics

At a substrate temperatures of 150–450°C, the growth rate is ~1.2 nm/min and is only weakly temperature dependent due to the limited precursor feed rate. With increasing water partial pressure, the growth rate steadily decreases (Fig. 2). The reduction of the growth rate at higher water pressures is attributed to a shift of the competitive adsorption equilibria on the growth surface to a water-rich condition, away from the ratio that affords maximum rate.35 This behavior has the advantage that it can lead to films that are

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**Table I. Comparison between TiO_2 precursors for CVD (or ALD as labeled).**

<table>
<thead>
<tr>
<th>Precursor and coreactant</th>
<th>T_{source} (°C)</th>
<th>T_{sub} (°C)</th>
<th>Growth rate (nm/min)</th>
<th>Impurities (at. %)</th>
<th>T_{sub} and phase(^a)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(O-i-Pr)_4 or Ti(O-i-Pr)_4/O_2</td>
<td>170</td>
<td>350–1200</td>
<td>0.1–3000</td>
<td>C (&lt;1)</td>
<td>350-x</td>
<td>2</td>
</tr>
<tr>
<td>TiO(acac)_2/O_2</td>
<td>170</td>
<td>550–680</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti(O-i-Pr)_2(dpm)_2/O_2</td>
<td>150</td>
<td>300–900</td>
<td>13–500</td>
<td>C (3)</td>
<td>300-450-A</td>
<td>22</td>
</tr>
<tr>
<td>TiI_4/H_2O_2</td>
<td>105–110</td>
<td>230–490 (ALD)</td>
<td>0.03–0.12 nm/cycle</td>
<td>H (0.05–0.9)</td>
<td>275-A</td>
<td>23</td>
</tr>
<tr>
<td>Ti(dpm)_3(OCH_3)_2/O_2</td>
<td>90</td>
<td>350–650</td>
<td>0.5–7.0</td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>TiO-i-Pr_4</td>
<td>50–60</td>
<td>323–920</td>
<td>0.15–3.3</td>
<td></td>
<td>323-650-A</td>
<td>25</td>
</tr>
<tr>
<td>Ti(NO_3)_4</td>
<td>50–60</td>
<td>159–900</td>
<td>0.3–5.7</td>
<td></td>
<td>159-650-A</td>
<td>25</td>
</tr>
<tr>
<td>TiCl_4/H_2O</td>
<td>20</td>
<td>100–900</td>
<td></td>
<td></td>
<td>700-920-R</td>
<td></td>
</tr>
<tr>
<td>Ti(DMADB)_2/H_2O</td>
<td>25</td>
<td>150–450</td>
<td>1.0–1.3</td>
<td>B, N (&lt;0.5)</td>
<td>350-450-A/R</td>
<td>This work</td>
</tr>
</tbody>
</table>

\(x = \text{amorphous, A = anatase, R = rutile.}\)
highly conformal. 35 We previously reported a kinetic study of competitive adsorption and its effect on growth rate for a similar system, the growth of MgO films using Mg(DMADB)2 and H2O; for that system, the data fit well to a first-order adsorption-reaction model.36

C. Microstructure and crystallinity
Films deposited at 400 °C are continuous and dense (Fig. 3). The surface roughness results from crystallization and faceting at this growth temperature. TiO2 films deposited at 350 and 450 °C show preferred orientations for the anatase (004) and rutile (210) planes, indicated by the major peaks at 38° and 44° (Fig. 4). The rutile to anatase ratio increases at higher growth temperature. Additional small peaks occur in positions corresponding to reported suboxides,37 but a precise match is not obvious; we interpret that preferred orientation or defect states are responsible. Overall, the data indicate that CVD from Ti(DMADB)2 and H2O affords mixed phase TiO2 films at a relatively low temperatures, 350–450 °C. Similar results can be achieved using TiCl4 or TiI4 as the precursor,38,39 but the current method has the advantage of avoiding the presence of halogens, which as low level contaminants can be detrimental, e.g., they reduce the reliability of micro-electronic metallization.

IV. SUMMARY AND CONCLUSIONS
A recently synthesized precursor, Ti(DMADB)2, reacts with H2O to afford TiO2 films by CVD at modest temperatures. With sufficient water pressure, the films are stoichiometric with a total impurity content <1 at. %. Films grown at substrate temperatures of 350–450 °C consist of a mixture of anatase and rutile; the rutile content increases with temperature. The film growth rate is weakly dependent on temperature, and the pressure dependence of the growth rate is consistent with competitive adsorption of the Ti precursor and water on the growth surface. The Ti(DMADB)2–H2O system may be of technological interest due to the ready formation of mixed phase material at low temperature from a highly volatile halogen-free precursor.

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34. See supplementary material at http://dx.doi.org/10.1116/1.4894454 for high resolution XPS spectrum showing Ti subslet peaks for TiO2 film, and Gaussian fitting to the peaks.