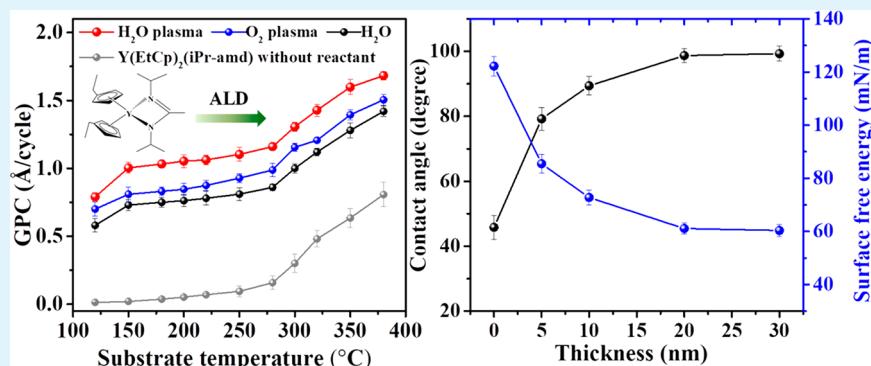


# Thermal and Plasma-Enhanced Atomic Layer Deposition of Yttrium Oxide Films and the Properties of Water Wettability

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 Supporting Information



**ABSTRACT:** The atomic layer deposition (ALD) of yttrium oxide ( $\text{Y}_2\text{O}_3$ ) is investigated using the liquid precursor  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  as the yttrium source with thermal ( $\text{H}_2\text{O}$ ) and plasma-enhanced ( $\text{H}_2\text{O}$  plasma and  $\text{O}_2$  plasma) processes, respectively. Saturation is confirmed for the growth of the  $\text{Y}_2\text{O}_3$  films with each investigated reactant with a similar ALD window from 150 to 300 °C, albeit with a different growth rate. All of the as-deposited  $\text{Y}_2\text{O}_3$  films are pure and smooth and have a polycrystalline cubic structure. The as-deposited  $\text{Y}_2\text{O}_3$  films are hydrophobic with water contact angles  $>90^\circ$ . The water contact angle gradually increased and the surface free energy gradually decreased as the film thickness increased, reaching a saturated value at a  $\text{Y}_2\text{O}_3$  film thickness of  $\sim 20$  nm. The hydrophobicity was retained during post-ALD annealed at 500 °C in static air for 2 h. Exposure to polar and nonpolar solvents influences the  $\text{Y}_2\text{O}_3$  water contact angle. The reported ALD process for  $\text{Y}_2\text{O}_3$  films may find potential applications in the field of hydrophobic coatings.

**KEYWORDS:** atomic layer deposition, plasma-enhanced, heteroleptic precursor, yttrium oxide, water contact angle

## 1. INTRODUCTION

Yttrium oxide ( $\text{Y}_2\text{O}_3$ ) offers material properties that are attractive to specific applications. Its high refractive index of 1.9 is useful for the fabrication of planar waveguides in solid-state and high-power lasers.<sup>1</sup> Bulk  $\text{Y}_2\text{O}_3$  has a high thermal conductivity of 0.27 W (cm K)<sup>-1</sup> at 300 K, a high melting point of 2430 °C, and a high mechanical strength, which makes it an interesting material for temperature- and wear-resistant coatings.<sup>2–5</sup>  $\text{Y}_2\text{O}_3$  has numerous applications in the fields of electronics and optoelectronics.<sup>6–9</sup> For example, thin films of  $\text{Y}_2\text{O}_3$  are suited as high- $k$  gate dielectrics due to the large intrinsic band gap in the range of 5.5 to 5.8 eV and the high dielectric constant of 14–18. For this reason,  $\text{Y}_2\text{O}_3$  thin films are intensively studied in metal oxide semiconductor field effect transistors (MOSFETs) as the thin high- $k$  gate material.<sup>10</sup> Moreover,  $\text{Y}_2\text{O}_3$  thin films have been employed as optical and protective coatings, buffer layers in ferroelectrics and superconductors, as well as dielectric insulators in electroluminescent devices.<sup>11–14</sup> For example, the rare-earth-doped  $\text{Y}_2\text{O}_3$  films, such as Eu: $\text{Y}_2\text{O}_3$ ,<sup>15,16</sup> Er: $\text{Y}_2\text{O}_3$ ,<sup>17</sup> Er:Eu: $\text{Y}_2\text{O}_3$ ,<sup>18</sup> and Er:Yb: $\text{Y}_2\text{O}_3$ ,<sup>19</sup> have been widely used in photonic devices, like optical amplifiers, sensors, up-converters,

light-emitting diodes (LEDs), organic LEDs, and thin-film electroluminescent devices. In addition,  $\text{Y}_2\text{O}_3$ -based films, such as yttria-stabilized zirconia (YSZ) and yttria-doped ceria (YDC), are applied as solid-state electrolytes for solid oxide fuel cells (SOFCs).<sup>20–25</sup>

There have been a variety of methods used to deposit thin films of  $\text{Y}_2\text{O}_3$ , including physical vapor deposition (PVD),<sup>26</sup> chemical vapor deposition (CVD),<sup>27</sup> plasma-enhanced chemical vapor deposition (PECVD),<sup>28</sup> and atomic layer deposition (ALD). Studies such as these have shown that important film properties such as crystallinity, residual carbon content, and electronic properties are influenced by the choice of deposition method as well as the particular precursor/reactant used. Among them, ALD has attracted much interest because it is able to produce high-quality, uniform, and conformal films with excellent composition and submonolayer thickness control, even at low growth temperatures based on self-limited surface reactions.<sup>29–31</sup> During ALD, the film grows through

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the surface reactions of vaporized precursors and reactant gases that are alternately supplied to the substrate surface. The choice of the proper metal precursor is crucial for a successful ALD process. The main requirements for ALD precursors concern a suitable vapor pressure at its supplying temperature, no self-decomposition at the process temperature, and an aggressive reaction with surface groups.<sup>32,33</sup>

In prior research on the ALD of  $\text{Y}_2\text{O}_3$ , thermal or plasma-enhanced techniques with various types of precursors have been explored, as summarized in Table 2. Cyclopentadienyl-(Cp-) based precursors,  $\text{Y}(\text{Cp})_3$ ,<sup>34</sup>  $\text{Y}(\text{MeCp})_3$ ,<sup>35</sup>  $\text{Y}(\text{EtCp})_3$ ,<sup>36</sup> and  $\text{Y}(\text{iPrCp})_3$ ,<sup>37</sup> are solid at room temperature (RT) and show high growth rates and reactivity toward water,  $\text{O}_2$  plasma, or  $\text{O}_3$  but suffer from poor thermal stability. O-coordinated  $\beta$ -diketonate  $\text{Y}(\text{thd})_3$ <sup>38</sup> is solid at RT and offers good thermal stability but requires sublimation over 130 °C while exhibiting a growth rate of only 0.23 Å per cycle at a high substrate temperature of 350 °C, and the deposited film was reported to contain carbon 1.4% impurities. To reduce the carbon level in the films, N-coordination and heteroleptic precursors have been evaluated, like  $\text{Y}(\text{DPDMG})_3$ ,<sup>39</sup>  $\text{Y}(\text{iPr}_2\text{-amd})_3$ ,<sup>40</sup> and  $\text{Y}(\text{iPrCp})_2(\text{iPr-amd})$ .<sup>41–43</sup>  $\text{Y}(\text{DPDMG})_3$  is solid at RT and requires sublimation over 130 °C, and the deposited film was reported to contain 3 at % N and 2 at % C impurities.  $\text{Y}(\text{iPr}_2\text{-amd})_3$  is solid at RT, and growth resulted in a film with a high O content (Y/O ratio of 0.5). Whereas solid precursors may have similar thermodynamic vapor pressures with liquid precursors, they are still limited by the slower kinetics of vaporization. Therefore, liquid precursors are preferred for ALD processes. The heteroleptic  $\text{Y}(\text{iPrCp})_2(\text{iPr-amd})$ , which consists of cyclopentadienyl and amidinate ligands, is the only liquid precursor reported so far in the literature. The  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  discussed in this work is also liquid at RT and will be shown to enable a significantly higher growth rate compared with  $\text{Y}(\text{iPrCp})_2(\text{iPr-amd})$ .

Hydrophobic coatings are widely used in applications ranging from industrial components to housewares.<sup>44,45</sup> Inorganic metal oxide hydrophobic coatings have attracted more and more interest because of the better mechanical durability and thermal stability than traditional polymer hydrophobic coatings.<sup>46</sup>  $\text{ZnO}$ <sup>47,48</sup> and  $\text{TiO}_2$ <sup>49,50</sup> are the most researched, but the hydrophobicity was not retained after either high-temperature annealing or UV exposure. Recently, rare-earth oxides were studied as hydrophobic materials. Varanasi et al.<sup>51</sup> and Kim et al.<sup>52</sup> reported that  $\text{Er}_2\text{O}_3$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Tb}_4\text{O}_7$ ,  $\text{Ho}_2\text{O}_3$ ,  $\text{Tm}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ , and  $\text{Lu}_2\text{O}_3$  films show high hydrophobicity with water contact angles >90°. Therefore, it can be concluded that rare-earth oxides have potential applicability as robust hydrophobic surfaces.

In this work, we report the ALD of  $\text{Y}_2\text{O}_3$  films from a liquid heteroleptic precursor, yttrium bis-ethylcyclopentadienyl-diisopropylacetamidinate,  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$ , for which the chemical structure is shown in Figure 1, with thermal ( $\text{H}_2\text{O}$ ) and plasma-enhanced ( $\text{H}_2\text{O}$  plasma and  $\text{O}_2$  plasma) processes, respectively. The ALD process conditions that are required to deposit  $\text{Y}_2\text{O}_3$  films are investigated and optimized. The morphology, conformality, crystallinity, and composition of the grown films are characterized. Finally, we investigated the water wettability of  $\text{Y}_2\text{O}_3$  films and the influence of exposure to different solvents (hexane, toluene, ethanol and isopropanol) on their wetting properties.

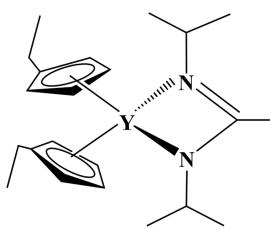


Figure 1. Chemical structure of the  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  precursor.

## 2. EXPERIMENTAL SECTION

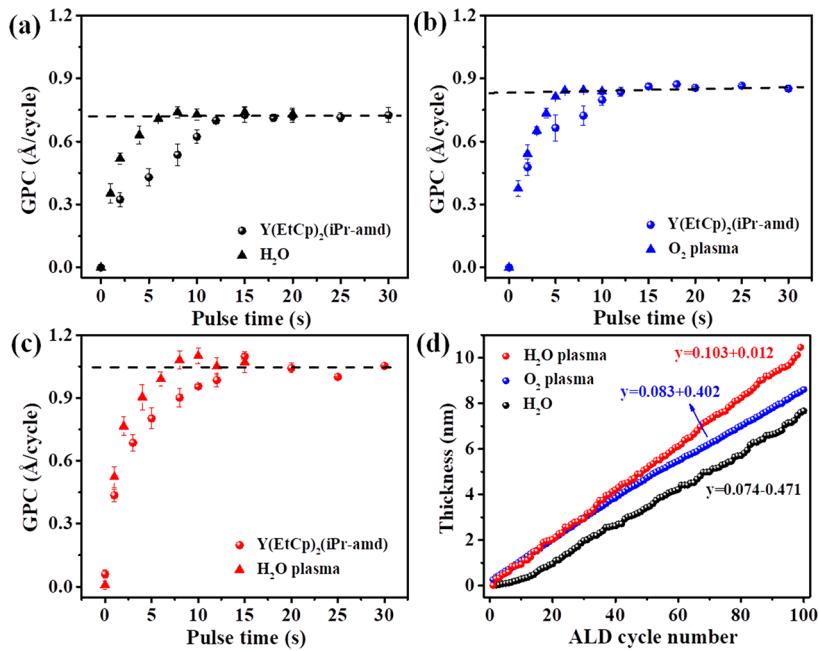
**2.1. ALD of  $\text{Y}_2\text{O}_3$  Thin Films.** The  $\text{Y}_2\text{O}_3$  films were grown on Si (100) substrates with a native oxide layer in a home-built high-vacuum ALD system with a base pressure  $<5 \times 10^{-6}$  mbar.<sup>53–55</sup> In the ALD process,  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  (supplied by AirLiquide) was used as the Y source. As reactant gases, water, oxygen plasma, and water plasma were tested, respectively. The oxygen and water plasma pulses of  $1 \times 10^{-2}$  mbar were performed with a radio frequency remote plasma source of 13.56 MHz and a power of 200 W. The ALD chamber and walls were heated to 100 °C. The  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  precursor was held in a stainless-steel container at 120 °C for optimal vapor pressure without decomposition, and the delivery line was maintained at 130 °C to avoid precursor condensation. Argon was used as the carrier gas for  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  precursor delivery to the ALD chamber. Water was kept at room temperature, and the delivery line was heated to 50 °C.

**2.2. Characterization of  $\text{Y}_2\text{O}_3$  Thin Films.** X-ray reflectometry (XRR) and X-ray diffraction (XRD) patterns were acquired on Bruker D8 diffractometers using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154$  nm). The film thickness and density were determined from XRR by fitting simulated patterns to the measured ones. In situ spectroscopic ellipsometry (SE) measurements were performed with a J. A. Woollam M-2000 ellipsometer with a wavelength from 245 to 1000 nm and using the CompleteEASE software for fitting and data analysis. Surface morphology was characterized by scanning electron microscopy (SEM, Quanta 200F FEI) and atomic force microscopy (AFM) in tapping mode by using a Bruker Dimension Edge system. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific Theta Probe XPS instrument using  $\text{Al K}\alpha$  ( $\lambda = 0.834$  nm) X-rays generated at 15 kV and 70 W and focused to a spot size of 0.3 mm by an MXR1 monochromator gun. The sample surface was etched by  $\text{Ar}^+$  ions at an acceleration voltage of 3 keV and a current of 2  $\mu\text{A}$ . After the measurements, the resulting spectra were analyzed with the CasaXPS software package for the calculation of atomic concentrations. Fourier transform infrared spectroscopy (FT-IR, Vertex V70 Bruker) was used to detect surface chemical functional groups. The data were collected from 600 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

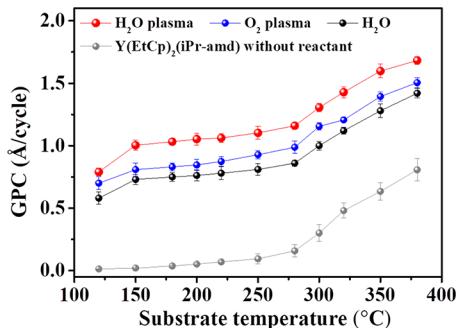
**2.3. Water Contact-Angle Measurements.** The water wettability of ALD  $\text{Y}_2\text{O}_3$  films was evaluated by the sessile drop technique using a contact-angle analyzer (Kruss, DSA30) with deionized water. Contact-angle images were acquired by a charge-coupled device video camera and Drop Shape Analysis software. The volume of each deionized water droplet used was 4  $\mu\text{L}$ . For the thermal stability experiments, ALD  $\text{Y}_2\text{O}_3$  films were annealed in a furnace at 500 °C for 2 h in the static air, after which the contact angle was measured. We used a dipping method to simulate the effect of different ambient conditions on the water wettability of  $\text{Y}_2\text{O}_3$  films.<sup>56</sup> Hexane, toluene, ethanol, and isopropanol were investigated as the dipping solvents, respectively. A 2 cm × 2 cm piece of Si wafer was immersed in the solvent for 24 h, taken out, and left to dry in the air naturally, after which we measured the water contact angle. All of the contact-angle values in this work are reported as the average value recorded by the analyzer system.

## 3. RESULTS AND DISCUSSION

**3.1. ALD of  $\text{Y}_2\text{O}_3$  with Thermal ( $\text{H}_2\text{O}$ ) and Plasma-Enhanced ( $\text{O}_2$  Plasma and  $\text{H}_2\text{O}$  Plasma) Process.** In a true



**Figure 2.** Saturation plots of ALD  $\text{Y}_2\text{O}_3$  films at a substrate temperature 200 °C with  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  and (a)  $\text{H}_2\text{O}$ , (b)  $\text{O}_2$  plasma, and (c)  $\text{H}_2\text{O}$  plasma as a reactant. (d) Film thickness determined by in situ SE versus the ALD cycle number under saturated conditions.



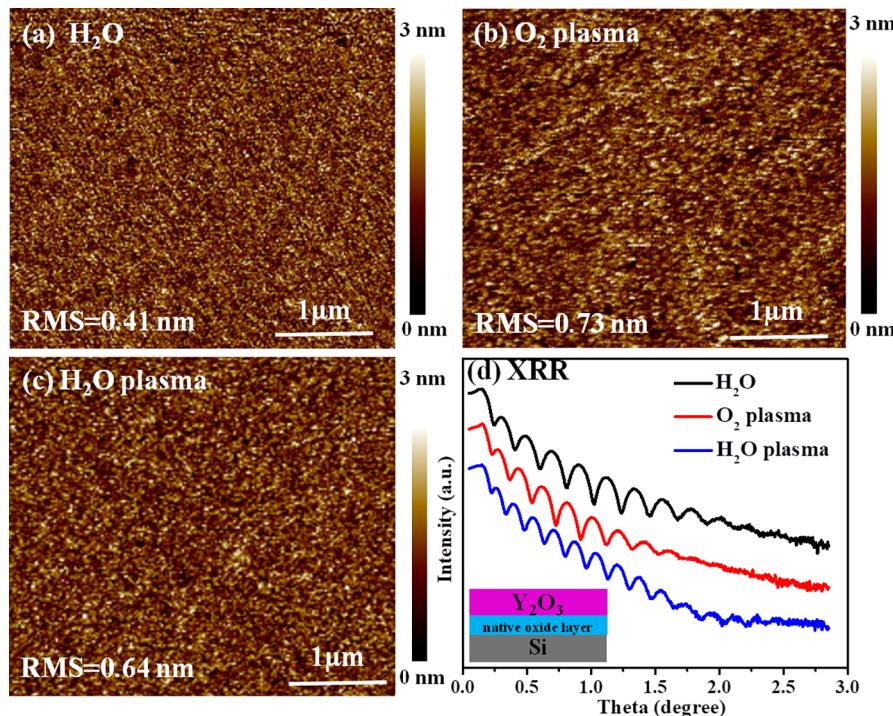
**Figure 3.** GPC as a function of substrate temperature.

ALD process, the precursor surface reactions must be self-terminating and complementary to yield a uniform, conformal, and high-quality  $\text{Y}_2\text{O}_3$  thin film. To verify that the surface reaction for  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  is really self-terminating, the effects of pulse time and substrate temperature were investigated. Figure 2a shows the results by monitoring the growth per cycle (GPC) as a function of both  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  and  $\text{H}_2\text{O}$  pulse times at a constant temperature of 200 °C. The GPC for  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  is saturated when the pulse time exceeds 15 s. This result indicates that  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  undergoes a self-terminating reaction with the  $\text{Y}_2\text{O}_3$  surface prepared by the reaction with  $\text{H}_2\text{O}$ . The  $\text{H}_2\text{O}$  pulse time is saturated when it exceeds at 10 s. This suggests that  $\text{H}_2\text{O}$  undergoes a self-terminating reaction with surface-absorbed  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  molecules. The saturated GPC is 0.74 Å/cycle. The plasma-enhanced process includes  $\text{O}_2$  plasma and  $\text{H}_2\text{O}$  plasma, showing similar behaviors characteristic of a saturated reaction. For the  $\text{O}_2$  plasma case, saturation was achieved after  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  12 s/ $\text{O}_2$  plasma 8 s and yielded a slightly higher GPC of 0.83 Å/cycle (Figure 2b). For  $\text{H}_2\text{O}$  plasma, saturation was achieved at a 1.03 Å/cycle of  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  15 s/ $\text{H}_2\text{O}$  plasma 8 s (Figure 2c). To understand the deposition kinetics, the

thickness was monitored as a function of the cycle number under the saturation conditions of  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  and the reactant at a constant temperature of 200 °C (Figure 2d). For the water thermal process, growth inhibition of ~15 cycles could be observed, but after ~15 cycles, the film thickness increased linearly as a function of the number of ALD cycles. The slope of the linear line is the GPC value, which corresponds to the GPC of the saturation time test (Figure 2a). For the plasma process ( $\text{O}_2$  plasma and  $\text{H}_2\text{O}$  plasma), no growth inhibition was observed, and the slopes were also consistent with the GPC mentioned under the saturated conditions (Figure 2b,c).

As shown in Figure 3, all three reactants ( $\text{H}_2\text{O}$ ,  $\text{O}_2$  plasma, and  $\text{H}_2\text{O}$  plasma) have the same type of temperature window, with a nearly constant GPC value between 150 and 300 °C. In addition, there is almost no growth when only  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  pulses without any reactant (gray dots), which indicates that the  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  precursor is stable and does not decompose between 150 and 300 °C. Below 150 °C, the GPC decreases slightly, whereas above 300 °C the GPC increases abruptly with increasing substrate temperature. This suggests that the  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  precursor molecules are chemisorbed with self-saturation on the surface at 150–300 °C, whereas an incomplete reaction occurs below 150 °C, and accelerated decomposition occurs above 300 °C. So in the mention of this work, we performed deposition at a substrate temperature of 200 °C.

Figure 4 shows the representative AFM images and corresponding XRR patterns. The resulting films were acquired after 250 ALD cycles of  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  with  $\text{H}_2\text{O}$ ,  $\text{O}_2$  plasma, and  $\text{H}_2\text{O}$  plasma, respectively. For the AFM images, the scanned area is  $3 \times 3 \mu\text{m}^2$ . The surface morphology appears homogeneous and exhibits relatively low root-mean-square (RMS) roughness of ~0.41 nm with  $\text{H}_2\text{O}$  (Figure 4a), ~0.73 nm with  $\text{O}_2$  plasma (Figure 4b), and ~0.64 nm with  $\text{H}_2\text{O}$  plasma (Figure 4c). From XRR and fitting results (Figure 4d), the density of the film is 4.88 g/cm<sup>3</sup> with  $\text{H}_2\text{O}$  as reactant,

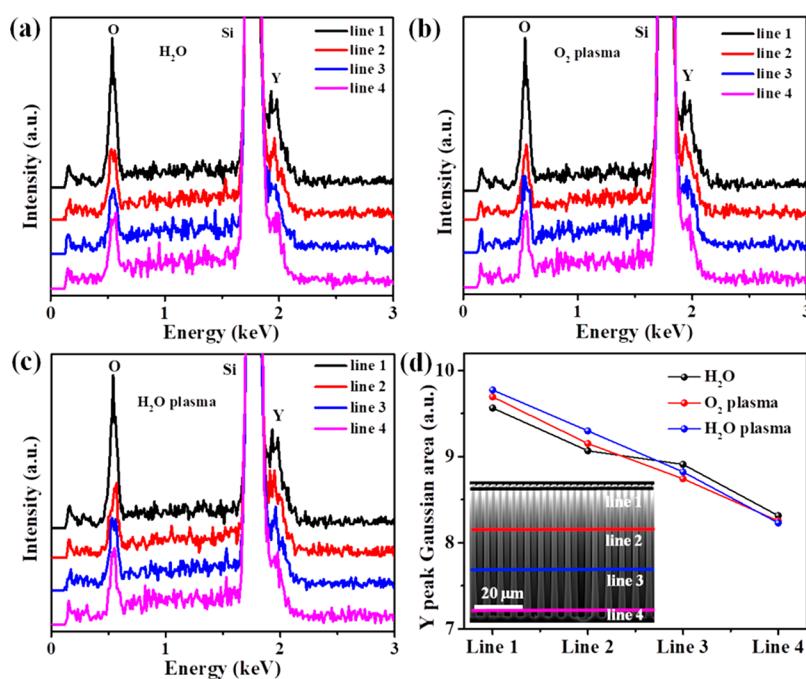


**Figure 4.** AFM images of Y<sub>2</sub>O<sub>3</sub> films for Y(EtCp)<sub>2</sub>(iPr-amd) with (a) H<sub>2</sub>O, (b) O<sub>2</sub> plasma, and (c) H<sub>2</sub>O plasma and (d) the corresponding XRR patterns.

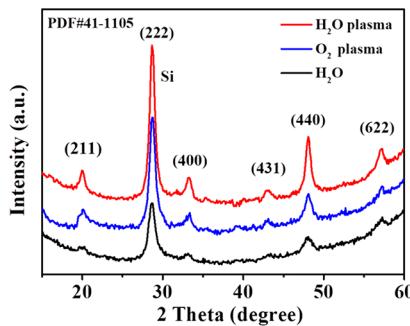
**Table 1. Thickness, Density, and Roughness of Y<sub>2</sub>O<sub>3</sub> Films after 250 ALD Cycles<sup>a</sup>**

ALD reactant	thickness determined by in situ SE (nm)	thickness determined by XRR (nm)	density determined by XRR(g/cm <sup>3</sup> )	roughness determined by XRR (nm)	roughness determined by AFM (nm)
H <sub>2</sub> O	18.5	19.4	4.88	0.43	0.41
O <sub>2</sub> plasma	21.0	21.6	4.97	0.95	0.73
H <sub>2</sub> O plasma	25.7	24.7	4.92	0.82	0.64

<sup>a</sup>Results are from measurements of SE, XRR, and AFM.



**Figure 5.** EDX spectra of the Y<sub>2</sub>O<sub>3</sub> coating layer at four different positions in silicon micropillar arrays (panel d inset) of (a) with H<sub>2</sub>O, (b) O<sub>2</sub> plasma, and (c) H<sub>2</sub>O plasma. (d) Y peak Gaussian area at four different depths acquired from EDX line scans.



**Figure 6.** XRD patterns of  $\text{Y}_2\text{O}_3$  films for  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  with  $\text{H}_2\text{O}$ ,  $\text{O}_2$  plasma, and  $\text{H}_2\text{O}$  plasma.

4.97  $\text{g}/\text{cm}^3$  with  $\text{O}_2$  plasma, and 4.92  $\text{g}/\text{cm}^3$  with  $\text{H}_2\text{O}$  plasma. These values are lower than the value of 5.03  $\text{g}/\text{cm}^3$  reported for the bulk density of  $\text{Y}_2\text{O}_3$ , which is probably related to the inclusion of  $-\text{OH}$ . The densities for the plasma-enhanced processes ( $\text{O}_2$  plasma and  $\text{H}_2\text{O}$  plasma) are slightly higher than that of the thermal process. The thickness determined by XRR is similar to the results of SE, indicating that the Cauchy model used for analyzing the *in situ* SE data is indeed suitable. The roughness determined by XRR is also close to the results of AFM. All results are summarized in **Table 1**.

Conformality is an important aspect of ALD process development, as it is the ability to conformally deposit a film on a substrate, especially for the 3D complex structures with ideally no variation in thickness along with the structure.<sup>29,30</sup> Here the conformality of the coating was investigated by depositing a 10 nm  $\text{Y}_2\text{O}_3$  film with  $\text{H}_2\text{O}$ ,  $\text{O}_2$  plasma, and  $\text{H}_2\text{O}$  plasma, respectively, on a high-aspect-ratio (AR) structure consisting of silicon micropillars with an AR of 25 (namely, 2  $\mu\text{m}$  wide, 50  $\mu\text{m}$  high, spaced 4  $\mu\text{m}$  center-to-center on a square lattice) etched into a silicon substrate, shown in **Figure 5**. The as-deposited samples were measured with SEM and energy-dispersive X-ray spectroscopy (EDX) to evaluate the amounts of yttrium at different depths (**Figure 5d**, inset). The EDX spectra in **Figure 5a** show the  $\text{Y}_2\text{O}_3$  coating from  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  with  $\text{H}_2\text{O}$  and clearly demonstrate the Y peak, indicating the presence of  $\text{Y}_2\text{O}_3$ . For the  $\text{O}_2$  plasma (**Figure 5b**) and  $\text{H}_2\text{O}$  plasma (**Figure 5c**), the samples show the same trend from top to bottom on the micropillars. To distinguish the Si and Y signals, we fitted the EDX spectra with a Gaussian equation (see the *Supporting Information*) to get the Y peak area as a function of depth along the pillars. At the second marker on the cross-sectional SEM image (line 2), which is 17  $\mu\text{m}$  deep along the pillars, the peak area of Y maintained  $\sim 94\%$  of the initial value on line 1, and even at the bottom of the pillars, the Y peak area is still  $> 85\%$  of its initial

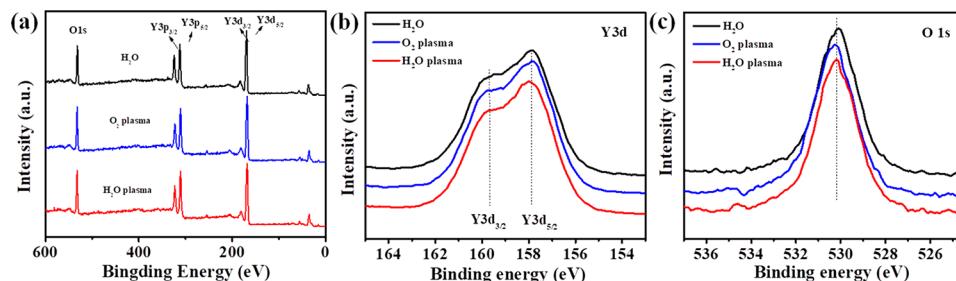
value (**Figure 5d**). These results indicated that for the thermal ( $\text{H}_2\text{O}$ ) and plasma-enhanced ( $\text{O}_2$  plasma and  $\text{H}_2\text{O}$  plasma) processes, the pillars are fully coated with a reasonable conformality, although the amounts are not perfectly constant as a function of the penetration depth.

The crystalline structure of 30 nm  $\text{Y}_2\text{O}_3$  films on Si substrates was determined by XRD. All three investigated reactants yield polycrystalline cubic  $\text{Y}_2\text{O}_3$  (JCPDS 41-1105).<sup>38</sup> The corresponding lattice planes are labeled for the different diffractions peaks in **Figure 6**. It demonstrates that the normal direction of the (222) plane is the most obvious, whereas the (211), (400), (431), (440), and (622) planes of cubic  $\text{Y}_2\text{O}_3$  are also clearly observed.

The chemical binding environments in as-deposited  $\text{Y}_2\text{O}_3$  films were studied by XPS, and the results are shown in **Figure 7**. All of the data were collected after  $\text{Ar}^+$  beam sputtering 20 s from the surface to remove carbon surface contaminants. **Figure 7a** shows that all of the films deposited using different processes contain Y and O, whereas no N is detected, suggesting that the N-coordination from the  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  molecule was not retained in the film. After sputtering, no C contamination in the bulk of the films could be detected. As shown in the Y 3d core-level spectrum of the as-deposited films (**Figure 7b**), the peak at 157.6 eV can be assigned to  $\text{Y}^{3\text{d}_{5/2}}$ , and the shoulder peak at 159.6 eV is identified as  $\text{Y}^{3\text{d}_{3/2}}$ . In **Figure 7c**, the peaks assigned to O 1s for the three reactants have some slight variations around 530.1 eV, possibly due to the different contents of  $\text{Y}-\text{O}$  and  $\text{Y}-\text{OH}$ .<sup>57</sup> The impurity content of C is  $< 0.5$  at %, and the atomic ratio of Y/O is 0.57 to 0.60 for the  $\text{Y}_2\text{O}_3$  films by the three processes, indicating the deposition of a high-purity  $\text{Y}_2\text{O}_3$  film.

From the above characterizations, we know that the as-deposited  $\text{Y}_2\text{O}_3$  films are pure (with C and N impurity levels below 0.5 at %) and smooth and have a polycrystalline cubic structure. To make a comprehensive assessment of our results, we summarized existing literature on the ALD of  $\text{Y}_2\text{O}_3$  using different precursors in **Table 2**. The  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  used in this research and  $\text{Y}(\text{iPrCp})_2(\text{iPr-amd})$  are the only liquid precursors reported so far. When compared with  $\text{Y}-(\text{iPrCp})_2(\text{iPr-amd})$ , the  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  explored in this work was demonstrated to offer a significantly higher growth rate as well as a wider temperature window. All other precursors listed in **Table 2** are solids, require a high source temperature, and suffer from a low GPC or from C/N impurities in the deposited films.

**3.2. Water Wettability of  $\text{Y}_2\text{O}_3$  Films.** **Figure 8** shows the measured water contact angle values as a function of the  $\text{Y}_2\text{O}_3$  film thickness varying from 5 to 30 nm for the investigated three different ALD processes. The water contact angle of the Si substrate with a native oxide layer is  $\sim 40^\circ$  without ALD

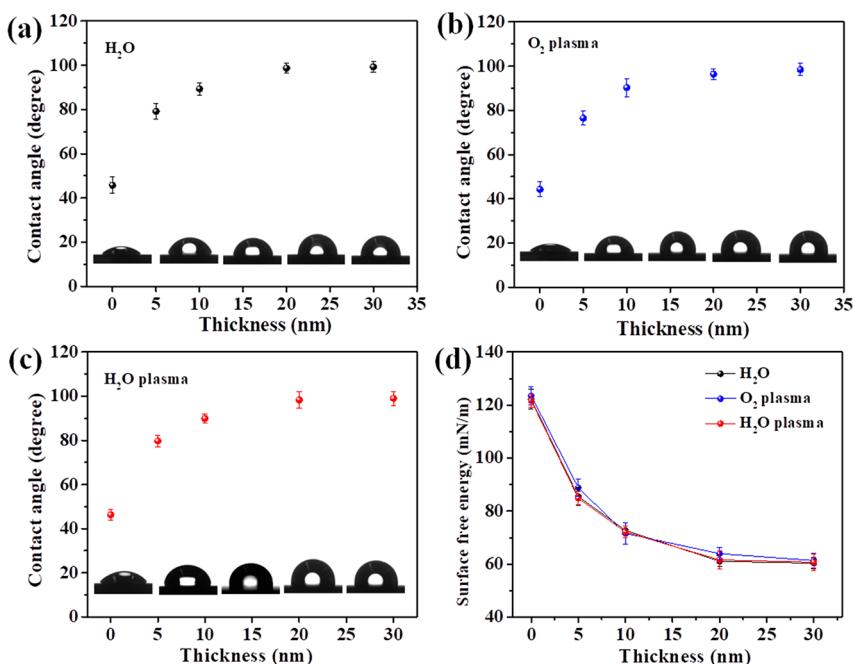


**Figure 7.** XPS spectra of  $\text{Y}_2\text{O}_3$  films of (a) survey, (b) Y 3d, and (c) O 1s for  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  with  $\text{H}_2\text{O}$ ,  $\text{O}_2$  plasma, and  $\text{H}_2\text{O}$  plasma.

**Table 2.** ALD of  $\text{Y}_2\text{O}_3$  Using Different Precursors and Relevant Process and Film Properties

precursor + reactant	precursor state at RT	bubbler temp (°C)	substrate temp (°C)	GPC (Å/cycle)	impurity (at %)	Y/O (at)	ref
$\text{Y}(\text{Cp})_3 + \text{H}_2\text{O}$	solid	150	250–400	1.5–1.7	C 0.5, 300 °C	~0.68, 300 °C	34
$\text{Y}(\text{MeCp})_3 + \text{O}_2$ plasma	solid	145	175–325	1.1–1.3	C 0.85, 300 °C	not reported	35
$\text{Y}(\text{EtCp})_3 + \text{H}_2\text{O}$	solid	120	250–280	1.5–1.7	C < 0.5, 250 °C	~0.64, 250 °C	36
$\text{Y}(\text{iPrCp})_3 + \text{O}_3$	solid	130	245–300	1.6–1.8	C < 0.5, 270 °C	~0.29, 270 °C	37
$\text{Y}(\text{thd})_3 + \text{O}_3$	solid	120	250–350	0.23	C 1.0–1.4, 350 °C	~0.62, 350 °C	38
$\text{Y}(\text{DPDMG})_3$	solid	130	175–250	1.1	C, 2; N 3, 225 °C	~0.5, 225 °C	39
$\text{Y}(\text{iPr}_2\text{-amd})_3 + \text{H}_2\text{O}$	solid	120	150–280	0.8	C, N < 0.5, 280 °C	~0.5, 280 °C	40
$(\text{iPrCp})_2\text{Y}(\text{iPr-amd}) + \text{H}_2\text{O}^a$	liquid	150	350–450	0.6	C, N < 0.5, 350 °C	~0.62, 350 °C	41
$\text{Y}(\text{iPrCp})_2 (\text{iPr-amd})^a + \text{H}_2\text{O}$	liquid	130	200–350	1.3	C 3.7 ± 0.4, 300 °C	~0.56, 300 °C	42
					C 5.6 ± 0.5, 300 °C	~0.48, 300 °C	
$\text{Y}(\text{iPrCp})_2(\text{N-iPr-amd}) + \text{H}_2\text{O}^a$	liquid	130	180–200	0.4	C, N ~0.1, 180 °C	not reported	43
$\text{Y}(\text{EtCp})_2 (\text{iPr-amd}) + \text{H}_2\text{O}$	liquid	120	150–300	0.74	C, N < 0.5, 200 °C	~0.57, 200 °C	this work
					0.83	C, N < 0.5, 200 °C	
					1.03	C, N < 0.5, 200 °C	

<sup>a</sup> $\text{Y}(\text{iPrCp})_2(\text{N-iPr-amd})$ ,  $(\text{iPrCp})_2\text{Y}(\text{iPr-amd})$ , and  $\text{Y}(\text{iPrCp})_2(\text{iPr-amd})$  have the same chemical structure.

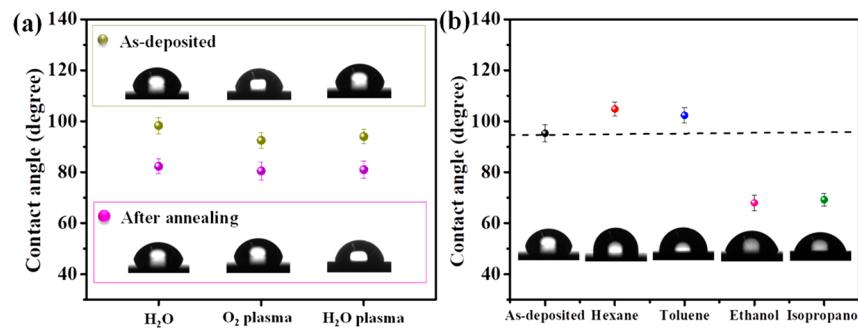


**Figure 8.** Water contact angles of as-deposited and  $\text{Y}_2\text{O}_3$  films with a thickness of 5, 10, 20, and 30 nm with (a)  $\text{H}_2\text{O}$ , (b)  $\text{O}_2$  plasma, (c)  $\text{H}_2\text{O}$  plasma, and (d) the surface free energy.

growth of  $\text{Y}_2\text{O}_3$ , showing the typically hydrophilic property. For the  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  with  $\text{H}_2\text{O}$  process (Figure 8a), the 20 and 30 nm  $\text{Y}_2\text{O}_3$  films yielded a water contact angle of ~95°. The water contact angle reduced to 87° for 10 nm  $\text{Y}_2\text{O}_3$  ALD films and even to 77° for 5 nm films. A similar thickness dependency was also observed for the other two reactants,  $\text{O}_2$  plasma (Figure 8b) and  $\text{H}_2\text{O}$  plasma (Figure 8c). Figure 8d shows the surface free energy calculated from the water contact angle of ALD  $\text{Y}_2\text{O}_3$  films with different thicknesses by the Young–Dupré equation<sup>58</sup>

$$W = \gamma(1 + \cos \theta)$$

where  $W$  is the surface free energy (N/m),  $\gamma$  is the surface tension of water, which is a constant of 0.072 J/m<sup>2</sup>, and  $\theta$  is the water contact angle. The three reactants show similar results. An inverse relationship between water contact angle values and the surface free energy is observed with increasing the thickness of  $\text{Y}_2\text{O}_3$ . The thinner the film, the smaller the water contact angle and the higher the surface free energy, which is more easily wetted with water. All of the investigated films with a thickness >20 nm have a stable water contact angle



**Figure 9.** Water contact angles of as-deposited 30 nm thick  $\text{Y}_2\text{O}_3$  surfaces (a) before and after annealing at 500 °C for 2 h in static air and (b) after treatment with hexane, toluene, ethanol, and isopropanol for 24 h.

of  $\sim 95^\circ$ , which indicates that they are with a hydrophobic surface. To obtain a stable water contact angle, the work described later about the water wettability was performed using 30 nm films.

To evaluate the effect of ALD post-annealing on the wettability of the  $\text{Y}_2\text{O}_3$  surfaces, we annealed the ALD  $\text{Y}_2\text{O}_3$  films at 500 °C for 2 h in static air. As shown in Figure 9a, the water contact angles of annealed ALD  $\text{Y}_2\text{O}_3$  films were slightly smaller than those of as-deposited samples but still maintained values around  $80^\circ$ , which indicates the quite robust behavior of the surfaces wettabilities.<sup>59</sup> The exact nature and composition of the surface are important factors for the material's water wettability. Adsorbed molecules can have a significant impact on the water contact angle.<sup>60–63</sup> Therefore, we investigated the influence of four different solvents (hexane, toluene, ethanol, and isopropanol) on the water contact angle of  $\text{Y}_2\text{O}_3$  films. After immersing  $\text{Y}_2\text{O}_3$  ALD films in these solvents for 24 h, the water wettability was evaluated. Figure 9b demonstrates that exposure of the  $\text{Y}_2\text{O}_3$  surface to typical nonpolar solvents like hexane and toluene enhanced the hydrophobicity, as the water contact angle increased to 104.8 and 102.3°, respectively, which is higher than the value of  $95^\circ$  measured for the as-deposited  $\text{Y}_2\text{O}_3$ . Exposure to polar solvents like ethanol and isopropanol induced a hydrophilic effect, decreasing the water contact angle to 68 and 69.2°, respectively. The FT-IR data of as-deposited  $\text{Y}_2\text{O}_3$  and after exposure to hexane, toluene, ethanol, and isopropanol are shown in Figure S3.

## 4. CONCLUSIONS

We have successfully fabricated ALD– $\text{Y}_2\text{O}_3$  films using a liquid heteroleptic Y precursor,  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$ , and investigated  $\text{H}_2\text{O}$ ,  $\text{O}_2$  plasma, and  $\text{H}_2\text{O}$  plasma as reactants, respectively. The growth of the  $\text{Y}_2\text{O}_3$  films with each investigated reactant can get saturated with a similar ALD window from 150 to 300 °C but with a different growth rate. All of the as-deposited  $\text{Y}_2\text{O}_3$  films are pure and smooth and have a polycrystalline cubic structure. Compared with other Y precursors,  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  is a liquid, requires a lower source temperature ( $\sim 120$  °C), offers a wide temperature window for ALD (150 to 300 °C), and enables the deposition of high-purity films (C/N impurities below 0.5 at %) at a high growth rate (0.74 to 1.03 Å/cycle), which renders it a promising precursor for industrial applications. The as-deposited  $\text{Y}_2\text{O}_3$  films are hydrophobic with a water contact angle of  $\sim 95^\circ$ . The hydrophobicity was retained during post-ALD annealing and could be altered by exposure to various solvents.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.9b18412>.

Figure S1. SEM image of 3D pillars coated with the  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$  and  $\text{H}_2\text{O}$  process and the EDX spectra for line scans as indicated on the SEM image. Figure S2. Gaussian fit spectra in Figure S1. Table S1. Y Gaussian peak area corresponding to the position of the Figure S1 SEM image. Table S2. Y peak area corresponding to the different depths on the cross-sectional SEM image for the  $\text{Y}(\text{EtCp})_2(\text{iPr-amd})$   $\text{O}_2$  plasma and  $\text{H}_2\text{O}$  plasma process. Figure S3. FT-IR spectra of a 30 nm thick  $\text{Y}_2\text{O}_3$  film, as-deposited and after exposure to hexane, toluene, ethanol, and isopropanol for 24 h (PDF)

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### Notes

The authors declare no competing financial interest.

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