

# Atomic Layer Deposition of Ruthenium Dioxide Based on Redox Reactions between Alcohols and Ruthenium Tetroxide

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Cite This: <https://doi.org/10.1021/acs.chemmater.2c02292>



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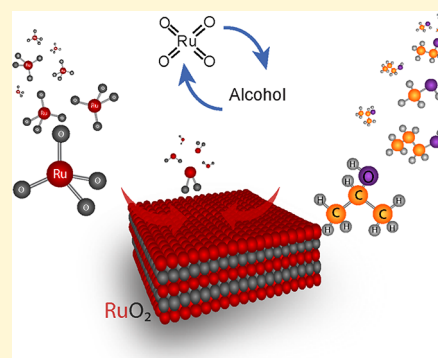


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**ABSTRACT:** Atomic layer deposition (ALD) of ruthenium dioxide ( $\text{RuO}_2$ ) thin films using metalorganic precursors and  $\text{O}_2$  can be challenging because the  $\text{O}_2$  dose needs to be precisely tuned and significant nucleation delays are often observed. Here, we present a low-temperature ALD process for  $\text{RuO}_2$  combining the inorganic precursor ruthenium tetroxide ( $\text{RuO}_4$ ) with alcohols. The process exhibits immediate linear growth at  $1 \text{ \AA}/\text{cycle}$  when methanol is used as a reactant at deposition temperatures in the range of  $60\text{--}120 \text{ }^\circ\text{C}$ . When other alcohols are used, the growth per cycle increases with an increasing number of carbon atoms in the alcohol chain. Based on X-ray photoelectron spectroscopy (XPS) and conventional X-ray diffraction, the deposited material is thought to be amorphous  $\text{RuO}_2$ . Interestingly, pair distribution function (PDF) analysis shows that a structural order exists up to  $2\text{--}3 \text{ nm}$ . Modeling of the PDF suggests the presence of Ru nanocrystallites within a predominantly amorphous  $\text{RuO}_2$  matrix. Thermal annealing to  $420 \text{ }^\circ\text{C}$  in an inert atmosphere crystallizes the films into rutile  $\text{RuO}_2$ . The films are conductive, as is evident from a resistivity value of  $230 \mu\Omega\text{-cm}$  for a  $20 \text{ nm}$  film grown with methanol, and the resistivity decreased to  $120 \mu\Omega\text{-cm}$  after crystallization. Finally, based on in situ mass spectrometry, in situ infrared spectroscopy, and in vacuo XPS studies, an ALD reaction mechanism is proposed, involving partial reduction of the  $\text{RuO}_2$  surface by the alcohol followed by reoxidation of the surface by  $\text{RuO}_4$  and concomitant deposition of  $\text{RuO}_2$ .



## INTRODUCTION

Ruthenium dioxide ( $\text{RuO}_2$ ) is known for its very low resistivity value ( $\sim 35 \mu\Omega\text{-cm}$ ), high chemical stability, and a work function even higher than metallic Ru ( $5.1 \text{ eV}$  for  $\text{RuO}_2$  and  $4.1 \text{ eV}$  for Ru).<sup>1–3</sup>  $\text{RuO}_2$ , in both amorphous and crystalline forms, is interesting for various applications, especially in electrochemical devices.<sup>4–8</sup> Crystalline  $\text{RuO}_2$  is a promising material for gas-evolving reactions,<sup>9–11</sup> such as hydrogen, oxygen, and chlorine evolutions, whereas amorphous ruthenium dioxide is suitable for electrochemical pseudocapacitor applications.<sup>5,8,12,13</sup> Over the past 40 years, it has been used as a dimensionally stable anode (DSA) for chlorine-alkali electrocatalysis.<sup>14–16</sup>  $\text{RuO}_2$ -based catalysts have emerged as promising heterogeneous catalysts for low-temperature dehydrogenation of molecules like  $\text{NH}_3$ ,<sup>17</sup>  $\text{HCl}$ ,<sup>18</sup> and methanol.<sup>19</sup> Among the different transition metal oxides (TMOs),  $\text{RuO}_2$  has attracted immense attention for supercapacitor applications owing to its high conductivity, excellent cyclic performance, and high specific capacitance.<sup>2,20–23</sup> To avoid the leakage current, a very high work function value for the metal electrode is necessary. This fact gives a clear advantage for  $\text{RuO}_2$  as electrodes for the capacitors in DRAM over the currently integrated TiN ( $\sim 4.2 \text{ eV}$ ) and even metallic Ru.<sup>1</sup> In addition, it has been used as a positive electrode material for

lithium ion batteries,<sup>24,25</sup> and thin  $\text{RuO}_2$  films act as excellent barriers against  $\text{O}_2$  diffusion.<sup>26</sup>

$\text{RuO}_2$  thin films have been grown for various purposes using techniques such as direct deposition by magnetron sputtering<sup>27,28</sup> or reactive sputtering of Ru.<sup>29</sup> The other commonly employed techniques are pulsed laser deposition,<sup>30,31</sup> electro-deposition from aqueous solution<sup>32</sup> or cyclic voltammetry,<sup>33</sup> sol-gel spin coating method,<sup>34</sup> metal organic chemical vapor deposition,<sup>35,36</sup> chemical vapor deposition (CVD),<sup>37,38</sup> pulsed-CVD,<sup>39</sup> and atomic layer deposition (ALD).<sup>40–50</sup> Among those techniques to prepare  $\text{RuO}_2$  thin films, ALD offers uniform and conformal growth over three-dimensional substrates without compromising the precise control over thickness and composition.<sup>51–53</sup>

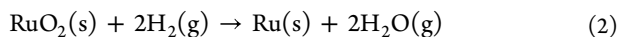
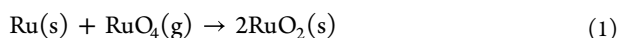
Previous reports on ALD of  $\text{RuO}_2$  employed organometallic precursors such as bis(cyclopentadienyl) Ru(II) [ $\text{RuCp}_2$ ],<sup>48</sup> bis(ethylcyclopentadienyl) Ru(II) [ $\text{Ru}(\text{EtCp})_2$ ],<sup>43,46,47,50,54,55</sup> and bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooc-

Received: July 28, 2022

Revised: September 9, 2022

tadiene) Ru(III) [Ru(thd)2(cod)],<sup>56</sup> the most commonly used precursor being [Ru(EtCp)<sub>2</sub>]. Recent reports make use of zero-valent ruthenium complexes like (1,5-hexadiene)(1-isopropyl-4-methylbenzene)ruthenium,<sup>40</sup> ( $\eta^4$ -2,3-dimethylbutadiene)(tricarbonyl)ruthenium,<sup>41</sup> and (ethylbenzene)(1,3-butadiene)ruthenium.<sup>44</sup> In almost all cases, the co-reactant used is molecular O<sub>2</sub>. The reaction mechanism proposed by Aaltonen et al. illustrates the main challenge for depositing RuO<sub>2</sub> by ALD using an organometallic precursor and O<sub>2</sub> gas.<sup>57</sup> The authors found that the precursor molecules are partially oxidized into H<sub>2</sub>O and CO<sub>2</sub> by (sub) surface oxygen atoms upon adsorption and the remaining part of the ligands are oxidized during the subsequent O<sub>2</sub> pulse. All the oxygen that adsorbs on the surface is used for the oxidation reaction with the precursor such that metallic ruthenium, and not ruthenium dioxide, is formed in the resulting films. Hence, several authors reported the necessity of high oxygen partial pressures to synthesize RuO<sub>2</sub> by ALD.<sup>46,50</sup> In addition to this, the formation of RuO<sub>2</sub> relies on different parameters including the deposition temperature<sup>58</sup> and the amount of Ru precursor adsorbed on the surface.<sup>46</sup>

Given the importance of RuO<sub>2</sub>, it is highly desirable to have ALD chemistries that offer solutions to the abovementioned drawbacks. In this scenario, we report the synthesis of RuO<sub>2</sub> using ruthenium tetroxide (RuO<sub>4</sub>) as the precursor and an alcohol as the co-reactant. In our previous works, we have demonstrated the suitability of RuO<sub>4</sub> as a Ru source for ALD of metallic Ru films, in combination with H<sub>2</sub><sup>59</sup> or H<sub>2</sub> plasma<sup>60</sup> as the co-reactant. The proposed reaction mechanism for the thermal process is given below:



The first reaction (1) shows the formation of a RuO<sub>2</sub> layer on a Ru surface when exposed to RuO<sub>4</sub>. This reaction saturates because RuO<sub>4</sub> cannot dissociate on a RuO<sub>2</sub> surface. The deposited RuO<sub>2</sub> surface layer is then reduced to metallic Ru by H<sub>2</sub> in the next reaction (2).

In this work, we use the same Ru source, i.e., RuO<sub>4</sub>, but in combination with alcohols to deposit RuO<sub>2</sub> films by ALD. Alcohols such as ethanol have been previously used as a reducing agent to remove unwanted CuO<sub>x</sub> layers formed on metallic Cu films upon ambient exposure.<sup>61</sup> Some of the ALD processes in the literature have also benefited from the use of alcohols as a reducing agent.<sup>62–64</sup> So, the starting hypothesis in this work was to use alcohols to partially reduce the RuO<sub>2</sub> surface formed upon the introduction of RuO<sub>4</sub>. This would create a surface that is again oxidizable, enabling reaction with RuO<sub>4</sub> and resulting in the deposition of stoichiometric RuO<sub>2</sub>. Indeed, the use of methanol in combination with RuO<sub>4</sub> results in deposition of RuO<sub>2</sub> with a growth per cycle (GPC) of 1 Å per cycle, a value which is shown to increase by choosing a higher alcohol homologue such as ethanol, 1-propanol, and 2-propanol. The use of RuO<sub>4</sub> as the Ru source, which has a high vapor pressure and is liquid at room temperature, alleviates the need for organometallic precursors that are less reactive and require comparatively higher temperatures to convert into the gaseous phase. The issues with the careful tuning of the O<sub>2</sub> partial pressures are avoided by the oxidizing properties of RuO<sub>4</sub>, combined with the alcohol as a gentle reducing agent. The processes introduced in this work (different alcohols in combination with RuO<sub>4</sub>) do not show significant nucleation

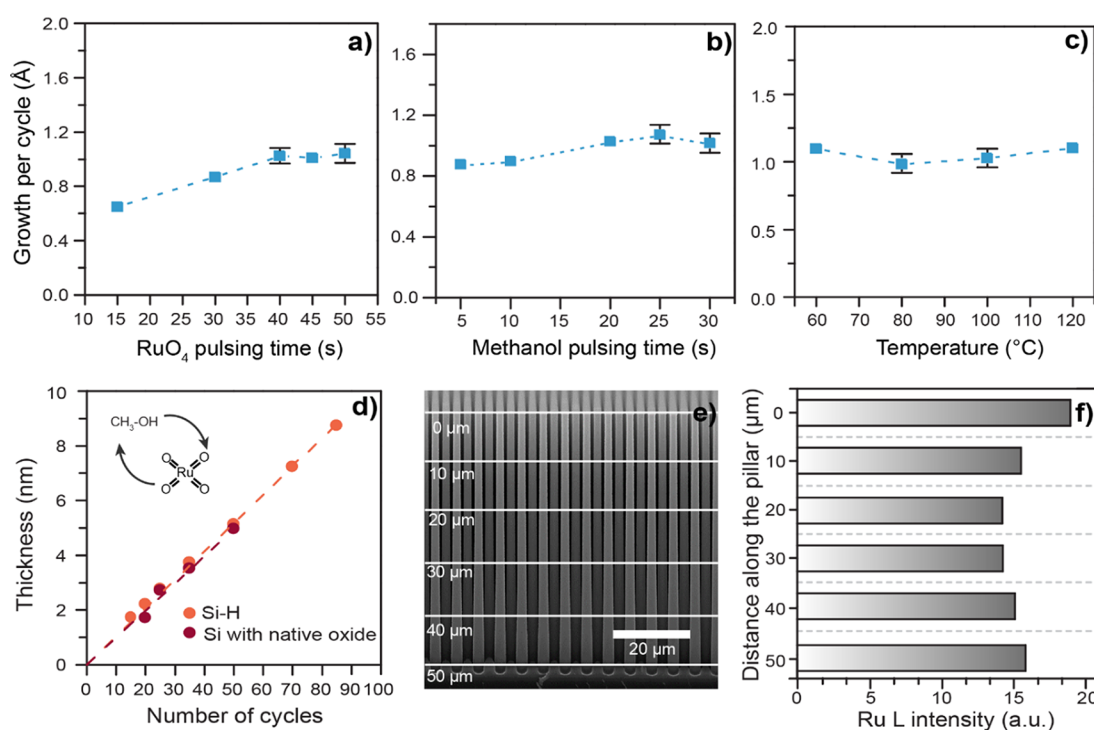
delays, whereas most processes reported so far suffer from very long nucleation delays,<sup>41</sup> up to several hundreds of cycles in some cases. Moreover, with deposition temperatures in the range of 60–120 °C, the RuO<sub>4</sub>/alcohol processes are compatible with temperature-sensitive substrates, offering another important advantage over the majority of processes that use metalorganic Ru precursors.

## EXPERIMENTAL SECTION

**ALD Synthesis.** The RuO<sub>2</sub> thin films were grown in a custom-built ALD reactor described elsewhere.<sup>65</sup> The setup is equipped with a turbomolecular pump, which is connected to the vacuum chamber through a gate valve, such that a base pressure of 10<sup>−6</sup> mbar is achieved. The sample is heated inside the chamber with a resistive heater. A solution of RuO<sub>4</sub> in a methyl-ethyl fluorinated solvent (ToRuS), developed and produced by Air Liquide, was used as the Ru source.<sup>66</sup> The alcohols used as the reactants in this work, namely, methanol (99%), ethanol (98%), 1-propanol (99%), and 2-propanol (98%), were purchased from Sigma Aldrich. No carrier gas was used to supply the alcohols or RuO<sub>4</sub> to the chamber. The precursor containers were not heated owing to the high vapor pressure of both precursors. The inlets of both precursors were kept at 65 °C. The chamber walls were kept at 90 °C to avoid condensation of the precursors. During both the precursor pulses and the co-reactant pulses, the gate valve to the turbomolecular pump was kept open, and the flow of the precursor gas was regulated by a needle valve, which caused the reactor pressure to increase to 4 × 10<sup>−3</sup> mbar. H-terminated Si (Si-H) substrates were obtained by dipping Si with native oxide in a 2.5% hydrogen fluoride solution for approximately 60 s and after that, they were put in deionized water to wash away any remaining fluoride impurities. Then, they were immediately transferred to the reactor for depositions. Metallic Ru films that will be described in this work are prepared by the RuO<sub>4</sub>-H<sub>2</sub> ALD process, as reported before.<sup>59</sup>

**Material and Process Characterization.** X-ray reflectivity (XRR) and X-ray diffraction (XRD) measurements were performed using a Bruker D8 diffractometer<sup>67,68</sup> with Cu K $\alpha$  radiation. The post-annealing of the deposited films in He and air was performed in a custom-built heating chamber mounted on a Bruker D8 diffractometer to enable in situ XRD characterization.<sup>69</sup> A linear detector was used to collect the diffracted X-rays at 2 s time intervals. SEM was performed using an FEI Quanta 200F instrument combined with an EDAX silicon drift detector to perform energy-dispersive X-ray spectroscopy (EDX). To verify the conformality of the RuO<sub>2</sub> ALD process, silicon micropillar substrates were used, which were prepared using the Bosch Deep Reactive Ion Etching process.<sup>70</sup> Atomic force microscopy (AFM) was used in tapping mode to determine the roughness of the samples and was done using a Bruker Dimension Edge system.

Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements of the samples were performed at the NCD-SWEET beamline of the ALBA Synchrotron, Spain. The X-ray energy used was 12.4 keV with a collimated beam size at the sample position of 50 × 150  $\mu\text{m}^2$  ( $V \times H$ ). The X-ray beam incident angle was set at 0.5°, and a Rayonix Ix255-HS area detector with a pixel size of 88.54 × 88.54  $\mu\text{m}^2$  was employed to record the scattering pattern. The reciprocal space was calibrated using Cr<sub>2</sub>O<sub>3</sub> as the standard, obtaining the detector tilts and a sample-to-detector distance of 101.44 mm. Grazing incidence total X-ray scattering measurements<sup>71</sup> of the samples were performed at the ID15A beamline of the European Synchrotron Radiation Facility (ESRF), France.<sup>72</sup> The beam energy was 64 keV, and the beam was focused to a size of 2.5–3  $\mu\text{m}$  ( $V$ ) by 6  $\mu\text{m}$  ( $H$ ) using refractive lenses in the beam path 3 m before the sample. Data were acquired with a Pilatus3 X CdTe 2M detector for an incidence angle of the order of 0.025–0.035° and a sample-to-detector distance of 222.29 mm, calibrated using NIST standard Cr<sub>2</sub>O<sub>3</sub> powder. Measurements of a blank Si sample were also acquired for background subtraction. The intense diffraction spots originating from Si were masked in the 2D diffraction patterns followed by



**Figure 1.** ALD characteristics: (a) GPC as a function of RuO<sub>4</sub> pulse time using a fixed pulse time of 25 s for methanol. (b) GPC as a function of methanol pulse time, with the RuO<sub>4</sub> pulse time kept fixed at 40 s. (c) Temperature window of the ALD process showing the growth per cycle as a function of substrate temperature as obtained from XRR. Note that for the data points with error bars, the mean of the data points measured in each case is plotted and the error bar corresponds to the standard deviation of the data. (d) Thickness vs the number of ALD cycles as determined from XRR on Si-H and Si with native oxide substrates at 100 °C (inset: schematic illustration of the ALD process). (e) Cross-sectional SEM image of the RuO<sub>2</sub>-coated micropillars indicating the different depths where the EDX was measured. (f) Normalized Ru L intensity at different depths of the pillars as obtained from EDX.

azimuthal integration. The background subtracted 1D patterns were transformed into pair distribution functions (PDF) using PDFgetX3,<sup>73</sup> applying a  $Q_{\max}$  value of  $22.0 \text{ \AA}^{-1}$ . PDF refinements were carried out in TOPAS Academic version 7.74. The fit residual is defined as  $R_p = [\sum_i (Y_{O,i} - Y_{C,i})^2 / \sum_i (Y_{O,i})^2]^{1/2}$ , with  $Y_{O,i}$  and  $Y_{C,i}$  as the experimental (observed) and calculated data in point  $i$ , respectively.

For gas-phase analysis of the reaction products, in situ quadrupole mass spectrometry (QMS, Hiden Analytical) was performed. Gas species were ionized with an energy of 70 eV and detected with a secondary electron multiplier detector. Before the QMS characterization was done, the chamber and sample stage were precoated by several hundreds of RuO<sub>2</sub> ALD cycles. Temperatures were the same as for the regular depositions. For the characterization of the RuO<sub>4</sub> pulse, 100 iterations of the following cycle were carried out: (open valve to mass spectrometer) + (20 s wait time) + 3 × (40 s RuO<sub>4</sub> + 40 s pump time) + (close valve to mass spectrometer) + (20 s wait time) + (25 s methanol + 20 s pump time). For the characterization of the methanol pulse, the following variation was used as well 100 times: (open valve to mass spectrometer) + (20 s wait time) + 3 × (25 s methanol + 20 s pump time) + (close valve to mass spectrometer) + (20 s wait time) + (40 s RuO<sub>4</sub> + 40 s pump time). After data analysis according to a method described earlier in more detail,<sup>75</sup> a time-resolved spectrum of the full range of masses was obtained (see Figure S9). Relevant slices of this spectrum, resembling conventional, time-resolved measurements at specific  $m/z$  are presented in the main manuscript as they are more straightforward to interpret.

In vacuo XPS experiments were performed in order to obtain the oxidation state of Ru in the deposited films. The experiments were performed on a dedicated ALD-XPS setup consisting of a Theta Probe XPS instrument (Thermo Fisher Scientific Inc.) directly connected to a custom-built ALD reactor.<sup>76,77</sup> This allows sample transfer between the ALD reactor ( $10^{-7}$  mbar) and XPS ( $10^{-10}$  mbar)

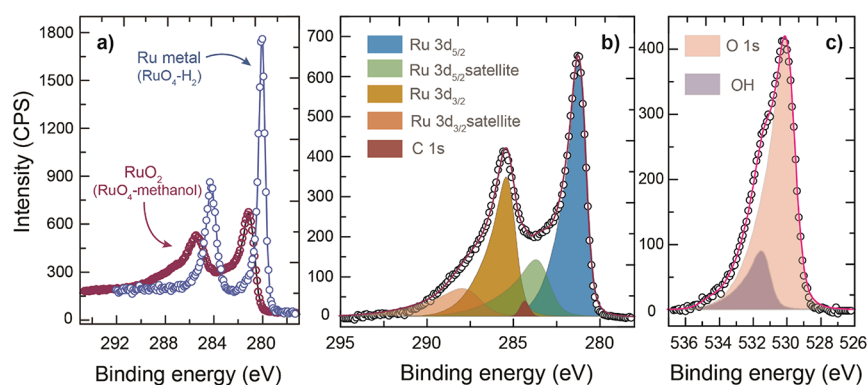
in less than a minute and without (high) vacuum break. The XPS spectra were calibrated with respect to the Si 2p<sub>3/2</sub> peak at 99.4 eV.

A Vertex 70v vacuum spectrometer from Bruker was used to measure the mid-IR spectra of the thin films in transmission mode during the ALD process on double-polished Si wafer. Each mid-IR spectrum is the average of 200 scans, resulting in a measurement time of ca. 200 s. Spectra were collected at the start of every experiment, after each ALD reaction, and at the end of the process. The FTIR spectra were analyzed using the OPUS software package from Bruker.

## RESULTS AND DISCUSSION

In this section, we first present the ALD characteristics and thin film properties for the process using RuO<sub>4</sub> and methanol as the reactants. Next, we show that the RuO<sub>2</sub> growth rate can be tuned by selecting a different type of alcohol, more specifically for ethanol, 1-propanol, and 2-propanol. Finally, we propose a reaction mechanism for the process based on the learnings acquired by in situ QMS, in situ FTIR, and in vacuo XPS studies.

**Growth Characteristics of the RuO<sub>2</sub> ALD Process.** The self-limiting behavior of the two reactions is an important aspect of an ALD process. Saturation experiments for the RuO<sub>4</sub>-methanol process were performed on Si-H substrates at a substrate temperature of 100 °C. Figure 1a,b shows the saturation curves for RuO<sub>4</sub> and methanol, respectively. First, the pulse time of RuO<sub>4</sub> was varied while keeping the methanol pulse time fixed at 25 s. Saturation of the surface reaction with RuO<sub>4</sub> was achieved at 40 s, with a GPC of 1 Å/cycle. Similar experiments were conducted to reveal the saturation behavior of the surface reaction with the methanol precursor at a fixed pulsing time of 40 s for the RuO<sub>4</sub> precursor. These



**Figure 2.** (a) Comparison of the in vacuo XPS spectra in the Ru 3d region for metallic Ru (RuO<sub>4</sub>-H<sub>2</sub> ALD process)<sup>58</sup> and RuO<sub>2</sub> (RuO<sub>4</sub>-methanol process, this work). (b, c) XPS peak deconvolution of the Ru 3d and O 1s signals, respectively, for the RuO<sub>4</sub>-methanol process.

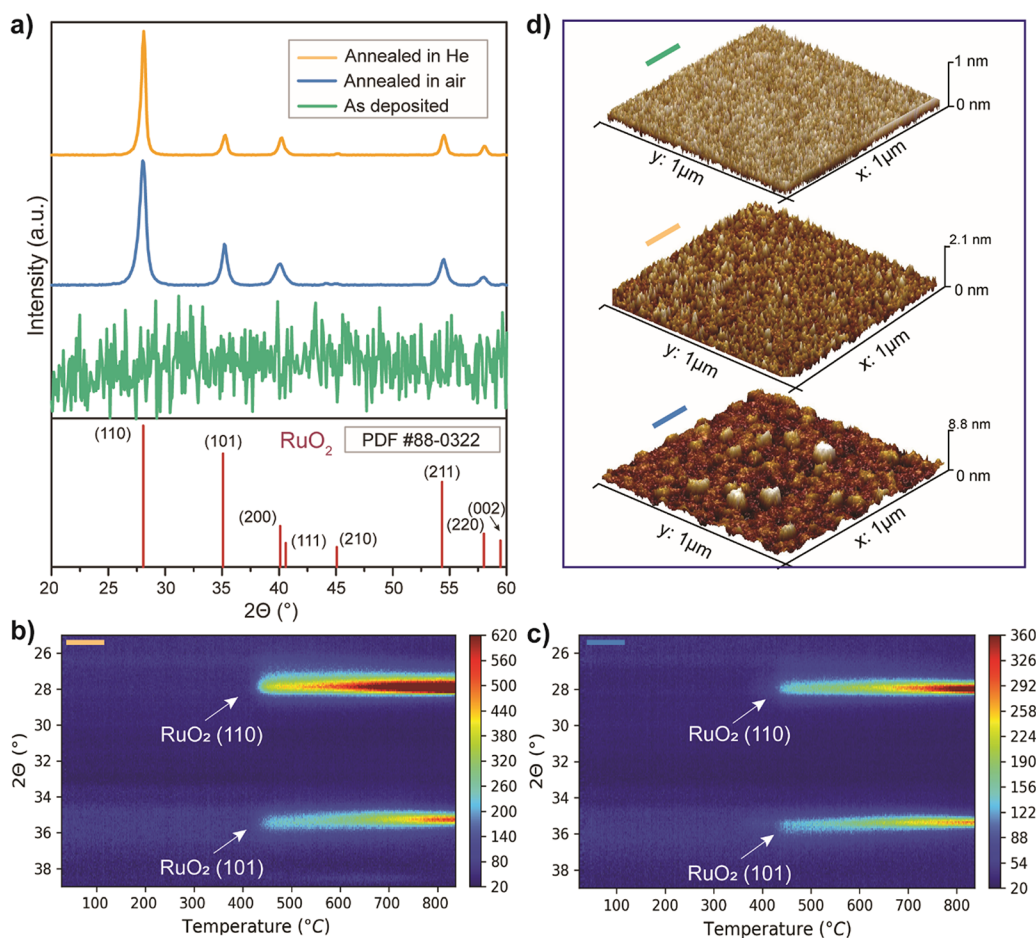
experiments indicated saturation for the methanol reaction at about 20 s. Next, the dependence of ALD growth on the temperature was evaluated using the saturated conditions for both reactions. Only temperatures below 125 °C were studied as the RuO<sub>4</sub> precursor is known to thermally decompose above this substrate temperature.<sup>59</sup> The GPC remained the same throughout the temperature range studied (60–120 °C), slightly above 1 Å/cycle (Figure 1c).

The linearity of the process was studied by ex situ XRR (Figure 1d). Depositions with different cycle numbers were performed on both Si-H and Si with native oxide substrates at a deposition temperature of 100 °C. The pulse time for methanol was 25 s and for RuO<sub>4</sub>, the pulse time was 40 s. These experiments revealed that the thickness of the films increased linearly with the number of ALD cycles with an average GPC of 1 Å per cycle on both substrates and without a significant nucleation delay. Comparing the nucleation behavior of the RuO<sub>4</sub>-methanol process with the RuO<sub>4</sub>-H<sub>2</sub> process,<sup>76</sup> it can be concluded that both processes behave similarly on H-terminated Si, demonstrating swift nucleation. In contrast, for ALD on Si with a native oxide, the RuO<sub>4</sub>-H<sub>2</sub> process was marked by initial inhibited growth, while this is not observed in Figure 1d for the RuO<sub>4</sub>-methanol process. As RuO<sub>4</sub> is a strong oxidizer, the immediate growth on Si-H was explained by RuO<sub>4</sub> oxidizing the Si during the first exposure, while the lack of a surface that can be further oxidized explains the inhibited growth on SiO<sub>2</sub>. We reported that one single prepulse of TMA on an oxide surface allows the growth of Ru metal without growth inhibition as RuO<sub>4</sub> will oxidize the CH<sub>3</sub> groups of the adsorbed TMA molecules.<sup>76</sup> The linear growth on Si with native oxide observed in Figure 1d suggests that methanol molecules reside on the surface following the first exposure, which can act as similar nucleation sites for RuO<sub>4</sub> as the aforementioned TMA molecules.

The conformality of an ALD process is very important as it is the ability to deposit films on high-aspect-ratio (AR) structures, with preferably no variation in the amount and the composition of the material deposited along the structures.<sup>51,78</sup> The conformality of the RuO<sub>2</sub> coating was evaluated by depositing 100 cycles on silicon micropillars with an equivalent AR (EAR) of approximately 10 (namely, 2 μm wide and 50 μm high pillars, spaced at a 4 μm center-to-center distance on a square lattice) etched into a silicon substrate as shown in Figure 1e.<sup>78</sup> After the deposition, the sample was analyzed in cross section with scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) to evaluate the

amount of ruthenium at different depths along the pillar. The EDX spectrum (Figure 1f) indicated clear ruthenium signals at all depths. Although there is a slight variation in the Ru signal at different depths, the signal intensity at 50 μm depth is still comparable with the Ru signal intensity at the top of the pillar, which suggests a decent conformality of the process (note that variations can be due to the slightly conical shape of the pillars).

**Material Characterization.** To verify that the films deposited using the RuO<sub>4</sub>-methanol process are ruthenium dioxide, in vacuo XPS measurements were carried out. For reference purposes, first, a metallic Ru film was deposited using the previously reported RuO<sub>4</sub>-H<sub>2</sub> ALD process.<sup>59</sup> In a second experiment, a film was deposited using the RuO<sub>4</sub>-methanol ALD process under study. In both cases, 15 cycles were performed on a Si-H substrate and the samples were transferred to the XPS analysis chamber immediately after deposition and without high vacuum break. The XPS spectra were calibrated by placing the Si 2p<sub>3/2</sub> peak of the substrate at 99.4 eV.<sup>79</sup> The XPS signal from the substrate is visible as the films have a thickness of about 2 nm, which is below the information depth for XPS.<sup>80</sup> Inspection of the Ru 3d XPS spectra clearly indicates differences in binding energy and shape between the two films (Figure 2a). For metallic Ru, the Ru 3d<sub>5/2</sub> and Ru 3d<sub>3/2</sub> peaks are observed at 280.4 and 284.6 eV, respectively, and the peaks have an FWHM of 0.6 and 0.9 eV, consistent with Ru(0) (see Figure S1).<sup>81</sup> For the film deposited with the RuO<sub>4</sub>-methanol process, the Ru 3d<sub>5/2</sub> and Ru 3d<sub>3/2</sub> peaks are positioned at 281.1 and 285.3 eV, respectively, and they are much broader compared to metallic Ru. The 0.7 eV shift of the Ru 3d<sub>5/2</sub> peak toward higher binding energy compared to Ru(0) is consistent with a + 4 oxidation state of the Ru atoms.<sup>82–84</sup> The broad nature of the Ru 3d peaks is also expected for pure RuO<sub>2</sub> and originates from satellite peaks induced by XPS final-state effects.<sup>85</sup> Morgan<sup>81</sup> performed a detailed XPS study on Ru-containing materials, and the models they reported for metallic ruthenium and ruthenium dioxide were used to deconvolute and fit the Ru 3d and O 1s peaks (Figure 2b,c, respectively). The O 1s spectrum contains two different components, attributed to Ru–O and Ru–O–H bonds<sup>81,86,87</sup> (Figure 2c). The results of the fits are tabulated in the Supporting Information, and the good agreement with the earlier reported models allows us to conclude that the films deposited with the RuO<sub>4</sub>-methanol process are RuO<sub>2</sub>.<sup>81</sup> Concerning the impurity content of the RuO<sub>2</sub> films, we note that determining the carbon content in



**Figure 3.** (a) Lab-based ex situ X-ray diffractograms of as-deposited, He-annealed, and air-annealed RuO<sub>2</sub> films with a thickness of 20 nm. (b, c) In situ XRD patterns acquired during the annealing in helium and air, respectively. (d) 3D AFM images of an as-deposited 20 nm RuO<sub>2</sub> film on a Si-H substrate (top), the same film after annealing in He to 800 °C (middle), and after annealing in air to 800 °C (bottom). Note the different scales along the z axis (height).

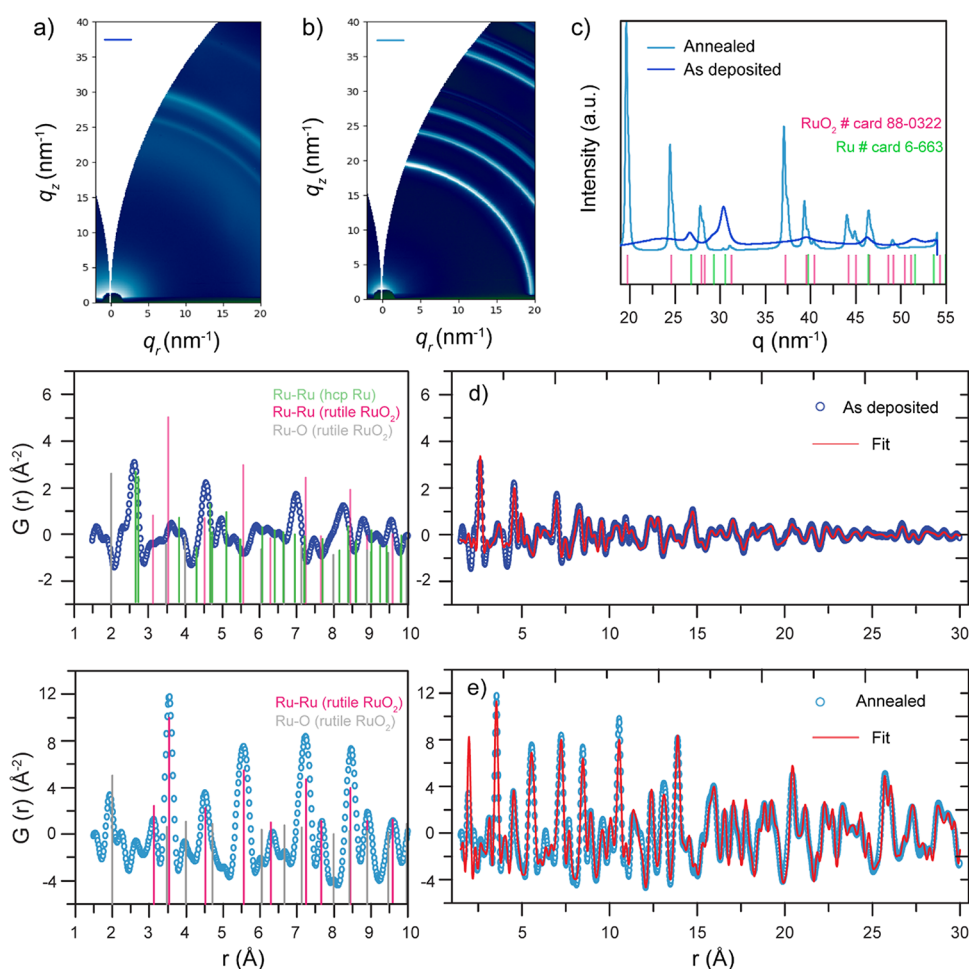
the films with XPS is a challenge due to the overlap of the C 1s with the Ru 3d region and the complex satellite structure of the Ru 3d spectrum. The peak fitting results, where the constraints used in the model are based on the reference work by Morgan,<sup>81</sup> yielded a carbon concentration below 5%, providing an indication that the carbon contamination in the as-deposited RuO<sub>2</sub> thin films is acceptably low. Fluorine impurities (2 atom %) were also detected with in vacuo XPS, most likely deriving from the methyl-ethyl fluorinated solvent used in the ToRuS precursor.<sup>66</sup> The fluorine could be removed by short Ar<sup>+</sup> ion etching, which suggests that the fluorine is not built into the films and is only present at the surface. No other impurities than carbon and fluorine were detected.

The crystallinity of the RuO<sub>2</sub> films was investigated by various X-ray scattering methods. Conventional lab-based XRD measurements did not reveal any diffraction signal for as-deposited films of 20 nm thickness (Figure 3a), suggesting that the as-deposited RuO<sub>2</sub> thin film would be amorphous. As several of the applications require crystalline RuO<sub>2</sub>, we investigated the crystallization of the RuO<sub>2</sub> films by post-deposition thermal annealing. For this, 20 nm RuO<sub>2</sub> films deposited on Si-H were annealed up to a temperature of 800 °C in helium and in air, both with a ramp rate of 0.2 °C/s. During each anneal, the RuO<sub>2</sub> crystallization was monitored by lab-based in situ XRD (Figure 3b,c). At around 420 °C, clear

diffraction peaks originating from crystalline rutile RuO<sub>2</sub> start to appear during both anneals. After cooling down to room temperature, ex situ XRD measurements were performed, and the data are displayed in Figure 3a (blue and yellow pattern), showing that the diffraction peaks can be identified based on the rutile RuO<sub>2</sub> diffractogram (JCPDS 88-0322). To learn more about the carbon content in the RuO<sub>2</sub> thin films before and after crystallization, SIMS measurements were carried out and the results are presented in Figure S2. SIMS revealed a lower level of carbon impurities in the film after annealing.

The film morphology of the as-deposited and the post-annealed RuO<sub>2</sub> films was studied by atomic force microscopy (AFM). The as-deposited film (20 nm thick, prepared using the RuO<sub>4</sub>-methanol process) was found to be relatively smooth with an RMS roughness value of 0.48 nm (Figure 3d, top). The roughness value increases to 0.88 nm after annealing in He (Figure 3d, middle). The air annealed films show an even higher roughness value of 2.85 nm (Figure 3d, bottom). The increase in roughness after annealing can be attributed to grain formation during crystallization. The higher roughness for the air-annealed films could potentially be related to the diffusion of oxygen atoms (in the air ambient) into the film during annealing.<sup>88,89</sup>

Finally, the crystallization of as-deposited RuO<sub>2</sub> was compared with the formation of crystalline RuO<sub>2</sub> by the oxidation of metallic Ru films (grown with the RuO<sub>4</sub>-H<sub>2</sub> ALD



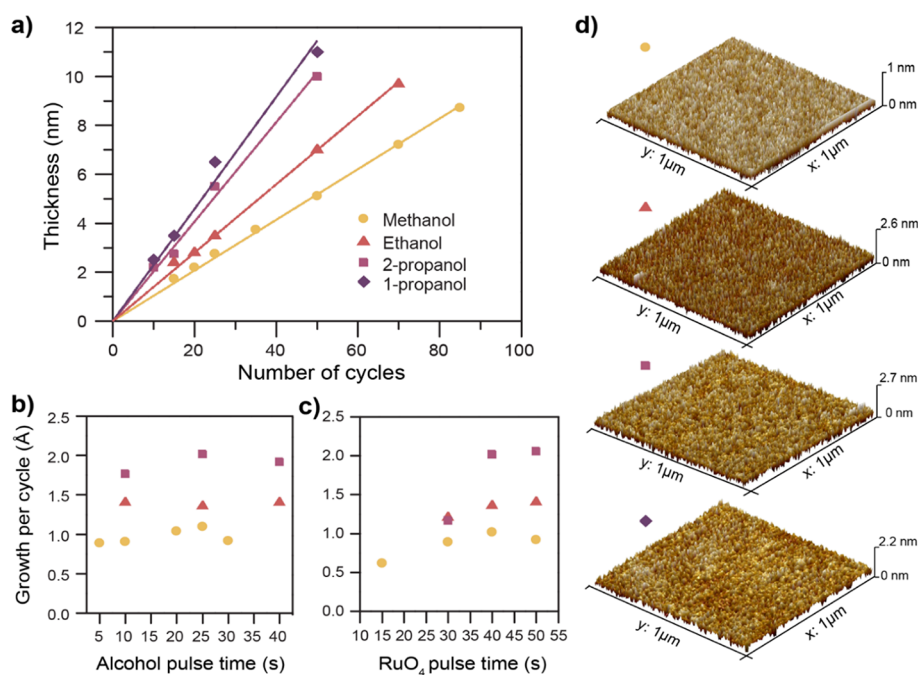
**Figure 4.** (a, b) Synchrotron-based 2D GIWAXS patterns of a 50 nm as-deposited film and of the same film annealed in helium. (c) Azimuthal integration of the GIWAXS data for the two films. (d, e) PDFs of the as-deposited and the annealed films, resulting from the grazing incidence total X-ray scattering patterns shown in Figure S4. The respective zoomed images are provided in the left side of the plots.

process) as depicted in Figure S3a. The crystallization of as-deposited  $\text{RuO}_2$  occurred around 400–450 °C, whereas the oxidation of metallic Ru to crystalline  $\text{RuO}_2$  requires temperatures as high as 600 °C. Moreover, the former process resulted in smoother films and the latter in rough  $\text{RuO}_2$  layers, as evidenced from the SEM images in Figure S3b. The rough  $\text{RuO}_2$  layer formation is likely related to the volume change associated to oxidation.

To further investigate the structural properties of the as-deposited and annealed  $\text{RuO}_2$  thin films, GIWAXS measurements and grazing incidence total X-ray scattering measurements with pair distribution function analysis (GIPDF) were carried out for 50 nm-thick films before and after annealing in helium. Figure 4a,b shows the 2D GIWAXS patterns for the as-deposited and annealed layer that were recorded at the NCD-SWEET beamline of the ALBA Synchrotron, Spain. Intense diffraction rings can be observed for the annealed sample, as expected, while also for the as-deposited layer, diffraction rings are visible, with broader and less intense signals. In Figure 4c, the azimuthal integrated patterns are shown. In line with the lab-based XRD measurements, the diffraction peaks of the annealed thin film can be identified based on the rutile  $\text{RuO}_2$  phase. In contrast, the broad diffractions for the as-deposited material match the diffractogram of the Ru hcp metal. Together with the XPS results confirming the growth of  $\text{RuO}_2$ , this suggests a microstructure of amorphous  $\text{RuO}_2$  with

nanocrystalline Ru inclusions that could not be detected with lab-based XRD.

Total scattering experiments employing a grazing incidence geometry have recently been proposed to access the local and medium-range order of atoms in thin films, whether crystalline or not, via PDF analysis. Here, we applied the emerging GIPDF method<sup>71,73</sup> to further clarify the structure of the as-deposited  $\text{RuO}_2$  thin films by comparing its PDF to the one of the crystalline annealed material. Figure 4d,e shows the extracted PDF for the as-deposited and annealed sample, respectively. The zooms on the left side include the bond distances for ideal bulk rutile  $\text{RuO}_2$  and Ru hcp metal.<sup>90,91</sup> The PDF for the annealed sample exhibits significant oscillations to at least 50 Å, indicative of long-range order, as expected, for a crystalline thin film (Figure S5). The Ru–Ru bond lengths dominate the PDF of the rutile  $\text{RuO}_2$  structure due to the larger scattering power of Ru compared to O. It can be seen that the positions of the dominant peaks in the experimental PDF agree with the expected Ru–Ru bond lengths in an ideal rutile  $\text{RuO}_2$  structure.<sup>91</sup> Fitting the data against models of rutile  $\text{RuO}_2$  and Ru hcp in the range between 1.5 and 30 Å confirms that the thin film structure resembles that of the rutile  $\text{RuO}_2$  structure. A good agreement with the experimental PDF is obtained for a model assuming 99 wt % of  $\text{RuO}_2$  ( $R_p = 0.24$ ). The peaks in the PDF for the as-deposited sample decay to zero faster, yet the presence of clear features up to 22 Å



**Figure 5.** (a) Thickness against the number of ALD cycles for the methanol-, ethanol-, 1-propanol-, and 2-propanol (isopropanol)-based processes as obtained from XRR. (b, c) Saturation curves for the RuO<sub>4</sub> surface reaction and the alcohol surface reaction, respectively, for these different processes. (d) 3D-AFM images obtained for the methanol-, ethanol-, 2-propanol-, and 1-propanol-based processes (from top to bottom, respectively) after 85, 70, 50, and 50 ALD cycles, respectively. Note the different scales along the *z* axis (height).

indicates that the film exhibits local structural order. The observed pair correlations, however, differ in position and amplitude when compared with the structure that is adopted after thermal annealing. In this case, the experimental PDF, especially the features at larger *r* values, can be fitted best against a model that is dominated by the hexagonal Ru structure (96 wt %,  $R_p = 0.30$ ), in line with the reciprocal space data revealing diffractions corresponding to hcp Ru. Comparison of the pattern with the ideal model of rutile RuO<sub>2</sub> in the range up to 4 Å also reveals some resemblance. A peak can be observed at  $\sim 1.95$  Å, which corresponds to the first Ru–O bond distance in rutile RuO<sub>2</sub>. The second Ru–Ru peak, expected to be the most intense Ru–Ru correlation, at  $\sim 3.54$  Å, is also visible. A weak feature, corresponding to the first Ru–Ru bond distance, can be discerned at  $\sim 3.1$  Å. For these *r* values, no overlap with Ru–Ru correlations in hcp Ru is expected. Overall, this hints toward amorphous RuO<sub>2</sub> that exhibits only short-range order at the level of the nearest neighbors, while the structural order seen for larger distances is mostly a consequence of the nanocrystalline Ru hcp inclusions. Nevertheless, this investigation highlights that ALD-grown thin films that are easily classified as “amorphous” based on lab-based XRD measurements can actually present structural medium- to long-range order that may often remain under the radar.

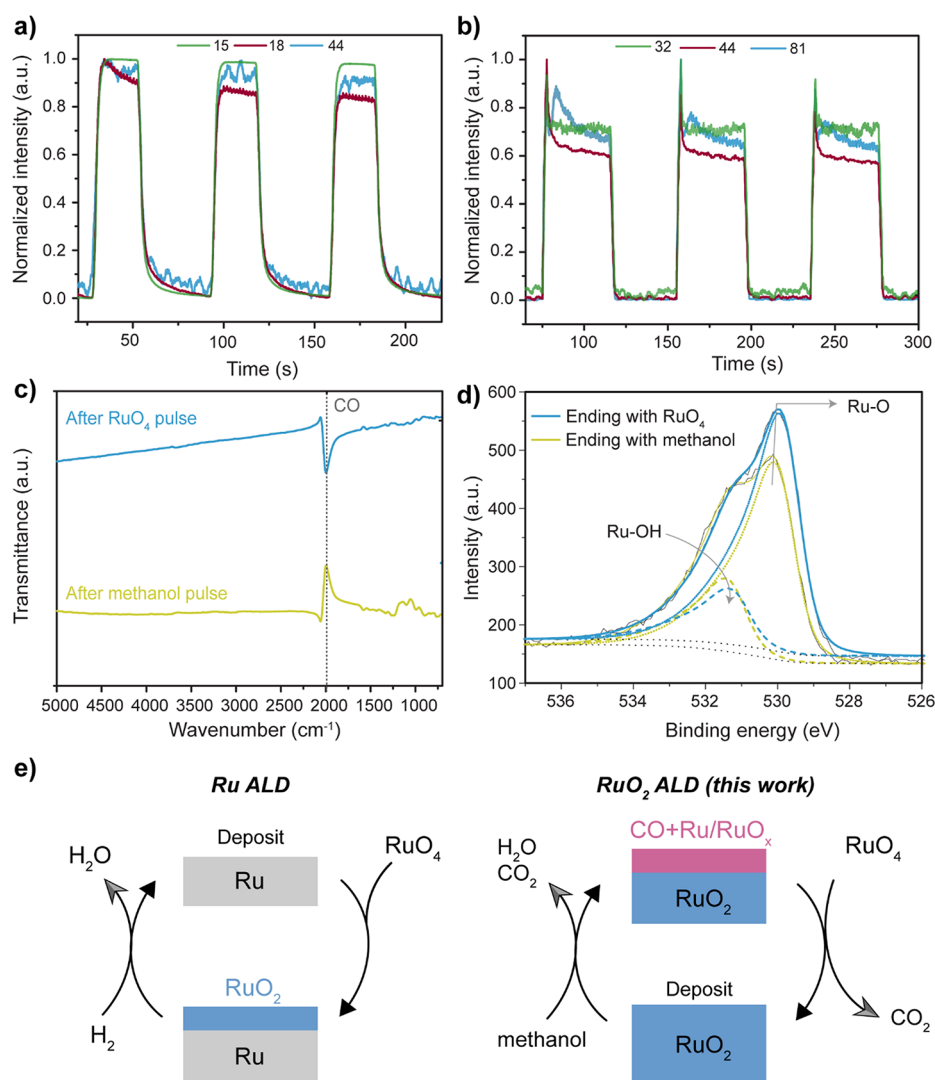
The electrical resistivity of the films was determined using four-point probe measurements. The resistivity of an as-deposited 20 nm RuO<sub>2</sub> film (on Si with a native oxide substrate) was found to be 230 μΩ·cm. The resistivity values improved upon thermal annealing to 800 °C in both air and He. After annealing in air, the resistivity value decreased to 199 μΩ·cm and after annealing in He, the resistivity was 123 μΩ·cm. These values indicate a fairly conductive RuO<sub>2</sub> film, and they are comparable with existing literature reports for ALD-synthesized RuO<sub>2</sub>.<sup>41</sup> The resistivity improvement after

annealing may be associated with the introduction of crystallinity in the samples and decrease in carbon content.

The optical properties were assessed by performing ex situ transmittance measurements using spectroscopic ellipsometry for the RuO<sub>2</sub> (ca. 15 nm) film deposited on a quartz substrate. The results and analysis details are explained in the Supporting Information (Figure S6). A value of 1.9 eV was obtained as the band gap for the RuO<sub>2</sub> films, comparable with other reports.<sup>92,93</sup>

**Growth Using Other Alcohols as the Co-reactant.** The ALD characteristics and film properties of the RuO<sub>4</sub>-methanol process have been explained in detail. It is known that RuO<sub>4</sub> can react with both primary and secondary alcohols in solution, and different byproducts are obtained depending on the choice of the alcohol.<sup>94</sup> Therefore, we performed a series of depositions combining RuO<sub>4</sub> with ethanol, 1-propanol, and 2-propanol (isopropanol) as the co-reactants. The depositions were performed on H-terminated Si substrates at a temperature of 100 °C. As shown in Figure 5a, growth occurred for each of the alcohols under the conditions studied. Interestingly, the growth rate increases with the carbon chain length. While the growth rate for the methanol-based process is 1 Å/cycle, the growth rates for the ethanol- and 1-propanol-based processes increase to 1.4 and 2 Å/cycle, respectively. The 2-propanol-based-process displays the same growth rate as the 1-propanol-based process.

The saturation behavior of these processes was investigated. Just like the experiments with methanol, H-terminated silicon was chosen as the substrate, and it was kept at 100 °C. From Figure 5b,c, it follows that the saturation conditions are independent of the choice of the alcohol. Saturation was achieved after 40 s for the RuO<sub>4</sub> pulses and 25 s for the alcohol pulses in all cases. To reveal if the choice of the alcohol influences the roughness of the films, ex situ AFM measurements were performed on samples of similar thickness (Figure



**Figure 6.** (a, b) In situ mass spectrometry data obtained during successive methanol pulses and successive RuO<sub>4</sub> pulses, respectively. (c) In situ FTIR difference spectra for the methanol (blue) and RuO<sub>4</sub> half cycles (red). The methanol difference spectrum is acquired by subtracting the FTIR spectrum acquired after the RuO<sub>4</sub> pulse from that acquired after the subsequent methanol pulse, and vice versa. (d) *In vacuo* XPS spectra acquired in the O 1s region. The blue and yellow spectra indicate processes ending with RuO<sub>4</sub> and methanol, respectively. The dotted lines indicate the Ru–O components, and the dashed lines indicate the Ru–OH components. (e) The proposed reaction mechanisms for Ru ALD and RuO<sub>2</sub> ALD (this work).

5d). It was found that the RMS roughness of the as-deposited RuO<sub>2</sub> increases with an increase in the length of the carbon chain. More specifically, for methanol, a 20 nm film had a roughness of 0.48 nm. For the ethanol-, 2-propanol-, and 1-propanol-based processes, the RMS values were 0.81 nm (9.7 nm film), 1.2 nm (10 nm film), and 0.92 nm (11 nm film), respectively.

Lab-based ex situ XRD before and after annealing, and in situ XRD measurements during annealing, did not reveal significant differences in the crystallization behavior of films deposited with different alcohols. No diffraction peaks could be observed for the as-deposited films, which crystallize into rutile RuO<sub>2</sub> by annealing either in an inert atmosphere or in air. The ex situ XRD patterns recorded after annealing reveal differences in preferential crystallographic orientation with different annealing atmospheres (Figure S7), which was not observed for the RuO<sub>2</sub> material deposited with methanol (Figure 3a). The onset of crystallization was around 420 °C in all cases (Figure S8). This latter result provides an indirect

indication that the carbon content in the films grown with different alcohols is comparable as a larger carbon contamination is known to often result in an increase in crystallization temperature.<sup>95</sup> The resistivity values for the films deposited using methanol (12 nm RuO<sub>2</sub>), ethanol (9.7 nm), and 2-propanol (10 nm) were 245, 282, 322 μΩ·cm respectively, which are also comparable.

**Mechanism of the Developed ALD Process.** In situ QMS, in situ FTIR, and in vacuo XPS were used to gain insights into the mechanism of the developed process by probing the gas phase reaction products and surface chemistry. In QMS, data can only be obtained for a single mass at a time, and the common approach in ALD research is to follow a couple of selected masses to confirm or disprove a certain hypothesis on the reaction mechanism. Recently, our group showed that it is possible to exploit the cyclic nature of ALD to obtain full mass-over-charge spectra, in a time-resolved fashion, to screen for the formation of any reaction products during the two reactions in the ALD cycle.<sup>66</sup> Time-resolved full-range



mass spectra were collected during the methanol and RuO<sub>4</sub> surface reactions with the methodology described in our earlier work (Figure S9). Relevant parts from those full-range spectra are shown in Figure 6a for the methanol reaction and in Figure 6b for the RuO<sub>4</sub> reaction, respectively. During the collection of mass spectra, molecules entering the spectrometer will be ionized and fragmented. It is relevant to note that different fragments of the same parent molecule may have a different absolute intensity, but the time evolution of this intensity will be very similar as it is directly correlated to the partial pressure of the parent molecule.

Methanol ( $m/z$  32) will be fragmented in the mass spectrometer (Figure 6a); hence, the CH<sub>3</sub> fragment with  $m/z$  15 presents a reference for the partial pressure of methanol. The water signal ( $m/z$  18) is transient, which identifies it as a reaction product. The fragment at  $m/z$  44 can be attributed to CO<sub>2</sub>. It is not transient, but because it is heavier than methanol, it must be a reaction product as well. No other signals above  $m/z$  32 were observed during the methanol pulse. The appearance of H<sub>2</sub>O and CO<sub>2</sub> in the spectrum can therefore be attributed to the oxidation of methanol by the RuO<sub>2</sub> surface. This observation is backed up by other reports, showing that under vacuum conditions, CH<sub>3</sub>OH is oxidized to CO<sub>2</sub> on a RuO<sub>2</sub> surface.<sup>96</sup> As a result, the RuO<sub>2</sub> surface will be partially reduced.

During the RuO<sub>4</sub> pulse, a myriad of fragments is present in the time-resolved, full-range spectrum. Most of those fragments do not originate from the RuO<sub>4</sub> molecule itself but from the proprietary solvent complex that is used for the safe handling of the precursor. When analyzing all fragments, three distinct types of time evolutions were discerned (Figure 6b). The first type of time evolution that we observed was linked to the partial pressure of an unreacted precursor in the chamber. As the signal for the Ru atom itself ( $m/z$  101) had a very low intensity, the fragment with  $m/z$  32 (possibly O<sub>2</sub>) is shown in Figure 6b. Most fragments that are related to the solvent showed this type of time evolution. A second type of time evolution was observed for mass 44. As can be seen in Figure 6b, this signal shows a transient behavior, and the first peak is longer-lasting (broader in time) and more intense than that of the RuO<sub>4</sub>/solvent type. This kind of time evolution was only observed for  $m/z$  44 and can be attributed to the formation of CO<sub>2</sub> as a reaction product during the RuO<sub>4</sub> pulse. Hence, there must be carbon left at the surface after the methanol pulse. Finally, a third, distinct shape of time evolution was found for some fragments of the solvent complex. As an example, the fragment with  $m/z$  81 is presented in Figure 6b. As can be seen in the time evolution of this fragment, a peak arises with a time delay relative to the peak of the CO<sub>2</sub> signal, and it also displays a transient behavior. We can explain this as follows: The RuO<sub>4</sub> molecules enter the chamber in a complex with the solvent molecules. Upon reaction of this RuO<sub>4</sub>-solvent complex with the surface, CO<sub>2</sub> is formed as a reaction product, and RuO<sub>x</sub> is incorporated into the film. After this reaction, the solvent molecules leave the surface, leading to a time delay in the QMS data.

To investigate if carbon species are accumulating on the surface during the methanol pulse and are removed during the RuO<sub>4</sub> pulse (as seen by CO<sub>2</sub> evolution in the mass spectrometry), in situ FTIR experiments were performed (Figure 6c). The changes that occur at the surface during the methanol pulse (referenced to the previous RuO<sub>4</sub> pulse) and RuO<sub>4</sub> pulse (referenced to the previous methanol pulse) are

shown in difference spectra in Figure 6c. The positive features represent the chemical groups that are being added and negative features the groups that are being removed during each pulse. During the methanol pulse, the significant peak that appeared (positive feature, marked by a dotted line) was around 2000 cm<sup>-1</sup>, which is attributed to CO adsorbed on the RuO<sub>2</sub> surface during the methanol oxidation on RuO<sub>2</sub>. This peak has been previously linked to CO adsorption on coordinatively unsaturated Ru on RuO<sub>2</sub> surfaces.<sup>97</sup> The complete removal of this peak was observed during the RuO<sub>4</sub> pulse as seen by the negative feature in the same region, indicating that CO is oxidized to CO<sub>2</sub>, corroborating the mass spectrometry data. There are, however, some weak features to be seen after the methanol pulse around 1147 and 1049 cm<sup>-1</sup>, which are most likely related to the methoxy species (CH<sub>3</sub>-O)<sup>98</sup> originating from the oxidation of methanol on the RuO<sub>2</sub> surface.

To further support the QMS data, in vacuo XPS measurements were carried out. The RuO<sub>4</sub>-methanol process was conducted on a Si-H substrate for 100 cycles, and the sample was transferred to the XPS without (high) vacuum break after the RuO<sub>4</sub> pulse followed by the acquisition of the O 1s spectrum (Figure 6d). After this, the same sample was transferred back to the ALD chamber to perform two additional ALD cycles, this time for the process ending with methanol, after which again the O 1s spectrum was acquired. In both cases (for the process ending with RuO<sub>4</sub> and for the one ending with methanol), the spectra can be deconvoluted into two different components, one at a binding energy of 529.7 eV and the other at 530.1 eV. The one at 529.7 eV can be attributed to a Ru-O bond<sup>81,86</sup> and the one at 531.1 eV to Ru-O-H<sup>81,87,99</sup> bonds. Note that the contribution of the Si substrate (oxidized during the growth) in the O 1s signal is excluded by the absence of a Si 2p peak measured after 100 cycles of the methanol-RuO<sub>4</sub> process (see Figure S10). Inspection of the O 1s spectra in the figure clearly indicates a lower oxygen signal for the process ending with methanol compared to the one ending with RuO<sub>4</sub>. This in turn suggests that during the methanol pulse, the top surface of the RuO<sub>2</sub> film is reduced to RuO<sub>x</sub> ( $0 \leq x < 2$ ). The OH component was not found to be affected by the RuO<sub>4</sub> or methanol treatment. Han et al. reported the CVD of RuO<sub>2</sub> using RuO<sub>4</sub> and H<sub>2</sub> gas where they proposed that hydroxyl groups can be formed due to the interaction of H<sub>2</sub> with RuO<sub>2</sub>. Such groups can also favor the chemisorption of RuO<sub>4</sub>. In contrary, we did not find a substantial decrease in OH intensity after the RuO<sub>4</sub> pulse, indicating less (no) reaction of RuO<sub>4</sub> with hydroxyl groups on the surface. However, a similar mechanism to our case was observed when methanol decomposition was studied on a RuO<sub>2</sub> surface, where, RuO<sub>2</sub> catalyzes the oxidation of methanol to different products, depending on the conditions chosen and as a result of this, the RuO<sub>2</sub> top layer is reduced to metallic Ru or RuO<sub>x</sub>.<sup>100</sup> Similar to the O 1s regions, the Ru 3d regions (for the processes ending with RuO<sub>4</sub> and for the one ending with methanol) were also examined, as shown in Figure S11. However, no useful inference can be drawn in this case due to the complex satellite structure of the Ru 3d region.

These experiments helped us put forward a plausible mechanism for the developed process. A schematic illustration is provided in Figure 6e, which includes also the inferred mechanism of the Ru ALD<sup>59</sup> process for comparison. For Ru ALD with RuO<sub>4</sub> and H<sub>2</sub>, in the first half cycle, the Ru surface is oxidized by the RuO<sub>4</sub> molecules, bounding RuO<sub>2</sub> to the surface

in a self-saturating way. In the second reaction, H<sub>2</sub> gas enables the reduction of RuO<sub>2</sub> to metallic Ru. For RuO<sub>2</sub> ALD with RuO<sub>4</sub> and methanol, our results indicate that the alcohol (during the alcohol pulse) is oxidized into CO<sub>2</sub> and H<sub>2</sub>O on a RuO<sub>2</sub> surface. As a result of this oxidation, CO remains present at the surface. The oxidation of methanol in turn leads to the reduction of the surface RuO<sub>2</sub> to a slightly O<sub>2</sub>-deficient RuO<sub>2</sub> surface. The detection of nanocrystalline Ru inclusion in the as-deposited material provides another hint that the alcohol indeed leads to a reduction of the RuO<sub>2</sub> surface. RuO<sub>4</sub> can easily nucleate on such a reduced RuO<sub>x</sub>/Ru surface layer, which helps in oxidizing (during the next RuO<sub>4</sub> pulse) the surface again to a thicker and oxygen-rich RuO<sub>2</sub>. The CO that was present on the surface is oxidized and leaves the surface as CO<sub>2</sub>.

## CONCLUSIONS

We have demonstrated a novel ALD synthesis strategy for depositing RuO<sub>2</sub> thin films utilizing the reaction between RuO<sub>4</sub> and alcohols. The reaction of methanol with RuO<sub>4</sub> yielded a GPC of 1 Å/cycle, exhibiting all typical characteristics of an ALD process, without a significant nucleation delay. Interestingly, the GPC could be tuned by altering the alcohol counterpart. The GPC was found to be 1.4 Å/cycle when using ethanol, and it was around 2 Å/cycle when using 1-propanol and 2-propanol. Irrespective of the chosen alcohol, amorphous RuO<sub>2</sub> thin films were deposited. Structural characterization with synchrotron-based grazing incidence X-ray scattering methods revealed the presence of nanocrystalline Ru metal inclusions in the as-deposited amorphous RuO<sub>2</sub> films. However, post-deposition annealing either in He or in air yielded crystalline rutile RuO<sub>2</sub> around 420 °C. Highly conductive films were obtained as evidenced from a resistivity value of 230 μΩ·cm for the as-deposited films of 20 nm thickness, and this value is found to improve after annealing. The as-deposited films were found to be smooth with an RMS roughness of 0.48 nm. Annealing in He resulted in only slight increase in the roughness (0.88 nm), whereas after annealing in air, the RMS roughness increased to a value of 2.8 nm. The mechanism of the developed ALD process was investigated with in situ mass spectrometry, in situ FTIR, and in vacuo XPS. This indicated oxidation of methanol on the RuO<sub>2</sub> surface, yielding CO<sub>2</sub> and H<sub>2</sub>O as byproducts and concomitant reduction of the RuO<sub>2</sub> top layer to metallic Ru or RuO<sub>x</sub>. The methanol pulse also leaves some CO residues on the surface. The reduced RuO<sub>2</sub> surface is then oxidized back to a thicker RuO<sub>2</sub> surface again during the next RuO<sub>4</sub> pulse with the removal of CO on the surface as CO<sub>2</sub>.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.2c02292>.

Ru 3d XPS spectrum of Ru metal, XPS fitting parameters, and details; SIMS data before and after annealing, ex situ and in situ XRD for processes using different alcohols, total X-ray scattering data, and PDF data for the annealed film; band gap calculation of RuO<sub>2</sub> films, in situ mass spectrometry data heat maps, and in vacuo XPS spectra acquired in the Si 2p and Ru 3d region (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement no. 765378. The authors would like to acknowledge Air Liquide for supplying the ToRuS precursor. We thank Ranjith. K. Ramachandran for useful discussions. M.M.M. and A.W. would like to thank the Flemish Research Foundation (FWO-Vlaanderen). The Special Research Fund BOF of Ghent University (GOA 01G01513) is also acknowledged. Dr. Alexander Merkulov is thanked for performing the SIMS measurements. The ESRF is acknowledged for provision of beamtime under proposal number MA-4987 ([doi.esrf.fr/10.15151/ESRF-ES-538779994](https://doi.esrf.fr/10.15151/ESRF-ES-538779994)). The GIWAXS experiments were performed at the NCD-SWEET beamline at ALBA Synchrotron with the collaboration of ALBA staff.

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