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Atomic layer deposition of ruthenium using an ABC-type process: Role of oxygen exposure during nucleation

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ABSTRACT
Atomic layer deposition (ALD) of ruthenium is of interest for various applications in nanoelectronics and is currently gaining attention for its potential role in interconnect technology in future technology nodes. This work provides insights into the influence of the O2 pulse time on the film nucleation on SiO2 and on the resulting material properties. Ru thin films were deposited using a three-step ALD process consisting of ethylbenzene(1,3-butadiene)Ru(0) precursor, O2 gas, and H2 gas pulses. It is shown that the addition of an H2 pulse to a conventional two-step process reduces any RuOx formed during the O2 pulse to metallic Ru. This provides the opportunity to employ longer O2 pulses, which enhances nucleation, leading to faster growth initiation and smooth films. Using this process, the deposition of Ru films at 225 °C with a low oxygen impurity level (<4 at. %) and a resistivity of 26 ± 2 μΩ cm is demonstrated. The data illustrate that the dosing time required for saturation during the nucleation phase can substantially deviate from the conditions required for the steady-growth phase.

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I. INTRODUCTION
Ru is a noble metal with a high work function (4.7 eV) and a low bulk-resistivity (7.4 μΩ cm), it has a conductive oxide (the resistivity of RuO2 is 20 μΩ cm) and is relevant for various applications, most importantly in nanoelectronics and catalysis.1–3 It has been considered as an electrode in dynamic random access memory (DRAM) and as a gate metal in metal-oxide-semiconductor transistors (MOSFETs).3–10 In the back-end-of-line (BEOL), Ru has been employed as a seed layer for Cu electroplating, as well as a diffusion barrier for Cu interconnects.11–17 More recently, Ru is receiving considerable attention for use as the conducting interconnect material itself due to superior resistivity at dimensions relevant for sub-5 nm semiconductor devices.18,19 Finally, Ru films, and especially Ru nanoparticles, find widespread application in catalysis, where precise control of the film thickness or particle size distribution is essential.3,20–24

Growth of Ru thin films using chemical vapor deposition (CVD) and atomic layer deposition (ALD) has been studied extensively.25,26 When optimizing Ru thin film deposition processes for device applications, there are several key metrics to consider in terms of processing conditions and desired material properties. Deposition at low temperatures is often preferred, especially for BEOL applications. Ultrathin continuous films without any voids are needed when Ru is used as a diffusion barrier for Cu interconnects.27–30 The application of Ru as a conducting interconnect material requires Ru with low resistivity and low impurity contents.18

ALD processes typically consist of the alternating dosing of precursor and coreactant gasses that interact with a substrate through self-limiting surface reactions. In comparison to CVD, ALD generally offers conformal growth over three-dimensional nanostructures.
and more precise thickness control.\textsuperscript{31–34} While several coreactants have been explored such as NH\textsubscript{3}, H\textsubscript{2}, and O\textsubscript{2}, most Ru ALD processes utilize O\textsubscript{2} gas as the coreactant in an AB-type (i.e., two-step) ALD recipe.\textsuperscript{25,35,36} To date, a variety of Ru precursors have been examined for Ru ALD including metallocenes, β-diketonates and their derivatives,\textsuperscript{12,37} and recently, zerovalent precursors.\textsuperscript{12,47−49} Typically, Ru ALD from metallocene or β-diketonate precursors suffers from long nucleation delays.\textsuperscript{25} In addition to requiring a longer process time, recipes with long nucleation delays can result in films with rough interfaces as a result of island formation during the initial growth.\textsuperscript{44,45} It has been claimed that zerovalent precursors lead to deposition after a negligible nucleation delay on a variety of substrates,\textsuperscript{5,29,45} although only limited experimental results supporting this claim have been reported so far. Currently, these precursor molecules are being explored for their potential to deposit ultrathin, smooth films.

In Ru AB-type ALD processes using molecular O\textsubscript{2} as the coreactant, the growth mechanism relies on catalytic combustion and dehydrogenation reactions.\textsuperscript{42−45} During the O\textsubscript{2} pulse, the Ru surface catalyzes dissociative chemisorption of O\textsubscript{2}.\textsuperscript{13,44} Subsequently, during the adsorption of the metal-organic precursor, chemisorbed O species participate in the combustion of the precursor ligands,\textsuperscript{34} while dehydrogenation reactions releasing H\textsubscript{2} proceed when O is consumed.\textsuperscript{45} A layer of partly dehydrogenated carbonaceous species eventually blocks further surface reactions and thereby causes the self-limitation of the precursor pulse.\textsuperscript{43,46,47} Ru is a particularly complex material because of its propensity to form subsurface O species, which can lead to more O incorporation in the final film.\textsuperscript{33,34} In many AB-type recipes, the primary difference between deposition of RuO\textsubscript{2} versus Ru metal is the ratio between the Ru precursor and O\textsubscript{2} pulse times or partial pressures,\textsuperscript{6,42} suggesting that short O\textsubscript{2} pulse times and/or low O\textsubscript{2} pressures should be employed to deposit metallic Ru. However, Methaapanon et al. have shown that higher O\textsubscript{2} pressures enhance nucleation, which, in turn, is important in determining the grain size of the final crystalline Ru film.\textsuperscript{33} They reported that smaller grain sizes were obtained when increasing the duration of the O\textsubscript{2} pulse, but past a certain point, longer O\textsubscript{2} pulse times eventually lead to O incorporation into the film. Deposition of films with small grains can be preferred for some applications because of their low surface roughness. On the other hand, in films with large grains, there is less charge carrier scattering at grain boundaries, resulting in lower resistivity.\textsuperscript{48–54}

Temperature also plays a critical role in determining whether Ru or RuO\textsubscript{2} is deposited. Generally, low deposition temperatures (<~200 °C) promote the deposition of RuO\textsubscript{2}.\textsuperscript{25} However, depending on the abovementioned ratio between the precursor and O\textsubscript{2} exposures, RuO\textsubscript{2} and Ru ALD can have overlapping temperature windows,\textsuperscript{37,38,55,56} meaning that careful attention to process parameters is required to prevent O as an impurity in Ru films. Hämäläinen et al. and Knoops et al. developed ABC-type ALD processes for noble metal ALD, whereby an H\textsubscript{2} gas step is added after the coreactant step (O\textsubscript{2}, O\textsubscript{3} plasma, or O\textsubscript{2}) to reduce the deposited film during each cycle.\textsuperscript{25,37–39} These processes generally allow for deposition of the metallic material at low temperatures, even down to room temperature.\textsuperscript{46,48} Other works on the nucleation of Pt and Pd ABC-type ALD processes have examined to what extent process parameters such as the number of cycles and substrate temperature can be used to tune particle size for catalysis applications.\textsuperscript{51,62} Regarding Ru, Lu et al. developed an ABC-type thermal ALD recipe consisting of successive exposures of bis-(ethylcyclopentadienyl) ruthenium ([Ru(ETCp)\textsubscript{2}], O\textsubscript{3}, and H\textsubscript{2} to deposit metallic Ru on Ru substrates at temperatures as low as 150 °C.\textsuperscript{63} Using quadruple mass spectrometry measurements, they demonstrated that for low temperatures, an H\textsubscript{2} step is necessary to reduce the deposited RuO\textsubscript{2} to metallic Ru.\textsuperscript{63} In a seminal study by Lu et al., various combinations of ABC-type cycles for Ru, Pd, and Pt ALD were employed to synthesize supported bimetallic nanoparticles with accurate control of the composition, size, and structure.\textsuperscript{64}

While the growth of Ru and RuO\textsubscript{2} films by ALD has been studied extensively, the nucleation of Ru ALD is not well understood.\textsuperscript{65} Because Ru ALD starts on most substrates as island growth, the chemical and physical reactions occurring during the nucleation phase can be very different from the steady-growth phase. This is especially relevant considering that the nucleation phase is important in ensuring deposition of a continuous layer and can also affect the resulting roughness.\textsuperscript{65,66} In previous studies, it has been demonstrated that oxygen plays a key role in the nucleation of noble metal ALD in AB-type processes. In our earlier work on Pt ALD, enhanced nucleation was observed for high O\textsubscript{2} pressures or extended O\textsubscript{2} pulse times.\textsuperscript{67} These observations were explained in more detail recently by Grillo et al. by considering that the combustion of precursor ligands leads to the release of heat, which can unpin nanoparticles from a specific location and thereby contribute to nanoparticle diffusion and sintering in large metal clusters.\textsuperscript{68,69} Furthermore, they observed that the removal of ligands from the oxide surface is the limiting factor, requiring a large O\textsubscript{2} exposure.\textsuperscript{68} As mentioned, Methaapanon et al. have shown that extended O\textsubscript{2} pulses result in smaller grain sizes and that high O\textsubscript{2} pressures are critical to achieving successful nucleation of the Ru film.\textsuperscript{33,34} Nevertheless, adjusting these parameters requires careful optimization to avoid oxygen incorporation into the film.\textsuperscript{13,44} The development of an ABC-type ALD process that includes an H\textsubscript{2} pulse gives the opportunity to extend the O\textsubscript{2} dose, without oxidizing the deposited Ru to RuO\textsubscript{2}.

In this work, we examine the growth and nucleation of Ru thin films deposited using the zerovalent precursor ethylbenzene (1,3-butadiene)Ru(0) (EBCHDRu) in an ABC-type ALD process that includes an H\textsubscript{2} pulse. In particular, we look at how the duration of the O\textsubscript{3} and H\textsubscript{2} pulses influences the growth and nucleation of the film and how these parameters can be used to manipulate the material properties. Differences between the saturation of the half-reactions during the nucleation and steady-growth phases are discussed.

II. EXPERIMENT

A. ALD reactor and film deposition

All depositions were performed in a homebuilt ALD reactor with a base pressure of 10\textsuperscript{−6} Torr as described in detail in previous work.\textsuperscript{2} The ethylbenzylcyclohexadiene Ru(0) precursor (EBCHDRu, 99.995% purity) was purchased from Hansol Chemical, Korea and was heated to 90 °C. The manifold lines were
heated to 110 °C and the reactor walls to 80 °C. Before each set of experiment, the reactor chamber was conditioned with at least 100 cycles of Al2O3 ALD followed by 500 cycles of RuOx ALD. The recipe for RuOx ALD consisted of a 15 s EBCHDRu dosing, 5 s Ar purge, 30 s O2 gas exposure (O2 pressure of 0.7 Torr), and 7 s Ar purge.

Depositions were performed on single-side polished Si substrates with a thermal oxide of 430–460 nm thick. All SiO2 substrates were cleaned using an O2 plasma (100 W) at 15 mTorr for 1 min to remove any organic residue. An O2 pressure of 15 mTorr and an H2 pressure of 1.5 × 10² mTorr were used for all Ru ALD experiments. Unless stated otherwise, 15 s EBCHDRu, 15 s O2 gas, and 5 s H2 gas pulses were employed as the standard recipe, which was performed with the substrate table set to a temperature of 225 °C. We employed the same recipe in our recent work on area-selective ALD of Ru.²

For noble metal ALD processes with a substantial nucleation delay, it is important to recognize that there is a difference between the average growth per cycle (GPC) determined from the ex situ measurement of the final thickness divided by the number of cycles (here referred to as the average GPC), and the GPC determined from the slope of a nucleation curve collected using in situ measurements. The average GPC is typically lower since it includes the effect of the nucleation delay, while the GPC from in situ measurements can be used to more accurately describe the steady-growth regime.

A Ru seed layer was used as the starting substrate for the measurement of the saturation curves of Fig. 1. Using a Ru seed layer instead of an SiO2 substrate ensures that the effect of the nucleation delay is minimized. To prepare this seed layer, 500 cycles of a Ru ABC-type process consisting of 15 s EBCHDRu, 15 s O2, and 15 s H2 pulses were carried out at a temperature of 275 °C, resulting in approximately 16 nm of Ru. No O2 plasma treatment was performed prior to deposition on the Ru seed layer to avoid any etching.

B. Characterization

In situ spectroscopic ellipsometry (SE) was conducted using a J. A. Woollam, Inc. M2000U ellipsometer (1.2–5.0 eV photon energy) with SE measurements performed after every five cycles for the saturation curves of Fig. 1 and after every 10 cycles for all other depositions. Ex situ measurements were carried out using a J. A. Woollam M2000D ellipsometer (1.2–6.5 eV) at variable angles of 60°, 70°, and 80°. The dielectric functions of the deposited Ru metal films were fitted using a B-spline model and matched those found by Leick et al.⁵ The surface oxidation of the Ru film due to the exposure to air was not taken into account in the ellipsometry model, and consequently, the thickness measured using ex situ SE was ~2 nm thicker than the value obtained from in situ analysis. In situ SE was also employed to determine the actual temperature of the substrate by modeling the temperature of a bare Si substrate during a control experiment as described in Fig. S1.⁷⁻⁹⁻¹⁵⁻¹⁹

Four-point probe (FPP) measurements were carried out using a Keithley 2400 Sourcemeter and Signatron probe to determine the electrical resistivity of each sample. For composition analysis, x-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermoscientific KA1066 system with monochromatic Al Kα x-rays (1486.6 eV). Each sample was sputtered with Ar⁺ ions (500 eV) for 60 s to remove any adventitious carbon and surface oxidation. It was found that a 60 s sputter time was sufficiently long to remove these contaminants without causing a significant decrease in the Ru peak intensity. To examine surface morphology and roughness, atomic force microscopy (AFM) measurements were performed using a Veeco Dimension 3100. The surface roughness was determined using the open source software package Nanoscope Analysis.¹¹ Low frequency noise and sample tilt effects were removed prior to image analysis.

To investigate the nucleation behavior, Ru ALD was performed on TEM windows and studied by scanning transmission electron microscopy (STEM) in a high angle annular dark field (HAADF) mode using an aberration-corrected microscope (JEOL JEM ARM200F). Si₃N₄ TEM windows were prepared by coating them with approximately 10 nm of SiO₂ in an Oxford Instruments FlexAL ALD reactor such that the TEM windows resemble the surface conditions of the samples used in other depositions. The samples were then transferred to the homebuilt ALD reactor where they were cleaned with 1 min O₂ plasma (100 W) at a pressure of 15 mTorr prior to Ru deposition.

**FIG. 1.** Growth per cycle (GPC) as a function of (a) EBCHDRu pulse time (using 15 s O₂, 15 s H₂), (b) O₂ pulse time (15 s EBCHDRu, 15 s H₂), and (c) H₂ pulse time (15 s EBCHDRu, 15 s O₂) on Ru seed layers at 225 °C.
III. RESULTS AND DISCUSSION

To determine the effect of using an ABC-type recipe on the saturation of the subcycles, a series of depositions with various EBCHDRu, O2, and H2 pulse times was performed. As mentioned, a Ru film of approximately 16 nm in thickness was used as the initial seed layer to measure the GPC without having to take nucleation effects into account. Figure 1 shows the saturation curves revealing that the O2 subcycle saturated after just 1 s and the H2 subcycle after 5 s. It is noted that beyond 15 s EBCHDRu dosing, the GPC increased slightly and showed more variation. We attribute this to changes in the substrate temperature during the cycle as verified by additional in situ SE measurements (see Fig. S175).

The recipe including a 15 s EBCHDRu pulse was found to have a GPC that is constant and reproducible at 0.033 ± 0.002 nm, and thus a 15 s precursor pulse was used for all other depositions. This GPC is lower than the value reported in the literature for the two-step ALD process using EBCHDRu and O2 (0.1 nm/cycle),12 which can be explained by the removal of chemisorbed O during the H2 pulse.46,63

The reaction mechanism of this process is expected to be similar to what has been reported for Ru ABC-type cycles with Ru (EtCp)2, O3, and H2 pulses.63 The main role of the H2 pulse is to ensure that metallic Ru is deposited instead of RuOx. Figure 2 deals with the influence of the H2 pulse time on the oxygen contents of the Ru film, showing the Ru 3p and O 1s XPS peaks for films deposited using 500 Ru ALD cycles on SiO2. For the film prepared using a 1 s H2 pulse, there is no Ru peak at 470.9 eV, which is a satellite peak characteristic of metallic Ru, suggesting that using only a 1 s H2 pulse results mostly in RuOx deposition. In the corresponding O 1s spectrum [Fig. 2(b)], an intense and broad Ru –Op eak is present. Fitting of the Ru–O peak shows that there is approximately 47 at % O in this film. When using H2 pulse times of 5 s or longer, the O content is in the range 5–8 at. %, which includes O that is incorporated during postdeposition oxidation in atmosphere. Thus, an H2 pulse of 5 s or longer is required to reduce the film to metallic Ru.

Figure 3 shows TEM images of Ru on SiO2-coated TEM windows representing the nucleation phase, prepared by employing various numbers of Ru ALD cycles using the standard recipe with 15 s O2 and 5 s H2 pulses. As the number of cycles increases, the Ru islands increase both in density and size. Figures 3(a)–3(c) depict that the islands are not monodisperse and aggregate into larger clusters, resembling previous nucleation studies for noble metal ALD.62,66,77,78 Both small and large islands are present, corresponding to a broad particle size distribution, which suggests that the formation of nuclei does not solely occur during the first few cycles but throughout the deposition process. Figures 3(d) and 3(e) illustrate that when the islands grow in size, eventually island coalescence and film closure occurs.

To explore whether the reactions during the O2 and H2 subcycles are also in saturation during the nucleation phase, 500 cycles of Ru ALD using different O2 and H2 pulse times were performed on SiO2 substrates. The final film thicknesses were determined using SE and are shown in Fig. 4. Because these measurements were taken ex situ, the film thicknesses include the contribution of nucleation delays on the SiO2 substrate, as well as surface oxidation following removal of the sample from the reactor (see Sec. II).

Contrary to the depositions performed on the Ru seed layer where the O2 subcycle saturates after only 1 s, on SiO2 approximately 45 s of O2 exposure is needed for saturation. Furthermore, for O2 pulses up to 15 s, the average GPC on SiO2 is lower than the GPC on the Ru seed layer. For example, 500 cycles of the standard recipe (15 s EBCHDRu, 15 s O2) at 225 °C using various H2 pulse times on SiO2. All samples were sputtered with Ar for 60 s prior to analysis.
data suggest that a long O₂ pulse time is needed to enhance the nucleation of Ru on SiO₂ in order to form a continuous film. Once this continuous film has been formed, shorter pulse times should be sufficient to achieve saturation, as can be concluded from the data of Fig. 1.

Figure 4(b) examines the effect of the H₂ pulse time on the final film thickness. For a 1 s H₂ pulse, a thickness as high as 35 ± 2 nm was measured, while saturation is reached after 5 s yielding a thickness of approximately 14 ± 2 nm. If viewed in conjunction with the XPS results (Fig. 2), it can be deduced that the higher thickness for the film deposited using 1 s H₂ is likely due to incomplete reduction of RuOₓ. Overall, the saturation behavior of the H₂ subcycle in Fig. 4(b) is similar to the saturation for the steady-growth phase shown in Fig. 1(c). Note that in both cases, an O₂ pulse time of 15 s was employed.

The observation that for O₂ pulse times ≥45 s the average GPC [Fig. 4(a)] is higher than the GPC from in situ data requires more attention. Although a 5 s H₂ pulse is sufficient for saturation when using a 15 s O₂ pulse [Fig. 4(b)], this appears not to be the case when using longer O₂ pulses. A likely explanation is that incomplete reduction of RuOₓ leaves chemisorbed O at the surface that can promote precursor adsorption, thereby leading to a higher growth rate. In contrast to growth on a Ru film, the Ru nuclei present during the nucleation on SiO₂ are expected to oxidize to a larger extent, requiring longer H₂ dosing for reduction to metallic Ru. The data, therefore, suggest that a 5 s H₂ pulse may not be sufficient during the nucleation on SiO₂ in the case when O₂ pulse times ≥45 s are used.
Figure 5 shows XPS that was performed on the same films as used to collect the data of Fig. 4(a), deposited with various O$_2$ pulse times. For the film prepared using a 1 s O$_2$ pulse, there is an Si–O peak in addition to a relatively large Ru–O peak in the O 1$s$ spectrum, which is because a thin and discontinuous RuO$_x$ film is deposited for this condition. For all other films deposited using O$_2$ pulse times of 15 s and longer, metallic Ru is obtained with a low O content that is constant at 7 ± 1 at. % (which includes postdeposition oxidation). Importantly, increasing the O$_2$ pulse time from 15 to 60 s, while using the same 5 s H$_2$ pulse time, does not result in incorporation of more O into the final film. This implies that O contained in the initial Ru nuclei (see discussion above) is eventually consumed in the surface reactions when the nuclei coalesce and evolve into a continuous film.

Taken together, the data of Figs. 4 and 5 lead to the important conclusion that a longer O$_2$ pulse time can be used in the developed Ru ABC-type ALD process, as a parameter to further tune and optimize the nucleation and material properties of the film, without resulting in RuO$_x$ deposition. To examine the effect of the O$_2$ pulse time on the initial Ru nucleation more closely, 100 cycles of Ru ALD using various O$_2$ pulse times were performed on SiO$_2$-coated TEM windows, and the resulting plan-view TEM images are depicted in Figs. 6(a)–6(d). A 1 s O$_2$ pulse leads to a nonuniform distribution of Ru islands as shown in Fig. 1(a). As the O$_2$ pulse time increases from 1 to 45 s, the Ru islands increase in size, while the fraction of visible SiO$_2$ decreases. These TEM images clearly illustrate that when using a longer O$_2$ pulse time, Ru evolves more quickly into a continuous film. Based on previous works on the nucleation of Pt ALD, it can be expected that increasing the O$_2$ pressure has a similar effect and that the O$_2$ exposure (O$_2$ pressure × O$_2$ pulse time) governs the nucleation behavior.

The dependence of the nucleation on the O$_2$ pulse time can potentially be exploited for enhancing the microstructure of the film. AFM, SEM, and FPP measurements were performed on the samples that were also used for Figs. 4(a) and 5, prepared by 500 Ru ALD cycles using various O$_2$ pulse times. In agreement with the results from Methaapanon et al., the SEM results depicted in Fig. 7.
suggest that the grain size decreases as the O$_2$ pulse time is extended from 1 to 45 s. The SEM image for 60 s O$_2$ dosing deviates from this trend, which is likely related to incomplete reduction of RuO$_x$ during the nucleation phase as discussed above. AFM analysis presented in Table S1 and Fig. S2 revealed relatively smooth films with roughness values of 0.5 ± 0.2 nm for O$_2$ pulse times of 30–45 s. In addition, Fig. 8(a) shows that the resistivity decreases with the O$_2$ pulse time until reaching a value of 33 ± 1 $\mu$Ω cm. The resistivity also decreases with the H$_2$ pulse time as depicted in Fig. 8(b), corresponding to the decrease in the oxygen content as shown by XPS (Fig. 3). From the results reported in the literature for AB-type processes using EBCHDRu precursor, the low-resistivity films are expected to consist of polycrystalline grains of hexagonal close-packed Ru without a RuO$_2$ fraction. A thicker film (24 ± 2 nm) deposited using an optimized process of 700 ALD cycles with extended O$_2$ and H$_2$ dosing times of 45 and 15 s, respectively, showed nearly negligible oxygen contents (4 at. %) and a resistivity of 26 ± 2 $\mu$Ω cm. These results are comparable to state-of-the-art values published in the literature for Ru ALD. For example, resistivity values of 14–20 and 29–36 $\mu$Ω cm have been reported for AB-type ALD processes using zerovalent EBCHDRu and (1,5-hexadiene)(1-isopropyl-4-methylbenzene)ruthenium precursors, respectively. In summary, the analysis of the material properties suggests that using a longer O$_2$ pulse time improves the nucleation of Ru on SiO$_2$, leading to smooth films.

IV. CONCLUSIONS

A more robust method for Ru ALD of smooth films with low resistivity and negligible O incorporation was demonstrated. By reducing surface RuO$_x$ every cycle, the additional H$_2$ pulse allows for employing longer O$_2$ pulse times. This opens up the possibility of using the O$_2$ pulse time or the O$_2$ pressure as a parameter to control the nucleation of the film, and it was shown that extended O$_2$ dosing results in substantially enhanced nucleation of the Ru film. Considering that a similar dependence on O$_2$ exposure has been reported for Pt ALD, we believe that this approach of using...
ABC-type cycles that include an H$_2$ pulse can also be employed to enhance the nucleation and improve the material properties of other noble metals.

The influence of the O$_2$ pulse time on the nucleation behavior might be even more pronounced than the selection of the precursors. However, the strong dependence on processing conditions makes it difficult to compare the results obtained for specific precursors (e.g., zerovalent versus metallocene precursors) in different laboratories. Future research should, therefore, focus more on comparing precursors using the same coreactant dose. Evidently, the data presented in this work suggest that optimizing the dosing conditions requires more attention when aiming for Ru ALD with a minimal nucleation delay.

This work also demonstrates that to ensure the saturation of the half-reactions, different conditions are required during the nucleation phase as compared to the steady-growth phase. An increase of the final film thickness indicating a shorter nucleation delay was observed for O$_2$ pulse times up to 45 s, while the O$_2$ half-reaction was shown to saturate already at 1 s O$_2$ dosing when performing deposition on Ru itself. These observations are consistent with previous results on the saturation during the synthesis of noble metal nanoparticles and imply that the surface reactions of Ru nucleation are substantially different as compared to those of the steady-growth phase, possibly due to the contribution of surface diffusion of deposited atoms and catalytic surface reactions. The data also suggest a longer H$_2$ pulse time is needed for the reduction of RuO$_x$ islands during nucleation as compared to the reduction of a RuO$_x$ surface layer during the steady-growth phase. As a general conclusion, it can be stated that to achieve a uniform and conformal deposition of noble metals, it is essential to also investigate the saturation of the surface reactions during the nucleation phase.

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