Atomic layer deposition and selective etching of ruthenium for area-selective deposition

Citation for published version (APA):

Vos, M. F. J., Chopra, S. N., Ekerdt, J. G., Agarwal, S., Kessels, W. M. M., & Mackus, A. J. M. (2021). Atomic layer deposition and selective etching of ruthenium for area-selective deposition: Temperature dependence and supercycle design. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films*, 39(3), [032412]. <https://doi.org/10.1116/6.0000912>

Document license:
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DOI:
[10.1116/6.0000912](https://doi.org/10.1116/6.0000912)

Document status and date:
Published: 01/05/2021

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Atomic layer deposition and selective etching of ruthenium for area-selective deposition: Temperature dependence and supercycle design

Cite as: J. Vac. Sci. Technol. A 39, 032412 (2021); doi: 10.1116/6.0000912

Submitted: 5 January 2021 · Accepted: 12 March 2021 ·

Published Online: 9 April 2021

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Note: This paper is a part of the Special Topic Collection on Area Selective Deposition.

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ABSTRACT

For future sub-5 nm technology nodes, the fabrication of semiconductor devices will likely involve the use of area-selective atomic layer deposition (ALD). While area-selective ALD processes have been reported for a variety of materials, most approaches yield a limited selectivity, for example, due to growth initiation at defects or impurities on the non-growth area. Recently, we demonstrated that Ru ALD can be combined with selective etching to achieve area-selective ALD of metal-on-metal with high selectivity. Cycles consisting of an O₂ plasma and an H₂ gas dose were integrated in an ALD-etch supercycle recipe to remove unwanted nuclei on the SiO₂ non-growth area, while obtaining deposition on the Pt or Ru growth area. The current work discusses the challenging compromise that needs to be made between selectivity and net deposition, considering that the material is also removed from the growth area. After investigating deposition between 100 and 200 °C on SiO₂, Al₂O₃, Pt, and Ru in terms of selectivity and net deposition, a substrate temperature of 150 °C was selected since the difference in Ru thickness on Pt and SiO₂/Al₂O₃ was maximum at this temperature, even though still some deposition occurred on the SiO₂ and Al₂O₃ non-growth areas. Different ALD-etch supercycles were studied, using varying O₂ plasma etch times and etch frequencies. The amount of the (undesired) material deposited on the SiO₂ non-growth area was quantified, demonstrating that the selectivity improved for longer O₂ plasma times. On the basis of the results, a simple mathematical description of the nucleation, growth, and etching effects during ALD-etch supercycles is discussed, which can assist the design of future area-selective deposition processes. Overall, this work illustrates how ALD and etch processes can be tuned to simultaneously obtain a high selectivity and a high net deposition of the material at the desired locations.

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I. INTRODUCTION

As integrated circuit manufacturing is moving toward sub-5 nm technology nodes, there is an ongoing effort to develop alternative fabrication techniques that can meet the increasingly demanding patterning requirements.¹ Traditionally, semiconductor devices are fabricated by repetition of deposition, lithography, and etch steps.² This top-down approach, while highly sophisticated, becomes challenging to use for next generation devices due to

misalignment of device features.^{3,4} Bottom-up fabrication methods that are characterized by the deposition of materials only where needed, can possibly solve alignment issues by making some lithography-based patterning steps obsolete.^{5,6} For this reason, area-selective deposition is regarded as an alternative, bottom-up approach to device fabrication. The industry has been employing area-selective chemical vapor deposition (CVD) processes, including selective epitaxy of Si and SiGe and selective capping of Cu interconnects by Co.^{7,8} In recent years, with the wide-scale

implementation of atomic layer deposition (ALD) in semiconductor manufacturing, especially area-selective ALD has emerged as a promising method for area-selective deposition.^{9,10} ALD is a vapor-phase thin film deposition technique based on cycles consisting of sequential precursor and coreactant exposures that are separated by purge steps.¹¹ The technique relies on self-limiting surface reactions, allowing for deposition with precise thickness control, good uniformity, and high conformality, which gives area-selective ALD several advantages over area-selective CVD.^{12–16}

Although several methods have been developed to achieve area-selective ALD, the selective growth can typically only be retained for a limited number of ALD cycles until selectivity is lost due to nucleation of material at defects or impurities on the non-growth area.¹⁰ Industrial applications of area-selective ALD require high selectivity for thicknesses on the growth area of up to ~10 nm, which is often not achievable.¹⁷ To obtain a sufficiently high selectivity, it is necessary to employ methods that involve an intermittent correction or cleaning step to remove material from the non-growth area during the deposition process.^{10,18–21}

Interestingly, the use of “cleaning steps” has already been reported several decades ago for area-selective epitaxy of Si.^{22,23} By adding an etchant gas such as HCl to the Si source gas, unwanted Si nuclei on SiO₂ or Si₃N₄ are removed, resulting in area-selective CVD of Si on Si growth areas.^{22–24} Methods that improve the selectivity of ALD by correcting for the deposition on the non-growth area have only recently been considered in the ALD community. Hashemi *et al.* proposed a lift-off strategy for the area-selective ALD of Al₂O₃ films on SiO₂ in the presence of Cu.²⁵ ALD on Cu areas was deactivated using a self-assembled monolayer (SAM) and postdeposition etching of the SAM layer using acetic acid resulted in the removal of any Al₂O₃ that was deposited on the Cu/SAM, thereby leading to an improvement of the selectivity. Using etch steps integrated during the deposition process Vallat *et al.* achieved area-selective deposition of Ta₂O₅ and TiO₂ on TiN.^{18,19} After a number of ALD cycles, they used an O₂/NF₃ plasma etch step to remove nuclei from Si and SiO₂ non-growth areas, and to simultaneously inhibit growth on these surfaces in subsequent ALD cycles through the formation of unreactive Si-F surface groups.^{18,19} More recently, Parsons and co-workers demonstrated area-selective ALD of TiO₂ on SiO₂ in the presence of H-terminated Si as the non-growth area by integrating atomic layer etching (ALE) cycles in ALD-ALE supercycles.^{20,21} The ALE cycles consisting of WF₆ and BCl₃ doses resulted in the removal of TiO₂ deposited on the H-terminated Si non-growth area, which enabled selective deposition of up to ~12 nm TiO₂ on SiO₂.²⁰

The method of combining deposition and etching is highly promising, since it allows for significant improvement of the selectivity that can be achieved. The etch step unfortunately also results in the removal of the deposited material from the growth area (where deposition is actually desired). However, the ALD-etch supercycle can be repeated as often as required in order to obtain the target thickness on the growth area. Nevertheless, considerably more material should be deposited than etched during one supercycle, such that the method provides a sufficiently high net deposition. It is noted that *growth-area selectivity* and *etch selectivity* are the two main parameters that are important for the approach.²⁶ Growth-area selectivity refers to preferential deposition of a

material on the growth area, while the non-growth area is left blank. Etch selectivity refers to preferential removal of a material with respect to a mask, underlying material, or other materials present in a device. For example, O₃ etches Ru and photoresist with high selectivity toward the Ru (i.e., Ru is etched faster).

Recently, we extended the approach based on ALD-etch supercycles to area-selective ALD of metal-on-metal, in this case, Ru on Pt or Ru.²⁶ Ru has a low bulk resistivity of 7.1 μΩ cm and its oxide, RuO₂, also exhibits a low resistivity as compared to other metal oxides.^{27,28} Area-selective ALD of Ru is relevant for industrial applications, since Ru is investigated for use in metal interconnects, either as a diffusion barrier for Cu (which demonstrates a low solubility in Ru), or as the conducting wire material itself.^{29–34} Ru also has applications as an electrode in dynamic random access memory (DRAM), gate metal in transistors, and seed layer for electroplating.^{35–40}

Although area-selective ALD is in an early stage of development, there are several reports on area-selective ALD of Ru. For example, Minjauw *et al.* recently reported on the thermal ALD process using RuO₄ and H₂, which demonstrates inherent selectivity by allowing for deposition on H-terminated Si in the presence of SiO₂ as a non-growth area.⁴¹ Park *et al.* patterned octadecyltrichlorosilane self-assembled monolayers (SAMs) to block Ru ALD, in order to obtain Ru lines on SiO₂ and HfO₂ surfaces.²⁹ In addition, Ru was selectively deposited on SiCN by Zyulkov *et al.*, while inhibiting growth on amorphous C (a-C) by using an H₂ plasma treatment prior to ALD.⁴² The H₂ plasma exposure results in the formation of CH₃ surface groups on a-C, which are not reactive toward the (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)Ru precursor (EBECHRu). Färm *et al.* achieved the area-selective ALD of Ru by patterning a seed layer of RuCl₃ using microcontact printing.⁴³ This RuCl₃ seed layer was oxidized to RuO_x, which was successfully used to activate subsequent Ru ALD growth at 250 °C. Finally, ALD of Ru on Pt was demonstrated by Junige *et al.*, where Pt was locally deposited on the SiO₂ substrate using electron-beam induced deposition.⁴⁴

In our previous work, a thermal Ru ALD cycle was combined with a selective etch cycle to remove Ru deposited on the SiO₂ non-growth area. The ALD-etch supercycle allowed for area-selective deposition of Ru on Pt and Ru, while obtaining a clean SiO₂ surface.²⁶ The Pt starting surface was primarily used to achieve elemental contrast when employing chemical analysis techniques (e.g., x-ray photoelectron spectroscopy and energy-dispersive x-ray spectroscopy), whereas the area-selective ALD of Ru on Ru is more relevant for semiconductor device manufacturing. The thermal Ru ALD process shows considerable growth on catalytic Pt and Ru at low deposition temperatures and less growth on dielectric SiO₂. This difference in growth behavior served as the starting point for the development of the area-selective deposition process and was explained by the fact that the Pt and Ru substrates facilitate the catalytic dissociation of O₂.^{26,45,46} O formed on Pt or Ru can participate in the combustion of the Ru precursor ligands, whereas SiO₂ does not demonstrate catalytic activity for this reaction.^{45,46} In order to improve the selectivity, Ru nuclei formed on the SiO₂ non-growth area were removed using an etch cycle which is based on an O₂ plasma exposure, leading to the formation of volatile RuO₄. An H₂ gas dose was added after the O₂ plasma to reduce the formed surface RuO_x to metallic Ru. This etch process results in the removal of only Ru and not Pt or SiO₂, and is therefore selective.^{47,48}

In this work, a detailed study of the ALD and etch processes for Ru is provided in the context of area-selective deposition. Specifically, the temperature dependence of the thermal Ru ALD process is investigated, as well as the effect of the O₂ plasma etch process on the net deposition of Ru on Pt. To assess the selectivity as a function of O₂ plasma etch time, the deposition on the SiO₂ non-growth area is characterized using various techniques. The O₂ plasma etch time and the etch frequency were varied, in order to find conditions for which a clean SiO₂ non-growth area is obtained, while the deposition on the growth area is maximized (corresponding to high “net deposition”). Based on the insights obtained from these experiments, general design principles are discussed to provide guidelines for the optimization of ALD-etch cycles for area-selective deposition.

This publication is structured as follows. First, the experimental conditions concerning the ALD and etching of Ru, as well as the characterization of the deposited films are described in Sec. II. This is followed in Sec. III by the experimental results: in Sec. III A the results on the effect of the deposition temperature on the ALD growth are presented and Sec. III B then addresses the characterization of the ALD-etch supercycle; both the net deposition on Pt and the selectivity are evaluated as a function of O₂ plasma time. Section IV discusses a mathematical description of the ALD-etch supercycles and provides a general discussion on how a high selectivity and a high net deposition can simultaneously be obtained when using supercycle recipes. Finally, the main conclusions are presented in Sec. V.

II. EXPERIMENTAL METHODS

A. Thermal atomic layer deposition and plasma etching of Ru

Ru films were deposited using a thermal ABC-type ALD process as described in detail elsewhere.⁴⁹ The ABC-type cycle is illustrated in Fig. 1(a) and consists of a 15 s ethyl-benzenecyclohexadiene Ru(0) (EBCHDRu) precursor dose (“A”), a 15 s O₂ gas dose (“B”), and a 5 s H₂ gas dose (“C”). Due to the addition of a reducing H₂ dose to the cycle, the ABC-type process results in the deposition of metallic Ru at temperatures below 200 °C.^{50–52}

The unwanted Ru present on the non-growth area was etched using an O₂ plasma. The etching of Ru occurs through the formation of volatile RuO₄, as is illustrated in Fig. 2. The Ru film on the growth area is also exposed to this O₂ plasma, and some material is, therefore, also removed from the growth area. Furthermore, the Ru surface region is simultaneously oxidized. For this reason, every O₂ plasma etch step is followed by a reducing H₂ gas exposure. These exposures together form the etch cycle which is implemented either as a postdeposition etch [i.e., after the complete deposition, see Fig. 1(b)], or after a number of Ru ALD cycles in a supercycle fashion [see Fig. 1(c)].

B. ALD reactor and conditions

Ru film deposition and etching was performed using a home-built ALD reactor.⁵³ The EBCHDRu precursor (Hansol Chemical, Korea) was contained in a stainless steel canister heated to 90 °C and Ar was used as a carrier gas. To avoid condensation of the precursor, the dosing line and the walls of the reactor were heated to

FIG. 1. Different types of recipes used in this study: (a) the “standard” thermal Ru ALD recipe, consisting of EBCHDRu precursor, O₂ gas, and H₂ gas doses, (b) an ALD recipe followed by a post-deposition etch cycle consisting of an O₂ plasma and an H₂ gas dose, and (c) a supercycle recipe with the same etch cycle included after a certain number ($10 \times \alpha$) of thermal Ru ALD cycles. Spectroscopic ellipsometry (SE) measurements were performed after every 10 ALD cycles and after every etch cycle.

105 and 100 °C, respectively. Prior to Ru metal deposition, the reactor chamber was conditioned with 500 thermal ALD cycles of Al₂O₃ followed by 500 thermal ALD cycles of RuO_x. For the RuO_x process, a 15 s EBCHDRu dose and a 60 s O₂ gas dose (at 0.75 Torr) were used.

Ru growth was investigated on Ru, Pt, SiO₂, Al₂O₃, Co, and TiN substrates at temperatures between 100 and 200 °C. Wafer pieces with the corresponding materials were loaded in the reactor simultaneously. Single-side polished Si wafers with a thermal oxide of ~430–450 nm were used as the SiO₂ substrates. The Pt film (~15 nm) was deposited by performing 360 ALD cycles at 300 °C on thermal SiO₂, using an ABC-type cycle consisting of (methylcyclopentadienyl)-trimethylplatinum (MeCpPtMe₃) precursor, O₂ plasma, and H₂ plasma exposures.⁵⁴ The Al₂O₃ film (~20 nm) was deposited with TMA [Al(CH₃)₃] and O₂ plasma using 150 ALD cycles at a temperature of 200 °C. The Co sample (~25 nm) was prepared by performing 1000 ALD cycles at 450 °C using CoCp₂ and an NH₃ plasma.⁵⁵ For the TiN substrate (~13 nm), 450 cycles were carried out at 200 °C using Ti(NMe₂)₄ (TDMAT) and an Ar/H₂ plasma.⁵⁶ Prior to experiments using only Ru ALD (without etching) the substrates were pretreated using H₂ gas for 30 s, while the pretreatment for ALD-etch supercycles was

FIG. 2. Schematic illustration of the etch cycle used to remove unwanted nuclei on the SiO_2 surface. Exposing the surfaces to an O_2 plasma leads to the formation of volatile RuO_4 . After the O_2 plasma exposure, the Ru on the Ru or Pt growth area is slightly oxidized, and the subsequent H_2 gas exposure results in reduction of the surface. The O_2 plasma does not etch the SiO_2 or Pt substrates, hence the etch step is selective.

done using an O_2 plasma (100 W) for 1 min, followed by a 30 s reducing H_2 gas exposure. It was decided to include the O_2 plasma exposure in order to minimize effects related to surface contamination, which can vary from sample to sample. The O_2 and H_2 pressures during all experiments were set to 15 and 150 mTorr, respectively. The O_2 plasma etching step was performed using a plasma power of 100 W, and different O_2 plasma exposure times of 5, 15, 30, and 60 s were investigated. The O_2 plasma exposure was followed by an H_2 gas dose of 15 s, which was previously found to be sufficiently long to reduce the surface back to metallic Ru after oxidation occurred during the O_2 plasma exposure.²⁶

C. Sample characterization

In situ spectroscopic ellipsometry (SE) data were collected using a J.A. Woollam, Inc. M2000U ellipsometer to monitor the deposition and etching of Ru. The data were fit using a B-spline model in the wavelength range of 1.2–4.5 eV.^{57,58} Depositions on SiO_2 were modeled by first defining the thickness and dielectric function of the SiO_2 substrate using a wavelength point-to-point exact numerical inversion of the experimental data.⁵⁷ For deposition of Ru on Pt, a B-spline model was used to fit the optical

response and thickness of the Pt substrate. The Ru thickness evolution was fit by first modeling the last *in situ* measurement. Subsequently, this fit was used as input for the first-to-last measurement, and this procedure was then repeated for all preceding measurements (i.e., dynamically fit backwards in time), while including the optical parameters in the fit.⁵⁸ *Ex situ* SE measurements were taken at angles of 60°, 70°, and 80° with a J.A. Woollam, Inc. M2000D ellipsometer (1.2–6.5 eV) to determine the final Ru thicknesses on SiO_2 , Al_2O_3 , and Pt at each deposition temperature. Since Ru growth starts out as island growth on SiO_2 and Al_2O_3 , the thickness determined from SE represents an average or effective value and therefore the term *apparent thickness* is used in this case. *Ex situ* x-ray photoelectron spectroscopy (XPS) was used to quantify the deposited Ru on the various substrates and was carried out with a Thermo Scientific KA1066 spectrometer, using monochromatic Al $K\alpha$ x-rays with an energy of 1486.6 eV. The Ru XPS signal can be used as an indication for the amount of Ru present, as long as the thickness is below the detection depth (~ 10 nm). For this XPS analysis, the Ru3p peak instead of the Ru4d peak was used, since the Ru3d and C1s XPS peak regions overlap.⁵⁹ Although the sensitivity for the Ru3p peak is slightly lower, detection of Ru in the presence of C is more accurate using the Ru3p peak, especially for low Ru coverages on SiO_2 and Al_2O_3 .⁶⁰ Scanning electron microscopy (SEM) images were taken using a Zeiss Sigma with a beam voltage of 5 kV, which allowed for the identification of Ru nuclei due to the differences in density and conductivity between Ru and SiO_2 .⁶¹

III. RESULTS

A. Temperature dependence

To investigate whether the deposition temperature could be tuned to obtain selectivity, Ru ALD on SiO_2 , Al_2O_3 , and Pt substrates was investigated at different temperatures between 100 and 200 °C using *ex situ* SE and XPS. Figure 3 shows the final thickness and the Ru3p XPS peak area after performing 400 ALD cycles as a function of deposition temperature. For 200 °C, the amount of Ru deposition was approximately the same on all substrates, with thickness values around 9 nm, and similar Ru3p peak areas. As the deposition temperature was decreased, a difference in the Ru deposition on Pt versus SiO_2 and Al_2O_3 was observed. For a temperature of 150 °C, the amount of Ru on Pt is significantly higher than on SiO_2 and Al_2O_3 . As can be seen in Fig. 3(a), 8.4 nm of Ru was deposited on Pt, as compared to 2.7 and 0.5 nm on SiO_2 and Al_2O_3 , respectively. In addition, Fig. 3(b) shows a much higher Ru peak area for the Pt substrate than for SiO_2 and Al_2O_3 . Further decreasing the temperature resulted in considerably less growth on the Pt substrate (3 nm for 125 °C and 0.7 nm for 100 °C), and negligible deposition on both SiO_2 and Al_2O_3 . For the depositions at temperatures of 100 and 125 °C, no Ru was detected on SiO_2 and Al_2O_3 using both SE and XPS (see the [supplementary material](#),⁷⁷ Fig. S1 for the XPS spectra). Note that a nonlinear relation exists between the peak area and the film thickness, since the measured XPS peak area on Pt saturates at higher temperatures, for which the film thicknesses are in the same order as the detection depth. Nevertheless, Figs. 3(a) and 3(b) show a similar trend, with a large difference in film growth for a deposition temperature of 150 °C.

FIG. 3. (a) (Apparent) Ru thickness from SE and (b) Ru3p XPS peak area (in counts per second · eV) as a function of deposition temperature after 400 ALD cycles, on Pt, SiO₂, and Al₂O₃ substrates. The lines serve as guides to the eye. Note that the term *apparent thickness* is used in the case of nuclei on SiO₂ and Al₂O₃, since the thickness determined from SE represents an average or effective value.

Based on the results of Fig. 3, 150 °C was selected as the optimum deposition temperature to achieve area-selective deposition of Ru onto Pt, since the difference in thickness between Pt and SiO₂/Al₂O₃ is maximum at this temperature, and further decreasing the deposition temperature would lead to an impractically low growth rate on the Pt substrate. In addition, the growth of Ru on Co and TiN was investigated at 150 °C. XPS analysis showed that only limited growth occurred on the Co and TiN substrates, comparable to the growth on SiO₂ and Al₂O₃ (see Fig. S2, [supplementary material](#)⁷⁷). It is noted that these substrates are

likely oxidized due to the O₂ doses of the ALD cycle, meaning that the growth of Ru on CoO_x and TiO_x surfaces was in fact investigated. SE analysis however revealed that the Ru ALD process showed immediate growth on a Ru substrate. These findings corroborate that the catalytic activity of Ru and Pt is leading to more growth of Ru on these substrates than on SiO₂, Al₂O₃, Co, and TiN. After selecting 150 °C as the optimum temperature, the material deposited on SiO₂ was studied in more detail using SEM (see Fig. S3, [supplementary material](#)⁷⁷). The SEM images reveal that Ru nuclei are present on SiO₂, which motivates the combination of this ALD process with etching steps to remove these nuclei.

B. Supercycle design

Prior to studying the ALD-etch supercycle approach, a postdeposition O₂ plasma treatment was investigated as a potential alternative method to improve the selectivity at 150 °C. 500 Ru ALD cycles were performed at 150 °C, followed by a postdeposition etch cycle consisting of 3 min O₂ plasma exposure and 30 s H₂ gas [see Fig. 1(b)]. It was found that while the O₂ plasma etch step removed some Ru nuclei from SiO₂, a significant number of islands remained on the surface (see Fig. S3, [supplementary material](#)⁷⁷), which was corroborated by SE analysis. Since it can be expected that small Ru nuclei are more easily etched than large Ru islands, it is beneficial to perform etch steps earlier on during the ALD process instead of postdeposition. More importantly, the cyclic nature of ALD is highly suitable for the implementation of correction steps during the deposition process.

An etch cycle was incorporated into a supercycle recipe as illustrated in Fig. 1(c). The supercycle recipe consisted of 400 ALD cycles and the etch cycle of O₂ plasma and H₂ gas steps was included after every 100 ALD cycles. As shown in Fig. 4, without including etch cycles there was approximately 4 nm of Ru growth on the SiO₂ layer [Fig. 4(a)], as compared to ~9 nm on the Pt substrate [Fig. 4(b)]. The thickness on SiO₂ was slightly higher than in Fig. 3(a), due to a different pretreatment prior to ALD (see Sec. II B). Adding an etch cycle with 5 s O₂ plasma exposure after every 100 ALD cycles resulted in etching of approximately 1 nm of Ru from SiO₂ in each supercycle. Nevertheless, an apparent thickness of about 2 nm was measured on the SiO₂ surface after four supercycles. For a supercycle recipe using 15 s O₂ plasma exposures, there was no detectable Ru on the SiO₂ substrate and a net deposition of ~5 nm on the Pt substrate. Prolonging the O₂ plasma exposure to 30 and 60 s led to Ru thicknesses on the Pt substrate of approximately 4 and 2.4 nm, respectively, while again no Ru was detected on SiO₂ using SE. These results suggest that a plasma duration of between 5 and 15 s is optimal, since such an O₂ plasma would result in minimal to no deposition on SiO₂ and a net Ru deposition on Pt of ~5–6 nm.

When investigating the Ru thickness on SiO₂ as a function of ALD cycles in more detail [Fig. 4(a)], several observations can be made. It can be seen that the first 10 ALD cycles after each etch cycle led to more Ru deposition on both SiO₂ and Pt than the subsequent 90 cycles. This enhanced deposition is attributed to the surface modification during the O₂ plasma and H₂ gas steps, causing a higher reactivity of the surface with the precursor in the following 10 ALD cycles. The data also show that the decrease in

FIG. 4. Thickness as a function of ALD cycles for growth on (a) SiO₂ and (b) Pt using ALD-etch supercycles with different etch times of 0, 5, 15, 30 and 60 s. 4 ALD-etch supercycles were performed, with the etch cycle after every 100 ALD cycles. SE measurements were done every 10 ALD cycles and after every etch cycle. The deposition temperature was 150 °C.

Ru film thickness on Pt per etch cycle depends on the O₂ plasma duration, as is addressed later (see Fig. 7). Moreover, it is observed that the GPC increases with the number of cycles when no etch cycles were performed (especially around 100 ALD cycles). In our previous work, it was discussed that the enhancement of the GPC as a function of the number of ALD cycles is possibly caused by an increase in the surface roughness, which can result in an effective increase in the surface area available for precursor adsorption.^{26,62} This enhancement of the GPC is likely suppressed by the etch cycles. The etching can lead to smoothing of the Ru film, since regions locally protruding from the surface are more easily etched than smooth regions of the film.^{26,63,64} A follow-up study is ongoing in which smoothing as a result of etching is analyzed using AFM in order to gain more insight on the effect of the etch cycles on the surface roughness.

To evaluate the obtained selectivity as a function of O₂ plasma time, the Ru surface coverage on SiO₂ was determined using SEM. Figure 5 shows SEM images collected after performing four supercycles on SiO₂ with O₂ plasma times between 0 and 60 s. Due to differences in density and conductivity, the Ru areas appear bright in the SEM images and by processing the images with analysis software (IMAGEJ), the density of nuclei n , and the surface coverage θ were determined.⁶⁵ Subsequently the selectivity was calculated according to $S = (\theta_{Pt} - \theta) / (\theta_{Pt} + \theta)$.¹⁷ The density of nuclei n , the surface coverage θ , the selectivity S , and net Ru thickness on Pt are listed in Table I. Note that a higher value for the selectivity does not necessarily indicate an improvement, as the obtained net growth on Pt should also be taken into account.¹⁷

Figure 5(a) shows that the SiO₂ surface was almost fully covered with Ru nuclei when no etch cycles are performed. Analysis of the nuclei yields a surface coverage θ of 0.7, which corresponds to a selectivity of 0.18.¹⁷ A supercycle recipe with an O₂ plasma duration of 5 s resulted in fewer Ru nuclei [see Fig. 5(b)], but the nuclei still account for a coverage fraction of 0.13 and the obtained selectivity is 0.77 (Table I). For O₂ plasma times of 15 and 30 s, nearly all Ru nuclei were removed, and the selectivity increased to 0.988 and 0.997, respectively. At the same time, the film thickness on the Pt substrate decreased to 4.8 and 4.3 nm, respectively. Finally, Fig. 5(e) shows that a practically clean SiO₂ surface was obtained using an O₂ plasma time of 60 s, corresponding to a selectivity of 0.9996. Nevertheless, the thickness of Ru on Pt was only 2.4 nm, and additional ALD-etch supercycles would be required to obtain a thicker Ru film on the growth area. XPS was additionally

TABLE I. Number density of nuclei n and surface coverage θ of Ru on the SiO₂ non-growth area, selectivity S and Ru thickness on the Pt growth area t_{Pt} after 4 supercycles using O₂ plasma times between 0 s and 60 s. The selectivity was calculated according to $S = (\theta_{Pt} - \theta) / (\theta_{Pt} + \theta)$, where θ_{Pt} was 1 (representing a closed film) for all samples (Refs. 17 and 66). No nuclei density value is listed for 0 s, since the nuclei cannot be distinguished accurately from each other.

O ₂ plasma time (s)	Number density $n(\mu\text{m}^{-2})$	Coverage θ	Selectivity S	$t_{Pt}(\text{nm})$
0	—	0.7 ± 0.1	0.18 ± 0.07	9.4 ± 0.2
5	$(1.1 \pm 0.1) \cdot 10^3$	0.13 ± 0.05	0.78 ± 0.08	6.3 ± 0.2
15	$(1.0 \pm 0.3) \cdot 10^2$	0.006 ± 0.002	0.988 ± 0.004	4.8 ± 0.2
30	$(3 \pm 1) \cdot 10^1$	0.0013 ± 0.0005	0.997 ± 0.001	4.3 ± 0.2
60	3 ± 1	0.0002 ± 0.0001	0.9996 ± 0.0002	2.4 ± 0.2

FIG. 5. Top-view SEM images after 4 Ru ALD-etch supercycles on SiO₂ with an etch cycle after every 100 ALD cycles. O₂ plasma times between 0 s and 60 s were investigated.

employed to investigate the Ru deposited on SiO₂, which yielded similar results (see Fig. S4, [supplementary material](#)⁷⁷).

In order to obtain the maximum net deposition, both the O₂ plasma etch duration and the etch frequency should be optimized (i.e., the ratio of ALD and etch cycles). Figure 6(a) shows that four supercycles with an O₂ plasma of 5 s after every 100 ALD cycles resulted in almost 2 nm deposition on the SiO₂ non-growth area. In contrast, no Ru was detected using SE on SiO₂ for the same O₂ plasma exposure of 5 s after every 50 ALD cycles [see Fig. 6(b)]. Likewise, no Ru deposition was detected on SiO₂ for supercycles with an O₂ plasma duration of 15 s after every 100 ALD cycles [see Fig. 6(c)]. On Pt, the final Ru thickness was approximately 1 nm lower when using a 5 s O₂ plasma after every 50 ALD cycles, as compared to when using a 15 s O₂ plasma after every 100 ALD cycles. Upon close examination of Figs. 6(b) and 6(c), it can be seen that the growth rate on Pt (i.e., the slope of the thickness

FIG. 6. (Apparent) Ru film thickness as a function of ALD cycles for deposition on SiO₂ and Pt using ALD-etch supercycles with an O₂ plasma etch step of (a) 5 s after every 100 ALD cycles, (b) 5 s after every 50 cycles, and (c) 15 s after every 100 ALD cycles. The deposition temperature was 150 °C, and the H₂ gas dose after every O₂ plasma exposure was 15 s. Note that the data of (a) and (c) are also shown in Fig. 4.

versus ALD cycles) was slightly lower for 5 s O₂ plasma after every 50 ALD cycles than for 15 s every 100 ALD cycles. For instance, between 360 and 400 ALD cycles, the average growth rates were ~0.17 and ~0.20 Å/cycle, respectively. The lower growth rate for etching after every 50 ALD cycles is likely due to the smoothing effect and corresponding reduced precursor adsorption. The smoothing effect is believed to be more pronounced when the etch cycle is included after 50 cycles, because the etch step is performed more often as compared to when etching after 100 ALD cycles. The combination of the lower average GPC and the additional etching results in a lower final thickness on Pt for 5 s O₂ plasma after every 50 ALD cycles. These observations suggest that performing the etch cycle after more ALD cycles, but using a longer O₂ plasma time, is beneficial in terms of net deposition, as also discussed in Sec. IV.

Insight into the etch behavior was obtained by evaluating the Ru thickness decrease on Pt as a function of O₂ plasma exposure time based on the data shown in Fig. 4(b). As can be seen in Fig. 7(b), the amount of Ru removed from the Pt growth area depends on the duration of the O₂ plasma etch step. The gradual decrease in the film thickness indicates that the etching by the O₂

FIG. 7. (a) The selectivity, (b) the average Ru thickness decrease from SE on the Pt growth area per etch cycle, and (c) the net deposition from SE on the Pt growth area after 4 supercycles as a function of the O₂ plasma time, with an etch cycle performed after every 50 or 100 ALD cycles. The horizontal axis represents the O₂ plasma time per etch cycle. The selectivity values in (a) are also listed in Table I. The reported thickness decrease in (b) is the decrease after the complete etch cycle, i.e., after the H₂ gas dose and indicates that the etch process demonstrates quasi self-limiting behavior. Note that an additional experiment was performed to determine the thickness decrease for 0.5 s of O₂ plasma (corresponding data not shown in Fig. 4).

plasma exposure is not a self-limiting reaction. The etch per cycle is however not linearly increasing and slows down as a function of O₂ plasma exposure time, i.e., the etch rate (in nm/s) is higher at the start of the O₂ plasma. As the film gets more oxidized, the etching appears to become more difficult. This quasi self-limiting etch behavior suggests that the etching of a RuO₂ film is less favorable than etching of metallic Ru, in line with the literature.^{47,67} Etching of metallic Ru has been performed using both O₃ gas and O₂ plasma and is believed to be driven by O radicals.^{47,48,68} Etching of RuO₂, on the contrary, requires energetic ions from an O₂ plasma and is mostly reported using reactive-ion etching.^{67–70}

Figure 7(c) shows the net deposition (after 400 ALD cycles) as a function of the O₂ plasma time. Due to the fact that the etch per cycle does not saturate, the net deposition continues to decrease for longer plasma times. However, because the etch behavior is quasi self-limiting, the etched thickness is not linearly increasing with the plasma time and the data point for an O₂ plasma etch of 5 s after every 50 ALD cycles (40 s etching in total), shows a lower net deposition (~3.9 nm) than the data point for 15 s after every 100 ALD cycles (60 s etching in total, ~4.8 nm). This observation indicates that the etch frequency has a larger effect on the net deposition than the etch duration. Furthermore, the dependence of the etch rate on the etch time implies that both the O₂ plasma duration and the etch frequency should be optimized such that no material is deposited on SiO₂, while obtaining a maximum thickness on the Pt substrate.

IV. DISCUSSION

The results presented in Sec. III B demonstrate that ALD-etch supercycles offer an interesting opportunity to improve the selectivity of area-selective ALD processes. However, the implementation of etch cycles results in a decrease in the deposition on the growth area, meaning that generally a trade-off should be made between selectivity and net deposition. To understand how the effect of this trade-off can be minimized, a mathematical description of the ALD-etch supercycles will be presented in this section. As is mentioned in Sec. I, ALD-etch supercycles have previously been reported for area-selective deposition of Ta₂O₅ and TiO₂.^{18–20} Vallat *et al.* used the nucleation delay of Ta₂O₅ and TiO₂ growth on Si and SiO₂ as a starting point for the development of ALD-etch supercycles, while in the work of Song *et al.*, the initially low growth rate of TiO₂ deposition on H-terminated Si was exploited.^{18–20} Although both studies demonstrated a high selectivity with ALD-etch supercycles, it remains to be determined which ratio of deposition and etching cycles in the supercycle yield the optimal results in terms of selectivity and net deposition.

For the Ru ALD-etch supercycles studied in this work, it was found that the selectivity *S* increased with the O₂ plasma time, while the net Ru deposition on the Pt growth area decreased (see Fig. 7). The data in Table I suggest that a supercycle using an etch cycle with 30 s O₂ plasma after 100 ALD cycles is close to the optimal ALD-etch supercycle configuration, obtaining a selectivity of 0.997 and a net deposition of 4.3 nm of Ru on Pt. However, further investigation is also required in this case, in order to verify whether this is the optimum, or whether performing the etch cycle after slightly more ALD cycles would increase the obtained net thickness (see the text related to Fig. 6). Since the optimum supercycle recipe has not

been determined so far for the different ALD-etch supercycles reported here and in the literature, it is relevant to discuss some guidelines for the optimization of ALD-etch supercycles. Several observations made for the Ru ALD and etch processes in Sec. III, and Fig. 4 in particular, are important for such a discussion:

- At a deposition temperature of 150 °C, the Ru growth starts immediately on both the Pt growth area and on the SiO₂ non-growth area, but the growth rate on SiO₂ is lower than on Pt.
- The etch cycle results in the removal of Ru from the SiO₂ non-growth area as well as from the Pt growth area. However, close inspection of Fig. 4 reveals that the etch rate of Ru on SiO₂ is higher than of Ru on Pt. For example, for an O₂ plasma time of 5 s, the Ru thickness decrease is around 1 nm on the SiO₂ non-growth area, as compared to ~0.5 nm on the Pt growth area.
- On both SiO₂ and Pt, the growth rate depends on the number of performed ALD cycles, due to the change in Ru surface coverage on the SiO₂ substrate (i.e., Ru island growth on SiO₂ differs from Ru growth on a closed Ru film), or development of the surface roughness, respectively.

In Sec. I, we elucidated that growth-area selectivity is required for the ALD-etch supercycle approach to work, which means that the growth should occur preferentially on the growth area. We can thus define different parameters for the growth per cycle (GPC) for growth on the growth area (GPC_G) and on the non-growth area (GPC_{NG}). When aiming for perfect selectivity ($S = 1$), the net deposition on the non-growth area after performing N supercycles should be equal to zero,

$$D_{net,NG} = \alpha \cdot N \cdot GPC_{NG} - \beta \cdot N \cdot EPC = 0, \quad (1)$$

where α and β are the number of deposition and etch cycles in one supercycle, respectively, and EPC is the etch per cycle. For simplicity, it is first assumed that the GPC values on the two areas are constant, and that the etch rate is the same for etching material on the growth area as for the non-growth area. The requirement that there should be no net deposition on the non-growth area [Eq. (1)] determines the cycle ratio κ , which is the ratio between the number of deposition and etch cycles in one supercycle,

$$\kappa = \frac{\alpha}{\beta} = \frac{EPC}{GPC_{NG}}. \quad (2)$$

The deposition on the growth area can be calculated using

$$D_{net,G} = \alpha \cdot N \cdot GPC_G - \beta \cdot N \cdot EPC. \quad (3)$$

The following relation for the net deposition on the growth area can be derived by combining Eqs. (1) and (3),

$$D_{net,G} = \alpha N [GPC_G - GPC_{NG}]. \quad (4)$$

Equation (4) represents the simple etch-back strategy for which the amount of material removed from the growth area equals the amount of material that needs to be removed from the non-growth area to obtain perfect selectivity. For this case, it is evident that the growth rate on the non-growth area GPC_{NG} should be as low as

possible to maximize the net deposition on the growth area. This is schematically elucidated in Fig. 8 for two different values of GPC_{NG} . Comparison of the plots in Figs. 8(a) and 8(b) illustrates that a lower value for GPC_{NG} yields a higher net deposition on the growth area D_G , since fewer etch cycles are needed.

So far it was assumed that material from the non-growth area is removed at the same rate as from the growth area [see Eq. (4)]. However, if we define EPC_G and EPC_{NG} for the etching of materials from the growth area and the non-growth area, respectively, the following equation holds:

$$D_{net,G} = \alpha N \left[GPC_G - GPC_{NG} \frac{EPC_G}{EPC_{NG}} \right]. \quad (5)$$

FIG. 8. Calculated film thickness as a function of ALD cycles for ALD-etch supercycles assuming a growth rate on the non-growth area GPC_{NG} which is (a) 0.4 times and (b) 0.2 times GPC_G . A lower value for GPC_{NG} can allow for a higher net deposition on the growth area, because less etching is necessary. Note that the cycle ratio κ is the ratio between ALD cycles α and etch cycles β .

Equation (5) illustrates which strategies can be taken to maximize the net deposition on the growth area. First of all, as already discussed, the most straightforward strategy is to reduce the growth rate on the non-growth area as much as possible. In addition, it can be seen that it is beneficial to aim for a higher etch rate on the non-growth area, i.e., a low value for the ratio between the etch rates EPC_G/EPC_{NG} . From Eq. (5), it also becomes evident that selectivity can even be achieved in case the growth rates on the growth and non-growth area are the same, but there is a significant difference in etch rates instead.

A difference in etch rate can, for example, be obtained if the surface morphology of materials on the non-growth area deviates from the morphology of materials on the growth area. Interestingly, the concept of a higher etch rate for nuclei as compared to films is already exploited in practice for selective epitaxial growth of Si.⁷¹ As was briefly mentioned above for the case of the Ru ALD-etch supercycles, material on the non-growth area seems to be etched faster than on the growth area. The Ru thickness decrease was approximately double on SiO₂ as compared to Pt during the etch cycle when using a 5 s O₂ plasma exposure (see Fig. 4). Such a difference in etch behavior can, for example, be due to differences in morphology. Due to a large contrast in surface energy between Ru and SiO₂, the Ru nucleation on SiO₂ starts out as island growth (Volmer–Weber growth),^{72–74} while the surface energies for Ru and Pt are more similar.^{75,76} A higher etch rate for Ru nuclei is in line with the observed smoothing effect, as it indicates that areas protruding from the surface (including nuclei or islands) are etched faster than the bulk of the film.

To illustrate the concept of using different etch rates, Fig. 9(a) shows an example where $EPC_{NG} = 2 \times EPC_G$. By comparing Fig. 8(a) to Fig. 9(a), it can be seen that a higher etch rate for material on the non-growth area indeed allows for a higher net deposition. Note that except for the etch rate, the same values are used for Figs. 9(a) and 8(a).

Although the situation depicted in Fig. 9(a) represents an improvement as compared to Fig. 8(a), in the ideal case only nuclei on the non-growth area are affected by the etch cycles. This potential strategy is illustrated in Fig. 9(b) and offers an interesting approach to circumvent the trade-off between high selectivity and high net deposition. It is important to realize that the etch rate of nuclei on the non-growth area EPC_{NG} likely depends on the nuclei size, as it can be expected that small nuclei are more easily removed than bigger nuclei or particles. Because the nuclei size typically increases with the number of performed ALD cycles (α), the etch rate should also depend on the number of performed ALD cycles, i.e., $EPC_{NG} = f(\alpha)$. In the most likely scenario, GPC_{NG} increases with the number of ALD cycles α (e.g., when there is a nucleation delay), while EPC_{NG} decreases as a function of α . The situation where material on the growth area is not removed can hypothetically be approached by etching relatively frequently when small nuclei or individual atoms are present on the non-growth area, and only a mild etch step is sufficient to remove those. Finally, it is noted that if the material on the growth area is not (or very slightly) etched during the etch cycle, an etch process can be employed that does not exhibit self-limiting surface reactions, since the uniformity and conformality of the film on the growth area are not (significantly) affected by the etch process.

FIG. 9. Calculated film thickness as a function of ALD cycles assuming a growth rate on the non-growth area GPC_{NG} which is $0.4 \times GPC_G$, (a) for $EPC_{NG} = 2 \times EPC_G$, and (b) for the ideal situation where $EPC_G = 0$. Note that a different etch chemistry, or different etch conditions might be required to obtain the situation depicted in (b), meaning that the etch process for (b) is not necessarily the same as in (a).

An aspect that has not been addressed so far in this discussion is the time-dependence of the etch rates (i.e., $EPC = f[t]$). As was shown in Fig. 7(a), the Ru etch process shows a quasi self-limiting behavior, and the etch rate slows down with time. In general, an etch process can also demonstrate self-limiting behavior, i.e., when considering an ALE process, the etch time would not affect the amount of material etched (as long as saturation is assured), and the number of etch cycles is thus the only parameter which can be used to change the amount of materials removed. However, for quasi self-limiting etching, it becomes more complicated [see Fig. 7(b)]. In this case, doubling the etch time results in less than twice the amount of removed material. For example, for the Ru ALD-etch supercycles, it was found that an O₂

plasma time of 15 s resulted in etching of 0.73 nm of Ru, while 30 s leads to a decrease of 0.89 nm. Finally, effects of the etch cycles on the GPC, such as smoothing and enhanced surface reactivity, also play a role in the optimization.²⁰ Because of these effects, estimation of the optimal number of deposition and etch cycles in a supercycle recipe typically requires more than taking just the sum of the deposition and etch components of the individual processes.

The discussion above, and Eq. (5) in particular, helps to clarify which information is required to design an optimal ALD-etch supercycle. Logically, the growth rate on the growth area should be known when developing an ALD process. In addition, it should be investigated how the growth rate changes on the non-growth area as a function of ALD cycles (e.g., whether there is a nucleation delay). Generally, these are aspects which are studied when developing an area-selective ALD process. The evolution of the nuclei size on the non-growth area and the etch rate of these nuclei as a function of their size are however usually not studied in detail and thus require additional investigation.

V. CONCLUSION

In this work, area-selective deposition was achieved by combining a Ru ALD process, which demonstrated a limited selectivity, with an etch cycle consisting of O₂ plasma and H₂ gas exposures. When using the thermal ALD process without etching, a deposition temperature of 150 °C allowed for the largest difference in growth between the Pt/Ru growth areas and the SiO₂/Al₂O₃ non-growth area. In order to characterize the ALD-etch supercycle, the O₂ plasma etch duration and frequency were varied. The selectivity of the different ALD-etch supercycle configurations was determined by measuring the Ru coverage on SiO₂ using SEM images. The selectivity was found to increase with the O₂ plasma exposure time, although the net deposition on the Pt growth area decreased significantly. This observation illustrates the trade-off between selectivity and net deposition which generally has to be made when employing ALD-etch supercycles.

On the basis of a mathematical description, it was discussed that several strategies can be taken to simultaneously maximize the net deposition and obtain a high selectivity. An obvious strategy is to reduce the growth rate on the non-growth area as much as possible, as this lowers the number of required etch cycles. In addition, the impact of the trade-off between selectivity and net deposition can be minimized by identifying conditions for which the etch rate of material on the non-growth area is much higher than on the growth area. The analysis also illustrates that for the development of novel processes based on ALD-etch supercycles, it is important to understand how the ALD and etch cycles influence each other, for instance whether there is a growth or etch delay when switching from one process to the other. Overall, the obtained insights on ALD-etch supercycles can benefit the future application of area-selective deposition processes in semiconductor device fabrication.

ACKNOWLEDGMENTS

The authors would like to thank C. A. A. van Helvoirt, J. J. A. Zeebregts, C. O. van Bommel, and J. J. L. M. Meulendijks for their technical assistance. This work was financially supported by the Netherlands Organization for Scientific Research (NWO) through

the *Zwaartekracht* program “Research Centre for Integrated Nanophotonics.” In addition, the work of S.N.C. was made possible through the National Science Foundation (NSF) Graduate Research Opportunities Worldwide program, the Netherlands Organization for Scientific Research (NWO), and a NASCENT Whaley fellowship.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#). Additional data are available from the corresponding author upon reasonable request.

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