Area-selective deposition of Ruthenium by combining atomic layer deposition and selective etching

Citation for published version (APA):

DOI:
10.1021/acs.chemmater.9b00193

Document status and date:
Published: 22/05/2019

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.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 14. Aug. 2019
Area-Selective Deposition of Ruthenium by Combining Atomic Layer Deposition and Selective Etching

Martijn F. J. Vos, † Sonali N. Chopra, †‡ Marcel A. Verheijen, † John G. Ekerdt, †§ Sumit Agarwal, ‡ Wilhelmus M. M. Kessels, † and Adriaan J. M. Mackus†§

†Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
‡McKetta Department of Chemical Engineering, The University of Texas at Austin, 200 East Dean Keeton Street, Stop C0400, Austin, Texas 78712, United States
§Department of Chemical and Biological Engineering, Colorado School of Mines, 1613 Illinois Street, Golden, Colorado 80401, United States

Supporting Information

C urrent nanopatterning techniques used for integrated circuit fabrication typically rely on a combination of deposition, lithography, and etch steps. Due to alignment issues, nanopatterning is becoming very challenging as device dimensions approach sub-5 nm scales.1−4 In recent years, area-selective atomic layer deposition (ALD) has emerged as an alternative, bottom-up approach to nanomanufacturing.5,6 By limiting the deposition to specific areas, area-selective ALD enables self-aligned fabrication and can reduce the number of processing steps during device manufacturing, such as patterning and chemical mechanical polishing. Since ALD operates in a surface-reaction-controlled regime with sequential precursor and co-reactant exposures, separated by purge steps, area-selective ALD is also characterized by growth with precise thickness control and high conformality.5,6

Currently, one of the main challenges for industrial application of area-selective ALD is obtaining a sufficiently high selectivity.7 The selectivity is generally limited to a few tens of ALD cycles due to eventual nucleation on the area where no deposition is desired (“non-growth area”). Cleaning based on etching has previously been implemented in industrial selective epitaxy processes,8 which serves as inspiration here for exploring novel combinations of area-selective ALD and selective etching. For example, during the selective epitaxial growth of Si by chemical vapor deposition (CVD), an etchant gas, typically HCl, is added to the CVD gas mixture to remove unwanted nucleation on SiO2 or Si3N4 nongrowth areas.9,10 Due to the cyclical nature of ALD, it is especially valuable to develop deposition processes that involve an intermittent correction or cleaning step to increase the growth selectivity.

Area-selective ALD of metal-on-metal is of interest for applications in metal interconnects in semiconductor devices. In particular, ALD of Ru is significant, since Ru (bulk resistivity of 7.1 μΩ cm) is considered either as a Cu diffusion barrier or as a replacement for Cu lines.11−15 Furthermore, Ru is used as an electrode in dynamic random access memory, a gate metal in transistors, and a seed layer for electroplating.16−21 Area-selective ALD of Ru on metal seed layers can simplify device processing for these applications. Several processes for area-selective ALD of Ru already exist and depend on inherent selectivity, area activation, or area deactivation.22−26 Here, we demonstrate a method for area-selective ALD of Ru on Pt or Ru (metal-on-metal) with SiO2 as the nongrowth area, which exploits the inherent selectivity between the two different substrate materials.

Our approach to achieve area-selective ALD with high selectivity is based on deposition and cleaning and consists of periodic selective etch steps integrated into an ALD process as illustrated in Figure 1. The resulting supercycle of ALD and etch steps offers a promising opportunity to improve the growth selectivity of ALD processes. An essential requirement for this approach is that there should be an initial difference in nucleation behavior on the different substrate areas or materials.27 After a certain number of cycles, nuclei start to form on the nongrowth area, and the addition of etch steps can lead to removal of these nuclei. Typically, some material is also removed on the growth area, where deposition is actually desired. However, as long as substantially more material is deposited than etched on the growth area per supercycle, this approach can provide a sufficiently high net growth rate, while improving the overall growth selectivity. By repeating such a

Figure 1. Schematic illustration of the concept of combining ALD with periodic etching to achieve area-selective deposition with a high selectivity. (i) When using an ALD process with an (insufficient) inherent selectivity, ALD leads to film growth on the growth area (gray, e.g., Pt, Ru), and island formation on the nongrowth area (blue, e.g., SiO2). (ii) Inclusion of etch steps in a supercycle recipe results in removal of the unwanted deposition on the nongrowth area. (iii) By repeating the supercycle, a film with the desired thickness can be obtained selectively on the growth area.

Received: January 15, 2019
Revised: May 20, 2019
Published: May 22, 2019
supercycle of ALD and etching as many times as required, the desired thickness can be obtained on the growth area.

It is important that the following two requirements are met when combining ALD with etching to improve the selectivity of the deposition process: (i) growth-area selectivity, which refers to an initial difference in nucleation behavior (in terms of nucleation delay or growth per cycle) between the growth and nongrowth areas, and (ii) etch selectivity, where only the deposited material is etched, with almost no etching of the substrate material or other materials that are present. Several additional aspects are desirable and can lead to a more ideal area-selective ALD process. First, to retain the merits of ALD, the etching process is preferred to be self-limiting and isotropic. In the case of plasma etching, this means that the ion contribution should be insignificant. The conformal nature of ALD on 3D structures is especially preserved by combining ALD with isotropic atomic layer etching (ALE). Second, the etch step should have a negligible effect on the neighboring materials and underlying substrate, for instance, in terms of roughening or incorporation of impurities. Furthermore, possible impurities should be easily removed, or at least not inhibit growth on the growth area in the subsequent ALD cycles. Note that having inhibiting species on the non-growth area can actually be beneficial for the selectivity. Third, the ALD and etch processes should be compatible, meaning that they can be performed at similar conditions, such as temperature and pressure. Fourth, ideally the etch rate of the nuclei or islands on the non-growth area is higher than the etch rate of the material on the growth area, such that a high net growth rate on the growth area is obtained. In addition to considering these aspects, both the repetition frequency and the duration of the etch step should be optimized, in order to obtain the highest net growth rate.

Recently, Vallat et al. demonstrated a combination of ALD and selective etching to improve the overall selectivity of area-selective ALD. In an O₂-plasma-enhanced ALD process for Ta₂O₅ that shows an inherent growth selectivity for a TiN surface over Si or SiO₂, NF₃ etching gas was added to the O₂ plasma step during every ninth cycle. The addition of the NF₃ allowed for the removal of Ta₂O₅ on Si and/or SiO₂ nongrowth areas such that the area-selective deposition of Ta₂O₅ on TiN could be achieved.

All deposition and etching experiments were performed using a home-built ALD reactor with an inductively coupled plasma source operated at a radio frequency (RF) of 13.56 MHz. The reactor walls and manifold lines were heated to 100 and 105 °C, respectively. After using the reactor for deposition of a different material, the chamber was first conditioned with 500 cycles of Al₂O₃ ALD followed by 500 cycles of thermal RuOₓ ALD (using a 60 s O₂ gas dose at 1 mbar as coreactant step). This procedure yielded reproducible Ru film growth. All substrates were cleaned after being loaded into the reactor and prior to the deposition using a 60 s O₂ plasma (100 W), followed by a 30 s reducing H₂ gas treatment. Small coupons of single-side polished Si wafers with thermally grown SiO₂ of ~430–450 nm and ALD-grown Pt or Ru on SiO₂/Si were used as SiO₂/Pt, and Ru substrates. In addition, a sample consisting of Pt lines on top of ~450 nm thick thermally grown SiO₂ was used to characterize the area-selective growth through scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) elemental mapping. The lines of 1, 2, and 3 µm width were patterned by electron-beam lithography (EBL) using poly(methyl meth-
seed layers.\textsuperscript{37,38} For the case of Ru ALD, Pt, as well as Ru, also facilitate the dissociation of O\textsubscript{2}, and the formed O can subsequently lead to the combustion of the precursor ligands.\textsuperscript{39} Since a similar pathway does not occur on the inert SiO\textsubscript{2} surface, this provides the growth selectivity of Ru on noble metals at low deposition temperatures.

To improve the selectivity of the ALD process, an etch cycle was integrated into the ALD process as illustrated in Figure 1. A supercycle recipe was performed in which one etch cycle was included after every 100 ALD cycles, using O\textsubscript{2} plasma and H\textsubscript{2} gas exposure times of 30 and 15 s, respectively. As can be seen in Figure 2a, a recipe consisting of 4 supercycles resulted in a negligible amount of Ru on SiO\textsubscript{2}, while the Ru thickness on the Pt substrate was approximately 4.3 nm, as determined from SE. Approximately 1 nm of Ru is removed after each etch cycle, both on the SiO\textsubscript{2} and the Pt. However, since the GPC of Ru on Pt is higher than on SiO\textsubscript{2}, the supercycle recipe results in net growth selectivity. The SEM image in Figure 3a shows a clean SiO\textsubscript{2} surface in between the Pt lines, further demonstrating the selectivity of the approach. In addition, Ru was only detected by EDX on top of the Pt lines (see Figure 3b). Furthermore, XPS measurements in the region corresponding to C 1s/Ru 3d (294 eV–276 eV, see Figure S3) only revealed a small C 1s singlet peak, whereas no Ru 3d doublet peak was detected. The XPS detection limit for Ru on top of SiO\textsubscript{2} was estimated to be below 0.01 monolayer, or 1.7 \times 10^{13} \text{atoms/cm}^2.\textsuperscript{32} Interestingly, the data demonstrates that the sensitivity for Ru nuclei detection is higher for SEM than for XPS.

After demonstrating the principle of the supercycle approach on blanket substrates, deposition was done onto a SiO\textsubscript{2} substrate with patterned Pt lines. A supercycle recipe of 800 ALD cycles was performed with an etch cycle after every 100 ALD cycles using an O\textsubscript{2} plasma time of 20 s. An etch time of 20 s was used, since this was found to be sufficiently long to obtain selectivity. The SEM image in Figure 3a shows a clean SiO\textsubscript{2} surface in between the Pt lines, further demonstrating the selectivity of the approach. In addition, Ru was only detected by EDX on top of the Pt lines (see Figure 3b). Furthermore, the cross-sectional TEM image and EDX mapping in Figure 4a,b (of the sample as used for Figure 3) reveal that the Ru film on the evaporated Pt (∼50 nm) is approximately 8 nm thick and conformally coats the Pt. The EDX mapping in Figure 4c, collected at the edge of one of the Pt lines, demonstrates that the Ru only covers the Pt and not the SiO\textsubscript{2} substrate, corroborating that a high selectivity is achieved.

The obtained material properties were investigated to further assess the potential of the ALD-etch supercycle approach. XPS measurements revealed a Ru film of high purity, and only a small O 1s peak was detected after every 100 ALD cycles was sufficient to remove nearly all the Ru islands formed on SiO\textsubscript{2}, which corroborates the results of Figure 2a.

Analysis of the nuclei visible with SEM yields a surface coverage \( \theta \) on the nongrowth area of 0.0013, which corresponds to a selectivity factor \( S \) of 0.997 for a Ru thickness of 4.3 nm on the Pt growth area.\textsuperscript{31} Furthermore, XPS measurements in the region corresponding to C 1s/Ru 3d (294 eV–276 eV, see Figure S3) only revealed a small C 1s singlet peak, whereas no Ru 3d doublet peak was detected. The XPS detection limit for Ru on top of SiO\textsubscript{2} was estimated to be below 0.01 monolayer, or 1.7 \times 10^{13} \text{atoms/cm}^2.\textsuperscript{32} Interestingly, the data demonstrates that the sensitivity for Ru nuclei detection is higher for SEM than for XPS.

After demonstrating the principle of the supercycle approach on blanket substrates, deposition was done onto a SiO\textsubscript{2} substrate with patterned Pt lines. A supercycle recipe of 800 ALD cycles was performed with an etch cycle after every 100 ALD cycles using an O\textsubscript{2} plasma time of 20 s. An etch time of 20 s was used, since this was found to be sufficiently long to obtain selectivity. The SEM image in Figure 3a shows a clean SiO\textsubscript{2} surface in between the Pt lines, further demonstrating the selectivity of the approach. In addition, Ru was only detected by EDX on top of the Pt lines (see Figure 3b). Furthermore, the cross-sectional TEM image and EDX mapping in Figure 4a,b (of the sample as used for Figure 3) reveal that the Ru film on the evaporated Pt (∼50 nm) is approximately 8 nm thick and conformally coats the Pt. The EDX mapping in Figure 4c, collected at the edge of one of the Pt lines, demonstrates that the Ru only covers the Pt and not the SiO\textsubscript{2} substrate, corroborating that a high selectivity is achieved.

The obtained material properties were investigated to further assess the potential of the ALD-etch supercycle approach. XPS measurements revealed a Ru film of high purity, and only a small O 1s peak was detected after every 100 ALD cycles was sufficient to remove nearly all the Ru islands formed on SiO\textsubscript{2}, which corroborates the results of Figure 2a.
(corresponding to <5 atomic % O), which is comparable in
intensity as for ALD only (see Figure S4). Furthermore, four-
point-probe measurements yielded a resistivity of ~22 μΩ cm
(after correcting for the Pt resistance) for 8 nm of Ru depos-
ited using ALD-etch supercycles.

Comparing the growth on Pt with and without etch cycles in
Figure 2a, it is clear that the GPC increases with the number of
cycles when no etching is performed, while this effect seems to
be suppressed by the periodic etch cycles (see also Figure S5).
Note that the GPC is essentially given by the slope of the plot
for the thickness versus ALD cycles. The gradual increase in
GPC for the normal ALD recipe is attributed to an increase in
surface roughness as the film thickness increases, which
manifests as an effective increase in the surface area available
for growth.43 We speculate that this increase in GPC is sup-
pressed by the etch cycles, as the radical-assisted O₂ plasma etching leads to smoothing of the Ru film. This
smoothing effect can be explained by the fact that Ru regions
protruding from the surface are more easily etched by the O₂
plasma than smooth regions of the Ru film. Smoothing of thin
films, including Ru, by ALE has been reported previously, and
the O₂ plasma etching process used in this work can be
qualified as quasi-ALE.44 To confirm this hypothesis, Ru films
of ~8 nm were analyzed by AFM, yielding root-mean-square
roughness values of 1.3 and 0.9 nm for films deposited without
and with etch cycles, respectively. The inclusion of the etch
cycles thus has the benefit of smoothing the Ru film, in
addition to enhancing the selectivity.

In summary, it was demonstrated that area-selective ALD
with high selectivity can be obtained by combining ALD with
selective etching. Specifically, a Ru ALD process was combined
with etch cycles of O₂ plasma and H₂ gas to remove unwanted
growth on SiO₂. Approximately 8 nm of Ru was deposited on
Pt patterns, while both EDX and SEM confirmed that the
neighboring SiO₂ was clean. In addition, it was found that
inclusion of the etch cycles leads to smoothing of the Ru film,
as evidenced by a lower surface roughness than for ALD only.
This study provides valuable insight into how area-selective
ALD can be combined with selective etching to deposit
materials on a surface with high selectivity, while maintaining
the ALD merits of high conformality and precise thickness
control. Finally, the general requirements and guidelines for
ALD-etch supercycles discussed in this work can help to
extend the approach to other material systems.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the
ACS Publications website at DOI: 10.1021/acs.chemmater.9b00193.

Information on the process flow for the Pt pattern fabrication, additional experimental details, O 1s and Ru 3d XPS spectra collected on Pt and SiO₂, and Ru film thickness versus ALD cycles on Pt, with and without etch cycles (PDF)

AUTHOR INFORMATION
Corresponding Author
*(A.J.M.M.) E-mail: a.j.mackus@tue.nl.

ORCID
Martijn F. J. Vos: 0000-0002-7380-5032
John G. Ekerdt: 0000-0002-1788-5330
Wilhemus M. M. Kessels: 0000-0002-7630-8226
Adriaan J. M. Mackus: 0000-0001-6944-9867

Author Contributions
M.J.J.V. and S.N.C. performed the experiments and M.A.V.
the TEM analysis. The manuscript was written through
contributions of all authors. All authors have given approval
to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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. R. Mahlouji, B. Barcones Campo,
and D.A. Kane are acknowledged for preparation of the Pt lines
on SiO₂, the TEM lamella, and AFM measurements,
respectively. 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
and a NASCENT Whaley fellowship. Solliance and the Dutch
province of Noord-Brabant are acknowledged for funding the
TEM facility.

REFERENCES
(1) Schuegraf, K.; Abraham, M. C.; Brand, A.; Naik, M.; Thakur, R.
Semiconductor Logic Technology Innovation to Achieve sub-10 nm
(2) Thoms, S.; Macintyre, D. S.; Docherty, K. E.; Weaver, J. M. R.
Alignment Verification for Electron Beam Lithography. Microelectron.
Eng. 2014, 123, 9–12.
(3) Fang, M.; Ho, J. C. Area-Selective Atomic Layer Deposition:
Conformal Coating, Subnanometer Thickness Control, and Smart
(4) Mackus, A. J. M.; Bol, A. A.; Kessels, W. M. The Use of Atomic
Layer Deposition in Advanced Nanopatterning. Nanoscale 2014, 6,
10941–10960.


