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Area-Selective Atomic Layer Deposition of Metal Oxides on Noble Metals through Catalytic Oxygen Activation

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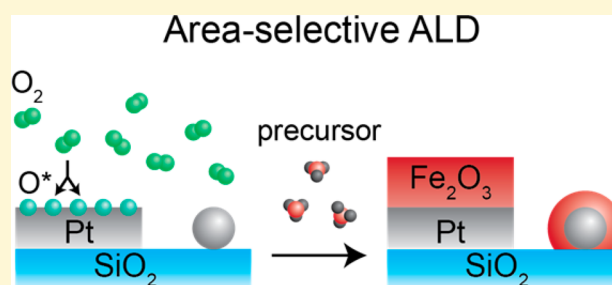
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Supporting Information

ABSTRACT: Area-selective atomic layer deposition (ALD) is envisioned to play a key role in next-generation semiconductor processing and can also provide new opportunities in the field of catalysis. In this work, we developed an approach for the area-selective deposition of metal oxides on noble metals. Using O₂ gas as co-reactant, area-selective ALD has been achieved by relying on the catalytic dissociation of the oxygen molecules on the noble metal surface, while no deposition takes place on inert surfaces that do not dissociate oxygen (i.e., SiO₂, Al₂O₃, Au). The process is demonstrated for selective deposition of iron oxide and nickel oxide on platinum and iridium substrates. Characterization by *in situ* spectroscopic ellipsometry, transmission electron microscopy, scanning Auger electron spectroscopy, and X-ray photoelectron spectroscopy confirms a very high degree of selectivity, with a constant ALD growth rate on the catalytic metal substrates and no deposition on inert substrates, even after 300 ALD cycles. We demonstrate the area-selective ALD approach on planar and patterned substrates and use it to prepare Pt/Fe₂O₃ core/shell nanoparticles. Finally, the approach is proposed to be extendable beyond the materials presented here, specifically to other metal oxide ALD processes for which the precursor requires a strong oxidizing agent for growth.



INTRODUCTION

Area-selective deposition plays an increasingly important role in the development of nanostructured materials for semiconductor processing^{1,2} and catalysis.^{3,4} In semiconductor processing, conventional fabrication of multilayer device structures is facing the challenge of aligning the layers with nanometer accuracy. Use of area-selective deposition allows for control over where deposition takes place without requiring photolithography for every device layer.¹ Consequently, the number of lithography steps can be reduced, which eliminates these alignment errors while lowering the fabrication costs.

In catalysis, there is a desire to create highly controlled bimetallic or core/shell nanoparticles that are monodisperse and of high purity. Conventional synthetic methods have difficulty ensuring a consistent bimetallic composition.^{5–8} Large improvements can be expected if the deposition of the second material occurs selectively on the first material only, and not on the surrounding support substrate. This ensures that all particles are covered uniformly, while preventing the formation of monometallic particles of the second material.

Atomic layer deposition (ALD) utilizes self-limiting reactions of precursor and co-reactant gases to achieve highly controlled deposition. ALD has many favorable attributes including high conformality, good spatial uniformity, and Å-level thickness control. Since the chemical reactions occur only on the substrate surface, area-selective ALD can be achieved by either blocking or activating the growth on specific areas or materials. Prior reports have shown that such selectivity can be obtained by chemically modifying surfaces to prevent growth.^{1,2,9–15} Alternatively, ALD growth can be activated on an inert substrate by locally catalyzing the surface reactions of an ALD process.^{8,16–18} Etching can be added as part of the area-selective ALD process to improve the selectivity.^{19,20}

Prior work has shown that area-selective ALD by area activation can be achieved by choosing a suitable co-reactant.^{3,8,16–18,21} For example, a mildly oxidizing co-reactant such as O₂ gas may allow for area-selective growth on certain

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surfaces, while more strongly oxidizing co-reactants such as ozone or O₂ plasma generally result in growth on any surface and are therefore not suitable for area-selective deposition. Weber et al. used this approach to synthesize Pt/Pd and Pd/Pt core/shell nanoparticles supported on Al₂O₃ substrates.^{16,18} Selective deposition of Pt on Pd particles was achieved by using O₂ gas as the co-reactant. The Pd particles are able to catalyze the surface reactions of subsequent Pt ALD. More specifically, noble metal surfaces catalyze the dehydrogenation and combustion of precursor ligands.^{8,16,18,22} The latter is driven by dissociative chemisorption of O₂ into O* (chemisorbed O). These catalytic surface reactions allow for deposition of Pt only on the Pd particles and not on the surrounding Al₂O₃ substrate. In a similar way, Pd deposition on Pt particles was enabled by using H₂ gas, where this time the Pt particles catalyze the formation of H* reactive sites. Lu et al. expanded this methodology by exploiting the selective chemisorption of O₂ and H₂ to synthesize bimetallic PdPt, RuPt, and RuPd nanoparticles on Al₂O₃.⁸

In this work, we extend this approach to area-selective ALD of metal oxides by demonstration of selective iron oxide and nickel oxide deposition on catalytic Pt and Ir substrates. We focus particularly on Pt-Fe based materials since this system has key applications in catalysis and magnetic devices. For example, Pt-Fe can be used for carbon nanotube growth,^{23–26} the oxygen reduction reaction,²⁷ and room temperature CO oxidation.²⁸ Furthermore, the use of ALD to prepare these materials may allow them to be integrated into next-generation catalyst designs³ and take advantage of ALD's favorable attributes for catalyst synthesis.^{3,4,21,29–32} As a result of their magnetic properties, Pt-Fe based materials have key applications for creating memory^{33,34} and spintronic devices,³⁵ and are used in medical imaging.³⁶

Area-selective ALD is achieved by exploiting the catalytic activation of O₂ on Pt and Ir substrates, which enables deposition of iron oxide and nickel oxide from *t*-butyl ferrocene (TBF) and nickelocene precursors, respectively. These precursors are relatively unreactive and usually require strongly oxidizing co-reactants such as ozone or O₂ plasma to combust the ligands and result in deposition.^{37,38} However, in this work, we show that deposition can also be achieved with O₂ gas when a catalytic substrate such as Pt or Ir is used. On such catalytic metals, O₂ gas is catalytically activated through dissociative chemisorption (Figure 1). The reactive O* species are in this case formed at the catalytic substrate instead of supplied by the ozone or O₂ plasma. On the other hand, deposition does not take place on materials such as SiO₂, Al₂O₃, and Au as these

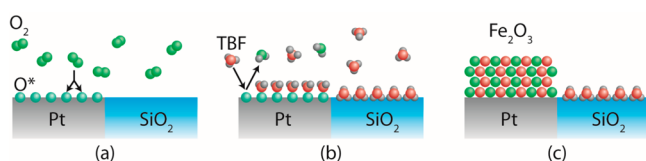


Figure 1. Schematic illustration of the proposed mechanism by which area-selective ALD occurs. As an example, we illustrate Fe₂O₃ deposition from *t*-butyl ferrocene (TBF)/O₂ on Pt. (a) Pt surfaces allow for the dissociative chemisorption of O₂ to O* (chemisorbed oxygen), whereas SiO₂ surfaces do not catalyze this reaction. (b) While TBF adsorption may occur on both surfaces, TBF only fully reacts where O* is present and therefore only leads to deposition on Pt. (c) In this way, a film of Fe₂O₃ can be deposited selectively by ALD on the Pt.

materials do not dissociate the O₂ gas. In this way, by using O₂ gas, area-selective deposition is achieved on the catalytic Pt and Ir substrates, while no growth is obtained on noncatalytic substrates such as SiO₂. In this mechanism of catalytic dissociation by the substrate metal, one might expect growth of the transition metal oxide to terminate when all the surface Pt or Ir sites are covered by the growing film. However, as shown in this work, we observe sustained growth even after depositing a film of 20 nm in thickness. Two potential mechanisms are proposed to explain these results. Using this process, we successfully synthesize patterned bilayer thin films as well as core/shell nanoparticles.

METHODS

In this work, we performed several processes in three different ALD reactors, located at Eindhoven University of Technology (TU/e) and Stanford University. The TU/e reactor was used for Fe₂O₃ film depositions on planar substrates but not on particles. The experiments include *in situ* spectroscopic ellipsometry (SE) measurements on various substrates (Figure 2a), and deposition on patterned Pt squares (Figure 5). The Stanford reactors were used for Fe₂O₃ deposition on supported Pt particles (Figure 6, Figure 7, and Figure S3), and Fe₂O₃ and NiO deposition on patterned Ir substrates (Figure S2). We note that the similar results obtained in the TU/e high-vacuum reactor and the Stanford low-vacuum reactors supports the robustness of our approach.

The TU/e reactor is a high-vacuum system that is evacuated by combination of a rotary and a turbomolecular pump to a base pressure of $\sim 10^{-6}$ Torr. The system has been extensively described in previous work.³⁹ Fe₂O₃ depositions were performed using *t*-butyl ferrocene precursor (TBF, 98%, Strem Chemicals) and O₂ gas. The TBF was kept at 100 °C to ensure adequate vapor pressure and was dosed using Ar carrier gas through a delivery line heated to 120 °C. Each cycle consisted of 1–20 s TBF exposure (as indicated in the results), 10 s pump time, 10 s O₂ exposure, and 10 s pump time. The reactor walls were kept at 100 °C, and the substrate table was heated to 300 °C. Due to poor thermal contact in vacuum, however, the actual temperature of the samples during the process is typically lower.⁴⁰ For the area-selective process, a high O₂ pressure of 750 mTorr was used to improve the thermal contact, giving a sample temperature of ~ 250 °C as measured by spectroscopic ellipsometry (see below).

The Stanford reactors were of two types: a custom-built, low-vacuum system and a commercial Arradiance Gemstar low-vacuum system. Processes were developed for NiO and Fe₂O₃ depositions on planar samples using the custom system (Figure S2). Typical oxygen pressures on the order of 1–10 Torr were used. Depositions were performed at a 1 Torr N₂ operating pressure. For NiO ALD, the substrates were heated to 250 °C and the nickelocene precursor was heated to 70 °C. Each cycle consisted of 7 s nickelocene exposure, 40 s purge time, 3 s O₂ exposure, and 30 s purge time. For Fe₂O₃ ALD, the substrates were heated to 225 °C and the TBF precursor was heated to 95 °C. Cycles consisted of 8 s TBF exposure, followed by 10 s holding time, 10 s purge time, 3 s O₂ exposure, and 30 s purge time.

The selectivity of the process was checked in the TU/e reactor by *in situ* SE on five different substrate materials: (1) Pt, (2) Au, (3) Fe₂O₃, (4) SiO₂, and (5) Al₂O₃. These substrates will be referenced in the results, but details are described here. (1) The Pt films were 20 nm in thickness and were deposited by plasma-assisted ALD on thermal SiO₂.⁴¹ (2) The Au films were 16 nm in thickness and were deposited by electron-beam evaporation. (3) Fe₂O₃ films were ~ 5 nm in thickness (without an underlying Pt substrate) and were deposited by plasma-assisted ALD of Fe₂O₃ on SiO₂, using the process reported by Ramachandran et al.⁴² Due to the use of O₂ plasma, this is a conventional, nonselective process which allows for deposition on noncatalytic substrates. (4) SiO₂ substrates consist of as-received 450 nm thermal SiO₂ on Si. (5) The Al₂O₃ films (20 nm) were deposited on SiO₂ by ALD. The *in situ* SE measurements were performed using a J.A. Woollam, Inc. M2000 ellipsometer (1.2–5.0 eV photon range).⁴³

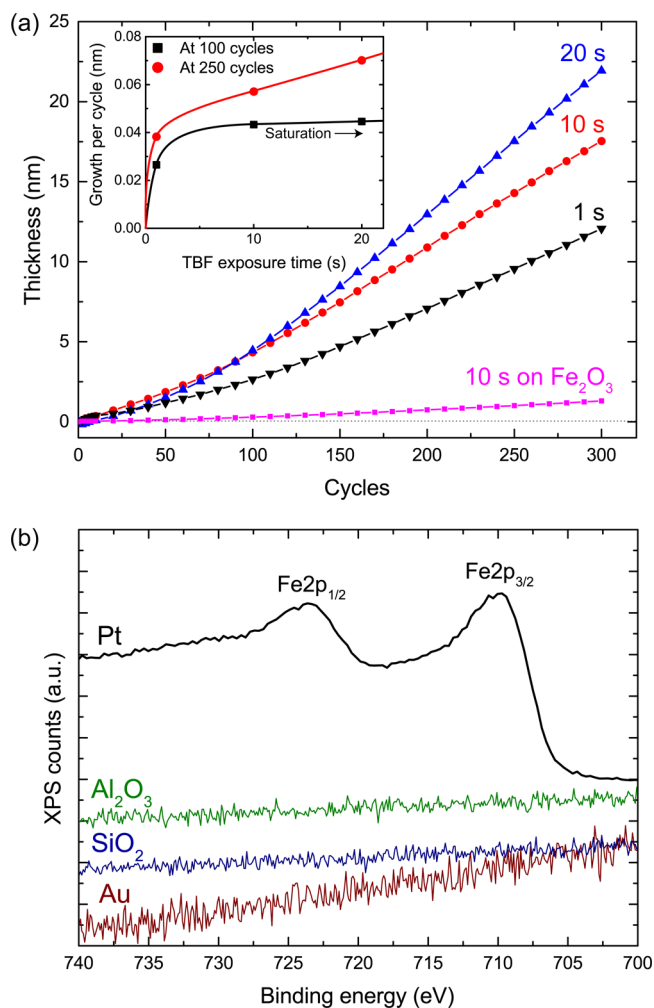


Figure 2. (a) Thickness measured by *in situ* SE during deposition of Fe₂O₃ from TBF/O₂ on Pt with various TBF exposure times, with growth on Fe₂O₃ shown for comparison. Almost negligible growth is observed on the Fe₂O₃ substrate. (a, inset) Saturation curves showing the growth per cycle of Fe₂O₃ deposited on Pt substrates, extracted at 100 and at 250 cycles from the *in situ* SE data. The growth per cycle is determined by dividing the thickness at 100 or 250 cycles of deposition by the number of cycles performed. (b) X-ray photoelectron spectroscopy (XPS) scans showing the Fe_{2p} region after 300 ALD cycles of Fe₂O₃ on Pt, Au, SiO₂, and Al₂O₃ substrates. A clear Fe_{2p} signal is observed on Pt, but no Fe above the detection limit is detected on the catalytically inactive substrates.

Prior to the experiments, the sample temperature was determined by SE. A Si wafer with native oxide was measured using SE for different O₂ pressures, and modeled using a J.A. Woollam temperature-sensitive optical model.

For XPS and cross-sectional TEM measurements, planar Fe₂O₃ films were deposited on electron-beam evaporated Pt films (~16 nm). Cross-sectional TEM images were obtained at TU/e using a JEOL JEM-ARM200F system. The TEM lamella was cut from the sample by focused ion beam (FIB) milling. Prior to FIB milling, a protective layer of SiO₂ was deposited by electron-beam induced deposition. Cross sections were imaged in bright-field and high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) modes. Energy-dispersive X-ray spectroscopy (EDS) was performed using this microscope (Figure 3).

Auger electron spectroscopy was performed at Stanford using a PHI-700 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were done at TU/e using Thermo Scientific KA1066 and at Stanford PHI Versaprobe III spectrometers with mono-

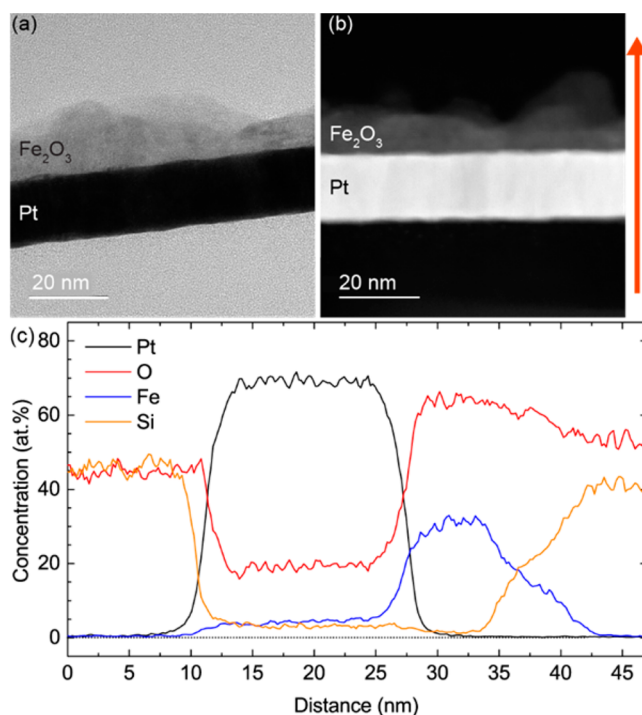


Figure 3. Cross-sectional TEM micrographs of Fe₂O₃ deposited on a Pt substrate as recorded using (a) bright-field TEM and (b) HAADF-STEM. (c) Elemental concentrations determined using EDS line scan in cross-sectional view, along the vertical direction as indicated by the arrow in (b). The elemental concentrations measured are averaged over a ~40 nm lateral distance. The Si signal for distances > 33 nm results from the protective SiO₂ layer deposited prior to FIB milling.

chromatic Al K α X-rays in both cases, and using Ar⁺ sputtering for depth profiling.

Core/shell Pt/Fe₂O₃ nanoparticles were deposited at Stanford by ALD on Aerosil OX50 silica powder, which was cleaned using UV irradiation and ozone. The powder was contained in a custom stainless steel cup with lid based on a design by Libera et al.⁴⁴ A standard Pt ALD process was used to deposit Pt nanoparticles with the Stanford Arradiance system.⁴⁵ Fe₂O₃ was deposited in the Stanford custom system using alternating exposures of TBF and O₂ gas, with the silica powder heated to 250 °C. To saturate the high surface area of the powder, for these experiments, cycles consisted of 10–15 s TBF exposure, followed by 20 s holding time, 120 s purge time, 1.5 s O₂ exposure, followed by 30 s holding time, and 120 s purge time.

TEM of the prepared nanoparticles was performed at Stanford using an FEI G2 F20 Tecnai TEM (Figure 6) and an FEI Titan environmental transmission electron microscope (Figure 7 and Figure S3). Scanning transmission electron microscopy (STEM) and energy-dispersive spectroscopy (EDS) were carried out on the Titan microscope. The SiO₂ nanospheres on which the nanoparticles were prepared were dropcast onto Cu TEM grids with lacey or ultrathin Cu.

RESULTS

ALD Growth and Substrate Selectivity. *In situ* SE was performed to characterize the selectivity and growth properties of the area-selective Fe₂O₃ process. Depositions were carried out on a number of different starting substrates to verify the need for a catalytically active film. The substrates include Pt, Au, Fe₂O₃, SiO₂, and Al₂O₃ (as described in the Methods section). Plots of the thickness as a function of cycle number are presented in Figure 2a for the Pt and Fe₂O₃ substrates, using various TBF exposure times. On the Pt substrates, growth of Fe₂O₃ is clearly observed. The growth rate increases during

the initial 100 cycles until a constant growth rate is achieved. This behavior is typical for the growth of polycrystalline films.⁴⁶ In the inset of Figure 2a, the saturation curve for the TBF exposure is shown as determined at 100 cycles or 250 cycles. At low film thicknesses up to ~ 5 nm (around 100 cycles), the process appears to be in saturation after 10 s TBF exposure and reaches a growth rate of 0.045 nm/cycle. For thicker films at 250 cycles, however, the growth rate for 20 s TBF exposure (0.070 nm/cycle) is higher than for 10 s TBF exposure (0.057 nm/cycle), suggesting that the process is no longer in saturation. This observation will be explained in terms of a possible reaction mechanism in the Discussion section below. We note that the growth rate of 0.070 nm/cycle is similar to results observed for ALD using TBF and O₂ plasma.⁴²

It is evident from the growth curves of Figure 2a that negligible growth occurs on as-deposited Fe₂O₃ substrates (with no Pt underneath, substrate "3" as described in the Methods section), with a growth rate of only 0.005 nm/cycle for 10 s TBF exposure. This is an important observation as it confirms that the Fe₂O₃ film itself is not catalyzing the deposition of additional Fe₂O₃.

Figure 2b shows XPS scans of the Fe_{2p} region on the Pt, Au, SiO₂, and Al₂O₃ substrates after a deposition of 300 cycles. Fe is detected on the Pt substrate, with the Fe 2p_{3/2} peak located at 711.0 eV, in good agreement with Fe(III) in Fe₂O₃ (710.9 eV).⁴⁷ In addition, the spin orbit splitting between Fe 2p_{1/2} and Fe 2p_{3/2} is 13.6 eV as expected for Fe(III) in Fe₂O₃.⁴⁷ Prior work on ALD of Fe₂O₃ films using ferrocene precursors found that the films consisted of either α -Fe₂O₃ or amorphous Fe₂O₃.^{37,42,48,49} Furthermore, no Fe is detected after deposition on the Au, SiO₂, and Al₂O₃ substrates. These results demonstrate that the process has excellent selectivity, with immediate growth on Pt substrates (Figure 2a) and no indication of any growth on SiO₂ or Al₂O₃ substrates (Figure 2b). Furthermore, the lack of growth on Au substrates indicates that a metal catalytically active for O₂ dissociation, such as Pt or Ir, is required.

We also note another interesting observation: on Pt substrates, the Fe₂O₃ layer can deposit to at least 20 nm in thickness without noticeable attenuation of the growth rate. This is in contrast to the expectation that the growth will stop once the catalytic surface has been covered. This behavior is discussed in detail in the Discussion section.

Microstructure and Composition. Bright-field and dark-field cross-sectional TEM micrographs of a Fe₂O₃ film deposited with 300 Fe₂O₃ ALD cycles on a Pt substrate are provided in Figure 3. The Fe₂O₃ layer has completely covered the Pt substrate. However, the layer appears to be polycrystalline, resulting in grain boundaries and a high roughness. The images show a clearly defined interface between the underlying Pt substrate and the Fe₂O₃ film. Furthermore, Figure 3c shows the elemental concentrations as measured by EDS in the cross-sectional orientation. EDS likewise supports a clearly defined interface between the Pt and the Fe₂O₃ layers with no detectable Pt within the Fe₂O₃ layer. A plan-view scanning electron micrograph is shown in Figure S1, in which the polycrystallinity and resulting roughness is clearly visible.

The stoichiometry and chemical structure of Fe₂O₃ films on Pt substrates were investigated using XPS depth profiling by Ar⁺ ion sputtering. Figure 4 shows the concentration of Pt, C, O, and Fe in a 17 nm Fe₂O₃ film as a function of the sputtering time (representing the depth). The initial surface measurement before any sputtering shows atomic concentrations of 60% O,

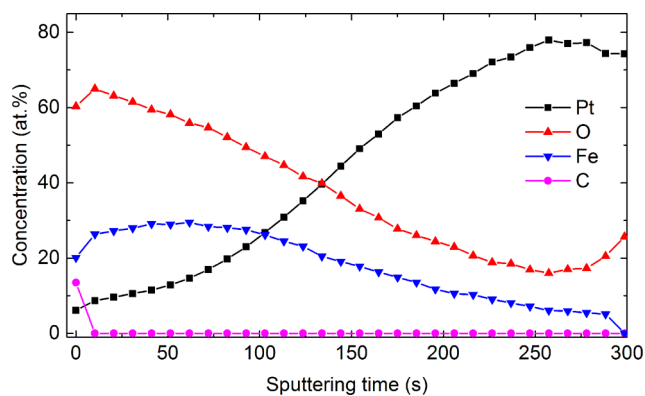


Figure 4. XPS sputter depth profile of a 17 nm thick Fe₂O₃ film on a Pt substrate.

20% Fe, 13% C (adventitious), and 6% Pt. Initially, the Fe concentration remains constant while there is a reduction in O concentration most likely resulting from preferential sputtering of O.⁵⁰ The small amount of C present on the surface is fully removed after the first sputtering cycle, indicating it is only present on the surface and is the result of adventitious C contamination. The detection of Pt in the initial surface measurement is likely caused by the probing of the underlying Pt film, and not from possible Pt in the Fe₂O₃ film itself. Due to the high roughness of the Fe₂O₃ film, there are some regions of the film where the thickness is low enough (~ 10 nm) for XPS to detect the underlying substrate. The absence of significant Pt signal in the cross-sectional EDS measurement (Figure 3c) further supports that the 6% Pt originates from the substrate and not the Fe₂O₃ film itself.

Selectivity on Patterned Samples. We employed AES to investigate the selectivity of the deposition process on microstructured patterns. AES maps and line scans of Fe₂O₃ deposited on SiO₂ substrates with patterned Pt squares are presented in Figure 5. The high spatial correlation between Pt and Fe elemental signals in the AES maps further supports the

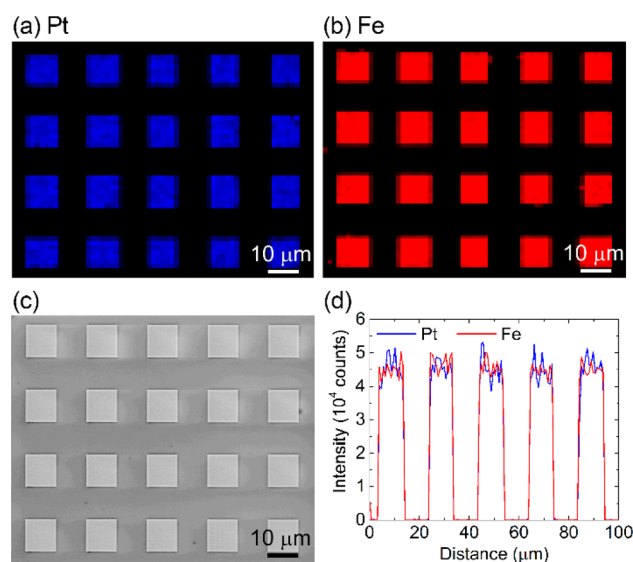


Figure 5. AES elemental maps for (a) Pt and (b) Fe of Fe₂O₃ deposited on patterned Pt substrates. (c) Corresponding SEM image. (d) Line scan showing Pt and Fe counts. The AES maps show excellent correlation between the Pt and Fe signals.

preference for deposition on Pt over SiO₂ surfaces. On the basis of the ratio of observed elemental counts in the Pt and SiO₂ regions of the substrate, the selectivity for deposition on Pt versus SiO₂ is 2000:1.

The area-selective deposition of NiO and Fe₂O₃ on SiO₂ substrates with patterned Ir was similarly investigated by AES, and the results are presented in Figure S2. There is also a very high correlation between the Fe and Ir, and likewise the Ni and Ir signals. Very low Ni and Fe levels are detected in the SiO₂ regions where Ir is not present, giving selectivities of 200:1 for Ni and 900:1 for Fe.

Synthesis of Core–Shell Nanoparticles. The area-selective ALD process reported here is ideal for the preparation of core/shell nanoparticles, as a metal oxide shell can be deposited selectively on catalytically active core particles. As a demonstration, we prepared core/shell Pt/Fe₂O₃ nanoparticles. The Pt core particles were deposited by performing 50 cycles of Pt ALD on a SiO₂ nanosphere support, and subsequently, the Fe₂O₃ shell was deposited using either 25 or 50 cycles of the area-selective Fe₂O₃ ALD process. Bright-field TEM micrographs of these nanoparticles are shown in Figure 6. The

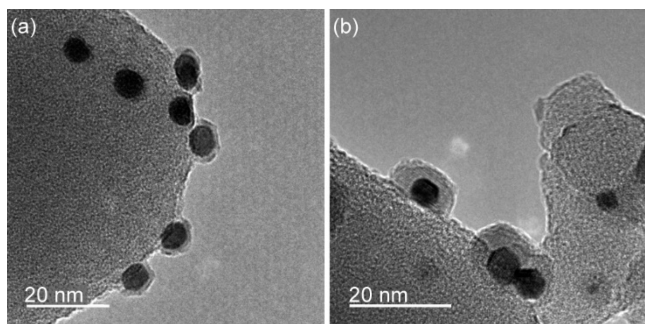


Figure 6. Bright-field TEM images of Pt/Fe₂O₃ core/shell nanoparticles supported on SiO₂ nanospheres prepared by 50 cycles of Pt ALD, followed by (a) 25 cycles and (b) 50 cycles of Fe₂O₃ ALD from TBF/O₂.

micrographs indicate a dark, strongly diffracting core with a lighter, weakly diffracting shell. The core is assigned to Pt and the shell to Fe₂O₃, as follows. Lattice fringes spaced by 0.23 Å in the dark core correspond to the Pt(111) crystal plane spacing. Strong lattice fringes are not observed in the shell, which may be due to limited crystallinity and the lower atomic number (*Z*) of Fe. Where fringes are observed, they are spaced by 0.27 Å corresponding closely to the Fe₂O₃(104) crystal plane spacing which agrees with the XPS results discussed above. As expected, the thickness of the Fe₂O₃ shell increases in going from 25 to 50 cycles. An annular dark-field (ADF) micrograph and a corresponding STEM-EDS line scan are shown in Figure 7. The dark-field image shows a strongly scattering core in each particle and a weakly scattering shell, which corresponds to a high *Z* Pt core and a low *Z* Fe₂O₃ shell. During the line scan (direction indicated in Figure 7a), the Fe signal appears before the Pt signal is observed, also in support of a core/shell structure with an Fe-containing shell and a Pt core. A STEM-EDS map and corresponding ADF micrograph are presented in Figure S3. In the elemental map, there is a high correlation between the Pt and Fe signals supporting area-selectivity. Very few Fe counts are observed in regions where only Si is present.

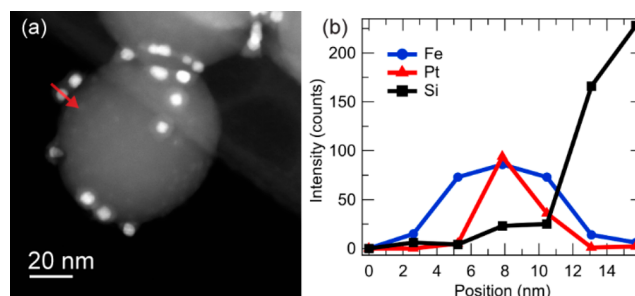


Figure 7. (a) ADF micrograph and (b) STEM-EDS line profile of Pt/Fe₂O₃ nanoparticles supported on SiO₂ prepared using 50 cycles of Pt ALD, followed by 50 cycles of Fe₂O₃ ALD from TBF/O₂. The large SiO₂ sphere is decorated with smaller Pt nanoparticles that in turn are coated with Fe₂O₃. The location and direction of the line scan in (b) is marked on the ADF micrograph in (a).

DISCUSSION

The selective growth of Fe₂O₃ and NiO on Pt and Ir surfaces was demonstrated. No growth of Fe₂O₃ and NiO was observed on SiO₂, Al₂O₃, and Au surfaces. The mechanism of this deposition process will now be discussed.

We propose a reaction mechanism closely related to the mechanism for ALD of Pt-group metals, most notably the ALD process for Pt using MeCpPtMe₃ and O₂ gas which was demonstrated to involve the chemisorption of oxygen.^{22,51} In each cycle of this Pt ALD process, oxygen dissociatively chemisorbs on the Pt surface during the oxygen half reaction, and the chemisorbed oxygen oxidizes the ligands from the MeCpPtMe₃ precursor. These combustion-like reactions happen during both the MeCpPtMe₃ and oxygen half-reactions.^{52–54}

Similarly, we propose a mechanism (Figure 1) where, in each Fe₂O₃ or NiO ALD cycle, oxygen dissociatively chemisorbs during the oxygen half-reaction on the catalytic Pt or Ir substrate and not on surfaces inactive for oxygen activation (e.g., Au, SiO₂, Fe₂O₃, or Al₂O₃). On the catalytic Pt or Ir, dissociatively chemisorbed oxygen species then combust the ligands of the nickelocene and *t*-butyl ferrocene. The lack of chemisorbed oxygen on the inactive substrates is the reason why no deposition occurs on these surfaces. Importantly, the lack of growth on Au substrates supports the requirement of a catalytically active substrate for the growth, since Au films are not catalytically active toward oxygen dissociation (except in small Au clusters).^{55–57}

In this mechanism, one might expect the growth of the transition metal oxide to attenuate when the catalytically active substrate becomes covered by the growing metal oxide film. However, in the case of Fe₂O₃ on Pt shown in Figure 2, linear growth is sustained for at least 300 cycles (resulting in >200 nm growth), at which point the Pt substrate is already fully covered by Fe₂O₃ (as can be concluded from TEM images; see Figure 3). Figure 2a also shows that the growth is almost negligible on Fe₂O₃ substrates, where the initial Fe₂O₃ film is grown using nonselective ALD with TBF/O₂ plasma. This indicates that the Fe₂O₃ material itself does not provide a significant catalytic contribution to the growth.

The mechanism of the sustained growth is currently not fully understood. One key hypothesis is that, during the oxygen half-reaction, oxygen diffuses into the Fe₂O₃ film, reaches the Pt substrate, and is dissociated there. This diffusion is likely enhanced by the presence of grain boundaries resulting from

the polycrystalline nature of the film as seen in Figure 3 and Figure S1. If the dissociated O* can diffuse back toward the surface, it could react with the TBF precursor during the subsequent precursor half-cycle. In this way, the Fe₂O₃ film could act as a reservoir for oxygen. A similar phenomenon was observed during SiO₂ ALD on Ag, where Ag₂O is formed and releases O species, resulting in increased SiO₂ deposition.⁵⁸ The saturation behavior of our process as shown in the inset of Figure 2a provides some evidence for this mechanism. For thin Fe₂O₃ films up to 100 cycles, saturated growth is observed. In contrast, however, for thicker films such as at 250 cycles, the growth rate increases going from 10 to 20 s of TBF exposure. This supports the proposed mechanism, as thicker Fe₂O₃ films would have a higher oxygen uptake capacity, allowing for increased amounts of oxygen to be released. Consequently, a higher TBF dose would be required for the growth to saturate. We expect saturation to eventually occur if the TBF exposure time is increased.

An alternative explanation may be the presence of a small amount of Pt in or on the Fe₂O₃ film. Diffusion of Pt from the substrate toward the top of the Fe₂O₃ layer may be possible at the elevated growth temperature, and this Pt may be catalyzing the growth. However, no Pt is detected in the Fe₂O₃ layer in the cross-sectional EDS measurement (Figure 3c), which makes this explanation less likely. As mentioned previously, the observation of Pt in the XPS depth profiling (Figure 4) is likely due to detection of the Pt substrate through thinner regions of the Fe₂O₃ film. Therefore, we do not expect surface Pt species to play a key role in the continued growth; however, we cannot conclusively rule out the presence of trace amounts of Pt below the EDS detection limit.

The process of area-selective ALD that we demonstrate here should be extendable to a variety of systems. First, we have shown that selectivity can be achieved for two different transition metal oxide ALD systems (Fe₂O₃ and NiO) on two different catalytic substrates (Pt and Ir). Moreover, the ability to perform these selective depositions in ALD reactors of different designs and on both flat and nanoparticle substrates supports the robustness of our processes. By using Pt-group metal surfaces such as Pt, Ir, Pd, and Ru as the substrate to catalyze the oxidant reaction, we expect that area-selective deposition can be achieved through a similar mechanism for almost any metal oxide ALD system that uses a precursor requiring a strong oxidizing agent for growth (i.e., does not react with molecular O₂) such as Co₃O₄,⁵⁹ In₂O₃,⁶⁰ and MoO₃.⁶¹ Likewise, there are other materials that can chemisorb and catalyze oxygen dissociation, and this may allow for selective growth even on non-noble metals such as Cu.⁶² Furthermore, similar mechanisms may be possible with other co-reactants such as hydrogen,⁸ as demonstrated by the selective deposition of Pd on Pt particles via hydrogen dissociation.¹⁶

CONCLUSIONS

We studied the area-selective ALD of Fe₂O₃ and NiO on Pt and Ir surfaces, using *t*-butyl ferrocene and nickelocene precursors, which conventionally require strong oxidizing agents. When using molecular O₂ gas as the co-reactant, ALD growth can only be obtained on catalytically active surfaces, a phenomenon that was exploited for achieving area-selective ALD. These substrates catalyze dissociative chemisorption of O₂, leading to activated O* that participates in the ALD reactions, while no growth occurs on substrates that do not possess catalytic

activity for O₂ dissociation including Au, SiO₂, and Al₂O₃. Area-selective deposition is thereby achieved through the catalytic activity of the underlying substrate.

Process characterization was performed using *in situ* spectroscopic ellipsometry. XPS measurements on Au, SiO₂, and Al₂O₃ show no indication of any Fe presence after 300 ALD cycles of Fe₂O₃ ALD, which confirms the high selectivity of the process. Area-selective ALD was demonstrated by successfully depositing Fe₂O₃ and NiO on micron-scale Pt and Ir patterns. AES measurements on these patterned samples yielded selectivity values of 2000:1 for Fe₂O₃ on Pt with respect to SiO₂, and 200:1 for NiO on Ir. Furthermore, Pt/Fe₂O₃ core/shell nanoparticles were synthesized by performing area-selective ALD of Fe₂O₃ on Pt nanoparticles.

Finally, the demonstrated area-selective deposition of both Fe₂O₃ and NiO, as well as the similarity of results obtained in different reactors, supports the robustness of the process. This approach holds promise for the area-selective deposition of a wide range of other metal oxides for which the precursor does not react with molecular oxygen, for example, processes relying on O₂ plasma or ozone as co-reactant. In particular, the Fe/Pt-based results may be applied for preparation of magnetic or spintronic devices, or catalyst particles for the synthesis of carbon nanotubes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b03818.

SEM micrograph of Fe₂O₃/Pt, AES lines scans on Ir, and STEM-EDS mapping of Fe₂O₃/Pt (PDF)

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Notes

The authors declare no competing financial interest.

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