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Area-Selective Atomic Layer Deposition of SiO₂ Using Acetylacetone as a Chemoselective Inhibitor in an ABC-Type Cycle

Alfredo Mameli,*† Marc J. M. Merkx,** Bora Karasulu,†§ Fred Roozeboom,*† Wilhelmus (Erwin) 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
‡TNO-Holst Centre, High Tech Campus 31, 5656 AE Eindhoven, The Netherlands

ABSTRACT: Area-selective atomic layer deposition (ALD) is rapidly gaining interest because of its potential application in self-aligned fabrication schemes for next-generation nanoelectronics. Here, we introduce an approach for area-selective ALD that relies on the use of chemoselective inhibitor molecules in a three-step (ABC-type) ALD cycle. A process for area-selective ALD of SiO₂ was developed comprising acetylacetone inhibitor (step A), bis(diethylamino)silane precursor (step B), and O₂ plasma reactant (step C) pulses. Our results show that this process allows for selective deposition of SiO₂ on GeO₂, SiNx, SiO₂, and WO₃, in the presence of Al₂O₃, TiO₂, and HfO₂ surfaces. In situ Fourier transform infrared spectroscopy experiments and density functional theory calculations underline that the selectivity of the approach stems from the chemoselective adsorption of the inhibitor. The selectivity between different oxide starting surfaces and the compatibility with plasma-assisted or ozone-based ALD are distinct features of this approach. Furthermore, the approach offers the opportunity of tuning the substrate-selectivity by proper selection of inhibitor molecules.

KEYWORDS: self-aligned fabrication, area-selective deposition, chemoselective inhibition, atomic layer deposition (ALD), silicon oxide, nanomanufacturing, density functional theory
other hand, in self-aligned fabrication, a partially processed device architecture is taken as the starting point, where patterning has been performed in a previous processing step. Thus, the sample surface consists of several different materials, and the challenge is to selectively deposit on the surface of only one or a subset of these materials. The area-selective ALD processes developed so far often concern metal-on-metal or oxide-on-oxide deposition. However, self-aligned fabrication can also require other material combinations to be deposited in an area-selective manner. For example, some applications might demand area-selective ALD on a specific metal oxide in the presence of other oxide surfaces.

In this work, an approach for area-selective ALD is introduced. It is based on a three-step (ABC-type) ALD cycle, where step A is the exposure of the surface to inhibitor molecules, and B and C are the steps of a regular ALD process. Earlier investigations in chemical vapor deposition illustrate some of the advantages of using inhibitors for achieving area-selective deposition. Our approach is inspired by the work of Yanguas-Gil et al., who used inhibitor molecules (e.g., ethanol, acetone, hexane) in ABC-type ALD cycles to improve the doping efficiency in ALD-grown materials. Instead of reducing the growth per cycle by partial blocking of the adsorption sites for the precursor molecule, we intend to completely block precursor adsorption on specific starting materials.

Our approach for achieving area-selective ALD is illustrated in Figure 1. In step A, we use an inhibitor molecule that selectively adsors on certain materials on which no deposition is desired (referred to as the non-growth area). The inhibitor blocks the precursor adsorption during the subsequent step B. The cycle is completed in step C by removing the precursor ligands together with the inhibitor molecules and by activating the surface for the next cycle. This approach should ideally allow for area-selective ALD on surfaces where the inhibitor does not adsorb (referred to as the growth area).

A pronounced benefit of this approach is that the selectivity no longer relies solely on the chemoselective adsorption of an ALD precursor on a specific surface. Chemoselective adsorption is decoupled from the precursor by inserting an inhibitor step, and this will therefore yield more freedom for developing area-selective ALD processes. Similar to previous work on the application of self-assembled monolayers (SAMs) for area-selective ALD, this approach relies on the blocking of surface sites for precursor adsorption. However, the main difference is that the inhibitor molecules are reapplied every single cycle, which can potentially lead to a more robust approach that does not suffer from a gradual degradation of the blocking layer. Another advantage of reapplying the inhibitor every cycle is that it renders area-selective deposition compatible with (or accessible to) more types of ALD processes, including plasma-assisted or ozone-based ALD. This will therefore extend the set of materials that can be deposited by ALD in an area-selective manner.

In this article, we demonstrate a proof-of-concept for using ABC-type ALD cycles to achieve area-selective ALD of SiO₂, a low-κ material that is ubiquitous in many devices. The process consists of acetylacetone (abbreviated in the literature as Hacac) as the inhibitor, bis(diethylamino)silane (BDEAS) as the Si precursor, and O₂ plasma as the co-reactant. In contrast to previous area-selective ALD studies in which typically only two surfaces were considered, the nucleation behavior of this ABC-type ALD process is investigated here on as many as 14 different starting surfaces. As a proof-of-concept, the process was tested on patterned Al₂O₃/GeO₂ samples, and the selectivity was probed using surface analysis techniques. Theoretical calculations as well as in situ studies were performed to determine the mechanistic aspects of the chemoselective inhibitor adsorption and the precursor blocking. The basic understanding obtained this way can be used to further improve the selectivity of the current approach. Finally, the opportunities enabled by this area-selective ALD approach will be discussed.

RESULTS AND DISCUSSION

Impact of Hacac Adsorption on SiO₂ Nucleation.

Saturation curves for the ABC-type ALD cycle, included in the Supporting Information (Figure S1), demonstrate that the saturation behavior and the growth per cycle are not influenced by the addition of the Hacac step. ABC-type ALD cycles of SiO₂ were carried out on various starting surfaces to identify on which surfaces deposition of SiO₂ is obtained and on which ones it is blocked. Figure 2 depicts the nucleation curves as measured by in situ spectroscopic ellipsometry (SE). The graph shows that SiO₂ grows without any nucleation delay on GeO₂, SiO₂, WOₓ, and SiNₓ. On these substrates a growth per cycle of approximately 0.09 nm/cycle was obtained. This is comparable to the growth per cycle of the regular two-step ALD process, consisting of BDEAS precursor and O₂ plasma pulses (referred to as the BC process). Figure 2 also shows that growth delays for ABC-type ALD of SiO₂ are observed on Al₂O₃ (15 cycles), TiO₂, and HfO₂ (both 10 cycles). The growth delay of 15 cycles is that obtained when using the ABC-type cycles on Al₂O₃ means that a SiO₂ film of ~1 nm thickness can be selectively deposited on GeO₂ in the presence of Al₂O₃. Nucleation curves for the BC process are shown in Figure S2, demonstrating that there is no nucleation delay for the regular
The selectivity was further investigated on a patterned Al₂O₃/GeO₂ sample. To this end, an ALD-prepared Al₂O₃ layer
was patterned on a GeO₂ surface using a regular lift-off method. Figure 4a–c show the TOF-SIMS elemental mapping images for the Ge⁺, Al⁺, and Si⁺ secondary ions for the patterned sample after 15 ABC-type ALD cycles of SiO₂. The mappings confirm that ALD of SiO₂ occurred predominantly on the GeO₂ regions. The line scans, presented in Figure 4d, show a high Si⁺ signal in the regions not covered by Al₂O₃, indicating area-selective deposition of SiO₂ on GeO₂. Only a very small amount of Si is also present on Al₂O₃, which was quantified to correspond to a 0.01 nm thick SiO₂ layer, as derived from calibration measurements (see the Methods section). Also, lateral broadening of ~1 nm, the so-called mushrooming effect, is expected to take place given the nature of the ALD technique. This will mainly impact (and be observable for) nanoscale patterns, and the effect will be investigated on such samples in future work.

Surface Chemistry of the ABC SiO₂ ALD Process. In order to investigate the Hacac and BDEAS adsorption on SiO₂ and Al₂O₃ starting surfaces, in situ infrared absorption spectroscopy experiments were performed on pellet-pressed SiO₂ powder using a Fourier transformed spectrometer (FTIR). To this end, the SiO₂ powder was first coated using...
30 ALD cycles of SiO₂ or Al₂O₃, respectively. FTIR spectra were collected after coating the powder and after the subsequent Hacac and the BDEAS dosing steps. Figure 5a shows the results on Al₂O₃ as difference spectra, using the spectrum collected after Al₂O₃ coating as the reference. The results confirm that Hacac adsorbs on Al₂O₃ as indicated by the absorption peaks in the wavenumber range 1300–1650 cm⁻¹. Subsequent dosing of BDEAS precursor causes only a minor change in the spectrum, which confirms that the preadsorbed Hacac molecules act as inhibitors and block the impinging BDEAS molecules from chemisorbing onto the Al₂O₃ surface. It is estimated that the minor change corresponds to a fraction of ~8% of the amount of BDEAS molecules adsorbed on bare Al₂O₃. This indicates that Hacac is not fully effective in blocking the precursor adsorption.

A similar experiment on the SiO₂-coated sample, using identical Hacac and BDEAS dosing times, revealed a distinctly different behavior, as shown in Figure 5b. Now, only 8% of Hacac adsorbs on SiO₂ as compared to the amount that adsorbs on the Al₂O₃-coated surface. Consequently, the adsorption of BDEAS is not significantly affected on this surface, as shown by the large (positive) absorption peaks. BDEAS adsorption results in positive peaks in the wavenumber ranges 2800–3000 cm⁻¹ and 1610–1620 cm⁻¹, originating from the C=H and Si–H stretching vibrations of the adsorbed BDEAS molecules. Concurrently, there is a loss of absorbance around 3740 cm⁻¹, characteristic for the O–H stretching vibrations of the surface hydroxyl groups that are consumed during BDEAS precursor adsorption.

In conclusion, the FTIR studies confirm that Hacac selectively adsorbs on Al₂O₃ and subsequently inhibits the BDEAS adsorption. Yet, the studies also provide insights for further improvement of the process that will be discussed below.

**Mechanism Underpinning the Chemoselective Adsorption of the Hacac Inhibitor.** Density functional theory (DFT) calculations were performed to better understand the mechanism of the chemoselective Hacac adsorption at a molecular level. Hydroxylated surfaces of Al₂O₃ (0001) and SiO₂ (0001) were employed to represent the experimentally used Al₂O₃ and SiO₂ surfaces. The calculations revealed that Hacac prefers to bind in a chelate configuration on both surfaces, with both of its oxygen atoms bonded to Al³⁺/Si⁴⁺ surface sites. Alternative binding configurations were also found, as discussed below. Concretely, H₂O is predicted to form as a byproduct on both surfaces through a proton transfer to a hydroxyl surface group. The H₂O byproduct is expected to stick to the surface, where it plays an important role in stabilizing the chemisorbed acac⁻ product through H-bond interactions (see Supporting Information, Figure S7 and the accompanying discussion).

The structures and associated relative energies were calculated for the stationary points along the suitable reaction pathways (i.e., minimum energy paths) for the adsorption of the Hacac inhibitor on Al₂O₃ and SiO₂ (Figure 6). For the first step in Hacac binding, i.e., physisorption, two distinct binding orientations were identified by the DFT calculations (horizontal and vertical; see Figure S6 and detailed description in the Supporting Information). As evident from Figure 6a, the dissociative binding of Hacac on Al₂O₃ is associated with an overall exothermic reaction with an energy gain of 0.49 eV. The chemisorption involves the formation of an intermediate complex through a slightly exothermic (∆E = –0.07 eV) process with near-zero barrier (Eₚ ≈ 0.01 eV). The intermediate complex comprises Hacac that is bonded to the Al³⁺ site through one of its oxygen atoms (Figure S7a). This intermediate species is predicted to lose its hydroxyl proton through a kinetically accessible process (Eₚ = 0.25 eV), producing a monodentate adduct (type A, Figure S7b) alongside H₂O. However, this adduct corresponds to a transition-state species on the energetically downhill path that yields the chelate end-product (type B, Figure S7c) through binding of acac⁻ via its second oxygen to the same surface Al³⁺ site. Considering that the Hacac would have already gained.

**Figure 6.** DFT (GGA/PBE-D3) level minimum energy paths for the Hacac adsorption on (a) Al₂O₃ and (b) SiO₂ surfaces, as described by the corresponding chemical equations. Minimum energy structures of the important steps are also shown (yellow, green, and blue dots and corresponding chemical equations). Minimum energy structures of the important steps are also shown (yellow, green, and blue dots and corresponding chemical equations).
sufficient kinetic energy by physisorbing on the Al₂O₃ surface (i.e., \( \Delta E_p = -0.75 \) eV, physisorption energy), it would readily overcome the overall barrier of 0.25 eV and be converted to the chelate (type B) end-product. Therefore, none of the monodentate (type A) species (intermediate or adduct) are expected to accumulate on the Al₂O₃ surface.

Similar to the Al₂O₃ case, a chelate (type B, Figure S7d) species is the end-product of Hacac adsorption on SiO₂, whereas the monodentate (type A) complex is only a transition state (Figure 6b). More importantly, the overall chemisorption reaction on SiO₂ is calculated to be endothermic and to require an energy of 0.98 eV, accompanied by an extremely high kinetic barrier \( (E_k = 2.35 \text{ eV}) \). In accordance with the SE and FTIR results, these DFT findings suggest that Hacac binds readily on hydroxylated Al₂O₃, while the overall reaction on hydroxylated SiO₂ is both thermodynamically and kinetically hindered. This explains the selectivity of Hacac adsorption on Al₂O₃ as opposed to SiO₂ during the ABC-type ALD of SiO₂.

**Role of Surface Acidity on Hacac Adsorption.**

The chemoselective adsorption of Hacac on various starting surfaces can also be interpreted in terms of surface acidity.⁶¹ This allows explaining the results obtained on the experimentally used starting surfaces. Hacac has a pKₐ value of 9.0 in aqueous solution at 25 °C, and therefore it should behave as a weak acid.⁶² A reaction with Hacac is not likely to occur with the hydroxyl groups that possess an acidic character (e.g., SiO₂).³³ Conversely, hydroxyl groups with more basic character can react with Hacac. In this framework, an acid/base surface reaction between Hacac and the surface hydroxyl groups of a given oxide (e.g., Al₂O₃) can be written as

\[
\text{M-OH}^* + \text{Hacac}_{(g)} \rightarrow \text{M(acac)}^* + \text{H}_2\text{O}_{(g)}
\]  

(1)

where M is a generic atom of the oxide (either metal or nonmetal) and the asterisks represent the surface species. A generalization can be made in order to explain which surfaces allow for the chemoselective adsorption of the Hacac inhibitor (and potential blocking of the precursor) and which surfaces will lead to immediate deposition instead. The acidity of an oxide can be predicted from the electronegativity of the cation element, M.⁶⁴ The relative acidity of several oxide surfaces was calculated using Sanderson’s electronegativity scale and the electronegativity equalization principle, in order to explain the data of Figures 2 and S3, as presented in Figure S8. The agreement of the calculated values with the experimental data underlines that the distinct acidic/basic behavior of different oxide compounds governs the chemoselective adsorption of Hacac. Therefore, this provides a framework for predicting the area selectivity on different starting surfaces.

**Merits and Opportunities Provided by the Approach.**

The approach introduced in this article shows similarities with recent work by Engstrom and co-workers in which inhibitor molecules are co-injected into the reactor together with the precursor.³⁵ Also that approach relies on influencing the precursor adsorption by an inhibitor molecule. The benefit of dividing the inhibitor and precursor exposure over two different dosing steps is that the adsorption of both molecules can reach saturation independently, without suffering from competitive adsorption effects. Consequently, similar to regular two-step ALD processes, an ABC-type ALD process should allow for the deposition of conformal films on nanostructured surfaces.

A more natural approach for achieving area-selective ALD would be to design dedicated ALD precursors to enable chemoselective adsorption on materials on which deposition should occur. However, in practice this is extremely challenging because the precursor molecule has to contain the atom to be deposited, while also satisfying other requirements to behave as an effective ALD precursor (in terms of stability, volatility, and self-limiting adsorption). By using two different molecules in an ABC-type ALD cycle, the inhibitor provides the selectivity in step A, without compromising the properties of the precursor dosed in step B.

When the ABC-type ALD approach is compared to other area-selective ALD approaches, several distinctive aspects can be identified. As discussed in the introduction, reapplying the inhibitor molecules every cycle can be beneficial from a reliability point-of-view, while it also makes the approach compatible with plasma-assisted or ozone-based ALD. Moreover, an important merit of this approach is that it distinguishes between the growth on different oxide surfaces (e.g., GeO₂/SiO₂ versus Al₂O₃/HfO₂/TiO₂).

The FTIR studies revealed that the selectivity of the Hacac adsorption is not perfect, since some adsorption was also observed on SiO₂. However, the amount of Hacac on SiO₂ is sufficiently small such that it does not influence the deposition on the growth area, as we concluded from the in situ SE measurements (Figures 2 and S1). Moreover, a small amount of BDEAS adsorption was detectable on Al₂O₃ after dosing the Hacac inhibitor. Ex situ XPS and TOF-SIMS also confirmed that a minor amount of SiO₂ was deposited on Al₂O₃ after 15 cycles, suggesting that the adsorbed Hacac does not completely block the precursor adsorption. This incomplete precursor blocking can occur most likely due to the presence of (i) surface defects or impurities that can negatively influence the ideal inhibitor adsorption behavior; (ii) surface reactive sites that remain accessible to the precursor; and (iii) physisorbed water molecules on the surface that can compete with the Hacac chemisorption, as discussed in the DFT calculations in the Supporting Information, Figure S7. This implies that the selectivity of the ABC-type ALD process can be further improved by exploring different surface preparation procedures and by optimizing the deposition conditions. In addition, alternative inhibitors, different inhibitor dosing strategies, or co-dosing two or more inhibitor molecules can be considered for improving the selectivity. All these parameters offer physicochemical pathways to enhance the inhibitor surface coverage and, therefore, maximize the blocking effect during the precursor dose step. For these reasons, we foresee that it should be possible to significantly improve the selectivity to the extent it meets the requirements of semiconductor manufacturing.

The ABC approach provides the opportunity of tailoring the substrate-selectivity of an ALD process by selection of the chemoselective inhibitor molecule. There is a wealth of information in surface science and catalysis literature about the adsorption of organic molecules on inorganic surfaces,³⁶,³⁷ which can serve as a good starting point for selecting suitable inhibitor molecules.²⁵ The ideal case would be to use an inhibitor molecule that adsorbs on all surfaces, except for the particular surface on which deposition is needed. Additional research is required to investigate whether such selectivity is achievable and to further explore the toolbox of using inhibitor molecules for area-selective ALD. We expect that this approach can enable area-selective ALD for different materials by using other precursors and for example H₂ or NH₃ plasma co-reagents. To this end, the interaction of the inhibitor with the material to be deposited and with the plasma needs to be
studied. In view of the large set of possibilities, this will be the subject of a follow-up study.

CONCLUSIONS

We have demonstrated the use of chemoselective inhibitors in ABC-type ALD cycles as a route for area-selective ALD. Area-selective ALD of SiO2 was achieved using a process consisting of alternated Hacac inhibitor, BDEAS precursor, and O2 plasma pulses on a GeO2 substrate with patterned Al2O3 features. SiO2 was investigated as starting surfaces in this study. Al2O3, HfO2, TiO2, studies revealed that area-selective (i.e., uninhibited) growth can also be obtained on WO3, SiO2, SiNx, and Pd, while there are nucleation delays of 10−15 cycles on TiO2, HfO2, CoO2, and MoO2. The selectivity originates from the chemoselective adsorption of the Hacac inhibitor molecule. This was corroborated in detail by in situ SE and FTIR experiments, as well as by DFT calculations, and generalized by correlating the Hacac adsorption to the acidoxy of the starting surface. SE and FTIR experiments confirmed that adsorbed Hacac blocks the subsequent BDEAS precursor adsorption, thereby resulting in area-selective deposition of SiO2 on those surfaces on which Hacac does not adsorb.

The presented results establish a proof-of-concept for the introduced approach and provide insight into how the selectivity can be further improved. The SiO2 ABC-type process offers an exceptional substrate-selectivity, by distinguishing between different oxide starting surfaces. We expect that the compatibility of the approach with ozone-based or plasma-assisted ALD, as well as the ability to tune the substrate-selectivity by selection of the inhibitor molecule, will extend the compatibility of the approach with ozone-based or plasma-assisted ALD, as well as the ability to tune the substrate-selectivity by selection of the inhibitor molecule, will extend the portfolio of materials that can be deposited by ALD in an area-selective manner.

METHODS

ALD Processes. The depositions were carried out in an Oxford Instruments FlexAL reactor, which is described in detail in ref 38. In short, it is a vacuum vessel equipped with a remote inductively coupled plasma (ICP) source, a 200 mm substrate table, a turbo-molecular pump, and a loadlock. The SiO2 plasma-assisted ALD recipe with BDEAS (H2Si[N(C2H5)2]3) precursor (also known as SAM24) and O2 plasma pulses, characterized by Dingemans et al.,24 was used as the starting point. The recipe was changed to an ABC-type ALD process by adding a step of Hacac dosing before the precursor step. The Hacac inhibitor was kept at room temperature (∼25 °C), and it exists in two tautomeric forms: keto and enol. In gas phase, the tautomeric equilibrium is shifting toward the enol form,10 which was the form considered in the DFT calculations. The Hacac inhibitor was kept at room temperature in a stainless steel container and vapor drawn into the chamber using 3 pulses of 5 s each. All experiments were carried out at a substrate temperature of 150 °C.

Substrate Preparation Methods. A set of 14 different materials was investigated as starting surfaces in this study. Al2O3, HfO2, TiO2, WO3, CoO2, MoO2, FeO2, ZnO, Pt, Pd, Ru, and SiNx samples were prepared by ALD in our lab using standard ALD recipes. In addition, crystalline Si and Ge substrates were used. All these substrates were cleaned by 5 min O2 plasma exposure (8 mTorr O2, 200 W) prior to the deposition, with the exception of SiNx. Because of this O2 plasma cleaning step, the Si and Ge substrates are referred to as SiO2 and GeO2, respectively, in this article.

Analytical Methods. In situ SE was performed using a J.A. Woollam M2000D ellipsometer as the main diagnostic technique to characterize the process and to measure the nucleation curves, using a Cauchy parametrization to model the data. In the case of SiNx, O2 plasma oxidation occurs during the SiO2 deposition, which was taken into account in the modeling of the data of Figure 2. The nucleation delay was defined as the number of cycles until the first data point that showed a measurable increase in thickness. The dielectric function of a monolayer of adsorbed Hacac molecules was not taken into account, and the same Cauchy parametrization as used to describe the deposited SiO2, was employed to model the subcycle SE data of Figures 3 and S4. In these results, the thickness obtained from modeling the data after Hacac exposure is therefore represented as “apparent thickness”.

XPS measurements were performed using a K-Alpha system from Thermo Scientific. TOF-SIMS analysis was performed at Philips Innovation Laboratories using an Ion-Tof TOF-SIMS IV instrument, which was operated in positive mode to measure Al+ (m/z = 27), Si+ (m/z = 28), and Ge+ (sum of m/z = 70, 72 representing the most abundant isotopes of Ge). In addition, TOF-SIMS mapping was performed on patterned GeO2/Al2O3 samples by applying burst-alignment with long pulses of 200 ns, resulting in high lateral resolution (∼0.3 μm), but low mass resolution (∼1 m/z). A series of 2, 5, and 10 regular ALD cycles for SiO2 deposition was performed on Ge substrates to calibrate the TOF-SIMS signals for thickness quantification. These samples were probed using the high-current bunched mode, which allows for measurement with high mass resolution. Note that the thickness of the deposited SiO2 on the GeO2 regions is already beyond the linearity limit of TOF-SIMS, meaning that the ratio of the Si+ intensity of the GeO2 and Al2O3 regions in the line scans underestimates the selectivity.

In situ FTIR experiments were carried out in a home-built ALD setup, which is very similar to the FlexAL reactor in terms of the plasma source and pumping system. This home-built setup is equipped with a Bruker Vector FTIR spectrometer with a mid-infrared light source (Globar, ~10 000−50 cm−1) and a liquid N2 cooled mercury cadmium tellurium detector with a spectral range of 12 000−500 cm−1, a translational and rotational sample manipulator, and KB-9 windows that can be isolated from the chamber with gate valves. FTIR measurements were performed on Aerosil OX50 SiO2 powder that was pellet-pressed on a tungsten mesh. The powder was heated to 150 °C by passing a current through the mesh. To account for the accessible surface area of the powder, the spectra were normalized to the peak intensities of regular saturated TMA or BDEAS adsorption on the same substrate before the Hacac dosing.

Computational Methods. All electronic structure calculations were performed using the projector-augmented wave function22–23 as implemented in Vienna Ab Initio Simulation Package (VASP) v.5.3.5.34–44 First-principles calculations were carried out using the generalized gradient approximation to the DFT.35,46 Perdew–Burke–Ernzerhof (PBE) exchange−correlation functionals47 were employed, and the van der Waals interactions were also accounted for on an empirical basis (PBE-D3).48 Hydroxylated α-Al2O3 and α-SiO2 clusters were used as approximations of the amorphous hydroxylated Al2O3 and SiO2 used in the experiments. Additional computational details including the model system preparation can be found in the Supporting Information and also elsewhere.17,49

ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b04701.

Additional characterization data, computational details, and supporting figures (PDF)

AUTHOR INFORMATION

Corresponding Author

E-mail: a.j.m.mackus@tue.nl.

ORCID

Alfredo Mameli: 0000-0001-9175-8965
Bora Karasulu: 0000-0001-8129-8010
Wilhelmus (Erwin) M. M. Kessels: 0000-0002-7630-8226
Adriaan J. M. Mackus: 0000-0001-6944-9867

Present Address
3Department of Physics, University of Cambridge, Cavendish Laboratory, 19 J. J. Thomson Avenue, CB3 0HE, Cambridge, United Kingdom.

Notes
The authors declare no competing financial interest.

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