Self-Correcting Process for High Quality Patterning by Atomic Layer Deposition

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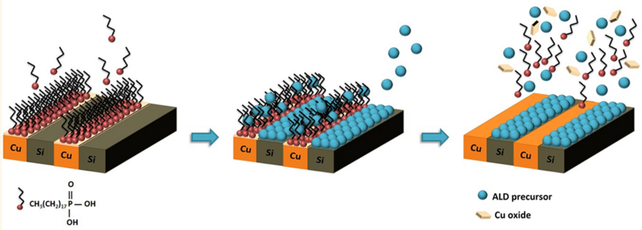

ABSTRACT Nanoscale patterning of materials is widely used in a variety of device applications. Area selective atomic layer deposition (ALD) has shown promise for deposition of patterned structures with subnanometer thickness control. However, the current process is limited in its ability to achieve good selectivity for thicker films formed at higher number of ALD cycles. In this report, we demonstrate a strategy for achieving selective film deposition *via* a self-correcting process on patterned Cu/SiO_2 substrates. We employ the intrinsically selective adsorption of octadecylphosphonic acid self-assembled monolayers on Cu over SiO_2 surfaces to selectively create a resist layer only on Cu. ALD is then performed on the patterns to deposit a dielectric film. A mild etchant is subsequently used to selectively remove any residual dielectric film deposited on the Cu surface while leaving the dielectric film on SiO_2 unaffected. The selectivity achieved after this treatment, measured by compositional analysis, is found to be 10 times greater than for conventional area selective ALD.

KEYWORDS: area selective ALD · self-assembled monolayers · etching · Al_2O_3

As the sizes of electronic and optoelectronic devices continue downward scaling, novel processing methods are needed to meet the increasingly difficult materials challenges associated with new devices. Bottom-up fabrication of patterned structures requires many steps consisting of deposition and etching which makes the process time-consuming and expensive. On the other hand, selective deposition of robust films during fabrication processes may play an important role in significantly reducing process complexities associated with 3-D nanoelectronic and sensing devices. The ultimate adoption of selective deposition approaches in device fabrication will require a technique that can provide for deposition of different materials with a variety of thicknesses while maintaining the selectivity up to high thickness limits.

Atomic layer deposition (ALD) is a good choice for selective deposition applications in which the thickness, conformality and uniformity of the deposited film need to be well controlled over large areas. The ALD process is based on self-limiting reactions between gas phase precursors and specific functional groups at the growth surface. This chemical specificity provides a means to achieve selectivity in ALD on a spatially patterned substrate, since the surface functional groups can be manipulated prior to deposition to either block or allow film growth as desired.[1,2] It is also a widely used deposition method in the fabrication of today's electronic devices.[3,4] A variety of steps in electronic and optoelectronic device fabrication could thus benefit from nanopatterning using area selective ALD (AS-ALD), including those involved in making metal/dielectric patterns. These patterns are prevalent in integrated circuits, impacting structures ranging from FinFETs to interconnects.

In some studies of area selective ALD, unreactive and thermally stable polymer films have been used as a blocking layer in the regions where ALD was not desired.[5−9] However, more commonly, the surface of the substrate is chemically modified with self-assembled monolayers (SAMs). SAMs are well-studied organic monolayer films that form spontaneously on solid surfaces

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Received for review May 24, 2015 and accepted July 16, 2015.

Published online July 16, 2015
10.1021/acsnano.5b03125

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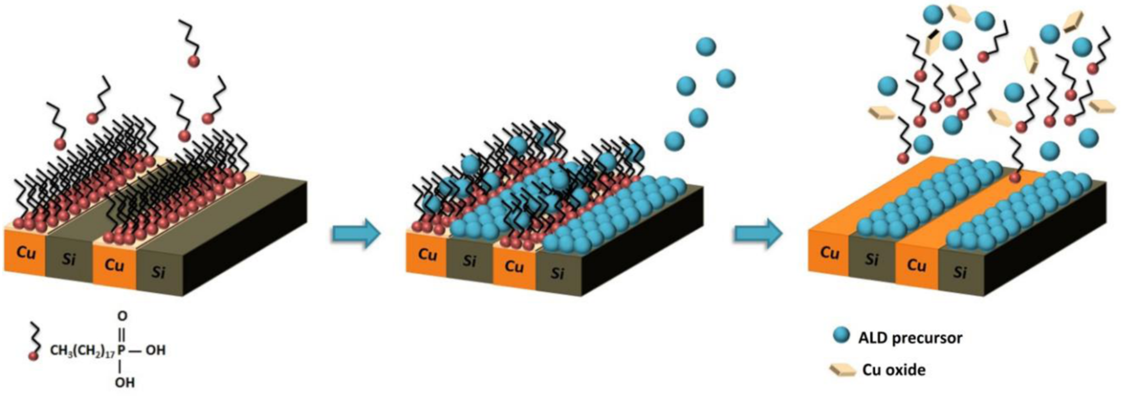

Figure 1. Schematic demonstrating self-aligned patterning through a combination of selective deposition (using ODPA SAM blocking layer on Cu oxide) and selective removal (using acid) of dielectric material.

and have been used to modify the physical, chemical, and electrical properties of semiconducting, insulating and metallic surfaces.[10,11] SAMs have been used for different applications including chemical sensing and protection of metals against corrosion.[12] They have also shown promise as an organic blocking layer for area selective ALD. For example, octadecylphosphonic acid (ODPA) has been used to direct area selective ALD on a metal/metal oxide pattern. ODPA forms a well packed layer on surfaces of copper in a variety of states, *i.e.*, CuO, Cu_2O and Cu,[13,14] but it does not chemically attach on a SiO_2 surface at room temperature.[15−19] Hence, on the basis of this intrinsically selective adsorption, area selective ALD of ZnO on ODPA-treated Cu/SiO_2 patterned substrates has been achieved for film thicknesses up to 36 nm.[20]

However, even with a successful system like ODPA on Cu/SiO_2, there are several factors limiting the use of SAM passivation layers for area selective ALD. First, due to the diverse chemical nature of the precursors involved in dielectric film deposition, the selectivity achieved using SAMs as the blocking layer may be limited to only few nanometers of dielectric films, depending on the material. Second, the deposition time to form a well-packed SAM passivation layer that can prevent ALD has been shown to be above 48 h for a variety of SAMs, including both ODPA and octadecyltrichlorosilane (ODTS).[20−22] Although the water contact angle (WCA) on the substrate increases dramatically when treated by ODPA or ODTS solution even for 1 h, confirming the formation of a hydrophobic SAM on the surface, it has been found that this monolayer is not capable of preventing ALD.[20,21] The need for long SAM exposure makes the selective deposition process using SAMs time-consuming. Finally, removal of the residual SAM from the surface after the selective deposition is necessary for many applications, but it has not been well studied. Here, we propose a new strategy to resolve all these issues on metal/dielectric patterns by introducing a combined process of selective deposition and selective etching. We use Cu/SiO_2 as model substrate.

The blocking ability of SAMs in area selective ALD is typically limited by interaction of the ALD precursor with the SAM, leading to deposition on or within the SAMs. Because the loss of selectivity on a Cu/SiO_2 substrate will originate from the onset of ALD onto the SAMs at the Cu region (which consists of copper oxide at its surface), we expect to see a significant enhancement in selectivity if the oxide layer on Cu and the associated SAM layer containing the ALD film can be selectively removed from the Cu without altering the properties of the deposited film on the Si surface. This then is the strategy that we adopt. Figure 1 illustrates the proposed approach.

Several methods can be used to remove SAMs or the copper oxide layer from the surface of copper.[23−25] One is by electrochemical dissolution, and our group has recently demonstrated the selective removal of SAMs from oxidized copper by electrochemical reduction of the copper, resulting in an increase in the selectivity for MLD and ALD films.[22] However, an electrochemical sweep is not compatible with many electronic device fabrication processes. A promising new approach that we introduce here is the removal of the copper oxide layer using a mild etchant. A mild etchant would avoid the use of electrochemical processing and provide a simple and easily deployed route to selective removal of the residual ALD film. There are numerous reports on dry or wet cleaning of Cu substrates by removal of copper oxide.[26−31] Strong acids such as hydrochloric acid or nitric acid can remove the Cu oxide in a matter of seconds but could also roughen the surface of the metal. Our atomic force microscopy (AFM) results show that the rms roughness on the Cu substrate increased from 0.8 to 6.7 nm after treatment with diluted hydrochloric acid for only 30 s. These acids can also etch the deposited dielectric film from a Cu/dielectric pattern. In contrast, a mild acid such as acetic acid can gradually remove copper oxide in several minutes without attacking the copper film.[26] Compared to dry and more aggressive approaches such as plasma etching,[28] acetic acid can remove the

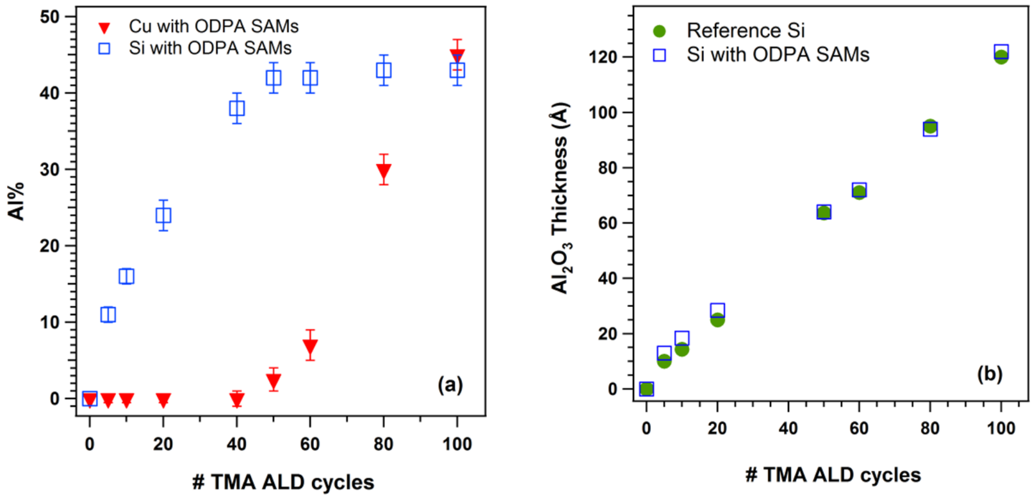

Figure 2. (a) Auger composition analyses on Si and Cu substrates treated with ODPA SAMs for 48 h after different numbers of Al_2O_3 ALD cycles. (b) Ellipsometry results comparing Al_2O_3 thickness on Si wafers dipped in ODPA solution and reference Si substrates after different numbers of cycles of Al_2O_3 ALD.

oxide at low temperature. Acetic acid also has a low surface tension (27.8 dyn/cm), allowing facile removal from the Cu surface.[26] From a variety of different acids and etchants, we selected acetic acid because it can controllably reduce the Cu surface without affecting nearby SiO_2 regions (see Supporting Information).

In this paper, we combine the selective ALD and selective etch steps to develop a new self-correcting process that leads to high quality patterning. We demonstrate the process *via* selective ALD of Al_2O_3 using ODPA SAMs on patterned Cu/dielectric substrates. Al_2O_3 was chosen as model metal oxide for selective ALD due to its tremendous potential in various fields such as optics, electronics, and energy harvesting.[32−36] We demonstrate, for the first time, that a combination of selective deposition using ODPA SAMs followed by chemical etching can provide the ability to significantly increase the selectivity of deposited dielectric materials on a metal/dielectric pattern for thicknesses above 60 nm. We also show that selective deposition requires much shorter formation times for the ODPA SAMs when the combined process is used, mitigating the need for long exposure times to the ODPA SAMs. This approach can be applied to selective deposition of a variety of different dielectric materials, opening up the possibility for new applications.

RESULTS AND DISCUSSION

The extent to which ODPA SAMs could prevent Al_2O_3 ALD on copper by a standard process was first investigated. The presence of ODPA SAMs as a blocking layer on the Cu regions of a Cu/SiO_2 patterned substrate allows for selective dielectric deposition on the samples for up to 50 cycles of trimethylaluminum (TMA), corresponding to 6 nm thickness of Al_2O_3, as evidenced by the data in Figure 2. Figure 2a shows the Al composition results from Auger electron spectroscopy (AES) on both the Cu and Si regions of patterned wafers treated with ODPA SAMs for 48 h (WCA: 110°) following different numbers of Al_2O_3 ALD cycles. Initially, no Al signal is detected on Cu while the Al signal on Si is increasing (Figure 2a). After around 50 cycles of Al_2O_3 ALD, the Al% on the ODPA-covered Cu surface begins to rise. The Al% is correlated to the amount of Al_2O_3 on the surface. Due to the electron escape depth, once the thickness of the Al_2O_3 film reaches a few nanometers, signal from the underlying substrate (Cu or Si) is no longer detectable and the Al% saturates at ∼40%, corresponding to stoichiometric Al_2O_3. On the other hand, ellipsometry results (Figure 2b) show identical growth of Al_2O_3 on ODPA-treated Si as on the reference Si substrates.

Although some selectivity is observed, Figure 2 reveals that selective deposition is limited on these patterns to approximately 50 cycles, or 6 nm, of Al_2O_3 film. To increase the selectivity, the samples were treated with the selective etching process. The results are shown in Figure 3. Elemental Al distribution maps on the ODPA-treated patterns after 60, 80, 250, and 550 cycles of Al_2O_3 ALD were obtained by scanning AES (Figure 3b,e,h,k, respectively). Figure 3b (60 cycles) reveals that only moderate to poor selectivity is achieved on the substrate as a result of treatment with ODPA without the selective etch process. The selectivity decreases as the number of ALD cycles increases from 60 to 550. Almost no selectivity is observed by AES on the patterns after 250 cycles of TMA (∼31 nm Al_2O_3 growth). On the other hand, the Al Auger maps of the samples after sonication in acetic acid (Figure 3c,f,i,l) show remarkably better selectivity, demonstrated by the difference in the intensity of Al signal on Si *versus* Cu. Auger composition analysis on the patterned samples shows an Al concentration of 35% on Si *versus* less than 0.1% on Cu after the acetic acid treatment (Al ratio 350:1).

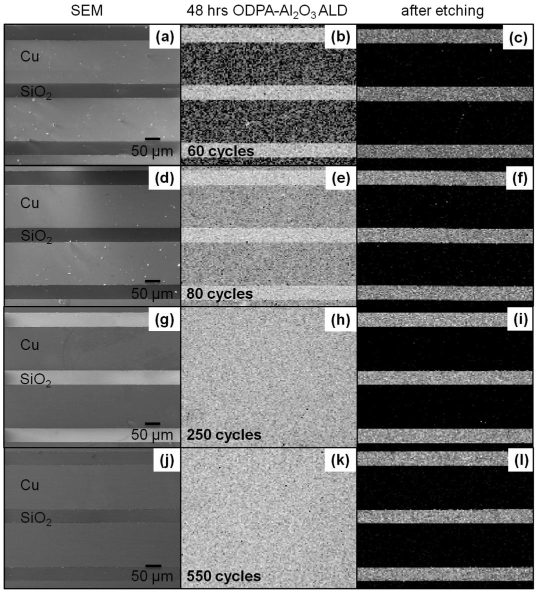

Figure 3. (a, d, g, j) SEM images on the patterned Cu/Si substrates treated as described below. (b, e, h, k) Al Auger maps of the patterned Cu/Si substrates treated with ODPA for 48 h followed by (b) 60, (e) 80, (h) 250, and (k) 550 cycles of Al_2O_3 ALD. (c, f, i, l) Al Auger maps after sonication of the corresponding substrates in acetic acid for 10 min.

Importantly, the highest limit of the selective deposition of Al_2O_3 film has increased at least 10 times, from 6.1 to 60 nm (550 ALD cycles). Higher thicknesses of Al_2O_3 ALD films have not been explored, but due to the reliability and robustness of the proposed process, we believe that this process has the potential to work on Al_2O_3 films with thicknesses even greater than 60 nm.

Auger line scans (Figure 4) confirm the removal of deposited Al_2O_3 from the samples. Figure 4a is a representative SEM image of the typical Cu/SiO_2 patterned substrate that was used for selective deposition. The red line indicates the direction at which the Auger Al line scans were acquired. Panels b, c, and d of Figure 4 show the Al line scans on ODPA-treated samples after 60, 80, and 550 cycles of Al_2O_3 ALD (blue line), respectively, and after the same samples have been subjected to 10 min of acetic acid sonication (red line). In this series of studies, all of the samples were dipped in ODPA for 48 h. The results show clear differences between the Al concentration on the Cu regions of the substrate *versus* the Si regions, with the Al signal going to zero in the Cu regions only after acid treatment. The absence of Al signal on the Cu stripes after acetic acid sonication provides clear evidence for the removal of the Al_2O_3 layer from Cu as a result of the etching process.

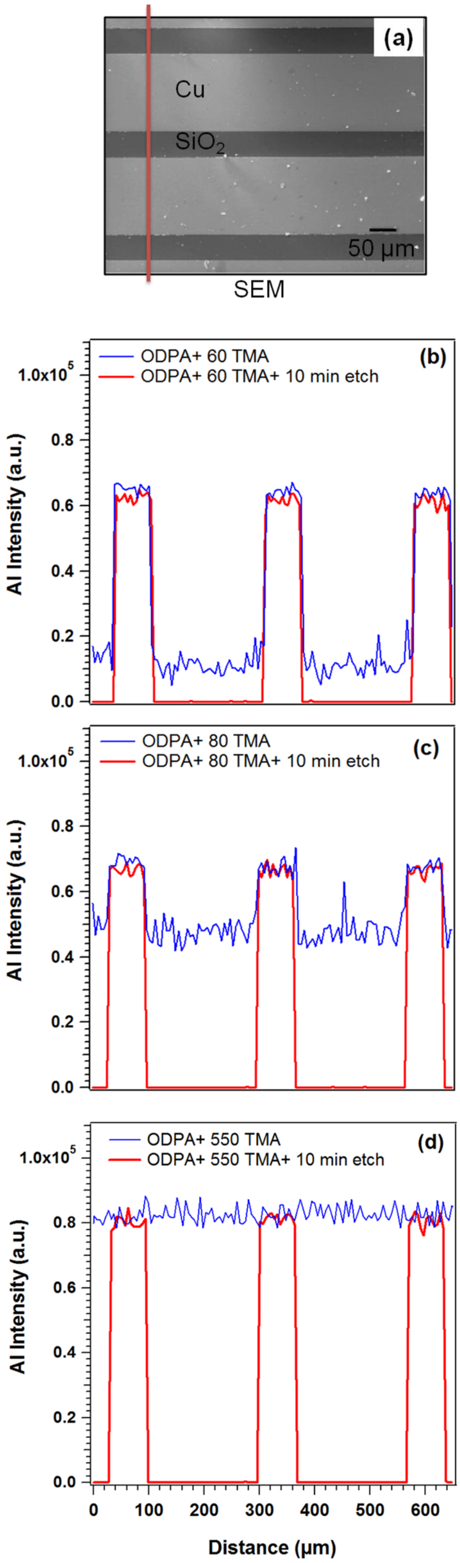

Figure 4. (a) SEM image of the pattern subjected to 48 h of ODPA exposure followed by Al_2O_3 ALD and acetic acid sonication. The red line designates the direction of the Auger line scan. Auger Al line scan on the samples after 60 (b), 80 (c), and 550 (d) cycles of Al_2O_3 ALD before (blue) and after (red) acetic acid sonication.

We propose the following model to explain the improvement in selectivity after the etch process. The phosphonic acid monolayer deposits upon a copper oxide layer present at the copper surface. Acetic acid can etch off the copper oxide layer.[26] As the samples are sonicated in acetic acid, the etching agent attacks the Cu oxide layer, removing not just part of the Cu oxide but also the ODPA SAM and the dielectric materials deposited on top of or within it. On the other hand, acetic acid does not react strongly with silicon, leaving intact any ALD film deposited on the silicon regions of the substrate. To address the question of whether the ODPA SAM is necessary for this process to work, we performed experiments in which the same ALD process was carried out on patterns without initial SAM passivation and then subjected to the same etching process. The results show that no selectivity is observed either before or after the etch process when ODPA is not used (see Supporting Information). This result indicates that the ODPA passivation layer is necessary for this combined selective deposition-selective etch process. We propose that the presence of the ODPA layer helps restrict the Al_2O_3 deposition to that of a thinner, less uniform film which is permeable to acetic acid, allowing the acid to attack the underlying copper oxide.

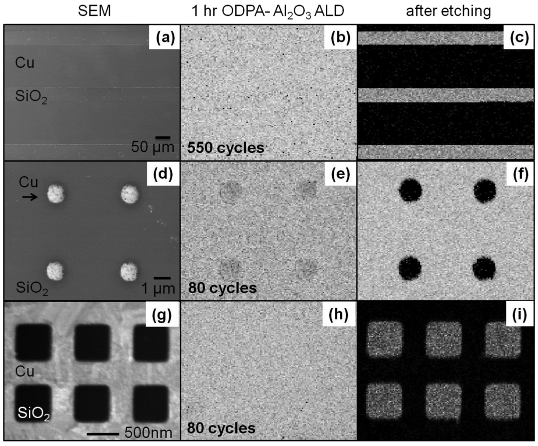

Figure 5. (a, d, g) SEM image of the patterned Cu/SiO_2 substrate. (b, e, h) Al Auger map of the patterned Cu/SiO_2 substrate treated with ODPA for 1 h and (b) 250, (e) and (h) 80 cycles of Al_2O_3 ALD. (c, f, i) Al Auger map after sonication of the substrates in acetic acid for 10 min.

To further explore what quality of ODPA SAM is necessary for the selectivity to be achieved after the selective etch, we investigated the process with ODPA SAMs formed for a shorter exposure time. Patterns were dipped in ODPA solution for 1 h instead of 48 h. The Cu substrate shows a relatively high water contact angle (105°) after 1 h of treatment with the ODPA solution. Figure 5a shows the SEM image and Al Auger map of the Cu/SiO_2 pattern after 1 h of ODPA deposition and 550 cycles of Al_2O_3 ALD before and after the sample was sonicated in acetic acid. It is clear from the results that although the selectivity is poor directly after ALD, it is recovered as a result of using the etchant. The compositional analysis on the samples passivated with ODPA for 48 h (Figure 4l) and for 1 h (Figure 5c) show the same amount of Al (<0.1%) remaining on the Cu regions of the substrate after etching, indicating that the same degree of selectivity can be achieved using both deposition times. This study shows that a high quality ODPA SAMs is not required for the selective etching process. We have also performed ALD of 10 nm of Al_2O_3 followed by the same etching process on finer Cu/SiO_2 patterns, again passivated with ODPA for only 1 h (Figure 5d,g). These results, carried out on patterns with 500 nm Si and 1 μm Cu feature sizes, confirm that the selective deposition can be performed at a variety of length scales while eliminating the need for the time-consuming process of dense SAM formation.

The effectiveness of this new selective patterning method is summarized in Figure 6. Auger composition analyses after the acetic acid treatment on 48 h ODPA passivated samples confirm that for all the different thicknesses of Al_2O_3, we are able to completely remove the dielectric layer from Cu (Figure 6a) because the Al detected on the Cu regions of all the samples is below the detection limit (0.1%). Meanwhile, ellipsometry results on Si show no change in the thickness of

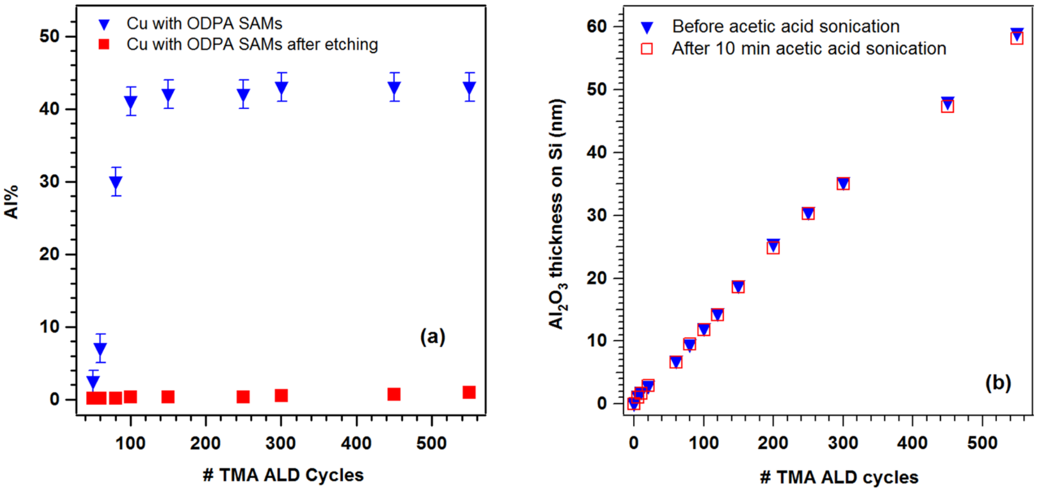

Figure 6. (a) Auger elemental analysis on Cu substrate before and after acetic acid etching. (b) Ellipsometry results on Si wafers before and after etching.

Al_2O_3 before and after etching (Figure 6b), indicating that the film in these regions remains intact as desired, agreeing with the previous reports of robustness of aluminum oxide thin films against etching processes.[37,38] To determine if the properties of the Al_2O_3 film are affected by the acetic acid exposure, we have measured the optical and electronic properties of the ALD Al_2O_3 using spectroscopic ellipsometry and capacitance measurements, respectively. Bulk Al_2O_3 has a refractive index of 1.6−1.7 at 1.96 eV.[39−41] The refractive index (n) measured by ellipsometry on different ALD Al_2O_3 films before any treatment was found to be 1.64 ± 0.02, and the refractive index after acetic acid sonication was 1.63 ± 0.02 (see Supporting Information). On the basis of the measured refractive indices, the dielectric constant (ε_1) of ALD Al_2O_3 samples after acetic acid treatment remains unchanged. To further investigate the electronic properties of the Al_2O_3 films before and after acetic acid treatment, we fabricated MOS capacitors using a 47.3 ± 0.8 nm thick Al_2O_3 layer deposited on a Si substrate. One capacitor was fabricated using the as-deposited Al_2O_3 layer, while a second capacitor was fabricated after the substrate was sonicated in acetic acid for 10 min and rinsed with water. The average capacitance was 68.1 ± 2 pF on the as-deposited Al_2O_3 film and 71.8 ± 5 pF on the acetic acid-treated film. The small difference in the capacitance of the samples may be due to the slight difference in the thickness of the films. Nonetheless, these results further confirm the stability of the Al_2O_3 film under acetic acid treatment.

CONCLUSIONS

We demonstrate a method for enhancing selective deposition of dielectric films to reach thickness limits that conventional area selective ALD is not capable of achieving. We propose and test a combined selective deposition-selective etch approach, and show that it improves the film thickness for which selective deposition can be performed by at least 10 times. The process is inherently self-correcting, because undesired deposition can be cleanly removed in the second step, allowing for high quality patterning. Moreover, the required formation time of the SAM resist can be significantly reduced from 48 h to at most 1 h, making the process much more efficient. Performing the etching process also removes the SAMs from the metal surface, allowing for subsequent processing steps to be performed without the interference of an organic SAM layer. This process has the potential to be extended to a variety of systems, including selective deposition of multiple dielectric layers on an initial pattern and also other dielectric and metal films that are currently used in microelectronics applications. The method of selective deposition and etch has the potential to facilitate bottom-up fabrication of nanoscale patterns for many applications.

MATERIALS AND METHODS

Experiments were performed on Cu/Si patterned wafers provided by collaborators. Patterned Cu-on-Si substrates were prepared *via* conventional lithography, with the Cu approximately 50 nm thick and the Si covered by SiO_2. Copper features on the patterns vary in size from 1 to 100 μm. Silicon wafers with a native oxide layer of *ca.* 1.5 nm were used for ellipsometry measurements and also as the reference substrates for ALD. Blanket Cu films sputter-deposited on silicon wafers using an argon-based plasma, with thickness of a few hundred nanometers, were used for water contact angle measurements. All the copper surfaces contain a thin layer of native oxide. The surface roughness of these Cu substrates measured by AFM was 0.8 nm. Prior to SAM deposition, the patterned substrates were sonicated in ethanol and acetone for 10 min to remove organic contaminants, dried with nitrogen, and then subjected to 15 min of UV/ozone for the final cleaning. After cleaning, samples were immediately immersed into a 1 mM solution of ODPA (Sigma-Aldrich) in *tert*-butanol (Fisher Scientific) for 1− 48 h. Since the melting point of *tert*-butanol is *ca.* 26 °C, the SAM growth was done at a controlled temperature of *ca.* 30 °C to prevent the solution from solidifying. After SAM formation was completed, samples were rinsed thoroughly with pure methanol (Fisher Scientific) and dried under flow of nitrogen. Substrates that were not immediately transferred to the reactor for ALD were typically kept inside a sealed container and stored inside a dry, air-purged glovebox.

ODPA-coated substrates were transferred into the reactor for the ALD processes. Al_2O_3 ALD was performed in a GemStar 6 reactor (Arradiance Inc.) using trimethylaluminum (TMA) and water as precursors. Al_2O_3 was grown at 150 °C with reactant exposure times of 30 ms for both precursors, and nitrogen purge times of 10 s between exposures. After film deposition, samples were removed from the reactor for *ex situ* characterization and analysis. The etching process was performed using glacial acetic acid (Fisher Scientific). During etching, samples were sonicated in acetic acid for 10− 15 min and rinsed with water afterward.

Film thickness on the Si substrates was measured using an Alpha-SE ellipsometer by J. A. Woollam Co. with a spectral range of 380−900 nm at three different angles of incidence (65°, 70° and 75°) and with the polarizer set to 45°. A standard Cauchy model has been used to describe the aluminum oxide layer. Auger electron mapping and line scans on patterned substrates were performed on a PHI 700 Scanning Auger Nanoprobe. Water contact angle (WCA) measurements were performed with an FTA 200 instrument. Five microliters of deionized water (Millipore) was brought into contact with the samples to analyze the wettability of the films on the surfaces. Due to the proximity of Cu (3p and 3s) and Al (2p and 2s) binding energies in XPS, elemental composition of the Cu/Si patterns was also determined through Auger electron spectroscopy. A PHI Versa Probe Scanning XPS Microprobe with Al Kα radiation of 1486 eV was used for other compositional analyses. The X-ray beam diameter was 200 μm with 42 W power. Atomic force microscopy (AFM) was performed on a Park System XE-70 in a noncontact mode with a scan size of 5×5 μm. Capacitors were fabricated using the Al_2O_3 layer deposited by ALD on single sided Si substrates. A Au contact layer with a thickness of 60 nm was deposited on the Al_2O_3 film by thermal evaporation using a 3×3 cm shadow mask with an array of circular holes 300 μm in diameter. The capacitance measurements were performed using an Agilent E4980A Precision LCR Meter at a frequency of 735 Hz on more than five points on each sample.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Figure S1, XPS results on Cu and Si substrates treated with acetic acid; Figure S2, SEM and Al Auger map on Cu/Si patterns with no ODPA SAMs after 50 cycles of Al_2O_3 ALD and after being sonicated in acetic acid; Table S1, ellipsometry results on substrates before and after acetic acid cleaning; Figure S3, refractive index and extinction coefficient on samples before and after acetic acid cleaning. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b03125.

Acknowledgment. This publication was based on work supported by the Semiconductor Research Corporation (SRC) and Intel Corporation. F.S.M.H acknowledges funding from the Kodak Graduate Fellowship.

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