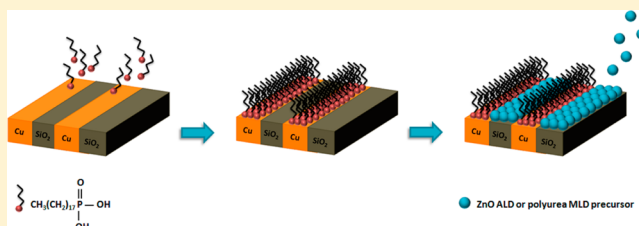


A New Resist for Area Selective Atomic and Molecular Layer Deposition on Metal–Dielectric Patterns

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Supporting Information

ABSTRACT: Both area selective atomic layer deposition (ALD) and area selective molecular layer deposition (MLD) are demonstrated on Cu/SiO₂ patterns using octadecylphosphonic acid (ODPA) self-assembled monolayers as a resist layer. X-ray photoelectron spectroscopy and Auger electron spectroscopy confirm that during a metal oxide ALD process, no growth occurs on ODPAs-protected Cu, whereas the metal oxide grows on SiO₂ regions of the substrate, for up to 36 nm of metal oxide. The results also show that ODPAs blocks the Cu surface from MLD, preventing polyurea deposition for up to 6 nm of film thickness.



1. INTRODUCTION

Electronic devices consisting of metal/dielectric patterns are widely used in integrated circuits, impacting structures ranging from nonplanar, double gate field effect transistors (FinFETs) to interconnects. As the size of microelectronic devices continues downward scaling, difficult new materials challenges are introduced, and new materials processing methods are being explored to meet these challenges. Importantly, selective deposition of robust films in transistor fabrication may play an important role in significantly reducing process complexities associated with 3-D nanoelectronic and sensing devices whose critical dimensions are on the 10 nm length scale.

Area selective deposition requires a technique that can provide deposition of different materials at a variety of thicknesses, including the ability to maintain the selectivity up to higher thickness limits. Selective deposition of metal or dielectric materials on different dielectric films has been previously studied.^{1–4} However, due to the different properties of metal and dielectric surfaces and difficulties in applying the conventional methods, there have been only few reports^{5–8} on selective deposition of dielectric materials on metal/dielectric patterns. In addition, the selectivity achieved in previous work has mainly been reported up to a couple of nanometers.^{1–4,7,8} There are not many studies that show selective deposition for thicker films of up to 10 nm and or more.⁵

Two promising film growth techniques for selective deposition are atomic layer deposition (ALD) and its analogue, molecular layer deposition (MLD). With ALD (or MLD), the thickness, conformality, and uniformity of the deposited film can be well controlled over large areas. In addition, both techniques are outstanding choices for selective deposition because they are based on self-limiting reactions between gas phase precursors and specific functional groups at the growth surface.^{9–15} As a result, both processes are very sensitive to the

conditions of the substrate surfaces, and consequently, the surface functional groups can be manipulated prior to deposition to carry out an area-selective process.

In some area selective ALD processes, unreactive and thermally stable polymer films have been used as a mask layer in the regions where ALD was not desired.^{16–20} However, more commonly, the surface of the substrate is chemically modified with self-assembled monolayers (SAMs). SAMs are monolayer organic films that form spontaneously on solid surfaces.²¹ SAMs have been well studied and used to modify the physical, chemical, and electrical properties of semiconducting, insulating, and metallic surfaces. A variety of applications have been investigated for SAMs including chemical sensing and protection of metals against corrosion.^{21–23} Alkanethiols and organophosphonic acids have been reported to form well-packed SAMs on metal surfaces and to block them from corrosion and other contamination. Octadecylphosphonic acid (ODPA) has been shown to protect different metals, including Cu and Al,^{24–26} and reports have shown that ODPAs is capable of forming a well-packed layer on surfaces of copper in a variety of states, i.e., CuO, Cu₂O, and Cu.^{25,27} On the other hand, numerous studies have shown that ODPAs does not chemically attach on an SiO₂ surface at room temperature.^{28–31} This poor grafting may arise from the high activation barrier between the head group of phosphonic acid and the SiO₂ surface.³¹ This makes the P–O–Si bond less favorable at the temperature at which the SAM deposition is performed (~30 °C). It has been shown that in order to bond the phosphonic acid to SiO₂, elevated surface temperatures (near 140 °C) are required.³² In addition, due to the hydrogen bonding of the OH groups on

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the fully hydroxylated SiO₂ surface, the phosphonic acid molecule must deform to connect the P and O atoms at the transition state, making the attachment less favorable.³¹ Recognizing this intrinsically selective adsorption of ODPA SAMs on Cu over SiO₂ suggests that we can use ODPA on patterned metal–dielectric substrates to prevent deposition by either ALD or MLD on the metal surface, while letting the ALD or MLD film grow naturally on the dielectric regions.

In this report, we illustrate a method to effectively grow ODPA SAMs on the surface of Cu and describe measurements to accurately determine the quality of these SAMs on the Cu surface. We demonstrate, for the first time, the use of ODPA as a resist layer for area selective deposition in both ALD and MLD. ZnO was chosen as model metal oxide material for selective ALD due primarily to its facile ALD process and tremendous potential in various fields such as optics, electronics, and energy harvesting.³³ To test the ability of ODPA to block MLD, we chose polyurea because of its potential application in lithography^{34,35} and our recent success in area selective MLD of this film on an SiO₂ surface using another type of SAM.³⁶ The results from X-ray photoelectron spectroscopy (XPS), water contact angle measurement, and Auger electron spectroscopy all confirm that both ALD and MLD films selectively deposit on dielectric regions of the test structures but are blocked at the ODPA-protected Cu regions. The selectivity of both processes was also compared, and it was found that, despite more reactive precursors used for ZnO ALD deposition, a higher selectivity could be achieved from ZnO ALD than from polyurea MLD.

2. EXPERIMENTAL METHODS

Unless otherwise noted, all chemicals were purchased from Sigma-Aldrich and used as received.

Blanket and patterned Cu substrates were obtained from collaborators. Cu films were sputter deposited on silicon wafers using an argon-based plasma and are a few hundred nanometers thick. High-temperature post-sputter annealing of the Cu substrates was performed to enable recrystallization and improve film quality. The surface roughness of Cu wafers measured with atomic force microscopy was less than 1 nm (rms roughness = 0.8 nm). Silicon wafers with a native oxide layer of ca. 18 Å were used for the SiO₂ substrates. Prior to SAM deposition, Cu and SiO₂ substrates were sonicated in ethanol and acetone for 10 min to remove organic contamination, dried with nitrogen, and then subjected to 15 min of UV/ozone for the final cleaning. After the cleaning and ozone treatment, the Cu substrates remain covered with a copper oxide layer. (For detailed compositional analysis of the Cu surface, see Supporting Information.)

After cleaning, samples were immediately immersed into a 1 mM solution of ODPA in *tert*-butanol for 48 h, unless otherwise specified. 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 and dried with compressed air. The roughness of the Cu wafers after ODPA deposition measured with atomic force microscopy was 1.1 nm (rms: 1.1 nm). If they were not immediately transferred to the reactor for ALD or MLD, samples were typically kept inside a sealed container and stored inside a dry air-purged glovebox. The water contact angle of the SAM-coated substrates after days of storage in the dry container was similar to that of freshly prepared SAMs, suggesting rather

stable ODPA SAMs on the surface of Cu. Patterned Cu-on-SiO₂ substrates were prepared via conventional lithography. The thickness of Cu wires on this pattern was about 20 μm. The cleaning procedures and SAM formation on the patterned substrates were similar to those of Cu blanket materials.

After SAM formation was complete, substrates were transferred into the reactor for either ALD or MLD processes. ZnO ALD was performed in a GemStar 6 reactor (Arradance Inc.) by using diethylzinc (DEZ) and water as precursors. ZnO was grown at 150 °C using reactant exposure times of 30 ms for both precursors and nitrogen purge times of 10 s between exposures. Polyurea MLD films were grown following the published procedures.^{36,37} Following MLD, samples were quickly rinsed with acetone to remove extra particles of polyurea that may have agglomerated on the surface and blown dry with dry air. The thickness of the MLD film was roughly estimated by measuring the thickness of the film grown on SiO₂ control samples placed concurrently in the chamber during MLD. The measured growth rate of the MLD film on SiO₂ was 0.55 nm/cycle, similar to the previously reported value.^{36,37} After film deposition, samples were removed from the reactor for ex-situ characterization and analysis.

Static water contact angle (WCA) measurements were performed with an FTA 200 instrument. 1 μL of deionized water (Millipore) was brought into contact with the samples to analyze the wettability of the films on the surfaces. Each measurement was done in three replications per sample, and the average value is used to represent the hydrophobicity of the film. All electrochemical measurements were made on a Biologic VMP3 potentiostat equipped with a 1 MHz frequency analyzer. A three-electrode setup was used by employing Cu that had ODPA absorbed on it as a working electrode, platinum wire as a counter electrode, and Ag/AgCl in saturated KCl(aq) as a reference. Experiments were performed with a solution containing 0.1 M LiClO₄ in dry methanol. For electrochemical impedance spectroscopy (EIS) measurements, experiments were performed without applying bias on the working electrode.

Film thickness was measured on 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°. Thicknesses were measured on the silicon wafers on at least three spots to ensure the uniformity of the film. Elemental composition of the film was determined through XPS spectroscopy using a PHI VersaProbe scanning XPS microprobe with Al Kα radiation of 1486 eV. 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 100 × 100 μm. Auger electron mapping on patterned substrates was performed on a PHI 700 scanning Auger nanoprobe.

3. RESULTS AND DISCUSSION

The ability of ODPA to block deposition by ALD and MLD was first evaluated on blanket Cu and SiO₂ substrates. Following the formation of the ODPA SAM, water contact angle goniometry and EIS were utilized to probe its quality. It was found that the water contact angle on Cu increased with SAM formation time until it reached a value of 110° at dipping times longer than 12 h (Figure 1b). This value of water contact angle is also in good agreement with other types of SAMs that have the same alkane tail group.^{4,36,38} It also suggests that well-packed SAMs were formed at a dipping time of 12 h. In

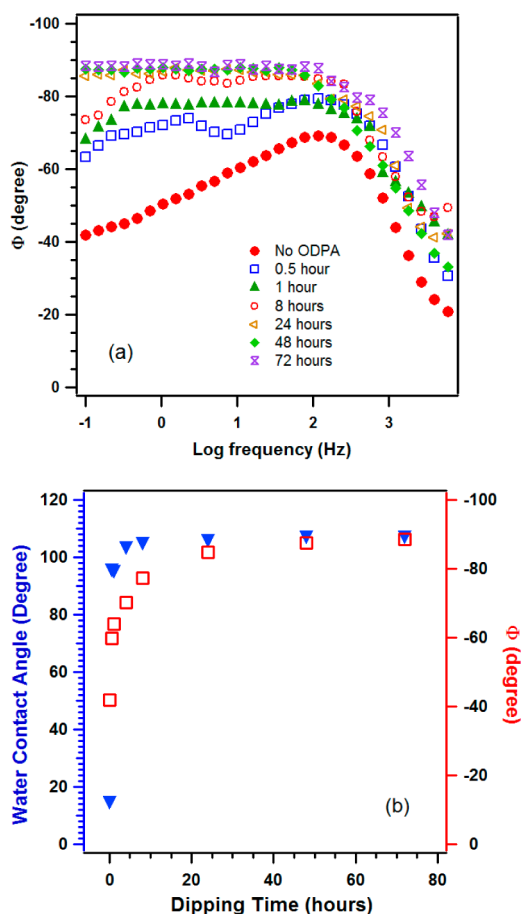


Figure 1. (a) Bode phase plot of Cu substrates with different ODPA deposition times. (b) Water contact angle and the Bode phase angle (at 0.1 Hz frequency) as a function of dipping time of Cu substrates in ODPA solution.

contrast, the water contact angle of ODPA on the SiO_2 surface remains similar to that of clean SiO_2 (WCA: $30^\circ \pm 2$), indicating that there is no attachment of ODPA onto the SiO_2 surface (see Supporting Information).

Water contact angle goniometry has been commonly used to gauge the hydrophobicity of SAMs due to the facility of this measurement. However, previous results from our group suggested that this method yields only a rough approximation of the quality of the SAMs, especially toward ALD.³⁹ For example, some alternative cleaning treatments that we tested on the wafers resulted in very high WCA after ODPA deposition but were found to not provide good blocking against dielectric deposition. Treatments that roughen the film may be expected to result in a more hydrophobic surface. But since the molecules of the SAM are not well packed on a rough surface compared to a smooth surface, such a SAM does not provide good blocking against the ALD precursors. EIS, on the other hand, has been demonstrated in several reports as an alternative measurement to effectively probe the quality of SAMs on electrodes.^{40–43} When SAMs are created on an electrode, they increase its capacitance. In addition, if a densely packed SAM is formed on the surface of the electrode, this thin layer will prevent any ions in solution from reaching the surface. As a result, when measuring the impedance of densely packed SAMs, the phase angle ϕ will become close to 90° . We can therefore measure the quality of the SAM by measuring this value. Figure 1a shows a typical Bode phase plot of an ODPA

SAM-covered Cu electrode at various ODPA dipping times. It is evident that the Bode phase plot of ϕ measured at 0.1 Hz (-1 on the log axis), which correlates to a time scale in which ions in the electrolyte react with the metal surface,^{40,42} increases as the dipping time increases.

Figure 1b shows a comparison between the water contact angle and the phase angle ϕ from the Bode plot as a function of ODPA dipping time. The results from water contact angle measurement suggest that well-packed SAMs are formed in as few as 12 h. We find, however, that the SAMs formed for this period of time are not able to fully prevent deposition (data not shown here). On the other hand, the results from EIS measurement indicate that densely packed SAMs do not form until a deposition time of close to 48 h, similar to results we observed previously with other types of SAMs.^{2–4,39} We also show (vide infra) that at this dipping time ODPA SAMs are capable of preventing ALD and MLD deposition. We therefore use this dipping time of 48 h throughout our experiments.

After SAM formation was completed, substrates were transferred to the reactor for ALD or MLD deposition. ZnO ALD was performed for 5–300 cycles, corresponding to growth of ZnO films from 0.9 to 54 nm thick. Figure 2a shows the Zn/(Zn + Cu) atomic ratio at the Cu substrate measured by XPS

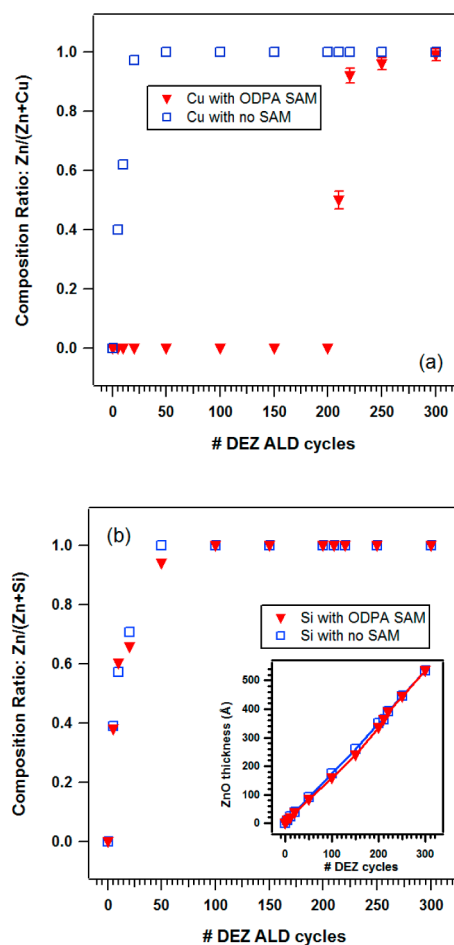


Figure 2. (a) XPS results showing the Zn/(Zn + Cu) atomic ratio at the Cu wafers after different numbers of DEZ ALD cycles. (b) XPS results showing the Zn/(Zn + Si) atomic ratio at the silicon wafers after different numbers of DEZ ALD cycles. Inset: ellipsometry results comparing ZnO thickness on SiO_2 wafers with ODPA SAM and without ODPA SAM after different numbers of DEZ ALD cycles.

after ALD as a function of cycle number. The figure compares a Cu substrate treated with the ODPA SAM with an untreated, bare Cu substrate. The data confirm the growth of Zn on the bare Cu wafer, as indicated by the increase in the Zn/(Zn + Cu) ratio with the number of ALD cycles from 5 to 300. The apparent saturation on the bare surface occurs because after 50 cycles of ALD, which corresponds to 9 nm ZnO growth, Cu can no longer be detected at the surface, and only Zn signal is measured. In contrast, no Zn is detected on the ODPA-treated Cu samples, and the Zn/(Zn + Cu) ratio remains zero for up to 200 cycles of DEZ (ZnO film of 36 nm thick). For higher numbers of DEZ ALD cycles, ZnO starts to grow on ODPA-protected Cu substrate, and the Zn/(Zn + Cu) ratio increases gradually until it saturates after 300 cycles of DEZ. XPS results on these samples also show a large C signal arising from the long alkane chain of the ODPA molecules. A small intensity of Cu signal is also observed after as many as 200 ALD cycles, confirming that no metal oxide deposition is taking place on the substrates, and the Cu signal can be still detected from under the 25 Å long ODPA molecules (see Supporting Information).

Because it is of interest to study selective deposition on patterned Cu/SiO₂ surfaces, the behavior of ODPA and its effect on ALD or MLD at the SiO₂ surface must also be investigated. Figure 2b shows the XPS results on SiO₂ substrates, comparing the Zn/(Zn + Si) ratio on ODPA-treated SiO₂ and on untreated SiO₂. The results show an increase followed by saturation of the Zn/(Zn + Si) signal on both of the samples, with no difference observed between the two types of samples, proving that ODPA is not blocking growth on the SiO₂ substrate. In addition, ellipsometry results shown in the inset of Figure 1b confirm the constant growth of ZnO on the SiO₂ substrate. Metal oxide growth on the ODPA-treated SiO₂ substrate is comparable to that on the untreated SiO₂ samples. The data in Figure 2 therefore confirm the blocking by ODPA of metal oxide (ZnO) growth on metal (Cu) samples while retaining the growth on dielectric (SiO₂) samples for up to 36 nm in thickness of the metal oxide.

To test the robustness of the ODPA blocking layer on Cu, we also performed experiments to assess its ability to prevent polyurea MLD. Figure 3 shows results of water contact angle measurements of MLD films grown on ODPA-treated and untreated, bare Cu substrates. On the bare Cu surface, the water contact angle increases from 24° with no MLD cycles (an

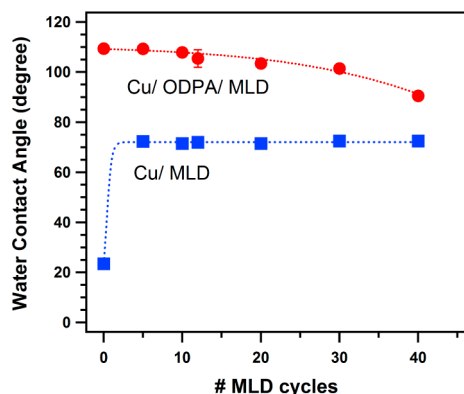


Figure 3. Plot of water contact angle of the organic film as a function of MLD cycles on untreated Cu (square) and ODPA SAM-coated Cu (circle). A representation of the uncertainty of the measurement is also shown at 12 cycles of MLD.

expected value for the hydrophilic copper surface) to 73° after 5 MLD cycles, staying at this value for up to 40 MLD cycles. These results indicate good growth of MLD on the bare Cu surface. On the Cu samples containing ODPA SAMs, before any MLD deposition (zero cycles), the water contact angle is close to 110°. When exposed to low numbers of MLD cycles (less than 12 cycles), this value remains nearly constant. However, at 12 cycles, equivalent to ca. 60 Å of MLD on the SiO₂ control, a slight drop of the water contact is observed. Because the MLD film has a lower contact angle than does the ODPA SAM, this result suggests that some polyurea MLD was deposited on this surface. In addition, we also observed a small nitrogen peak in XPS scans of the sample after 12 cycles (see Supporting Information). This may indicate that an upper limit of the blocking ability of polyurea MLD by ODPA SAMs was reached. At higher MLD cycles (more than 30 cycles), the decrease in the water contact angle becomes more prominent. XPS analysis also shows a significant peak of nitrogen at this number of cycles.

Once the blocking ability of ODPA SAMs was established on the blanket materials, we performed ODPA SAM formation on patterned samples consisting of 50 μm wide Cu strips on a silicon wafer (Figure 4, left). The patterned substrates were

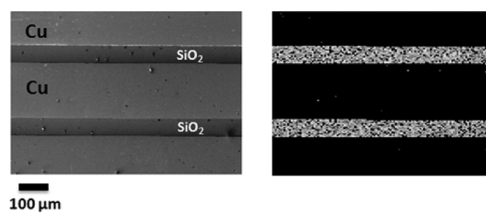


Figure 4. (left) SEM image of Cu/SiO₂ patterned sample. (right) AES elemental mapping of Zn on the patterned sample after 19 nm ZnO growth.

cleaned then immersed in the ODPA solution for 48 h. After rinsing the substrate with methanol, 100 cycles of ZnO (ca. 19 nm) were deposited. Auger electron spectroscopy (AES) was performed to give a map of Zn content at the surface (Figure 4, right). It can clearly be seen from Figure 4 that ZnO deposits only on the SiO₂ regions of the sample without any deposition on the Cu strips, confirming excellent area selective ALD enabled by the ODPA SAMs.

Substrates from the same batch of ODPA SAM-modified patterned samples were also tested for area selective MLD using polyurea deposition. After 12 cycles of MLD (ca. 60 Å thick), patterned substrates were probed for selectivity by N Auger electron mapping. The result is shown in Figure 5.

Figure 5 reveals that while polyurea MLD is mostly deposited on the dielectric part of the pattern, scattered N

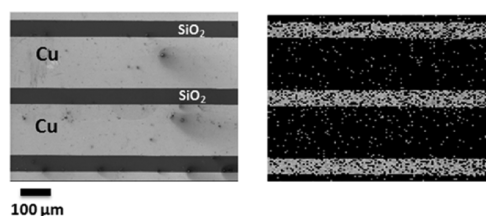


Figure 5. (left) SEM image of Cu/SiO₂ patterned sample. (right) AES elemental mapping of N on the patterned sample after 6 nm MLD growth.

signal can still be observed on the Cu strips. The results were replicated with two additional data sets, and similar outcomes were obtained, suggesting that only moderate selectivity in polyurea MLD could be achieved by these SAMs. In addition, AES line scans also show a poor spatial resolution of the nitrogen signal from polyurea MLD compared to the Zn signal from ZnO ALD (see Supporting Information). Moreover, according to the blanket studies in Figures 2 and 3, the selectively deposited MLD film has a lower thickness (6 nm) compared to the ALD film (36 nm). If we use the maximum thickness of the deposited film blocked by ODPAs as a measure of selectivity, the results suggest that, despite the more reactive precursors used for ZnO ALD than for polyurea MLD, the selectivity achieved from the ALD process is roughly 6 times higher. The lower selectivity observed in polyurea MLD could arise from the slightly stronger interaction between the end group in the SAM (methyl-terminated) and the organic precursors used for MLD deposition. This may lead to partial deposition of MLD on (or within) the SAM layer. Investigations are currently being performed to better understand this partial deposition of MLD on SAM-terminated substrates.

4. CONCLUSIONS

We have demonstrated the use of ODPAs SAMs as a resist layer for selective deposition on metal–dielectric patterns by testing on Cu and SiO₂. We found that ODPAs selectively adsorb on the metal surface, determined by WCA measurement. The quality of ODPAs SAMs on the metal surface could be sensitively assessed by EIS. Fully packed ODPAs SAMs were subsequently used as a resist layer for selective deposition of ZnO ALD and polyurea MLD. XPS and ellipsometry results confirm growth of ZnO on SiO₂ while no ZnO is deposited on ODPAs-protected Cu substrates, for up to 36 nm of deposited ZnO. WCA and Auger electron spectroscopy are applied to show the blocking limit of ODPAs against polyurea MLD growth. The selectivity of ALD and MLD processes was also compared, and a significantly higher selectivity was achieved for the ZnO ALD process. We believe that the method we presented here illustrates the tremendous potential of ODPAs SAMs as a resist layer for selective layer-by-layer deposition on metal and dielectric surfaces.

■ ASSOCIATED CONTENT

Supporting Information

High-resolution XPS results from cleaned Cu substrate; plot of water contact angle on Cu and SiO₂ substrates as a function of ODPAs dipping time; survey XPS results from ODPAs-treated Cu substrate after 200 cycles of ZnO ALD; high-resolution XPS results from ODPAs-on-Cu substrate after 20 cycles of polyurea MLD; Auger electron spectroscopy nitrogen and zinc line scans on patterned Cu/SiO₂ substrate treated with ODPAs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Jiang, X.; Bent, S. F. Area-Selective ALD with Soft Lithographic Methods: Using Self-Assembled Monolayers to Direct Film Deposition. *J. Phys. Chem. C* **2009**, *113*, 17613–17625.
- (2) Chen, R.; Kim, H.; McIntyre, P. C.; Porter, D. W.; Bent, S. F. Achieving Area-Selective Atomic Layer Deposition on Patterned Substrates by Selective Surface Modification. *Appl. Phys. Lett.* **2005**, *86*, 191910–191913.
- (3) Chen, R.; Kim, H.; McIntyre, P. C.; Bent, S. F. Self-Assembled Monolayer Resist for Atomic Layer Deposition of HfO₂ and ZrO₂ High-κ Gate Dielectrics. *Appl. Phys. Lett.* **2004**, *84*, 4017–4019.
- (4) Chen, R.; Bent, S. F. Chemistry for Positive Pattern Transfer Using Area-Selective Atomic Layer Deposition. *Adv. Mater.* **2006**, *18*, 1086–1090.
- (5) Gordon, R. G.; Hong, D. Selective Sealing of Porous Dielectric Materials, US Patent No. 2008/0032064, 2008.
- (6) Elina, F.; Marko, V.; Mikko, R.; Markku, L. Passivation of Copper Surfaces for Selective-Area ALD Using a Thiol Self-Assembled Monolayer. *Semicond. Sci. Technol.* **2012**, *27*, 074004–074009.
- (7) Tao, Q.; Jursich, G.; Takoudis, C. Selective Atomic Layer Deposition of HfO₂ on Copper Patterned Silicon Substrates. *Appl. Phys. Lett.* **2010**, *96*, 192105.
- (8) Tao, Q.; Overhage, K.; Jursich, G.; Takoudis, C. On the Initial Growth of Atomic Layer Deposited TiO₂ Films on Silicon and Copper Surfaces. *Thin Solid Films* **2012**, *520*, 6752–6756.
- (9) George, S. M.; Yoon, B.; Dameron, A. A. Surface Chemistry for Molecular Layer Deposition of Organic and Hybrid Organic–Inorganic Polymers. *Acc. Chem. Res.* **2009**, *42*, 498–508.
- (10) Sankur, H. O.; Gunning, W. Deposition of Optical Thin Films by Pulsed Laser Assisted Evaporation. *Appl. Opt.* **1989**, *28*, 2806–2808.
- (11) Ritala, M.; Leskelä, M. *Handbook of Thin Films*; Nalwa, H. S., Ed.; Academic Press: Burlington, 2002; Chapter 2, pp 103–159.
- (12) Ritala, M.; Kukli, K.; Rahtu, A.; Räsänen, P. I.; Leskelä, M.; Sajavaara, T.; Keinonen, J. Atomic Layer Deposition of Oxide Thin Films with Metal Alkoxides as Oxygen Sources. *Science* **2000**, *288*, 319–321.
- (13) Mikko, R.; Markku, L. Atomic Layer Epitaxy - A Valuable Tool for Nanotechnology? *Nanotechnology* **1999**, *10*, 19–24.
- (14) Wen-Jie, Q.; Nieh, R.; Byoung Hun, L.; Onishi, K.; Laegu, K.; Yongjoo, J.; Lee, J. C.; Kaushik, V.; Bich-Yen, N.; Prabhu, L.; Eisenbeiser, K.; Finder, J. In *Performance of MOSFETs with Ultra Thin ZrO₂ and Zr Silicate Gate Dielectrics*; VLSI Technology, 2000. Digest of Technical Papers. 2000 Symposium on 13–15 June 2000; 2000; pp 40–41.
- (15) Zhou, H.; Bent, S. F. Fabrication of Organic Interfacial Layers by Molecular Layer Deposition: Present Status and Future Opportunities. *J. Vac. Sci. Technol., A* **2013**, *31*, 040801–18.
- (16) Sinha, A.; Hess, D. W.; Henderson, C. L. Area Selective Atomic Layer Deposition of Titanium Dioxide: Effect of Precursor Chemistry. *J. Vac. Sci. Technol., B* **2006**, *24*, 2523–2532.
- (17) Sinha, A.; Hess, D. W.; Henderson, C. L. Transport Behavior of Atomic Layer Deposition Precursors through Polymer Masking Layers: Influence on Area Selective Atomic Layer Deposition. *J. Vac. Sci. Technol., B* **2007**, *25*, 1721–1728.
- (18) Färm, E.; Kemell, M.; Ritala, M.; Leskelä, M. Selective-Area Atomic Layer Deposition Using Poly(methyl methacrylate) Films as Mask Layers. *J. Phys. Chem. C* **2008**, *112*, 15791–15795.
- (19) Färm, E.; Kemell, M.; Santala, E.; Ritala, M.; Leskelä, M. Selective-Area Atomic Layer Deposition Using Poly(vinyl pyrrolidone) as a Passivation Layer. *J. Electrochem. Soc.* **2010**, *157*, K10–K14.

- (20) Gay, G.; Baron, T.; Agraffail, C.; Salhi, B.; Chevolleau, T.; Cunge, G.; Grampeix, H.; Tortai, J. H.; Martin, F.; Jalaguiet, E.; Salvo, B. D. CMOS Compatible Strategy Based on Selective Atomic Layer Deposition of a Hard Mask for Transferring Block Copolymer Lithography Patterns. *Nanotechnology* **2010**, *21*, 435301.
- (21) Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* **1996**, *96*, 1533–1554.
- (22) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; et al. Molecular Monolayers and Films. A Panel Report for the Materials Sciences Division of the Department of Energy. *Langmuir* **1987**, *3*, 932–950.
- (23) Jennings, G. K.; Laibinis, P. E. Self-Assembled Monolayers of Alkanethiols on Copper Provide Corrosion Resistance in Aqueous Environments. *Colloids Surf., A* **1996**, *116*, 105–114.
- (24) DiBenedetto, S. A.; Facchetti, A.; Ratner, M. A.; Marks, T. J. Molecular Self-Assembled Monolayers and Multilayers for Organic and Unconventional Inorganic Thin-Film Transistor Applications. *Adv. Mater.* **2009**, *21*, 1407–1433.
- (25) Cabritaajavaara, J. F.; Viana, A. S.; Abrantes, L. M. Copper Protection by Phosphonic Acid Self-Assembled Monolayers. *Corros. Prot. Mater.* **2010**, *29*, 114–119.
- (26) Ma, H.; Acton, O.; Hutchins, D. O.; Cernetic, N.; Jen, A. K. Y. Multifunctional Phosphonic Acid Self-Assembled Monolayers on Metal Oxides as Dielectrics, Interface Modification Layers and Semiconductors for Low-Voltage High-Performance Organic Field-Effect Transistors. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14110–14126.
- (27) Fonder, G.; Minet, I.; Volcke, C.; Devillers, S.; Delhalle, J.; Mekhalif, Z. Anchoring of Alkylphosphonic Derivatives Molecules on Copper Oxide Surfaces. *Appl. Surf. Sci.* **2011**, *257*, 6300–6307.
- (28) Nie, H. Y.; McIntyre, N. S.; Lau, W. M. Selective Removal of Octadecylphosphonic Acid (OPA) Molecules from Their Self-Assembled Monolayers (SAMs) Formed on a Si Substrate. *J. Phys.: Conf. Ser.* **2007**, *61*, 869.
- (29) Nie, H. Y.; McIntyre, N. S.; Lau, W. M.; Feng, J. M. Optical Properties of an Octadecylphosphonic Acid Self-Assembled Monolayer on a Silicon Wafer. *Thin Solid Films* **2008**, *517*, 814–818.
- (30) Nie, H. Y.; Walzak, M. J.; McIntyre, N. S. Bilayer and Odd-Numbered Multilayers of Octadecylphosphonic Acid Formed on a Si Substrate Studied by Atomic Force Microscopy. *Langmuir* **2002**, *18*, 2955–2958.
- (31) Thissen, P.; Peixoto, T.; Longo, R. C.; Peng, W.; Schmidt, W. G.; Cho, K.; Chabal, Y. J. Activation of Surface Hydroxyl Groups by Modification of H-Terminated Si(111) Surfaces. *J. Am. Chem. Soc.* **2012**, *134*, 8869–8874.
- (32) Hanson, E. L.; Schwartz, J.; Nickel, B.; Koch, N.; Danisman, M. F. Bonding Self-Assembled, Compact Organophosphonate Monolayers to the Native Oxide Surface of Silicon. *J. Am. Chem. Soc.* **2003**, *125*, 16074–16080.
- (33) Özgür, Ü.; Alivov, Y. I.; Liu, C.; Teke, A.; Reshchikov, M. A.; Doğan, S.; Avrutin, V.; Cho, S.-J.; Morkoç, H. A Comprehensive Review of ZnO Materials and Devices. *J. Appl. Phys.* **2005**, *98*, 041303.
- (34) Zhou, H.; Bent, S. F. Molecular Layer Deposition of Functional Thin Films for Advanced Lithographic Patterning. *ACS Appl. Mater. Interfaces* **2011**, *3*, 505–511.
- (35) Zhou, H.; Blackwell, J. M.; Lee, H.-B.-R.; Bent, S. F. Highly Sensitive, Patternable Organic Films at the Nanoscale Made by Bottom-Up Assembly. *ACS Appl. Mater. Interfaces* **2013**, *5*, 3691–3696.
- (36) Prasittichai, C.; Zhou, H.; Bent, S. F. Area Selective Molecular Layer Deposition of Polyurea Films. *ACS Appl. Mater. Interfaces* **2013**, *5*, 13391–13396.
- (37) Loscutoff, P. W.; Zhou, H.; Clendenning, S. B.; Bent, S. F. Formation of Organic Nanoscale Laminates and Blends by Molecular Layer Deposition. *ACS Nano* **2009**, *4*, 331–341.
- (38) Hong, J.; Porter, D. W.; Sreenivasan, R.; McIntyre, P. C.; Bent, S. F. ALD Resist Formed by Vapor-Deposited Self-Assembled Monolayers. *Langmuir* **2007**, *23*, 1160–1165.
- (39) Chen, R.; Kim, H.; McIntyre, P. C.; Bent, S. F. Investigation of Self-Assembled Monolayer Resists for Hafnium Dioxide Atomic Layer Deposition. *Chem. Mater.* **2005**, *17*, 536–544.
- (40) Boubour, E.; Lennox, R. B. Insulating Properties of Self-Assembled Monolayers Monitored by Impedance Spectroscopy. *Langmuir* **2000**, *16*, 4222–4228.
- (41) Cai, X.; Baldelli, S. Surface Barrier Properties of Self-Assembled Monolayers as Deduced by Sum Frequency Generation Spectroscopy and Electrochemistry. *J. Phys. Chem. C* **2011**, *115*, 19178–19189.
- (42) Janek, R. P.; Fawcett, W. R.; Ulman, A. Impedance Spectroscopy of Self-Assembled Monolayers on Au(111): Evidence for Complex Double-Layer Structure in Aqueous NaClO₄ at the Potential of Zero Charge. *J. Phys. Chem. B* **1997**, *101*, 8550–8558.
- (43) Kaur, I.; Zhao, X.; Bryce, M. R.; Schauer, P. A.; Low, P. J.; Katak, R. Modification of Electrode Surfaces by Self-Assembled Monolayers of Thiol-Terminated Oligo(Phenyleneethynylene)s. *ChemPhysChem* **2013**, *14*, 431–440.