Area-Selective Atomic Layer Deposition for Resistive Random-Access Memory Devices

Il-Kwon Oh, Asir Intisar Khan, Shengjun Qin, Yujin Lee, H.-S. Philip Wong, Eric Pop, and Stacey F. Bent*

ABSTRACT: Resistive random-access memory (RRAM) is a promising technology for data storage and neuromorphic computing; however, cycle-to-cycle and device-to-device variability limits its widespread adoption and high-volume manufacturability. Improving the structural accuracy of RRAM devices during fabrication can reduce these variabilities by minimizing the filamentary randomness within a device. Here, we studied area-selective atomic layer deposition (AS-ALD) of the HfO$_2$ dielectric for the fabrication of RRAM devices with higher reliability and accuracy. Without requiring photolithography, first we demonstrated ALD of HfO$_2$ patterns uniformly and selectively on Pt bottom electrodes for RRAM but not on the underlying SiO$_2$/Si substrate. RRAM devices fabricated using AS-ALD showed significantly narrower operating voltage range (2.6 X improvement) and resistance states than control devices without AS-ALD, improving the overall reliability of RRAM. Irrespective of device size ($1 \times 1$, $2 \times 2$, and $5 \times 5$ $\mu$m$^2$), we observed similar improvement, which is an inherent outcome of the AS-ALD technique. Our demonstration of AS-ALD for improved RRAM devices could further encourage the adoption of such techniques for other data storage technologies, including phase-change, magnetic, and ferroelectric RAM.

KEYWORDS: area-selective atomic layer deposition, dielectrics, resistive random-access memory, filament confinement, data storage device
contributes to reduced complexity and a smaller number of lithographic exposure or etching steps.

In this work, we investigated the AS-ALD of HfO$_2$ dielectrics for the fabrication of RRAM devices. For the AS-ALD of HfO$_2$ (active material of the RRAM) patterns on Pt (bottom electrode), the SiO$_2$ surface regions of a Pt/SiO$_2$/Si substrate were selectively modified with inhibitors of self-assembled monolayers (SAMs), as confirmed by water contact angle (WCA) measurement, followed by HfO$_2$ ALD. The chemical composition and elemental mapping of HfO$_2$ were probed by Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS), further confirming the selectivity of HfO$_2$ deposition between Pt and SiO$_2$ substrates. RRAM devices were fabricated with AS-ALD HfO$_2$, and device performance was evaluated compared to those with nonselective ALD of HfO$_2$.

**EXPERIMENTAL SECTION**

Prior to SAM coating, the p-doped Si substrate was sonicated in acetone for 10 min, followed by 10 s in isopropanol to remove organic contaminants on the surface, and dried under flowing nitrogen. The sample was subsequently treated with either O$_2$ plasma (dry treatment) or H$_2$O (wet treatment) for 10 min under vacuum conditions of ~100 mTorr in an ALD reactor to produce a high concentration of surface hydroxyl groups. For patterned substrates used for RRAM devices, we first deposited 50 nm-thick Ti layers on the SiO$_2$/Si substrate for adhesion improvement below the bottom electrode material. Pt. Pt films of 100 nm in thickness were next electron-beam evaporated onto the Ti-coated SiO$_2$/Si substrate, followed by the definition of the patterns using a lift-off process. The patterning process includes the coating of the surface with photoresist, followed by optical photolithography and the subsequent development of the patterns. The deposited Ti/Pt metal films were then lifted off via solvent stripper to finalize the patterns. These patterned Pt/SiO$_2$ substrates were used for AS-ALD of HfO$_2$. After surface treatment, SAMs were coated on the Pt/SiO$_2$ patterns. An octadecyltrichlorosilane (ODTS) SAM was used as an inhibitor for HfO$_2$ growth. The samples were immersed in a 1 mM solution of ODTS in toluene for 48 h at room temperature. After SAM coating, samples were sonicated for 10 min in toluene to remove physisorbed SAMs, followed by drying with N$_2$. The ODTS-coated substrates were transferred to ALD reactors for AS-ALD. We used two ALD reactors for HfO$_2$ AS-ALD: a custom reactor at Stanford University was used for feasibility tests, and an Atomic Premium, CN1 Co. reactor at Ajou University was used for large-area demonstration. For the HfO$_2$ ALD processes, a tetrakisdimethylamino hafnium (TDMAH) precursor and deionized water counter reactant were pulsed at a growth temperature of 200 °C. The Hf precursor was held at 55 °C to maintain sufficient vapor pressure for delivery to the ALD reactor.

WCA goniometry measurement (SEO Co.) was performed to confirm SAM deposition. The chemical composition of the films on the surface was measured by XPS (ThermoFisher Scientific Co.), SEM (Physical Electronics Co.) and AES (Physical Electronics Co., PHI700) mappings were also conducted. The thickness and refractive index of the films were measured by spectroscopic ellipsometry (Ellipso technology Co.).

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**Figure 1.** Growth characterization of area-selective ALD HfO$_2$. (a) Growth per cycle of HfO$_2$ on Si with SiO$_2$ native oxide as a function of precursor exposure. (b) Thickness of HfO$_2$ with the number of ALD cycles. (c) Water contact angle before and after ODTS solution dipping according to wet and dry treatment processes on SiO$_2$/Si. (d) Water contact angle with ODTS solution dipping time.
After selective ALD, the SAM was removed by 1 min of O$_2$ plasma exposure before depositing the top electrodes of the RRAM devices. TiN/Pt films with a thickness of 40 nm/20 nm were deposited (reactive sputtering of TiN and direct current (dc) sputtering of Pt) and defined by standard lift-off as the top electrodes. Thus, the fabricated RRAM devices were in a typical crossbar structure with a 5 nm-thick HfO$_2$ switching layer sandwiched between the metal electrodes. We also fabricated control HfO$_2$ RRAM devices by performing standard ALD of HfO$_2$, followed by patterning and etching to define the device region (no AS-ALD involved). The thickness of selective and uniform HfO$_2$ on Pt was measured by an ellipsometer, showing nearly the same results of about 5 nm. The fabrication process flow for the RRAM device with AS-ALD is presented in Figure S1 in the Supporting Information. The schematics of the fabricated RRAM devices are presented in Figure S2. Comparing to a selective HfO$_2$ case (Figure S2a), uniform HfO$_2$ (Figure S2b) shows a larger program area. The reduced variability in our RRAM devices fabricated by using AS-ALD can be attributed to the better areal confinement of the HfO$_2$ switching region on the top of the bottom electrode compared to that for uniform ALD devices, enhancing the confinement and stability of filaments.

Electrical characteristics (current–voltage curves) of RRAM devices with and without AS-ALD HfO$_2$ were evaluated by using an Agilent B1500A Semiconductor parameter analyzer. The electrode sizes of the devices were varied between 1 × 1, 2 × 2, and 5 × 5 μm$^2$. Initially, the devices were in a high resistance state and needed to be activated with a forming process. A positive voltage was applied to the top electrode to switch the device to a low resistance state (LRS) or ON state, while a reverse biased voltage switched it back to a high resistance state (HRS) or OFF state.

**RESULTS AND DISCUSSION**

Figure 1a,b shows the growth characteristics of HfO$_2$ ALD using TDMAH and H$_2$O as the precursor and counter reactant, respectively. Figure 1a shows that the growth per cycle (GPC) gradually saturates at 1.3 Å/cycle as the precursor exposure time is increased. Therefore, the precursor undergoes...
a self-limiting reaction. Figure 1b shows that the thickness increases linearly as the number of ALD cycles increases, indicating the possibility of thickness control by adjusting the number of ALD cycles. Figure 1c,d shows the WCA values of the Si substrate with SiO₂ for different substrate treatment processes (dry and wet) and the SAM solution dipping time. A significant increase of WCA is observed after dipping the SiO₂ substrates, indicating hydrophobic SAM coating on the Si surface with SiO₂ (Figure 1c). These WCA values (above 100°) are comparable with previous reports on AS-ALD. Both dry and wet treatments are effective in allowing inhibitor coating on SiO₂/Si, with a slight difference of WCA values. Figure 1d shows that the WCA values saturate with increasing solution dipping time for the SiO₂/Si substrate prepared by dry treatment. For the subsequent experiments, we chose 24 h to ensure sufficient coating of the SAM layers on the SiO₂/Si substrate made by dry treatment.

Figure 2a shows the relative concentration change of Hf on ODTS-SAM-coated Pt and SiO₂ substrates as the number of ALD cycles increases. Even after the SAM coating, the concentration of Hf gradually increases on a Pt substrate. The result indicates that SAM blocking is not effective for the Pt substrate, which we attribute to a low concentration on the Pt noble metal surface of O–H groups, which are needed for bonding to the SAM headgroup, leading to poor packing of the SAM on Pt. This conclusion is consistent with WCA measurements showing almost no difference of WCA on Pt before and after SAM coating (58°–60°) (data not shown).

On the other hand, the concentration of Hf remains nearly zero up to 75 cycles of HfO₂ ALD on a SAM-coated SiO₂/Si substrate. The result suggests that ODTS SAMs are packed well enough to block the adsorption of Hf precursor to the substrate, in agreement with the high WCA value shown in Figure 1c,d. The resulting selectivity of HfO₂ ALD to Pt over the SiO₂/Si substrate is in alignment with a previous report. The calculated selectivity of HfO₂ on Pt versus SiO₂/Si is 97.5 and 96.6% at 50 and 75 cycles, respectively, estimated using \( R_{gs} = (R_{gs} - R_{ns})/(R_{gs} + R_{ns}) \), where \( R_{gs} \) is the selectivity after \( x \) ALD cycles, and \( R \) represents the atomic composition of the deposited material as a function of the substrate. Specifically, \( R_{gs} \) represents the atomic composition ratio of Hf/(Hf + Pt) for the growth surface (gs), and \( R_{ns} \) represents Hf/(Hf + Si) for the nongrowth surface (ns). Figure 2b shows an XPS survey spectrum after 50 cycles of HfO₂ ALD on ODTS-coated SiO₂/Si. No notable Hf peak can be seen, confirming that AS-ALD HfO₂ was successfully performed.

Figure 2c shows an SEM image of 5 nm-thick ALD-HfO₂ deposited on SAM-coated Pt/SiO₂ patterns. The dark region represents the SiO₂/Si substrate, whereas Pt is present in the light-colored regions. The same sample was used for elemental mapping analysis by AES, as shown in Figure 2d–g. Figure 2d–g confirms that the Hf signal is only detectable on the Pt areas of the pattern. Also, in Figure 2f, the carbon signal is observed principally in SiO₂/Si areas of the substrate and not on Pt, consistent with selective ODTS SAM formation on SiO₂/Si. In contrast, when HfO₂ ALD is performed without a SAM inhibitor on the same Pt/SiO₂ patterns, the Hf signal is detected across the entire substrate pattern, as shown in Supporting Information Figure S3, although we note that there is some inherent selectivity for growth on Pt observed even without the SAM (which could possibly arise from a catalytic effect of the Pt substrate). Thus, with ODTS-assisted AS-ALD, HfO₂ films are successfully deposited only on Pt, a bottom electrode for the RRAM devices, and not on the SiO₂/Si substrate. Additionally, we compare the impurity content in both HfO₂ films by XPS because impurities such as carbon can degrade device performance (Figure S4 and Table S1 in the Supporting Information). The results show only a very small amount of carbon impurity for selective HfO₂ (~0.4%), and no carbon or nitrogen impurities in uniform HfO₂ with respect to the detection limits.

This technique is not limited to the fabrication of bottom electrodes for RRAM devices; rather, it can be readily used for fabricating the ultrascaled and precise bottom electrodes of other competing memory technologies such as phase-change RAM, magnetic RAM, and ferroelectric RAM. In each case, since AS-ALD is based on the specific chemical reactions at the surface, it will be necessary to select an appropriate combination of inhibitor and precursor depending on the type of substrate and material to be deposited.

Figure 3a,b shows current (I)–voltage (V) plots of RRAM devices (1 × 1 μm² active device regions) taken across 50 consecutive cycles on RRAM with uniform (i.e., non-area-selective) and AS-ALD of HfO₂, respectively. The switching voltage of the AS-ALD RRAM devices shows a significant reduction in cycle-to-cycle variation compared to their nonselective counterparts, in which the HfO₂ was more uniformly grown on Pt/SiO₂ patterns. Considering the cycle-to-cycle variation, the SET voltage (the voltage at which the transition occurs from HRS to LRS) distribution in the selective ALD RRAM device shows a significantly narrower range (~0.5 V) compared to the nonselective design (~1.3 V), an improvement of ~2.6X. The reduced variability in our RRAM devices fabricated by using AS-ALD can be attributed to the better areal confinement of the HfO₂ switching region on top of the bottom electrode, thus enhancing the
confinement and stability of filaments (as further detailed below).

A similar benefit for selective ALD RRAMs can also be discerned for the resistance distributions in the LRS and HRS, with a 280 and 292% reduction in the distribution variation, respectively, compared to the nonselective ALD devices. We further explored the applicability and consistency of the selective ALD deposition technique in different cell sizes of the RRAM devices. Figure 3b–d plots I vs V for area-selective-ALD RRAM devices of different sizes (1 × 1, 2 × 2, and 5 × 5 μm²) each measured for 50 consecutive cycles, confirming the reproducibility of stable device operation as well as low cycle-to-cycle variation irrespective of the device dimension. I vs V data for ten different devices (Figures S5 and S6 in Supporting Information) show that device-to-device variability is also reasonably low for our selective-ALD RRAM devices, showing the proof-of-concept reliability of the AS-ALD technique for RRAM device fabrication. We further note that the design (e.g., geometry of the electrodes) and fabrication process flow could be further optimized for large arrays and reliable high-volume manufacturing of future ultrascaled RRAM devices.

Figure 4a–c summarizes the statistical variation of SET voltage, LRS, and HRS comparing our selective ALD and uniform ALD RRAM devices. The average SET voltage for selective ALD RRAM devices (15 devices and 25 switching cycles for each device) is 1.67 ± 0.16 V, whereas for uniform ALD devices (15 devices and 25 switching cycles for each device), the average SET voltage is 1.87 ± 0.27 V (Figure 4a). Thus, the standard deviation of SET voltage is 40% lower in selective ALD RRAM devices, compared to control uniform ALD devices. The interquartile ranges of the SET voltage for selective ALD RRAM devices, compared to control uniform ALD devices, are 0.28 and 0.45 V respectively, further underscoring the lower SET voltage variability in selective ALD RRAM devices. Figure 4b shows lower LRS variability in the selective ALD devices (~2.4 ± 1.3 kΩ, interquartile range ~1.7 kΩ) compared to the control uniform ALD devices (~4.5 ± 6.15 kΩ (skewed data distribution), interquartile range ~3.8 kΩ). The average HRS of our selective ALD RRAM devices is ~53 ± 30 MΩ (interquartile range ~48.9 MΩ), whereas for our uniform ALD RRAM, the average HRS is ~61 ± 42.6 MΩ with an interquartile range of 60.5 MΩ (Figure 4c). Thus, we also estimate ~78% and ~28% smaller standard deviations in the low and high resistance states of our selective ALD RRAM devices, respectively, compared to the control devices without selective-ALD, improving the overall reliability of RRAM devices. The reset voltage (i.e., the stopping voltage) is similar for both selective ALD and uniform ALD RRAM devices.

The reduced variability in our RRAM devices fabricated using AS-ALD can be attributed to the better areal confinement of the HfO₂ switching region (i.e., confinement of the possible locations of the filaments) on top of the bottom electrode compared to that for uniform ALD devices, thus enhancing the confinement and stability of filaments (Figure S2). Figure S2b shows a conventional crossbar RRAM device with nonselective ALD HfO₂, demonstrating the possible formation paths of random filaments due to the extended presence of the HfO₂ active region beyond the size of the electrodes. In contrast, the oxygen vacancies inside filaments in an AS-ALD HfO₂ RRAM device would be physically confined to a smaller region compared to uniform ALD RRAM devices, as illustrated in Figure S2a, which can reduce the variability by negating excess conductivity during the electrical bias application. This further renders filaments more controllable under the electrical field imposed by the electrodes compared to the nonselective case.

Previous studies on the device performance of RRAM showed a dependence on device size because the number density of formed filaments increases as the device size increases, making it hard to control device performance precisely. In addition, the projected area of HfO₂ outside of the electrodes increases with the device area, therefore increasing the possible filament formation paths, which can introduce more variability. In contrast, compared to a conventional top-down process, this size-insensitive phenomenon may be attributed to an inherent characteristic of the AS-ALD process. Namely, the patterned HfO₂ films grow vertically, directly following the underlying pattern of the growth substrate, such that patterning resolution (pattern size) should not be limited, ideally. This performance consistency independent of active device size further shows the promise of AS-ALD for future three-dimensional (3D) heterogeneous integration of ultrascaled multilayer RRAM technology with low variability and higher reliability. Similar to vertical NAND flash memory, the separation of the active insulator will be required for further scaling down of 3D structures, which cannot be achieved by a conventional top-down fabrication based on photolithography. Also, the AS-ALD process can be utilized multiple times, which enables the deposition of nanolaminate layers.

Even though we did not directly compare HfO₂ films patterned by photolithography, the expectation is that AS-ALD reduces EPE compared to a conventional patterning process by preventing material from depositing in unwanted areas. As an outlook, the reduced EPE can be useful to mitigate interdevice interference and variations in a high-density array of RRAM.
In summary, we studied the area-selective ALD of HfO$_2$ dielectrics as the active layer for RRAM devices. We developed an AS-ALD process for depositing HfO$_2$ uniformly and selectively on patterned Pt bottom electrodes on an underlying SiO$_2$/Si substrate. Using the developed process, RRAM devices were fabricated, and their electrical characteristics were systematically compared. The devices with AS-ALD show significantly lower variability in terms of SET voltages and resistance states compared to their nonselective counterparts. These findings demonstrate the promise of the AS-ALD technique for reliable and high-density RRAM with ultrascaled devices and should further encourage the adoption of AS-ALD for other emerging memristor technologies.

**CONCLUSIONS**

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The area-selective atomic layer deposition development was supported in part by NEW LIMITS, a center in nCORE, a Semiconductor Research Corporation (SRC) program sponsored by NIST, through award no. 70NANB17H041. This work was partially supported by the National Research Foundation of Korea (MSIT) (nos. 2021R1F1A1063671 and 2021R1A4A1033155). E.P. and H.S.P.W. acknowledge support from the member companies of the Stanford Non-Volatile Memory Technology Research Initiative (NMTRI). A.I.K. acknowledges support from the Stanford Graduate Fellowship. The authors thank R. Islam for useful discussions at the initial phase of this work during its conceptualization. A.I.K. is thankful to M. Chen for the lab support.

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**Figure S1.** Device fabrication process flow for area-selective atomic layer deposition (ALD) of HfO\textsubscript{2} RRAM. Abbreviation: PR = photoresist, SAM = self-assembled monolayer
Figure S2. Schematics of fabricated RRAM devices. a and b, Top-view images for AS-ALD and uniform HfO₂. TE and BE represent top and bottom electrodes, respectively. Program area should be under TE, but for understanding program area easily, the area of TE on program area is removed. c, Cross-sectional image of a RRAM device for both AS-ALD and uniform HfO₂.
Figure S3. Spatial Auger electron spectroscopy (AES) images of a, hafnium, b, silicon, and c, platinum signals for 50 cycles of ALD of HfO$_2$ performed without a self-assembled monolayers (SAM) inhibitor on Pt/SiO$_2$ patterns which are the same as in Figure 2c. Hf signal is observed on both the Pt and SiO$_2$ regions of the substrate, unlike in the AS-ALD case of Figure 2c for which it is observed only on the Pt.
Figure S4. XPS core level spectra: a, C 1s and b, N 1s for selective HfO$_2$; c, C 1s and d, N 1s for uniform HfO$_2$. Impurity contents in HfO$_2$ films are compared, to confirm the incorporation of any other impurity when using SAM layers.
Table S1. Atomic concentration of Hf, O, C, and N in selective and uniform HfO$_2$ films and their stoichiometric ratios measured by XPS.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic concentration (%)</th>
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<tr>
<td></td>
<td>Hf</td>
<td>O</td>
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<tr>
<td>Selective HfO$_2$</td>
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Figure S5. Electrical measurements of additional area-selective ALD RRAM devices. a–h, Current (I) - voltage (V) curves of eight additional RRAM devices fabricated using selective ALD showing low variability in the SET voltage, low and high resistance states (also see Figure 4 in the main text). All the devices are of 1 x 1 µm² in size. Compliance current for the measurements is 100 µA for all the devices.
Figure S6. a and b, Current (I) - voltage (V) curves of two additional RRAM devices with 2 x 2 µm² in size fabricated using selective ALD. Compliance current for the measurements is 100 µA for all the devices.