Controlling Cu Migration on Resistive Switching, Artificial Synapse, and Glucose/Saliva Detection by Using an Optimized AlO\textsubscript{x} Interfacial Layer in a-CO\textsubscript{x}-Based Conductive Bridge Random Access Memory

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**ABSTRACT:** The Cu migration is controlled by using an optimized AlO\textsubscript{x} interfacial layer, and effects on resistive switching performance, artificial synapse, and human saliva detection in an amorphous-oxygenated-carbon (a-CO\textsubscript{x})-based CBRAM platform have been investigated for the first time. The 4 nm-thick AlO\textsubscript{x} layer in the Cu/AlO\textsubscript{x}/a-CO\textsubscript{x}/TiN\textsubscript{O}/TiN structure shows consecutive >2000 DC switching, tight distribution of SET/RESET voltages, a long program/erase (P/E) endurance (>10\textsuperscript{8} cycles) at a low operation current of 300 \mu\text{A}, and artificial synaptic characteristics under a small pulse width of 100 ns. After a P/E endurance of >10\textsuperscript{9} cycles, the Cu migration is observed by both ex situ high-resolution transmission electron microscopy and energy-dispersive X-ray spectroscopy mapping images. Furthermore, the optimized Cu/AlO\textsubscript{x}/a-CO\textsubscript{x}/TiN\textsubscript{O}/TiN CBRAM detects glucose with a low concentration of 1 pM, and real-time measurement of human saliva with a small sample volume of 1 \mu\text{L} is also detected repeatedly in vitro. This is owing to oxidation-reduction of Cu electrode, and the switching mechanism is explored. Therefore, this CBRAM device is beneficial for future artificial intelligence application.

**INTRODUCTION**

The conductive bridge resistive random access memory (CBRAM)\textsuperscript{1,2} has been considered as one of the memristors\textsuperscript{3} that will meet the technological requirements\textsuperscript{4} such as miniaturization, long program/erase (P/E) endurance (>10\textsuperscript{9} cycles\textsuperscript{5,6}) high speed (~10 ns), and low energy operation (~10 pt). To achieve the above requirements, various types of materials like HiO\textsubscript{2},\textsuperscript{5,6} Ta\textsubscript{2}O\textsubscript{5},\textsuperscript{7} insulating polymers,\textsuperscript{10} carbon-based materials,\textsuperscript{11-14} and so on have been reported. Recently, amorphous carbon (a-C)-based switching materials (SMs) are beneficial owing to its wafer-scale fabrication,\textsuperscript{15} wide energy gap (2–5 eV),\textsuperscript{15} and high metal diffusivity with low activation energy (0.76 eV for Cu).\textsuperscript{16} Tao et al. have reported the resistive switching by using a Cu/dual-layer-nanoporous-carbon/Pt structure, and a P/E endurance of 10\textsuperscript{5} cycles under a high current of 1 mA is shown.\textsuperscript{14} Similarly, the a-CO\textsubscript{x} based materials are also useful because they have shown good chemical stability,\textsuperscript{17} high electrical resistivity,\textsuperscript{17} and a high dielectric constant of ~15.\textsuperscript{12} As compared to Ta\textsubscript{2}O\textsubscript{5} SM, the a-CO\textsubscript{x} material is scalable and low cost for CBRAM application.\textsuperscript{17} Murdoch et al. have investigated resistive switching using a Ag/a-CO\textsubscript{x}/Pt structure under a high current compliance (CC) of 10 mA.\textsuperscript{18} Xu et al. have reported the resistive switching in Cu/a-CO\textsubscript{x}/Pt atomic switches at a CC of 500 \mu\text{A}.\textsuperscript{19} Although the a-CO\textsubscript{x} is a favorable material, however, a single switching layer is insufficient to control Cu migration, and a long P/E endurance at a low operation current is a challenging task.

Therefore, interface engineering by choosing a suitable material like Ti,\textsuperscript{10,21} Al\textsubscript{2}O\textsubscript{3},\textsuperscript{22-25} nanopore graphene,\textsuperscript{26} and porous Ir\textsuperscript{18} is an effective approach to control the Cu migration, and the switching performance should be improved drastically. In addition, the oxidation of Cu electrode (i.e., Cu to CuO\textsubscript{2}) in CBRAM produces higher Cu migration due to weak Cu–O bonding than pure Cu–Cu bonding (1.5 eV vs 2 eV).\textsuperscript{22} Considering the Gibbs free energy of CO/CO\textsubscript{2} (~137.16 and 394.39 kJ/mol), CuO/CuO (~149 and ~129.7 kJ/mol), and Al\textsubscript{2}O\textsubscript{3} (~1582.3 kJ/mol) at 300 K,\textsuperscript{27} Al can work as an interfacial layer, which could react with oxygen from the CuO\textsubscript{x}/a-CO\textsubscript{x} interface and form an AlO\textsubscript{x} layer. Moreover, the high thermal conductivity of Al\textsubscript{2}O\textsubscript{3} (15 W/m·K)\textsuperscript{28} is another advantage for conductive filament (CF) formation/dissolution in low thermal conductivity materials like a-C (~1 W/m·K).\textsuperscript{29} In addition, the Al\textsubscript{2}O\textsubscript{3} thin film has a higher energy gap of >7 eV, which will help to maintain a high resistance.
ratio and serves an interfacial layer. Shin et al. have reported self-CC of 10 nA by using Al2O3 in the Cu/CuO/LT-Al2O3/HT-Al2O3/Pd structure and a P/E endurance of 10⁴ cycles under a long pulse width of 5 ms. Kumar et al. have reported a DC endurance of >1.6 × 10⁴ cycles using the Cu/Ta/SiCN/Al2O3/TiN structure at a high CC of 500 μA. Barci et al. have reported a P/E endurance of 10⁵ cycles using the CuTeₓ/GdOₓ/Al2O3/metal structure at a long pulse of 1 μs. Vishwanath et al. have reported a P/E endurance of 2 × 10³ cycles using the Cu/AlOₓ/Al2O3/Pt structure at an operation current of 100 μA to 10 mA. Therefore, we have investigated an optimized AlOₓ IL in the Cu/a-COₓ-based CBRAM device to achieve the controlled Cu migration and a longer P/E endurance at a small P/E pulse width of 100 ns.

Recently, the research in the field of CBRAM is also focused on brain-inspired neuromorphic computing. In neuromorphic computing, the CBRAM device can act as the two terminal artificial synapses between pre-synaptic neuron and post-synaptic neuron. At the artificial synapse, a low energy of 10 fJ is required for every signal transport from pre- to post-neurons. Due to high scalability, fast switching, and good endurance (>10⁹ cycles) of the CBRAM devices, the a-C-based resistive switching material is one of the potential candidates for neuromorphic applications; however, the research on these devices has not extended yet. Bachmann et al. have reported the Pt/a-COₓ/W memristor with 16 conducting states at sub-picojoule energy consumption. Although, the CBRAM devices have shown low power operation, the switching variability due to high metal migration is a disadvantage for neuromorphic applications. Therefore, the interface engineering is needed to obtain good synaptic characteristics. Raeber et al. have reported the Pt/ta-C/a-COₓ/Ag structure with consecutive 100 switching cycles at a high CC of 5 mA, and paired-pulse inhibition at biorealistic time scales of <100 ms is also evaluated. Lim et al. have achieved consecutive 100 depression states using the Cu/Cu₂−ₓS/WO₃−ₓ/W structure. Jo et al. have investigated the Pt nanowire/AgSi/a-Si/Si/W structure, and they have achieved 100 long-term potentiation (LTP) states and 100 long-term depression (LTD) states under a long pulse width of 300 μs. Therefore, an optimized AlOₓ IL in a-COₓ-based CBRAM device will be beneficial for neuromorphic application.

On the other hand, diabetes is one of the serious chronic diseases in humans, which is caused by the insufficient insulin production or the excessive rise of blood glucose. Due to lack of known cure methods, it is necessary to monitor the blood glucose in our body to overcome its complications through appropriate medication or early diagnosis of blood sugar level. Self-monitoring the blood glucose through disposable blood glucose test strips is currently one of the widely using methods. However, its invasive sensing method involves blood sampling from finger pricking, which is an inconvenience for the patients to monitor the number of required tests. Recent advancements in noninvasive glucose sensing through contact lenses and tattoos have shown promising approaches; however, it requires further validation for commercial application. Other non-invasive sensing approaches have been proposed to sense glucose in body fluids such as sweat and tears. Liu et al. have reported a Au gate/In₂O₃/PET field-effect transistor sensor for enzymatic glucose monitoring in various body fluids with a linear range of 10 nM to 1 mM. The glucose levels in these fluids are much lower than in blood. Therefore, a highly sensitive glucose sensor is necessary for the continuous glucose monitoring. Several research groups have reported different types of glucose sensors. Cella et al. have reported glucose detection using a single-walled carbon nanotube (SWCNT)-

Figure 1. (a) Schematic representation of glucose/saliva detection using the Cu/AlOₓ/a-COₓ/TiNₒₓ/TiN via-hole structure. (b) HRTEM image of the pristine S2 device. The inset of (b) shows the FFT and IFFT images corresponding to the Cu (111) plane. (c) HAADF image and elemental mapping images of Al, C, and Cu. (d) EDS line profile of the S2 device.
based field-effect transistor, and they have used cyclic voltammetry.\textsuperscript{14} Chang et al.\textsuperscript{15} have used a flower-like Ag nanocrystals (NCs)-based electrochemical sensor for glucose sensing.

Recently, saliva has been considered as one of the useful non-invasive methods due to its easy collection without any pain. Glucose can directly be detected by using natural human saliva without sample preparation owing to a negligible interference effect also.\textsuperscript{16} Saliva has a high correlation with blood glucose concentrations.\textsuperscript{17} Therefore, saliva can be used as alternative diagnosis to monitor the glucose levels of the diabetes patients.\textsuperscript{18–21} Jia et al.\textsuperscript{18} have reported Au nanoparticles-decorated Au NP/CTS/CoO/GCE electrodes. Chakraborty et al.\textsuperscript{22} have reported CuO porous nanostructure electrodes for non-enzymatic salivary glucose detection with a range of 5–225 μM. However, sensing concentrations of these reports are still high. To detect low concentrations for early diagnosis of a disease, the CBRAM platform has been chosen due to low cost Cu and a small device area. In this report, we propose a Cu/AlO\textsubscript{x}/a-CO\textsubscript{y}/TiN CBRAM device as a highly sensitive glucose sensor with a minimum detection of 1 pM, and a small sample volume of 1 μl is used. This approach is useful to monitor real-time human saliva in the future.

In this article, we conduct a detailed study on the resistive switching characteristics and controlled Cu migration by inserting an optimized AlO\textsubscript{x} IL in the a-CO\textsubscript{y}-based CBRAM device for the first time. The CBRAM device with a 4 nm-thick AlO\textsubscript{x} IL shows consecutive >2000 I–V switching, and a long P/E endurance (>10\textsuperscript{6} cycles) at a P/E current of 300 μA and a small P/E pulse width of 100 ns is applied. The Cu migration is investigated through ex situ TEM analysis after >10\textsuperscript{8} P/E pulse width of 100 ns is applied. The Cu migration can contribute for nanoscale memory, bioinspired device for the AlO\textsubscript{x} inserting an optimized AlO\textsubscript{x} a-CO\textsubscript{y}/TiN surface and observed at a-CO\textsubscript{y}/TiN interface. Chakraborty et al.\textsuperscript{49} have reported CuO porous nanostructure for diabetes patients.\textsuperscript{48} Moreover, the sensing of Cu active electrode. Therefore, these combined results by using a single Cu/AlO\textsubscript{x}/a-CO\textsubscript{y}/TiN structure can contribute for nanoscale memory, bioinspired synapse, and human saliva detection in the future.

\section{RESULTS AND DISCUSSION}

CBRAM devices using a-CO\textsubscript{y} SM in the Cu/AlO\textsubscript{x}/a-CO\textsubscript{y}/TiN\textsubscript{y}/TiN structure with different AlO\textsubscript{x} IL thicknesses of 4 nm (S2), 7 nm (S3), or 10 nm (S4) were fabricated, as described in Table S1. The devices without an Al interfacial layer or AlO\textsubscript{x} IL (S1) and without an Al capping layer (S5) were fabricated for glucose/saliva detection.

\textbf{Schematic View with Glucose Sensing Mechanism and TEM with Elemental Analysis}. A schematic view shows typical Cu/AlO\textsubscript{x}/a-CO\textsubscript{y}/TiN\textsubscript{y}/TiN structure including the glucose/saliva detection mechanism (Figure 1a). The CBRAM device is also beneficial for glucose and human saliva detection repeatedly, which is explained later. Figure S1a represents the cross-sectional TEM image of the pristine Al/Cu/AlO\textsubscript{x}/a-CO\textsubscript{y}/TiN\textsubscript{y}/TiN device with an area of 0.4 x 0.4 μm\textsuperscript{2}, whose size is smaller than required.\textsuperscript{1} Figure 1b depicts the HRTEM image of the S2 device, captured from a marked region of Figure S1a. The Cu TE, Al interfacial layer, a-CO\textsubscript{y} SM, and TiN BE are observed clearly. After the deposition of TiN, partially crystalline TiN\textsubscript{y} is formed on the TiN surface and observed at a-CO\textsubscript{y}/TiN interface (Figure 1b). From the HRTEM image, the thicknesses of Al IL, a-CO\textsubscript{y} SM, and TiN\textsubscript{y} are found to be 4–5, 4.3, and 2.9 nm, respectively. Both the a-CO\textsubscript{y} and Al layers are amorphous. The inset of Figure 1b shows the fast Fourier transformation (FFT) and inverse fast Fourier transformation (IFFT) images of the Cu TE at the marked region in Figure 1b. The d-spacing value is 2.09 Å, which is attributed to the Cu (111) plane, and this is similar to the reported value (2.08 Å).\textsuperscript{6} To understand the elemental composition of our device, the high-angle annular dark-field imaging (HAADF) is employed by scanning TEM (STEM) from the BE to TE (Figure 1c). The elemental mapping and EDS line profiles are shown in Figure 1c,d and Figure S1b–i. The a-CO\textsubscript{y} layer is well defined with other deposited layers. The elemental mapping of oxygen (Figure S1) and the EDS line profile reveal the presence of oxygen in Al IL, the a-CO\textsubscript{y} and TiN\textsubscript{y} layers, and the corresponding mass percentage values are 30, 27, and 19%, respectively. In addition, the presence of oxygen is observed in the a-CO\textsubscript{y} films owing to available oxygen in a chamber. Due to the low Gibbs free energy of Al\textsubscript{2}O\textsubscript{3} (−1582.3 kJ/mol) than CO (−137.16 kJ/mol) or CO\textsubscript{2} (394.39 kJ/mol) at 300 K,\textsuperscript{27} the Al IL consumes oxygen from both the a-CO\textsubscript{y} and CuO layers. The mass % of oxygen and Al at the a-CO\textsubscript{y}/Cu TE interface are 30 and 24%, respectively. This forms AlO\textsubscript{x} IL. The small amount of C (5 mass %) in a-CO\textsubscript{y} layer is found (Figure 1c,d) because of the thin layer. The presence of Cu (15 mass %) is observed in the AlO\textsubscript{x} IL, suggesting that Cu is partially diffused through the AlO\textsubscript{x} layer during the deposition. Therefore, AlO\textsubscript{x} IL behaves as a buffer layer,\textsuperscript{17} which controls the Cu migration through a-CO\textsubscript{y} SM. In addition, XPS shows the carbon-to-oxygen bonding in the a-CO\textsubscript{y} film and the oxidation states in Cu (Figure S2). In the narrow scan Cu2p\textsubscript{3/2} spectra, the peak at a binding energy of 932.5 eV represents the pure metallic Cu film with “0” oxidation state.\textsuperscript{52} Under the external bias, this pure Cu TE through oxidation—reduction (Cu ↔ Cu+ + z e−, z = 1, 2) properties is the reason for resistive switching, potentiation/depression, and glucose/saliva detection. First, the bipolar resistive switching characteristics are discussed below.

\textbf{Resistive Switching Characteristics}. Figure 2a represents consecutive 2000 I–V switching cycles without any failure at a low CC of 300 μA. The voltage sweeping directions are denoted by arrows accordingly 1 → 2 → 3 → 4. Figure S3 shows cumulative probability distribution of formation voltage (V\textsubscript{form}) of the S1, S2 S3, and S4 devices. The V\textsubscript{form} increases with increasing AlO\textsubscript{x} thickness.\textsuperscript{53} The operation voltages of all devices are optimized manually and measured DC cycles. The SET voltage (V\textsubscript{SET}) and RESET voltage (V\textsubscript{RESET}) of the S2 devices are approximately 0.6 and −0.47 V, respectively. I–V characteristics of the S1, S3, and S4 devices at a CC of 300 μA are shown in Figure S4; however, those devices show large dispersions of high resistance state (HRS) and low resistance state (LRS). From the I–V curves, the HRS and LRS values of all devices are plotted, as shown in Figure 2b,c. It is observed that the LRS of the S2 device is highly stable throughout the 2000 DC cycles because of thin and stable CF formation for every SET process. The HRS is slightly dispersed due to the variation in the dissolution length of the CF. The HRS and
LRS values of the S2 devices at 50% probability are found to be 75.5 and 2.1 kΩ, respectively. A good resistance ratio of approximately 37 is obtained. On the other hand, the HRS value of the S1 device is gradually decreased after 400 cycles and fails after 600 cycles. However, both S3 and S4 devices show longer 1000 DC cycles with LRS variation from 4 kΩ to 100 Ω owing to non-uniform CF formation, which leads to a higher CC. The HRS values for the S1, S3, and S4 devices at 50% probability are 62.5, 20.5, and 61.3 kΩ, while the LRS values are 1.75, 1.61, and 1.52 kΩ, respectively. To further understand the effect AlOx IL thickness, I–V characteristics of the S1, S2, S3, and S4 devices are measured at a higher CC of 1 mA (Figure S5). The S2 device shows consecutive 2000 DC cycles with the uniform HRS and LRS, suggesting well-controlled Cu migration. The S1 and S4 devices fail after 549 and 900 cycles, respectively. Interestingly, the S3 device also shows consecutive 2000 DC cycles without any failure. This indicates that the S3 device works well at a higher CC of 1 mA, suggesting that the high energy is required to control the Cu migration. The LRS values for the S1, S2, S3, and S4 devices are found to be 419, 516, 476, and 382 Ω, respectively. The LRS values at the CC of 1 mA are less than 300 μA CC owing to the formation of a large-diameter CF. On the other hand, the LRS value decreases with increasing the thickness of the AlOx layer. In our previous report, the Cu migration under the applied electric field is higher in thicker AlOx oxide-electrolyte than the thinner one. Therefore, thicker interfacial layers have a higher RESET current and poor DC cycles owing to a randomly formed larger diameter of CFs. On the other hand, the S1 device has a CuOx interfacial layer, which allows higher Cu migration, and unstable DC cycles are observed.

**Uniformity and Comparison with Reported Results.**

Figure S6 shows device-to-device cumulative distribution of the HRS and LRS of the S2 devices at CCs of 300 μA and 1 mA, respectively. Arbitrarily, 25 devices have been chosen for this study. The HRS/LRS shows good uniformity in cycle-to-cycle and device-to-device. The DC cycles are comparable even it is better than the reported results (Table 1). Zhao et al. have reported 1000 DC cycles using the Cu/a-C/Pt structure at a CC of 10 mA. The VSET and VRESET distributions of DC cycles are plotted, as shown in Figure 2d and Figures S7 and S8. At 300 μA CC, the S2 device shows tight distributions of VSET (from 0.4 to 0.5 V, 92%) and VRESET (from −0.38 to −0.475 V, 90%) for more than 2000 cycles. The VSET distribution for the S1, S3, and S4 devices are 0.2−0.9 V, 0.3−0.9 V, and 0.2−1.2 V, while the VRESET distribution for those devices are −0.1 to −0.9 V, −0.19 to −0.95 V, and −0.1 to −0.9 V, respectively (Figure 2d and Figure S7). The S1, S3, and S4 devices show wide distributions of VSET and VRESET. On the other hand, both S2 and S3 devices at a CC of 1 mA show tight distributions of VSET (0.4−0.6 V, 96% and 0.5−0.7 V, 90%) and VRESET (−0.38 to −0.57 V, 94% and −0.2 to −0.4 V, 96%), as shown in Figure S8. However, the S1 and S4 devices show a wide distribution (Figure S8). The tight distribution of VSET and VRESET represents the uniform formation/dissolution of CF, and a long P/E endurance at a low operation current is achieved, which is discussed later. To understand the device performance, the current transport mechanism is explained below.

**Transport Characteristics.** A typical I–V curve of the S2 device at a low CC of 300 μA is fitted for different conduction mechanisms (Figure S9). The HRS current under −Ve bias is replotted in ln(I/V) vs √E scale, and this shows the Schottky conduction. The dynamic dielectric constant (ε(\(\lambda\))) and Schottky barrier height (\(\phi_b\)) are calculated from the slope and intercept in eqs 1 and 2 below:

\[
slope = \left(\sqrt{\frac{q^3}{4\pi \varepsilon_{\text{F\text{\hbox{-}\text{ch}}}} k_B T^2}}\right)
\]

Table 1. Comparison of CBRAM Performance with Various Materials/Structures

| device structure         | operation current (μA) | DC endurance (#) | HRS/LRS ratio | P/E voltage (V) | P/E pulse width (ns) | P/E endurance (#) | retention (s) |
|--------------------------|------------------------|------------------|---------------|-----------------|----------------------|--------------------|---------------|---------------|
where \( q \) is the electronic charge, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_{\text{sch}} \) is the relative permittivity of dielectric medium, \( k_B \) is the Boltzmann’s constant, \( T \) is the absolute temperature, and \( \phi_B \) is the Schottky barrier height. The \( \varepsilon_{\text{sch}} \) and the \( \phi_B \) values are found to be 5.32 and 0.28 eV, respectively. The refractive index \( n \) value is 2.3, which follows the equation \( \varepsilon_{\text{sch}} = n^2 \). Stagg et al. have reported that the \( n \) value of a-C is 2.32 at a wavelength of 500 nm. The \( n \) value of our device is similar to the reported one. The LRS current is well fitted in \( \ln(J) \) vs \( \ln(V) \), which exhibits ohmic conduction with a slope of 0.95. In our previous report, we have reported the Schottky conduction at the HRS and ohmic conduction at the LRS using the Cu/Ir/TiN structure.5

**Program/Erase Endurance.** The P/E endurance characteristics of the S1, S2, S3, and S4 devices are shown in Figure 3 and Figure S10. A small P/E pulse width of 100 ns is applied. To obtain a long P/E endurance, the P/E voltages are optimized for all the devices. A long P/E endurance of more than \( 10^9 \) cycles is achieved without resistance verification circuit for the S2 devices at a low operation current of 300 \( \mu \)A (Figure 3a). A long P/E endurance of \( >1.5 \times 10^8 \) cycles under an operation current of 1 mA is also obtained. The energy consumptions of the device during program and erase are 36 and 24 pf, respectively. In Figure 3a, it is found that variation of the LRS/HRS at initial cycles is observed, and it has plausible random formation or complete dissolution of CFs in a-CO\(_x\) SM. During these initial cycles, continuous stress is developed, and the heat enhances the sp\(^2\) cluster formation in a-CO\(_x\) SM. Zhao et al.\(^{11}\) have reported that the degree of sp\(^2\) clustering is increased after a current of 100 \( \mu \)A using the Cu/a-C/Pt structure. The sp\(^2\) clustering helps to create uniform CFs also.\(^{11}\) The S2 device shows a long P/E endurance owing to the key role of the optimized AlO\(_x\) interface layer, and the enhancement of the sp\(^2\) clustering under the continuous SET/RESET pulses. On the other hand, the P/E endurance at a high operation current of 1 mA does not show fluctuation at initial cycles because the sp\(^2\) clustering is formed. Although the enhancement of the sp\(^2\) cluster occurs in the S3 and S4 devices, the Cu migration is higher due to defective thicker AlO, ILs and restricts the performance. In contrast to the S2 device, the S1 device fails after \( 5 \times 10^7 \) cycles (Figure 3b). The S3 device shows a slightly longer P/E endurance of \( 2 \times 10^8 \) cycles than the S1 and S4 devices (\( 5 \times 10^7 \) cycles). However, both S2 and S3 devices at the programming current of 1 mA are shown to have a long P/E endurance of more than \( 10^9 \) and \( 6 \times 10^8 \) cycles, respectively (Figure S10). On the other hand, the S1 and S4 devices fail after \( 4 \times 10^7 \) and \( 8 \times 10^7 \) cycles, respectively. Table 1 shows the comparison of our P/E endurance with recently reported results using various SMs.\(^{5,6,11,14,23,24,55}\) In addition, the CO\(_x\)-based device shows a longer P/E endurance than the Ta\(_2\)O\(_5\)-based CBRAM (\( >10^9 \) vs \( 10^8 \) cycles).\(^{58}\) The S2 devices show uniform and stable data retention of over \( 10^4 \) s at an operation current of 300 \( \mu \)A (Figure S11). The stable data retention is explained by measuring the activation energy (Figure S12). The HRS value decreases with increasing temperature, suggesting the defect-dependent current conduction. The activation energy is 0.26 eV, which is similar to the reported value of 0.28 eV.\(^{59}\) The LRS value increases with increasing temperature, which confirms the typical metallic behavior or ohmic (Figure S9). The activation energy at the LRS is 0.17 eV. The low activation energy of the Cu filament depends on various factors, such as hopping distance, migration speed, and temperature.\(^{59}\) Rehman et al. have reported a similar activation energy value of 0.14 eV for Cu CF in the Al/Cu2Se/Pt structure.\(^{60}\) For further understanding of the Cu migration-based CF, the ex situ TEM analysis is employed as discussed below.

**Cu Filament by HRTEM Analysis.** After forming the S2 devices at a CC of 10 \( \mu \)A, the cross-sectional TEM image is obtained (Figure S13). The inset of HRTEM image demonstrates the FFT and IFFT images, which are captured from the marked regions. The \( d \)-spacings of the AlO\(_x\)/a-CO\(_x\) region is 2.06 Å, which corresponds to the Cu(111) plane.\(^{6}\) The elemental composition at this region is also characterized by EDS line scan profiling and elemental mapping (Figures S14 and S15). The Cu content at the a-CO\(_x\)/AlO\(_x\) interface is lower (12%), suggesting the controlled Cu migration by AlO\(_x\) IL. The Cu content is 27% in a-CO\(_x\) SM, which represents the accumulation of migrated Cu. The surface of TiN BE is likely TiO\(_x\) and a small Cu amount of 5% is observed. Alén et al. have reported that the 3-nm-thick TiO\(_2\) layer works as a diffusion barrier of Cu.\(^{63}\) Thus, a small amount of Cu is found in the TiO\(_2\) layer. From the evidence of Cu migration, these results reveal the formation of Cu CFs. After operating at \( >10^8 \) P/E cycles and keeping the device to SET, the strong Cu migration is observed (Figure S16). Figure 4 shows the HRTEM image, which is captured at the marked region II (Figure S16b). The a-CO\(_x\) and AlO\(_x\) layers are amorphous, except a crystalline region is observed, as shown in the marked region. The \( d \)-spacings of the crystal region is also referred to the Cu (111) plane.\(^{6}\) From the EDS line profile (Figure S17), the Cu counts at the a-CO\(_x\)/AlO\(_x\) interface, a-CO\(_x\) and TiO\(_2\) are 20, 40, and 11%, respectively. Those values are higher than those of the forming device. The higher Cu counts in the a-CO\(_x\) and AlO\(_x\) layers have been observed in elemental mapping (Figure S18). Therefore, this suggests that the Cu concentration in CF increases with increasing P/E
cycles. Lv et al. have analyzed the similar phenomena after DC cycles in the Cu/HfO2/Pt structure.5

**Switching Mechanism.** The resistive switching mechanism is also explained schematically, as illustrated in Figure S19. During the SET process (Figure S19b), a 4 nm-thick AlOx interfacial layer controls the Cu²⁺ ion migration. The generated Cu ions (Cu⁰ → Cu²⁺ + 2e⁻; Cu¹ → Cu⁺ + e⁻) at the AlOx/a-COx interface are observed by cyclic voltammetry (CV), as shown in Figure S20. The Cu oxidation using the Cu/Ta₂O₅/Pt structure is also reported by Tsuruoka et al.62 The Cu ions are migrated through a-COx, also confirmed by both CV and ex situ TEM images. The Cu ions are reduced at the a-COx/TiN interface because electrons are tunneled through the TiN layer from the TiN BE. The TiN layer shows a less amount of oxygen (19%), which is metallic-like.63 Considering the work functions of TiO₂ (~4.8 eV) and TiN (4.3–4.65 eV),65 the work function difference at the TiN/O₂/TiN BE is relatively low, which leads to ohmic. Therefore, a large number of electrons pass through this thin TiN/O₂ layer and reduces the Cu²⁺ ions into Cu⁰. Considering the work function of Al (4.06–4.26 eV), a positive built-in potential (0.24–0.39 eV) in the Al/a-COx/TiN structure helps to control Cu ion migration. On the other hand, a negative built-in potential (~0.35 eV) in the Cu/a-COx/TiN structure does not control Cu migration, even oxidation of the CF is possible during SET. Therefore, the Cu ions are migrated randomly for the S1 devices. Similarly, the thicker AlOx interfacial layers show also a huge amount of Cu migration and thicker CF formation in the a-COx SM. Many research groups have reported that the thin Al₂O₃ layer, which works as a Cu diffusion barrier.22,66 It is known that the thermal conductivity of Al₂O₃ (15 W/m-K) is higher than a-C (0.01–0.1 W/m-K) and TiO₂ (8.5 W/m-K).67 During the RESET process (Figure S19c), heat will be transferred easily through the AlOx buffer layer than the a-COx SM, and the temperature rises at the low thermal conductive a-COx layer. The CF temperature increases at the AlOx/a-COx interface. Therefore, the CF dissolves at the AlOx/a-COx interface first and leaves a small part of the CF at the a-COx/TiN interface. During the next SET process, the residual CF in the a-COx layer enhances the electric field and therefore allows us to form uniform CF at the dissolved region. However, the degree of sp² clustering also helps restricted Cu migration through a-COx after certain P/E cycles. Therefore, these lead to high resistive switching memory performance.

**Artificial Synapse Characteristics.** Due to the long P/E endurance ability, good conductance modulation (i.e., potentiation/depression) is expected, which is essential to emulate the biological synaptic behavior. Typical analog I–V characteristics of the S2 device are demonstrated by applying a positive voltage for potentiation (Figure 5a) and a negative voltage for depression (Figure 5b). By considering the V_SET and V_RESET distributions of all the devices (Figure S8), the

**Figure 4.** HRTEM image of the stressed S2 device. The S2 device after a P/E endurance of 10⁹ cycles (stressed) is used for the TEM analysis. The d-spacing from FFT and IFFT images (inset images) corresponds to the Cu (111) plane. The image at region II is captured from Figure S16b.

**Figure 5.** Conductivity modulation of the S2 device: (a) potentiation, (b) depression, (c) the corresponding conductance vs number of DC sweeps plots for randomly picked three devices, and (d) typical LTP and LTD characteristics.
optimized voltages have been chosen to avoid the abrupt switching. During the potentiation, the device undergoes partial SET to initiate the CF or incremental filament formation, as shown in the inset of Figure 5a. When consecutive voltage sweeps ($0 \rightarrow 0.5$ V) are applied on the S2 devices, the conductance gradually increases for each voltage sweep, and a maximum of 37–40 distinguished states are obtained. When consecutive negative voltage sweeps ($0 \rightarrow -0.4$ V) are applied, the conductance gradually decreases for each sweep. Hence, a maximum of 48–54 distinguished states are obtained. During depression, the CF experiences incremental dissolution due to the subsequent application of constant negative voltage. This leads to a gradual decrease of current conduction. The potentiation/depression of the S2 device are replotted as conductance vs number of DC sweeps (Figure 5c), where the gradual increase or decrease of the conductance can be seen clearly. Obviously, the conductivity modulations of the S1, S3, and S4 devices are inferior, as shown in Figures S21 and S22. Sun et al. have reported 16 conducting states during gradual SET (0.6 V, 10 V/s) and 30 conducting states during gradual RESET (−0.8 V, 13 V/s) by using the Ag/GeSe/TiN structure. In our previous report, we have reported potentiation/depression characteristics with the maximum of 10 and 25 conductance states by using the Cu/Ir/Ta-based subquantum CBRAM.30,32 Due to the achievement of considerable conductance states in the S2 and S3 devices, the artificial synaptic behavior is further evaluated by applying a short pulse width of 100 ns (Figure 5d and Figure S23). The conductance amplitudes of the S2 and S3 devices are applied similarly as 0.6−1 V read of ±0.2 V (2 ms pulse width). The conductance in the S2 and S3 devices increases with increasing the number of applied positive pulses (LTP), while it decreases with increasing the number of applied negative pulses (LTD). The LTP/LTD conductance states in the S2 devices are stable up to 59/101 consecutive positive/negative pulses, while those states for the S3 devices are 25/65. Those numbers can be improved further by using 1T1R (one transistor one resistor) configuration because the current overshoot effect can be reduced also. The energy consumption range of the S2 device during the LTP is 6.7–13.3 pJ, and it is lower than the S3 devices (13.4–32.5 pJ). Our data is compared with the recently reported results (Table 2).30,32–36 Shi et al. have demonstrated 256 conducting states using the ZrTe/AlO$_x$/Ta-based subquantum CBRAM.30 Chen et al. have reported 190/140 conducting states using the Cu/SiO$_2$/W structure.34 However, our S2 device shows comparable energy consumption with other reported results, which is beneficial for future brain-inspired neuromorphic application.

**Glucose Sensing and Mechanism.** Due to the oxidation/reduction properties of Cu, the S5 device with an optimized AlO$_x$ interfacial layer is used for glucose/saliva detection. The glucose/human saliva detection is also shown schematically in Figure 1a. First, pH 7.4 solution with a sample volume of 1 μL is dropped on 4 × 4 μm$^2$ via-hole. Then, $I−V$ characteristics within sweeping voltages of $±2$ V are shown in Figure 6a. The sweeping voltage paths are shown in arrows from 1 $→$ 2 $→$ 3 $→$ 4. For biosensing, we are using the pristine CBRAM device before the SET/RESET voltage. The paths 1 and 2 are fitted to the Schottky conduction mechanism (Figure S24). The $\phi_B$ values are calculated from the intercept (eq 2) and plotted with respect to the sweeping voltages (Figure 6b). As the sweeping voltage increases, the $\phi_B$ values of path 1 are almost the same, and the current conduction in the device is constant owing to the reduction of Cu TE. However, the $\phi_B$ values of path 2 are gradually increased with increasing sweeping voltage. This increment value of $\phi_B$ controls the current conduction owing to the partial oxidation of Cu TE. The $\epsilon_{sch}$ values with applied

| device structure | number of states (#) | pulse amplitude (V) | pulse width | energy consumption |
|------------------|----------------------|--------------------|-------------|-------------------|
| Cu/AlO$_x$/a-CO$_2$/TiN$_2$/TiN (this work) | 59/101 | 0.5/−0.4 | 100 ns/100 ns | 6.7−13.3 pJ |
| ZrTe/AlO$_x$/Ta-based subquantum CBRAM | 256 | 2/2 | 1 μs/1 μs | ~0.1−10 pJ |
| Ag/i-SiGe/p-Si | 500/500 | 5/−3 | 5 μs/5 μs | 300 μs/300 μs |
| Cu/Cu$_{2}$/WO$_{3}$//W | /100 | −2.5 | /1 μs | ~225−500 pJ |
| Cu/SiO$_2$/W | 190/140 | 0.79−1.15/−0.75 to −1.01 | 10 μs/10 μs | ~2 nJ |
| Ag/GeSe/TiN | 200/200 | 0.6/−1 | 60 μs/60 μs | ~300 pJ to 12 nJ |
| Pt NWs/Ag/Si/a-Si/Si/W NWs | 100/100 | 3.2/−2.8 | 300 μs/300 μs | ~24 fJ to 0.38 pJ |

**Figure 6.** (a) $I−V$ hysteresis characteristics in the presence of buffer solution (pH 7.4) with different sweeping voltages from $±1$ to $±2$ V. (b) Barrier height ($\phi_B$) vs applied negative voltage plot. (c) Plot of normalized current shift vs glucose concentration from 1 pM to 1 nM. (d) $I−t$ response of pH 7.4 and human saliva. (e, f) Repeatable human saliva detection of (e) the same device and (f) device-to-device after a short response time of 5 s.
voltage differences of −1, −1.5, and −2 V are 6.5, 5.35, and 7.53, while the n values are 2.55, 2.34, and 2.74 for the path 1, respectively. These n values are similar to the reported value of CuO (2.73 at a wavelength of 600 nm). The ε_s values are 4.4, 5.24, and 2.24, while the n values are 2.09, 1.8, and 1.49 for the path 2, respectively. These n values are similar to the reported value of CuO (∼1.6 at a wavelength of 546 nm). Typical I−t characteristics of the device in the presence of buffer solution (pH 7.4), buffer plus glucose oxidase, and 1 mM glucose solutions are measured at a V_end of −0.2 V (Figure S25). The current levels are similar when pH 7.4 and 15 units GOx enzyme are dropped on the device. However, the saturated current level is suddenly decreased when 1 pM glucose is added. The glucose in the presence of GOx enzyme produces gluconic acid and H₂O₂, as shown in eq 3 below:

\[
d - \text{glucose} + O_2 \xrightarrow{\text{glucose oxidase}} \text{gluconic acid (H}^+\text{)} + H_2O_2
\]

As the glucose concentration increases from 1 pM to 1 nM, the production of H₂O₂ content increases. This H₂O₂ oxidizes Cu TE from Cu⁰ to Cu⁺ (where z = 1, 2), and the φ_d value at the Cu/AIOₓ interface increases, and therefore the current decreases. As compared to the buffer plus GOx, the saturated current level in the I−t plot drops gradually as the concentration of glucose increases from 1 pM to 1 nM. From the I−t plot, we have replotted the glucose concentration vs normalized current (ΔI/I_0) (where ΔI = I_pM glucose − I_0, I_0 is the current at a time response of 5 s for buffer plus oxidase), as shown in Figure 6c. We have fitted the glucose concentration vs normalized current plot in eq 4 below:

\[
M_{\text{Glucose}} = \exp \left( \frac{1}{S} \left( \frac{\Delta I}{I_0} - G \right) \right)
\]

The slope (S) and intercept (G) values are found to be −0.05642 and −0.498, respectively. As glucose the concentration increases from 1 pM to 1 nM, the normalized current is decreased from −0.475 to −0.874. A high sensitivity of 0.475 pM⁻¹ is achieved for a low concentration of 1 pM glucose. Table 3 shows a comparison of our glucose sensing and glucose in saliva detection in the literature. Our result is comparable, and it is even better than the reported values.

Saliva Detection. This highly sensitive glucose sensor is beneficial for noninvasive sensing of body fluids such as human saliva. The S5 device is used to detect glucose in human saliva. At first, we have mixed 50 μL of human saliva in 50 μL of GOx (25 units). The 1 μL sample solution in vitro is used for each real-time measurement (pH 7.4 and human saliva plus GOx).

Figure 6d shows typical I−t response of pH 7.4 and human saliva plus GOx. The saturated current of pH 7.4 solution is approximately 48 nA at 5 s. In comparison to pH 7.4, the current is decreased to 3.3 nA for the human saliva plus GOx. This suggests that the GOx reacts selectively with available glucose in human saliva and produces H₂O₂, and the saturated current decreases by Cu oxidation. The current of human saliva plus GOx is similar to 100 pM glucose (13.3 nA), as shown in Figure 6c. By using eq 4, the glucose concentration in saliva from a human is approximately 70 pM. Repeatable measurements of human saliva with respect to pH 7.4 buuffer are shown in Figure 6e. The same device can detect saliva more than three times. A typical current value at pH 7.4 for the first time is slightly higher than the next measurement (∼50 nA vs ∼42 nA). This suggests that Cu TE is partially reduced to Cu⁰ in the presence of pH 7.4 after saliva measurement. Further study is needed to reach a pristine current. However, our device shows repeatable saliva detection, and this shows good detection for the device-to-device also (Figure 6f). The currents of devices are 13 ± 1 and 44 ± 3 nA for saliva plus GOx and pH 7.4 after 5 s, respectively. In this study, the Cu electrode in the novel Cu/AIOₓ/a-COₓ/TiOₓ/NiO/TiN CBRAM device is used to detect human saliva even if a small sample volume of 1 μL has been used in vitro. The optimized AIOₓ IL-based CBRAM device shows excellent resistive switching characteristics with a P/E endurance of >1.5 × 10⁹ cycles, artificial synapse characteristics (LTP and LTD), and glucose/human saliva detection under lower concentration levels, which opens a wide window for future new application.

CONCLUSIONS

In conclusion, the role of a thin AIOₓ IL is controlling Cu migration, and the resistive switching memory performance, superior artificial synapse, and human saliva detection using a Cu/AIOₓ/a-COₓ/TiOₓ/NiO/TiN CBRAM memory platform are investigated for the first time. The AIOₓ layer and a-COₓ layers are observed by both TEM and EDS analyses. As compared to other thicknesses of IL, the 4 nm-thick AIOₓ layer controls Cu migration and exhibits stable switching of more than 2000 DC cycles, uniform distribution of SET/RESET voltages, and a long P/E endurance of >1.5 × 10⁹ cycles under an operation current of 300–10⁵ μA, and a small P/E pulse width of 100 ns is applied. The evidence of Cu migration is observed by ex situ HRTEM, which is owing to the Cu filamentary-based resistive switching. In addition, the S2 device shows superior conductance modulation with long LTP/LTD states of 59/...
101 under a small pulse width of 100 ns, and a low energy of 6.7–13.3 pJ is required. The CBRAM device detects glucose with a low concentration of 1 pM, which is owing to good oxidation—reduction of Cu. Similarly, the Cu migration in the CBRAM is due to oxidation—reduction of Cu under external bias, and conductive filament formation/dissolution is obtained. It is noted that human saliva with a small sample volume of 1 μL is also detected repeatedly in vitro by using the CBRAM. This will be useful to find the sugar level of a diabetic patient using this easy method, or this will help in diagnosis at an early stage of other human diseases in the future. This Cu/AlOx/a-COx/TiN/Ox/TiN-based CBRAM paves a way for future possible AI application.

**EXPERIMENTAL SECTION**

**Memory Device Fabrication.** First, a 200 nm-thick SiO2 layer on Si was deposited by thermal oxidation. Then, a 40 nm-thick TiN as a bottom electrode (BE) on 160 nm-thick Ti was deposited. To create the 0.4 × 0.4 μm2 size via-holes, a 150 nm-thick SiO2 layer was deposited on the TiN/Ti/SiO2/Si stack. The a-COx oxide-electrolyte SM with a thickness of 5 nm was deposited by radio frequency sputtering. The carbon target with a purity of 99.95% was used. During deposition, the chamber pressure, Ar flow rate, and radio frequency power were maintained at 9 × 10−6 Torr, 10 sccm, and 100 W, respectively. To optimize the resistive switching performance, Al IL (which will form AlOx) with a thickness of 4, 7, or 10 nm was deposited on the a-COx SM by thermal evaporation. Finally, a 40 nm-thick Cu as a top electrode (TE) and 160 nm-thick Ti as a capping layer were deposited by using thermal evaporation. Then, a lift-off process was performed to obtain the CBRAM devices with different AlOx IL thicknesses (S2, S3, and S4), as shown in Table S1. For comparison, the device without AlOx IL (S1) was also fabricated. For glucose/saliva detection, the device without an Al capping layer (SS) was fabricated. The Al capping layer does not detect glucose because it is oxidized easily on the surface owing to a lower Gibbs free energy of Al2O3. Therefore, the Cu TE was used, which proves also the oxidation—reduction mechanism to detect glucose/saliva and resistive switching. A typical Cu/AlOx/a-COx/TiN/Ox/TiN structure was fabricated for glucose/saliva detection, as shown in Figure 1a. The CBRAM structure and chemical composition of a-COx were examined by HRTEM, energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). The current—voltage (I−V) characteristics were obtained by applying sweeping bias on the Cu TE, while the TiN BE was grounded. Memory characteristics were measured by using an Agilent Technologies B1500 Semiconductor Device Analyzer.

**Glucose and Glucose Oxidase Preparation.** For the glucose sensing, glucose and glucose oxidase (GOx) enzyme were purchased from Sigma-Aldrich. At first, 0.054 g of glucose was dissolved in 30 mL of deionized water to obtain the 10 mM main stock solution. By dissolving the main stock in phosphate buffer solution (pH 7.4), the concentration of the glucose solution was reduced to desired concentrations (1 pM to 1 nM). Similarly, GOx enzyme with 110 units stock solution was prepared by dissolving it in 500 μL of phosphate buffer solution. The GOx enzyme with optimum concentrations of 15 and 25 units were used for the glucose and human saliva measurements, respectively. Finally, buffer, GOx enzyme plus different concentrated glucose from 1 pM to 1 nM were added each time to the CBRAM via-hole device and measured current—time (I−t) response. In this case, a small sample volume of 1 μL was used to investigate glucose/saliva in the Cu/AlOx/a-COx/TiN/Ox/TiN structure. The B1500 Semiconductor Device Analyzer was used to measure current—time (I−t) characteristics.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00795. (Table S1) Split table of the devices; TEM image and EDS mapping of the S2 device; XPS spectra of a-COx and Cu thin films; forming voltage distribution; I−V switching characteristics and DC endurance; device-to-device cumulative probability; cycle-to-cycle Vset/Vreset distribution; current transport mechanism; P/E endurance; data retention; temperature-dependent HRS/LRS and Arrhenius plot; TEM image and EDS mapping after the forming process; TEM image and EDS mapping after the P/E endurance of >108 cycles; schematic representation of the switching mechanism; oxidation—reduction of Cu TE for the via-hole devices; conductance modulation; Schottky conduction at pH solution; and current—time (I−t) characteristics of glucose (PDF)

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**Author Contributions**

S.G. performed experiments and measurements and wrote the first manuscript. S.G. analyzed data by helping S.M. Glucose/saliva detection is analyzed by helping J.T.Q. S.M. modified the manuscript. All authors contributed their part and given approval to the final version of the manuscript.

**Notes**

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ABBREVIATIONS

IL, interfacial layer; SM, switching material; HRTEM, high-resolution transmission electron microscopy; Al, artificial intelligence; CBRAM, conductive bridge random access memory; a-C, amorphous carbon; CC, current compliance; CF, conducting filament; LTP, long-term potentiation; LTD, long-term depression; TE, top electrode; BE, bottom electrode; EDS, energy-dispersive X-ray spectroscopy; XPS, X-ray photoelectron spectroscopy; GOx, glucose oxidase; FFT, fast Fourier transformation; IFFT, inverse fast Fourier transformation; X-ray photoelectron spectroscopy; TiN, titanium nitride; NPs, nanocrystals; CNTs, carbon nanotubes; GCE, glassy carbon electrode; PN, porous nanostructures; ITO, indium tin oxide; CTS, chitosan.

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