

Reduced Stochastic Resistive Switching in Organic-Inorganic Hybrid Memristors by Vapor-Phase Infiltration

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Resistive random-access memory (RRAM) is promising for next-generation data storage and non-von Neumann computing hardware. However, tuning device switching characteristics and particularly, controlling their stochastic variation remain as critical challenges. Here, new organic-inorganic hybrid RRAM media are reported whose bipolar switching characteristics and stochasticity can be controlled by vapor-phase infiltration (VPI), an ex situ hybridization technique derived from atomic layer deposition. Hybrid RRAMs based on AlOx-infiltrated SU-8 feature facile tunability of device switching voltages, off-state current, and on-off ratio by adjusting the amount of infiltrated AlO_x in the hybrid. Furthermore, a significant reduction in the stochastic, cycle-to-cycle variations of switching parameters is enabled by AlO_x infiltration, driven by the infiltration-induced changes in mechanical, dielectric, and chemical properties of organic medium and their influence on the dimension and formation characteristics of conductive filaments. Finally, multi-level analog switching potentially useful for neuromorphic applications are demonstrated, along with direct, one-step device patterning exploiting the negative-tone resist feature of SU-8. With the demonstrated control over switching characteristics and stochastic variation, combined with analog switching and one-step patterning capabilities, the results not only present a novel hybrid medium for RRAM applications but also showcase the utility of VPI for developing new, high-performance hybrid RRAM devices.

1. Introduction

The advent of digital era has generated large amounts of data and information, resulting in the ever-increasing demand for ultrahigh-density data storage (UHDDS).^[1] In principle, this can be achieved by scaling down current Si-based memory cells and improving the device integration.^[2] However, the miniaturization by the existing microelectronics manufacturing capabilities is becoming increasingly challenging due

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to factors such as processing complexity, high fabrication cost, and high-power consumption.^[3] These limitations have encouraged the development of alternate information storage technology that can address the current technical constraints and eventually realize next-generation UHDDS.^[4] Among the various emerging non-volatile memory technologies, the resistive random-access memory (RRAM), or memristor, holds great potential for its excellent device performances including high storage capacity, stable data retention, excellent cycling stability, low power consumption, fast data transfer rate, short access time, multi-year retention, and scalability.^[5] A typical RRAM cell has a simple two-terminal structure consisting of solid electrolyte sandwiched by top and bottom electrodes and switch between high resistance state (HRS) and low resistance state (LRS) to store, retrieve, and erase information (i.e., resistive switching).^[6] They can be incorporated with existing 3D memory device architecture.^[7] such as the 3D stackable crossbar architecture which has an ideal memory cell area (4F², with F being the minimum feature size of the

chip manufacturing process) and enables high density data storage.^[7,8] RRAM technology is also promising for processing data within the memory (processing-in-memory architecture) and can significantly enhance memory speed and efficiency when handling large datasets.^[9]

Among the types of RRAM, the redox-process-based memory cells are most mature and typically rely on the formation of conductive filaments between the electrodes, mediated by electrochemical reactions occurring in conjunction with the motion of ions in ion-conductive materials.^[5c] Depending on ionic species that contribute to the filament formation, redox-based RRAM cells can be of two types, namely, the valence change memory (VCM) cells and the electrochemical metallization (ECM) cells. The VCM cell typically utilizes metal oxides, such as $TaO_{xp}^{[10]}$ TiO_x^[11] and HfO_x,^[12] as the resistive switching media and mobile ionic species in the host lattice, such as oxygen ion (i.e., oxygen anions) or metal cation, whose migration induces a local stoichiometry change and a redox reaction accompanied with a valence change in the cation sublattice, hence leading to a change in the electrical conductivity.^[5c]

ECM cells meanwhile use the oxidation and reduction of electrochemically active metal cations and their migration in

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the switching medium. Different kinetic factors of the material system, including ion mobilities and redox rates, give rise to different filament growth directions and switching properties,^[13] wherein the Gibbs free energy of formation for the metal cations is closely related with switching properties as well as reliability.^[14] Therefore, a wide variety of material combinations have been investigated to favorably control the interaction that occurs between switching medium and metal ions, and to tune the switching characteristics. Metals such as Ag, Cu, Al, Au, Fe, Ni, Ta, Ti, V, Zr, Ru, Pd, and Pt have been employed as electrodes for injecting cations, while inorganic materials including oxides (SiO₂, TaO₂, ZrO₂, HfO₂, TiO₂, WO₃, GeO₃₂ CuO/Cu2O), sulfides (Cu2S, Ag2S), iodides (RbAg4I4, AgI), selenides (GeSex), and tellurides (Cu-Ge-Te), have been investigated as switching media in ECM RRAM devices.^[8d] The summary of the memory properties of such systems can be found in recent review articles.^[6b,15]

More recently, organic and organic-inorganic hybrid materials have been given much attention as RRAM switching media because they can display tunable, mixed material properties and offer unique advantages such as flexibility, simple fabrication process, disposability, biocompatibility, and tunable memory properties achievable by changing the inorganic composition within the organic matrix.^[16] For instance, Kim et al. have shown configurable RRAM device using Au nanoparticle (NP)-egg albumin hybrid with low operating voltage (≈ 0.5 V), long data retention (>10⁴ s), and good endurance properties and reproducibility.^[17] Other notable developments also include perovskite NP-polyethylene oxide (PEO) hybrid memory devices with high on-off ratio,^[18] Ag NP-carboxymethyl: *κ*-carrageenan hybrid RRAMs demonstrating ultralow-power (≈0.35 µW) operation,^[19] inkjet-printing-based scalable PEO-AgClO₄ hybrid memory devices with reproducible performance,^[20] and methylammonium-bismuth iodide hybrid RRAMs featuring neuromorphic memory effects, mimicking synaptic plasticity and meta-plasticity.^[21]

Despite the advantages offered by the various ECM systems introduced above, many of them are generally plagued with stochastic variation in operating voltages ("SET" and "RESET" voltages (V_{SET} and V_{RESET})) that dictate device resistance states (LRS and HRS, respectively)), reliability (endurance and retention), and reproducibility (device-to-device variabilities), which are fundamentally caused by the random growth and rupture of conductive filaments.^[22] Accordingly, several strategies have been explored in various inorganic switching media to control and confine the conductive filament and make performance of RRAM more reliable and practical.^[23]

One approach is based on the electrode engineering. Liu et al., for instance, were able to control the Ag filament formation in ZrO₂ by decorating Pt bottom electrodes with Cu nanoclusters (CuNCs) that guide the Ag filament growth direction, demonstrating narrower V_{SET} and V_{RESET} distributions compared with control devices without CuNCs.^[24] Shin et al. also fabricated a pyramid-tip-structured Ag/Al₂O₃/Pt resistive switching device in which the Ag filament formation was spatially controlled near the pyramid tip, leading to low V_{SET} and V_{RESET} along with improved endurance and retention than the conventional planar geometry device.^[25] Similarly, insulating SiO₂ nanodots patterned by block copolymers between the top

Pt electrode and NiO switching medium in the Pt/SiO₂/NiO/Ni RRAM device was shown to reduce the standard deviation (SD) for V_{SET} and V_{RESET} by 77% and 60%, respectively with a 99% reduced SD for HRS compared to the base Pt/NiO/Ni device.^[26] Recently, Zhao et al. used a nanoporous graphene as an interlayer between the top Cu electrode and the HfO₂ switching medium to confine the formation of filament and thus improved the uniformity of HRS current level.^[27]

Another strategy being implemented is engineering the switching medium itself by either alloying elements, dispersing nanoparticles, or incorporating atomic-scale conduits that can control the filament formation and growth. For example, Yeon et al. recently have reported a dramatic reduction in the temporal (i.e., cycle-to-cycle) variation (relative SD) of $V_{\rm SET}$ from 16.4% to 3.3% when doping Cu in the Si resistive switching medium.^[28] Dispersing Ag nanoparticles into the BaTiO₃ switching medium was also shown effective in increasing the on-off ratio and decreasing the switching voltage.^[29] Furthermore, Choi et al. recently demonstrated physically confining the conductive filament growth in epitaxial SiGe through dislocations, reducing the absolute temporal variation in $V_{\rm SET}$ to as low as 1.7% and enabling improved neuromorphic device operation.^[30]

Similar to the inorganic RRAM devices, the stochasticity issues in the hybrid RRAM are primarily associated with the non-homogeneous size and spatial distributions of the inorganic elements within the organic matrix, which causes non-uniform electric field and, thus, affects the underlying electrochemical process. However, unlike inorganic RRAM devices wherein various approaches have been explored to mitigate the issue, there have been only a few reports that attempt to address the stochastic switching in the hybrid RRAM. For instance, Hong et al. have shown that the size of polypyrrole NPs embedded in poly(vinyl alcohol) (PVA) switching layers could control the switching characteristics by affecting the charge trapping.^[31] Kim et al. also demonstrated that the incorporation of poly(vinylpyrrolidone) (PVP) capping agent on Au NPs dispersed in the albumin-based hybrid switching media could improve the device switching variability by suppressing the physical agglomeration of the Au NPs.^[17] Developing further advanced strategies suitable for improving the control over the structural, physical, and chemical properties of hybrid switching media would enable further improved high-performance hybrid RRAMs with reliable and predictable memory characteristics.

Here, we report a novel hybrid switching media consisting of SU-8, a common negative-tone photoresist, hybridized with molecular network of AlO_x incorporated by vapor-phase infiltration (VPI),^[32] an emerging materials hybridization technique derived from atomic layer deposition (ALD), and demonstrate a facile tunability of device resistive switching parameters combined with a significantly reduced device operational stochasticity. Organic-inorganic hybrid materials generated by VPI have been studied for their mechanical,^[33] gas adsorption,^[34] molecular sieving,^[35] electronic doping,^[36] and triboelectric properties,^[37] but their application as an active component media in electronic devices has been rarely attempted.^[32c,d] The resulting hybrid RRAM device, comprising the AlO_x -infiltrated SU-8 hybrid doped with Ag perchlorate (AgClO₄), with Ag and



Pt top and bottom electrodes, featured actively tunable resistive switching parameters, such as the reduced magnitudes of required V_{SET} and V_{RESET} , and the decreasing HRS current level and concomitantly enhanced device on-off ratio, by controlling the amount of AlO_x infiltrated into SU-8 by up to 10 wt%. Significantly, the stochastic variations of the switching parameters could be decreased by the AlO_x infiltration, for example, reducing the SD of V_{SET} and V_{RESET} by 25% and 70%, to 40 and 25 mV, respectively, and the relative RSD of HRS current level to 17% (SD \approx 100 pA), which was accompanied by an ability to operate at lower SET compliance currents, reducing the required device operation power down to 15 μ W for 100 \times 100 mm² active area (i.e., 1.5 fW nm⁻²). Finally, we demonstrated a multilevel analog switching potentially suitable for neuromorphic applications by controlling the SET compliance current, as well as a direct, one-step lithographic patterning of the hybrid RRAM device by utilizing the negative-tone photoresist characteristics of SU-8. These results represent not only a novel strategy to control and address the resistive switching properties and their stochastic variation in hybrid memristors but also a new, scalably patternable hybrid RRAM system.

2. Results and Discussion

2.1. Optimization of the Switching Performance of Base SU-8Ag RRAM

Among the organic-based resistive switching devices, solid polymeric electrolyte (SPE) switching media generally display high resistance in natural form and an ability to support ionic transport under applied voltage. Here we use SU-8 as a base switching medium for its ability to support ionic conduction and facile lithographic patterning. SU-8 is a well-known, chemically amplified, negative-tone photoresist based on bisphenol-A novolac epoxy resin^[38] with eight epoxy (EO) units incorporated in its monomer (Figure 1a). Similar to PEO, a typical SPE matrix for various applications involving electrochemical processes including RRAM devices,^[20,39] the EO units in SU-8 are expected to be able to complex with alkali metal salts, promoting ionic conductivity as in the PEO mixed with AgClO₄.^[40] Furthermore, SU-8 can be directly patterned by either ultraviolet (UV) or electron-beam lithography with negative tone, providing additional advantages for device patterning and integration. Despite these potential benefits as a RRAM switching media, no report is available so far investigating the use of SU-8 or other equivalent photoresist systems for RRAM devices.

We first experimentally confirm the efficacy of the base SU-8 layer doped with $AgClO_4$ (SU-8_{Ag}) without AlO_x infiltration as an effective RRAM medium. The SU-8Ag device, based on a cross-point, metal/insulator/metal (MIM) structure, consists of a 30 nm-thick $SU-8_{Ag}$ layer sandwiched between bottom Pt (ground) and top Ag electrodes (Figure 1b,c). The resistive switching properties of SU-8_{Ag} were found to be strongly dependent on the doping concentration of AgClO₄ (0, 5, 10, and 15 wt% with respect to SU-8, mixed in the SU-8 solution, see Experimental Section for more details). Figure 2 shows typical direct-current (DC), current-voltage (I-V) cycling characteristics (from 0 to 10 to -10 V and to 0 V, applied on Ag electrode) at 250 mA current compliance (I_{CC}) . The pure SU-8 without any AgClO4 features low currents (<100 pA) with no discernable switching action within a ± 10 V bias window (Figure 2a). Only when the AgClO₄ concentration was increased to 5 wt%, the SU- 8_{Ag} device starts exhibiting a bipolar resistive switching within a ± 1.5 V window (Figure 2b), but, with a large variation in the HRS current level (I_{OFF}, Figure S1a, Supporting Information), indicating that the amount of AgClO₄ within the polymer matrix was insufficient to form a stable filament.

At 10 wt% AgClO₄ concentration, the SU- 8_{Ag} hybrid now showed a more consistent switching within a further reduced required switching voltage window (≈±0.8 V) during 100 repeated switching cycles (Figure 1c), which is accompanied by a significantly more consistent cycle-to-cycle *I*_{OFF} (Figure S1b, Supporting Information), evidenced by a steep rise of cumulative probability ($P_{\text{cumulative}}$) distribution and a drastic reduction in their statistical variation compared with the 5 wt% AgClO₄ case (Figure S1c,d, Supporting Information)-an indication of a stable filament formation. This also led to an excellent retention of both HRS and LRS during 100 reading cycles (using 10 mV reading voltage (V_{READ})) with ≈ 200 on-off ratio (Figure S2a, Supporting Information) and a temporal (cycle-to-cycle) variation of 0.91 and 0.069 for HRS and LRS current levels, respectively (Figure S1b, Supporting Information). A reasonable device-to-device (i.e., spatial) variation was also achieved among 10 separately tested devices (Figure S2b, Supporting Information) with 0.41 and 0.028 variation for HRS and LRS current levels. We note that the variations of currents are described using RSD (=SD/ μ , μ being mean value), which allows the comparison of the intrinsic spreads of different data sets, unlike SD whose comparison is not meaningful if the mean values of compared data sets are not in the same order of magnitude.



Figure 1. a) SU-8 monomer molecular structure. Schematics of: b) The fabricated hybrid RRAM device arrays, and c) the device cross-section.





Figure 2. Representative cyclic I-V switching characteristics of Ag/SU-8_{Ag}/Pt RRAM devices with varying AgClO₄ doping concentration: a) 0 wt%, b) 5 wt%, c) 10 wt%, and d) 15 wt%. Red traces denote the first sweep and grey in (b) and (c) 99 consecutive sweeps after the first sweep.

Overall, the results not only confirm the optimized base SU- 8_{Ag} is an effective resistive switching medium but also hint at the importance of controlling the filament formation for mitigating the switching stochasticity. Meanwhile, at 15 wt% AgClO₄ concentration, no resistive switching was observed, which is likely caused by the formation of a permanent percolative conductive network (Figure 1d).

While the optimized base SU-8_{Ag} hybrid RRAM device exhibits consistent I_{OFF} during repeated DC switching cycles, it still features a large variation in the device V_{SET} and V_{RESET} as evident in Figure 2c (i.e., varying grey I-V sweep traces). This is most likely originating from a non-uniform distribution of randomly mixed AgClO₄ in SU-8 matrix affecting a stochastic formation and a disruption of conductive filaments as shown previously in the albumin-based hybrid RRAM in which the agglomeration of Au NPs caused poor, inconsistent switching performance.^[17] We indeed confirm a non-uniform distribution of AgClO₄ in the SU-8 matrix by cross-sectional transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS), featuring a visible agglomeration of AgClO₄ (Figure S3, Supporting Information).

2.2. Stochastic Variation of the Resistive Switching Characteristics in AlO_x-Infiltrated SU-8_{Ag} Hybrid RRAM

We discover that the incorporation of molecular AlO_x network by VPI into the $SU-8_{Ag}$ matrix could not only significantly

suppress the variation of device switching parameters, including V_{SFT} and V_{RESET} , but also enable their control by adjusting the amount of infiltrated AlO_x . The infiltration of AlO_x into the SU-8_{Ag} matrix was implemented through the sequential exposure of trimethyl aluminum (TMA) and water vapors under a static vacuum in a commercial ALD system, with an intermediate N₂ purge step between the two precursor exposure steps (Scheme 1). During the infiltration process, Lewis-acidic TMA molecules are expected to bind to Lewis-basic moieties available in SU-8, such as EO groups^[41] or residual solvent molecules,^[42] and be converted to AlO_x during the following water vapor exposure step, with the total amount of infiltrated AlO_x controlled by the precursor exposure duration. As we have shown previously, a similar incorporation of metal oxides in SU-8 by VPI could lead to novel hybrid properties, including ultrahigh elastic energy storage capacity^[33c] and enhanced gravimetric chemical sensing capability,^[34] as well as the arbitrary patterning of metal oxide nanostructures and devices.[43]

2.2.1. Impact of Infiltration on the Stochastic Variation of I_{OFF} and I_{ON}

We find that the AlO_x infiltration into the $SU-8_{Ag}$ (10 wt% $AgClO_4$ unless specified otherwise hereon) switching medium gives rise to a significant impact on device operation variables, I_{OFF} , on-off ratio, and, most importantly, the variation of device switching parameters, as a function of the amount of infiltrated

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Scheme 1. Illustration of the process flow for generating AIO_x-infiltrated hybrid SU-8 RRAM media. a) Spin-coating of a 30 nm-thick SU-8_{Ag} layer. b) The first half cycle of VPI for infiltrating TMA molecules in the SU-8_{Ag} layer. c) The next half cycle of VPI infiltrating water molecules into the TMA-infiltrated SU-8_{Ao} layer to generate a molecular network of AlO_x imbedded in the SU-8_{Ao}. d) Potential binding reactions available between infiltrated AlO_x and SU-8 matrix, including reactions with epoxy (1), ether (2), and residual cyclopentanone (solvent) molecule (3).

 AlO_x controlled by the precursor exposure duration (100–400 s). For instance, while the base $SU-8_{Ag}$ device did not require a separate electroforming step for the formation of conductive filaments, the AlOx-infiltrated SU-8Ag device did so under I_{CC} of 100 μ A (Figure S4a–c, Supporting Information), where the I_{OFF} at $V_{READ} = 10$ mV (before the electroforming step) was only sub-100 pA regardless of the AlO_x infiltration duration (amount), in contrast to $I_{\rm OFF}$ of >10 nA in the base SU-8_{Ag} hybrid without infiltration. The RSD of IOFF determined from 10 different devices (i.e., spatial variation) immediately after the forming process also decreased down to 0.645 after 100 s AlO, infiltration from 1.198 of the non-infiltrated control (Figure S4d, Supporting Information), the first sign of the alleviation of the device switching stochasticity by the AlO_x infiltration. Similarly, AlO_x infiltration for 200 s and 400 s led to a decrease in the spatial RSD of I_{OFF} after the forming process to 0.634 and 0.577, respectively (Figure S4d, Supporting Information).

In the meantime, the I_{OFF} of the SU-8_{Ag} memory cell after the electroforming process decreased as a function of AlO_x infiltration amount as clearly visible in the representative DC switching I-V characteristics and the I_{OFF} and LRS current level $(I_{\rm ON})$ obtained at $V_{\rm READ}$ = 10 mV during 100 DC switching cycles (Figure 3a-d). Specifically, the I_{OFF} decreased from 100 nA down to 10 pA as the AlO_x infiltration duration increased from 0 s to 400 s, thus by approximately a decade decrease in I_{OFF} per 100 s increase in AlO_x infiltration duration. Since the I_{ON} is dictated by the prescribed I_{CC} (100 mA), the decreasing I_{OFF} also leads to a commensurate increase in the device on-off ratio, from 100 of the base $SU-8_{Ag}$ device without infiltration up to 10^6 at 400 s AlO_x infiltration duration, thus marking a four-decade increase.

We find that the AlO_x infiltration, under an optimized amount, reduced the variation of switching parameters in the hybrid SU-8_{Ag} memory device as evidenced by decreasing SD and RSD of I_{OFF} with increasing AlO_x infiltration duration (Figure 3e,f), the SD value decreased monotonously by orders of magnitude (from $\approx 10^{-8}$ to $\approx 10^{-11}$) with increasing infiltration time up to 400 s as shown in Figure 3e. Again, the comparison of intrinsic spreads of I_{OFF} for different conditions is possible by comparing RSD, the RSD decreased from 0.911 of the base hybrid SU-8_{Ag} to 0.621 after 100 s AlO_x infiltration and further to 0.532 after 200 s infiltration (Figure 3f), indicating a reduced degree of stochastic switching. However, extending the AlO_x infiltration duration to 400 s rather increased the RSD of I_{OFF} to 0.802 (Figure 3f). We attribute this to the low measured I_{OFF} (≈pA) that is increasingly comparable to the instrumental noise under the fast current measurement condition used. Meanwhile, the changes of SD and RSD of I_{ON} were relatively minor with respect to AlO_x infiltration duration (Figure S5, Supporting Information). The observed reduction in the RSD of I_{OFF} in response to the varied AlO_x infiltration amount (at least up to 200 s infiltration) is indicative of infiltrated AlO_x affecting the physical properties of the SU-8 organic matrix and, subsequently, Ag filament formation within the SU-8 matrix, which we will discuss in detail in a later section.

2.2.2. Impact of Infiltration on the Stochastic Variation of V_{SET} and V_{RESET}

The VSET and VRESET of RRAM are other important device switching parameters whose stochastic variation is desired and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons







Figure 3. a) Representative cyclic *I*–*V* switching characteristics of AlO_x-infiltrated SU-8_{Ag} (10 wt% AgClO₄) RRAM with varying AlO_x infiltration duration, from 0 s (red), 100 s (green), 200 s (orange), and to 400 s (blue). HRS and LRS current levels (I_{OFF} and I_{ON}) determined from 100 consecutive switching cycles of AlO_x-infiltrated SU-8_{Ag} hybrid RRAM with varying AlO_x infiltration duration from b) 100 s to c) 200 s and to d) 400 s. e) Temporal (cycle-to-cycle) SD of I_{OFF} . f) Temporal RSD of I_{OFF} as a function of AlO_x infiltration duration.

to be reduced. We find that AlO_x infiltration into the SU-8_{Ag} also significantly reduced the variation of V_{SET} and V_{RESET}. At the outset, the V_{SET} required for the initial electroforming of a conductive filament (V_{SET,forming}) increased with increasing AlO_x exposure duration (Figure S6a,b, Supporting Information), from ~0.2 V of the un-infiltrated base SU-8_{Ag} to ~1 V for either 100 s or 200 s AlO_x infiltration duration and finally up to ~10 V after 400 s AlO_x infiltration implicates an infiltration of more robust and continuous AlO_x network within the SU-8 matrix interferes with the initial formation of Ag conductive filaments. Similarly, the magnitude of V_{RESET,forming}) increased, but, modestly from around -0.4 to -0.7 V after 400 s AlO_x infiltration).

Intriguingly, after the very first electroforming cycle of the AlO_x-infiltrated SU-8_{Ag} device, the actual V_{SET} and V_{RESET} required for the following memory device operation decreased with increasing AlO_x infiltration duration, which was accompanied by drastically reduced cycle-to-cycle variations: As evident in **Figure 4**a, V_{SET} measured during 100 DC switching cycles decreased from ~0.3 V down to ~0.15 V with an apparently reduced width of V_{SET} distribution as the AlO_x infiltration duration, especially for 400 s. The corresponding rise of $P_{\rm cumulative}$ distribution was therefore rendered steeper by the AlO_x infiltration, especially for 400 s duration (Figure 4b). Consequently, the cycle-to-cycle SD of V_{SET} is reduced to ~40 mV after 400 s AlO_x infiltration, compared with ~53 mV of non-infiltrated base SU-8_{Ag} device (Figure 4b). As shown in Figure 4c, the AlO_x infiltration also decreased the magnitude







Figure 4. Temporal (cycle-to-cycle) variance of V_{SET} and V_{RESET} of the AlO_x-infiltrated SU-8_{Ag} (10 wt% AgClO₄) RRAM devices with varying AlO_x infiltration duration (0–400 s). a) Distribution of V_{SET} and b) corresponding $P_{\text{cumulative}}$ distribution and absolute SD. c) Distribution of V_{RESET} and d) corresponding $P_{\text{cumulative}}$ distribution and absolute SD. c) Distribution of V_{RESET} and d) corresponding $P_{\text{cumulative}}$ distribution and absolute SD. c) Distribution of V_{RESET} and d) corresponding $P_{\text{cumulative}}$ distribution and absolute SD.

of V_{RESET} from -0.23 V of the un-infiltrated control to -0.14 to -0.15 to -0.17 V after the AlO_x infiltration for 100 s, 200 s, and 400 s, respectively, while suppressing its variability significantly, it not only eliminated the bimodal distribution of V_{RESET} of the base SU-8_{Ag} but also significantly reduced the SD of V_{RESET} from ≈88 mV of the base SU-8_{Ag} device to ≈25 mV after AlO_x infiltration regardless of the infiltration duration (Figure 4d).

2.3. Fundamental Origin of the Infiltration-Induced Variation in Switching Parameters

So far, we have clearly demonstrated the drastic impacts of AlO_x infiltration on the switching characteristics of $SU-8_{Ag}$ RRAM and their stochastic variation. Next, we investigated the fundamental causes of such impacts by combining physico-chemical





and structural characterizations of the AlO_x-infiltrated SU-8_{Ag}. First, we quantified the amount of infiltrated AlO_x for each AlO_x infiltration duration by using the in situ quartz crystal microbalance (QCM) measurement performed during VPI (see Experimental Section for more details). The QCM measurement confirmed the increasing AlO_x mass gain in the SU-8_{Ag} hybrid with increasing AlO_x infiltration duration, the mass uptake caused by the incorporation of AlO_x in the SU-8 matrix increased from 1.08 to 1.21 and to 1.37 µg cm⁻² as the infiltration duration extended from 100 s to 200 s and to 400 s (**Figure 5**a).

The temporal mass gain and chamber pressure profiles measured during the VPI of AlO_x (Figure 5b–d) showed the predominant mass gain (≈92% of the final mas gain) was reached during the TMA exposure regardless of the infiltration duration, consistent to the typical behavior observed during VPI in SU-8^[42] and other polymers with similar reactive moieties.^[41,44] Considering the molecular weight of TMA (114.18 g mol⁻¹) and the initial thickness of base SU-8_{Ag} layer (≈33 nm), the mass gain of 1 µg cm⁻² would correspond to the sorption of ≈1.6 TMA molecules nm⁻³ in SU-8_{Ag}. We also find that the

infiltration of AlO_x accompanies a swelling of the SU-8_{Ag} film. The cross-sectional TEM of AlO_x-infiltrated SU-8_{Ag} films clearly showed that the film thickness increased by up to $\approx 24\%$, from 33 to 41 nm as the AlO_r infiltration duration extended from 0 s to 400 s (Figure 5a,e). We expect that the observed AlO_x -infiltration-induced thickness change was most likely a minor factor on the switching properties, previous reports have shown that the resistive switching characteristics of organic-based hybrid memristors remained nearly unchanged unless there was a large thickness increase, up to over a few folds. For instance, Ling et al. found no difference in the switching characteristics of polyvinylcarbazole (PVK) based devices when the active layer thickness was varied between 25 and 360 nm,[45] and similar observations have been reported for memristors based on mixed biopolymers^[46] and PEO.^[20] Rather, it was the property modification in the hybrid medium itself, such as moisture content, inorganic concentration, and the presence of stabilizers,^[20,39b,47] that led to a significant change in the device resistive switching characteristics. Considering these, we expect the change in other physical properties of SU-8 matrix, induced



Figure 5. a) Variation of mass gain (red) and thickness (blue) of AlO_x -infiltrated SU-8_{Ag} with respect to the VPI exposure duration. Temporal mass gain (red) and pressure (blue) profiles during VPI of AlO_x in SU-8_{Ag} for varying infiltration exposure duration: b) 100 s, c) 200 s, and d) 400 s. e) Cross-sectional TEM micrographs of AlO_x -infiltrated SU-8_{Ag} hybrids (0 s, 100 s, 200 s, and 400 s, from left to right). All scale bars denote 10 nm.

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Figure 6. Schematic illustration of conductive filament formation during: a) forming process and b) post-forming switching processes. It is noted that both red and yellow spheres indicate Ag atoms. The different colors are chosen to differentiate the segment of filament that participates in the post-forming SET and RESET processes.

by the AlO_x infiltration, to have more critical influences. In the following, particularly we consider the modification of dielectric constant and mechanical modulus of SU-8 affecting the resistive switching characteristics by influencing the formation of conductive filaments and their dimensions.

We hypothesize that I_{ON} (at $V_{READ} = 10 \text{ mV}$) after the initial electroforming step is directly dependent on the dimension of a single conductive filament controlled by the mechanical modulus and free volume of the infiltrated hybrid matrix. The initial electroforming of ECM-based RRAM devices is likely initiated by the random nucleation of multiple filaments at the bottom electrode (Figure 6a, first and second panels). However, the subsequent competitive growth of these filaments, enabled by the supply of Ag⁺ ions electromigrated from the top electrode by electric field, cannot be uniform because any fluctuations of filament growth rate will render the electric field concentrated on the tallest filament at any given moment, accelerating the supply of Ag⁺ ion toward the filament, leading to its dominant growth over others. Eventually, this single filament will be connected to the top electrode, stopping the growth of other shorter filaments due to the absence of electric field (i.e., the top and bottom electrodes are now short-circuited). This now creates the first SET state of the memristor (Figure 6a, second and third panels). When the bias is reversed, it would be again this single filament that ruptures to bring the device to the RESET state (Figure 6a, fourth panel).

After the initial forming processes described above, the subsequent device SET switching is driven by the reconnection of the ruptured, two ends of the filament since the electric field is most concentrated due to the shortest distance (Figure 6b first panel, depicted by yellow spheres). This explains why the post-forming V_{SET} is smaller than $V_{\text{SET,Forming}}$ as observed in our data. The following RESET switching is again realized by the re-rupture of this filament (Figure 6b second panel). It is noted that there exist previous studies that have suggested multiple filaments or conductive channels may contribute to the memristor device operation, which generally manifests itself by a gradual device RESET.^[10a,46] In our study, the un-infiltrated base SU-8_{Ag} system did display a gradual RESET (Figure 2c) indicating the possible presence of multiple filaments or conducting channels, but the AlO_x-infiltrated hybrid SU-8_{Ag} memristor showed an abrupt, not gradual, RESET characteristic (Figure 3a), strongly supporting that the resistive switching action in the AlO_x-infiltrated hybrid memristor was controlled by a single filament.

Considering a single filament is responsible for the device switching operation, the filament diameter (d) can be estimated based on the device I_{ON} read at $V_{READ} = 10$ mV because it determines corresponding $R_{\rm ON}$ via $R_{\rm ON} = V_{\rm READ}/I_{\rm ON}$, and, thus, d via $R_{\rm ON} = \rho L / \pi (d/2)^2$ with ρ being Ag resistivity at room temperature ($\approx 1.6 \times 10^{-8} \Omega \text{ m}^{-1}$) and *L* being SU-8 film thickness. The Ohmic relation between V_{READ} and I_{ON} is supported by the clearly linear device switching I-V characteristics observed during SET and RESET operations, as evidenced by the near unity slope in double-logarithmic I-V plots at the low bias range for all the AlO_x infiltration durations (Figure S7, Supporting Information). We find that the average R_{ON} determined from I_{ON} was increasing up to $\approx 1.4 \text{ k}\Omega$ after AlO_x infiltration for 400 s, compared with ${\approx}1~k\Omega$ of the un-infiltrated control (Figure 7a)—a 40% increase that cannot be fully accounted for by the 24% increase in L after infiltration. The calculated average d appears to be decreasing from 1.04 to 0.88 nm with increasing amount of AlO_x infiltration (Figure 7b), which alone would account for $\approx 40\%$ increase in $R_{\rm ON}$. We note that there was a large statistical variation in the determined d (Figure 7b), which is likely influenced by a non-uniform d of a filament along the film thickness in reality. Despite the uncertainty in comparing absolute values, these observed qualitative trends nevertheless are consistent to the notion that the infiltrated AlO_x was influencing the dimension of the formed conductive



www.advelectronicmat.de C) a) 1.8 b) TMA/H₂O 1 12 10 Exposure Time: 16 0 s 1.04 $R_{\rm ON}~(\kappa\Omega)$ d (nm) I_{OFF} (A) 14 100 s 10-6 200 s 0.96 1.2 300 s0.88 10-1 1.0 0.80 0.8 10-13 0.3 0.6 0.9 0.0 1.2 1.5 0.3 0.6 0.9 ^{2.2} ^{2.4} *E*_v (GPa) 0.0 1.2 1.5 2.0 2.6 Mass Gain (µg/cm²) Mass Gain (µg/cm2)

Figure 7. The effect of the varying amount of infiltrated AlO_x (mass gain) controlled by infiltration duration on a) R_{ON} ($V_{READ} = 10 \text{ mV}$), b) estimated conductive Ag filament diameter, d, and c) I_{OFF} of the SU-8_{Ag} RRAM.

filament, such as L and d, consequently affecting the device switching characteristics.

In general, as the amount of infiltrated inorganic component increases, a hybrid medium generated by VPI becomes denser due to the occupation of the free volume of organic matrix by the infiltrated inorganic component,^[48] likely reducing the volume available for the conductive filament formation during the device resistive switching. In addition, the hybrid medium will be rendered mechanically stiffer, increasing Young's modulus (E_y) and yield strength (s_y) as we have shown previously for the AlOx-infiltrated SU-8.^[33c] For example, based on the Halpin-Tsai model that correlates E_v with the inorganic volume fraction in an organic-inorganic hybrid nanocomposite, $[^{33c]}E_{y}$ is expected to increase by 30% from ≈2 GPa of pure SU-8 to \approx 2.6 GPa after 400 s AlO_x infiltration (Figure S8, Supporting Information). Similarly, the overall electrical resistivity of the hybrid medium is likely increasing with increasing amount of infiltrated AlO_x, which would explain the large decrease (four decades) in I_{OFF} under HRS after 400 s AlO_x infiltration (Figure 7c).

Other important aspects of the AlO_x-infiltrated SU-8 hybrid medium that could have influenced the memristor switching parameters, particularly V_{SET} and V_{RESET} are the intertwined effects of the modified dielectric properties of the hybrid, combined with the change in electrochemical processes affected by the presence of hydroxyl ions present in the AlO_x-infiltrated SU-8 matrix. Considering the experimentally measured amount (mass gain) of infiltrated AlO_x, the effective relative dielectric constant of the AlO_x-infiltrated SU-8 matrix (ε_{eff}) can be estimated using the Maxwell-Garnett mixing rule:^[49]

$$\varepsilon_{\rm eff} = \varepsilon_{\rm SU8} + 3 f \varepsilon_{\rm SU8} \frac{\varepsilon_{\rm AIO_x} - \varepsilon_{\rm SU8}}{\varepsilon_{\rm AIO_x} + 2\varepsilon_{\rm SU8}} \tag{1}$$

where *f* is volume fraction of infiltrated AlO_x in SU-8 matrix (deduced from the measured mass gain), and ε_{AlO_x} and ε_{SU8} the nominal dielectric constants of AlO_x and SU-8, respectively ($\varepsilon_{AlO_x} \approx 9.34$ and $\varepsilon_{SU8} \approx 3$). We find that ε_{eff} would increase by $\approx 12\%$, from 3 to 3.37, as the AlO_x infiltration exposure duration (i.e., the amount of AlO_x infiltrated into SU-8) increases to 400 s (mass gain of ≈ 1.37 mg cm⁻²), a natural trend given the higher dielectric constant of AlO_x compared with SU-8. This

increase in ε_{eff} in principle should facilitate the electrochemical reduction of Ag⁺ to Ag (i.e., conductive filament growth) and its reverse process (oxidation, i.e., filament disruption) due to an increased capacitance (C_h) of the hybrid media (i.e., $C_h \propto \varepsilon_{\text{eff}}$) that leads to a greater amount of charge (Q_h) available for completing the electrochemical reactions for a given applied bias. For example, if Q_c is the critical amount of charge required for the electrochemical formation (or disruption) of a conductive filament, V_{SET} (or V_{RESET}) would decrease as $\varepsilon_{\text{reff}}$ increases (e.g., $V_{\text{SET}} = Q_c / C_h \propto 1/\varepsilon_{\text{eff}}$). For the 12% increase in ε_{eff} after 400 s AlO_x infiltration in SU-8, this would correspond to a commensurate 12% decrease in V_{SET} observed in the experiment after 400 s AlO_x infiltration (from 0.3 to 0.15 V).

We expect the remainder of the V_{SET} (or V_{RESET}) reduction is caused by the presence of hydroxyl ions (-OH) generated during the AlO_x infiltration into SU-8, the AlO_x infiltration based on the sequential exposure of TMA and water results in the formation of aluminum hydroxide (Al(OH)₃) via, for example, the following reaction: Al(CH₃)₂ + 2H₂O \rightarrow $Al(OH)_2 + 2CH_4$, where one of the three methyl groups of the starting TMA is assumed to be reacted with SU-8, similar to the reaction of diethylzinc with SU-8 during ZnO infiltration.^[42] It is well known that hydroxyl ions can enhance the switching dynamics of a hybrid memristor by affecting the oxidation rate and cation mobility that control the electrochemical processes preceding the resistive switching.^[50] Additionally, they can act as charge carriers, increasing the total conductivity of the switching media, hence decreasing V_{SET} required for turning the memristor device on.^[47e,51] While the overall discussions provided above addressed why the device switching characteristics in SU-8_{Ag} hybrid memristors could be controlled by the AlO_x infiltration, the exact origin of the reduced stochastic variation in switching parameters by the infiltration remains unclear. We suspect the discussed, reduced free volume and increased mechanical stiffness of SU-8 after AlO_x infiltration as the most likely factors associated with the observed reduced stochastic switching because they can directly regulate the conducive filament formation. Examining such possibilities would require more dedicated experimental investigation preferably complemented by computational modeling, which is out of scope of the current work.

2.4. Multi-Level Resistive Switching and Direct Patternability of AIO_x -Infiltrated SU-8_{Ag} Hybrid RRAM

One of the most important emerging applications of RRAM is the artificial, analog synaptic switching device toward the lowpower neuromorphic computing.^[52] Such synaptic devices must support a multi-level resistive switching behavior to store more than two data levels in one cell and thus increase the memory capacity.^[12b,53] We confirmed that the AlO_x -infiltrated SU-8_{Ag} hybrid memristor could support the multi-level switching by controlling the I_{CC} imposed during the device SET operation. In particular, we obtained five distinct LRS levels by using I_{CC} of 1 mA, 500, 250, 100 or 10 μ A in the 200 s AlO_x-infiltrated SU-8_{Ag} RRAM (Figure 8a). The resistance of HRS ($V_{\text{READ}} = 10 \text{ mV}$) was nearly unaffected by different I_{CC} only with a minor fluctuation, but the LRS resistance ($V_{READ} = 10 \text{ mV}$) clearly increased in response to the decreased I_{CC} , demonstrating the tunability of the LRS level and, thus, the multi-level LRS (Figure 8b). A stable retention of these data states was also identified, as the device could well distinguish the five LRS levels without any sign of degradation during a continuous 2000 s reading operation (Figure 8c,d). Since the multi-level switching was controlled by varying current compliance (I_{CC}) imposed on the device SET operation during which the supplied current is used to reduce Ag+ cations to bridge a ruptured portion of a filament, I_{CC} essentially controls how many Ag⁺ ions are reduced and, therefore, the resulting diameter of the reconnected segment (Figure S9a, Supporting Information; left panel), as $I_{\rm CC}$ increases, so would the diameter of the newly formed filament segment (Figure S9a, Supporting Information; right panel). Indeed we find that the filament diameter *d* increased monotonically from \approx 0.18 nm at $I_{\rm CC}$ = 10 µA to \approx 2 nm at $I_{\rm CC}$ = 1 mA (Figure S9b, Supporting Information).

Finally, we demonstrate the facile one-step lithographic patterning capability of the AlOx-infiltrated SU-8Ag hybrid RRAM device utilizing the negative-tone resist characteristics of SU-8 matrix. The patterning of conventional RRAM media, such as inorganic metal oxides, typically involves multiple process steps consisting of, for example, a lithographical patterning of photoresist mask (or more added steps for creating a hard mask), its transfer to the RRAM media by certain etching processes (e.g., reactive ion etching), and the removal of the remaining mask, again, by etching processes. To fabricate patterned AlOx-infiltrated SU-8Ag RRAM devices, we first imparted the negative tone in SU-8 (i.e., cross-linkable by photon or electron exposure) by adding a photoacid generator (PAG), triarylsulfonium hexafluoroantimonate salt (10 wt% with respect to SU-8), into SU-8 $_{Ag}$ in solution, which was spin-cast on a base device substrate with pre-patterned Pt electrode. The spincast SU-8Ag layer was then patterned via ultraviolet (UV) light exposure using a shadow mask and solution development, followed by the AlO_x infiltration by VPI and the deposition of Ag top electrode through a shadow mask, completing the device fabrication (Figure 9a). The patterned, AlO_x -infiltrated (100 s)



Figure 8. a) Representative *I*–V switching characteristics of the AlO_x-infiltrated SU-8_{Ag} RRAM (10 wt% AgClO₄ and 200 s AlO_x infiltration) during the setting process under different I_{CC} of 1 mA (dark green), 500 μ A (magenta), 250 μ A (blue), 100 μ A (red), and 10 μ A (black). b) Multi-level LRS resistances, with a nearly constant HRS resistance, obtained during 25 consecutive switching cycles by varying I_{CC} . At every five switching cycles, I_{CC} was increased with I_{CC} values. c) Retention characteristics of multi-level data states of during a 2000 s reading operation. d) Magnified retention characteristics shown in (c) for I_{CC} of 1 mA (dark green), 500 μ A (magenta), 250 μ A (blue), and 100 μ A (red).





SU-8_{Ag} RRAM showed the device *I*–*V* switching characteristics (Figure 9b) similar to those of the non-patterned (uncross-linked) counterpart without PAG we have discussed earlier, it featured the initial $V_{\text{SET,forming}} \approx 1.5$ V, which was accompanied by $V_{\text{SET}} \approx 0.24 \pm 0.049$ V and $V_{\text{RESET}} \approx -0.18 \pm 0.033$ V (measured during 100 consecutive switching cycles) (Figure 9c), with stable I_{ON} and I_{OFF} (on-off ratio ≈ 2400) (Figure 9d) as well as the multi-level switching controlled by varying I_{CC} (Figure 9e,f).

We note that PAG is a charged molecule and potentially can have influences on the memristor device characteristics. In our experiment, we find that for the PAG concentration (10 wt%) needed for a complete crosslinking of SU-8 (see Table S1, Supporting Information), there was a negligible difference in the device switching parameters when compared with the uncrosslinked counterpart. To clearly demonstrate this, we have tested both crosslinked and un-crosslinked SU-8_{Ag} memristors infiltrated with AlO_x (100 s exposure duration) and found that all switching parameters, including I_{ON} , I_{OFF} , V_{SET} , and V_{RESET} values, were very similar each other, except that I_{OFF} in the un-crosslinked device was somewhat noisier compared to the crosslinked counterpart (Figure S10a,b, Supporting Information). Furthermore, both devices could operate at various current compliances (Figure S10c,d, Supporting Information), demonstrating a similar capability for multi-level switching



Figure 9. a) Top-view optical micrographs of a fabricated AlO_x-infiltrated SU-8_{Ag} RRAM device array and a magnified patterned device area (100 s AlO_x infiltration, 10 wt% AgClO₄, 100 μ m electrode width). b) Representative cyclic *I*–V switching characteristics of a patterned AlO_x-infiltrated SU-8_{Ag} RRAM displaying the initial electroforming and the following 100 cycles of the set-reset switching operation. c) Histograms depicting the temporal (cycle-to-cycle) variations of V_{SET} and V_{RESET} of the patterned AlO_x-infiltrated SU-8_{Ag}. d) LRS and HRS currents levels (*I*_{ON} and *I*_{OFF}) of the patterned AlO_x-infiltrated SU-8_{Ag} RRAM measured during 100 consecutive switching cycles. e) Representative *I*–V switching characteristics of a patterned AlO_x-infiltrated SU-8_{Ag} RRAM during the setting process under different *I*_{CC} of 1 mA, 500, 250, 100, and 10 μ A. f) Retention characteristics of multi-level data states of a patterned AlO_x-infiltrated SU-8_{Ag} RRAM during a 2000 s reading operation (at *V*_{READ} = 10 mV).

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(Figure S10e,f, Supporting Information). Overall, these show that PAG had negligible impact on the AlO_x -infiltrated SU-8_{Ag} hybrid memristor, thus enabling the direct one-step patterning. As to the higher measurement noise in I_{OFF} for the un-crosslinked device, it is most likely attributed to the lower mechanical hardness of the un-crosslinked SU-8 and its larger mechanical deformation exerted by an electrical prober, which is known to be able to affect the stability of electrical probing on memristor devices.^[54]

3. Conclusion

In summary, we have developed a novel AlO_x -infiltrated SU-8_{Ag} hybrid RRAM switching medium using VPI hybridization technique and demonstrated a facile tunability of device resistive switching parameters combined with a significantly reduced device operational stochasticity, a multi-level analog switching, and a one-step lithographic patternability. We first confirmed the feasibility of the base SU-8 as an effective organic medium that could support the resistive switching when an optimized amount of AgClO₄ (10 wt%) was added. We discovered that the following incorporation of molecular network of AlO_x into the SU-8_{Ag} hybrid RRAM matrix by VPI led to not only an active control over device switching parameters, such as the reduced magnitudes of VSET, VRESET, and IOFF, and the increased on-off ratio with respect to the AlO_x infiltration amount, but also a significant reduction in their stochastic variations, as exemplified by the reduction of the variabilities (SD or RSD) of V_{SET} , V_{RESET} , and I_{OFF} by 25%, 70%, and 74%, respectively, compared with the un-infiltrated base $SU-8_{Ag}$ RRAM. The achieved tunability and reduced variation of device resistive switching characteristics were attributed to the AlO_x-infiltration-induced, physicochemical changes of the SU-8 organic matrix that affected the Ag conductive filament formation characteristics and dimension, including active hybrid layer thickness, mechanical modulus, and dielectric constant. Finally, we showcased a multi-level analog switching capability as well as a convenient, one-step direct lithographic patterning of the AlO_x-infiltrated SU-8_{Ag} hybrid RRAM device by exploiting the negative-tone resist nature of SU-8. The results not only deliver a novel hybrid RRAM medium with controllable switching characteristics and significantly reduced variability but also highlight the potentials of combining conventional polymeric resist materials and the VPI process for developing scalable, new class of highperformance hybrid RRAM materials for future memory and computing applications.

4. Experimental Section

Device Fabrication: Devices with 100 \times 100 μm^2 active areas were fabricated using the cross-point architecture on SiO₂ (300 nm)/Si substrates following the steps shown in Figure S11, Supporting Information. Cr/Pt (20 nm/20 nm) bottom electrodes were deposited by electron-beam evaporation through a shadow mask. 1 wt% SU-8 solution (in cyclopentanone) with varying concentrations of AgClO₄ (0, 5, 10, and 15 wt% with respect to the polymer) was spin-cast on the base device substrate to form a SU-8_{Ag} film with ~30 nm thickness (measured by an interferometer (Filmetrics)). Next, the AlO_x VPI was applied to SU-8_{Ag} as

described below. Finally, Ag top electrodes (50 nm thick) capped with a protective Ti/Au (15/10 nm) layer were deposited by thermal evaporation through a shadow mask.

 AlO_x VPI: AlO_x was infiltrated into the SU-8_{Ag} thin film via VPI process using a commercial ALD system (Cambridge Nanotech, Savannah S100) at 85 °C. TMA and water were used as Al and O precursors, respectively. A single AlO_x infiltration cycle was applied to the SU-8_{AG} film with varying TMA and water exposure times (100, 200, or 400 s). The infiltration protocol consists of a) TMA exposure under a static vacuum (~13 Torr), b) chamber purging by N₂ (100 sccm) for 100 s, c) water exposure under a static vacuum (~35 Torr), d) chamber purging by N₂ (100 sccm) for 100 s.

Materials Characterization: The as-AlO_x-infiltrated SU-8_{Ag} hybrid films were characterized using TEM (JEOL 2100, 200 kV), and scanning TEM (FEI Talos F200X, 200 kV, equipped with the energy dispersive spectroscopy (EDS) elemental mapping capability). The cross-sectional TEM samples were prepared by using a standard in situ lift-out procedure using Ga ion milling in a focused ion beam system (FEI Helios 600 Nanolab).

Patterning of SU-8_{Ag}: To enable negative-tone photo-induced crosslinking of SU-8 matrix, a PAG, triarylsulfonium hexafluoroantimonate salt (Sigma Aldrich), was mixed with SU-8_{Ag} (10 wt% of SU-8) in cyclopentanone. The solution was spin-cast on the base device substrate with pre-patterned bottom Cr/Pt electrode to form a ~30 nm thick SU-8_{Ag} film with PAG and exposed to ultraviolet (UV) light through a shadow mask for 5 min under N₂ using a UV light chamber equipped with a lowpressure mercury lamp (American Ultraviolet Co.), followed by the postexposure thermal bake for 5 min at 95 °C in ambient air. After the baking step, the unexposed hybrid film regions were removed by rinsing in the film in cyclopentanone. The patterned SU-8_{Ag} was then subjected to the AlO_x VPI and/or the Ag top electrode deposition as described earlier.

Electrical Characterization: The electrical properties of the fabricated hybrid RRAM devices were measured by a semiconductor parameter analyzer (4156C, Agilent) at room temperature in ambient air. During the measurement, the top Ag electrode was biased against the bottom Pt electrode, which was grounded.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

A.S. and C.-Y.N. perceived the concept. C.-Y.N. supervised the project and data analysis. A.S. performed the synthesis of hybrid resistive media, device fabrication, electrical characterization, and data analysis. N.T. assisted the device fabrication. K.K. performed the TEM characterization. A.S. and C.-Y.N. cowrote the manuscript. All authors reviewed and finalized the manuscript. ADVANCED SCIENCE NEWS

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

hybrid, memristor, photoresist, stochastic switching, vapor-phase infiltration

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- [1] C. L. Philip Chen, C.-Y. Zhang, Inf. Sci. 2014, 275, 314.
- [2] J. Kim, A. J. Hong, S. M. Kim, K. S. Shin, E. B. Song, Y. Hwang, F. Xiu, K. Galatsis, C. O. Chui, R. N. Candler, S. Choi, J. T. Moon, K. L. Wang, *Nanotechnology* **2011**, *22*, 254006.
- [3] a) E. P. DeBenedictis, Computer 2019, 52, 114; b) R. F. Service, Science 2018, 361, 321.
- [4] Y. Li, Q. Qian, X. Zhu, Y. Li, M. Zhang, J. Li, C. Ma, H. Li, J. Lu, Q. Zhang, InfoMat 2020, 2, 995.
- [5] a) R. Waser, M. Aono, *Nat. Mater.* 2007, *6*, 833; b) F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, *Mater. Sci. Eng.*, *R* 2014, *83*, 1; c) R. Dittmann, J. P. Strachan, *APL Mater.* 2019, *7*, 110903; d) Y. Li, Z. Wang, R. Midya, Q. Xia, J. J. Yang, *J. Phys. D: Appl. Phys.* 2018, *51*, 503002.
- [6] a) J. J. Yang, M. D. Pickett, X. Li, D. A. A. Ohlberg, D. R. Stewart, R. S. Williams, *Nat. Nanotechnol.* 2008, *3*, 429; b) R. Waser, R. Dittmann, G. Staikov, K. Szot, *Adv. Mater.* 2009, *21*, 2632; c) D. S. Jeong, R. Thomas, R. S. Katiyar, J. F. Scott, H. Kohlstedt, A. Petraru, C. S. Hwang, *Rep. Prog. Phys.* 2012, *75*, 076502; d) H. Akinaga, H. Shima, *Proc. IEEE* 2010, *98*, 2237.
- [7] J. Y. Seok, S. J. Song, J. H. Yoon, K. J. Yoon, T. H. Park, D. E. Kwon, H. Lim, G. H. Kim, D. S. Jeong, C. S. Hwang, *Adv. Funct. Mater.* 2014, *24*, 5316.
- [8] a) C. Kügeler, M. Meier, R. Rosezin, S. Gilles, R. Waser, Solid-State Electron. 2009, 53, 1287; b) G. C. Adam, B. D. Hoskins, M. Prezioso, F. Merrikh-Bayat, B. Chakrabarti, D. B. Strukov, IEEE Trans. Electron Devices 2017, 64, 312; c) C. Li, L. Han, H. Jiang, M. H. Jang, P. Lin, Q. Wu, M. Barnell, J. J. Yang, H. L. Xin, Q. Xia, Nat. Commun. 2017, 8, 15666; d) D. Jana, S. Roy, R. Panja, M. Dutta, S. Z. Rahaman, R. Mahapatra, S. Maikap, Nanoscale Res. Lett. 2015, 10, 188.
- [9] a) P. Chi, S. Li, C. Xu, T. Zhang, J. Zhao, Y. Liu, Y. Wang, Y. Xie, in 2016 ACM/IEEE 43rd Annual Int. Symp. on Computer Architecture (ISCA), IEEE, Piscataway, NJ 2016, pp. 27–39; b) D. Ielmini, H. S. P. Wong, *Nat. Electron.* 2018, 1, 333.
- [10] a) J. H. Yoon, J. Zhang, P. Lin, N. Upadhyay, P. Yan, Y. Liu, Q. Xia, J. J. Yang, Adv. Mater. 2020, 32, 1904599, b) J. P. Strachan, A. C. Torrezan, F. Miao, M. D. Pickett, J. J. Yang, W. Yi, G. Medeiros-Ribeiro, R. S. Williams, IEEE Trans. Electron Devices 2013, 60, 2194.
- [11] a) D. B. Strukov, G. S. Snider, D. R. Stewart, R. S. Williams, *Nature* 2008, 453, 80; b) D. H. Kwon, K. M. Kim, J. H. Jang, J. M. Jeon, M. H. Lee, G. H. Kim, X. S. Li, G. S. Park, B. Lee, S. Han, M. Kim, C. S. Hwang, *Nat. Nanotechnol.* 2010, *5*, 148; c) M. Prezioso, F. Merrikh-Bayat, B. D. Hoskins, G. C. Adam, K. K. Likharev, D. B. Strukov, *Nature* 2015, *521*, 61.
- [12] a) S. Z. Rahaman, Y. D. Lin, H. Y. Lee, Y. S. Chen, P. S. Chen, W. S. Chen, C. H. Hsu, K. H. Tsai, M. J. Tsai, P. H. Wang, *Lang-muir* **2017**, *33*, 4654; b) C. Li, M. Hu, Y. Li, H. Jiang, N. Ge, E. Montgomery, J. Zhang, W. Song, N. Dávila, C. E. Graves, Z. Li, J. P. Strachan, P. Lin, Z. Wang, M. Barnell, Q. Wu, R. S. Williams,



J. J. Yang, Q. Xia, *Nat. Electron.* **2017**, *1*, 52; c) C. Li, D. Belkin, Y. Li, P. Yan, M. Hu, N. Ge, H. Jiang, E. Montgomery, P. Lin, Z. Wang, W. Song, J. P. Strachan, M. Barnell, Q. Wu, R. S. Williams, J. J. Yang, Q. Xia, *Nat. Commun.* **2018**, *9*, 2385.

- [13] Y. Yang, P. Gao, L. Li, X. Pan, S. Tappertzhofen, S. Choi, R. Waser, I. Valov, W. D. Lu, *Nat. Commun.* **2014**, *5*, 4262.
- [14] M. Lübben, I. Valov, Adv. Electron. Mater. 2019, 5, 1800933.
- [15] a) S. Slesazeck, T. Mikolajick, Nanotechnology 2019, 30, 352003;
 b) Z. Wang, H. Wu, G. W. Burr, C. S. Hwang, K. L. Wang, Q. Xia,
 J. J. Yang, Nat. Rev. Mater. 2020, 5, 173.
- [16] a) B. Hwang, J.-S. Lee, Adv. Electron. Mater. 2019, 5, 1800519;
 b) B. Mu, H.-H. Hsu, C.-C. Kuo, S.-T. Han, Y. Zhou, J. Mater. Chem. C 2020, 8, 12714; c) N. Raeis-Hosseini, J.-S. Lee, J. Electroceram. 2017, 39, 223.
- [17] S.-J. Kim, B. Hwang, J.-S. Lee, Adv. Mater. Interfaces 2018, 5, 1800882.
- [18] E. Ercan, J.-Y. Chen, P.-C. Tsai, J.-Y. Lam, S. C.-W. Huang, C.-C. Chueh, W.-C. Chen, Adv. Electron. Mater. 2017, 3, 1700344.
- [19] M. K. Kim, J. S. Lee, ACS Appl. Mater. Interfaces 2018, 10, 10280.
- [20] S. R. Mohapatra, T. Tsuruoka, K. Krishnan, T. Hasegawa, M. Aono, J. Mater. Chem. C 2015, 3, 5715.
- [21] T. Mazur, P. Zawal, K. Szacilowski, Nanoscale 2019, 11, 1080.
- [22] a) S. Long, C. Cagli, D. Ielmini, M. Liu, J. Suñé, J. Appl. Phys. 2012, 111, 074508; b) F. G. Aga, J. Woo, S. Lee, J. Song, J. Park, J. Park, S. Lim, C. Sung, H. Hwang, AIP Adv. 2016, 6, 025203; c) X. Xu, H. Lv, H. Liu, T. Gong, G. Wang, M. Zhang, Y. Li, Q. Liu, S. Long, M. Liu, IEEE Electron Device Lett. 2015, 36, 129; d) Y. Y. Chen, M. Jurczak, R. Degraeve, B. Govoreanu, S. Clima, L. Goux, A. Fantini, G. S. Kar, D. J. Wouters, G. Groeseneken, IEEE Electron Device Lett. 2013, 34, 626.
- [23] T. Li, H. Yu, S. H. Y. Chen, Y. Zhou, S.-T. Han, J. Mater. Chem. C 2020, 8, 16295.
- [24] Q. Liu, S. Long, H. Lv, W. Wang, J. Niu, Z. Huo, J. Chen, M. Liu, ACS Nano 2010, 4, 6162.
- [25] K.-Y. Shin, Y. Kim, F. V. Antolinez, J. S. Ha, S.-S. Lee, J. H. Park, Adv. Electron. Mater. 2016, 2, 1600233.
- [26] B. K. You, W. I. Park, J. M. Kim, K.-I. Park, H. K. Seo, J. Y. Lee, Y. S. Jung, K. J. Lee, ACS Nano 2014, 8, 9492.
- [27] X. Zhao, S. Liu, J. Niu, L. Liao, Q. Liu, X. Xiao, H. Lv, S. Long, W. Banerjee, W. Li, S. Si, M. Liu, *Small* **2017**, *13*, 1603948.
- [28] H. Yeon, P. Lin, C. Choi, S. H. Tan, Y. Park, D. Lee, J. Lee, F. Xu, B. Gao, H. Wu, H. Qian, Y. Nie, S. Kim, J. Kim, *Nat. Nanotechnol.* 2020, 15, 574.
- [29] K. Au, X. S. Gao, J. Wang, Z. Y. Bao, J. M. Liu, J. Y. Dai, J. Appl. Phys. 2013, 114, 027019.
- [30] S. Choi, S. H. Tan, Z. Li, Y. Kim, C. Choi, P. Y. Chen, H. Yeon, S. Yu, J. Kim, Nat. Mater. 2018, 17, 335.
- [31] J.-Y. Hong, S. O. Jeon, J. Jang, K. Song, S. H. Kim, Org. Electron. 2013, 14, 979.
- [32] a) Q. Peng, Y. C. Tseng, S. B. Darling, J. W. Elam, Adv. Mater. 2010, 22, 5129; b) Q. Peng, Y. C. Tseng, S. B. Darling, J. W. Elam, ACS Nano 2011, 5, 4600; c) A. Subramanian, N. Tiwale, C.-Y. Nam, Jom 2019, 71, 185; d) A. Subramanian, N. Tiwale, W.-I. Lee, C.-Y. Nam, ACS Nano 2021, https://doi.org/10.3389/fnano.2021.766690.
- [33] a) S.-M. Lee, E. Pippel, U. Gösele, C. Dresbach, Y. Qin, C. V. Chandran, T. Bräuniger, G. Hause, M. Knez, *Science* 2009, *324*, 488; b) K. E. Gregorczyk, D. F. Pickup, M. G. Sanz, I. A. Irakulis, C. Rogero, M. Knez, *Chem. Mater.* 2015, *27*, 181; c) K. J. Dusoe, X. Ye, K. Kisslinger, A. Stein, S. W. Lee, C. Y. Nam, *Nano Lett.* 2017, *17*, 7416.
- [34] E. S. Muckley, L. Collins, A. V. Ievlev, X. Ye, K. Kisslinger, B. G. Sumpter, N. V. Lavrik, C. Y. Nam, I. N. Ivanov, ACS Appl. Mater. Interfaces 2018, 10, 31745.
- [35] a) E. K. McGuinness, F. Zhang, Y. Ma, R. P. Lively, M. D. Losego, *Chem. Mater.* 2019, *31*, 5509; b) E. Barry, A. U. Mane, J. A. Libera,

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

J. W. Elam, S. B. Darling, *J. Mater. Chem. A* **2017**, *5*, 2929; c) S. Greil, A. Rahman, M. Liu, C. T. Black, *Chem. Mater.* **2017**, *29*, 9572.

- [36] a) W. Wang, C. Chen, C. Tollan, F. Yang, Y. Qin, M. Knez, J. Mater.
- Chem. C 2017, 5, 2686; b) W. Wang, C. Chen, C. Tollan, F. Yang, M. Beltran, Y. Qin, M. Knez, ACS Appl. Mater. Interfaces 2017, 9, 27964.
- [37] a) Y. Yu, Z. Li, Y. Wang, S. Gong, X. Wang, Adv. Mater. 2015, 27, 4938; b) Y. Yu, X. Wang, Extreme Mech. Lett. 2016, 9, 514.
- [38] J.-H. Pai, Y. Wang, G. T. A. Salazar, C. E. Sims, M. Bachman, G. P. Li, N. L. Allbritton, Anal. Chem. 2007, 79, 8774.
- [39] a) F. Verbakel, S. C. J. Meskers, R. A. J. Janssen, Chem. Mater. 2006, 18, 2707; b) K. Krishnan, T. Tsuruoka, M. Aono, Jpn. J. Appl. Phys. 2016, 55, 06GK02; c) S. Wu, T. Tsuruoka, K. Terabe, T. Hasegawa, J. P. Hill, K. Ariga, M. Aono, Adv. Funct. Mater. 2011, 21, 93.
- [40] a) P. Johansson, *Polymer* 2000, 42, 4367; b) S. Cheng, D. M. Smith,
 C. Y. Li, *Macromolecules* 2014, 47, 3978; c) Z. Xue, D. He, X. Xie, *J. Mater. Chem. A* 2015, *3*, 19218.
- [41] D. H. Yi, C.-Y. Nam, G. Doerk, C. T. Black, R. B. Grubbs, ACS Appl. Polym. Mater. 2019, 1, 672.
- [42] X. Ye, J. Kestell, K. Kisslinger, M. Liu, R. B. Grubbs, J. A. Boscoboinik, C.-Y. Nam, *Chem. Mater.* 2017, 29, 4535.
- [43] a) C.-Y. Nam, A. Stein, K. Kisslinger, J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.-Process., Meas., Phenom. 2015, 33, 06F201;
 b) C.-Y. Nam, A. Stein, K. Kisslinger, C. T. Black, Appl. Phys. Lett. 2015, 107, 062404; c) C. Y. Nam, A. Stein, Adv. Opt. Mater. 2017, 5, 1700807.
- [44] N. Tiwale, A. Subramanian, K. Kisslinger, M. Lu, J. Kim, A. Stein, C.-Y. Nam, J. Mater. Chem. C 2019, 7, 8803.

[45] H. Ling, M. Yi, M. Nagai, L. Xie, L. Wang, B. Hu, W. Huang, Adv. Mater. 2017, 29, 1701333.

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www.advelectronicmat.de

- [46] N. Raeis-Hosseini, J. S. Lee, ACS Appl. Mater. Interfaces 2016, 8, 7326.
- [47] a) K. Krishnan, A. Gubicza, M. Aono, K. Terabe, I. Valov, T. Tsuruoka, J. Mater. Chem. C 2021, 9, 11198; b) K. Krishnan, S. M. Tauquir, S. Vijayaraghavan, R. Mohan, RSC Adv. 2021, 11, 23400; c) K. Krishnan, M. Aono, K. Terabe, T. Tsuruoka, J. Phys. D: Appl. Phys. 2019, 52, 445301; d) K. Krishnan, M. Aono, T. Tsuruoka, Nanoscale 2016, 8, 13976; e) I. Valov, T. Tsuruoka, J. Phys. D: Appl. Phys. 2018, 51, 413001.
- [48] R. Z. Waldman, D. J. Mandia, A. Yanguas-Gil, A. B. F. Martinson, J. W. Elam, S. B. Darling, J. Chem. Phys. 2019, 151, 190901.
- [49] A. Sihvola, Subsurf. Sens. Technol. Appl. 2000, 1, 393.
- [50] a) T. Fu, X. Liu, H. Gao, J. E. Ward, X. Liu, B. Yin, Z. Wang, Y. Zhuo, D. J. F. Walker, J. Joshua Yang, J. Chen, D. R. Lovley, J. Yao, Nat. Commun. 2020, 11, 1;, b) S. J. Krumbein, IEEE Trans. Compon., Hybrids, Manuf. Technol. 1988, 11, 5.
- [51] T. Tsuruoka, K. Terabe, T. Hasegawa, I. Valov, R. Waser, M. Aono, Adv. Funct. Mater. 2012, 22, 70.
- [52] a) D. Marković, A. Mizrahi, D. Querlioz, J. Grollier, Nat. Rev. Phys. 2020, 2, 499; b) K. Roy, A. Jaiswal, P. Panda, Nature 2019, 575, 607.
- [53] a) Z. Wang, S. Joshi, S. E. Savel'ev, H. Jiang, R. Midya, P. Lin, M. Hu, N. Ge, J. P. Strachan, Z. Li, Q. Wu, M. Barnell, G. L. Li, H. L. Xin, R. S. Williams, Q. Xia, J. J. Yang, *Nat. Mater.* 2017, *16*, 101;
 b) M. A. Zidan, J. P. Strachan, W. D. Lu, *Nat. Electron.* 2018, *1*, 22.
- [54] Y. Zuo, H. Lin, J. Guo, Y. Yuan, H. He, Y. Li, Y. Xiao, X. Li, K. Zhu, T. Wang, X. Jing, C. Wen, M. Lanza, *Adv. Electron. Mater.* **2020**, *6*, 1901226.