Resistive Switching Memory



Intrinsically Stretchable Resistive Switching Memory Enabled by Combining a Liquid Metal–Based Soft Electrode and a Metal–Organic Framework Insulator

Xiaohui Yi, Zhe Yu, Xuhong Niu, Jie Shang,* Guoyong Mao, Tenghao Yin, Huali Yang, Wuhong Xue, Pravarthana Dhanapal, Shaoxing Qu, Gang Liu,* and Run-Wei Li*

Mechanical flexibility and electrical reliability establish the fundamental criteria for wearable and implantable electronic devices. In order to receive intrinsically stretchable resistive switching memories, both the electrode and storage media should be flexible yet retain stable electrical properties. Experimental results and finite element analysis reveal that the formation of 3D liquid metal galinstan (GaInSn) calabash bunch conductive network in poly(dimethyl siloxane) (PDMS) matrix allows GaInSn@PDMS composite as soft electrode with the stable conductivity of >1.3 \times 10³ S cm⁻¹ at the stretching strains of >80% and a fracture strain extreme of 108.14%, while the third-generation metal-organic framework MIL-53 thin film with a facial rhombohedral topology enables large mechanical deformation up to a theoretical level of 17.7%. Combining the use of liquid metal-based electrode and MIL-53 switching layer, for the first time, intrinsically stretchable RRAM device Ag/MIL-53/GaInSn@PDMS is demonstrated that can exhibit reliable resistive switching characteristics at the strain level of 10%. The formation of fluidic gallium conductive filaments, together with the structural flexibility of the GaInSn@PDMS soft electrode and MIL-53 insulating layer, accounts for the uniform resistive switching under stretching deformation scenario.

1. Introduction

Along with the rapid development of smart healthcare and medical services over the past few years, wearable and implantable electronic gadgets have been receiving increasing amount of attention from both the academic and industrial communities.^[1–3] This requires all the circuit components including information storage devices to be stretchable, allowing free contacts to and conformal deformation with the complex curvilinear surfaces of human skin and internal organs.^[2,4–6] Resistive switching memories (or RRAM in short), which use bistable resistance states to encode and storage binary digital data, are considered as one of the most promising candidates for the next-generation information storage technology.^[7–9] They are also widely explored for flexible applications due to their unique advantages of the simple two-terminal structure and versatile range of materials' selection.^[10-14] For instance, by depositing

hafnium oxide directly on plastic substrate, Shang et al. successfully made flexible RRAM device that can be bent to the strain level of 3.18%.^[15,16] Using parylene-C, etc., as the switching media, complementary metal oxide semiconductor (CMOS)compatible memories are also made possible by Huang et al. with organic materials.^[11,17] Nevertheless, the limited adaptability of inorganic materials to large strains obviously hinders their application for stretchable electronics, while the soft organic materials bear poor resistance to the changing environments of atmosphere moisture and oxygen.^[18–21] Fabrication of stretchable resistive switching memories that juggles both the electrical and the mechanical stability is still a technical challenge at the moment.

Generally, resistive switching memories are composed of electrode/insulator/electrode (or MIM) sandwich structures. The development of high-performance flexible RRAM devices is thus highly depending on the rational design of both electrode and insulator materials with intrinsic stretchability and established electronic properties. With this concern, the 3D hybrid materials that inherit the unique features of the parenting inorganic and organic building blocks appear good choices. In recent years, liquid metals (LMs) such as eutectic gallium–indium (EGaIn) and gallium–indium–tin ("galinstan," GaInSn) alloys with good electrical conductivity and room-temperature fluidity

Dr. X. Yi, Z. Yu, X. H. Niu, Prof. J. Shang, Dr. H. L. Yang, Dr. W. H. Xue, Dr. P. Dhanapal, Prof. G. Liu, Prof. R.-W. Li CAS Key Laboratory of Magnetic Materials and Devices Ningbo Institute of Materials Technology and Engineering Chinese Academy of Sciences Ningbo 315201, P. R. China E-mail: shangjie@nimte.ac.cn; liug@nimte.ac.cn; runweili@nimte.ac.cn Dr. X. Yi, Z. Yu, X. H. Niu, Prof. J. Shang, Dr. H. L. Yang, Dr. W. H. Xue, Dr. P. Dhanapal, Prof. G. Liu, Prof. R.-W. Li Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology Ningbo Institute of Materials Technology and Engineering Chinese Academy of Sciences Ningbo 315201, P. R. China Z. Yu. X. H. Niu College of Materials Science and Opto-Electronic Technology University of Chinese Academy of Sciences Beijing 100049, P. R. China Dr. G. Mao, T. Yin, Prof. S. Qu State Key Laboratory of Fluid Power and Mechatronic System Key Laboratory of Soft Machines and Smart Devices of Zhejiang Province Department of Engineering Mechanics Zhejiang University Hangzhou 310027, P. R. China DOI: 10.1002/aelm.201800655



ADVANCED ELECTRONIC MATERIALS www.advelectronicmat.de

are emerging as important soft electrode candidates for flexible electronics.^[22-24] Packaging of liquid metal with elastic materials such as poly(dimethyl siloxane) (PDMS) into a 3D network nanostructure can form soft composites with an extremely high conductivity of \approx 24 100 S cm⁻¹ and fracture strains of \approx 225%.^[25] Application such as stretchable sensors has been demonstrated with LM-based composite conductor, in which their stable electrical property during stretching is realized by designing 3D conductive network of LMs in matrix.^[26] On the other hand, Pan et al., Huang et al., Yoon et al., and Liu et al. have independently demonstrated that the long-range 3D porous structure endows metal-organic frameworks (MOFs) with both resistive switching characteristics and mechanical flexibility.^[13,14,27-29] In particular, the hydrogen bonding-facilitated expansion and contraction of the third-generation breathing MOFs (e.g., MIL-53) offers them a theoretical large deformation capability of up to 17%.^[30,31] Therefore, combining the liquid metal-based soft electrode and metal-organic framework insulator may provide a great privilege for constructing intrinsically stretchable resistive switching memories.

In this contribution, we report the first intrinsically stretchable RRAM device that can retain resistive switching characteristics at the stretching strain of 10%, which is realized by using GaInSn@PDMS soft composite electrode and MIL-53 insulator. Due to the formation of 3D gallium-indium-tin alloy calabash bunch conductive network with room-temperature fluidity and thus intrinsic deformation capability in soft PDMS matrix, GaInSn@ PDMS composites demonstrate an unaffected high conductivity of $>1.3 \times 10^3$ S cm⁻¹ at strains of >80% and a fracture strain of 108.14%. Utilizing the liquid phase self-assembly approach to deposit flexible MIL-53 nanofilm with lozenge pore structure on top of the soft electrode, Ag/MIL-53/GaInSn@ PDMS device exhibits resistive switching behavior with good reproducibility at the stretching strain of 10%. Further experiments reveal that galinstan not only provides fundamental conductivity and stretchability in the elastic electrode, but also participates in the formation of soft conductive filament through the switching layer directly. The present finding suggests that organic-inorganic hybrid materials, either conducting or insulating, may play a crucial role in developing high-performance intrinsically stretchable electronics.

2. Results and Discussions

Considering the MIM sandwich structure of the resisitive switching memories, electrode that accounts for current conduction and sometimes formation of conductive filaments is an indispensable component of the devices. It should also be soft for the stretchable applications. Currently, elastic composite conductors have been widely explored for flexible electronics,^[32] most of which are based on solid conductive fillers and polymer matrix.^[33–35] However, due to the mismatch between the elastic modulus and conductivity of the rigid and soft materials, the preparation of stretchable electrodes that can endure large strain and repeated deformation yet without sacrificing their electrical performance remains a technical dilemma.^[36–38] In order to realize stretchable RRAM devices, herein we employ LMs' alloy galinstan (GaInSn, with 68.5% Ga, 21.5% In, and

10% Sn by weight) as the conductive component to achieve soft electrodes. The room-temperature fluidic nature of the eutectic alloy allows it to possess fully conformal deformation with the PDMS matrix.^[22–24] therefore, leading to the formation of all-soft GaInSn@PDMS composite with high mechanical flexibility and electrical conductivity. The preparation of the soft electrode is illustrated in Figure S1 (Supporting Information). Upon rigorous mixing of the galinstan alloy and PDMS prepolymer with the curing agent at an elevated temperature of 60 °C, the precursor solution is poured into a home-made Teflon mold for solidification. Cross-sectional scanning electron microscope (SEM) image (Figure S2a, Supporting Information) indicates that the as-formed soft electrode has a typical bilayer structure. The relatively thinner top layer is about 300 µm in thickness and shows a clear calabash bunch network of the liquid alloy filler in the polymer matrix (inset of Figure S2a in the Supporting Information), while the underneath layer is pure in PDMS with a featureless thickness of 700 µm. The width of the galinstan network, exposed on the top surface of the composite (Figure S2b, Supporting Information), is \approx 45 µm. Note that the SEM images are taken by peeling the solidified sample off the mold and flipping it up and down, the presence of a composite GaInSn@PDMS conducting layer residing on top of a pure PDMS supporting layer can thus be understood in terms of natural sedimentation of the relatively heavier metallic components in the mixture slurry during solidification. In addition to the composite GaInSn@PDMS conducting layer that is responsible for providing metallic conductivity of the soft electrode, the existence of the thicker PDMS supporting layer may also provide an elastic support to maintain the electrode intact during deformation.

As visualized in Figure S3 (Supporting Information), the liquid metal-based soft electrode GaInSn@PDMS composite is fully stretchable, with a Young's modulus of ≈ 0.66 Mpa and a stretching fracture strain of 108.14%, which is slightly lower than that of the pure PDMS film (Figure S3, Supporting Information), wherein the minor discrepancy is arising from the addition of high surface tension liquid metal into soft polymer matrix. Four-wire measurement suggests that the GaInSn@ PDMS composite has a bulk conductivity of $\approx 1.46 \times 10^3$ S cm⁻¹, and a small sheet resistance of $\approx 18.79 \text{ m}\Omega \square^{-1}$ (Figure S4, Supporting Information). More importantly, the resistance variation of the soft electrode upon deformation is only ≈4.13% as measured at the stretching fracture strain of 108.14% (Figure 1a), which is 2-5 orders of magnitude lower than that of the solid filler-based composite conductors reported in the literatures.^[32,33] After 1000 stretching cycles, the hysteresis coefficient of the resistance-strain curve is only 0.079 at the deformation level of 100%, while a negligible resistance change of 4.45% during 1000 stretching cycles is maintained (Figure S5, Supporting Information), offering promising reliability for elastic electrode upon loading and reloading of external strains.

In order to clarify the origin of the strain–insensitive resistance response of the GaInSn@PDMS composite, we perform finite element analysis (FEA) with a simplified model to simulate the mechanics of the liquid filler–soft matrix networks (Figure 1b–d).^[25] During simulation, the GaInSn calabash bunch structures have been aligned at an angle θ with respect to the stretching direction (upper panel of Figure 1b). Four







Figure 1. a) Resistance variation of the GaInSn@PDMS electrode as a function of the stretching strain at different deformation levels. Inset shows the optical images of the soft electrode in its initial (upper panel) and stretched (lower panel) states, respectively. b) GaInSn calabash bunch structures aligned in different directions with respect to the horizontal stretching strains. Upper panel shows the initial orientations of the calabash bunch structures wherein the current is flowing along the axial direction of the calabash bunch. Lower panel shows the stress distribution of the calabash bunch structures when subjected to 100% horizontal stretching strain. c) Calculated results of the resistance variation of the GaInSn calabash bunch structure when being stretched at 0° (orange) and 90° (blue) with respect to the axial direction of the calabash bunch structure. The overall resistance variation of a 0° aligned calabash bunch structure connected in series are also displayed with the red dashed line. d) Distribution of stress of a GaInSn@PDMS soft composite with a network of calabash bunch structures being subjected to 100% stretching strain.

different angles, viz. 0° , 30° , 60° , and 90° , were selected during simulation. Lower panel of Figure 1b shows the distribution of the stress in the calabash bunch structures when being oriented in different directions and under horizontal stretching strains. It is found that when the angle θ is close to 0° , the length of the calabash increases while its radius decreases. The resistance of the GaInSn calabash will increase during stretching deformation, according to the equation

$$\mathrm{d}R = \rho \times \mathrm{d}l / \left(\pi r^2\right) \tag{1}$$

where d*R* is the differential resistance of calabash with length d*l*, radius *r*, and the resistivity ρ . On the contrary, when the angle θ is close to 90°, the length of the calabash decreases while the radius increases, respectively. Consequently, its resistance will decrease. Upon integrating the above equation (Equation (1))

over the entire GaInSn calabash bunch structures, the variation curve of the sample resistance versus stretching strain is calculated and plotted in Figure 1c. Results show that the horizontally aligned calabash bunch demonstrates a significant increase in its resistance, while the vertically oriented calabash bunch structure becomes more conductive. If we connect a horizontal calabash bunch structure with a vertical calabash bunch structure in series, the resistance of the combined sample will decrease first and then increase with the increase in stretching strains. This trend is consistent with the experimental observation shown in Figure 1a. The calabash bunch structures being oriented in all directions and interconnecting with each other inside the GaInSn@PDMS layer form a continuous conductive network of the soft electrode (Figure 1d). When the conductive network is stretched to 100% strain, we can find that the horizontal calabash bunch structure (θ close to 0°) becomes



slim and the vertical one (θ close to 90°) becomes stubby, with their individual resistances being increased and decreased, respectively. When the current flow through the network, it will pass both the horizontal calabash bunch structures and the vertical ones as shown in Figure 1c. As a result, the variation of the overall resistance of the entire conductive network can be ignored, because of the presence of various orientated calabash bunch structures and their respective resistance variations during stretching deformation. As such, the soft GaInSn@ PDMS composite exhibits stable and metallic conductivity even at high strains, which qualifies a competent candidate for stretchable electrodes.

Very recently it is demonstrated that by manipulating the molecular and ionic species encapsulated inside the 3D-ordered nanopores of the metal-organic frameworks, this family of organic-inorganic hybrid materials can exhibit resistive switching properties in either single crystal or in thin-film forms.^[27-29] Using plastic as soft substrates, flexible RRAM devices with bending extremes of 2.8% and thermally stable memory performance are also made possible with HKUST-1 and ZIF-8 nanofilms.^[13,14] In order to further enhance the deformation capability of the hybrid switching media, the third-generation soft MOF crystals with structural multistability should be employed to replace their first- and second-generation counterparts that carry rigid frameworks.^[39,40] MIL-53 is a family of 1D breathing MOFs constructed from 1,4-benzenedicarboxylate (BDC) linker and trivalent metal ions (e.g., Al, Fe, and Cr).^[30,31,41] They are generally synthesized through a hydrothermal method, and have a facial rhombohedral topology in their 3D network (Figure 2a). The presence of the residual water solvent and terephthalic acid template molecules can form hydrogen bonds with the metal octahedra, the exclusion and reinclusion of which (for example upon heating and rehydration at room temperature) can activate the rotation of the O-metal-O planes around the metal-metal axis of the spring-like framework. Thus, the variation of the dihedral angles endows MIL-53 materials large structural deformation and mechanical flexibility, not only by modulating the molecular scale hydrogen bonding interaction between the MOF framework and guest molecules, but also through macroscopic analog of external mechanical stresses.

Aluminum-based MIL-53 nanofilm is prepared on GaInSn@ PDMS stretchable electrodes through a modified liquid phase self-assembly approach and subsequently dried at 363 K. The entire process is done automatically in a home-designed apparatus to facilitate the formation of the MOF nanofilm.^[13] Figure 2b depicts the X-ray diffraction (XRD) patterns of the MIL-53 film grown on top of the liquid metal-based soft electrodes. In comparison to the simulated spectrum with data (CCDC numbers: 220 475, 220 476, and 220 477) obtained from the Cambridge Crystallographic Data Centre (CCDC), it is indicated that the as-prepared nanofilm is polycrystalline, whereas an obvious diffractive peak located at the 2θ of 8.3° and a preferential (011) crystalline direction is observed. Drying the sample at elevated temperature can drive part of the solvent and template molecules out to receive MIL-53 in its large pore (lp) form.^[31] The resultant increasing amount of free space is also essential to accommodate the modifications of the steric hindrance of the MOF constituents during deformation. Fourier transformed infrared (FTIR) spectra (Figure 2c)



exhibit absorption peaks at the wavenumbers of 1589, 1511, and 1423 cm⁻¹, which can be ascribed to the stretching vibration of the carbonyl mojeties of BDC linkers, respectively.^[42] The peaks distributed from 1250 to 900 cm⁻¹ correspond to the stretching vibration of the Si-O bonds in the GaInSn@ PDMS soft electrode.^[43] The lack of obvious absorption peaks at the wavenumber of $\approx 3500 \text{ cm}^{-1}$ indicates the absence of water molecules in the as-prepared MIL-53 film and shows the open form of the MOF nanopores. The experimental XRD and FTIR spectra thus confirm the successful synthesis of MIL-53 film on GaInSn@PDMS composite. SEM observation reveals that the MIL-53 nanofilm is ≈150 nm in thickness with a closely packed granular nature (Figure 2d,e). The Young's modulus of the MIL-53/GaInSn@PDMS multilayer structure is 0.83 Mpa (Figure S6, Supporting Information), similar to that of the liquid metal soft composite electrode. The MIL-53/ GaInSn@PDMS structure remains complete without obvious cracks formed upon being stretched up to 10% strain level (Figure 2f), allowing the fabrication of intrinsically stretchable resistive switching memories. It is noteworthy that although the MIL-53 nanofilm shows a preferential (011) crystalline direction with a facial rhombohedral topology as shown in Figure 2, the horizontal diagonal of the lozenge structure can be distributed randomly in all the in-plane directions. In case the stretching strain is applied along the horizontal diagonal direction, the MOF film may reach the theoretical deformation extremes of 17.7% as predicted in the literature.^[40] If the horizontal stretching strain is applied perpendicularly to the diagonal direction, the film may not be stretchable at all. With the random alignment of the lozenge structures in all in-plane directions, the overall deformation capability is compromised to be smaller than the maximum value, and stretching the sample to 12% will result in cracking in the MIL-53 nanofilms. Future effort in controlling the in-plane orientation of the MOF structure and its matching with the strain direction may further improve the deformation capability of the MIL-53 nanofilm and devices.

Silver is employed as top electrode through deposition of elargo on the surface of MIL-53 nanofilm to produce the Ag/ MIL-53/GaInSn@PDMS sandwich structure device, and all the devices were sealed with PDMS to avoid being oxidized in the ambient environments during electrical measurements. The memory performance of the device is first examined in its pristine state, which demonstrates forming-free bipolar switching characteristic (Figure 3a) with small programming voltages of -1.2 and 0.3 V (applied to the Ag electrode) and an ON/OFF ratio of ≈200. Such a forming-free resistance switching behavior with low operating voltages is highly desirable for reducing the complexity and power consumption of the entire integrated circuits. In order to refrain the device from potential permanent breakdown during the set process, a compliance current preset of ≈1 mA was employed to restrain the fast and over growth of the conductive filaments. During the reset process, the compliance current was removed, and the electrical-induced Joule heating effect will annihilate the filament and return the device to the original state. As such, the device can be switched repeatedly in a bipolar manner. It should be noted that a higher reset current may also lead to the eventual failure of the device. This adverse effect can be







Figure 2. a) Crystal structure of MIL-53 (left panel), projection along the nanopore direction illustrating stimulus facilitated structural variation (right panel), and dihedral connection between the aluminum chains and the terephthalate ions (inset). Aluminum ions are depicted in green, oxygen in red, and carbon in gray. b) X-ray diffractive pattern and c) Fourier transformed infrared spectrum of the as-synthesized MIL-53 nanofilm on GaInSn@PDMS composite. d) Scanning electron microscopic cross-sectional and e) top view images of the as-prepared MIL-53 nanofilm. f) SEM top view images of the MIL-53 nanofilm upon being stretched from 0% to 10% strain levels.

eliminated by reducing the parasitic capacitance in the circuit through one transistor and one resistor (1T1R) structure,^[44] or by controlling the growth of the conductive filament through rationally designing the electrode composition^[45] or insulator/ electrode interface.^[46,47] Both the high- and low-resistance states (HRS and LRS read at -0.1 V) are programmable, accessible, and stable in the repeated switching cycles, and can be readily retained for >10⁵ s (Figure 3b). The long retention of the memory device over 24 h again suggests that neither was the encapsulated top Ag electrode nor the bottom GaInSn@PDMS

conductive substrates oxidized with worsened electrical behaviors. The memory performance of the present device made from hybrid materials can be repeated with fairly good accuracy, and both the programing voltages and HRS/LRS resistances are distributed uniformly (Figure 3c,d).

In order to evaluate the mechanoelectronic performance of the resistive switching memory constructed from hybrid materials, the Ag/MIL-53/GaInSn@PDMS device is stretched with a manual mold retrofitted from commercial micrometer caliper during electrical measurements (Figure S7, Supporting







Figure 3. a) Room-temperature current–voltage (*I–V*) characteristics and b) retention and endurance performance of the unstretched Ag/MIL-53/ GaInSn@PDMS device. Uniform distribution of c) the programming voltages and d) HRS/LRS resistances of the memory device. Insets of panels (c) and (d) illustrate the Set/Rest process and HRS/LRS, respectively.

Information). As shown in **Figure 4**a, the memory device well retains its forming-free bipolar resistive switching behavior when being stretched up to from the 0% to 10% strain levels. During stretching, only slight fluctuations in the switching

voltages and the ratio of HRS and LRS (or ON/OFF ratio in shot) are observed (Figure 4b,c). At the strain level of 10%, the device shows promising endurance in the pulse-mode operation (Figure 4d), as well as when being stretched-relaxed



Figure 4. a) Room-temperature current–voltage characteristics of the Ag/MIL-53/GaInSn@PDMS device under the stretching strains of 2–10%. Evolution of b) the switching voltages and c) HRS/LRS resistances of the Ag/MIL-53/GaInSn@PDMS device as a function of the strain level. d) Endurance, e) continuous stretching fatigue, and f) retention performance of the device at the stretching strain level of 10%.





for up to 50 cycles (Figure 4e). Considering the bulk conductivity of $\approx 1.46 \times 10^3$ S cm⁻¹ and a small sheet resistance of ≈18.79 m Ω \Box^{-1} , the GaInSn@PDMS conductive substrate has very small resistance as compared to that of the MIL-53 nanofilm. Even in the LRS, the MOF film resistance is estimated as ≈200 times larger than that of the liquid metal-based composite electrodes. Therefore, although the electrode resistance varies between ± 3.5% during deformation, it will not influence the HRS and LRS resistances of the memory device significantly. Consequently, both the HRS and LRS resistances are unaffected during the dynamic stretching-relaxing process (Figure S8, Supporting Information; with stretching/ relaxing rates of 0.25 mm s⁻¹) and can be retained for at least 10^4 s at room temperature under stretching (Figure 4f). At the stretching strain of 13%, the MIL-53 nanofilm cracks and exfoliates from the GaInSn@PDMS soft electrode as shown in Figure S9a (Supporting Information). As a result of the MIL-53/GaInSn@PDMS structure delamination, it is no longer able to apply external voltage onto the MOF nanofilms

from the two electrodes, consequently resulting in "programming failure" wherein the device cannot be switched ON any more (Figure S9b, Supporting Information). This deformation extreme is slightly lower than that of the theoretical value, and can be explained by the grain boundary–assisted crack formation in the MIL-53 insulating layer. Deposition of single crystalline MIL-53 film might help to minimize the crack formation and further extend the deformation capability of the MOF devices. Nevertheless, the extreme strain level of 10%, at which the Ag/ MIL-53/GaInSn@PDMS memory is still working, is superior to that of most of the organic and inorganic counterparts.^[19,48]

Finally, we try to elucidate the switching mechanism of the Ag/MIL-53/GaInSn@PDMS device through probing the local electrical behavior with conductive atomic force microscope (C-AFM) and the formation of conductive filaments with X-ray photoelectron spectroscopic (XPS) analyses. For C-AFM measurements, the current map of the MIL-53/GaInSn@ PDMS structure is monitored with a Pt/Ir-coated conductive tip (grounded). Under a low biased voltage of -0.5 V, the



Figure 5. Conductive atomic force microscopic current maps of the MIL53/GaInSn @PDMS structure in its a) initial high state and b) after being set at -3 V. c) XPS depth-profiling analyses of the Pt/MIL-53/GaInSn@PDMS device in its initial and low-resistance states. d) Schematic illustration of switching mechanism in Ag/MIL-53/GaInSn@PDMS device.



C-AFM current map does not show any obvious features in the scanning area of $2 \times 2 \ \mu m^2$, suggesting that the pristine MIL-53 film has poor conductivity (Figure 5a). After applying a biased voltage of -3 V and recording the current response at -0.5 V, several bright spots with the diameter of ≈ 10 nm are observed, which indicate the filamentary mechanism of the device (Figure 5b). Once a biased voltage of 2 V is applied onto the same area, these conductive areas disappear completely, thus mimicking the write-read-erase cycles of the Ag/MIL-53/ GaInSn@PDMS devices. In order to verify the chemical identity of the conductive filament, XPS depth-profiling analysis is performed in the Pt/MIL-53/GaInSn@PDMS structure in their respective initial (high)-resistance states (IRS or HRS) and low-resistance states. Here, to avoid the introduction of foreign atoms from the top electrodes into the MOF layer upon argonion etching, chemically inert platinum is used instead as the top electrode. Before the application of external electric field, the top electrode layer should not contain any Al content either. As shown in the XPS depth-profiling spectra of the pristine device plotted in Figure S10a (Supporting Information), aluminum species start to appear after the first three etching treatments, which exactly locate the position of the Pt/MIL-53 interface. Remembering that the thickness of the Pt top electrode is \approx 50 nm, the overall etching time of 1320 s for the first three treatments indicates that the etching operation is conducted at an estimated rate of 0.038 nm s⁻¹. Figure 5c plots the intensity versus etching depth relationships for different elements as derived from Figure S10a (Supporting Information), revealing a clear and sharp interface at the Pt top electrode/MIL-53 layer. Coincidently, the gallium and aluminum signals appear at the same location when the device is switched to the low-resistance state, suggesting that Ga of the galinstan alloy is injected from the soft electrode into the MOF matrix. As shown in the LRS core-level XPS spectra of Figure S10b (Supporting Information), the Ga $2p_{1/2}$ and Ga $2p_{3/2}$ species at the binding energies (BEs) of 1143.45 and 1116.69 eV confirm that the injected gallium has been electrochemically reduced to metallic Ga atoms and consists the elastic conductive filaments that connect the anode and cathode.

Based on the above analysis, a phenomenological model of resistive switching observed in the Ag (or Pt)/MIL-53/ GaInSn@PDMS stretchable memory device is proposed and illustrated in Figure 5d. When a negative voltage is applied to the top electrode, oxidation of the gallium atoms into the Ga³⁺ cations occurs in the GaInSn@PDMS soft composite electrode, which could be described as $Ga \rightarrow Ga^{3+} + 3e^{-}$. With the relative more positive standard electrode potential of In/In³⁺ and Sn/ Sn^{2+} (-0.3382 and -0.1325 V, respectively) than that of Ga/Ga³⁺ (-0.549 V), indium and tin cations are less likely to be formed. Under the applied electric field, the Ga³⁺ cations migrate across the MIL-53 layer and are reduced by electrons injected from the Ag electrode, i.e., $Ga^{3+}+3e^- \rightarrow Ga$. The consecutive sedimentation of Ga metal atoms on the Ag electrode consequently leads to the growth of Ga filaments, which finally reach the GaInSn@PDMS electrode to form highly conductive filaments in the ON state. Since the standard electrode potential of Ga/ Ga^{3+} is also more negative than that of Ag/Ag⁺ (0.7669 V), Ga atoms will be oxidized more easily by the electric field than Ag atoms. Therefore, when a positive voltage is applied to the Ag



electrode during the reset process, an electrochemical dissolution of Ga atoms occurs at the weakest point of conductive filaments and primarily gives rise to an HRS device. Under external mechanical stresses, the stretching strains are mainly released through the facial rhombohedral topology of the MOF nanofilm, thus making the as-formed Ga fluidic conductive filaments and memory performance of the Ag/MIL-53/ GaInSn@PDMS device almost unchanged. It is noteworthy that due to the moderate coordination bond strength between the metal cation and the carboxylic groups of the aromatic linkers, Al³⁺ in MIL-53 nanofilm may also migrate as driven by the applied electric field (as indicated in Figure 5c by the minor lowering in the interfacial concentration of the Al species in the low-resistance state in comparison to that in the initial resistance state). As reported in our previous work,^[13] the negatively charged vacancies in the MOF nanofilm are relatively less stable, and the carboxylic groups can be removed from the aromatic linkers upon Joule heating. The resultant coupling of the neighboring benzene rings, and the subsequent formation of sp²-hybridized carbon-rich channels can facilitate the charge carrier transport through a localized conjugated system, in comparison to the hopping between the Al³⁺ ions or the organic linkers, contributing to additional carbon-based conductive filaments beyond the Ga metallic counterparts.

3. Conclusion

To summarize, intrinsically stretchable resistive switching memory has been developed thanks to the combination of the liquid metal-based soft composite electrode GaInSn@PDMS and the third-generation MIL-53 nanofilm. Uniform and reproducible resistive switching effect, which can be sustained at the stretching strain of 10%, is observed for the first time with the hybrid conducting and insulating materials. Through C-AFM and XPS depth-profiling analyses, it is proposed that the electric field-induced generation and migration of the Ga³⁺ ion, which lead to the formation of fluidic and highly conducting filaments across the MOF matrix, give rise to the observed resistive switching in this system. Future advances in the epitaxial deposition of single crystalline MIL-53 nanofilm, together with the utilization of stretchable top electrodes including silver nanowire (AgNW)-polymer nanocomposite or even intrinsically conductive polymers, may further extend the deformation capability of the stretchable memory device toward the theoretical extreme of the flexible MOF materials. The finepatterning of the GaInSn@PDMS conductive substrates into stripe electrodes of bit and word lines, as well as the thinning of their thickness down to tens of nanometers through deposition process optimization, should be conducted to incorporate the stretchable memory devices into high-density crossbar array and even 3D stacks.

4. Experimental Section

Preparation of GaInSn Liquid Metal Alloy and GaInSn@PDMS Soft Composite Electrode: High-purity metal gallium (99.99%), indium (99.995%), and Tin (99.99%), all purchased from Beijing Founde Star



Sci. & Technol. Co. Ltd, were mixed in the mass ratio of 68.2:21.8:10 upon heating and stirring at 60 °C for 30 min to receive the GaInSn liquid metal alloy. Then the GaInSn alloy and PDMS prepolymer (Sylgard 184 silicone elastomer base, Dow Corning Corporation) were mixed in the volume ratio of 1:4. Upon adding the curing agent (Sylgard 184 silicone elastomer curing agent, Dow Corning Corporation) in a mass content of 10% to the PDMS prepolymer and stirring for another 5 min, the mixture was poured into a home-made Teflon mold and stood at room temperature for 60 min to allow the natural sedimentation of the LM microdroplets. Afterward the mixture was cured at 60 °C for 4 h for solidification and finally peeled off the mold to obtain the GaInSn@ PDMS soft composite electrode. The size of the soft electrode is determined by the dimension of the mold and can be cut into arbitrary shapes at will.

Deposition of MIL-53 Nanofilm on GaInSn@PDMS Soft Composite Electrode: The GaInSn @PDMS soft composite electrode was first treated with oxygen plasma at 100 W and 200 mTorr for 5 min to generate hydroxyl groups on the surface. Then the surface functionalized composite electrode was immerged in a 50×10^{-3} M water solution of AlCl₃ in a home-designed reactor and sealed with a rubber stopper for 10 min. After removing the solution, the sample was then soaked with excess amount of water for 5 min to remove the unreacted AlCl₃, and blow-dried in the reactor with a nitrogen stream. Subsequently, the sample was immerged in a saturated water solution of terephthalic acid (H₂BDC) for 10 min. Then, the sample was washed again with water for 5 min, and blow-dried with the nitrogen stream. The same procedure was repeated for 200 times, all performed automatically at 90 °C in the home-designed apparatus to avoid exposing the reaction environment to the ambient atmosphere, which might introduce contamination onto the samples.^[13] The total thickness of the sample can also be controlled by adjusting the total number of the assembly cycles.

Materials' Characterization: The crystalline structure of the as-grown MIL-53 nanofilms was investigated by X-ray diffraction measurement on a Bruker AXS D8 ADVANCE DAVINCI instrument using Cu K α radiation. The diffractive patterns were recorded with a step of 0.01° in the range of 5°–30°. FTIR spectra of the MOF film were recorded on an Agilent Cary 600 series FTIR spectrometer in the wavenumber range 3800–900 cm⁻¹. The cross-sectional and top view SEM images of the samples were recorded using field-emission scanning electron microscopy (FESEM, Hitachi, S-4800). The bulk conductance/resistance of the GaInSn@PDMS soft composite electrode was measured using a DC current source (Keithley 6221) and nanovoltmeter (Agilent 3442A) with a standard four-wire method. The sheet resistance of the soft electrode was measured using a standard four-point probe method. The stretching strains for soft electrode characterization were applied with a universal material testing machine (Instron 5943).

Device Fabrication and Characterization: The Ag/MIL-53/GaInSn@ PDMS structure device was fabricated by placing elargo onto the MOF nanofilm manually with a diameter of \approx 500 µm, directly. The Pt/MIL-53/ GaInSn@PDMS structure device was prepared by magnetron sputtering of platinum onto the MOF nanofilm through a metal shadow mask with the diameter of 100 μ m and a thickness of 50 nm. The as-prepared devices were sealed with PDMS (1 mm in thickness) to avoid being oxidized in the environmental atmosphere. The current-voltage (I-V)characteristics of the devices were measured on a Lakeshore probe station equipped with a precision semiconductor parameter analyzer (Keithley 4200) in dc sweep or pulse mode. Scanning probe microscope (Veeco, Dimension 3100 V) equipped with a Pt/Ir coated cantilever was employed for conductive atomic force microscopic measurements of the MIL-53/GaInSn@PDMS structures. Depth-profiling analysis of the elemental distribution in the Pt/MIL-53/GaInSn@PDMS structure was performed using ion-etching treatment during XPS (SHIMADZU, Axis Ultra Dld) measurements. A monochromatic Al K α X-ray source (1486.6 eV photons) was used at a constant dwell time of 100 ms. A pass energy of 80 or 40 eV was employed for the wide and core-level spectra scans, respectively. The X-ray source was run at a reduced power of 150 W (15 kV and 10 mA). The pressure in the analysis chamber was maintained at 10⁻⁸ Torr or lower during each measurement. All BEs were



referenced to the C 1s hydrocarbon peak at 284.6 eV. The elemental sensitivity factors were calibrated using stable binary compounds of well-established stoichiometries. Each ion-etching operation unveiled a brand-new surface and the XPS spectra provided the means of analyzing the composition of these surfaces.

Finite Element Analysis: The mechanical behavior of the GalnSn@ PDMS soft composite conductor was simulated as a simplified calabash bunch structure made of liquid metal surrounded by PDMS substrate using ABAQUS software. The calabash bunch structure was similar to that observed via SEM and consisted of four spheres representing the liquid metal droplets and connected in sequence. The liquid metal was simulated as an incompressible fluid without viscosity, and the PDMS substrate was simulated as an incompressible hyperelastic material. The Mooney–Rivlin material model was used to predict the mechanical behavior of the PDMS substrate, and the energy density of Mooney– Rivlin material (*W*) was described as

$$W = C_1(I_1 - 3) + C_2(I_2 - 3)$$
⁽²⁾

where C_1 and C_2 are two material constants, and the ratio $C_1/C_2 = 0.5$ was set. I_1 and I_2 are two strain invariants, $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ and $I_2 = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3 + \lambda_1^2 \lambda_3^2$, where λ_1 , λ_2 , and λ_3 are three primary stretch components. In the simulation, the entire composite material was subjected to a simple tension test, in which the composite material was stretched along one direction and the boundary on other sides was free. The stress states and resistances of the deformed composite conductors were calculated during the stretching process, with the calabash bunch structures being aligned in different orientations with respect to stretch direction.

Supporting Information

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

Acknowledgements

X.Y., Z.Y., and X.N. contribute equally to this work. This work was supported by the National Key R&D Program of China (2017YFB0405604 and 2016YFA0201102), National Natural Science Foundation of China (Grant Nos. 61722407, 61774161, 61674153, 61504154, 51525103, and 11474295), the K. C. Wong Education Foundation (RCZX0800), the Natural Science Foundation of Zhejiang Province (LR17E020001), the Public Welfare Technical Applied Research of Zhejiang Province (2017C31100), the Ningbo Natural Science Foundation (2015B11001).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

liquid metal, metal-organic frameworks, resistive switching, stretchable memory

Received: September 22, 2018 Revised: November 12, 2018 Published online:

 S.-T. Han, H. Peng, Q. Sun, S. Venkatesh, K.-S. Chung, S. C. Lau, Y. Zhou, V. A. L. Roy, *Adv. Mater.* 2017, *29*, 1700375.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [2] Y. Liu, M. Pharr, G. A. Salvatore, ACS Nano 2017, 11, 9614.
- [3] D. H. Kim, N. S. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. D. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T. I. Kim, R. Chowdhury, M. Ying, L. Z. Xu, M. Li, H. J. Chung, H. Keum, M. McCormick, P. Liu, Y. W. Zhang, F. G. Omenetto, Y. G. Huang, T. Coleman, J. A. Rogers, *Science* **2011**, *333*, 838.
- [4] T. Q. Trung, N. E. Lee, Adv. Mater. 2017, 29, 1603167.
- [5] M. Amjadi, A. Pichitpajongkit, S. Lee, S. Ryu, I. Park, ACS Nano 2014, 8, 5154.
- [6] D. H. Ho, Q. Sun, S. Y. Kim, J. T. Han, D. H. Kim, J. H. Cho, Adv. Mater. 2016, 28, 2601.
- [7] 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.
- [8] J. J. Yang, D. B. Strukov, D. R. Stewart, Nat. Nanotechnol. 2013, 8, 13.
- [9] J. Lee, W. D. Lu, Adv. Mater. **2018**, 30, 1702770.
- [10] N. R. Hosseini, J.-S. Lee, ACS Nano 2015, 9, 419.
- [11] R. Huang, Y. Tang, Y. Kuang, W. Ding, L. Zhang, Y. Wang, IEEE Trans. Electron Devices 2012, 59, 3578.
- [12] N. R. Hosseini, J.-S. Lee, Adv. Funct. Mater. 2015, 25, 5586.
- [13] L. Pan, Z. Ji, X. Yi, X. Zhu, X. Chen, J. Shang, G. Liu, R.-W. Li, Adv. Funct. Mater. 2015, 25, 2677.
- [14] Y. Liu, H. Wang, W. Shi, W. Zhang, J. Yu, B. K. Chandran, C. Cui, B. Zhu, Z. Liu, B. Li, C. Xu, Z. Xu, S. Li, W. Huang, F. Huo, X. Chen, *Angew. Chem., Int. Ed.* **2016**, *55*, 8884.
- [15] J. Shang, W. Xue, Z. Ji, G. Liu, X. Niu, X. Yi, L. Pan, Q. Zhan, X.-H. Xu, R.-W. Li, *Nanoscale* **2017**, *9*, 7037.
- [16] J. Shang, G. Liu, H. L. Yang, X. J. Zhu, X. X. Chen, H. W. Tan, B. L. Hu, L. Pan, W. H. Xue, R.-W. Li, *Adv. Funct. Mater.* **2014**, *24*, 2171.
- [17] M. Lin, Q. Chen, Z. Wang, Y. Fang, J. Liu, Y. Yang, W. Wang, Y. Cai, R. Huang, *Polymers* **2017**, *9*, 310.
- [18] G. Liu, C. Wang, W. Zhang, L. Pan, C. Zhang, X. Yang, F. Fan, Y. Chen, R.-W. Li, Adv. Electron. Mater. 2016, 2, 1500298.
- [19] C. C. Hung, Y. C. Chiu, H. C. Wu, C. Lu, C. Bouilhac, I. Otsuka, S. Halila, R. Borsali, S. H. Tung, W. C. Chen, Adv. Funct. Mater. 2017, 27, 1606161.
- [20] X. M. Lu, Y. N. Xia, Nat. Nanotechnol. 2006, 1, 163.
- [21] B. Hu, X. Zhu, X. Chen, L. Pan, S. Peng, Y. Wu, J. Shang, G. Liu, Q. Yan, R.-W. Li, J. Am. Chem. Soc. 2012, 134, 17408.
- [22] L. Sheng, J. Zhang, J. Liu, Adv. Mater. 2014, 26, 6036.
- [23] J. Zhang, Y. Yao, L. Sheng, J. Liu, Adv. Mater. 2015, 27, 2648.
- [24] S.-Y. Tang, I. D. Joshipura, Y. Lin, K.-Z. Kourosh, A. Mitchell, K. Khoshmanesh, M. D. Dickey, Adv. Mater. 2016, 28, 604.
- [25] J. Park, S. Wang, M. Li, C. Ahn, J. K. Hyun, D. S. Kim, D. K. Kim, J. A. Rogers, Y. Huang, S. Jeon, *Nat. Commun.* **2012**, *3*, 916.
- [26] Z. Yu, J. Shang, X. H. Niu, Y. W. Liu, G. Liu, P. Dhanapal, Y. N. Zheng, H. L. Yang, Y. Z. Wu, Y. L. Zhou, Y. X. Wang, D. X. Tang, R.-W. Li, *Adv. Electron. Mater.* **2018**, *4*, 1800137.

- [27] L. Pan, G. Liu, H. Li, S. Meng, L. Han, J. Shang, B. Chen, A. E. Platero-Prats, W. Lu, X. Zou, R.-W. Li, J. Am. Chem. Soc. 2014, 136, 17477.
- [28] S. M. Yoon, S. C. Warren, B. A. Grzybowski, Angew. Chem., Int. Ed. 2014, 53, 4437.
- [29] X. Huang, B. Zheng, Z. Liu, C. Tan, J. Liu, B. Chen, H. Li, J. Chen, X. Zhang, Z. Fan, W. Zhang, Z. Guo, F. Huo, Y. Yang, L.-H. Xie, W. Huang, H. Zhang, ACS Nano 2014, 8, 8695.
- [30] C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër, G. Férey, J. Am. Chem. Soc. 2002, 124, 13519.
- [31] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Ferey, *Chem. - Eur. J.* 2004, *10*, 1373.
- [32] M. Kuang, L. Wang, Y. Song, Adv. Mater. 2014, 26, 6950.
- [33] S.-M. Park, N.-S. Jang, S.-H. Ha, K. H. Kim, D.-W. Jeong, J. Kim, J. Lee, S. H. Kim, J.-M. Kim, J. Mater. Chem. C 2015, 3, 8241.
- [34] L. Cai, J. Z. Li, P. S. Luan, H. B. Dong, D. Zhao, Q. Zhang, X. Zhang, M. Tu, Q. S. Zeng, W. Y. Zhou, S. S. Xie, *Adv. Funct. Mater.* **2012**, *22*, 5238.
- [35] S. Q. Liang, Y. Y. Li, J. B. Yang, J. M. Zhang, C. X. He, Y. Z. Liu, X. C. Zhou, Adv. Mater. Technol. 2016, 1, 1600117.
- [36] H. Yang, D. Qi, Z. Liu, B. K. Chandran, T. Wang, J. Yu, X. Chen, Adv. Mater. 2016, 28, 9175.
- [37] D. McCoul, W. Hu, M. Gao, V. Mehta, Q. Pei, Adv. Electron. Mater. 2016, 2, 1500407.
- [38] M. D. Bartlett, N. Kazem, M. J. Powell-Palm, X. Huang, W. Sun, J. A. Malen, C. Majidi, Proc. Natl. Acad. Sci. USA 2017, 114, 2143.
- [39] G. Ferey, C. Serre, Chem. Soc. Rev. 2009, 38, 1380.
- [40] A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, R. A. Fischer, Chem. Soc. Rev. 2014, 43, 6062.
- [41] F. Millange, N. Guillou, R. I. Walton, J.-M. Greneche, I. Margiolaki, G. Ferey, Chem. Commun. 2008, 0, 4732.
- [42] J. M. Salazar, G. Weber, J. M. Simon, I. Bezverkhyy, J. P. Bellat, J. Chem. Phys. 2015, 142, 124702.
- [43] D. Cai, A. Neyer, R. Kuckuk, H. M. Heise, J. Mol. Struct. 2010, 976, 274.
- [44] K. Kinoshita, K. Tsunoda, Y. Sato, H. Noshiro, S. Yagaki, M. Aoki, Y. Sugiyama, *Appl. Phys. Lett.* **2008**, *93*, 033506.
- [45] L. Goux, K. Opsomer, R. Degraeve, R. Müller, C. Detavernier, D. J. Wouters, M. Jurczak, L. Altimime, J. A. Kittl, *Appl. Phys. Lett.* 2011, 99, 053502.
- [46] X. Zhao, J. Ma, X. Xiao, Q. Liu, L. Shao, D. Chen, S. Liu, J. Niu, X. Zhang, Y. Wang, R. Cao, W. Wang, Z. Di, H. Lv, S. Long, M. Liu, *Adv. Mater.* **2018**, *30*, 1705193.
- [47] F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, Mater. Sci. Eng., R 2014, 83, 1.
- [48] S. Kim, H. Y. Jeong, S. K. Kim, S.-Y. Choi, K. J. Lee, Nano Lett. 2011, 11, 5438.

