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Operando Direct Observation of Filament Formation in Resistive Switching Devices Enabled by a Topological Transformation Molecule

Kungi Hou, Shuai Chen, Cheng Zhou, Linh Lan Nguyen, Putu Andhita Dananjaya, Martial Duchamp, Guillermo C. Bazan, Wen Siang Lew,* and Wei Lin Leong*



electrode heights, which serves to enhance the understanding of switching behavior and their variability at device level. Therefore,



sistive random-access memory (ReRAM) is an emerging Renorvolatile memory technology which is of great interest for embedded device applications such as the Internet of Things (IoT), automobile and infotainment platforms, as well as neuromorphic computing,¹⁻⁶ In comparison to flash memory, ReRAM has the advantages of lower power consumption and higher operating speed. It also has low cost per bit and superior scaling capability.^{7,8} The filamentary model has been widely accepted in explaining the switching process, i.e., formation and rupture of conductive filaments (CFs) within a cell that is typically composed of an insulating oxide layer.^{9,10} The CF is composed of oxygen vacancies or defects generated within the oxide layer when under a voltage bias. The key challenges for wafer-level ReRAM have been the variability in device and array level due to the challenges in large area deposition of high-quality oxides, as well as the random electroforming process.

Locating CFs is important as it relates directly to the origin of oxygen vacancies and variabilities in switching.¹ Conductive-atomic force microscopy (C-AFM) technique has been used to localize the CF on the scanned current map after forming process.^{15–21} In situ transmission electron microscopy (STEM) technique has also been developed to learn the dynamics of defects generation and filament formation.^{15,22} While these characterization techniques provide important information about the physics of the CF in the nanoscale region, there are limitations such as the need for removal of top electrode and expertise in specimen preparation, or the use of specimen thinness which can produce an unrealistically small thermal conductance to ambient temperature and alter the switching mechanism,²³ as well as not suitable for large-area spatial filament mapping.²³ Direct observation and correlation between CF formation and its electrical behavior during repeated switching in real device operation remains elusive.

In resistive switching, several hundred degrees Celsius within the formed filament region can be reached due to the significant Joule heating effect. $^{13,24-27}$ On the basis of such a temperature effect, infrared microscopy is used to detect the existence of filamentary conduction by Uenuma et al.^{28,29} The main challenge of this infrared microscopy technique is the calibration of its signal to device temperature and the heat spreading across the top electrode which could limit its spatial resolution.²⁹ Another filament-detecting method involves spin-

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Figure 1. (a) Molecular structure of the TT molecule in the twisted state (left) and the planar state (right). (b) UV–vis absorption spectra of the TT film in the twisted (red) and the planar (blue) state. The peak shift from 335 and 520 nm to 375 and 580 nm, respectively. (c) Schematic demonstration of the working principle of this study. (d) Optical images of the fabricated sample and ReRAM device before and after coating of the TT molecule layer. The ReRAM device has a cross-point structure, with a bottom electrode (BE), oxide layer, and top electrode (TE). (e) Formation of conductive filament after switching on and the impact of generated Joule heating on the color of π -conjugated molecule layer.

coating a photoresist layer on the top of electrode, in which the photoresist layer will be burned out at the filament region due to the Joule heating effect, hence indicating the filament position.³⁰ However, the burn-out of the photoresist is permanent, and repeated observations of the filament formation during the reversible switching process cannot be carried out.

Herein, we introduce a simple-yet-effective approach to observe the filament formation in ReRAM device by utilizing an organic π -conjugated molecule, namely, (7,7'-(3,3'-dihexyl-[2,2'-bithiophene]-5,5'-diyl)bis(6-fluoro-4-(5-hexylthiophen-2-yl)benzo[c][1,2,5] thiadiazole)), referred to as "TT", which exhibits a topological transformation with temperature. As shown in Figure 1a, the TT molecule contains a flexible bithiophene central fragment and possesses unique phase transition properties. It presents the amorphous or twisted state in the initial film formation (red color) and can crystallize over time and ultimately adopting a planar configuration (dark blue color)^{31,32} (Figure 1b). Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements to support the

morphology change have also been reported in previous work.³³ Interestingly, the structural change of the TT film is reversible. Upon heating above 120 °C, the color of TT film changes back to red (amorphous) and to dark blue once the molecule crystallizes over time. At room temperature, this color change of the film took over a period of ~ 23 min. The detailed absorption spectra and color change during the film transition are also shown in Figure S1 and Video 1, respectively. Figure 1c,d presents the schematic illustration of the working principle of this work and the optical images of the fabricated cross-point ReRAM device, where the TT molecule film is placed on top of the top electrode (TE) of the ReRAM device. The CFs can be observed and visualized by TT molecule during the switching process since Joule heating the CF region induced the change of structural properties of TT molecule and therefore color change of the TT film. Figure 1e shows a representative optical image using this technique, where the location of a conductive filament (red spot) is reflected in the optical image at 40 μ m \times 40 μ m device after the electrical setting process.



Figure 2. (a) Schematic drawing of ReRAM coated with filament-detection layer. The ReRAM structure of this work is (tungsten (10 nm)– hafnium oxide (10 nm)–Platinum (10 nm)) cross-point structure. (b) Cross-sectional TEM image of the stacked layers in ReRAM. (c) I-V curves of forming, before, and after spin-coating TT film of the ReRAM stack, and the 100, 300, 500, 1000 I-V data for the same device after depositing TT molecule with the reset stop voltage of 2 V under 1 mA compliance current condition. (d) Distribution of set and reset voltages of ReRAM device. (e) Cumulative probability graph of HRS and LRS among 128 × 6 direct current (dc) cycles with a -0.2 V read voltage. (f) Current waveform during the setting and resetting process, and the current value during the reading process when the device is in LRS and HRS with a 0.2 V read voltage. (g–l) Optical images of the ReRAM with the device area of 20 μ m × 20 μ m, using a 100× microscope. The red spots circled by the dashed lines in the images indicate the approximate locations of the CF, which disappear after the TT film transform to the planar state and reappear again during the setting process after 1 day and 5 months.

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Symmetry rotate T_{max} within filament 1400 b T_{max} on TE surface T (K) on TT surface 1200 т Quadratic fit 800 ГΊ **Femperature (K)** Pt 1000 700 800 сı HfO₂ 600 600 500 400 400 SiO 300 200 0.0 0.5 1.5 3.0 10 20 2.5 Current (mA) 200nm Formed filaments Revealed filaments by TT molecule Tip Photoresist Form the filaments using Depositing the tungsten electrode and TT Remove the photoresist and micro-tip in HfOx layer molecule squentialy on formed HfOx read the ReRAM device е 50um 40um 40um

Figure 3. (a) Structure of built 2D axisymmetric ReRAM COMSOL model. (b) Maximum temperature value and their fittings of CF (purple), TE surface (green), and TT surface (red) with varying applied current. (c) Structure of indium tin oxide substrate (ITO substrate)/HfO_x(12 nm)/ tungsten (the head of microtip) ReRAM stack and the operating procedures used in the microtip study. (d) Optical images of the 40 μ m \times 40 μ m ReRAM device during the filament setting and displaying, where the discoloration spots reflect the formed filaments. e) Triangle, diamond, and pentagon patterns created by the tip and reflected by TT film.

The ReRAM device used in this work comprises a tungsten (10 nm)-hafnium oxide (10 nm)-platinum (10 nm) crosspoint structure (Figure 2a,b). Hafnium oxide (HfO_x) is chosen in this study as it is one of the most commonly used oxide materials for ReRAM devices, and its filamentary switching nature has been well-studied.^{19,34-37} The working principle of such ReRAM stack is demonstrated in Figure S2. We first measured the current-voltage (I-V) curves for the ReRAM devices before and after depositing the TT molecule, to ensure that the TT molecule layer does not affect the performance of resistive switching. The tungsten bottom electrode (BE) was grounded, while the voltage bias was applied to the platinum top electrode (TE). As shown in Figure 2c, the I-V curves of the devices with and without the TT molecule are similar. We also tested six ReRAM devices containing the TT layers for 128 direct current (dc) cycles. Figure 2d shows the average set and reset voltage for each device. This ReRAM stack gives an average forming, set, and reset voltages of -2.08, -1.1, and 0.85 V respectively. The resistances of a high-resistance state (HRS) and low-resistance state (LRS) in each cycle were reviewed on I-V curves at -0.2 V. Figure 2e shows the cumulative probability of resistance states with a 86 463 Ω average HRS and a 817 Ω average LRS, yielding an average on-off ratio of ~106. The current dynamics of the ReRAM

stack with read-set pulse-read-reset pulse-read waveform are also presented in Figure 2f. Good endurance (>1000 cycles) and fast transient response (<20 μ s) of the ReRAM stack are observed (Figure S3). The ReRAM devices therefore showed stable resistive switching according to these electrical characterization results.

To observe the role of the TT molecule, we first compared the optical images of a 20 μ m \times 20 μ m ReRAM device before and after the electrical forming process (Figure 2g,h). The red spot circled by the dashed line in Figure 2h indicates the approximate location of the CF after the electrical forming process. The red spot gradually disappear once the TT film transformed to planar state (after around 1 day); see Figure 2i. We next switched the device to LRS again, and the CF is reflected at the same spot location (Figure 2j). This is most like due to the secondary formed CF growing from the tip of the previous partially ruptured CF, which has also been reported by previous studies.^{38,39} The reset processes can be done repeatedly even after 5 months (Figure 2k,l), which indicates that the partially ruptured CF remains in the oxide layer and the fabricated ReRAM device has good data retention. The color-changing spot appears from a small point and expands quickly to a larger size in hundreds of milliseconds because of the heat diffusion (see attached Videos

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Figure 4. (a) Optical images of 5 ReRAMs with varying color spot size. (b) Relationship between the color spot size and the read current value (blue), and resistance value in LRS (red). (c) Optical images of ReRAMs with different spot numbers. (d) Relationship between spot numbers and the shape of the I-V curve during the forming process.

S2 and S3). We note that the recovering time, i.e., the time for the red spot to disappear, can vary from around 12 h to 1 day. This is due to the generation of different sizes of CFs and therefore varying sizes of the color-changing spots (Figure S4). All filaments formed in different locations of ReRAM devices such as TE edge, BE edge, and center can be successfully detected using this approach (Figure S5).

The high current density associated with filamentary conduction can cause an increase in temperature due to local Joule heating. A COMSOL model with similar ReRAM device structure was built to further verify the temperature distribution inside the device upon applying the current in LRS. The schematic diagram of the model is shown in Figure 3a, where a 2D axisymmetric ReRAM model was built up in COMSOL. The detailed information on varying parameters used inside the model can be found in the Supporting Information (Note 1). The simulated maximum temperature values of CF, TE surface, and TT molecule surface as a function of applied currents were plotted in Figure 3b. The temperature (T) displays a quadratic relationship with the applied current (I), where $T \propto P = I^2 \times R$, where P refers to the power of Joule heating and R is the resistance. The simulations results showed that the temperature on the TT surface can reach 400 K (~127 °C) under the condition of a 1.6 mA read current, which is sufficient to modulate the topological state of the organic film (~120 $^{\circ}$ C). The simulation studies on varying CF sizes and TE thicknesses, as well as temperature diffusion dynamics were also conducted, which are shown in Figure S6. The simulation results therefore give qualitatively proof of the proposed method, where the

Joule heating generated can be used to optically modulate the TT film.

To further verify this new filament detection method, we carried filaments programming through a microtip before the deposition of the TT molecule. A tungsten microtip with ~ 5 μ m diameter was placed in direct contact with the HfO_x film, which was deposited on indium tin oxide (ITO) substrate. The ITO and the tungsten tip serve as BE and TE, respectively. The CFs can therefore be formed within the oxide laver by applying the voltage bias through the tip and ITO substrate (Figure S7). Thereafter, varying numbers of CFs could be formed in different locations. The tungsten tip is then removed, and the platinum TE and TT film were deposited sequentially. A read voltage is then applied to the ReRAM stack. The schematic diagram of this process is shown in Figure 3c. As presented in Figure 3d, the filament that is preset by the tungsten tip is reflected by the spot of color change on TT film. We also created more customized filaments using the microtip, where the formed filaments are in shapes of triangle, diamond, and pentagon, and all these formed filaments were reflected by TT film accurately (Figure 3e). Hence, this filament programming study gives quantitative confirmation of such filament detection method.

Besides the position, the size of formed CFs can also be monitored by the TT film, where a larger color spot larger indicates a larger size of CF due to the larger heat diffusion area (Figure 4a). We further correlate these different sizes of CFs with the resistance and read current values in LRS, where the resistance value decreases as the color spot size increases, and the read current (under a 0.2 V read voltage) showed a



Figure 5. (a) Spatial maps of the CF distribution for $10 \ \mu m \times 10$ to $50 \ \mu m \times 50 \ \mu m$ ReRAMs. (b) Statistical result on the CF number per device and P_{be} , and their relationship to the device area. (c) Value of P_{be} with respect to BE thickness. Forty ReRAM devices were measured for each BE thickness. (d) Variations of LRS in 32DC cycles for 18 ReRAM devices, and its relationship with the CF number.

positive relationship with the color spot size (Figure 4b), in agreement with previous studies.⁴⁰ Moreover, in some other devices, multiple color spots can be observed which indicates that more filaments were generated during the forming cycle. As shown in Figure 4c,d, multiple increment steps (resistance states) can be observed in the I-V curves for multiple CF-based ReRAMs (device 3 and 4), while the current value directly reached the compliance for single CF-based ReRAMs (device 1 and 2).

We further conducted a statistical study, which focuses on the spatial distribution of CFs to understand the relationship between filament-forming and ReRAM device geometry. Here, a total of 200 devices were fabricated with varying sizes (from 10 μ m × 10 to 50 μ m × 50 μ m) and BE thicknesses (10, 15, and 20 nm). The location of CFs for each device was recorded through the color-changing spot of TT film after the electroforming process. The detailed information on the procedure to obtain the filament coordinates is shown in Figure S8. Figure 5a shows the spatial mappings of the CF distribution with varying sizes (BE height was kept at 10 nm). In general, there is a trend that more filaments tend to be formed for larger-area devices (Figure 5b). In addition, the number of CFs formed at the edge of BE is found to increase significantly with decreasing device size. The probability of filament forming at BE edge (P_{be}) also displayed an inverse proportion to the device size (Figure 5b). We postulate that this is likely due to the device fabrication process where the BEs were directly deposited on substrates. This will cause an edge effect, where the thickness of deposited oxide film is not uniform and will induce thinner oxide thickness at the edge area of BE. This edge effect is also more pronounced with higher BE

thickness,^{30,41} where an increasing number of CFs are formed at the BE edge (\sim 24, \sim 31, and \sim 36%) for increasing BE thickness (10, 15, and 20 nm); see Figure 5c.

Multiple filaments based ReRAM are typically not desired as the setting process might not switch on every filament which will induce a larger uncertainty in LRS. Using this approach, we also compared the performance of ReRAM devices with varying number of filaments. Eighteen devices with varying filament numbers were conducted for 32 dc cycles. The variations in HRS and LRS were extracted from the cycling data. As shown in Figure 5d, a single-filament-based ReRAM is shown to exhibit a more stable resistance state in LRS. The average variation in LRS for a single-filament ReRAM is less than 20%, and the variation is found to increase with increasing filament numbers. The variations of HRS, set voltage, and reset voltage among these devices were also summarized in the Figures S9-11. Our results indicate that scaling down the device size is a way to control the filament number and minimize the variations.

In conclusion, an operando direct observation of filament formation and its properties for ReRAM at device level has been enabled by using a thermoresponsive conjugated molecule. The number, size, and position of CFs that formed within the oxide layer are revealed by the localized color change of the π -conjugated molecule layer. Such a method expands the filaments in the nanoscale to microscale by colorchanging spots, which were formed by the diffusion of localized Joule heating. Most importantly, the location can be easily observed and studied using a simple optical microscope. Notably, this organic molecule can display the CFs repeatably, which revealed the same filament multiple times over a 5 month interval. A 2D axisymmetric ReRAM model has been built up to confirm this filament positioning method, where the results showed that the temperature increment generated by the Joule heating effect can induce the structural transformation of the organic film. CFs were also deliberately programmed by the microtip, and the TT film was able to reflect the same CF locations, which confirms the viability of this approach. Finally, using this approach, we found the following: (1) Multiple CFs are relatively easier to form in devices with larger area. (2) There is a higher possibility of CFs formation at the edge of BE with decreasing device size and increasing BE thickness. (3) The variations in LRS for single filament devices were smaller. The resolution of this filament detection method can be further improved by limiting the amount of heat generation, which requires an accurate current limiter, e.g., transistor. If the amount of current/heat could be precisely controlled, then the colorchanging area will be confined to a smaller region. We believe the filament positioning method based on the topological transformation of TT molecule is a powerful technique to study filament properties and design of high-performing ReRAM devices.

EXPERIMENTAL SECTION

Experimental details on ReRAM device fabrication, electrical characterization, TT film preparation, and TEM sample preparation are shown in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c03180.

Methods and experimental details, absorption spectra during the transition of the TT film, heightmap of ReRAM device area characterized by AFM, endurance data, transient response during set process and reset process for fabricated ReRAM, COMSOL simulation results, optical images of color-changing spots I-Vcurves for filament programming, variations of HRS, set voltage, and reset voltage (PDF)

Video S1: Color-changing video of TT film heated on 125 $^{\circ}$ C hot plate (MP4)

Video S2: Formation and expansion of color-changing spot (MP4)

Video S3: Formation and expansion of color-changing spot (MP4)

AUTHOR INFORMATION

Corresponding Authors

- Wen Siang Lew School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore; orcid.org/0000-0002-5161-741X; Email: wensiang@ntu.edu.sg
- Wei Lin Leong School of Electrical and Electronic Engineering, Nanyang Technological University, 639798, Singapore; orcid.org/0000-0002-1402-0083; Email: wlleong@ntu.edu.sg

Authors

Kunqi Hou – School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore

- Shuai Chen School of Electrical and Electronic Engineering, Nanyang Technological University, 639798, Singapore; orcid.org/0000-0002-8562-5784
- **Cheng Zhou** Depertment of Chemistry, National University of Singapore, 117543, Singapore
- Linh Lan Nguyen School of Materials Science & Engineering, Nanyang Technological University, 639798, Singapore
- Putu Andhita Dananjaya School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore
- Martial Duchamp School of Materials Science & Engineering, Nanyang Technological University, 639798, Singapore; orcid.org/0000-0003-2105-3059
- Guillermo C. Bazan Depertment of Chemistry, National University of Singapore, 117543, Singapore

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.nanolett.1c03180

Notes

The authors declare no competing financial interest.

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