In situ imaging of the conducting filament in a silicon oxide resistive switch

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The nature of the conducting filaments in many resistive switching systems has been elusive. Through in situ transmission electron microscopy, we image the real-time formation and evolution of the filament in a silicon oxide resistive switch. The electroforming process is revealed to involve the local enrichment of silicon from the silicon oxide matrix. Semi-metallic silicon nanocrystals with structural variations from the conventional diamond cubic form of silicon are observed, which likely accounts for the conduction in the filament. The growth and shrinkage of the silicon nanocrystals in response to different electrical stimuli show energetically viable transition processes in the silicon forms, offering evidence for the switching mechanism. The study here also provides insights into the electrical breakdown process in silicon oxide layers, which are ubiquitous in a host of electronic devices.

Results

Figs. 1b–d shows the schematics of the device design and setup for the in situ imaging. The imaging region consists of a SiOₓ thin-walled structure covered by a layer of amorphous carbon (α-C), which is connected to...
external electrical inputs (Fig. 1b). By electrical breakdown in the α-C layer, a disruption region or nanogap can be produced as we described previously in planar carbon-coated SiOx devices12. The broken ends of α-C layer then serve as the electrodes for the SiOx in the nanogap region. The use of α-C as the electrode material eliminates possible extrinsic effects from metals13, and the electrical breakdown-generated nanogap provides an easy method for the fabrication of closely spaced electrodes atop a thin-walled structure. The confinement from the nanogap pre-localizes the switching site so that it can be constantly monitored from before the electroforming or filament formation and throughout the experiment. During imaging, the electron beam from the TEM system travels perpendicularly across the SiOx thin-walled structure. In this configuration, the SiOx and the α-C layer are spatially separated in the imaging plane, minimizing possible interference from the electrode material. Practically, for the successful passage of the electron beam across the nanogap region, a multi-stage design with the SiOx thin-wall structure is required (Fig. 1c). This multi-stage device is then vertically mounted on a home-built TEM stage (Supplementary Figs. S1, S2) that is capable of in situ electrical characterization (Fig. 1d). Note that while high vacuum environment (~10^-8 Torr) is involved in the TEM system, the multi-stage devices also work in the regular vacuum environment (~10^-3 Torr) in a probe station as was adopted for typical device testing13. It shows the same resistive switching behaviors (Supplementary Fig. S3) with no SiOx thin-wall thickness dependence, indicating the same switching mechanism intrinsic to SiOx as reported previously.

Figs. 2a–d shows a series of scanning electron microscopy (SEM) images of the multi-stage device (see Supplementary Fig. S2 for fabrication details). The thickness of the SiOx thin-walled structure is ~100 nm for the electron-beam transparency, and the length is ~1 µm to reduce the resistance of the α-C electrodes (~20 nm thick). The successful imaging of the pristine structure by TEM is shown in Fig. 2e. After electrical breakdown in the α-C layer, a nanogap is generated in the α-C layer atop the SiOx thin-walled structure (Fig. 2f).

Fig. 3 shows a series of high-resolution TEM images of the nanogap region (right panels) with respect to different I–V responses (left panels). Note that during the electrical characterization, the electron beam was temporarily blocked to exclude beam impact13. Immediately after the electrical breakdown in the α-C layer, a nanogap of ~15 nm is formed (Fig. 3a). Both the SiOx at the nanogap region and the SiOx far from the nanogap show amorphous silica features. Because of the disruption in the α-C layer, the device shows little conduction during the subsequent voltage sweep, until ~12 V the current suddenly increases (light grey curve in the plot of Fig. 3b). This conductance increase features the beginning of the electroforming process in SiOx. The device is subsequently electroformed, showing the characteristic I–V curve featuring current increase (at ~5 V) and decrease (at ~10 V) that define the typical set and reset processes, respectively (grey curve). The device is set to the ON state (red curve). The immediate TEM imaging shows morphological changes at the nanogap region (Fig. 3b), as is often associated with the electroforming process14. Specifically, out of the amorphous background, ~3 nm regions of nanocrystalline structure (based on the appearance of lattice fringes) appear at the nanogap (bounded region and inset in Fig. 3b). The apparent lattice spacing of the nanocrystal based on the fringes is distinct from that of the α-C, indicating a different material form.

Due to the beam impact (see below), the formed ON and switching states degrade after imaging (light grey curve in Fig. 3c). A subsequent re-electroforming process is involved to set the device back to ON (grey and red curves). The immediate imaging shows growth in the nanocrystal (bounded region and inset in Fig. 3c). The partially degraded ON state after this imaging is compensated by a set process (red curve in Fig. 3d). For the subsequent voltage sweep to 14 V, a sudden decrease in the conductance occurs at ~12 V, featuring the
typical reset process. The immediate imaging shows prominent shrinkage in the size of the nanocrystal (bounded region and inset in Fig. 3d).

**Discussion**

The nanocrystalline structures were persistently observed only at the nanogap region in the switching devices, indicating their correlation with the electroforming and switching processes. Selected area electron diffraction shows that the crystalline structures are consistent with Si nanocrystals (NCs) and not silicon carbide (Supplementary Fig. S4). As SiOₓ is the only source containing the Si element, the formation of the Si NCs shows that the energetically viable SiOₓ → Si process is associated with the electroforming process. The *in situ* recording of this process also excludes the possibility of processing-induced formation during the filament isolation as was involved in *ex situ* imaging. This TEM imaging process was studied over four different devices (Supplementary Figs. S4, S5), all yielding similar information.

As the ON state shows largely metallic conduction, questions arise regarding the composition of the conductor since conventional silicon is semiconducting. Lattice-spacing measurements and electron diffraction patterns from the Si NCs show evidence of structural deviation from the conventional diamond cubic Si-I phase. As shown in Fig. 4, the intersected lattice spacing of 0.33 and 0.32 nm with a nearly perpendicular angle is the feature of the Si-III phase, which is semi-metallic and often associated with other conducting phases. This indication can also be seen in Fig. 3; while the lattice spacing of 0.27 nm can be assigned to Si-I(200), Si-III(211) or Si-XII(11-2) faces, that of 0.33 nm (Fig. 3b) can only be associated with Si-III/Si-XII phases. In particular, as Si-I(200) is the forbidden plane for diffraction and multiple scattering is considerably weakened at the nanoscale crystalline size, the strong signal of 0.27 nm⁻¹ in the diffraction patterns is further indication of the conducting Si-III/Si-XII phases (Supplementary Figs. S4, S5). While these phase transitions in Si are typically induced by mechanical pressurization, here it is...
possible that the high electric field attained at the nanogap is inducing these phases. Indeed, the pressure induced by high electric field was revealed to induce structural distortion in silicon crystals. The stability of the formed silicon phases at ambient environment also accounts for the electronically nonvolatile property in SiOx resistive switching memory. Remarkably, the suppression of the electroforming and switching in SiOx at low temperature coincides with the fact that the Si-III phase cannot be formed at liquid-nitrogen temperature. Furthermore, the semi-metallic NCs suggest a rationale for failure to induce gating in three-terminal embodiments of these devices, which was originally proposed to be carbon switching and later clarified as SiOx-derived switching. Note that while the elementary composition of the Si filament was identified in our previous ex situ imaging study, its structural variation from the conventional Si form was not revealed due to the absence of a diffraction pattern. This revelation could have been further hindered by the alteration of the Si forms during sample preparation by FIB in the ex situ imaging, as the ion beam can potentially induce phase transitions in the Si forms.

From the devices studied, the filament in SiOx is not in the form of a continuous single crystal across the nanogap, as seen in TiOx switching systems. Instead, discrete Si NCs form across the nanogap. Imaging such a filament is challenging, because of its 3-dimensional structure (e.g., having different depth profiles perpendicular to the imaging plane), different crystalline orientations, and the possibility of narrower filamentary constrictions that are difficult to resolve from the environment. The growth of the Si NCs (Fig. 3c) indicates the general Si-rich nature along the nanogap in the electroformed device. This Si enrichment is also evidently correlated with the indentation and shrinkage of the volume at the nanogap region, likely a result of oxygen outgassing. The shrinkage of the Si NCs with respect to the conductance drop (Fig. 3d) indicates the possible amorphization process. This is consistent with the thermally induced amorphization observed in the metallic Si phases, as the reset process in unipolar resistive switching is largely thermally stress-driven. In particular, resistance increase is associated with the amorphization process. This provides a possible scenario for the filament rupture in the reset process.

We further take the electron-beam impact into consideration during the mechanistic interpretations. As mentioned above, the electron beam from the TEM system tends to degrade the conduction and switching state in SiOx. This does not indicate a charge-based mechanism though, as that was ruled out in the x-ray irradiation experiment and high temperature stability measurements. In fact, knock-on structural change in Si can be readily induced by an electron beam at the imaging energy (200 KeV), and the amorphization process can be induced. This accounts for the switching degradation after beam exposure (Fig. 3b) as structural changes along the entire filament are induced. While this is a further indication of structural change-induced conductance switching in the Si filament, it also implies that the structural transition needed for the switching can be subtle.

As was mentioned before, the SiOx resistive switching system shows a larger reset voltage than the set value (i.e., $V_{\text{reset}} > V_{\text{set}}$), which is different from typical unipolar systems that have $V_{\text{set}} > V_{\text{reset}}$. We suggest that the electric-field effect and thermal effect (by current local heating) are largely responsible for the set and reset processes, respectively, and that the competing process between the two effects results in this different behavior. The SiOx resistive switching system features a lower ON-state conductance compared to other unipolar systems. As a result, no current compliance is needed in the set process to suppress the thermal reset effect. The thermally driven reset process is induced at a higher voltage $V_{\text{reset}}$ ($V_{\text{reset}} > V_{\text{set}}$). Note that competition between the two processes persists in the region $V > V_{\text{reset}}$ with the thermal reset effect constant overrides the set process driven by the field effect. This dynamic competition is evident from the large current fluctuations in the $V > V_{\text{reset}}$ region, which sometimes even shows transient ON-state fluctuations (Supplementary Fig. S3a). This competition also explains why during a backward sweep the system goes back into ON state below $V < V_{\text{reset}}$ (ref. 9,12,27), because the field is sufficient to set the system to ON at $V > V_{\text{reset}}$, whereas the thermal effect is too weak to prevent this at $V < V_{\text{reset}}$. Note that while the thermal effect has been generally deemed responsible for the reset process in unipolar resistive switching systems, no direct observation has been made. Our in situ study provides further evidence and insights for this process.

In summary, the study here provides an overall picture of the intrinsic resistive switching in SiOx. The electroforming is through the SiOx→Si process with the semi-metallic Si state identified. The switching is indicated to be through the transition between the semi-metallic and amorphous Si forms. It also provides a general overview of electrical breakdown in silicon oxides. It should be noted that while a redox process was proposed to be responsible for the switching in our previous study, the current study suggests switching based on structural transitions of the Si. The degradation of the resistive switching state to a nonswitchable metallic state (hard breakdown) in SiOx is likely to be associated with the further aggregation of the metallic Si forms. The method described here can also be applied to other resistive switching materials for mechanistic investigation.

**Methods**

The multi-stage SiOx thin-wall structure as shown in Fig. 2 is fabricated from a silicon wafer (thickness ~ 500 μm) capped with 2 μm thermal SiOx ($x = 2$) on top. The n-C layer was grown by chemical vapor deposition method at 900°C using C2H2 as precursor gas. Electron-beam lithography, photolithography and reactive ion etching steps were involved for the definition of the multi-stage SiOx imaging structure (see Supplementary Information for more details). The fabricated structure was then mounted to a home-built TEM stage (Supplementary Figure S1) that is capable of electrical input, and electrically connected (through wire bonding) to an Agilent B1500 semiconductor parameter analyzer for the electrical characterizations. The imaging is carried out on a JEM-2100F TEM system with the beam energy at 200 KeV.

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**Figure 4** TEM and diffraction patterns from a different device. (a) High-resolution TEM image of the nanogap region from another SiOx switching device. (b) Selected-area diffraction pattern of the region shown in (a). (c) A fast Fourier transformed micrograph of the image shown in (a).
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Author contributions

J. Y. designed and carried out the experiment, did the data analysis and wrote the paper. L. Z., D. N. and J. M. T. oversaw the project and edited the manuscript.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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