Real-time in situ optical tracking of oxygen vacancy migration in memristors

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Resistive switches, which are also known as memristors, are low-power, nanosecond-response devices that are used in a range of memory-centric technologies. Driven by an externally applied potential, the switching mechanism of valence change resistive memories involves the migration, accumulation and rearrangement of oxygen vacancies within a dielectric medium, leading to a change in electrical conductivity. The ability to look inside these devices and understand how morphological changes characterize their function has been vital in their development. However, current technologies are often destructive and invasive. Here, we report a non-destructive optical spectroscopy technique that can detect the motion of a few hundred oxygen vacancies with nanometre-scale sensitivity. Resistive switches are arranged in a nanoparticle-on-mirror geometry to exploit the high optical sensitivity to morphological changes occurring in tightly confined plasmonic hotspots within the switching material. Using this approach, we find that nanoscale oxygen bubbles form at the surface of a strontium titanate memristor film, leading ultimately to device breakdown on cycling.
material strontium titanate (SrTiO$_3$), which is otherwise invisible to non-invasive electron microscopy techniques.

**Device structure and experimental set-up**

We fabricated cells with a conventional TiN/SrTiO$_3$ (TiN/STO) layer stack and a gold-nanoparticle (AuNP) top electrode (Fig. 1a,b). The STO acts as switching material, while the bottom conducting TiN layer forms the counter-electrode. Being widely adopted for ReRAM cells$^{28-30}$, STO is an ideal model material system. We emphasize that the optical properties of TiN follow a Drude-like behaviour, similar to Au, thus forming nanogaps with strong plasmonic field confinement when close to metallic nanoparticles (nanoparticle-on-mirror (NPoM) geometry$^{27}$; Fig. 1a).

The NPoMs were individually electrically contacted from the top using a flexible transparent Si$_3$N$_4$ tip-less cantilever coated with 3-nm Cr and 6-nm Au, yielding a resistance of $\approx 3 \Omega$ (Fig. 1b). This allowed unobserved observation of AuNP scattering under the cantilever through dark-field spectroscopy (Fig. 1b,c). The density of AuNPs (80-nm diameter) on the sample surface was further reduced in the deposition phase to ensure that the NPoM structures were individually contacted, with the large cantilever area ensuring edge scattering was not collected. Compared to the highly scattering atomic force microscopy (AFM) tips, this cantilever contacting allows optical access to the very inner regions of the device. To further ensure electrical connection only through the AuNP without any direct cantilever contact with the STO surface, the system was conformally coated with an insulating parylene layer, which was dry-etched to expose the AuNP crown while maintaining a pinhole-free insulating barrier over the surrounding surface (Methods).

The valence change mechanism is responsible for the switching process in this cell, with the oxygen vacancies experiencing drift under bias through the STO layer. Resistive switching is enabled by a voltage (typically 8 V–12 V) applied to the STO, thus forming nanogaps with strong plasmonic field confinement when close to metallic nanoparticles (nanoparticle-on-mirror (NPoM) geometry$^{27}$; Fig. 1a).

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In our measurements, the cantilever was gradually lowered into contact with the top of an isolated NPoM structure until it was locally parallel to the device top surface. The cantilever position and tilt orientation were controlled within $< 1 \text{nm}$ and $< 0.2^\circ$, respectively, using a piezoelectric stage while observing the wedged interference fringes created by the cantilever when approaching the Au mirror. Compared to the >10 GPa van der Waals forces across these nanometre-scale metal gaps, the cantilever makes little difference ($\approx 0.04 \text{ GPa}$) because it accommodates contact by bending along its 200$\mu$m length (Methods). The pressures used here are within a safe range where they play no role in the switching (Supplementary Section G).

We recorded the dark-field scattering spectra and voltage–current signals simultaneously. The localized plasmons of each AuNP couple to their image charges in the TiN film underneath the STO spacer layer, forming a confined plasmonic hotspot, similar to a nanoparticle dimer$^{29,30}$. The NPoM configuration has been investigated extensively$^{27}$. The optical response of this system was measured by illuminating the sample with a white-light beam incident at 60° and collecting the scattered light through a dark-field objective (Methods). Light was collected by a cooled spectrometer and a charge-coupled device (CCD) camera.

**Experimental optical investigation of switching cycles**

We focused our attention on two sets of samples with STO thicknesses of $d = 8 \text{ nm}$ (D8, Fig. 2a–c) and 4 nm (D4, Fig. 2d–i), respectively, as demonstrated via cross-sectional TEM (Supplementary Fig. 4). The results are representative, but the behaviour for each specific cell differs slightly in the details—spectral changes are consistently observed only upon switching, but the change in intensity or peak position can vary due to the nature of the switching mechanism (Supplementary Fig. 1), which involves stochastic processes and a complex interplay between electrochemical and diffusion effects (Supplementary Section H). The cells here switch to the LRS at a set voltage $V_{\text{SET}}$, defined as the voltage where the current abruptly changes from <40 pA to several nanoamperes (Fig. 2b) or microamperes (Fig. 2f). Applying a negative voltage results in a reset of the cell (switching back to the high-resistance off state, HRS).

For the D8 sample, the AuNP scattering spectra show a strong plasmon resonance at $\lambda_s \approx 610 \text{ nm}$ (Fig. 2a,c(I)). Focusing on times preceding the clear electrical switching event ($20 \text{ s} < t < 30 \text{ s}$), the longer-wavelength peak $\lambda_2 \approx 780 \text{ nm}$ grows (Fig. 2a,c(III)). After the set event at $t \approx 30 \text{ s}$, the total conductance reaches $10^{-10} \text{ G}_0$ ($30 \text{ s} < t < 70 \text{ s}$), well below that for an atomic point contact ($\text{G}_0 \approx 7.75 \mu\text{S}$ is the quantum conductance), as expected for ReRAM systems with narrow conductive filaments$^{26}$. In fact, the presence of oxygen vacancy paths in the dielectric gives extended bands in the gap$^{25}$, resulting in conductance $G \approx \text{G}_0$ for one vacancy path and $G \ll \text{G}_0$ when several vacancies are removed from the single-vacancy filament, hence positioning the energy of the first subband just above the electrode Fermi level$^{21}$. Although for this device the peak scattering $\lambda_2$ changes little with time, its intensity transiently halves following the switching event (Fig. 2a,c(III)). By contrast, the longer-wavelength peak $\lambda_1$ retains its intensity with a redshift of only a few nanometres. After the reset event ($t > 70 \text{ s}$), the $\lambda_1$ peak intensity increases to its value before switching, while the $\lambda_2$ peak remains unchanged (Fig. 2a,c(IV)). This highlights the non-reversibility of the ReRAM switching process, which is unable to bring the system back to the morphology of a pristine cell (I). Only three switching cycles are observed for the D8 sample.

**Fig. 1 | Memristive device in a plasmonic geometry.** a, ReRAM in an NPoM geometry, with plasmonic field tightly confined in the spacer material, STO, between an AuNP and the TiN film. b, Optical spectroscopy is performed through a transparent but electrically conductive cantilever that is used to contact each individual AuNP isolated by the surrounding insulating parylene layer. c, Dark-field top view of AuNPs on an STO layer, seen through the cantilever.
Turning our attention to the D₄ sample (Fig. 2d–i), we observe switching over multiple cycles when the applied voltage is repeatedly switched (Fig. 2e,g). Again, a shorter-wavelength mode λ₁ ≈ 630 nm is identified, with an intensity that reduces upon switching, as in the D₈ sample (Fig. 2d,h,i). A longer-wavelength peak λ₂ ≈ 750 nm is again visible upon switching (Fig. 2h, red), but, in contrast with the D₈ sample, it is much weaker and completely disappears upon reset (Fig. 2i, purple). The D₄ sample thus shows fully reversible switching cycles of the NPoM memristive cell.

Tracking oxygen vacancies drift and nanobubbles formation

To link the optical signatures observed experimentally with the various morphology regimes, we used a combination of density functional theory (DFT) calculations and finite-difference time-domain (FDTD) simulations (Methods) to meticulously analyse how oxygen vacancy drift influences the plasmonic modes in STO layers, and thus the experimentally measured spectra.

In the NPoM structure, aligning the lower nanoparticle facet (typically w = 20–30 nm wide) against the flat mirror (Fig. 3c,d) creates a thin plasmonic cavity that supports multiple ‘cavity’ resonances or gap modes. Plasmon oscillations in the nanoparticle, perpendicularly to the surface, induce image charges within the TiO₂ layer (confirmed by TEM; Supplementary Fig. 4), resulting from oxidation of the top few nanometres of TiN during STO growth (Fig. 3c,d). Figure 3b shows the field enhancement in the middle of the STO layer, where the energetically lowest mode appears at ~550 nm for both devices. The λ₁ mode radiates significantly, whereas the λ₂ mode absorbs, producing a dip in the radiative spectra. Hence, the scattering peak measured at longer wavelengths >800 nm is not in fact a resonance of the system, but is the result of the superposition of the dark mode λ₁ on the broad tail of the bright
mode $l_{10}$. Our experiments show narrower resonances, probably due to weaker absorption in the measured system than expected from literature dielectric constants \cite{10,s19}, but the resonances are fairly consistent between the experiment and simulation.

The oxygen vacancy bridge formed between the nanoparticle and the TiN mirror allows current to flow between the two structures when a bias is applied. The optical properties of the STO change when it fills with oxygen vacancies. To calculate this, we used DFT considering a $2 \times 2 \times 2$ supercell with 24 oxygens to simulate SrTiO$_3$. From the energy levels, we obtained the corresponding dielectric functions, with vacancy concentrations from $\alpha = 4$ to $20\%$ (1/24 to 5/24 in the supercell) (Supplementary Fig. 5).

To parameterize the influence of oxygen-vacancy-rich bridges on the spectral far-field response of the NPoM system, we incorporated these DFT optical properties into FDTD simulations of the bridge between TiN and an 80-nm AuNP with fixed circular facet diameter $w = 30$ nm (Fig. 3c). This was progressively conductively connected to the Au surface through a bridge with a content of 4% oxygen vacancies in the centre of the AuNP facet. The diameter of the cylindrical conductive bridge was varied from $b = 0$ to 30 nm, from no connection to a bridge with a size that equals the full facet, giving the optical spectra shown in Fig. 3e,f. The $l_{10}$ resonance blueshifts and its scattering amplitude decreases by up to ~30% as the vacancy bridge is formed. This corresponds well with the experiment (Fig. 2a,d), where the scattering of both devices decreases at 600 nm when current flows between the AuNP and the TiN mirror (that is, the device was on), although the peak positions are slightly shifted. Although the behaviour is qualitatively predicted, the intensity change (~150% for experiments in $D_4$; Supplementary Fig. 14) might be influenced by slight variations of refractive index from the DFT predictions.

By contrast, the peak at 840 nm is barely affected by the conductive vacancy bridge, indicating that an additional process, more dominant for $D_8$, occurs. To explain the observed spectral shifts we are forced to conclude that, with enough oxygen vacancies, the dense oxygen at the other electrode reversibly converts to O$_2$ gas, strongly perturbing the scattering response. As previously found, ultrathin oxide layers can reversibly form oxygen under high fields \cite{40}. To study the influence of O$_2$ content on the spectral far-field response, FDTD simulations were performed with a fixed facet diameter of $w = 30$ nm, fixed bridge size of $b = 30$ nm and thin dome-shaped oxygen bubble height at the STO interface that varied from $h = 0$ nm to 4 nm (Fig. 3g,h). These scattering spectra show that the O$_2$ reservoir has a very strong impact on the scattering strength at ~840 nm, but negligible change to the $l_{10}$ mode scattering peak at ~700 nm. Note that, for $D_8$, the scattering intensity at 840 nm is substantially brighter for larger O$_2$ reservoirs and reaches similar values to the $l_{10}$ mode scattering at ~700 nm. This behaviour is in agreement with the experimental results of Fig. 2a–c, where the $\lambda_2 \approx 800$ nm peak has stronger scattering intensity.

From our simulations, we thus conclude that changes to the main bright $l_{10}$ mode at $\lambda_1 \approx 600$ nm are due to the formation of the current-carrying vacancy bridge, which eventually turns the device on, while changes to the $\lambda_2 \approx 800$ nm peak come from superposed $l_{10}$ and $l_{11}$ modes arising from formation of an O$_2$ nanoreservoir at the STO/TiO$_2$ interface \cite{31}. Each spectral peak...
Fig. 4 | Numerical simulations of optical modes through the first switching cycle. **a**, Scattering intensities (a) of the structures in **b**: oxygen vacancies distributed through pristine sample (I), device pre-switching with $h = 2\,\text{nm}$ (II), device switched on with $h = 2\,\text{nm}$ and $b = 30\,\text{nm}$ (III) and resetting of the device into the off state with $h = 4\,\text{nm}$ (IV).

can be independently used as a signature for real-time and in situ readout of morphological changes occurring in the STO switching material, with few-nanometre resolution (lateral optical-mode full-width at half-maximum $\sqrt{\text{full}} \approx 11\,\text{nm}$ and $15\,\text{nm}$ for $D_2$ and $D_4$, respectively; Supplementary Fig. 12). Changes in $I_{s0}$ scattering intensity enable us to resolve the construction of these oxygen vacancy bridges for long times before the actual set event, even though the electrical signature only shows a sharp transition into the on state (Supplementary Fig. 14c). To highlight this ability to link nanoscale morphological changes to scattering spectra, we simulated the full evolution through a switching cycle (Fig. 4a). The pristine sample (no. 0), with no conductive bridge and no $O_2$ bubble, initially grows through (nos. 1–2) an $O_2$ reservoir of height $h = 2\,\text{nm}$ to a conductive bridge (on state, nos. 3–5) of $w = 30\,\text{nm}$ together with an $O_2$ reservoir of $h = 2–4\,\text{nm}$. Afterwards (reset, nos. 6–8), no conductive bridge remains, but an oxygen bubble of $h = 4\,\text{nm}$ is left behind. Although our model is necessarily simplistic, it is able to reproduce the experimental switching event depicted in Fig. 2a, with the corresponding spectra I, II, III and IV matching between experiment and simulations (Fig. 4), supporting our explanation. Comparing the intensity change for the $\lambda_i$ peak both in experimental and simulated scattering spectra enables us to optically track the bubble formation and its enlargement (Supplementary Fig. 13). The $\sim 90\%$ increase in scattering intensity at $\lambda_i$ in the pre-switching phase (II) of $D_8$ matches our FDTD simulations of the long-wavelength peak when an $8\,\text{nm} O_2$ bubble is formed in the STO layer. This highlights the substantial material transformation that characterizes the poor switching behaviour of $D_4$.

The first switching event of $D_8$ demonstrates non-reversible behaviour and shows the considerable stress built into the STO. This results in non-stable devices unable to perform multiple cycles, so that early breakage is observed. By contrast, $D_4$ (Fig. 2d–g) is characterized by continuous repeatable switching. From its spectroscopic signature, showing the plasmonic modes $\lambda_i$ consistently decreasing (oxygen vacancy accumulation) and $\lambda_1$ increasing ($O_2$ bubble formation) in intensity with switching over multiple cycles, we conclude that the $O_2$ reservoir is fully reabsorbed into the structure after every reset event. In our study, the devices with 8-nm STO thickness were more prone to fail than devices with 4-nm STO thickness, which could undergo hundreds of cycles (Supplementary Fig. 15d). The optical signatures of oxygen bubbles present in the 8-nm device (which possibly has a larger (thicker) STO reservoir of vacancies) suggest this plays a significant role in the failure mechanism.

Similar results were obtained for other devices, showing how spectroscopy is able to characterize the movement of oxygen vacancies before any electrical transport changes can be resolved (Supplementary Fig. 14c), as well as showing that oxygen nanobubble formation at the TiN/STO interface is a key cause of failure. We underline how such optical spectroscopy finally enables an improved understanding of the causes leading to device breakdown. This is achieved with an in situ technique that tracks, in real time, under ambient conditions and without perturbing the system, oxygen vacancy migration within a few nanometres of the switching layer, which can thus be combined with other techniques and environmental conditions.

Conclusions

We have linked the fields of nanoscale device engineering and plasmon-enhanced light–matter interactions to implement optically accessible resistive switches. A conductive transparent cantilever with nanoparticle-mediated electrical contacts provides a useful and non-destructive method to characterize the resistive switching effect in ReRAM devices. Avoiding the impact of electron beams and the need for lateral junctions (required for electron beams to access the region of the filament formation) are key benefits of this approach. Our experimental and numerical investigation generates new insight into the mechanism behind drift and accumulation of oxygen vacancies, the creation of a conductive channel between the electrodes, and formation of nanometre-size oxygen bubbles at the lower switching material interface. Our numerical framework couples each spectral peak to the drift of oxygen vacancies and to the formation of an $O_2$ reservoir at the STO/TiO$_2$ interface. The change of scattering intensity of the optical mode assigned to the bridge formation enables us to resolve the drift of oxygen vacancies in the $\sim 30$ s before the set event, showing only a sharp transition when the on state is reached. Our approach also helps to identify the breakdown mechanisms upon cycling. Future improvements in the technique will aim to decrease the switching voltages by reducing the dielectric spacer thickness, which has the additional benefit of trapping the light more tightly in the nanogap, thus increasing the spectroscopic signatures of filament dynamics and accessing faster timescales.

Methods

Sample preparation. Epitaxial SrTiO$_3$/TiN bilayer films were grown on (001)-oriented MgO substrates by pulsed laser deposition (PLD). Before growing the bilayer films, (001)-oriented MgO substrates were annealed in situ at 950 °C for 2h in vacuum. The TiN layer ($\sim 40\,\text{nm}$) was fabricated using a substrate temperature of 650 °C in an argon partial pressure of 1 mtorr with a laser fluence of 1.5 J cm$^{-2}$. The substrate temperature was then increased to 750 °C in an oxygen partial pressure of 1 mtorr for growing the SrTiO$_3$ layer. After deposition, the films were cooled to room temperature at a rate of 10°C min$^{-1}$ under an oxygen pressure of 1 mtorr. To further remove oxygen vacancies, some films were cooled under an oxygen partial pressure of 300 torr. The growth dynamics were investigated by real-time monitoring of the intensity variations of various features in reflection high-energy electron diffraction (RHEED) patterns. Gold nanoparticles (80–nm-diameter AuNPs in citrate buffer) from BBI Solutions were dropcast on the substrate to a number density of $\sim 10^{11}$ cm$^{-2}$ on the STO surface. A 350–nm layer of parylene-C (SCS Labcoter 2) was deposited on top of the entire sample and then etched with O$_2$ plasma to expose the top of the AuNPs while leaving a 20–nm insulating layer around the particles. Etching was performed in steps while monitoring the parylene thickness with an ellipsometer (Woollam alpha-SE).

Sample characterization. The phase and crystalline quality of the thin films were investigated by $\omega$–$2\theta$ X ray diffraction (using a high-resolution Panalytical Empyrean vertical diffractometer, Cu Kα radiation) and high-resolution transmission electron microscopy (HRTEM, FEI FEI Talos 200X TEM). The surface morphologies were examined by AFM. HRTEM images, selected area...
diffraction (SAD) patterns and EDX elemental maps (Supplementary Fig. 4) were used to estimate layer thicknesses and show the presence of the TiO₂ layer between conductive coating.

**Electrical measurements.** For electrical characterization, a Keithley 2635 source meter was used in a four-wire configuration with triaxial connections, which allows low-noise measurement of currents down to 10 pA. In all measurements, the Au top electrode was grounded. The voltage was ramped and a sweep rate of 0.18 V s⁻¹ was used. A measurement range of 100 μA was used to keep the integration time and sweep rate constant. All measurements were performed in air at room temperature.

**Cantilever contacting.** Transparent tip-less SiN AFM cantilevers were coated with 3-nm Cr and 6-nm Au by electron-beam evaporation, providing a transparent conductive coating. Tips were mounted on a custom-built mount controlled by piezoelectric positioners and integrated with the microscopy set-up. The cantilever spring constant was k = 35 nN m⁻¹ (as measured during manufacture), resulting in a pressure on our gap region of 0.04 GPa (Supplementary Section G).

**Numerical simulations.** DFT calculations were carried out using the plane wave pseudopotential code CASTEP. The optical dielectric functions were calculated by OpptDOS. A commercial simulator based on the FDTD method was used to perform calculations of the far-field scattering spectra and near-field distributions (Lumerical Inc., https://www.lumerical.com/products/).

**Data availability**

All source data for this work are available at https://doi.org/10.17863/CAM.55556.

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**References**


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**Author contributions**
Experiments were devised by G.D.M. and J.J.B. and performed by G.D.M., with support for the chemical nanoassembly and sample preparation from D.K. The custom-made cantilever contacting set-up was realized by D.K. W.L. synthesized the STO/TiN films, performed X-ray diffraction and atomic force microscopy, with support from X.W. and H.W. for the TEM measurements. DFT calculations were performed by B.Z., guided by W.L., and FDTD simulations by A.D. The data analysis was performed by G.D.M., with support from all authors. The manuscript was written with contributions from all authors.

**Competing interests**
The authors declare no competing interests.

**Additional information**
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