Quantized conductance coincides with state instability and excess noise in tantalum oxide memristors

Wei Yi1,2, Sergey E. Savel’ev3, Gilberto Medeiros-Ribeiro1,4, Feng Miao1,5, M.-X. Zhang1, J. Joshua Yang1,6, Alexander M. Bratkovsky1,7,8 & R. Stanley Williams1

Tantalum oxide memristors can switch continuously from a low-conductance semiconducting to a high-conductance metallic state. At the boundary between these two regimes are quantized conductance states, which indicate the formation of a point contact within the oxide characterized by multistable conductance fluctuations and enlarged electronic noise. Here, we observe diverse conductance-dependent noise spectra, including a transition from $1/f^2$ (activated transport) to $1/f$ (flicker noise) as a function of the frequency $f$, and a large peak in the noise amplitude at the conductance quantum $G_Q = 2e^2/h$, in contrast to suppressed noise at the conductance quantum observed in other systems. We model the stochastic behaviour near the point contact regime using Molecular Dynamics–Langevin simulations and understand the observed frequency-dependent noise behaviour in terms of thermally activated atomic-scale fluctuations that make and break a quantum conductance channel. These results provide insights into switching mechanisms and guidance to device operating ranges for different applications.
TaO\textsubscript{x}-based metal-oxide-metal devices exhibit voltage-induced resistance switching that represents a physical realization of the memristor electronic circuit element model\textsuperscript{13–15}. They are interesting for device and circuit applications\textsuperscript{4–12} because of their high ON-to-OFF switching endurance\textsuperscript{13,14}, sub-nanosecond switching times\textsuperscript{15,16}, and picosecond switching energies\textsuperscript{17}. At the same time, spectroscopically studies\textsuperscript{8}, transmission electron microscope analysis\textsuperscript{19} and temperature-dependent transport measurements\textsuperscript{8} have shown that the resistance switching mechanism in the TaO\textsubscript{x} system is significantly different from that in TiO\textsubscript{2}-based memristors\textsuperscript{21–24}. In particular, the primary state variable that determines the electronic transport mechanism in TaO\textsubscript{x} memristors has been identified to be the oxygen content in a TaO\textsubscript{x} channel running through the film\textsuperscript{19,20}. Other state variables, such as the internal temperature and the diameter of the conduction channel\textsuperscript{25}, may also influence the resistance. At low oxygen content (\textsim\textasciitilde 20\% O dissolved in Ta), the channel displays metallic conductivity, whereas at higher oxygen content (larger than 50\%, a suboxide, or reduced oxide) the channel can display a range of conduction behaviours, including activated semiconducting transport, barrier tunneling and hopping, all characteristic of a Fermi glass\textsuperscript{26}, which is reminiscent of the behaviour described by the Mooij rule for disordered transition metals\textsuperscript{27}.

An intermediate regime of electronic transport is characterized by quantized conduction, typically observed in mechanical break junctions\textsuperscript{28–30} but also in metal–insulator–metal resistive switches\textsuperscript{31–34}. Here we focus primarily on this regime, when the resistance of the memristor is in the 3 to 15 k\textOmega{} range (or in the range of a few conductance quanta $G_Q = 2e^2/h = 77.5 \mu$S = (12.9 k\textOmega{})\textsuperscript{−1}). We observe excess noise at conductance quanta for different samples and temperatures, several orders of magnitude above the baseline. The origin of excess noise is explained in terms of atomic instabilities at the contact. These results provide insight into switching mechanisms in memristors, as well as define regions for device operation for different applications.

**Results**

**Current voltage characteristics near quantum point contacts.** Our devices were sputter-deposited TaO\textsubscript{x} memristors with a bottom (grounded) Pt electrode and a top Ta electrode. We measured current controlled quasi-static current–voltage ($I$–$V$) sweeps, conductance as a function of time for constant applied voltage, and frequency-dependent noise spectra (see details in Methods, Supplementary Fig. 1 and Supplementary Note 1). The $I$–$V$ characteristics in Fig. 1a,b for SET and RESET operations display conspicuous telegraph-type dynamical fluctuations when the conductance is lower or equal to $G_Q$ (see also Supplementary Note 2). Thus, the device states near $G_Q$ are highly unstable, with the conductance hopping back and forth among several different and apparently discrete states as the current is ramped. The dynamical and stochastic nature of switching in this regime is shown in Fig. 1c, which displays the conductance versus time of a device held at a constant voltage of 50 mV. The conductance exhibited jumps at apparently random time intervals to more conductive states at essentially integer multiples of $G_Q$.

In Fig. 2 we illustrate how these fluctuations affect resistance switching by cycling a device between two different states over 100,000 times. The average conductance <$G>$ showed a significantly enhanced variance when we attempted to reset the device to a nominal value of $G_Q$.

**Noise spectra.** Figure 3 shows that the current noise spectral density in a device can be a few orders of magnitude larger than the background values for conductance values close to small integer numbers times $G_Q$. The detailed conductance and frequency dependence of the electrical noise in a TaO\textsubscript{x} memristor is exhibited in Fig. 3. The upper panel shows the noise normalized by the square of the current at 1 kHz for room temperature and 174 K. $S$ is the noise power spectral density in units of WHz\textsuperscript{−1},
while $S/f^2 = S_R$ gives the resistance noise spectral density in units of $\Omega \text{Hz}^{-1}$. The lower panel shows a 2D chart of the noise amplitude plotted as a function of device conductance and frequency for room temperature data. In both plots, there is a strong peak in the noise at $G_Q$, which rises three orders of magnitude above the baseline, and several minor peaks that appear primarily at integer values of $G_Q$. These general features were observed for similarly prepared samples, but the peak intensities and the presence or absence of a peak at particular integer multiples of $G_Q (nG_Q)$ varied from sample to sample (see Supplementary Fig. 2).

Figure 4 shows the measured frequency-dependent noise spectra over a wide range of conductance states. The frequency ($f$) dependence of the noise was $1/f$ for the high-conductance states and $1/f^2$ for the low-conductance states. However, in the quantized conductance regime, the noise amplitude was significantly above the background trend for $G = nG_Q$ ($n = 1$ and $2$). At $G = G_Q$, the noise displayed a $1/f^2$ dependence at high frequencies but flattened out at lower frequencies.

There is a vast literature on quantized conductance in Quantum Point Contacts (QPC) in mechanical break junctions (see, for example, refs 28–30 and references therein) that show similar behaviour to Fig. 1c. A single- or few-atom constriction can support few-electron eigenmodes that apparently suffer little back-scattering. Similar conductance steps have been observed in several thin film systems, for example, Ag$_2$S (ref. 31), AgI (ref. 32) and more recently in Ag/GeS$_2$/W (ref. 33), Ta$_2$O$_5$ (ref. 35), and Nb/ZrO/Pt (ref. 36), thus demonstrating that QPCs can also exist in metallic systems embedded in insulating matrices.

A phenomenological model reported by Ielmini et al. describes telegraphic noise during the transition from insulating to metallic regime. Telegraphic noise can depend on both the conducting channel width and applied voltage. However, enlarged noise behaviour at a QPC has not been revealed in any system to the best of our knowledge. The control
produces high local Joule heating, which in turn causes atomic fluctuations and severe electronic noise because of the disruption of the conductance channel. The noise peaks at \( nG_Q \) with \( n = 2, 3 \) and so on. may be caused by multiple point contacts in parallel or a single fluctuating contact that supports degenerate electron eigenstates.

The existence of a peak in the noise at a discrete conductance can be explained by a simple local bond model of a random network of resistances \( r_{st} = \{ r, \infty \} \) (ref. 44, and see Supplementary Note 3 and Supplementary Figs 3 and 4). When the concentration of the conducting bonds decreases to the critical value for disconnecting a conducting channel between the electrodes, the electronic noise diverges because the fluctuations of the conductance are determined by a small number of bonds at the point contact.

\[
\frac{S_R}{R^2} \propto \left( n - n_c \right)^{-x}.
\]

In a physical system, this divergence will be smoothed out by tunneling through the gap in the channel and by shunting around the gap through the surrounding matrix material (for example, the nearly stoichiometric oxide).

If there are several parallel conducting paths through the device, then the fluctuations of local conductances are uncorrelated and their contributions to the total conductance are averaged. We do not know exactly the microstructure of the growing embryonic conducting channels, but our observations are quite general to any geometry that includes point contacts. It is frequently assumed that they make a dendritic (or a stalagmite/stalactite) structure. In the case of the formation of a few parallel QPCs, the amount of local heating at each would obviously be lower than the single QPC case and may lead to a series of weaker noise peaks, since the amount of local heating in an ideal case for constant current would fall off with \( n^2 \), \( n \) being the number of parallel channels.

**Discussion**

We compare our theoretical expectations with the observed behaviour of the normalized noise spectra \( S/I^2 \) for resistance states around \( G_Q \) shown in Fig. 4. We observe three distinct regimes: a metallic, a semiconducting or insulating one and an intermediate regime characterized by conductances of \( nG_Q \). The metallic state with \( R = 1.28 \, k\Omega \) exhibits 1/f noise, while the semiconducting state shows 1/f² behaviour at high frequencies. In the 23 \( k\Omega \) sample (close to 0.5 \( G_Q \)), we observe the crossover from 1/f to 1/f² reproduced by our Molecular Dynamics–Langevin (MD-L) model (see Supplementary Fig. 5), and more resistive samples follow the 1/f² behaviour. The samples in the quantized conductance regime around 12 \( k\Omega \) exhibit the largest noise power compared with samples outside of this regime, exhibiting a Lorentzian distribution with \( <G> = G_Q \). For \( <G> = 2G_Q \) (\( R = 6.4 \, k\Omega \)), we observe a significantly lower power but also a Lorentzian behaviour. These results are in accord with discrete atomic fluctuators at the point contact, which is the predominant source of electronic noise level for the entire device.

Noise measurements can be a very sensitive probe of the internal dynamics of atomic-scale fluctuations in memristors and related devices. The observed multistable current–voltage characteristics and severe electronic noise in \( \text{TaO}_x \) memristors for quantized conductance states can be explained by a simple model of atomic thermal fluctuations that disrupt electronic eigenstates in a point contact of a conducting channel, and should be a general phenomenon in resistance switching based on atomic or ionic migration. Thus, although the possibility of having discrete conductance states in a device appears attractive, the inherent instability of the states can present a challenge for non-volatile
memory applications near point-contact regime. In previous work we showed that one can operate in quiet windows in between conductance quanta by controlling the write current or using a feedback write circuit. Nevertheless, there are applications where noise can be used as a resource. One example is stochastic feedback write circuit. Nevertheless, there are applications where noise in information processing. In the brain, cryptography and other applications such as stochastic quantum properties of light as the phenomenon generating conductance quanta by controlling the write current or using a nanoscale conduction channel reveals the mechanism of a high-performance memristor. Adv. Mater. 23, 5633–5640 (2011). Miao, F. et al. Continuous electrical tuning of the chemical composition of TaOx-based memristors. Ac. Nano 6, 2312–2318 (2012). Yang, J. J. et al. Memristive switching mechanism for metal/oxygen/metal nanodevices. Nat. Nano 3, 429–433 (2008). Miao, F., Yang, J. J., Borghetti, J., Medeiros-Ribeiro, G. & Williams, R. S. Observation of two resistance switching modes in TiO2 memristive devices electroformed at low current. Nanotechnology 22, 254007 (2011). Pickett, M. D. et al. Switching dynamics in titanium dioxide memristive devices. J. Appl. Phys. 106, 074508 (2009). Strukov, D., Abbott, F. & Stanley Williams, R. Thermostability/diffusion as a plausible mechanism for unipolar switching in metal/oxygen/metal memristors. Appl. Phys. A 107, 509–518 (2012). Strachan, J. P. et al. State Dynamics and Modeling of Tantalum Oxide Memristors. IEEE Trans. Electron. Devices 60, 2194–2202 (2013). Goldfarb, I. et al. Electronic structure and transport measurements of amorphous transition-metal oxides: observation of Fermi glass behaviour. Appl. Phys. A 107, 1–11 (2012). Mooij, J. H. Electrical conduction in concentrated disordered transition metal alloys. Phys. Status Solidi A 171, 521–530 (1997). Krans, J. M. et al. One-atom point contacts. Phys. Rev. B 48, 14721–14724 (1993). Bratkovsky, A. M. & Rashkeev, S. N. Electronic transport in nanoscale contacts with rough boundaries. Phys. Rev. B 53, 13074–13085 (1996). Scheer, E., Joyce, P., Devoret, M. H.,Esteve, D. & Urbina, C. What are Landauer’s conduction channels in an atomic-size metallic contact? Superlattices Microstruct. 23, 747–756 (1998). Terabe, K., Hasegawa, T., Nakayama, T. & Aono, M. Quantized conductance atomic switch. Nature 433, 47–50 (2005). Tappertzhofen, S., Valov, I. & Waser, R. Quantum conductance and switching kinetics of Ag-based microcrossbar cells. Nanotechnology 23, 145703 (2012). Jameson, J. R. et al. Quantized conductance in Ag/Ge/Si/W conductive-bridge memory cells. IEEE Electron Device Lett. 33, 257–259 (2012). Wedig, A. et al. Nanoscale cation motion in TaOx, HfOx and TiOx memristive systems. Nat. Nano 7, 67–74 (2016). Tsurukca, T., Hasegawa, T., Terabe, K. & Aono, M. Conductance quantization and synaptic behavior in a Ta 2 O 5 -based atomic switch. Nanotechnology 23, 435705 (2012). Zhu, X. et al. Observation of Conductance quantization in oxide-based resistive switching memory. Adv. Mater. 24, 3941–3946 (2012). Jelmini, D., Nardi, F. & Cagli, G. Resistance-dependent amplitude of random telegraph-signal noise in resistive switching memories. Appl. Phys. Lett. 96, 053503 (2010). Raghavan, N. et al. in Reliability Physics Symposium (IRPS), 2013 IEEE (2013). Reznikov, M., Heiblum, M., Shtrikman, H. & Mahalu, D. Temporal correlation of electrons: suppression of shot noise in a ballistic quantum point contact. Phys. Rev. Lett. 75, 3340–3343 (1995). van den Brom, H. E. & van Ruitenbeek, J. M. Quantum suppression of shot noise in atom-size metallic contacts. Phys. Rev. Lett. 82, 1526–1529 (1999). Dijkstra, D. & van Ruitenbeek, J. M. Shot noise measurements on a single molecule. Nat. Nano 6, 789–793 (2006). Machlup, S. Noise in semiconductors: spectrum of a two-parameter random process. J. Appl. Phys. 25, 341–343 (1954). Kogon, S. Electronic Noise and Fluctuations in Solids (Cambridge Univ. Press, 1996). Gaba, S., Sheridan, P., Zhou, J., Choi, S. & Lu, W. Stochastic memristive devices for computing and neuromorphic applications. Nanoscale 5, 5872–5878 (2013). Rammal, R. in Physics of Finely Divided Matter Vol. 5 Springer Proceedings in Physics (eds Boccara, Nino & Mohamed, Daoud) Vol. 5 Ch. 15 118–125 (Springer, 1985). Chen, C. C. & Chou, Y. C. Electrical-Conductivity fluctuations near the percolation threshold. Phys. Rev. Lett. 54, 2529–2532 (1985).
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Author contributions

A.M.B., G.M.-R. and R.S.W. conceived this study, W.Y. and F.M. performed the experimental measurements, M.X.Z., J.J.Y. made the samples and part of the electrical measurements, S.E.S. and A.M.B. performed the simulations, and all contributed to analysing the data and writing the manuscript.

Additional information

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