



## Electrochemical metallization ReRAMs (ECM) - Experiments and modelling: general discussion

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## DISCUSSIONS

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### Electrochemical metallization ReRAMs (ECM) - Experiments and modelling: general discussion

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## DISCUSSIONS

# Electrochemical metallization ReRAMs (ECM) - Experiments and modelling: general discussion

Elia Ambrosi, Philip Bartlett, Sanne Berg, Stefano Brivio, Geoffrey Burr, Sweetey Deswal, Jonas Deuermeier, Masa-aki Haga, Asal Kiazadeh, Gabriela Kissling, Michael Kozicki, Cina Foroutan-Nejad, Ella Gale, Yago Gonzalez-Velo, Anouk Goossens, Ludovic Goux, Tsuyoshi Hasegawa, Hans Hilgenkamp, Ruomeng Huang, Sherif Ibrahim, Daniele Ielmini, Tony Kenyon, Vladimir Kolosov, Yang Li, Sayani Majumdar, Gianluca Milano, Themistoklis Prodromakis, Niloufar Raeishosseini, Vikas Rana, Carlo Ricciardi, Monica Santamaria, Alexander Shluger, Ilia Valov, Rainer Waser, Stanley Williams, Dirk Wouters, Yuchao Yang and Andrea Zaffora

DOI: 10.1039/C8FD90059K

(1:[1]1) **Ella Gale** opened discussion of the introductory lecture by Rainer Waser: At the end of your talk you introduced complementary resistance switches, which you used for binary pattern matching. Do you have any insight into how you might use these systems to do computation in the real number space?

**Rainer Waser** answered: We are currently working on this.

(2:[2]2) **Ilia Valov** said: From your point of view, at the moment, what are the hottest points of research in memristive cells? What are the main challenges?

**Rainer Waser** answered: The hot points of research are the physical understanding of the reliability-limiting processes in conjunction with the material's treasure map and, from the application side, the development of a convincing neuromorphic circuit that shows clear benefit compared to standard CMOS solutions

(4:[4]4) **Hans Hilgenkamp** asked: Most memristor embodiments shown in the papers are based on stacked devices with the current flow perpendicular to the plane. Do all applications necessarily favour this type of configuration, or are there also applications for which an in-plane configuration would be preferred?

1           **Rainer Waser** responded: There are vertical 3D stack concepts, similar to the successful 3D-NAND flash, in which the memristive oxide switches between the stack layer and coverage of the stack. This is a lateral switching.

5           (5:[5]5) **Cina Foroutan-Nejad** said: I have a rather naïve question. Do you foresee an opportunity to reduce the variability of memristive devices by downsizing the memristors to the size of a molecule? Is there any attempt that you are aware of to design or make a monomolecular memristor?

10           **Rainer Waser** responded: This has been tried for years in the regime of molecular electronics. Unfortunately, these efforts were not successful, presumably it is just not possible to control the contact to a molecule, such as the angle, *etc.*, with sufficient precision.

15           (6:[6]6) **Philip Bartlett** asked: You touched on the effects of the interface in your answer to the earlier question. As the memory cells are made smaller in devices any effects of the interfaces between the ReRAM material and the walls of the cells may become more significant. Can you comments on these effects?

20           **Rainer Waser** responded: You are right. The effects of the walls of the cells will become more significant with shrinking cell size.

25           (7:[7]7) **Stanley Williams** queried: How much do you trust your simulation tools? Most commercial software programs were at least implicitly designed for linear systems near equilibrium. Pushing them into nonlinear systems far from equilibrium exposes them to realms for which they were not designed. How much do you trust the reliability of the simulation results?

30           **Rainer Waser** replied: Some of our simulation tools have been developed by ourselves, so that we were able to avoid any limitations. In others, we took care that we were able to use non-linear equations.

35           (8:[8]8) **Themistoklis Prodromakis** asked: You presented a variety of memory technologies that each bares its own performance benefits. Do you foresee any opportunities for combining distinct technologies for achieving new functionalities?

40           **Rainer Waser** replied: The concept of new functionalities has been presented in the Faraday Discussion articles included in this volume. Please consider the papers on in-memory computing and neuromorphic computing. Some people think about using memristive elements also in sensors.

45           (9:[9]9) **Vladimir Kolosov** said: Are there microstructure dependent factors somewhere in the metal oxide switching materials that you have covered in your presentation?

50           **Rainer Waser** responded: In my talk I had no time to cover the microstructure aspects. Still, microstructure is very important. There is a huge difference if an oxide material is single crystalline, polycrystalline (*e.g.* nanocrystalline), or

1 amorphous. It is partly covered in our papers, but also the subject of ongoing  
research.

5 (10:[10]10) **Michael Kozicki** opened a general discussion of the paper by  
Tsuyoshi Hasegawa: It's well known that the conductivity and other properties of  
silver chalcogenides are highly dependent on what  $\delta$  is in the  $\text{Ag}_{2+\delta}\text{S}$ . What is your  
 $\delta$ , and how did you measure it?

10 **Tsuyoshi Hasegawa** replied: We did not measure the  $\delta$  of our  $\text{Ag}_{2+\delta}\text{S}$  nanodot.  
Although there are several methods for measuring the  $\delta$  of a thin  $\text{Ag}_{2+\delta}\text{S}$ , they are  
hard to apply to a nanodot. The  $\delta$  of a nanodot should be different from a thin film  
even when we use the same sulfurization conditions. In the future, we would like  
to estimate our  $\delta$  by comparing with the  $\delta$  and resistivity of the bulk values.

15 (11:[11]11) **Stanley Williams** said: With respect to the nanowires, how stable  
are they? Do they want to essentially reform by Ostwald ripening and turn into  
spheres in order to minimize their surface area?

20 **Tsuyoshi Hasegawa** answered: Basically, the reformation of a Ag nanowire into  
a more stable structure, such as a sphere, should happen as in the question. The  
volatility of a Ag filament in Ag-based ECM cells seems to be caused by the effect,  
although a thicker Ag filament stably exists. However, the change in height of  
a grown Ag nanowire is rarely observed in our experiments using STM. When we  
25 grew Ag nanowires from  $\text{Ag}_2\text{S}$  by the e-beam of SEM, we also found that nanowires  
stably existed for a long time, as long as the e-beam was irradiated. The experi-  
mental results suggest that a STM/SEM induced electric field stabilizes a nano-  
wire. The other possibility is that the diameter of the nanowire is thicker than  
expected. We would like to consider some experiments to confirm what is  
30 happening.

35 (12:[12]12) **Ella Gale** enquired: In Fig. 3 of your paper (DOI: 10.1039/  
C8FD00099A), you compared your data to a theoretical model with a hexagonal  
symmetry that grew layer by layer, and the experimental results match it very well  
at the beginning and end of the measured growth process. Did you undertake any  
modelling of different geometries, for example a slightly slanted layer, to see if it  
accounts for that discrepancy?

40 **Tsuyoshi Hasegawa** answered: We did not try it. When we use a shape that has  
a wider cross-section in the lower layer, the expected height of the nanowire  
should become lower than that calculated using a cylindrical shape, seen in Fig. 3  
of our paper (DOI: 10.1039/C8FD00099A), and the mismatch becomes larger with  
growth. However, the mismatch is larger in the intermediate stage in the growth,  
45 suggesting other causes. We believe that not all of the Ag atoms expected to  
precipitate at each bias did precipitate as such, due to the incomplete inner ionic  
movement.

50 (13:[13]13) **Dirk Wouters** asked: When you are electrochemically removing  
dopant atoms on one electrode side of the nanodot, shouldn't there be a counter

1 reaction at the other electrode side? Similar to the reaction in a conductive  
bridging RAM and expected in general for electrochemical cells?

5 **Tsuyoshi Hasegawa** replied: In the removal or returning of dopant atoms, the  
following reactions should occur at the surface of the  $\text{Ag}_2\text{S}$  interface between the  
 $\text{Ag}_2\text{S}$  and Ag wire:  $\text{Ag} + \text{V}_\text{I}^\times \rightleftharpoons \text{Ag}_\text{I}^\cdot + \text{e}'$

The reaction can occur without any counter reaction at the other electrode side,  
which is the same as doping into semiconductor materials, or the counter reaction  
can be described as:  $\text{e}' + \text{V}_\text{I}^\times \rightleftharpoons \text{V}_\text{I}^\cdot$

10 The point of the experiment is that the Ag atoms that we removed are excess Ag  
atoms in the interstitial sites that do not make ionic bonds with sulfur atoms.  
When Ag atoms bond to sulfur atoms, a certain counter reaction is expected to  
occur for keeping the  $\text{Ag}_2\text{S}$  matrix, as in the question.

15 (14:[14]14) **Philip Bartlett** queried: You use nanosphere lithography to fabri-  
cate the  $\text{Ag}_{2+\delta}\text{S}$  nanodots. As a result the bases of each nanodot will have an  
approximately triangular shape and the bottom electrode contact to the Pt has  
a much larger area than the growing Ag column, is that correct? From the elec-  
20 trochemical perspective this is advantageous because the current density at the  
larger area contact at the base between the Pt and the nanodot will be much  
smaller than that at the interface between the growing Ag pillar and the nanodot,  
such that the Pt nanodot contact acts as a pseudo reference electrode and any  
changes you implement in the applied potential in the two terminal measure-  
25 ment, such as during the potential (bias) scans, mainly change the potential drop  
at the silver pillar/nanodot interface.

30 **Tsuyoshi Hasegawa** replied: Thank you for the comment. We deposited Ag  
through a space of nanospheres by EB-deposition. Since the height of the EB-  
deposited Ag film was 20 nm, which is smaller than the space, the difference in  
the area size between the top surface and bottom surface is negligible, as far as we  
observed by STM, AFM, and SEM. Although the sizes of the top surface and  
35 bottom surface are almost the same, the current densities at the top surface and  
the bottom surface are much different, as suggested. We would like to consider  
the effect when analyzing and doing further experiments.

40 (15:[15]15) **Philip Bartlett** said: Following on from my previous question, an  
obvious approach to ensure a relatively constant reference potential in this type of  
two electrode experiment would be to use a Ag electrode in place of Pt for the large  
area back contact.

45 **Tsuyoshi Hasegawa** replied: When a Ag electrode is used as a back electrode,  
Ag cations are supplied to the  $\text{Ag}_2\text{S}$  matrix, keeping the concentration of Ag  
cations constant and enabling continuous Ag nanowire growth. We reported such  
experimental results in our previous work.<sup>1</sup> In order to achieve atom by atom  
precipitation as a function of bias, we could not use Ag as a back electrode.

1 K. Terabe, T. Nakayama, T. Hasegawa and M. Aono, *J. Appl. Phys.*, 2002, **91**, 10110.

1 (16:[16]16) **Ilia Valov** remarked: The electronic conductivity of the low  
semiconductor form of  $\text{Ag}_2\text{S}$  is very sensitive to doping with Ag atoms.  $\text{Ag}_2\text{S}$  is  
5 a semiconductor with  $\sim 3$  eV bandgap. When Ag atoms dissolve in the sulfide  
matrix they dissociate to  $\text{Ag}^+$  ions and electrons. Whereas the ionic conductivity is  
not influenced by this doping, the electronic conductivity is significantly  
increased. Therefore, when one removes Ag atoms from  $\text{Ag}_2\text{S}$  nanodots (con-  
taining only a limited number of dopant atoms) we observe a discrete and  
significant change of the electronic conductivity.

10 (17:[17]17) **Gabriela Kissling** asked: How reversible is the formation of the  
silver nanowires? Do the silver ions get reabsorbed and evenly redistributed in the  
 $\text{Ag}_{2+\delta}\text{S}$  nanoparticle when the nanowire shrinks or does the silver form a kind of  
core-shell structure on the outside of the nanoparticle?

15 **Tsuyoshi Hasegawa** answered: Nanowire growth and shrinkage is repeatable,  
as we reported previously.<sup>1</sup> Since we remove the Ag atoms that only existed in the  
interstitial sites, they easily move back to the interstitial sites in the  $\text{Ag}_2\text{S}$  matrix.  
Removing the Ag atoms that bond to sulfur atoms breaks the  $\text{Ag}_2\text{S}$  matrix, making  
20 it impossible for the Ag atoms to return.

1 K. Terabe, T. Nakayama, T. Hasegawa and M. Aono, *J. Appl. Phys.*, 2002, **91**, 10110.

25 (18:[18]18) **Geoffrey Burr** asked: Have you considered using your technique for  
nano-stereo-lithography? That is, you would use the STM tip to pull some metal  
atoms out into a nanowire, then hold the potential while you deposited, very  
gently, a small number of dielectric atoms in the vicinity of the wire. This would  
require the formation of the filament to be stable enough that you can hold it in  
place while you "encase" it in non-conducting atoms and/or molecules.

30 **Tsuyoshi Hasegawa** replied: No, we have not considered using our technique  
for nano-stereo-lithography. This is because the chemical reaction that precipi-  
tates the Ag atoms occurs at the interface between a grown nanowire and a solid  
electrolyte, such as  $\text{Ag}_2\text{S}$ . This means that our technique cannot grow another  
35 branch from a nanowire surface.

(52:[19]19) **Asal Kiazadeh** remarked: Thanks for presenting your work at the  
Faraday Discussion. Since the nanowire is not stable enough and basically the  
retention time is low, I would like to know have you ever tried some other  
40 experiments, such as pulse train measurement by applying different amplitudes/  
frequencies, in order to study the plasticity of Ag dynamics? I mean, could you use  
the measurement set-up shown in Fig. 2 and 3 of the work by Kim and Lee<sup>1</sup> as  
a follow-up study?

45 1 M. Kim and J. Lee, *ACS Nano*, 2018, **12**, 1680–1687

**Tsuyoshi Hasegawa** responded: Ag nanowire growth and its stability, such as  
under pulse train, is partly reported in our previous work,<sup>1</sup> although the Ag  
nanowires grow in a molecular layer in the study. Regarding the experiment using  
50 STM in vacuum, we reported this previously.<sup>2</sup> Regarding the technique used, it

1 was used for the first time by ourselves in this article (DOI: 10.1039/C8FD00099A).  
In addition to this paper, we have also reported the STM and LTP characteristics  
previously.<sup>3-6</sup>

- 5 1 C. Arima, A. Suzuki, A. Kassai, T. Tsuruoka and T. Hasegawa, *J. Appl. Phys.*, 2018, **124**,  
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10 4 R. Yang, K. Terabe, G. Liu, T. Tsuruoka, T. Hasegawa, J. K. Gimzewski and M. Aono, *ACS*  
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5 A. Nayak, T. Ohno, T. Tsuruoka, K. Terabe, T. Hasegawa, J. K. Gimzewski and M. Aono, *Adv.*  
*Func. Mater.*, 2012, **22**, 3606.  
6 R. Yang, K. Terabe, T. Yao, T. Tsuruoka, T. Hasegawa, J. K. Gimzewski and M. Aono,  
*Nanotechnology*, 2013, **24**, 384003.

15 (19:[20]20) **Stanley Williams** opened a general discussion of the paper by  
Yuchao Yang: Have you looked for the threshold voltages in your anodic and  
cathodic reactions at the oxide/electrode interfaces? Is there a characteristic  
voltage or voltages below which you don't see one or the other? Can you control  
20 which reaction occurs?

**Yuchao Yang** replied: Thanks for raising this interesting question. Indeed, the  
occurrence of both anodic and cathodic reactions requires certain threshold  
voltages to be reached. We have performed a voltage dependent study on the  
25 anodic and cathodic reactions for the same Pt/HfO<sub>2</sub>/Pt system. It can be observed  
that the reactions start to take place above 8 V. However, there is difficulty in  
completely decoupling them since the anodic and cathodic processes happen  
simultaneously in order to maintain overall charge neutrality. As a result, we  
always saw the anodic and cathodic processes happening in parallel, otherwise no  
30 reactions occurred at low voltages. We expect that in the case of multiple anodic  
or cathodic processes, it could be possible to control their occurrence using the  
applied voltage.

35 (20:[21]21) **Masa-aki Haga** asked: You provide the *I-V* profile of the Pt/HfO<sub>2</sub>/Pt  
devices in Fig. 1*l* of your article (DOI: 10.1039/C8FD00113H) and you said that “a  
cathodic reaction must take place simultaneously with the anodic reaction”. How  
many volts are needed to cause such reactions? I am wondering why these reac-  
tions did not affect the current flow or *I-V* characteristics since holes were created  
40 during the potential scanning. I saw the reverse current was undulating in Fig 4*l*  
of your article. I expected similar undulation of the current when the holes were  
generated during the potential scanning.

**Yuchao Yang** replied: In Fig. 2b–e of our article (DOI: 10.1039/C8FD00113H),  
we have performed a voltage dependent study on the anodic and cathodic reac-  
45 tions for the same Pt/HfO<sub>2</sub>/Pt system. It can be observed that the reactions start  
to take place above 8 V. The undulation of the current may not always be observed,  
since the conductivities in the HfO<sub>2</sub> and TaO<sub>x</sub> based memristors are mainly  
provided by the localized conducting filaments instead of being a homogeneous  
effect. As a result, it can be found that the formation of holes/damage to the  
50 electrodes did not introduce current undulation in Fig. 1, 3, 5, and 6 of our article.

1 The only exception is the current undulating in the off state shown in Fig. 4I,  
which could be related to the occurrence of the redox reactions. The conductance  
of the device is fully dominated by the electronic current offered by the con-  
5 ducting filament once the device is switched to on state, and hence such undu-  
lation as a result of the redox processes cannot be observed.

(21:[22]22) **Masa-aki Haga** asked: How thin are the films on the Pt/HfO<sub>2</sub>/Pt  
devices?

10 **Yuchao Yang** responded: The thickness of the HfO<sub>2</sub> films in the Pt/HfO<sub>2</sub>/Pt  
devices is 30 nm.

(22:[23]23) **Rainer Waser** said: I wonder if you have changed the humidity in  
15 order to see if you can control the hydrogen evolution and suppress it using a dry  
atmosphere?

**Yuchao Yang** answered: This is a great suggestion. The experiments in this  
work were performed in air where the humidity level could not be controlled, but  
20 it is a very interesting suggestion to vary the level of moisture and examine the  
cathodic reactions.

(23:[24]24) **Alexander Shluger** remarked: What is the evidence that the water  
adsorbed on the hafnia surface does not dissociate by itself through adsorption  
and requires the reaction with the electrons in order to provide the OH<sup>-</sup> reaction,  
25 which is reaction 2 in the article (DOI: 10.1039/C8FD00113H)? Water tends to  
dissociate at surfaces consisting of SiO<sub>2</sub>, TiO<sub>2</sub>, and some other oxides.

**Yuchao Yang** answered: The necessity for the reaction of water with electrons  
30 originates from the general requirement for charge neutrality, since the anodic  
reactions described by eqn 1 of the article (DOI: 10.1039/C8FD00113H) will  
release electrons. This makes the generation of the OH<sup>-</sup> ions described by eqn 2  
in the article a more probable reaction at the cathode interface.

(24:[25]25) **Philip Bartlett** asked: Just to clarify, are you talking about the  
35 dissociation of water into H<sup>+</sup> and OH<sup>-</sup> on the oxide surface or a redox process that  
generates hydrogen, which is reaction 2 in the paper (DOI: 10.1039/C8FD00113H),  
or are you referring to one of the other reactions in the paper, for example reaction  
40 3 or 4?

**Alexander Shluger** replied: My question was, what is the evidence that the  
water adsorbed on the hafnia surface does not dissociate by itself through  
adsorption and requires the reaction with the electrons in order to provide OH<sup>-</sup>?  
45 Water tends to dissociate on the surfaces of SiO<sub>2</sub>, TiO<sub>2</sub>, and some other oxides.  
There have been suggestions regarding water dissociation on the surfaces of HfO<sub>2</sub>  
in the studies by Navrotsky *et al.*<sup>1</sup> and Driemeier and Gusev.<sup>2</sup> The nature of  
reaction 2 in the paper (DOI: 10.1039/C8FD00113H) is unclear. Such reaction  
takes place during the radiolysis of water, but how it may take place as "the  
50 cathodic reaction was suggested to be the reduction of moisture absorbed in the  
memristive oxides" is unclear. If water dissociates due to the interaction with the

1 surface, then H can be formed when the injected electrons interact with  $H^+$  at  
a certain Fermi level position.<sup>3</sup> You see damage caused, but you do not know  
whether it is caused by hydrogen or not. Do you have any evidence that hydrogen  
5 produces this damage?

1 G. Sharma, S. V. Ushakov, H. Liu, R. H. R. Castro and A. Navrotsky, *J. Phys. Chem. C*, 2017,  
121, 10392–10397.

2 C. Driemeier and E. P. Gusev, *Appl. Phys. Lett.*, 2006, 88, 201901.

3 M. Kaviani, V. V. Afanas'ev and A. L. Shluger, *Phys. Rev. B*, 2017, 95, 075117.

10 **Yuchao Yang** responded: The assumption of hydrogen evolution is based on  
previous experimental evidence in the literature showing that moisture is indis-  
pensable for cathodic reactions and forming was not possible without the pres-  
ence of moisture, such as in the papers by Lübben *et al.*<sup>1,2</sup> Since the oxidation of  
the oxygen ions at the anodic interface will create oxygen vacancies, a counter  
15 electrode reaction generating anions is required to keep the charge neutrality,  
thus suggesting the reduction of moisture to  $OH^-$  ions and accompanying  
hydrogen gas. Certainly, this is not direct evidence and it would be nice to directly  
analyze the chemistry of the gas products from the cathodic interface.

20 1 M. Lübben, S. Wiefels, R. Waser and I. Valov, *Adv. Electron. Mater.*, 2018, 4, 1700458.

2 M. Lübben, P. Karakolis, V. Ioannou-Sougleridis, P. Normand, P. Dimitrakis and I. Valov,  
*Adv. Mater.*, 2015, 27, 6202–6207.

25 (26:[27]27) **Tony Kenyon** asked: Have you tried to detect what gas is emitted  
during the forming and switching events? Related to that, what do you think the  
contribution is of local heating in producing the damage that you see?

30 **Yuchao Yang** answered: At this moment we do not have experimental means  
that can directly analyze the chemistry of the gas products during the forming and  
switching events. The contribution of local Joule heating is indeed present. In  
fact, the evolution of gas products from the anodic and cathodic interfaces is not  
expected to cause structural damage to the bottom electrode, which sits under-  
neath both interfaces. However, such damage was indeed observed in Fig. 1–6 of  
our article (DOI: 10.1039/C8FD00113H), which could be induced by the local  
35 heating effects. By lowering the current compliance and thus reducing the Joule  
heating, the damage to the bottom electrodes could be effectively prevented, as  
shown in Fig. 2f and 4m of our paper, further supporting this hypothesis. In  
addition, the periphery of the damaged area usually exhibits morphology that  
indicates a preceding melting process, *e.g.* in Fig. 1g, once again suggesting the  
40 role of Joule heating in producing the structural damage.

(27:[28]28) **Carlo Ricciardi** said: My question is about Fig. 7 of your article (DOI:  
10.1039/C8FD00113H). Can you specify if the ZnO film is amorphous or nano/  
polycrystalline? If it is the latter case, do you see any effect from the micro-  
45 structure like localization of the conductive filament in the grain boundaries?

50 **Yuchao Yang** responded: Thanks for raising this interesting point. The ZnO  
film in our device is nanocrystalline, as can be found from the topography of the  
films (Fig. 7a, d, g, and j). Although this work did not focus on the spatial  
correlation of the filament locations and grain boundaries, previous AFM and

1 CAFM studies on the Cu/ZnO/Pt devices have shown that Cu filaments tend to  
form at the ZnO grain boundaries, as seen in the work by Zhuge *et al.*,<sup>1</sup> demon-  
strating the validity of such correlation.

5 1 F. Zhuge, S. Peng, C. He, X. Zhu, X. Chen, Y. Liu and R. Li, *Nanotechnology*, 2011, **22**,  
275204.

(29:[29]29) **Iliia Valov** commented: I agree with you that charging of the thin  
films can be a source of instability. However, if you look at the images, there is  
development of gas at both electrodes. It's obvious that gas is developing. If  
there's damage then it's gas. It cannot be something else. It is an electrochemical  
reaction that takes place at both electrodes upon polarization. We have also  
observed H<sub>2</sub> and O<sub>2</sub> evolution during polarization in our work.<sup>1,2</sup>

15 1 M. Lübben, S. Wiefels, R. Waser and I. Valov, *Adv. Electron. Mater.*, 2018, **4**, 1700458.

2 I. Valov and T. Tsuruoka, *Phys. D Appl. Phys.*, 2018, **51**, 413001.

**Alexander Shluger** answered: The statement in the paper (DOI: 10.1039/  
C8FD00113H) that a cathodic reaction must take place simultaneously with the  
anodic reaction in both the ECM and VCM cells, in order to maintain charge  
neutrality, is not applicable to the open systems considered here. The charging of  
oxides in electronic devices is well known in the microelectronics community and  
leads to oxide degradation. The results provided in Fig. 1m of your paper (DOI:  
10.1039/C8FD00113H) show delamination of the Pt electrode but no H<sub>2</sub> gas is  
detected. Although some hydrogen gas formation may take place at the HfO<sub>2</sub>  
surface, see the work by Driemeier and Gusev<sup>1</sup> and Navrotsky *et al.*,<sup>2</sup> this paper  
does not provide proof of that happening and delamination can be caused, for  
example, by interfacial stress due to the structural changes caused by the  
significant loss of oxygen.

30 1 C. Driemeier and E. P. Gusev, *Appl. Phys. Lett.*, 2006, **88**, 201901.

2 G. Sharma, S. V. Ushakov, H. Li, R. H. R. Castro and A. Navrotsky, *J. Phys. Chem. C*, 2017,  
**121**, 10392–10397.

(30:[30]30) **Daniele Ielmini** remarked: The forming operation in your devices  
induces local bubbling and eruption. Do the samples still display resistance  
switching characteristics with set/reset operation after forming? Can you  
comment on the impact of scaling on the forming/set/reset behavior in your  
material system?

**Yuchao Yang** answered: The devices can be successfully set and reset after  
going through the gas eruptions and forming process. Similar phenomena have  
been observed in many previous studies<sup>1,2</sup> where the devices all showed normal  
set/reset operations after gas formation, indicating the generality of such  
behavior in oxide based memristors. As the device is scaled down, the number of  
filaments and the extent of interfacial reactions might be reduced to a certain  
extent. However, since the resistive switching is filamentary in such systems,  
instead of a homogeneous effect, the forming/set/reset behaviors are expected to  
be similar in general.

- 1 J. J. Yang, F. Miao, M. D. Pickett, D. A. A. Ohlberg, D. R. Stewart, C. N. Lau and R. S. Williams, *Nanotechnology*, 2009, **20**, 215201.  
2 D. Kwon, K. M. Kim, J. H. Jang, J. N. Jeon, M. H. Lee, G. H. Kim, X. Li, G. Park, B. Lee, S. Han, M. Kim and C. S. Hwang, *Nat. Nanotechnol.*, 2010, **5**, 148–153.

5 (44:[31]31) **Monica Santamaria** asked: Since you performed the voltage-current experiments under air exposure, did you consider the O<sub>2</sub> reduction as an additional faradaic process that can occur at the cathodic interface? The standard equilibrium potentials of the O<sub>2</sub>/H<sub>2</sub>O or O<sub>2</sub>/OH<sup>-</sup> equilibria are both more positive than the standard equilibrium potential of the H<sub>2</sub>O/H<sub>2</sub> equilibria, thus they are thermodynamically more favourable than the latter. This process can account for the lower volume of evolved gas at the cathode side.

15 **Yuchao Yang** answered: Thanks for the suggestion. We fully agree that the reduction of oxygen might also be responsible for the lower volume of gas evolved from the cathodic interface that we observed. The detailed cathodic process will be in the scope of future studies.

20 (45:[32]32) **Monica Santamaria** remarked: If you perform the *I-V* experiments under vacuum, you simultaneously reduce the moisture and oxygen concentrations. Did you check if the forming occurs under vacuum conditions?

25 **Yuchao Yang** answered: All the experiments were performed in ambient air in the present case. However, previous studies on similar material systems using vacuum conditions have revealed that the forming process is not possible when the device was placed in vacuum and heated to remove adsorbed moisture.<sup>1</sup>

1 M. Lübben, S. Wiefels, R. Waser and I. Valov, *Adv. Electron. Mater.*, 2018, **4**, 1700458.

30 (46:[33]33) **Ilia Valov** commented: If you use moisture free oxygen and oxygen free moisturized N<sub>2</sub> it can be possible to distinguish between these effects.

35 **Yuchao Yang** answered: Thanks for the suggestion. For the present study, all experiments were performed in air where the humidity level could not be controlled, but it will be a very interesting point to decouple the roles of oxygen and moisture in interfacial reactions based on this approach.

40 (47:[34]34) **Jonas Deuermeier** asked: Have you observed the bubbles occurring at the edges or rather in the centre of your devices? If so, was there a change when you used different polarities for switching?

45 **Yuchao Yang** answered: As can be found from Fig. 1–6 of our paper (DOI: 10.1039/C8FD00113H), in memristive systems with varied oxide, electrode combination, applied voltage, and current compliance, the bubbles are always emitted from the centre of the devices without showing preference to the edge of the electrodes. We have also adopted reversed voltage polarity in Fig. 4 and 5 of the article and the sites of bubble evolution showed generally the same results. However, by reversing the voltage polarity, it was found that the anodic reactions (now the bottom electrode in Fig. 4 and 5 of our paper) always resulted in more pronounced damage to the corresponding electrode, hence indicating the

1 possible existence of additional reduction processes that do not produce gaseous  
products.

5 (48:[35]35) **Ella Gale** commented: I did a similar study with much larger  
memristors and I saw bubbles start to form at the edge of the cross bars area, see  
Fig. 9 in my previous work in *Materials Chemistry and Physics*.<sup>1</sup> I thought this  
might be due to the increase in strain in the semiconductor and the top electrode  
at the edge of the cross-bar. It might be interesting to investigate that.

10 1 E. Gale, D. Pearson, S. Kitson, A. Adamatzky and D. L. Costello, *Mater. Chem. Phys.*, 2015,  
162, 20–30.

15 **Yuchao Yang** replied: Thanks for pointing out that interesting work. Yes, it is  
possible that the increased strain at the edges could contribute to the generation  
of bubbles, leading to gas evolution at the edges. Moreover, the electric field at the  
electrode edges is usually enhanced and might also play a role. However, it could  
still depend on the detailed conditions in the systems studied. As can be found  
20 from Fig. 1–6 in the article (DOI: 10.1039/C8FD00113H), in the present mem-  
ristive systems with varied oxide, electrode combination, applied voltage, and  
current compliance, the sites of bubble generation did not exhibit any specific  
preference to the edges but were distributed randomly on the top of the  
electrodes.

25 (49:[36]36) **Anouk Goossens** said: In Fig. 3–6 of your article (DOI: 10.1039/  
C8FD00113H), you show some global current–voltage measurements conducted  
over the entire electrode area. Have you also conducted any local current–voltage  
measurements in order to determine how the structural damage to the electrodes  
affects conductivity? How large is the difference in conductance between the areas  
30 with significant damage and the pristine regions?

35 **Yuchao Yang** responded: We did not measure the localized conductance in the  
present study, but previous studies showing similar structural damage have  
revealed enhanced conductivity (by a factor of  $\sim 4$ ) in the areas showing structural  
damage compared with the pristine region,<sup>1</sup> in agreement with the generation of  
oxygen vacancies in the reactions. We expect similar behavior holds in the present  
case.

40 1 K. Skaja, C. Bäumer, O. Peters, S. Menzel, M. Moors, H. Du, M. Bornhöfft, C. Schmitz, V.  
Feyer, C. Jia, C. M. Schneider, J. Mayer, R. Waser and R. Dittmann, *Adv. Funct. Mater.*, 2015,  
25, 7154–7162.

45 (50:[37]37) **Ruomeng Huang** asked: According to Fig.1a of your paper (DOI:  
10.1039/C8FD00113H), the probe for the  $I$ – $V$  measurements has been placed at  
the edge of each device. Is there any particular reason for this? Have you tried to  
place the probe in the centre of the device to see the impact the probe position  
might have on the bubble forming?

50 **Yuchao Yang** answered: The probe was placed at the edge of the device in order  
to minimize its influence on the observation of gas evolution and electrode  
damage. Also, qualitatively the same results have been observed when the probe

1 was placed in the centre of the electrode, as long as the loading force was kept at  
a low level.

5 (51:[38]38) **Ruomeng Huang** commented: The formation of bubbles means  
damage to the device. Did you observe this kind of damage in the subsequent SET  
and RESET processes or is it exclusive to the electro-forming process? In addition,  
you have demonstrated the damage can be mitigated by forming the device in an  
opposite polarity. In terms of the device performance, did you observe any  
10 difference in the performance for these two devices when using opposite forming  
polarities?

15 **Yuchao Yang** responded: The electrode damage was predominantly introduced  
in the forming process, while the subsequent set and reset processes are mainly  
caused by the redistribution of the ionic species introduced during forming. As  
a matter of fact, the redox processes were the same when the voltage polarity was  
reversed and only the positions for the anodic and cathodic reactions were  
switched, for example in Fig. 4 and 5 of the article (DOI: 10.1039/C8FD00113H).  
20 However, by reversing the voltage polarity, it was observed that the anodic reactions  
(now the bottom electrode) always resulted in more pronounced damage to  
the corresponding electrode, hence indicating the possible existence of additional  
reduction processes that do not produce gaseous products.

25 (53:[39]39) **Alexander Shluger** said: I have a general comment about the gas  
emission from these devices under high bias. This effect has already been  
observed in the sixties and seventies.<sup>1</sup> Whether bubbles are observed on the top of  
the top electrode or on the sides depends on the way that the electrode is  
deposited. Sputter deposition, often used in experiments, creates columnar  
structures with grain boundaries.<sup>2</sup> Oxygen can percolate through these grain  
30 boundaries creating bubbles on the top. If the electrodes have stronger adhesion  
to the oxide and less grain boundaries, the pressure of the oxygen gas can create  
delamination and bubbles on the sides of the electrode.

35 1 G. Dearnaley, A. M. Stoneham and D. V. Morgan, *Rep. Prog. Phys.*, 1970, **33**, 1129.

2 A. Mehonic, M. Buckwell, L. Montesi, M. S. Munde, D. Gao, S. Hudziak, R. J. Chater, S.  
Fearn, D. McPhail, M. Bosman, A. L. Shluger and A. J. Kenyon, *Adv. Mater.*, 2016, **28**, 7486.

40 **Yuchao Yang** responded: Thanks for sharing these important and relevant  
comments. The dependence of the gas emission sites on the microstructure and  
adhesion of the electrodes is highly plausible to us. In the present study all the  
electrodes were deposited by electron beam evaporation, which could give rise to  
similar microstructures to those in electrodes deposited by sputtering. It was  
found that the gas bubbles always emitted randomly from the top of the elec-  
trodes in our case, seen in Fig. 1–6 of our paper (DOI: 10.1039/C8FD00113H), and  
45 this might be related to the percolation of the gas molecules through the grain  
boundaries of the electrodes.

50 (54:[40]40) **Michael Kozicki** remarked: You have a pretty well defined  
mechanical system. Coming back to the gas evolution at the metal electrode, you  
know the material properties of the metal, shear strength, thickness, other

1 dimensions, *etc.* Do you have any idea of what the gas pressure is that's causing  
the electrode deformation and if that could be used to give clues about its  
evolution?

5 **Yuchao Yang** replied: Thanks for raising this point. It will be very interesting to  
estimate the gas pressure that leads to the observed electrode deformations and  
thus the extent of the preceding redox reactions. Nevertheless, construction of  
such a model is complicated by other factors, such as the varied local temperature  
10 during resistive switching, which evolves during the switching process and could  
significantly change the mechanical properties of the electrodes, making them  
different from that at room temperature. Such local temperature during resistive  
switching is not well documented yet.

15 (55:[41]41) **Philip Bartlett** said: In the paper (DOI: 10.1039/C8FD00113H), you  
used both Pt and Pd electrodes in different devices. Hydrogen evolution on Pd is  
different from Pt because the evolved hydrogen can dissolve into the Pd to make  
the alpha or beta phase palladium hydride. Did you see any evidence of different  
behavior for the Pt and Pd?

20 **Yuchao Yang** responded: Both the electrical behaviors and structural damage  
in the devices with Pt and Pd electrodes were very similar, as shown in Fig. 1–5 of  
the paper (DOI: 10.1039/C8FD00113H). The suggested hydrogen dissolution in Pd  
could play a role but did not appear to have a pronounced effect, which might be  
25 due to the fact that the reaction in eqn 2 of the paper was not the only cathodic  
process in the devices. Instead, our results indicated the possible existence of  
additional reduction processes that do not produce gaseous products, *e.g.* the  
reduction of Hf or Ta cations to their lower valence states.

30 (800:[42]42) **Andrea Zaffora** communicated: You mentioned that the extent of  
the redox processes in the Pt/HfO<sub>2</sub>/Pt device can be manipulated by the amplitude  
of the forming voltage. How can you change the forming voltage in this device  
without changing the oxide thickness or stoichiometry? It is clearly shown in  
35 Fig. 1a of the paper (DOI: 10.1039/C8FD00113H) that, for the device you  
mentioned, the forming voltage is higher than 12 V.

**Yuchao Yang** communicated in reply: The varied forming voltage in the  
present case refers to the amplitude of the voltage that was adopted during the  
forming process instead of the forming threshold, which was changed from 8 to  
40 14 V with a fixed current compliance. One can see that the extent of the redox  
processes and electrode damage gradually increased as the voltage amplitude was  
increased. It should be pointed out that such redox processes and electrode  
damage already occurred even before the forming threshold was reached (*e.g.* at 8  
45 V), as shown in Fig. 2 of the paper, indicating that the forming process is actually  
a consequence of such redox processes.

50 (801:[43]43) **Gianluca Milano** communicated: In your work, you have investi-  
gated interfacial redox processes in ECM systems by considering Cu/ZnO-based  
ECM devices. However, ZnO is well-known to be able to also switch in VCM  
configuration with an oxygen vacancy related mechanism. Indeed, as correctly

1 stated by the author, the formation of oxygen vacancies and oxygen ions cannot be  
excluded in ZnO. For example, as reported in previous work,<sup>1</sup> Cu/ZnO-based  
5 devices can be switched with a VCM mechanism by forming a conductive path  
with a positive polarity applied to the electrochemically inert electrode, instead of  
to the electrochemically active Cu electrode. These observations reveal that,  
besides the electrochemical reactions reported in eqn 6 and eqn 7 of your  
manuscript (DOI: 10.1039/C8FD00113H), the electrochemical reactions observed  
10 in VCM systems, such as eqn 1 in your manuscript, can be still present in Cu/ZnO-  
based devices. Did you observe any effect related to the VCM electrochemical  
reactions also in the Cu/ZnO ECM systems? Can you exclude an interdependence  
of both mechanisms in Cu/ZnO devices?

1 G. Milano, S. Porro, M. Y. Ali, K. Bejtka, S. Bianco, F. Beccaria, A. Chiolerio, C. F. Pirri and  
C. Ricciardi, *J. Phys. Chem. C*, 2017, **122**, 866–874.

15 **Yuchao Yang** communicated in reply: Thanks for raising a good point. We fully  
agree that the electrochemical reactions related to the valence change mechanism  
in ZnO can be present in the Cu/ZnO system. This issue was mitigated in the  
present study since the Cu electrode was adopted and positively biased. In this  
20 case, it is expected that the oxidation of the Cu metal atoms to Cu ions should be  
the dominant anodic process because the oxidation of the oxygen ions, described  
by eqn 1 in the manuscript (DOI: 10.1039/C8FD00113H), requires a much higher  
voltage. Indeed, the experimental results also revealed the migration of the Cu  
ions and subsequent nucleation at the cathodic interface, seen in Fig. 7 of the  
25 article, without showing clear evidence involving the VCM mechanism in the  
experimental conditions used in this work.

(31:[44]44) **Alexander Shluger** opened the discussion of the paper by Yago  
30 Gonzalez-Velo: How large is the effect of radiation with respect to the variability in  
the characteristics of your devices?

35 **Yago Gonzalez-Velo** responded: Variability is always a concern with ReRAM  
devices. In our case, we are careful to mention effects when an observed variation  
of an electrical parameter is large enough to be representative. Additionally,  
with the chalcogenide based PMCs (ReRAM) cells that we are able to make, we do find  
that the electrical parameters exhibit good repeatability and also that such  
40 a material system has been used for a long time even in commercially released  
ReRAM standalone memory. We previously performed total dose exposure of such  
commercial memory and limited effects were observed.<sup>1</sup>

1 Y. Gonzalez-Velo, H. J. Barnaby, M. N. Kozicki, C. Gopalan and K. Holbert, *IEEE Electron  
Device Lett.*, 2014, **35**, 205–207

45 (33:[46]46) **Stanley Williams** asked: Have you tried to make any estimates for  
the integrated energy deposited into your films by the radiation exposure that you  
deliver? I recommend that you calculate the deposited energy in terms of a more  
familiar quantity such as eV or whatever per atom within your film. This may be  
a useful exercise to go through to understand how the energy deposited into the  
50 system compares to the thermal energy.

1 **Yago Gonzalez-Velo** answered: The total dose provided is given as rad( $\text{Ge}_{30}\text{-Se}_{70}$ ) and Gray ( $1\text{Gy}=100\text{rad}$ ), which is the standard unit. They represent the amount of energy absorbed per unit mass. Consequently, the calculation of the amount deposited in the volume of the active ReRAM *via* is possible and can be  
5 done by the following: Total Dose  $\times$  mass. The *via* is about  $10\ \mu\text{m}$  in diameter and  $60\ \text{nm}$  in thickness, so its mass is close to  $23.5\ 10\text{E}^{-12}\ \text{kg}$  consisting of about  $5\ \text{gcm}^{-3}$ . This leads to an energy absorbed close to  $1.47\text{E}^{12}\ \text{eVMrad}^{-1}$  of the total ionising dose (TID), so in our case  $1.06\ \text{Mrad}$  leads to  $\text{Eabsorbed}(\text{TID}_1)=1.55\ 10\text{E}^{12}\ \text{eV}$  and  $2.38\ \text{Mrad}$  leads to  $\text{Eabsorbed}(\text{TID}_2)=3.49\ 10\text{E}^{12}\ \text{eV}$ .

10 (36:[48]48) **Ella Gale** queried: In Fig. 5 of your paper (DOI: 10.1039/C8FD00125A), you conclude that the radiation-dosage effect on annealed devices was monotonic (unlike the non-annealed devices), but why did you do only two different quantities of radiation? I do not think that you can conclude the dosage response is monotonic with only two dosages values.

15 **Yago Gonzalez-Velo** replied: In Fig. 5 of the article (DOI: 10.1039/C8FD00125A), you can observe the behavior as a function of TID for three points at increasing total dose ( $0\ \text{Mrad}$ ,  $1.06\ \text{Mrad}$ , and  $2.38\ \text{Mrad}$ ). As a consequence, we can say that experimentally, according to the results obtained and available, the response is monotonic, whereas it is not in the case of samples that were not annealed. The choice of 2 dose steps is based on setting up the experiment and being able to conduct the needed characterization in a timely manner, including the electrical testing of several devices repeatedly and XRD without having samples out of the irradiation chamber for long periods of time to minimize the relaxation effects

20 (36:[49]49) **Ella Gale** asked: Following on from my previous question, with the data that you have, can you tell me how long these devices would last in space?

25 **Yago Gonzalez-Velo** answered: How long a device lasts in space depends on where it is used in the space system (whether more or less shielding is provided), and in which orbit that space system is being flown. For commercial space applications, the total dose radiation related qualification is usually done for TID levels of  $150\ \text{krad}$  or lower. In the case of a challenging mission, such as research missions around Saturn or Jupiter, the TIDs are higher and in the range of  $300\ \text{krad}$  to  $1\ \text{Mrad}$ . That gives you an idea of the environment that designers will design towards, and the TID levels that we are testing these devices at are much  
40 higher.

30 (37:[50]50) **Gabriela Kissling** said: Have you performed any tests on the cyclability of your devices as a function of the radiation dose? Is there a difference in the lifetime of the devices or the amount of cycles you can perform before the devices break down as a function of the amount of radiation they have been exposed to?

35 **Yago Gonzalez-Velo** replied: In previous studies, we have conducted some assessment of the cyclability of chalcogenide based devices, however we did not look into the maximum number of cycles that could be obtained after exposure. Our previous work showed that the HRS/LRS ratio increases after total dose  
50

1 exposure and we also observed that the cycling lifetime was preserved or not  
2 changed after exposure to TID, *i.e.* we checked that the 10 kcycle operations  
3 occurring on the controls also occurred after exposure.<sup>1,2</sup> Such results were ob-  
4 tained on a given manufacturing process and would probably be process  
5 dependent. We did not conduct a broader study towards an optimization of  
6 cyclability with total dose.

1 Y. Gonzalez-Velo, H. J. Barnaby, M. N. Kozicki, P. Dandamudi, A. Chandran, K. E.  
2 Holbert, M. Mitkova and M. Ailavajhala, *IEEE Trans. Nucl. Sci.*, 2013, **60**, 4563–4569.

3 J. L. Taggart, Y. Gonzalez-Velo, D. Mahalanabis, A. Mahmud, H. J. Barnaby, M. N. Kozicki,  
4 K. E. Holbert, M. Mitkova, K. Wolf, E. Deionno and A. L. White, *IEEE Trans. Nucl. Sci.*, 2014,  
5 **61**, 2985–2990.

6 (38:[51]51) **Daniele Ielmini** commented: Regarding the annealing affect, your  
7 data show that the HRS resistance decreases during the annealing at high  
8 temperature, while the LRS resistance remains approximately constant. Can you  
9 comment on the possible mechanism behind such resistance drift?

10 **Yago Gonzalez-Velo** answered: This is an effect that we are interested in  
11 understanding better and it certainly requires additional characterization, which  
12 will need different techniques. However, as a comment, I would say that based on  
13 the results that we obtained I would look at having a better understanding of the  
14 existence and impact of nanocrystallite phases, such as Ag<sub>2</sub>Se, in the overall  
15 electrolyte resistance in the HRS state (Ag<sub>2</sub>Se has different bandgap and resistivity  
16 than the base chalcogenide film).

17 (39:[52]52) **Daniele Ielmini** asked: Again about the annealing-induced resis-  
18 tance drift, would it be possible that Ag gets clustered within the electrolyte, thus  
19 causing enhanced percolation in the film? Do you have evidence and information  
20 about the Ag content in the electrolyte before and after annealing?

21 **Yago Gonzalez-Velo** responded: Yes, that could be a possibility. We know that  
22 nanocrystallites form, we and other researchers in the literature have identified  
23 binary and ternary phases forming depending on the manufacturing recipe. The  
24 formation of silver cannot be dismissed, even though we have no characterization  
25 of it. Perhaps techniques such as transmission electron microscopy (TEM) could  
26 help in this case. We do not have information about the silver content before and  
27 after annealing, not at this point. It would be an interesting follow-up study.

28 (40:[53]53) **Philip Bartlett** said: I have a naïve question. Gamma rays are high  
29 energy, is there any difference in the absorption cross sections for the different  
30 materials? Are there any areas in the device where they will be absorbed more  
31 strongly, or are they just absorbed uniformly everywhere?

32 **Yago Gonzalez-Velo** responded: This is an interesting question. Gamma-rays,  
33 because they are high-energy photons, allow for dose reinforcement to be avoid-  
34 ed at the interface between the high-Z material and low-Z material. Such effects  
35 could occur with X-rays, for example, but not with gamma-rays, which enable  
36 minimization of the effect and are in part the reason for the use of a standard for  
37 device total dose qualification. Additionally, in our case the irradiator used is  
38

1 a Gammacell 220, where the configuration of the Co-60 sources provides photons impinging from all directions on the samples, also minimizing dose non-uniformities.

5 (41:[54]54) **Geoffrey Burr** commented: Your tests involve a particular device area. Would you expect to encounter more or less radiation-induced problems for larger or smaller-size devices? For instance, if a high-energy event can significantly increase conductance, then a larger area means more chance of this happening. What trend would you expect with different device areas?

10 **Yago Gonzalez-Velo** responded: This is a question that can be interpreted in several ways: if you are thinking of a high energy event, such as the heavy-ion interaction within the ReRAM cells, in the same way that people look at radiation effects and mention transient effects, such as single event effects, this is something that we have not fully characterized. I have focused here on total dose effects. However, an interaction by itself will lead to an absorption/deposition of energy, *i.e.* potentially leading to total dose effects (even the heavy-ion interaction). For devices with decreasing area the probability for an interaction to occur will decrease since the target volume will be smaller. However, if nanocrystallite growth occurs (as observed in the XRD characterization presented in this work) then, because the crystallites would grow in smaller ReRAM cells, the overall effect of the crystallite on the ReRAM cell might be higher in the case of a smaller ReRAM cell. My guess would be a trade-off/balance between having small ReRAM cells providing a lower cross-section or area to be seen by impinging particles, an increased number of cells within an array, and a possible increase of the TID impact on the ReRAM due to the crystallite growth. The impact of such crystallites still needs to be investigated and characterized though, and their dimensions and composition evaluated.

25 30 (42:[55]55) **Vladimir Kolosov** said: Why do you not do transmission electron microscopy (TEM) in addition to X-ray diffraction? Are there some specific problems with the sample preparations for TEM in your system?

35 **Yago Gonzalez-Velo** answered: We are interested in conducting TEM characterization of our samples, it will be very interesting indeed. It is a question of scheduling the different analysis, as the duration is incremental and it ends up taking a long time to perform. This is something that we plan on doing in the near future. Concerning the preparation of the samples for TEM, there are indeed some specific problems with sample preparation. We have conducted a couple of TEM studies of samples using the same material system and the issues, such as the time spent between lamella extraction and TEM visualization, are critical. It is also important to avoid keeping the electron beam on one spot for a long time as we have already observed electron beam induced crystallization on the cross section/lamella samples in previous cases. This, as an example, can have an impact on the EDS profiling done with TEM.

45 50 (43:[56]56) **Ruomeng Huang** asked: I have a question regarding the material preparation process. How uniformly has the Ag been incorporated into the GeSe layer after photodoping? Is it homogeneously doped? In addition, what is the

1 effect of the annealing process on the Ag doping profile in the GeSe layer? Is this  
2 photodoping process applicable to other metal and dielectric systems?

3 **Yago Gonzalez-Velo** responded: This is an interesting question. We do indeed  
4 conduct photodoping of the chalcogenide film with silver through UV light  
5 exposure.<sup>1,2</sup> This enables the formation of the electrolyte through the incorpora-  
6 tion of Ag inside the chalcogenide film. It has been shown in the literature that  
7 Ag exhibits a doping front in chalcogenide films that is quite constant (uniform  
8 doping with depth),<sup>3</sup> however I would comment that this is probably not appli-  
9 cable in the case of our ReRAM devices where the existence of the metal/  
10 electrolyte/metal structure might enable some electric field effect to occur due  
11 to the difference in work functions between the anode and cathode. A previous  
12 study conducted within our group showed that, using an EDS line scan on a TEM  
13 lamella, the Ag profile was not uniform throughout our films, with poor Ag doping  
14 close to the Ni cathode.<sup>4</sup> The photodoping would be applicable to chalcogenide  
15 films of various compositions where Ag or Cu are used as the active metals.<sup>2,3</sup>

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17 Holbert, M. Mitkova and M. Ailavajhala, *IEEE Trans. Nucl. Sci.*, 2013, **60**, 4563–4569.

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19 Goryll, T. L. Alford, J. L. Taggart and W. Chen, *IEEE Trans. Nucl. Sci.*, 2017, **64**, 2292–2299.

20 3 M. Frumar and T. Wagner, *Curr. Opin. Solid State Mater. Sci.*, 2003, **7**, 117–126.

21 4 D. Mahalanabis, Y. Gonzalez-Velo, H. J. Barnaby and M. N. Kozicki, *IEEE Trans. Electron  
22 Devices*, 2014, **61**, 3723–3730.

23 (56:[57]57) **Iliia Valov** said: These are nice results on the radiation effects in Ag-  
24 GeSe devices. What about the materials aspect? Is it the only material that shows  
25 this radiation resistant property? Do you have some idea which materials would  
26 be preferred?

27 **Yago Gonzalez-Velo** replied: In the last few years we have investigated the TID  
28 tolerance of systems such as Ag-Ge<sub>40</sub>S<sub>60</sub> (ref. 1) and Cu-SiO<sub>2</sub> (ref. 2) and both led to  
29 PMC/ReRAM/CBRAM cells that exhibited good resistive switching after exposure  
30 to high TID. However, we have not investigated the material changes occurring in  
31 these systems yet. It is also good to mention that there are several works that have  
32 been presented in the literature<sup>3–6</sup> not only on CBRAM but also on OxRAM that  
33 showed that such material systems also provided ReRAM cells that exhibited  
34 resistance switching at high TID. From a preference point of view, I think that  
35 there is work to be done to downselect but having a stable material with minimal  
36 crystallization would probably be my guess.

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40 Yu and W. Yu, *IEEE Trans. Nucl. Sci.*, 2015, **62**, 2404–2411.

41 3 E. DeIonno, M. D. Looper, J. V. Osborn, H. Barnaby and W. M. Tong, *Radiation effects  
42 studies on thin film TiO<sub>2</sub> memristor devices*, IEEE Aerospace Conference Proceedings, 2013.

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46 Electron Devices*, **58**, 2800–2805.

47 6 R. Fang, Y. Gonzalez-Velo, W. Chen, K. Holbert, M. N. Kozicki, S. Yu, *Appl. Phys. Lett.*, 2014,  
48 **104**, 183507.

1 (100:[100]100) **Gianluca Milano** opened a general discussion of the paper by  
Ludovic Goux: In your work, the device performances were associated to the  
empty volume of the chalcogenide layers. This means that the device perfor-  
5 mances, such as the writing speed, depend on the film density and porosity. As  
recently reviewed by Valov *et al.*,<sup>1</sup> moisture can be adsorbed and incorporated in  
nanoporous films both with or without chemical interaction, affecting the resis-  
tive switching behaviour. Indeed, besides impacting the electronic transport  
10 properties of the films, moisture can affect the electrochemical reactions (in  
particular the counter electrode reaction) and can thus regulate the switching  
kinetics. As reported by Tsuruoka *et al.*,<sup>2</sup> in the case of Ta<sub>2</sub>O<sub>5</sub>, lower film densities  
result in more water molecules being incorporated in the active material that may  
enhance the redox reactions at the metal-electrolyte interfaces, thus influencing  
15 the resistive switching properties, such as electroforming. Are the device perfor-  
mances observed in your chalcogenide films with different densities related to the  
different spatial constriction conditions that facilitate the migration of host ions  
in less dense chalcogenide electrolytes or to the different amounts of adsorbed  
moisture from the ambient environment that affect the switching kinetics?

1 I. Valov and T. Tsuruoka, *J. Phys. D*, 2018, **51**, 413001.

2 T. Tsuruoka, I. Valov, S. Tappertzhofen, J. V. D. Hurk, T. Hasegawa, R. Waser and M. Aono,  
*Adv. Funct. Mater.*, 2015, **25**, 6374–6381.

25 **Ludovic Goux** replied: That is a good point. We unfortunately have no infor-  
mation about whether the quantity of moisture varies with the density of our  
material, so it is difficult to assess whether it is the spatial condition or the  
moisture itself that is the origin of the properties. I would rather expect that it is  
the spatial conditions because moisture would fill the pores more and it would  
indeed reduce the switching speed but I would also expect that it would degrade  
30 retention, which is not what we observe. The question remains open still.

35 (101:[101]101) **Ilia Valov** commented: Have you performed experiments to  
determine the role of the short range order and also that of the density of the  
electrolyte materials? The particular surrounding in the cluster may also play  
a role in determining the performance. This could, for example, be studied using  
X-ray absorption experiments.

**Ludovic Goux** answered: This is indeed a good point. We have recently started  
some EXAFS experiments, however we have no results so far.

40 (102:[102]102) **Niloufar Raeishosseini** said: I have a question about the thermal  
stability. Considering GST as the phase change material, how do the authors  
confirm the phase of the material is stable during the experiment, specifically  
while the external voltage is applied? In Fig. 2 of the article (DOI: 10.1039/  
45 C8FD00115D), the sample prepared for XRD measurement should be prepared  
on a Si wafer rather than SiO<sub>2</sub> to avoid the XRD peak of the SiO<sub>2</sub> substrate, which  
is almost between 20 and 25. To be more concise, a high-temperature XRD is  
suggested; in this case, the authors can investigate the sample by elevating the  
temperature in steps until a transition temperature around 250 and 280 °C is  
50 reached. It seems just annealing the samples at 250 and taking the XRD will not

1 be enough to realize the stability of the samples. The MIT transition is likely to  
happen at 250–280 °C or even less annealing temperature depending on the  
samples.

5 **Ludovic Goux** responded: Thank you for the suggestion of this experiment. We  
agree that some parasitic local phase change of the GeTe material during  
switching is not excluded.

10 (103:[103]103) **Ella Gale** asked: You mention in your paper (DOI: 10.1039/  
C8FD00115D) that factor  $\gamma$  is a geometric factor from a random walk in 3-  
dimensions. Why did you use a 3-D random walk? 1-, 2-, and 3-D random walks  
15 have very different properties. For example, walkers can easily get stuck in a queue  
in 1-D, but this is much less likely in 3-D. If this is a conducting filament with ions  
hopping along it, would it be better modelled as a 1-D random walk? For example,  
the attempt frequency would be reduced if there was any queuing effect and  
crucially reduced by different amounts dependent on the number of walkers  
20 (ions) moving along the filament, so this would change as the device is used.  
Furthermore, there has been work in this field where the filaments are modelled  
as not 1-, 2- or 3-D but as fractals. See the work by J. S. Lee *et al.*<sup>1</sup> where the fractal  
dimension was found to be 2.54, so a fractal dimension is likely the best  
description of the filament structure.

25 1 J. S. Lee, S. B. Lee, S. H. Chang, L. G. Gao, B. S. Kang, M. -J. Lee, C. J. Kim, T. W. Noh and B.  
Kahng, *Phys. Rev. Lett.*, 2010, **105**, 205701.

30 **Ludovic Goux** responded: This is an interesting point. We actually do not think  
that 1-D walk would better describe the cation motion because field lines are not  
uniform. On the other hand, 3-D is also an overestimate, we agree. Probably the  
fractal dimension would indeed be the most appropriate. Anyway, we would like  
to note here that the equation was introduced only for the qualitative interpre-  
tation of the motion as a hopping mechanism.

35 (104:[104]104) **Iliia Valov** commented: Under applied voltage there won't be  
a chance to observe a random walk. At these conditions ion velocity is exponen-  
tially dependent on the electric field. I would suppose that there will be no 3D  
motion.

40 (105:[105]105) **Alexander Shluger** asked: What is the driving force for Cu to  
form a compact filament? Why do Cu atoms get together to form this type of  
a cylinder? What is the evidence that Cu-Cu interaction can assemble randomly  
diffusing Cu atoms into such structure?

45 **Ludovic Goux** answered: We performed *ab initio* simulations, which are  
unpublished, showing Cu that is thermodynamically more stable in clusters than  
as dispersed atoms. Besides, numerous works, including TEM imaging, have  
shown that Cu filaments or clusters are formed in CBRAM devices.

50 (106:[106]106) **Alexander Shluger** said: You put a lot of emphasis on free  
volume, which basically suggests that you think that Cu is moving by interstitial

1 hopping. Another mechanism is more efficient in some cases, such as when an  
interstitial atom pushes an atom out of its site and substitutes it, and other  
collective mechanisms, see the studies by Frank *et al.*<sup>1</sup> and F. Faupel *et al.*<sup>2</sup> The so  
5 called interstitialcy mechanism is very efficient, particularly for interstitial atom  
diffusion.<sup>3</sup> Why do you think that Cu is moving by hopping in this system? Did  
you consider other collective mechanisms? They will cause different free volume  
dependence.

10 1 W. Frank, A. Horner, P. Scharwaechter and H. Kronmuller, *Mater. Sci. Eng.*, 1994, **179**, 36–40.

2 F. Faupel, W. Frank, M. Macht, H. Mehrer, V. Naundorf, K. Rätzke, H. R. Schober, S. K. Sharma and H. Teichler, *Rev. Mod. Phys.*, 2003, **75**, 237.

3 B. Sadiq, T. J. Lenosky, S. K. Theiss, M. Caturla, T. D. Rubia and M. A. Foad, *Phys. Rev. Lett.*, 1999, **83**, 4341.

15 **Ludovic Goux** answered: This is an interesting remark, thank you for highlighting these previous studies. We did not have an *a priori* view of the cation motion mechanism, our interpretation of hopping through the empty volume just follows from our observation of faster motion in more porous matrix. However, in case the substitution scenario would be able to support our data, we would be open to considering it.

20 (107:[107]107) **Geoffrey Burr** said: I have a question about Fig. 11 in your paper (DOI: 10.1039/C8FD00115D). It's obvious that the bar chart drawing is a cartoon, but I noticed in the text that you report SET time as a function of the pulse-length that induces a SET state. However, it is possible that this SET event is influenced by the pulses that come before this final pulse, perhaps even the aggregate time exposure. This would imply that different pulse sequences or orders would end up producing a different "SET duration". I also would point out that in a memory application, it is most likely that this SET event, which we want to be fast, will come after the device has been sitting in an "unselected" state, which could mean a small negative polarity across the device. What has been your experience in terms of the dependence of the "SET time" on the time between pulses or on the polarity experienced by the device just before the SET pulse?

35 **Ludovic Goux** replied: This is a very good point indeed. For CBRAM devices, where switching is controlled by cation drift and redox, we typically observe that an ISPP write programming sequence is more efficient than a single write pulse having the same length as the last ISPP pulse, indicating that the sequence does something to the device that is not translated immediately in the electronic conduction. This can be expected from the impact on the cation drift and concentration profile. Obviously, opposite polarities will also affect this differently. This observation is also valid for OxRAM devices and I invite you to read a complete study of ours on this topic.<sup>1</sup>

45 1 "C.Y.Chen *et al.*, IEDM 2016"

50 (138:[108]108) **Dirk Wouters** said: In your presentation, interestingly, you attribute the better stability of the Ge-Se vs. Ge-Te based CBRAM device to the stronger bond of Cu with Se than with Te. As Cu has a stronger bond to Se than to Te, would that also affect the electrical conductivity of the filament, especially the

1 tiny filaments of similar size or number of Cu atoms, in the Ge-Se vs. Ge-Te matrix  
2 ?

5 **Ludovic Goux** answered: It is indeed possible that for tiny filaments, when the  
conductivity may no longer be described as originating from a Cu nanowire, the  
filament surface conductivity contributes. In that respect, I have no insight for the  
time being whether we would observe a difference between Ge-Se and Ge-Te  
electrolytes.

10 (110:[110]110) **Stanley Williams** opened a general discussion of the paper by  
Elia Ambrosi: Building on the talk earlier by Prof. Yuchao Yang about what  
happens to the electrodes when you apply such large voltages, such as are applied  
in your work, did you look at the electrodes using some type of microscopy during  
15 or after your experiments? Did you see any deformation in the electrodes when  
you applied these very large voltages? Were you blowing things up, blowing  
bubbles, *etc.*? Did you look for changes in the electrodes? If you don't look for  
them explicitly, you won't see them.

20 **Elia Ambrosi** answered: We have not performed microscopy observations in  
our device before or during the operation of the devices. However, we might safely  
rule out any bubbling effect because the operating voltage was much lower than  
reported in the previous work by Prof. Yuchao Yang.

25 (111:[111]111) **Stanley Williams** commented: I suggest strongly that you use an  
appropriate microscope and look at your devices as you're doing the switching or  
after the experiments are over, in the case of very small devices. We did that 10  
years ago and were rather astounded when we saw craters that had erupted out of  
our electrodes. Significant changes can occur, as we saw earlier from Prof. Yuchao  
30 Yang's talk. The structure that you have after you've applied these potentials can  
be completely different from what was originally built.

35 **Elia Ambrosi** responded: We thank you for your precious advice and we will  
look into studying the device structure before and after device operation by  
appropriate microscopy techniques.

40 (112:[112]112) **Daniele Ielmini** remarked: Regarding the possibility of bubble  
formation in our devices, although we have not inspected our devices for possible  
bubbling because of the extremely small active area of 70 nm diameter of the  
bottom electrode, I would rather exclude this possibility for several reasons. First,  
the devices formed at relatively low current, generally 10  $\mu\text{A}$ , thanks to the one-  
transistor/one-resistor (1T1R) structure with an integrated transistor. The low  
current forming allows the control of the local electrical parameters and Joule  
45 heating in the forming transient, thus preventing destructive thermal runaway.  
Second, the bubble sizes evidenced in the previous paper by Dr Yuchao Yang  
(DOI: 10.1039/c8fd00113h) are a few 100 nm at least, which makes even the  
smallest observed bubble much larger than the device itself. Third, our devices  
generally show endurance in the range of  $1\text{E}^7$  to  $1\text{E}^8$ , which alone makes the  
50 bubbling and its related degradation extremely unlikely.

1 (113:[113]113) **Dirk Wouters** said: In your work, you compare switching in  
different metal oxide layers, *i.e.* hafnium oxide and silicon oxide. However,  
5 another difference is that the  $\text{HfO}_2$  is stoichiometric, while the silicon oxide is  
substoichiometric ( $\text{SiO}_x$  and not  $\text{SiO}_2$ ). Why did you choose substoichiometric  
silicon oxide, what is the value of  $x$ , and did you examine the effect of different  
stoichiometries?

10 **Elia Ambrosi** responded: In our devices, silicon oxide is deposited by e-beam  
evaporation starting from a silicon monoxide solid target, thus  $x$  should be  
around 1. We chose sub-stoichiometric silicon oxide to increase the leakage  
current in the pristine state, thus reducing the forming voltage and improving the  
control of LRS/HRS. All our results with  $\text{SiO}_2$  instead of  $\text{SiO}_x$  led to excessive  
forming voltages and unstable RRAM operation.

15 (114:[114]114) **Dirk Wouters** remarked: In your paper, you compare the  
switching characteristics of different oxides based on the DC  $I$ - $V$  characteristics.  
Did you also perform kinetic analysis? Is the time behavior also similar?

20 **Elia Ambrosi** responded: We have conducted limited analysis of the pulsed  
behavior of the  $\text{SiO}_x$  and  $\text{HfO}_2$  RRAMs, from which it appears that the dynamic  
operation in the two materials is rather similar. For instance, we see a comparable  
increase of the set/reset voltages at decreasing pulse-width. A systematic analysis  
and comparison of the two materials is not yet completed.

25 (115:[115]115) **Tony Kenyon** said: When you deposit Ti on an oxide the Ti  
would usually oxidise, drawing oxygen out of the oxide and producing oxygen  
vacancies. This is typically used in Si oxide and Hf oxide, for example, to seed the  
interface with oxygen vacancies. In your case I would expect the same thing to  
30 happen, so how much of what you're seeing could be due to the Ti oxide layer  
rather than the silicon oxide? Could the switching be a bilayer effect?

35 **Elia Ambrosi** responded: Indeed, switching might be a two-layer effect because  
of the O gettering from the Ti top electrode. However, we observe strong differ-  
ences in the forming characteristics in Fig. 2 of our paper (DOI: 10.1039/  
C8FD00106E), which might indicate a central role of the bulk oxide, namely  
 $\text{HfO}_2$  or  $\text{SiO}_x$ , instead of the artificial  $\text{TiO}_x$ . Also, the LRS can become quite  
40 conductive at high compliance current, which suggests that the filament is  
metallic in both  $\text{SiO}_x$  and  $\text{HfO}_2$ , and that Ti (instead of O vacancy) might have  
a leading role in the formation of the conductive path.

45 (116:[116]116) **Yang Li** said: In Fig. 7 of your paper (DOI: 10.1039/  
C8FD00106E), you reported the negative set behavior of the  $\text{HfO}_2$  ReRAM and  
no negative set behavior in the  $\text{SiO}_x$  devices. In Fig. 8 of your paper, you showed  
the retention characterization of the devices and the  $\text{SiO}_x$  ReRAM showed larger  
resistance fluctuation. You attribute both the negative set and the resistance  
retention behavior to the energy barrier height for defect migration. I am just  
50 wondering if they're kind of contradictory, since if you have a higher energy  
barrier for defect migration in  $\text{SiO}_x$ , as explained for the negative reset behavior,

1 shouldn't we also expect less fluctuation for the SiO<sub>x</sub> devices in the retention  
experiment?

5 **Elia Ambrosi** replied: In both SiO<sub>x</sub> and HfO<sub>2</sub>, the HRS shows resistance fluctu-  
ations, although both oxide RRAMs show good data retention with no data loss  
even after 1 h annealing at 260 °C. Also note that the retention characteristics of  
the SiO<sub>x</sub> and HfO<sub>2</sub> RRAMs should be compared at equal resistance level, which is  
not possible for some relatively high resistance value in SiO<sub>x</sub> which we could not  
10 attain with a HfO<sub>2</sub> RRAM. Overall, the retention characteristics of the two RRAM  
devices look rather similar. Regarding the energy barrier for the negative set and  
retention, one should note that the two processes are rather different, therefore  
the relevant energy barrier might also have different values. For the negative set,  
the defects are activated by the application of a negative voltage at the top electrode.  
15 On the other hand, the data loss mechanism in the retention experiment is  
the spontaneous diffusion (no voltage applied) in the conductive path. In  
conclusion, given the different physical mechanisms involved in the negative set  
and retention experiment, the different behavior of the two RRAM devices in these  
experiments does not look like a contradiction.

20 (117:[117]117) **Alexander Shluger** commented: You state that the breakdown  
voltage of SiO<sub>x</sub> is 20 MVcm<sup>-1</sup>, which is much higher than the well-established  
breakdown voltage for SiO<sub>2</sub> films of about 10 MVcm<sup>-1</sup>, see for example work by  
Verweij and Klootwijk.<sup>1</sup> How do you explain why the SiO<sub>x</sub> in your system is much  
25 more stable with respect to dielectric breakdown than SiO<sub>2</sub> films?

1 J. F. Verweij and J.H. Klootwijk, *Microelectron. J.*, 1996, 27, 611–622.

30 **Elia Ambrosi** replied: There are at least two important differences between  
standard SiO<sub>2</sub> and the SiO<sub>x</sub> dielectric used in our RRAM devices. First, the device  
is SiO<sub>x</sub> with x equal to about 1. Second, the SiO<sub>x</sub> layer has already been subject to  
breakdown during the forming operation, as seen in Fig. 2 of our paper (DOI:  
10.1039/C8FD00106E). As a result, the breakdown event taking place during the  
negative set voltage can be viewed as a second breakdown, where the local  
35 conductive path is further degraded as a result of the application of a negative  
voltage. This is similar, for instance, to the hard breakdown event, compared to  
the soft breakdown event that occurred at forming.

40 (118:[118]118) **Alexander Shluger** asked: So this is not a real dielectric  
breakdown?

**Elia Ambrosi** replied: Indeed, we might view our estimated breakdown field of  
20 MVcm<sup>-1</sup> as an effective breakdown field for the onset of negative set, not to be  
compared to the known breakdown field of SiO<sub>2</sub>.

45 (130:[119]119) **Vikas Rana** enquired: How much current compliance has been  
used during the retention measurement?

50 **Elia Ambrosi** responded: Before the retention experiment, multiple ReRAM  
devices were initially prepared in various resistance states. Different HRS and LRS

1 values were obtained by changing the reset stop voltage  $V_{\text{stop}}$  and the compliance  
current  $I_C$ , respectively. The LRS was initially programmed in a range from about  
10 k $\Omega$  to 100 k $\Omega$ , corresponding to programming compliance currents between  
100  $\mu\text{A}$  and 10  $\mu\text{A}$ , respectively. During the retention experiment, after each  
5 annealing step, the resistance of each device was read using a  $-0.2$  V reading  
voltage at the top electrode, while keeping the series transistor biased at relatively  
large gate voltage to minimize the voltage drop across the transistor. So no  
compliance was used during the retention experiment, as the devices were read  
10 with a voltage much lower than the set/reset voltage.

(131:[120]120) **Vikas Rana** remarked: And what is the impact of the current  
compliance on your retention? What is the device size used in the retention test?

15 **Elia Ambrosi** responded: In Fig. 8 of our paper (DOI: 10.1039/C8FD00106E),  
both the  $\text{HfO}_2$  and  $\text{SiO}_x$  devices show slightly larger resistance fluctuations for  
a large initial LRS ( $R \approx 100$  k $\Omega$ ), namely for the resistance states obtained with  
a low programming compliance current  $I_C$ . However, both oxides show good  
retention with no data loss. The device size is about 70 nm  $\times$  70 nm.

20 (132:[121]121) **Jonas Deuermeier** asked: You're concluding that the forming  
process is very different, whereas the  $I$ - $V$  curves are very similar, although you're  
using different hafnium oxide thicknesses. The forming comparison was done  
looking at the 5 nm hafnium oxide, seen in Fig. 2 of your paper (DOI: 10.1039/  
25 C8FD00106E), whereas the  $I$ - $V$  comparison refers to the 10 nm hafnium oxide,  
*e.g.* Fig. 4 of your paper. It seems that the characteristics in general become  
similar by simply using a hafnium oxide twice as thick as the silicon oxide. In  
order to check this hypothesis, I was wondering if you tested the negative  
breakdown of the 10 nm hafnium oxide up to  $-10$  V, as you do for the silicon  
30 oxide.

**Elia Ambrosi** replied: In this work, we have not systematically tested the  
negative breakdown in 10 nm  $\text{HfO}_2$ , although the negative set voltage markedly  
increased with respect to the 5 nm thick  $\text{HfO}_2$ , as we could increase the stop  
35 voltage to a range (*e.g.*,  $-4$  V) which was not accessible with the 5 nm thick  $\text{HfO}_2$ .  
See Fig. 5c and d of our paper (DOI:10.1039/C8FD00106E).

(133:[122]122) **Jonas Deuermeier** said: Is the 10 nm hafnium oxide formed at  
40 4 V or at 8 V?

**Elia Ambrosi** replied: Forming of the 10 nm  $\text{HfO}_2$  occurred at about 8 V.

45 (134:[123]123) **Sherif Ibrahim** said: Regarding the observed negative set during  
the device cycling, did you manage to eliminate that negative set and get a proper  
reset of the device?

**Elia Ambrosi** replied: In general, we believe that the negative set can be  
50 explained by the breakdown of the bottom electrode interface with the dielectric  
layer, therefore the negative set can be attenuated or solved only by either  
increasing the characteristic breakdown field  $F_{\text{BD}}$  or by reducing the electric field

1 during reset below the critical threshold. In this work, we manage to eliminate the  
negative set in the  $\text{HfO}_2$  device by increasing the  $\text{HfO}_2$  thickness, hence reducing  
the field below  $F_{\text{BD}}$ . Another solution, also implemented in our work, is the  
5 adoption of relatively low  $V_{\text{stop}}$  values to reduce the operating electric field. On the  
other hand, we believe that the key approach to radically solve the negative set is  
to engineer the bottom electrode interface to increase  $F_{\text{BD}}$ . We are currently  
conducting some experiments to optimize the bottom electrode interface to  
improve  $F_{\text{BD}}$  in the  $\text{HfO}_2$ .

10 (136:[124]124) **Carlo Ricciardi** enquired: Why did you choose carbon as the  
bottom electrode? If the Ti ions are migrating, did you check for any Ti-C  
compound at the interface?

15 **Elia Ambrosi** answered: In general, it is good practice to adopt a rather inert  
bottom electrode for RRAM, as opposed to a rather oxidizable metal for the top  
electrode. This enables asymmetric structure and a polarity dependent operation  
of the device with positive-voltage set and negative voltage reset, with the voltages  
applied to the top electrode. Previous studies have also pointed out that the inert  
20 bottom electrode increases the immunity to the negative set.<sup>1</sup> Given the relevance  
of the negative set for improving the RRAM endurance, an inert electrode will thus  
strengthen the device against endurance failure.<sup>2</sup>

25 Carbon is known to be an inert material with low reactivity especially at high  
temperature. Our previous work also suggested that RRAM devices with a C  
bottom electrode were immune from negative set and showed a high endurance.<sup>3</sup>  
For these reasons, we adopted C as the bottom electrode in our RRAM. We did not  
check for the presence of Ti at the bottom electrode or for possible reaction of Ti  
with C. This is indeed possible, although metal carbides, such as TiC, are also  
30 known to be rather inert compounds that react with oxide only at relatively high  
temperature. Therefore, the reaction of Ti with C at the bottom electrode should  
not be critical for the negative set.

35 1 C. Y. Chen, L. Goux, A. Fantini, A. Redolfi, S. Clima, R. Degraeve, Y. Y. Chen, G. Groeseneken and M. Jurczak, *IEEE International Electron Devices Meeting*, Institute of Electrical and Electronics Engineers, San Francisco, 2014.

2 S. Balatti, S. Ambrogio, Z. Wang, S. Sills, A. Calderoni and N. Ramaswamy, *IEEE Trans. Electron Devices*, 2015, **62**, 3365–3372.

3 A. Bricalli, E. Ambrosi, M. Laudato, M. Maestro, R. Rodriguez and D. Ielmini, *IEEE Trans. Electron Devices*, 2018, **65**, 122–128.

40 (137:[125]125) **Stefano Brivio** said: You suggest that the operation of all the  
investigated devices relies on Ti drift and diffusion. The conduction mechanisms  
of the different devices in the various resistance states may reveal differences or  
additional similarities among the investigated systems. In this respect, have you  
analyzed and compared the conduction mechanisms of such devices in the  
45 various resistance states?

**Elia Ambrosi** responded: To test the conduction mechanism, we characterized  
the  $I$ - $V$  curves, which allow the assessment of the voltage dependence of resistance.  
In general, we found quasi-linear current, *i.e.* constant conductivity, for the  
50 LRS and a strongly non-linear transport in the HRS. The LRS showed an increased

1 non-linearity at increasing resistance or equivalently for lower compliance current  
of the set transition. In general, a linear increase of current with voltage can be  
attributed to a metallic conduction in the conductive path, whereas the non-linear  
5 behavior can be attributed to Poole-Frenkel conduction at the defects, such as  
metallic clusters, oxygen vacancies, or grain boundaries. More detailed  
temperature-dependent studies are currently being conducted to confirm this  
picture.

10 (140:[126]126) **Ilia Valov** said: About carbon, I think, there is an additional  
effect. It is supporting the way you suppress the oxygen reaction. We have seen  
this in our previous papers.<sup>1,2</sup> In addition, the mobility of Ti in HfO<sub>2</sub> has been  
documented by the group of G. Bersucker<sup>3</sup> and in a paper by Privitera *et al.*<sup>4</sup>

15 1 Nature Nanotechnology 2016.

2 Adv Mater 2015.

3 G. Bersucker *et al.*

4 Microelectronic engineering 2013.

20 **Elia Ambrosi** answered: We agree that C might prevent oxidation at the bottom  
electrode, hence contributing to the good performance under reset and the  
endurance of our RRAM devices.

25 (802:[127]127) **Asal Kiazadeh** communicated: Thanks for the work you have  
presented during the Faraday Discussion. Regarding Fig. 2 in your paper  
(DOI:10.1039/C8FD00106E), in the electroforming step of the pristine states of  
different devices, the compliance current (CC) alters almost two orders of  
magnitude. Does this mean that CC is not fixed through the gate of the series  
transistor for a certain level? In addition, it doesn't look like the reason for the  
30 changing CC is due to different leakage at the pristine state. Some with higher  
leakages reach lower CC values. Following the previous question, when the CC is  
higher, the required voltage is higher too, then how we can interpret the distri-  
bution of the forming voltages in a proper way? One needs to consider different  
sizes of filament during electroforming, right?

35 **Elia Ambrosi** communicated in reply: The reason for the different compliance  
currents in Fig. 2 of our paper ((DOI: 10.1039/C8FD00106E) is that various values  
of the gate voltage  $V_G$  were used for different devices. The compliance current is  
indeed controlled by the gate voltage, however  $V_G$  was deliberately changed, thus  
40 resulting in various compliance currents. Neither the compliance current was  
influenced by the initial leakage of the device, nor was the forming voltage  
influenced by the compliance current, which plays a role only to control the final  
resistance of the LRS after forming.

45 (803:[128]128) **Sweety Deswal** communicated: What are the conduction and  
switching mechanisms in the two HfO<sub>x</sub> and SiO<sub>x</sub> devices? How are these mech-  
anisms contributing for better performance of the SiO<sub>x</sub> device? Or what are the  
reasons for the better performance of the SiO<sub>x</sub> device?

1        **Elia Ambrosi** communicated in reply: The conduction mechanism is believed  
to be drift in the metallic Ti filament for the LRS and Poole-Frenkel in the HRS.  
The switching mechanism is most probably Ti migration induced by the electric  
5        field. The improved performance of the SiO<sub>x</sub> is because of the larger breakdown  
field for the negative set event, which enables a larger resistance window and  
a higher endurance.

10        (119:[129]129) **Ella Gale** opened the discussion of the paper by Masa-aki Haga:  
You stated that you had a pK<sub>a</sub> gradient that was generated and used as the driving  
force for proton movement. That is exciting. Did you design that at the start? How  
closely did it follow your design? And, if so, what are the design rules? If I wanted  
an arbitrary pK<sub>a</sub> gradient, how would I go about designing it?

15        **Masa-aki Haga** answered: We have published two papers concerning the  
energy storage based on proton-coupled electron transfer (PCET) reactions.<sup>1,2</sup>  
Based on the basic studies for the PCET reaction for the Ru(II) and Ru(III) states,  
we can expect a pK<sub>a</sub> change caused by the redox reaction. In the previous study,  
we reported a proton-rocking-chair-type redox capacitor with the same combi-  
20        nation of two RuNH-OH and RuCH-OH multilayer films on ITO electrodes  
sandwiched with neutral NaClO<sub>4</sub> aqueous solution. In this capacitor, under the  
galvanostatic condition, the stable charge-discharging process took place, see ref.  
36 in our paper (DOI: 10.1039/C8FD00098K), and during the charging process the  
electric energy was stored as a pH gradient between the two electrodes. For the  
25        discharging, the electric energy was released as a pH neutralization process. The  
guiding principle for the design of a protonic memristor arose from the idea of  
replacing the neutral aqueous solution in the previous redox capacitor with  
a proton-conducting polymer, such as P4VP, resulting in the charge storage  
memory device. The design role is to arrange the molecules with different pK<sub>a</sub>  
30        values each other. A better design for the system is that the molecules are  
hydrogen-bonded and arranged within the assembly. A list of the pK<sub>a</sub> values for  
the organic compounds is available and on the other hand you can find the pK<sub>a</sub>  
data set for the inorganic complexes, which is still limited. The proton pump in  
the biological membrane is the most studied system, so you will have a chance to  
35        get an idea for the new artificial system.

1 D. Motoyama, K. Yoshikawa, H. Ozawa, M. Tadokoro and M. Haga, *Inorg. Chem.*, 2017, **56**,  
6419–6428.

2 K. Yoshikawa, D. Motoyama, Y. Hiruma, H. Ozawa, S. Nagano and M. Haga, *ACS Appl.*  
*Mater. Interfaces*, 2018, **10**, 26990–27000.

40        (120:[130]130) **Ella Gale** remarked: Is that why you used Ru? I presume that it  
would be different if you chose different ions?

45        **Masa-aki Haga** replied: The redox chemistry of the ruthenium (II/III)  
complexes has been well known as a small reorganization energy system and the  
oxidation states of both Ru(II) and Ru(III) are substitutionally inert. Thanks to  
pioneers such as Nobel laureate Prof. H. Taube, Prof. T. J. Meyer, and Prof. R. W.  
Murray and their contribution in this field, we can easily design the functional Ru  
50        complexes by choosing the auxiliary ligands around the Ru ion. Therefore, we  
chose Ru complexes.



1 We have been studying the surface electrochemistry of the redox-active molecules immobilized on an ITO surface, and these studies have been extended into layer-by-layer (LbL) multilayer films. By the judicious selection of redox potentials in the molecules, photo responsive hetero LbL films through ET rectification have  
5 been achieved,<sup>4</sup> furthermore interesting humidity-controlled rectification switching in single molecular junctions for our Ru complexes has been recently found.<sup>5</sup> Through this study, the redox-active Ru LbL multilayer films are stable under the applied potential and thermally robust up to 200 °C. By changing the Ru complexes from RuNH-OH and RuCH-OH to the complex bearing N-methyl protected groups, RuNMe-OH and RuCMe-OH, see Fig. 2 in our paper (DOI: 10.1039/C8FD00098K),  
10 the *I-V* plots did not show little current flow, which indicated our devices are sensitive to the immobilized molecular structures. At this stage, we could not have any answer why the *I-V* plots in your work and ours showed similar hysteresis loop at almost the same voltages, even the film thickness is so different from each other. From the preliminary analysis of the *I-V* plots for our devices, the space-charge-limited conduction model is fitted for the low-to-high current transition. The energy barriers at the molecule/electrode interface through the hydrogen bonding between the RuNH-moieties and P4VP drastically changed under the voltage application and the charge accumulated at the interface by the p*K*<sub>a</sub> gradient.

1 D. R. Stewart, D. A. A. Ohlberg, P. A. Beck, Y. Chen, R. S. Williams, J. O. Jeppesen, K. A. Nielsen and J. Fraser Stoddart, *Nano Lett.*, 2004, **4**, 133–136.

2 G. Cao, H. G. Hong and T. E. Mallow, *Acc. Chem. Rev.*, 1992, **25**, 420–427.

3 E. L. Hanson, J. Guo, N. Koch, J. Schwartz and S. L. Bernasek, *J. Am. Chem. Soc.*, 2005, **127**, 10058.

4 T. Nagashima, H. Ozawa, T. Suzuki, T. Nakabayashi, K. Kanaizuka and M. Haga, *Chem. Eur. J.*, 2016, **22**, 1658–1667.

5 H. Atesci, S. J. van der Molen *et al.*, *Nature Nanotech.*, 2018, **13**, 117–1218.

(122:[132]132) **Stanley Williams** said: You have to be really careful in terms of the control experiments. We were using rotaxanes, for which a Nobel prize was awarded. We felt we were onto something. I worked on this for 6 years before I figured out we'd been fooling ourselves.

**Masa-aki Haga** responded: The surface redox-active coordination network system has a potential to pursue various functions not only for electronics but also photochemical and catalytic properties, therefore we will continue to study the surface molecular devices.

(123:[133]133) **Rainer Waser** said: We have shown, for two presumably molecular switching systems, both rose bengal and Cu TCNQ, that we could leave out the molecules completely and switch them in the same way. I've seen from your *I-V* curves that your currents go up to 4 mA. What kind of switching do you believe you have?

**Masa-aki Haga** responded: We have missed the literature survey for your rose bengal and Cu TCNQ systems. We should know these. If possible, please let me know these papers. Our device area is 0.95 cm<sup>2</sup>, which is relatively large. Therefore, the current density reached is ~ 4–10 mAcm<sup>-2</sup>. We have reported a proton-rocking-chair-type redox capacitor with the same combination of two RuNH-OH and RuCH-OH multilayer films on ITO electrodes sandwiched with neutral

1 NaClO<sub>4</sub> aqueous solution. In this capacitor, under the galvanostatic condition, the stable charge-discharging process took place<sup>1</sup> and, during the charging process, the electric energy was stored as a pH gradient between two electrodes. For the discharging, the electric energy was released as a pH neutralization process. The guiding principle for the design of a protonic memristor arose from the idea of replacing the neutral aqueous solution in the previous redox capacitor with a proton-conducting polymer, such as P4VP, resulting in the charge storage memory device. I propose the redox-induced switching of RuNH-OH and RuCH-OH on the acid-base pair hydrogen bonding site, as shown in Fig. 6 of our paper (DOI: 10.1039/C8FD00098K), induced the charge accumulation (proton or negative charge) at the hetero layer junction according to the pK<sub>a</sub> difference, becoming a stronger acid for one side and a on the other side a stronger base, which is the driving force for the high conducting state. This stayed until the reverse redox reaction occurred by the reverse potential bias. This process might be relevant to the ATP synthesis by the pH gradient in the biomembrane.

1 K. Yoshikawa, D. Motoyama, Y. Hiruma, H. Ozawa, S. Nagano and M. Haga, *ACS Appl. Mater. Interfaces*, 2018, **10**, 26990–27000.

20 (125:[134]134) **Philip Bartlett** said: To continue on that point, I think it would be better for this plot seen in Fig. 8 of your paper (DOI: 10.1039/C8FD00098K) to show the current density rather than the current. In your paper you focus on cations, the two Ru complexes on the two electrodes are both cationic and you focus on the movement of the protons. What are the compensating anions involved here? In both layers of the Ru complexes on the two electrodes you have some corresponding anions to maintain electroneutrality, and in the protonated poly(vinylpyridine) there will be some associated anions. Is it the same anion in the electrode layers and in the poly(vinylpyridine)? Have you looked at changing the anion? What effect does it have on the properties of the system?

30 **Masa-aki Haga** answered: Thank you for your comment. We have changed the *I*-*V* plots by converting the *y* axis to the current density from the current value. Regarding the cation/anion movement on the LbL films, the RuNH-OH and RuCH-OH complexes showed proton-coupled electron transfer (PCET) reactions on the ITO electrode. We have measured the electrochemical quartz crystal microbalance (EQCM) measurements for the Ru complexes having PCET reaction immobilized on the ITO EQCM chip in aqueous solution. Upon the oxidation of RuNH-OH from the Ru(II) to Ru(III) state, the charge imbalance was cancelled out by the proton release/capture on the redox reactions of the protonated Ru(II)-NH/deprotonated Ru(III)-N. On the other hand, RuNMe-OH showed large frequency change for the charge compensation by the captured fo anions. Under the solid state films, the ITO|(RuNH-OH)<sub>n</sub> electrodes were hydrogen bonded with P4VP, therefore little anion movement may take place on the ITO|(RuNH-OH)<sub>n</sub> layer, but in the P4VP polymer layer the proton movement is induced by the hydrogen-bonded water molecules, so the hydroxide anions play an important role. The study on the cation/anion effects for the *I*-*V* plots will be planned, in addition to the effect of deuterium water.

50 (126:[135]135) **Philip Bartlett** asked: If you look at Fig. 9 in your paper (DOI: 10.1039/C8FD00098K) this describes a kind of battery in which protons move

1 from the redox film on one electrode, through the electrolyte, to the redox film on the other electrode. You could make the same thing, for example with a lithium ion battery, replacing the mobile protons with  $\text{Li}^+$ .

5 **Masa-aki Haga** replied: Thank you for your comment. In our previous paper,<sup>1</sup> we reported a proton-rocking-chair-type redox capacitor composed of ITO|(RuNH-OH)<sub>n</sub>/aqueous neutral NaClO<sub>4</sub>/(RuCH-OH)<sub>n</sub>|ITO as two sandwiched electrode devices. By modifying the NH group to the other Li ion trapping one, a new type of Li ion battery will be realized.

10 <sup>1</sup> K. Yoshikawa, D. Motoyama, Y. Hiruma, H. Ozawa, S. Nagano and M. Haga, *ACS Appl. Mater. Interfaces*, 2018, **10**, 26990–27000.

15 (127:[136]136) **Niloufar Raeishosseini** said: Because humidity is the main factor in the proton conduction mechanism, I wonder if the authors measured the device under different conditions or not? The authors mentioned “the strong dependence of the *I-V* plots on the humidity and acid treatment of the P4VP film indicates that the protonated state of P4VP plays an important role for proton conduction,” therefore, it is expected that they show the relevant graphs and electrical measurements by discussing the effect of humidity. The authors also mentioned that “in order to elucidate the humidity effect on RuNH-OH/P4VP and RuCH-OH/P4VP, the proton conductivity was measured by changing the humidity RH values.” However, it is not clear which graph is related to changing the RH values? In Fig. 5 of the paper (DOI: 10.1039/C8FD00098K), it is suggested to determine the oxidation and reduction peaks of the cyclic voltammetry measurement and discuss the electrochemical property to attract the readers’ attention. In Fig. 8 and 10 of the paper, the cycles of the *I-V* sweeps are shown. How many cycles does the device endure? Under which condition is the device measured? Are all of the electrical measurements under a humid condition? In Fig. 9 of the paper, is the measurement done under the humid condition and, if so, what is the percentage of humidity? Did the authors compare the differences in the *I-V* curves for the humid condition and non-humid environment?

35 **Masa-aki Haga** responded: Thank you for your important question. I have not discussed details about the relative humidity effects on our P4VP devices in this paper due to still on-going experiments with my collaborator, Prof. Yuki Nagao at JAIST. With his permission, I have showed the preliminary results for the relative humidity (RH) dependence of the proton conductivities of P4VP with different layer-structured films, such as sapphire|P4VP, sapphire|(RuNH-OH)<sub>3</sub>/P4VP, and sapphire|(RuNH-OH)<sub>3</sub>/P4VP-HCl for the protonated state of P4VP by the mixing of P4VP polymer with hydrochloric acid before spin-coating (Fig. 2), in which the proton conductivities increased dramatically upon the protonation on P4VP. Furthermore, the EIS measurements of the ITO|(RuNH-OH)<sub>3</sub>/P4VP/(RuCH-OH)<sub>3</sub>-|ITO devices have been performed under different RH conditions (Fig. 3). When the relative humidity (RH) increased from 40% to 90%, the semicircle on the EIS spectra became smaller, indicating the resistivity became smaller, thus the conductivity increased. We are still continuing the RH effect on the conductivity, which will be published in a subsequent paper, including the reproducibility. All the *I-V* measurements in the paper have been carried out at the ambient

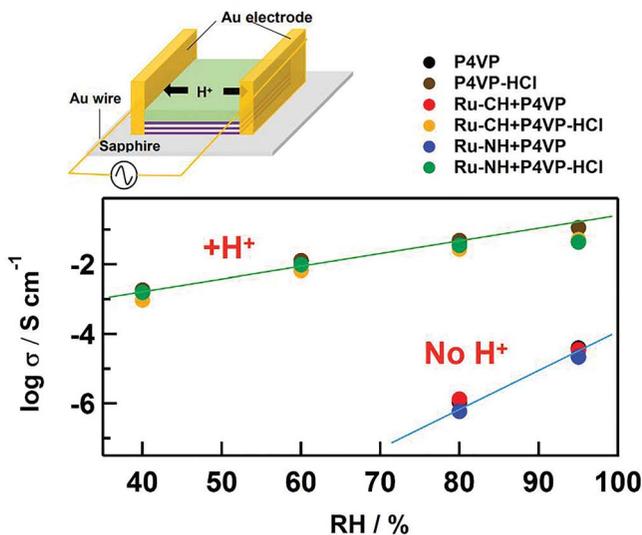


Fig. 2 Proton conductivities of P4VP with different layer-structured films on sapphire under different relative humidity (RH) environments. Protonated state of P4VP was prepared by the mixing of P4VP polymer methanol solution with hydrochloric acid.

condition at room temperature (RH  $\sim$  40 %). The  $I$ - $V$  sweeps were retained for about 40 cycles, after the cycles the hysteresis loops on the  $I$ - $V$  curves collapsed, leading to the non-linear  $I$ - $V$  curves. When the water vapor was blown to the

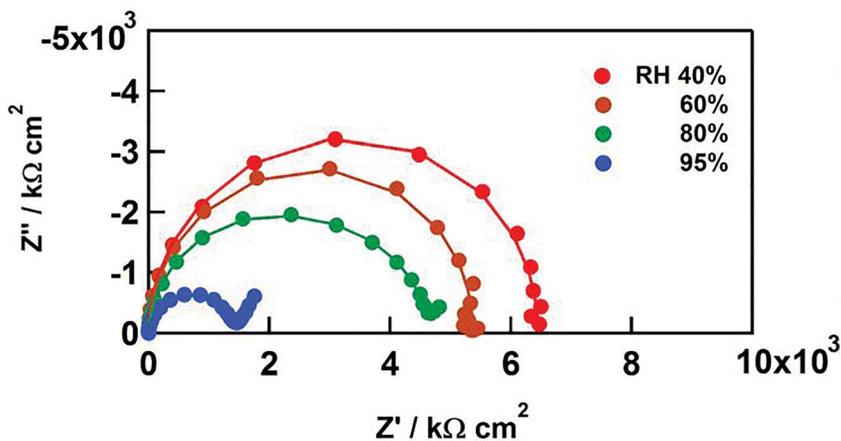


Fig. 3 Humidity (RH) dependence of the Nyquist plots for the ITO|(RuNH-OH)<sub>3</sub>/P4VP/(RuCH-OH)<sub>3</sub>|ITO device.

1 device, the increase of the current was observed. We need more quantitative  $I$ - $V$   
measurements under the controlled RH conditions in the near future.

5 (128:[137]137) **Sanne Berg** asked: You mentioned that you could maintain 50  
cycles for your devices, I was wondering if this is the stability limit and if  
breakdown of the device is observed after this point. If that is the case would you  
have suggestions on how to improve the stability and lifetime of your devices?

10 **Masa-aki Haga** answered: Regarding the device repeatability, the hysteresis  
loop became smaller on the  $I$ - $V$  plots after 50 cycles and finally only nonlinear  $I$ - $V$   
curve were obtained in the present devices. The present two-terminal device has  
not been sealed, so the device performance will be improved by the use of the  
sealant after clarifying the optimum humidity condition. In addition, the thick-  
15 ness of the sandwiched P4VP may be affected by the humidity and the proton-  
ation, which might influence the device stability.

20 (129:[138]138) **Daniele Ielmini** said: Is forming necessary to initiate switching  
in these devices or are they forming free?

**Masa-aki Haga** answered: No forming was applied for the fabrication. Two  
modified ITO electrodes were combined by pressing.

25 (135:[139]139) **Stanley Williams** remarked: You made a very interesting  
comment about the fact that your devices didn't require forming; neither did  
ours. It turns out that was a red herring. The molecules were actually reacting with  
the metals in the system. This actually gave us a great clue as to how to make  
forming free devices with oxides. You have to do some very intense control  
30 experiments with these molecular systems. Just the fact you have forming-free  
operation doesn't mean much. Chemical reactions between the molecules and  
electrodes may be important.

35 **Masa-aki Haga** responded: Chemical reactions or physisorption between the  
molecules and electrode surface induced the energy level alignment and the work-  
function change took place.<sup>1</sup> In particular, the surface modification of the ITO  
surface with phosphoric acid has been reviewed in the literature.<sup>2</sup> Therefore, the  
combination of the molecules bearing phosphoric acid with an ITO electrode is  
suitable for the forming-free devices for organic electronics.

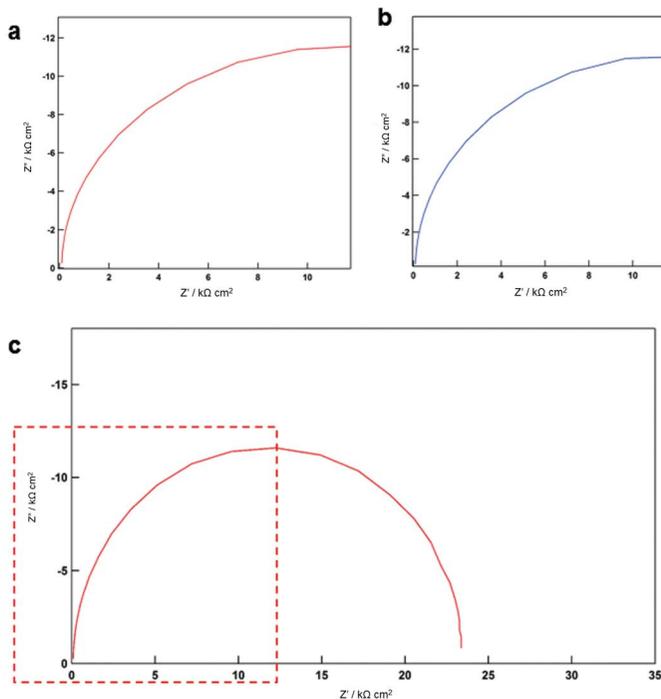
40 1 H. Ishii, K. Sugiyama, E. Ito and K. Seki, *Adv. Mater.*, 1999, **11**, 605–625.

2 S. A. Paniagua, A. J. Giordano, O. K. Smith, S. Barlow, H. Li, N. R. Armstrong, J. E. Pem-  
berton, J. L. Brédas, D. Ginger and S. R. Marder, *Chem. Rev.*, 2016, **116**, 7117–7158.

45 (139:[140]140) **Monica Santamaria** said: Fig. 10 of your paper (DOI: 10.1039/  
C8FD00098K) shows an impedance spectrum in the Nyquist representation  
(Fig. 10a) and the equivalent circuit you used to simulate the behaviour of the device  
(Fig. 10b). In the experimental section some details on how the spectra were  
recorded are missing. You stated in the experimental section that you employed an  
a.c. signal amplitude of 50 mV. This is usually a sinusoidal signal superimposed to  
50 a continuous signal. I have not referred to a reference as this was written by the

1 authors. Which was the latter? It is important to establish if such potential was lower  
or higher with respect to the switching potential. Further comments, the X and Y  
5 axes are in  $k\Omega$  not in  $k\Omega\text{cm}^2$ . Could you please normalize for the surface the real and  
imaginary components of the impedance in the spectrum? The magnitude of the  
employed constant phase elements and the corresponding best fitting exponents are  
not reported in the caption, therefore it is not possible to evaluate how physically  
reasonable the employed model is. Also, the reported spectrum looks like  
10 a depressed semicircle, thus it seems that only one time constant is enough to fit it.  
The authors should provide a zoom to show if other smaller semicircles are present.

**Masa-aki Haga** replied: For the impedance measurement, we employed the  
normal EIS measurement with a sinusoidal signal with an amplitude of 50 mV.  
15 The description in our paper (DOI: 10.1039/C8FD00098K) made you confused, so  
in the proof corrections we will delete several words; *i.e.* with respect to the  
reference. According to your comment, we will use a new y axis of  $k\Omega\text{cm}^2$  for  
Fig. 10 in our paper. Also, we will add the constant phase elements (CPE) fitting  
parameter in the caption of Fig. 10 of our paper. Also, I have provided the  
20 magnified version of the EIS spectra for your reference (Fig. 4).



50 Fig. 4 (a) Magnified raw data for the EIS spectra, (b) fitted data for the EIS spectra, and (c) raw data for the ESI spectra.

1 (142:[141]141) **Ella Gale** said: I can clearly see the bioinspiration in your work; however, what would a protonic coordination network or memristor offer technologically?

5 **Masa-aki Haga** responded: Although the present study was just a proof-of-concept for protonic molecular devices, my vision for the protonic coordination network or memristor devices is to fabricate large-area sensor devices at the environment-human interface to act as alternatives to the human five senses.

10 (143:[142]142) **Sayani Majumdar** said: I have a question about the switching time scales of the proton conducting devices. Have you measured the device switching response at different time scales? How fast can the device switch? In the humid environment, does the switching timescale change? A good control experiment to see if there is an effect of the molecule on the switching would be to look for the effect of the humidity on the switching times. Because, if there is no effect of the molecules, then humidity wouldn't affect the switching mechanisms.

20 **Masa-aki Haga** replied: Thank you for your question about the switching time. Our device is based on the surface molecular modified electrochemistry on ITO, so the switching time was controlled by the heterogeneous electron transfer rate between the Ru complexes and ITO electrode and the electron hopping within the LbL multilayer film.<sup>1</sup> Since the present device was composed of the molecular film and polymer films in the solid state, the response time became slower, however the switching timescale falls within a range of  $\sim 1$  ms for the positive bias and range of  $\sim 1$  s for the negative bias. I have shown the preliminary data for the current response under the pulse voltage (Fig. 5). We have not measured the

### Current on/off response upon the successive potential pulses

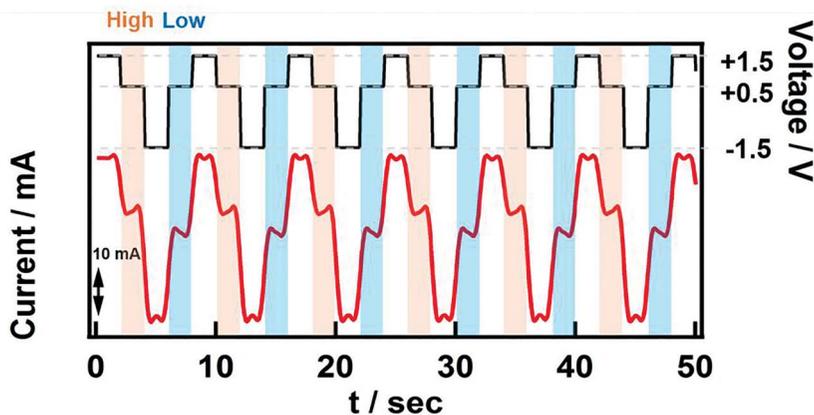


Fig. 5 Current on/off response upon the successive potential pulses.

1 switching time response upon the change of humidity, but further experiments  
are planned in the near future.

5 1 T. Nagashima, T. Suzuki, H. Ozawa, T. Nakabayashi, M. Oyama, T. Ishida and M. Haga,  
*Electrochim. Acta.*, 2016, **204**, 235–244.

## Conflicts of interest

10 There are no conflicts to declare.

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