



**Response to Comment on "Colossal Ionic  
Conductivity at Interfaces of Epitaxial ZrO<sub>2</sub>:Y<sub>2</sub>O<sub>3</sub>  
/SrTiO<sub>3</sub> Heterostructures"**

J. García-Barriocanal, *et al.*  
*Science* **324**, 465-b (2009);  
DOI: 10.1126/science.1169018

***The following resources related to this article are available online at  
www.sciencemag.org (this information is current as of June 17, 2009 ):***

**Updated information and services**, including high-resolution figures, can be found in the online version of this article at:

<http://www.sciencemag.org/cgi/content/full/324/5926/465-b>

A list of selected additional articles on the Science Web sites **related to this article** can be found at:

<http://www.sciencemag.org/cgi/content/full/324/5926/465-b#related-content>

This article **cites 4 articles**, 2 of which can be accessed for free:

<http://www.sciencemag.org/cgi/content/full/324/5926/465-b#otherarticles>

This article appears in the following **subject collections**:

Materials Science

[http://www.sciencemag.org/cgi/collection/mat\\_sci](http://www.sciencemag.org/cgi/collection/mat_sci)

Technical Comments

[http://www.sciencemag.org/cgi/collection/tech\\_comment](http://www.sciencemag.org/cgi/collection/tech_comment)

Information about obtaining **reprints** of this article or about obtaining **permission to reproduce this article** in whole or in part can be found at:

<http://www.sciencemag.org/about/permissions.dtl>

# Response to Comment on "Colossal Ionic Conductivity at Interfaces of Epitaxial $\text{ZrO}_2\text{:Y}_2\text{O}_3\text{/SrTiO}_3$ Heterostructures"

J. García-Barriocanal,<sup>1</sup> A. Rivera-Calzada,<sup>1</sup> M. Varela,<sup>2</sup> Z. Sefrioui,<sup>1</sup> E. Iborra,<sup>3</sup> C. Leon,<sup>1</sup> S. J. Pennycook,<sup>2</sup> J. Santamaría<sup>1\*</sup>

Guo suggests that the reported ionic conductivity of  $\text{ZrO}_2\text{:Y}_2\text{O}_3\text{/SrTiO}_3$  heterostructures might be due to the electronic conductivity from the  $\text{SrTiO}_3$ . We point out shortcomings in his reasoning and underscore that our results show that any electronic contribution to the conductance is at least three orders of magnitude lower than the ionic contribution determined by ac methods.

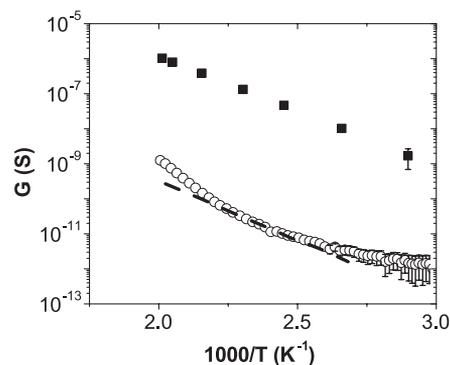
We recently reported strong enhancement of the ionic conductivity in  $\text{ZrO}_2\text{:Y}_2\text{O}_3\text{/SrTiO}_3$  (YSZ/STO) heterostructures with nanometer layer thickness grown on STO substrates (*1*). Guo (*2*) uses measurements of a bare commercial STO substrate to claim that our reported enhanced conductivity in the heterostructures "is most probably due to the p-type conductivity of STO." This possibility was already considered and ruled out by experimental evidence in our paper. Here, we rebut Guo's arguments and argue that neither the STO substrate nor the STO layers can account for the large ac conductance of our samples.

Guo (*2*) measured the conductivity of a commercial STO substrate annealed at 900°C in 3 mbar oxygen, obtaining the p-type conductivity and small electrode resistance characteristic of nominally undoped STO. As pointed out in his comment (*2*), the conductivity of commercial STO substrates is dominated by the electronic contribution. This is well known and was explicitly pointed out in our paper and the accompanying supporting online material (*1*). Our samples, as measured in the lateral geometry, are electrically the parallel association of the substrate and the heterostructure. The measured conductance is thus the sum of substrate and heterostructure contributions. As expected, the dc conductance of our samples measured using dc techniques is in fact very similar to that reported by Guo, which suggests that it is indeed due to the substrate. This is shown in Fig. 1, which is essentially our previous figure S2 in (*1*) but incorporates Guo's data for comparison. The slight differences (smaller activation energy) may simply be due to the different annealing conditions. First, the samples during growth are submerged into an energetic oxygen plasma, which certainly must contribute to their oxidation. Second, our

samples are grown at 3 mbar oxygen but are cooled down in 1 atmosphere oxygen pressure.

The large ac conductance of our samples, which is almost 4 orders of magnitude larger than the dc conductance (and absent in bare STO substrate data), must thus be due to the contribution of the heterostructure (in parallel). This contribution is in fact strongly blocked when frequency is lowered [see figure 2 in (*1*)] and does not amount to the dc conductance indicating its ionic origin. Most likely, this blocking occurs at grain boundaries and is especially strong due to the two-dimensional nature of the interface conduction process. In view of the strong blocking observed, there is no need for the Hebb-Wagner polarization experiment suggested by Guo (*2*), especially because, as stated in (*1*), conductivity measurements in air or nitrogen atmospheres showed similar results. The fact that Ag is not a completely blocking electrode for oxygen ions further strengthens our argument, because the electronic contribution from the STO substrate could be actually even lower than the dc conductance we measured in the dc polarization experiment.

Figure 2 in (*2*) indeed shows that the STO substrate fails to account for the large conductance



**Fig. 1.** Arrhenius plot of the dc conductance of the sample with a 1-nm-thick YSZ layer sandwiched between 10-nm STO layers obtained by dc (open circles) and ac (solid squares) measurements. The dashed line represents conductance data adapted to our geometry using conductivity values reported in (*2*).

measured in our heterostructures by almost 4 orders of magnitude. Unable to explain this large conductance of the heterostructures or its linear dependence on the number of interfaces (bilayers), Guo suggests that the 10-nm STO layers in the heterostructure might be responsible for the enhanced conductance, arguing that a conductivity enhancement has been observed previously in barium titanate (BTO) nanocrystalline samples. This conclusion, however, does not follow from Guo's measurements. First, the fact that BTO nanocrystalline samples show a conductivity enhancement does not mean that STO epitaxial thin films would show it also, as implied in (*2*). Guo even coauthored a paper (*3*) reporting a decrease of the (p-type) conductivity of epitaxial STO films when the thickness is reduced in the range of 3 microns to 250 nm. Second and most important, for the 10-nm-thick STO layers to account for the measured ac conductance of the heterostructures, its conductivity would have to be  $10^8$  times as high as the bulk STO (substrate) conductivity. This is clearly not the case, because it would also have been measured in the dc experiment. In addition, metallic behavior is expected for STO with such large conductivity values (*4*) as opposed to the measured semiconducting temperature dependence of the conductance in our samples. Moreover, figure S2 in (*1*) shows that the conductance of an YSZ substrate with a 10-nm-thick STO layer grown on top is the same as that of a plain YSZ substrate, thus demonstrating their negligible contribution to the measured ac conductance [see also the SOM discussion in (*1*)]. Therefore, contrary to what is claimed by Guo, electronic conductance of the STO layers can not account for the enhanced ac transport.

In summary, neither the experiment nor the arguments described in (*2*) relate the conductance of the STO substrate or the STO thin layers to the enhanced conductance of our YSZ/STO heterostructures. The conclusion of our original Report thus remains valid.

*Note added in proof:* Motivated by Gu's comment, we have measured STO substrates from two different suppliers (Crystal and Crystec) and found that one batch (34 out of 100 substrates) had substrates showing higher values of the conductivity than those shown by Guo, approaching values of the heterostructures at room temperature. The origin of this large conductivity is unknown. However, the conductivity dropped abruptly to the typical STO values (as reported by Guo and our dc experiment) when the temperature increased above 500 K. This should not affect our report because we conducted measurements cooling down after heating the sample above this temperature.

## References

1. J. García-Barriocanal *et al.*, *Science* **321**, 676 (2008).
2. X. Guo, *Science* **324**, 465 (2009); [www.sciencemag.org/cgi/content/full/324/5926/465a](http://www.sciencemag.org/cgi/content/full/324/5926/465a).
3. C. Ohly, S. Hoffmann-Eifert, X. Guo, J. Schubert, R. Waser, *J. Am. Ceram. Soc.* **89**, 2845 (2006).
4. O. N. Tufte, P. W. Chapman, *Phys. Rev.* **155**, 796 (1967).

5 December 2008; accepted 31 March 2009  
10.1126/science.1169018

<sup>1</sup>Grupo de Física de Materiales Complejos, Universidad Complutense de Madrid, Madrid 28040, Spain. <sup>2</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. <sup>3</sup>Escuela Técnica Superior de Ingenieros de Telecomunicaciones, Universidad Politécnica de Madrid, Madrid 28040, Spain.

\*To whom correspondence should be addressed. E-mail: [jacsan@fis.ucm.es](mailto:jacsan@fis.ucm.es)