Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Silicate conductive filaments assisted broadband light emission of HfO_2 high-k solid state incandescent devices

Yiwei Liu[a], Gang Niu[*b], Can Yang[a], Shengli Wu[*a], Liyan Dai[b], Haitao Wu[a], Jintao Zhang[a]

---

a Key Laboratory for Physical Electronics and Devices of the Ministry of Education, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an, 710049, China

b Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China

*Gang Niu: gangniu@xjtu.edu.cn

*Shengli Wu: slwu@xjtu.edu.cn

1. JV curve for ITO electrode device and silver paste electrode

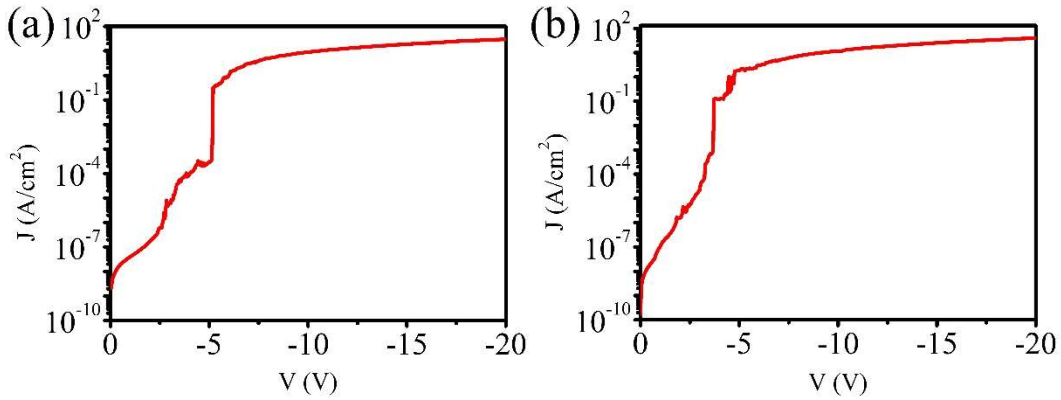

Figure S1 JV curve of (a) ITO electrode device, (b) silver paste electrode device

2. TEM and EDX line scan

Fig. S1 (a) shows the cross-sectional HRTEM views (bright-field) of Ti-embedded HfO_2 after RTA the thickness of the HfO_2-Ti-HfO_2 stack layer can be extracted as 9 nm. Fig.1 (b) shows the line scan from point A to point D of the energy dispersive X-ray spectrometry (EDXS) for the HfO_2-Ti-HfO_2 stack layer. It can be seen from Fig. S1 (a) that the layer with darker color (point B region) is related to the Ti-HfO_2 layer with a high Hf (with a higher atomic number) concentration (red curve in (b)), while the layer with brighter color correlates to the silicate layer (point C region) with a high Si (with a smaller atomic number) concentration (green curve in (b)). It can be noticed here that the Ti (black curve) has diffused into these two areas because of RTA procession thus the Ti-embedded layer cannot be observed in Fig. S1 (a).

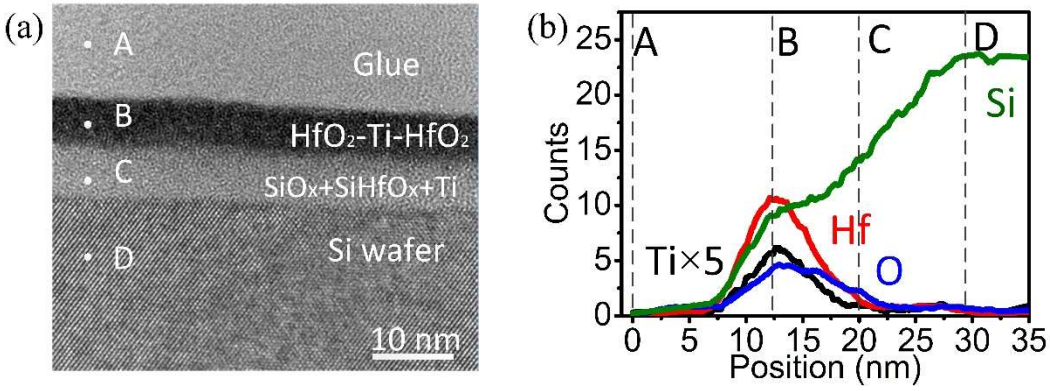

Figure S2 TEM image (a) and EDS line scan of Ti-embedded HfO_2 thin film after RTA

3. AFM and CAFM

The topography and current maps of HfO_2 thin film after stressed under -35 V are shown in Fig. S2 (a) and (b) respectively. After a careful searching on the large smooth surface of the HfO_2 surface, the pitted regions can be found. In Fig. S2(a), two black, rectangle regions with a size of ~900 nm×240 nm can be distinguished, corresponding to the deepest pits, the depth is ~7 nm extracted from the quantitative analysis. Fig. S2 (b) shows the current map of the same region shown in Fig. S2 (b). It is found that pits regions are conductive with a maximum current of approximately 12 nA and the conductive regions is exactly same as the pits shown in figure 5 (a). The other areas are insulating. After the dielectric hard breakdown, the current would only pass along these conductive paths which generate heat and emits light, quite similar as the current flow through the filaments.

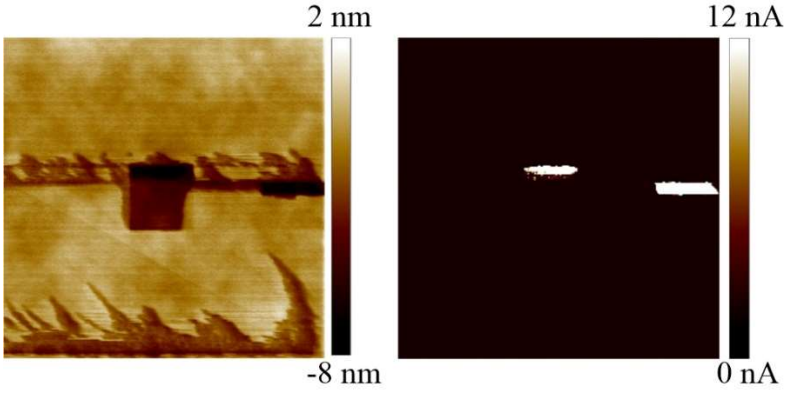

Figure S3 (a) Topography map and (b) current map of the surface of the HfO_2 thin film after hard breakdown;

4. First and second electrical measurement of devices

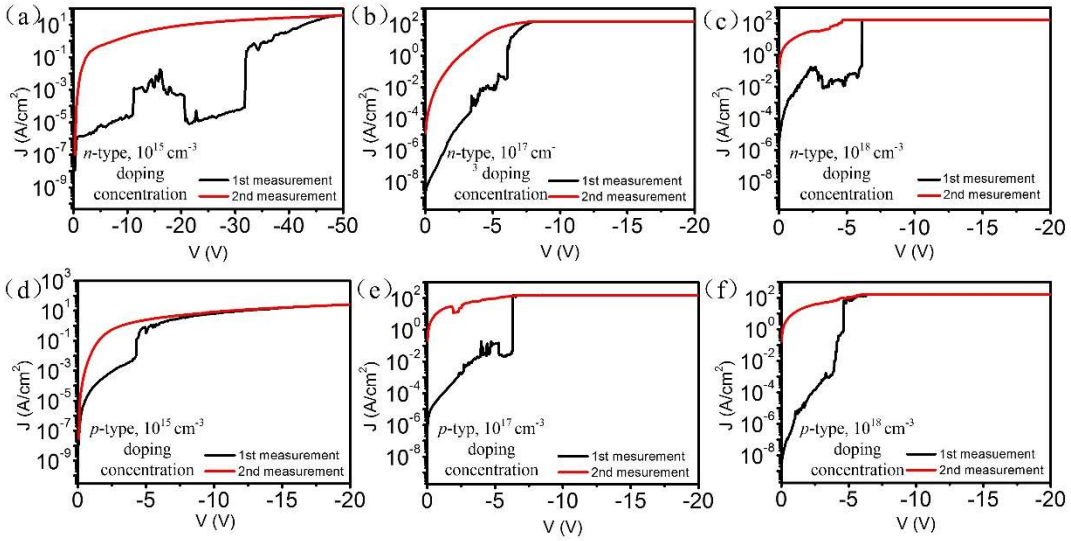

Figure S4 J-V curve for the devices fabricated on different substrates: *n*-type Si with (a)10^{15} cm^{-3}; (b) 10^{17} cm^{-3}; (c) 10^{18} cm^{-3} doping concentration; *p*-type Si with (d)10^{15} cm^{-3}; (e) 10^{17} cm^{-3}; (f) 10^{18} cm^{-3} doping concentration;

5. O 1s and Ti 2p XPS measurement of the Ti-HfO_2 thin film surface

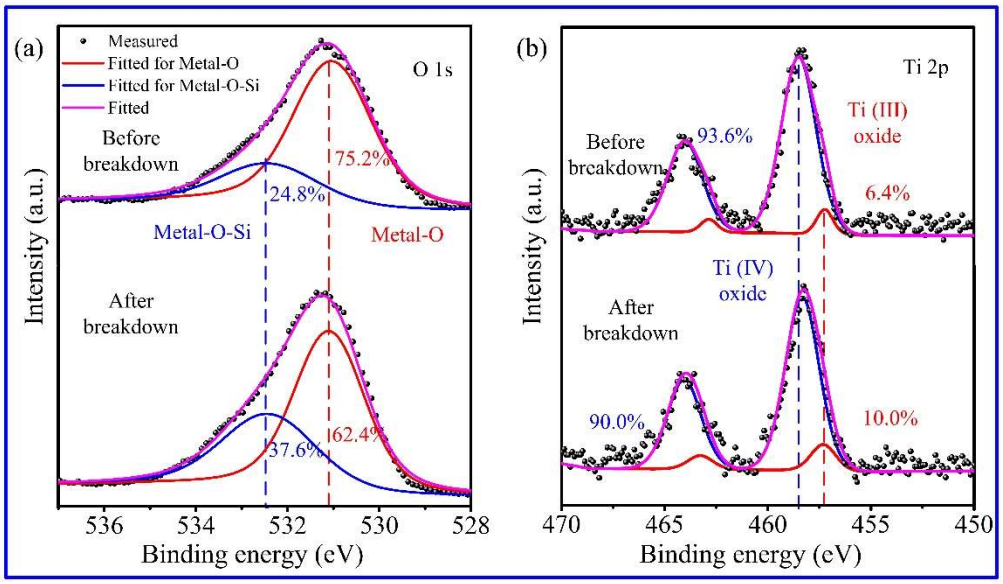

Figure S5 Deconvolutions of the spectra taken from HfO_2 thin film before and after breakdown, (a) O 1s (b) Ti 2p

In Fig. S5 (a), O 1s XPS spectra were fitted into two peaks. It should be noted here that the Metal-O-Si bonds observed from the sample before breakdown belong to the silicate located at interface between Si substrate and HfO_2, which was revealed by TEM in Fig. S2. One is located at 531.2 eV attributing to Metal-O bonds[1, 2] and the other located at 532.4 eV corresponding to Metal-O-Si bonds[1, 2]. As shown in Fig. S5 (b), the Ti 2p spectra consists Ti (VI)[3] located at 458.6 eV attributing to TiO_2 and Ti (III)[3] located at 457.1 eV corresponding to Ti_2O_3. The area ratio of Metal-O-Si increases from 24.8% to 37.6% and there is a slight augment of Ti (III) (from 6.4% to 10%). These results indicate the fact that the diffusion of Si ions into Ti-HfO_2 layer, which react with Ti-HfO_2 and cause the increase of Metal-O-Si. Numbers of O is got by Si ions thus lots of Ti (VI) being transformed into Ti (III) (reduction reaction).

Reference

1. D. Cao, X. Cheng, T. Jia, L. Zheng, D. Xu, Z. Wang, C. Xia and Y. Yu, *Nucl. Instrum. Meth. B*, 2013, **307**, 463-467.
2. R. Tan, Y. Azuma and I. Kojima, *Appl. Surf. Sci.*, 2005, **241**, 135-140.
3. M. C. Biesinger, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2010, **257**, 887-898.