ADVANCED
ELECTRONIC
MATERIALS

Supporting Information

for *Adv. Electron. Mater.*, DOI: 10.1002/aelm.201500286

Defining Switching Efficiency of Multilevel Resistive Memory with PdO as an Example

*K. D. M. Rao, Abhay A. Sagade, Robin John, T. Pradeep, and G. U. Kulkarni**

Supporting information

Defining switching efficiency of multi-level resistive memory with PdO as example

K. D. M. Rao[1], Abhay A. Sagade[1], Robin John[2], T. Pradeep[2], G. U. Kulkarni[3]†*

[1]Chemistry & Physics of Materials Unit and Thematic Unit of Excellence in Nanochemistry
Jawaharlal Nehru Centre for Advanced Scientific Research
Jakkur P.O., Bangalore 560 064 (India)
E-mail: kulkarni@jncasr.ac.in

[2]Department of Chemistry
Indian Institute of Technology Madras
Chennai - 600 036, INDIA

[3]Centre for Nano and Soft Matter Sciences
Prof. U. R. Rao Road, Jalahalli
Bangalore 560 013, INDIA
Email: guk@cnsms.res.in

†On lien from JNCASR, Bangalore

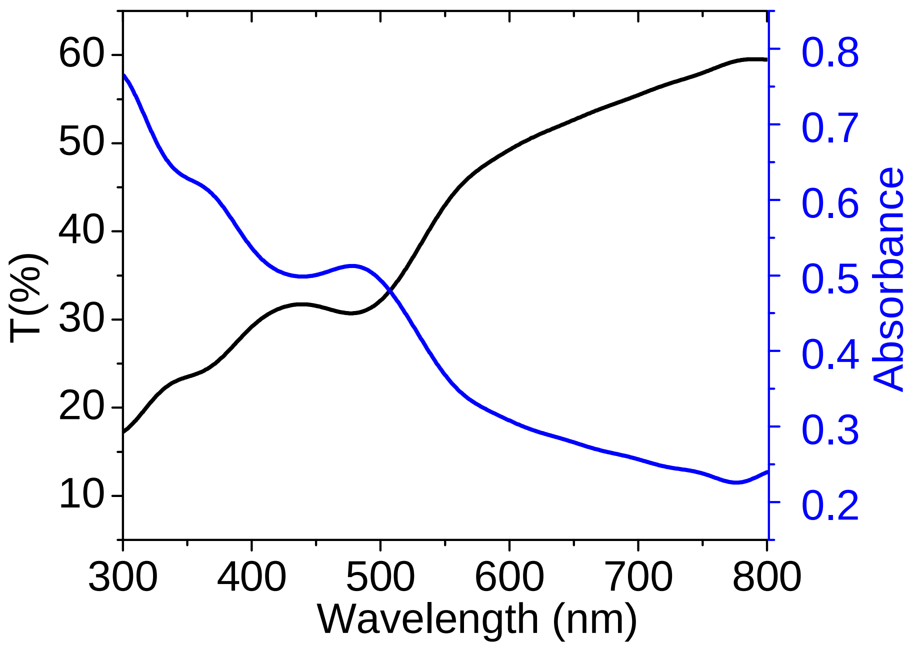

Figure S1: Transmittance and absorbance spectra of PdO thin film**.**

As shown in Figure S1, there is a small peak (450-550 nm) in the absorption /transmittance of the PdO thin film, which is not prominent. In case of nanocrystalline metal oxide thin films, such weak features are common (see for example, Journal of Applied Physics, **1999**, *85*, 7885). Importantly, such peaks have been used to estimate approximate bandgap.

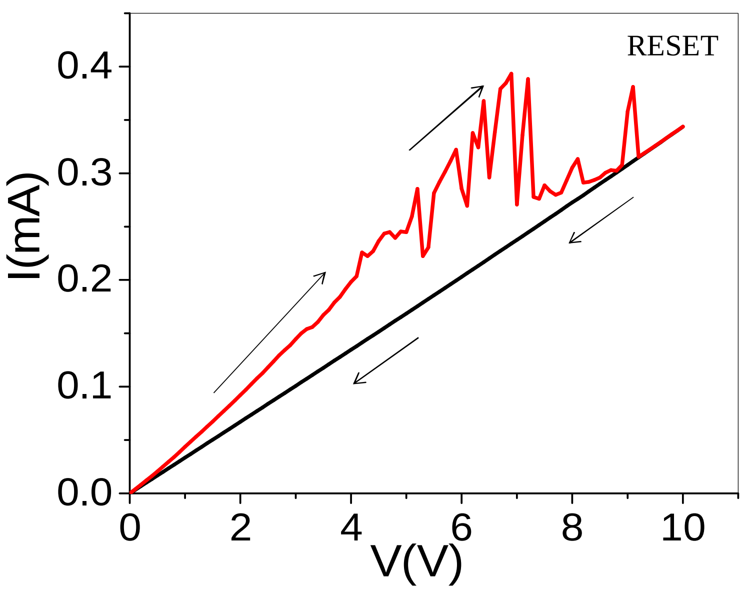

Figure S2: I-V characteristics of a PdO resistive switching device during the forming step, 0 to 10 V (red curve) and retrace, 10 to 0 V (black).

After forming process, in order to find the resistance state of the device, back sweeping of voltage was performed with a new device and the data is now added to the supporting information (Figure S3). After the reset process (0 to 10 V), as the voltage was retraced from 10 to 0 V, the current followed a linear behaviour as shown in Figure S3.

Note-1: Following is the sequence of voltage sweep/cycles employed in Figure 2c.

S.No.	Process	Voltage sweep/cycle employed	Colour of the curve	Memory state achieved
1.	RESET	0 to 8 V	Red	1
2.	SET	0 to 5 to 0 V	Red	0
3.	RESET	0 to 10 V	Green	2
4.	SET	0 to 5 to 0 V	Green	0
5.	RESET	0 to 12 V	Blue	3
6.	SET	0 to 5 to 0 V	Blue	0
7.	RESET	0 to 15 V	Brown	4
8.	SET	0 to 5 to 0 V	Brown	0

Note: Reading of the memory states was carried out with 0-1 V sweeps.

Note-2: Interstate switching has been carried out using voltage pulses; The following table provides details about the pulse width and amplitude.

S.No.	Process	Applied voltage pulse (V)	Voltage pulse width (ms)	Memory state
1.	SET	5	20	0
2.	RESET	8, 10, 12, 15	20	1, 2, 3, 4
3.	READ	0.01	20 (Each SET/RESET read ten times)	-

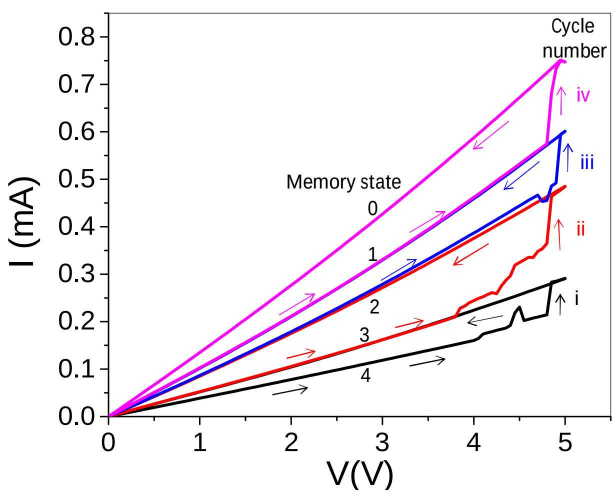

Figure S3: Consecutive voltage cycling from 0 to 5 to 0 V of a PdO device.

Initially, the device was RESET with a 0-15 V sweep and this high resistance state is marked as ‘4’ in the Figure S3. When a 0-5 V was performed on this state, a linear behaviour was observed (black curve) up to 4.8 V, beyond which (around 5 V), the current jumped and on completing the cycle (5–0 V), the current followed a linear curve in a lower resistance state termed ‘3’. Three more such loops could be obtained by sweeping the voltage in 0 to 5 to 0 V cycles where the currents in the linear regions were found overlapping. Likewise, it was possible to switch the resistance state totally four times. The voltage sweep for the fifth and the following cycles did not produce new states and the device was retained at ‘0’ state only. In short, the data clearly demonstrates interstate switching possibility with DC voltage cycles, although all switching events could not be realized even with higher voltage scan rates. More facile interstate switching was possible only with voltage pulsing (as is common with devices reported in literature), which forms the data in Figure 3a.

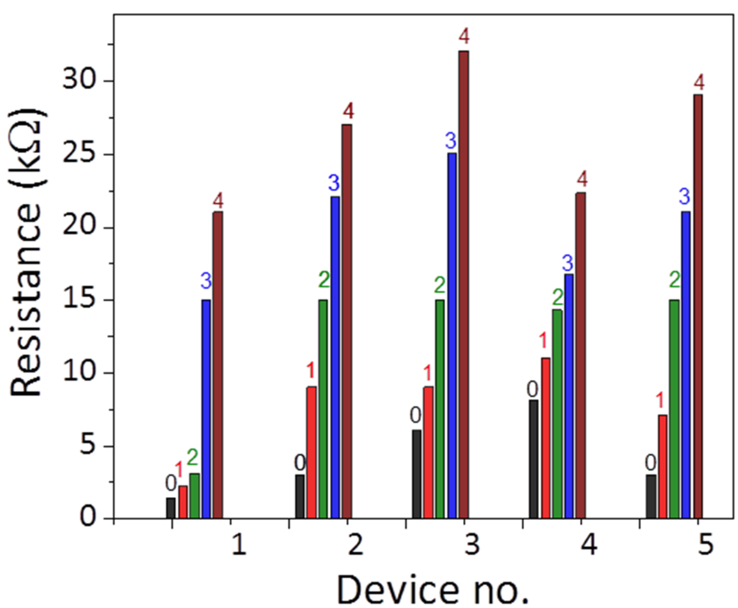

Figure S4: Multiple memory states and corresponding resistance of five devices.

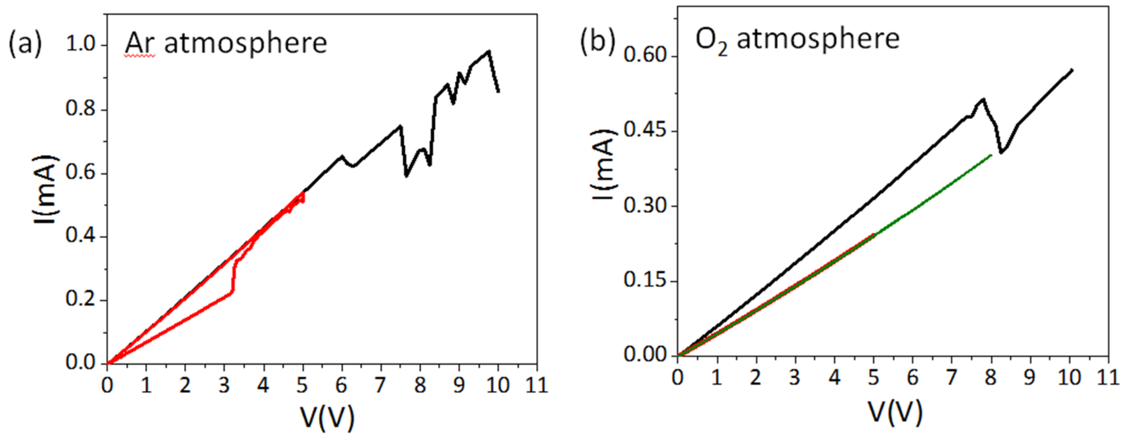

Figure S5: The RS of PdO MMS device in (a) Ar and, (b) O_2 atmospheres respectively.

In order to understand the RS mechanism, the switching was tried in different atmospheres such as Ar and oxygen (see Fig. S5). The device exhibited RS in Ar atmosphere as shown in Fig. S5a, however the after two cycles device did not switch. This indicates inert atmosphere is not favourable for switching. More interestingly, the device showed lower reset voltages (8V) with a clear jump towards high resistance state (HRS) in oxygen atmosphere as shown in Fig. S5b. Further, device did not switch back to LRS from HRS state even at higher voltages. It is clear that the device requires oxygen for reset process (LRS to HRS) whereas more oxygen is not favouring set process (HRS to LRS). Hence, PdO MRS device does exhibit switching only in presence of small amount of oxygen such as ambient conditions, which is more suitable for practical applications.

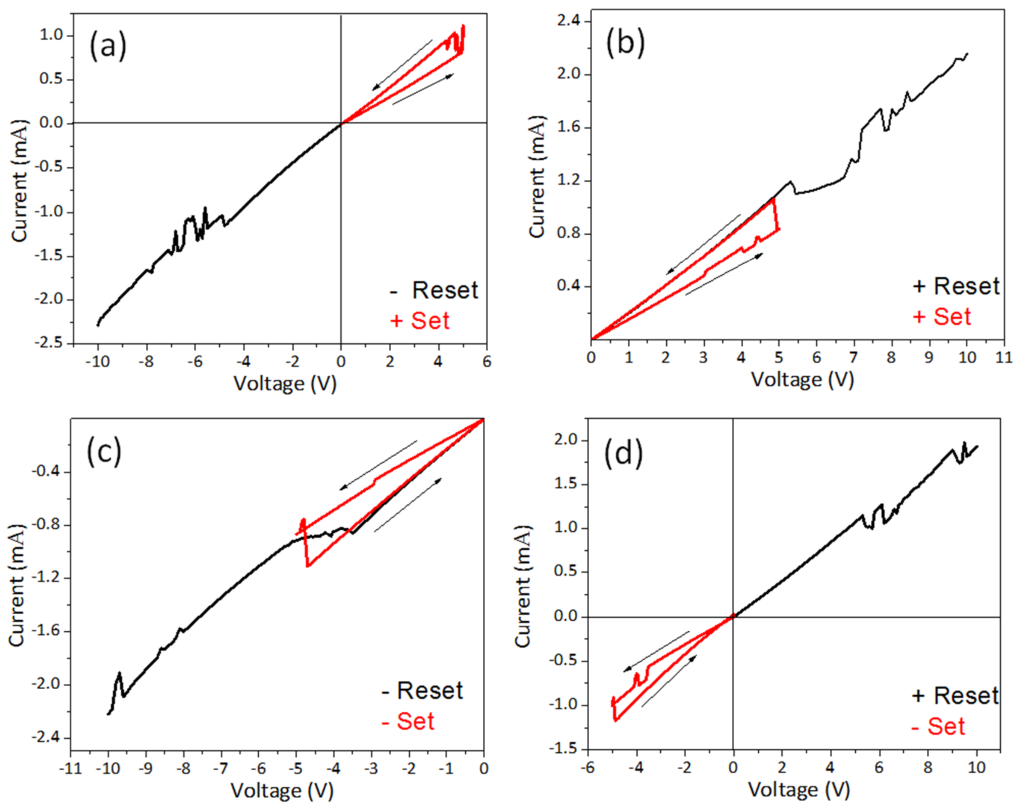

Figure S6: Non-polar resistive switching characteristics of PdO MMS device. The Reset and Set process performed at (a) negative-positive, (b) positive-positive, (c) negative-negative and (d) positive-negative bias polarities, respectively.

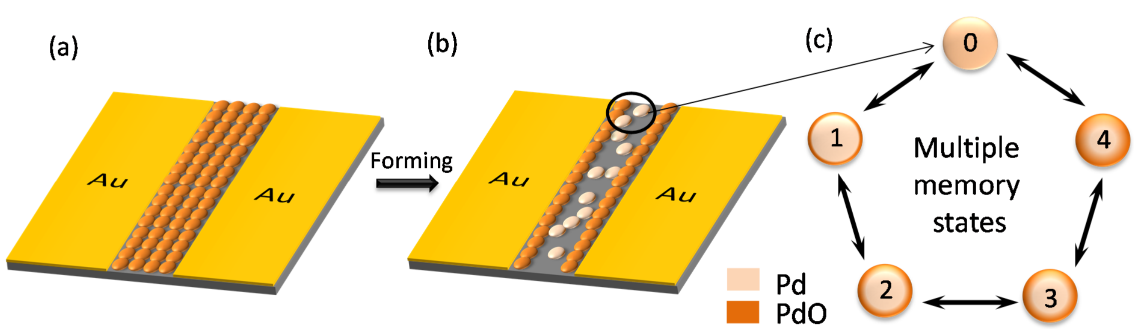

Figure S7: Resistive switching mechanism of PdO thin films (a) pristine, (b) after forming and (c) during RESET and SET process.

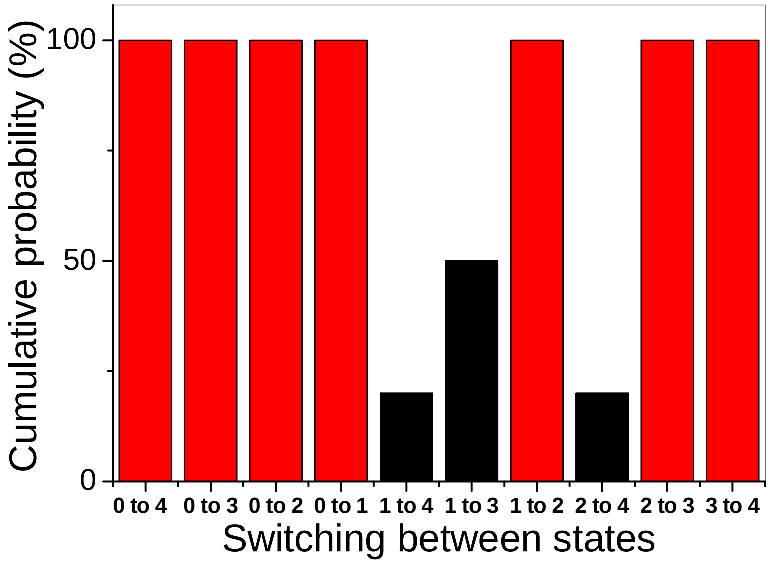

Figure S8: Cumulative probability of switching between the states, each probability is calculated over 20 events, in which 10 events are switching from n_1 to n_2 and other 10 events are switching from n_2 to n_1.

Table S1: Summary of the resistive switching devices made in this study

Device no.	**Resistance (kΩ)**	
	Low resistance state (LRS)	**High resistance state (HRS)**
1	1.4	2.2
2	8.1	11
3	3	9
4	6	9
5	9	13.3
6	7.1	4.2
7	11	25.1
8	2.1	3.5
9	9	12
10	6.1	9.3
11	3	7

Table S2: Comparative study of multi-level resistive switching devices reported in the literature

S.No.	Device Structure	Device geometry	On/Off ratio	Retention time for all states (s) and reading voltage (V)	Conduction in		No. of states	Temperature dependent resistivity for all states	Multiplex number (M)	Ref.
					On state	Off state				
1.	Ti/ZrO_2 /n^+-Si	Out of plane	10^4	-	Ohmic	Non-ohmic	3	yes	3.66	1
2.	Al/CNT/Al	Out of plane	10^2	10^5 and -1	Ohmic	Non-ohmic	3	no	3.66	2
3.	Cu/TaO_x/ Pt	Out of plane	10^4	-	Ohmic	Non-ohmic	3	yes	4	3
4.	ITO /AlQ_3 /Al_2O_3 /AlQ_3 /Al	Out of plane	10^4	10^3 and 1	Non-ohmic	Non-ohmic	3	no	3.66	4
5.	Au/SiO_2/Au	Out of plane	10^4	-	Ohmic	Non-ohmic	3	no	3.5	5
6.	ITO/MEH-PPV/Al	Out of plane	10^5	-	-	-	3	no	3.5	6
7.	Ag/PI/grapheneoxide:PI/PI /ITO	Out of plane	10^5	10^5 and 1			3	no	3.5	7
8.	Au /$Na_{0.5}Bi_{0.5}TiO_3$ /FTO	Out of plane	10		Non-ohmic	Non-ohmic	3	no	3.33	8
9.	Cu/HfO_2/Cu /Pt	Out of plane	10^7	10^5 and 0.1	Ohmic	Non-ohmic	4	yes	4.5	9
10.	$SrRuO_3$/$Ba_{0.7}Sr_{0.3}TiO_3$ /Pt	Out of plane	4	-	Non-ohmic	Non-ohmic	4	no	4.66	10
11.	ITO/PEDOT /organic/Al	Out of plane	10^3	10^6 and 1	Ohmic	Non-ohmic	4	yes	4.16	11
12.	Ag/organic/ITO	Out of plane	10^2	-	Non-ohmic	Non-ohmic	4	no	4.5	12
13.	Al/Alq_3/NiO /Al	Out of plane	10^3	10^5 and ~ 5	Non-ohmic	Non-ohmic	4	no	4.5	13
14.	Ag/Nb-doped $SrTiO_3$/Ti	Out of plane	10^4	-	Non-ohmic	Non-ohmic	4	no	4.41	14
15.	Ag/SiO_2/Pt	Out of plane	10^6	10^3 and 0.05	Non-ohmic	Non-ohmic	4	no	4.5	15
16.	Ti/ZrO_2/Pt	Out of plane	10^3		Ohmic	Non-ohmic	4	yes	4.41	16
17.	TiW/SiN/ $Ge_2Sb_2Te_5$ /TiW	Out of plane	10^3	10^5 and 0.2	-	-	4	no	4.83	17
18.	Si/SiO_x/ITO	Out of plane	10^6		Non-ohmic	Non-ohmic	4	no	4.41	18
19.	Au /$La_{0.7}Sr_{0.3}MnO_3$ /Au	In plane	10^2	10^3 and ~15	Non-ohmic	Non-ohmic	4	no	4.66	19

20.	Pt/PA-TsOH /Pt	Out of plane	10^4	10^2 and -0.5	Ohmic	Non-ohmic	4	no	4.5	20
21.	Pt/Cr_2O_3/TiN	Out of plane	10^2	-	Ohmic	Non-ohmic	4	no	4.5	21
22.	Cu /GeTe/W	Out of plane	2		Ohmic	Non-ohmic	4	no	4.66	22
23.	TiN/HfO_x /AlO_x/ Pt	Out of plane	10^2		Ohmic	Non-ohmic	4	no	4.25	23
24.	Au/$C_{10}H_{12}O_2$ /STM tip	Out of plane	10	10^3 and 0.2	Non-ohmic	Non-ohmic	4	no	4.25	24
25.	Pt/TiO_2/SiO_2/ Si/ SGO/Pt	Out of plane	10^2	10^3 and 0.1	Ohmic	Ohmic	4	yes	4.5	25
26.	Graphene/SiO_2	In plane	10^4	10^4 and 1	Ohmic	Non-ohmic	5	no	5.6	26
27.	Ti/Cu_xO/Pt	Out of plane	10^4	10^2 and 0.2	Ohmic	Non-ohmic	5	no	5.4	27
28.	Pt/TiO_2 /TiN	Out of plane	10^3	0.5 and 10	Non-ohmic	Non-ohmic	5	no	5.5	28
29.	Ti/AlOx/TiN	Out of plane	10	10^5 and 0.1	Non-ohmic	Non-ohmic	5	no	5.25	29
30.	Al/Fe_2O_3/Al	Out of plane	10^2	-	-	-	5		5.35	30
31.	Pt/NiO	Out of plane	10^5	--, 0.5	---	---	5	yes	5.4	31
32.	Cu/Cu_2S/Au	Out of plane	10^4	--, 0.5	---	---	5	no	---	32.
33.	Au/PdO/Au	In plane	10	10^3 and 0.01	Ohmic	Ohmic	5	yes	5.7	Present work

1. L. Ming, Z. Abid, W. Wei, H. Xiaoli, L. Qi and G. Weihua, *Applied Physics Letters*, 2009, **94**, 233106.

2. S. K. Hwang, J. M. Lee, S. Kim, J. S. Park, H. I. Park, C. W. Ahn, K. J. Lee, T. Lee and S. O. Kim, *Nano Letters,* 2012, **12**, 2217-2221.

3. Yang, Y. C.; Chen, C.; Zeng, F.; Pan, F. *Journal of Applied Physics* **2010,** 107, 093701.

4. V. S. Reddy, S. Karak and A. Dhar, *Applied Physics Letters*, 2009, **94**, 173304.

5. Y. Guanwen, C. Hsiang-Yu, M. Liping, S. Yue and Y. Yang, *Applied Physics Letters*, 2009, **95**, 203506.
6. M. Lauters, B. McCarthy, D. Sarid and G. E. Jabbour, *Applied Physics Letters*, 2006, **89**, 013507.
7. W. Chaoxing, L. Fushan, Z. Yongai, G. Tailiang and C. Ting, *Applied Physics Letters*, 2011, **99**, 042108.
8. T. Zhang, X. Zhang, L. Ding and W. Zhang, *Nanoscale Research Letters*, 2009, **4**, 1309-1314.
9. W. Yan, L. Qi, L. Shibing, W. Wei, W. Qin, Z. Manhong, Z. Sen, L. Yingtao, Z. Qingyun, Y. Jianhong and L. Ming, *Nanotechnology*, 2010, **21**, 045202.
10. R. Oligschlaeger, R. Waser, R. Meyer, S. Karthauser and R. Dittmann, *Applied Physics Letters*, 2006, **88**, 042901.
11. M. Colle, M. Buchel and D. M. de Leeuw, *Organic Electronics*, 2006, **7**, 305-312.
12. C. Jiangshan, X. Liling, L. Jian, G. Yanhou, W. Lixiang and M. Dongge, *Semiconductor Science and Technology*, 2006, **21**, 1121.
13. J. G. Park, W. S. Nam, S. H. Seo, Y. G. Kim, Y. H. Oh, G. S. Lee and U. G. Paik, *Nano Letters*, 2009, **9**, 1713-1719.
14. Y. Zhang, J. X. Shen, S. L. Wang, W. Shen, C. Cui, P. G. Li, B. Y. Chen and W. H. Tang, *Applied Physics A*, **109**, 219-222.
15. L. Lifeng, G. Bin, C. Bing, Y. Chen, W. Yi, K. Jinfeng and H. Ruqi, in *Solid-State and Integrated Circuit Technology (ICSICT), 2010 10th IEEE International Conference on*, pp. 1157-1159.
16. W. Ming-Chi, J. Wen-Yueh, L. Chen-Hsi and T. Tseung-Yuen, *Semiconductor Science and Technology*, 2012, **27**, 065010.
17. G. Ashvini and Y. Yee-Chia, *Journal of Applied Physics*, 2012, **112**, 104504.
18. M. Adnan, C. Sebastien, W. Maciej, H. Stephen, L. Christophe, R. Richard and J. K. Anthony, *Nanotechnology*, 2012, **23**, 455201.
19. H. K. Lau and C. W. Leung, *Journal of Applied Physics*, 2008, **104**, 123705.
20. B. Hu, X. Zhu, X. Chen, L. Pan, S. Peng, Y. Wu, J. Shang, G. Liu, Q. Yan and R. W. Li, *Journal of the American Chemical Society*, 2012, **134**, 17408-17411.
21. S. C. Chen, T. C. Chang, S. Y. Chen, H. W. Li, Y. T. Tsai, C. W. Chen, S. M. Sze, F. S. Yeh and Y. H. Tai, *Electrochemical and Solid-State Letters*, 2010, **14**, H103-H106.

22. S. J. Choi, G. S. Park, K. H. Kim, S. Cho, W. Y. Yang, X. S. Li, J. H. Moon, K. J. Lee and K. Kim, *Advanced Materials*, 2011, **23**, 3272-3277.
23. Y. Shimeng, W. Yi and H. S. P. Wong, *Applied Physics Letters*, 2011, **98**, 103514.
24. B. Anirban, K. Miki and Y. Wakayama, *Applied Physics Letters*, 2006, **89**, 243506.
25. Y. Sharma, P. Misra, S. P. Pavunny and R. S. Katiyar, *Applied Physics Letters*, 2014, **104**, 073501.
26. C. He, Z. Shi, L. Zhang, W. Yang, R. Yang, D. Shi and G. Zhang, *ACS Nano*, 2012, **6**, 4214-4221.
27. W. Sheng-Yu, H. Chin-Wen, L. Dai-Ying, T. Tseung-Yuen and C. Ting-Chang, *Journal of Applied Physics*, 2010, **108**, 114110.
28. Y. Chikako, T. Kohji, N. Hideyuki and S. Yoshihiro, *Applied Physics Letters*, 2007, **91**, 223510.
29. W. Yi, Y. Shimeng, H. S. P. Wong, C. Yu-Sheng, L. Heng-Yuan, W. Sum-Min, G. Pei-Yi, F. Chen and T. Ming-Jinn, in *Memory Workshop (IMW), 2012 4th IEEE International*, pp. 1-4.
30. Y. Jae Woo, H. Quanli, B. Yoon-Jae, C. Young Jin, K. Chi Jung, L. Hyun Ho, L. Do-Joong, K. Hyun-Mi, K. Ki-Bum and Y. Tae-Sik, *Journal of Physics D: Applied Physics*, 2012, **45**, 225304.
31. Y. C. Huang, P. Y. Chen, K. F. Huang, T. C. Chuang, H. H. Lin, T. S. Chin, R. S. Liu, Y. W. Lan, C. D. Chen and C. H. Lai, *NPG Asia Mater*, 2013, **6**, e85.