SAND2014-15536PE

New materials for memristive switching

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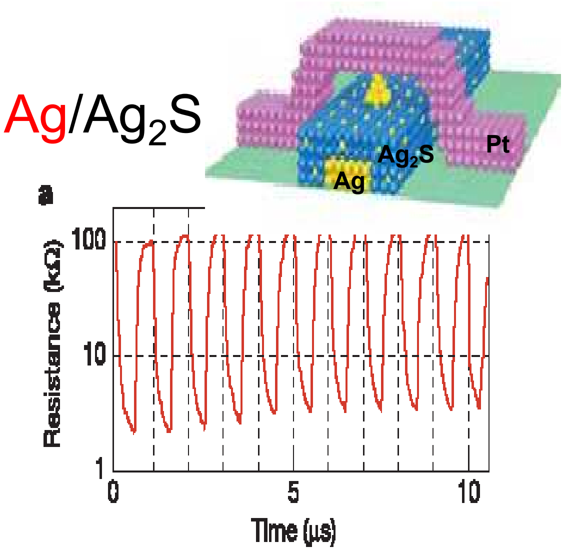
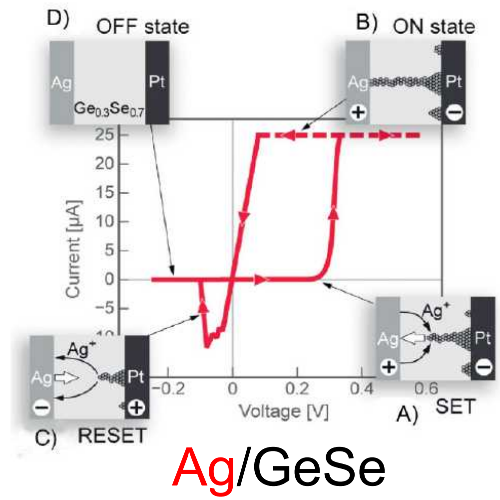
Outline

1. **Introduction: new switching materials**
2. **Non-oxide switching materials**
3. **Metal doped Switching Materials**
4. **Summary**

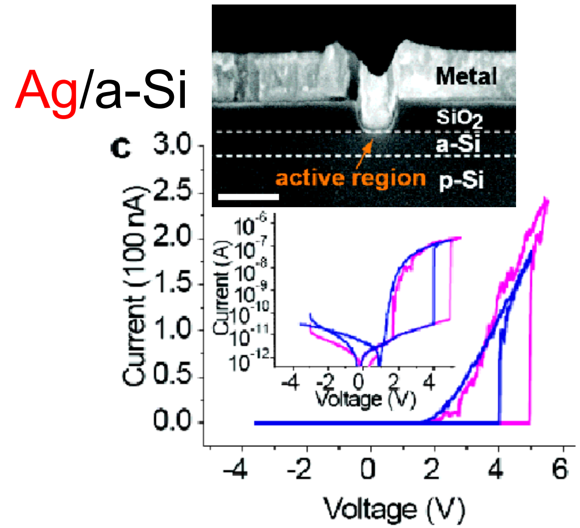
Introduction – ionic switching materials



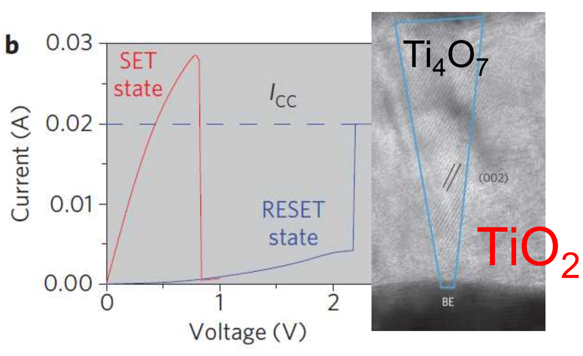
Terabe *et al*. Nature 433,47 (2005)



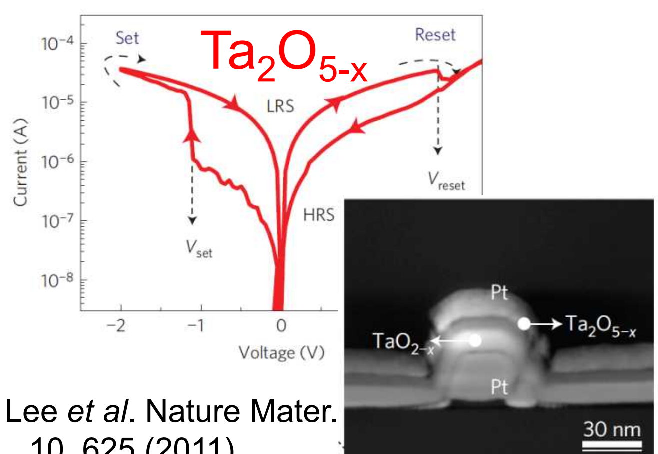
Waser *et al*. Adv. Mat. 21, 2632 (2009)



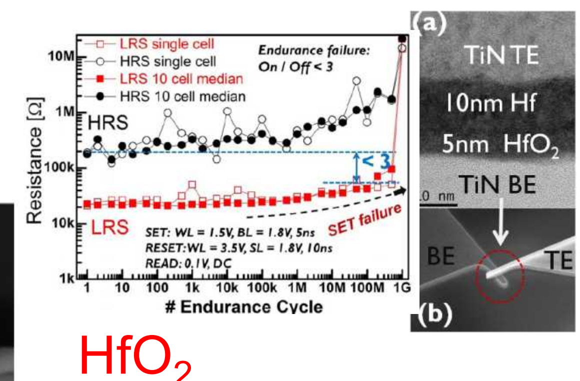
Jo & Lu, Nano Lett. 8, 392 (2008)



Kwon *et al*. Nature Nanotechnol. 5, 148 (2010)



Lee *et al*. Nature Mater. 10, 625 (2011)



Chen *et al*. '2012 IEDM

Summary of Anion based switching materials – valence change switching

Insulators	Bottom Electrode	Top electrode	Switching mode	reference
MgO	Pt	Pt	Unipolar	1
TiOx	Ru, Pt	Al, Pt	Non/Uni/Bipolar	2, 3
ZrO_x	P^+-Si , n^+-Si	Pt, Cr	Uni/Bipolar	4-6
HfO_x	TiN	TiN	Bipolar	7
VO_x	N/A	N/A	Threshold	8, 9
NbO_x	P^+-Si	Pt	Unipolar	10
TaO_x	Pt, Ta	Pt, Ta	Bipolar	11, 12
CrO_x	TiN	Pt	Bipolar	13
MoO_x	Pt	Pt-Ir	Uni/Bipolar	14
WO_x	W, FTO	TiN, Au	Bipolar	15, 16
MnO_x	Pt	Al, TiN	Bipolar	17, 18
FeO_x	Pt	Pt	Non/Bipolar	19, 20
CoO_x	Pt	Pt	Nonpolar	21
NiO_x	Pt	Pt	Nonpolar/Threshold	22, 23
CuO_x	TiN, TaN, SRO, Pt	Pt	Bipolar	24
ZnO_x	Pt, Au	TiN, Ag	Bipolar	25-27
AlO_x	Ru, Pt	Pt, Ti	Unipolar/Bipolar	28, 29
GaO_x	ITO	Pt, Ti	Bipolar	30
SiO_x	Poly-Si, TiW	Poly-Si, TiW	Unipolar	31
SiO_xN_y	W	Cu	Bipolar	32
GeO_x	ITO, TaN	Pt, Ni	Bipolar	33, 34
SnO_2	Pt	Pt	Unipolar	35
BiO_x	Bi	W, Re, Ag, Cu	Bipolar	36
SbO_x	Pt	Sb	Unipolar/Bipolar	37
SmO_x	TiN	Pt	Bipolar	38
GdO_x	Pt	Pt	Unipolar	39
YO_x	Al	Al	Unipolar	40
CeO_x	Pt	Al	Bipolar	41
EuO_x	TaN	Ru	Uni/Bipolar	42, 43
PrO_x	TaN	Ru	Bipolar	42, 43
ErO_x	TaN	Ru	Unipolar	42, 43
DyO_x	TaN	Ru	Unipolar	42, 43
NdO_x	TaN	Ru	Unipolar	42, 43
$Ba_{0.7}Sr_{0.3}TiO_3$	$SrRuO_3$	Pt, W	Bipolar	44
$SrTiO_3$	$SrRuO_3$, Au, Pt	Au, Pt	Bipolar	45
$SrZrO_3$	$SrRuO_3$	Au	Bipolar	46
$BiFeO_3$	$LaNiO_3$	Pt	Bipolar	47
$Pr_{0.7}Ca_{0.3}MnO_3$	YBCO, Pt, $LaAlO_3$	Ag	Bipolar	48
$La_{0.33}Sr_{0.67}FeO_3$	Au	Al	Bipolar	49
$Pr_yLa_{0.625-y}Ca_{0.375}MnO_3$	Ag	Ag	Bipolar	50
Nitrides (AlN)	Al, TiN, Pt	Al, TiN, Pt	Bipolar	51
Telluride (ZnTe)	Si	Au	Bipolar	52
selenide (ZnSe)	P^+-Ge	In, In-Zn	Bipolar	53
Polymers	Al, ITO, Cu	Al, ITO, Cu	Bipolar	54, 55

Most are oxides

Very few non-oxides

Even though non-oxide materials: 1) bigger pool
2) may even have better performance

J. Joshua Yang et al., Nature Nanotechnology **8,** 13 (2013)

New materials

May provide

1)Better compatibility with industry electrode materials[1]

2) Better control of conduction filament formation.[2]

[1] **B. J. Choi** et al. *Appl. Phys. A*, **109**, 1 (2012)
[2] **B. J. Choi** et al. *Nano Lett*. **13**, 3213 (2013)

Outline

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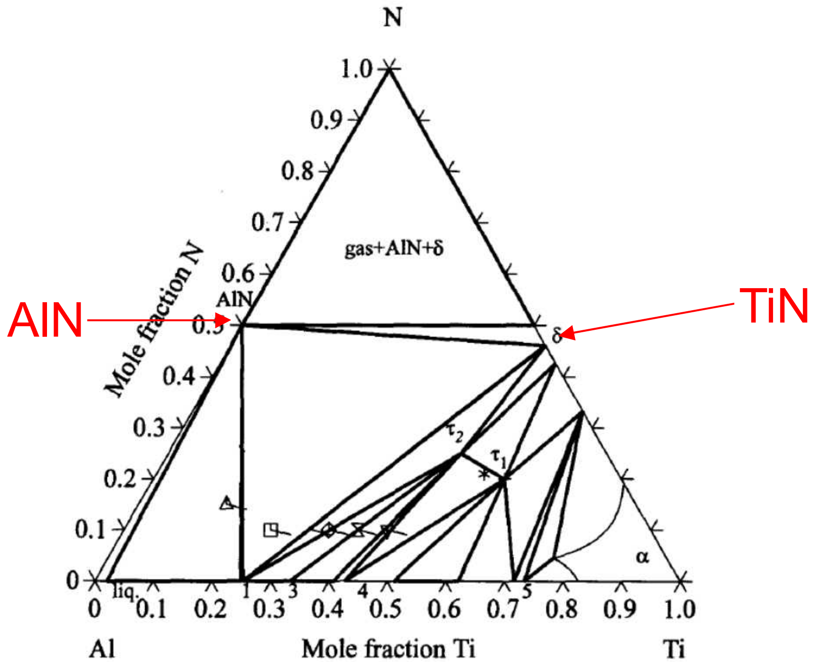
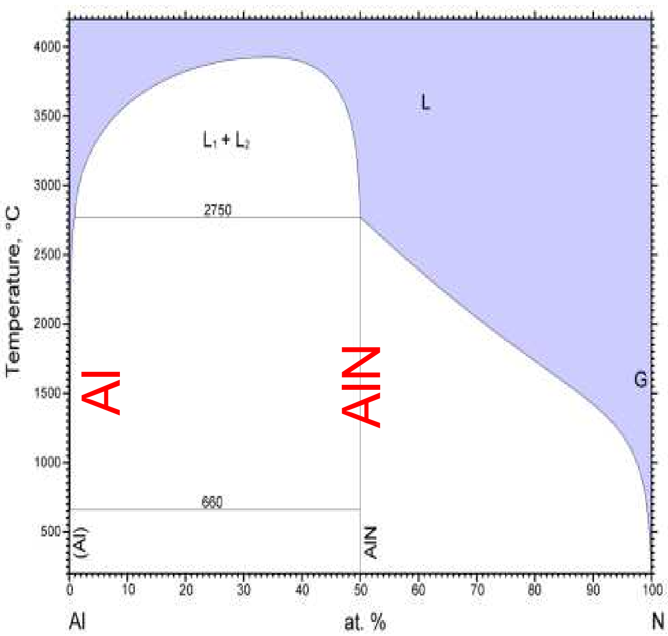
MOTIVATIONS: A Full - Nitride Memristor





TiN/AlN structure

1) TiN: fab preferred material

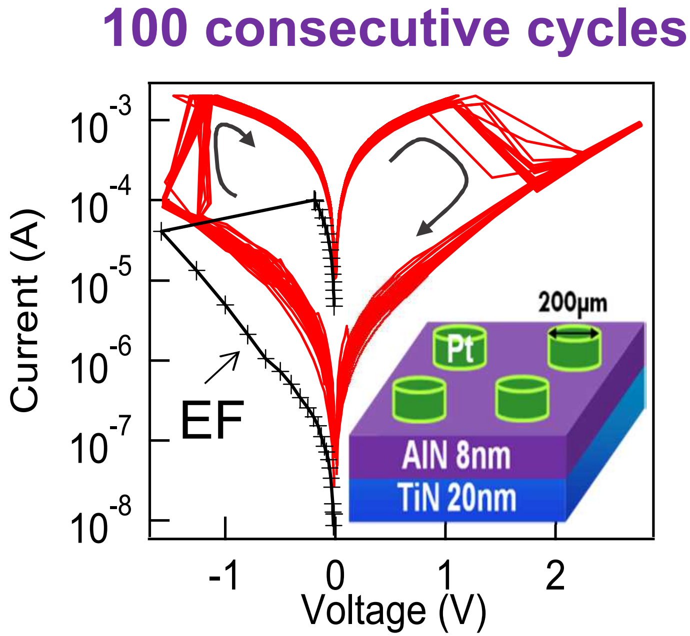
2) AlN and TiN: thermodynamic equilibrium between AlN and TiN

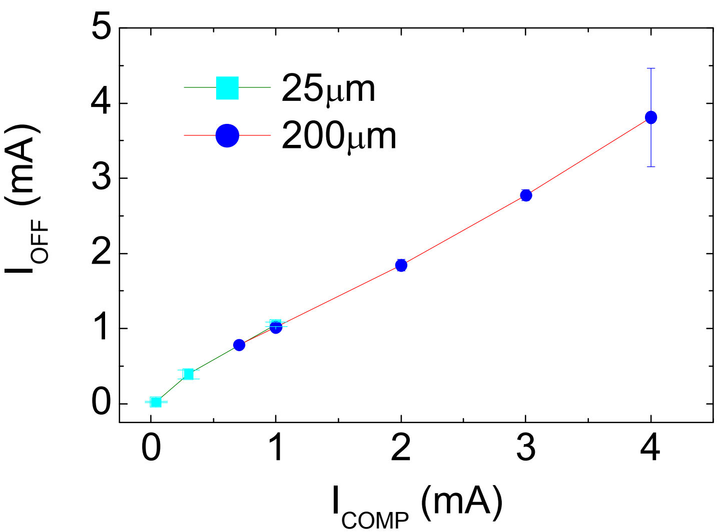
3) TiN: a large solubility of N → perfect electrode (serving as N reservoir)

4) AlN: only two stable solid phases →perfect switching material (a conducting phase + an insulting phase, same as Ta-O)

Device performance: repeatable

AlN memristor



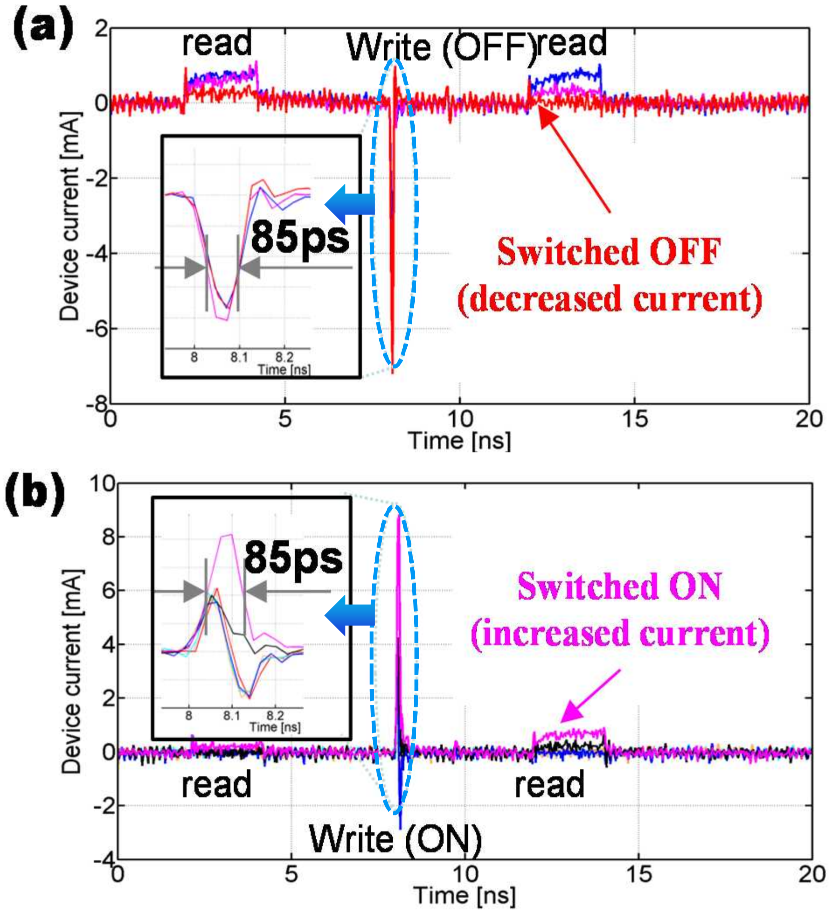


- Nitride memristors reported
- Stable and reproducible switching was observed after electro-forming
- Compliance current (I_{comp}) defines device resistance and I_{OFF}

Choi *et al.* Appl. Phys. A 109, 1 (2012)

Device performance: ultra-fast real-time switching

Bipolar device (2μm x 2μm) – OFF & ON switching



Pulse sequence	Quasi-DC device resistance [kΩ]
Initial	0.73
#3 (-2.0 V / 86 ps)	97.83 (OFF)

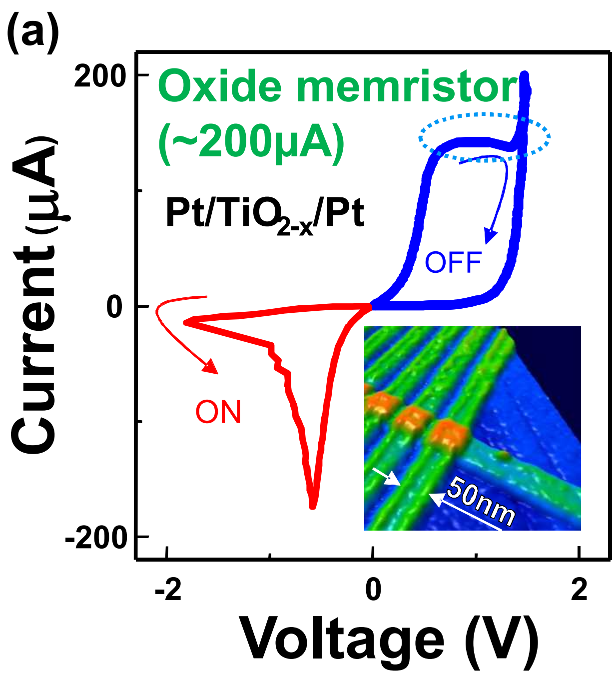
Initial	83 MΩ
#6 (+2.1 V / 87 ps)	2.56 kΩ (ON)
#7 (+2.1 V / 87 ps)	0.73 kΩ (ON)

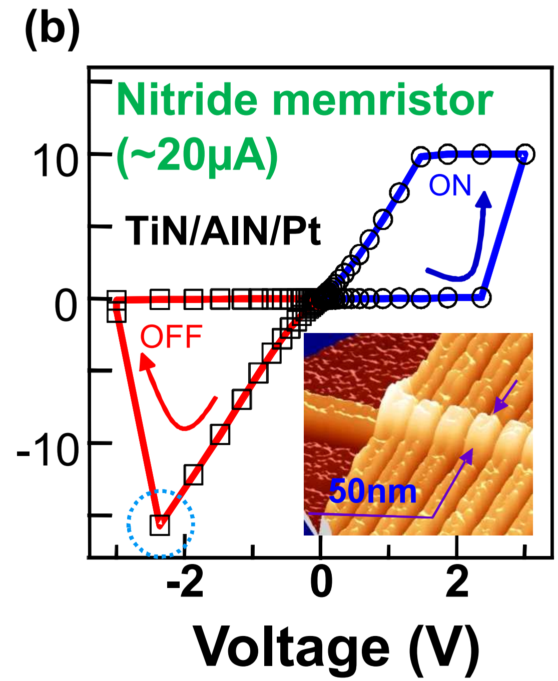
- Sub-100ps switching observed
- Strongly nonlinear switching dynamics

Experimental setup: A. C. Torrezan *et al*. *Nanotechnology* 22, 485203 (2011)

Device performance: scalability and low energy

50nm x 50nm nanodevice

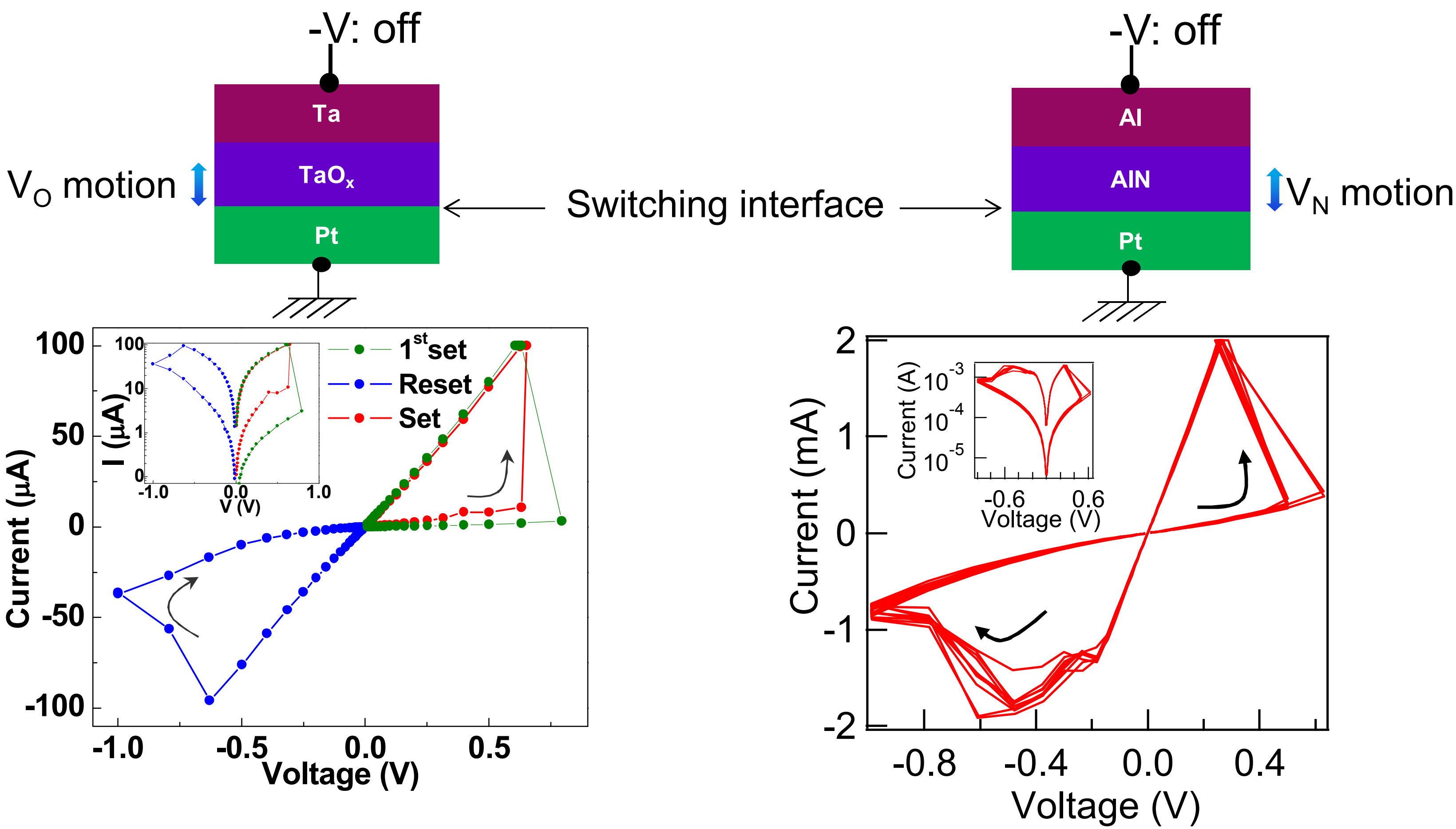




Low-energy device:
Lower current than TiOx and even TaOx

- OFF-switching current 10~20 μA
- High ON/OFF ratio (>100)

Mechanism: Analogous to oxide

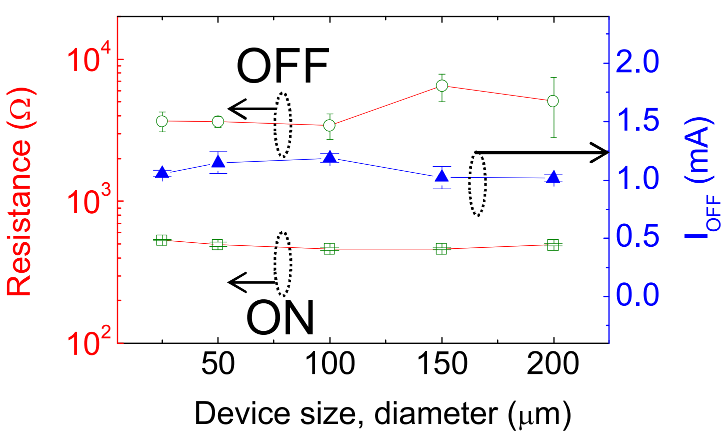


Inert interface favorable!

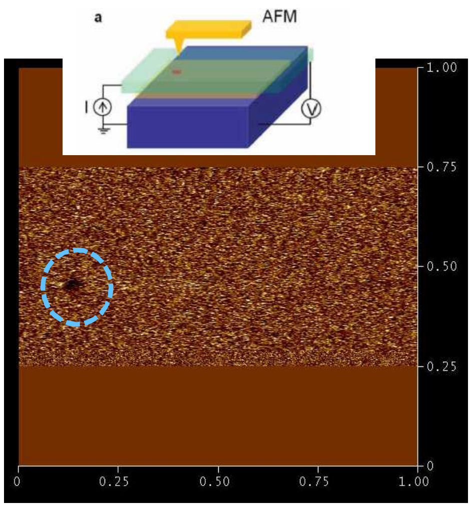
Yang et al. *Appl. Phys. Lett*. 97, 232102 (2010)
Miao et al. *Adv. Mater*. 23, 5633 (2012)

Mechanism: Localized channels

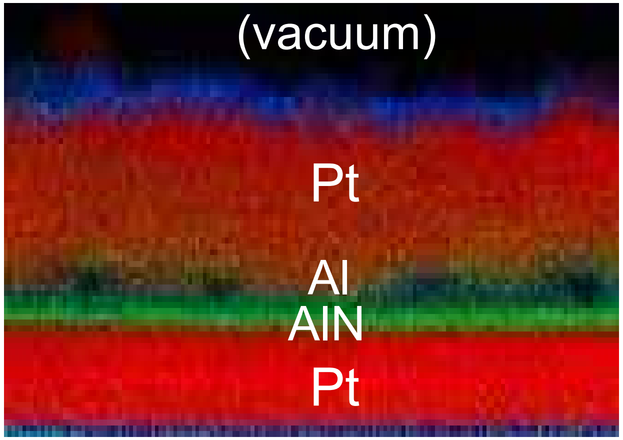
Various evidences



Irrelevance to area (Electrical test)



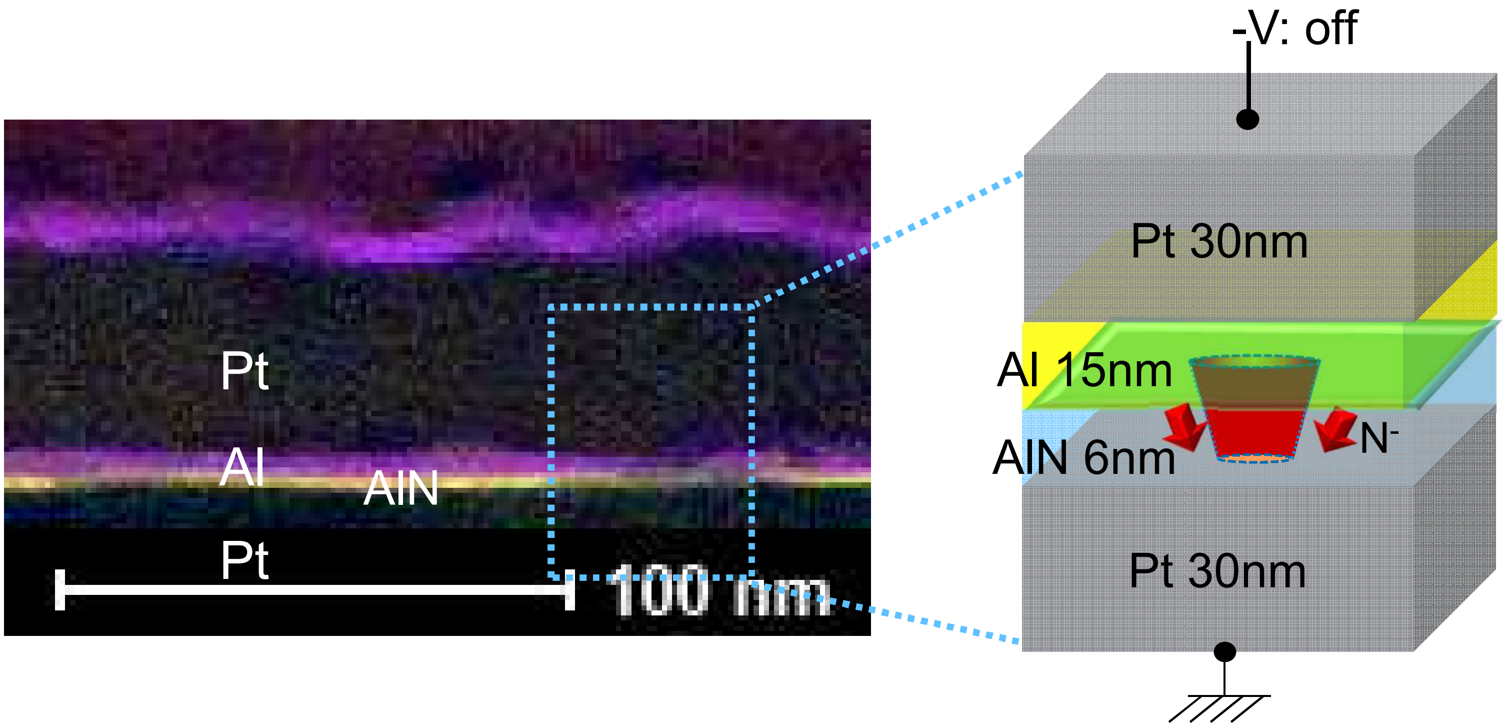
Localized conducting region detected (PMCM)



Chemical change (TEM-EDS)

Strachan et al. *Adv. Mater*. 22, 3573 (2010)
Miao et al. *Adv. Mater*. 23, 5633 (2012)

Mechanism: Al(N) channels



- Strongly localized heating
- Formation of N-deficient Al(N) → Localized channel

B. J. Choi et al. "Sub-100ps ultra-fast and energy-conservative nitride memristors", in preparation

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Engineered Materials

US008415652B2

(12) **United States Patent**
Yang et al.

(10) **Patent No.:** **US 8,415,652 B2**
(45) **Date of Patent:** **Apr. 9, 2013**

(54) **MEMRISTORS WITH A SWITCHING LAYER COMPRISING A COMPOSITE OF MULTIPLE PHASES**

(75) Inventors: **Jianhua Yang**, Palo Alto, CA (US); **Gilberto Ribeiro**, Menlo Park, CA (US); **R. Stanley Williams**, Portola Valley, CA (US)

(73) Assignee: **Hewlett-Packard Development Company, L.P.**, Houston, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 220 days.

(21) Appl. No.: **12/819,763**

(22) Filed: **Jun. 21, 2010**

FOREIGN PATENT DOCUMENTS

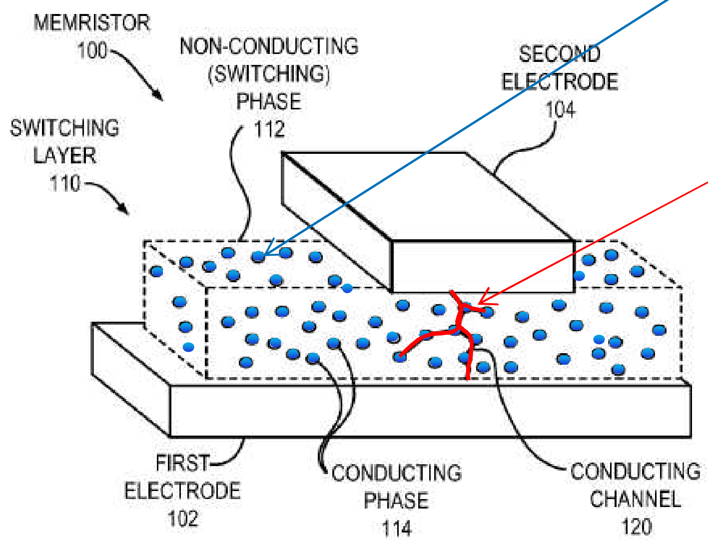
WO 2009114796 A1 9/2009

OTHER PUBLICATIONS

J. Yang et al., "The Mechanism of Electroforming of Metal Oxide Memristive Switches", Research Paper, Information and Quantum Systems Lab, Hewlett-Packard Laboratories; Department of Physics and Astronomy, University of California, Published 2009.
T. Driscoll et al., "5. Phase-Transition Driven Memristive System", Research Paper, University of California, San Diego. physics department; MIT—Device Team, ETRI. Daejeon 305-350, Republic of Korea.

* cited by examiner

Primary Examiner — Jami M Valentine
(74) *Attorney, Agent, or Firm* — David W. Collins

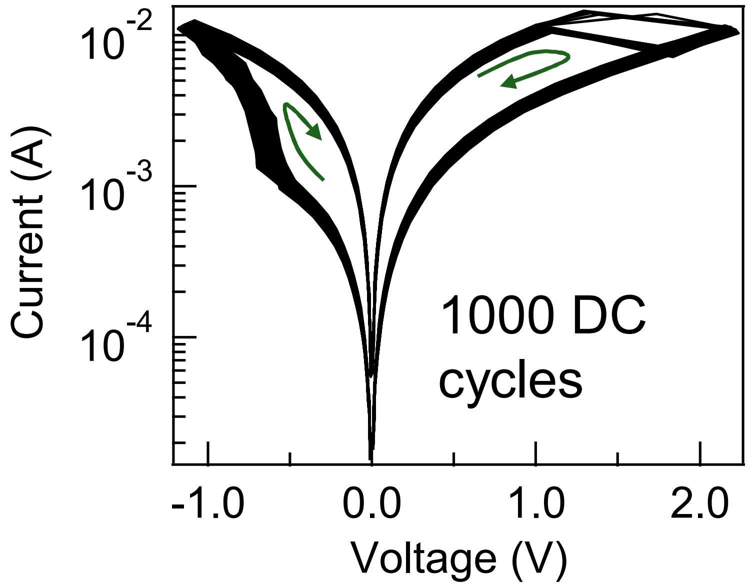


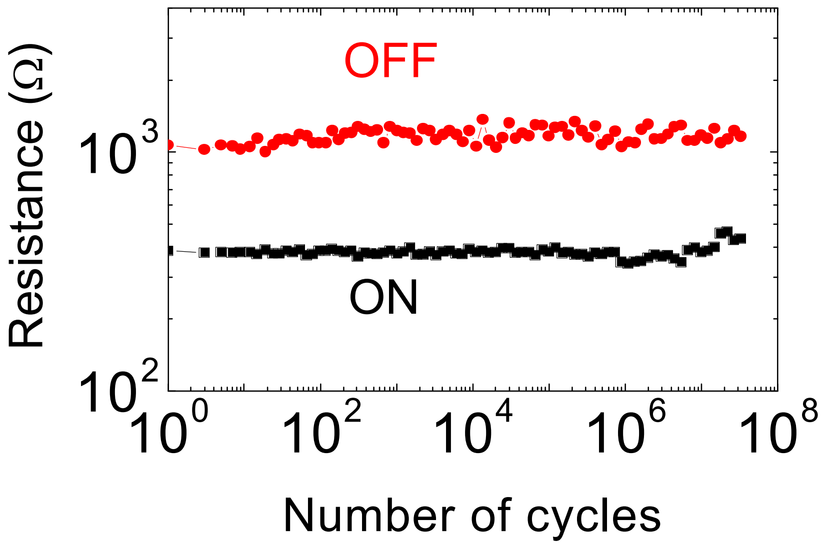
Origin:
Different switching channels in different devices.

Solution:
Plant similar seeds (nanoclusters) of switching channels in different devices

facilitate similar switching channels formed in every device.

Device performance: Reliable

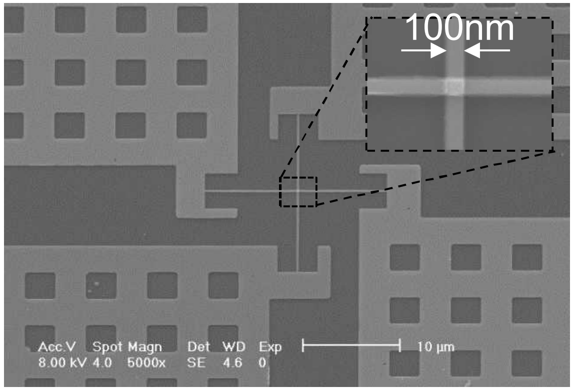


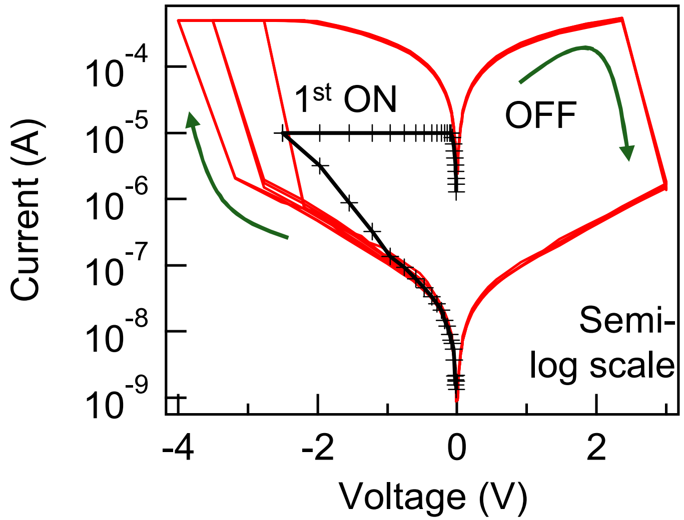


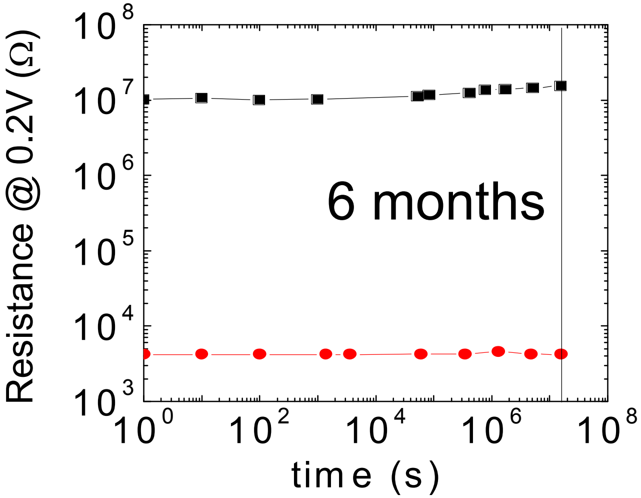
- Excellent uniformity and high durability
- Much reliable than binary oxide switching

B. J. Choi et al. ***Adv. Mater.* 23**, 3847 (2011)
B. J. Choi et al. ***Nano Lett*. 13**, 3213 (2013)

Device performance: Scalable



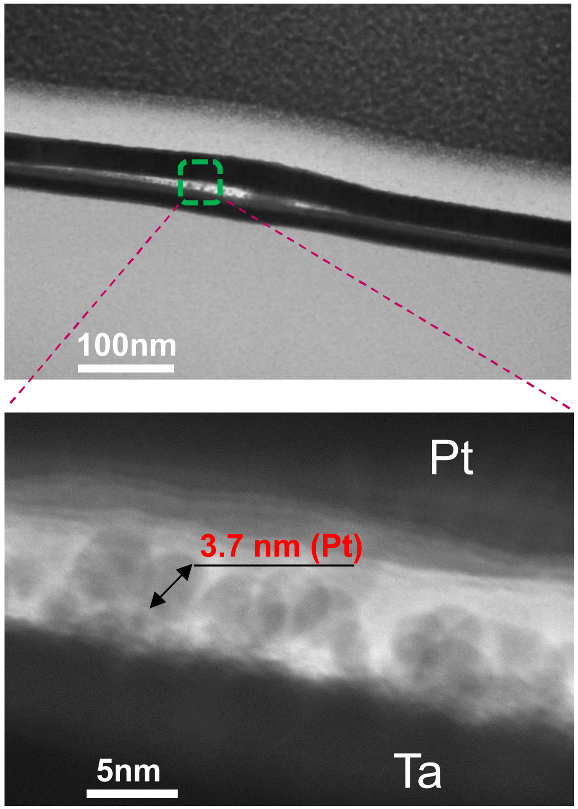


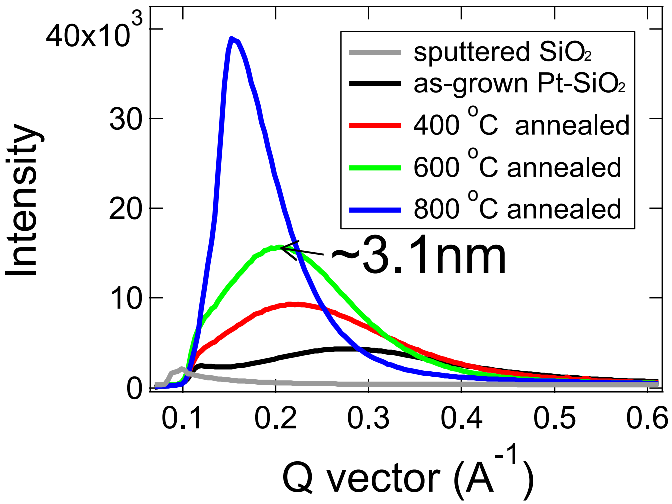


- Scalability proved down to $(100nm)^2$
- Uniform, high ON/OFF ratio
- No change up to 6 months

B. J. Choi et al. ***Nano Lett***. **13**, 3213 (2013)

Mechanism: Pt templated memristive switching





- Pt nanoparticle → rounder and bigger
- Joule heating and electric field
- Ionic switching effects are highly probable

<u>B. J. Choi</u> et al. ***Nano Lett***. **13**, 3213 (2013)

Summary

– *New switching materials for memristive switching*

- *Nitride memristors* demonstrated

- Fast switching (~85ps), scalability (50nm) with low energy consumption observed

- Switching at the more inert interface with localized conducting channel

- Switching interface is O-free after forming → Nitride Memristor!

- *ASM* (Artificial Switching Materials) are demonstrated

- Highly reproducible and uniform switching is observed

- Scaling with excellent device yield

- Possibly ANY metal into ANY insulator

Acknowledgements

HP Labs

John Paul Strachan
Douglas Ohlberg
Xuema Li / Ansoon Kim
Tan Ha / Cuong Le
Feng Miao / Matthew Pickett
Gary Gibson / Warren Jackson
Hans Cho / Yoocharn Jeon
Xia Sheng / Sity Lam
Tsung-Wen Lee / Steven Barcelo
Zhiyong Li
Dick Henze
Janice Nickel