FABRICATION AND CHARACTERIZATION OF ZnO THIN FILM MEMRISTOR USING ULTRA DILUTE ELECTRODEPOSITION METHOD

BY

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ABSTRACT

Memristor has become one of the alternatives to replace the current memory technologies. Instead of titanium dioxide (TiO_2), many researches have been done to explore the compatibility of others transition metal oxide (TMO) by using various deposition methods. Recently, the compatibility of zinc oxide (ZnO) to be used as the active layer of memristor has been widely explored. Meanwhile, the usage of organic materials in electronic device has shown a rapid growth as the size demand of devices is increasingly smaller and faster. Future electronics industry depends on the development of organic base semiconductor devices due to their advantages. In this study, the metal-insulator-metal (MIM) of Au/ZnO-Cu_2O-CuO/Cu and Au/ZnO/ITO/PET memristor were fabricated using dilute electrodeposition of zinc (Zn) and subsequent thermal oxidation methods at 773 K and 423 K respectively. The 15 s deposition gives the thinnest thin film, 80.67 nm for ZnO-Cu_2O-CuO on Cu and 68.10 nm for ZnO on ITO coated PET. The deposited thin film was characterized via X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). On Cu substrate, the XRD result indicates that Zn was oxidized to ZnO and has a wurzite structure. Meanwhile, Cu substrate also was oxidized to Cu_2O and CuO. There was formation of needle like structure observed through FESEM after thermal oxidation method. While on ITO coated PET substrate, Zn was oxidized to wurzite ZnO as shown in XRD result with nodule structure of ZnO after the thermal oxidation method. Both Au/ZnO-Cu_2O-CuO/Cu and Au/ZnO/ITO/PET sandwich memristive behavior were identified by the pinched hysteresis loop obtained from the *I-V* measurement. The high resistance state, HRS over low resistance state, LRS ratio of 1.110 and 1.067 respectively were obtained. Empirical study on thermodynamics of ZnO, Cu_2O, CuO and diffusivity of Zn^{2+} and O^{2-} in ZnO shows that zinc vacancy was formed in ZnO layer, thus giving rise to its memristive behavior. The synthesized Au/ZnO-Cu_2O-CuO/Cu and Au/ZnO/ITO/PET memristor show potential application in the production of a non-complex and low cost memristor. A flexible Au/ZnO/ITO coated PET memristor produces a comparable result to the Au/ZnO-Cu_2O-CuO/Cu memristor and other previous studies on memristor. The flexible memristor is applicable to be fabricated using dilute electrodeposition at room temperature with low thermal oxidation process.

ملخص البحث

أصبح memristor أحد البدائل لتكنولوجيات الذاكرة الحالية. تم دراسة تصنيع memristor ثاني أكسيد التيتانيوم (TiO_2) باستخدام مختلف أساليب الترسيب. إضافة إلى ذلك، في الاونة الأخيرة تم القيام بمزيد من الأبحاث لاستكشاف مدى توافق أكسيد المعدن الانتقالي (TMO) مثل أكسيد الزنك (ZnO) لاستخدامه كطبقة نشطة لmemristor. وفي الوقت نفسه أظهراستخدام المواد العضوية في الأجهزة الإلكترونية نموا سريعا، حيث أن حجم الطلب على الأجهزة متزايد بشكل أصغر وسرعة اعلى. إن صناعة الالكترونيات في المستقبل تعتمد على تطوير أجهزة الموصلات الجزئية ذات القاعدة العضوية نظرا لمزاياها. في هذه الدراسة، تم تصنيع المعدن عازل المعدنية باستخدام الترسيب الكهربائي ل-Au/ZnO-Cu_2O-CuO/Cu وAu/ZnO/ITO/PET memristor مخفف من الزنك (Zn) وطرق الأكسدة الحرارية اللاحقة. الترسيب ل 15 ثانية يعطي أنحف طبقة رقيقة و هي 80.67 نانومتر لZnO-Cu_2O-CuO و 68.10 نانومتر لZnO/ITO/PET . تم تشخيص الطبقة الرقيقة المرسبة من خلال الأشعة السينية (XRD) و المجهر الإلكتروني ذات حقل انبعاث الماسح الضوئي (FESEM). أظهرت نتائج XRD أن الزنك Zn أكسد لأكسيد الزنك ZnO و لديه تركيب wurzite. وفي الوقت نفسه، تم أكسدة ركيزة النحاس أيضا إلى Cu_2O وCuO. لقد لوحظ تشكيل إبرة مثل أكسيد الزنك ZnO خلال الأكسدة الحرارية عند درجة حرارة هي K773. تم تحديد سلوك شطيرة memristive لكل من Au/ZnO-Cu_2O-CuO/Cu و Au/ZnO/ITO/PET بواسطة حلقة التباطؤ الضيقة التي تم الحصول عليها عبر قياس *I-V*. نسبة التحويل المقاوم هو 1.110 و 1.067 على التوالي. تظهر الدراسة التجريبية على الديناميكا الحرارية لأكسيد الزنك ZnO، Cu_2O و CuO ، والانتشارية لZn^{2+} و O^{2-} في ZnO أن فراغ الزنك تشكل في طبقة أكسيد الزنك ZnO، مما أدى إلى سلوكها الmemristive. يبين توليف Au/ZnO- memristor Cu_2O-CuO/Cu و Au/ZnO/ITO/PET إمكانية التطبيق في إنتاج memristor بشكل غير معقد ومنخفض التكلفة. ينتج PET memristor المرن و المطلي بAu/ZnO/ITO نتائج مماثلة ل Au/ZnO-Cu_2O-CuO/Cu memristor ومماثل لدراسات أخرى سابقة على memristor. يمكن تصنيع memristor المرن باستخدام الترسيب الكهربائي المخفف في درجة حرارة الغرفة و مع عملية أكسدة حرارية منخفضة.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Materials Engineering).

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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

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May the blessing and peace of Allah be upon our prophet Sayyidina Muhammad ibn Abdullah (peace be upon him), and upon his families and upon his companions and upon all his godly followers.

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LIST OF ABBREVIATIONS

1-D	1-Dimensional
1T-1M	1Transistor- 1Memristor
A.u	Arbitrary unit
Ag/ AgCl	Silver chloride
Al	Aluminium
Al_2O_3	Aluminium (III) oxide
ALD	Atomic layer deposition
Au	Aurum
C	Carbon
CMOS	Complimentary metal-oxide-semiconductor
Cu	Copper
Cu_2O	Copper (I) oxide
CuO	Copper (II) oxide
CVD	Chemical vapor deposition
DC	Direct current
DRAM	Dynamic random access memory
EDX	Energy dispersion x-ray
FESEM	Field emission-scanning electron microscope
FTO	Fluorine doped tin oxide
FWHM	Full width at half width maxima
GO	Graphene oxide
HP	Hewlett-Packard

hr	Hour
HRS	High resistance state (same as R_{OFF})
In	Indium
ITO	Indium tin oxide
I-V	Current-voltage
JCPDS	Joint committee on powder diffraction standards
LRS	Low resistance state (same as R_{ON})
M	Molar
MRAM	Magnetoresistive RAM
MgO	Magnesium oxide
MIM	Metal-insulator-metal
min	Minute
n	Refractive index
N_2	Nitrogen
NAND	Not AND
Nb_2O_5	Niobium oxide
NBE	Near band edge
Ni	Nickel
NiO	Nickel (II) oxide
O_2	Oxygen
PCRAM	Phase change RAM
PET	Polyethylene terephthalate
PF	Poole-Frenkel
PL	Photoluminescence
PLD	Pulsed laser deposition
Pt	Platinum

RAM	Random access memory
RF	Radio frequency
RRAM	Resistive RAM
RT	Room temperature
RTP	Rapid thermal process
SCCM	Standard cubic centimeters per minute
SEM	Scanning electron microscope
Si	Silicon
SiO_2	Silicon dioxide
SRAM	Static random access memory
$SrZrO_3$	Strontium zirconate
Ti	Titanium
TiO_2	Titanium dioxide
TMO	Transition metal oxide
US	United States
UV	Ultraviolet
W	Tungsten
XRD	X-ray diffraction
Zn	Zinc
$ZnCl_2$	Zinc chloride
ZnO	Zinc oxide
ZrO_2	Zirconium dioxide

LIST OF SYMBOLS

ΔG	Gibbs reaction free energy change
ΔG°	Standard Gibbs reaction free energy change
θ	Theta
λ	Wavelength
ε_r	Optical dielectric constant
Ω	Ohm
$\mathscr{k}$	Reaction constant
φ_m	Magnetic flux
μm^2	Square micrometer
μ_v	Dopant mobility
A	Ampere
Å	Angstrom
atm	Standard atmospheric pressure
c	Concentration of oxygen
C_s	Storage capacitance
D	Diffusion coefficient (diffusivity)
d	Lattice distance
D	Thin film thickness
eV	Electron volt
fF	Femtofarads
G	Giga
I	Current

J	Diffusive flux
K	Kelvin
k	Kilo
k_p	Parabolic rate constant
L	Inductance
ℓ	Liquid
M	Memristance
m	Slope of straight line
mm^2	Square millimeter
ml	Milliliter
nm	Nanometer
P	Power
Pa	Pascal
P_g	Gas pressure
P_{O_2}	Oxygen partial pressure
q	Charge
R	Ideal gas constant
R_{OFF}	Off-state resistance (same as HRS)
R_{ON}	On-state resistance (same as LRS)
s	Seconds
s	Solid
sq	Square
T	Temperature
t	Time
V	Voltage

V	Volts
x	Displacement (position of length of diffusion)

CHAPTER 1

INTRODUCTION

1.1 LIMITATIONS OF CURRENT MEMORY TECHNOLOGIES

The reliance of people towards technology drove the development of computers and other technology devices. Innovation of smaller electronic devices with better performance and capacity give a huge impact to the memory storage system. As the technology developed, it can be seen that the size of the devices also are getting smaller. The smaller the device is, the more efficient it will be, but this brings forth the challenge in increasing the physical memory capacity. Presently used memory technologies such as dynamic random access memory (DRAM), static random access memory (SRAM), and NAND flash are facing design challenge due to the continued scale down in physical size.

The memory system is the most crucial component in any electronic devices. It is where the computer keeps its current programs and data that are in use. With the advances in the technology of electronic devices, the memory technology has met its maximum limit to keep on par with the demand for smaller size and higher capacity memory storage.

Figure 1.1 shows the trends in chip size, memory cell size and storage capacitance in response to DRAM generation by (Sunami, 2010). The increase of bit size of DRAM by a factor of 10^6 from 1 kbit to 1 Gbit caused the enlargement of the chip size up to 10 times. As mentioned previously, as the fabrication of increasingly smaller memory cell size grows harder, it could be expected to meet a limit on producing small chip sized with bigger DRAM size.

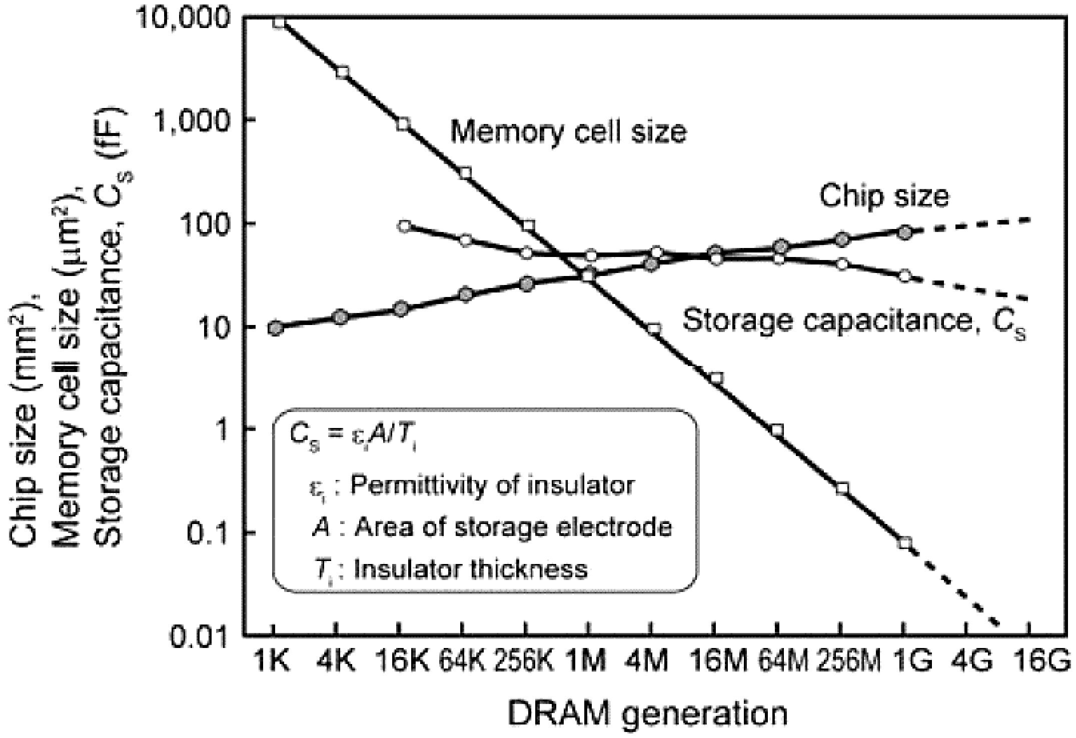

Figure 1.1 Memory cell size shrinkage at DRAM in volume production (Sunami, 2010)

On the other hand, the manufacturing cost of DRAM elevated up due to the improvement route in size and capacity to achieve the required specifications. Therefore, various development efforts have been focusing on reduction of manufacturing cost. Stated by Kwon in his thesis, worldwide DRAM industry has lost over 10 billion US Dollars during 2006 to 2008 because of the technological innovations and DRAM scaling. The cell size of DRAM has to be reduced every year by 30 % to satisfy the latest market demand while the price per bit of DRAM drops 26 % annually. This will end up in a big loss for the DRAM manufacturer (Kwon, 2013). A significant portion of the total system power and the total system cost is spent in the memory system with the increasing size of the memory system (Qureshi, Srinivasan, and Rivers, 2009). Figure 1.2 shows the overall current trend of the memory system where the target size approaches 10 nm, with higher capacity and speed. But as to reduce the size and improve the performance of the device, the manufacturing cost increases because of the increase in power consumption by the device itself and its cooling system itself as the structure of the device more complex.

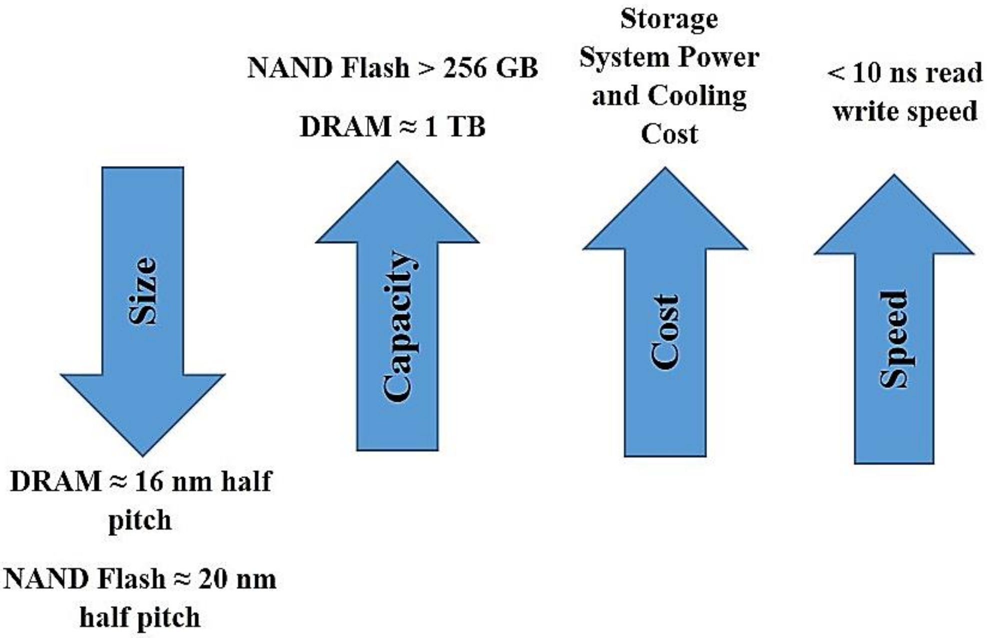

Figure 1.2 Overall current trend of memory system technology

The memory system is one of the most critical components of modern computers. Dynamic random access memory (DRAM) and static random access memory (SRAM) are the main system memory used in any electronic devices. They can be considered as the crucial components of the memory system with fast response and good performance.

But, DRAM and SRAM are the volatile memory system which they cannot store the memory data without the power supply (Perez and De Rose, 2010; Lian, 2014). The current memory devices cost billions dollars to keep pace with the current trend and capacity. It has reaching their maximum physical limitation when demands of the smaller size memory devices arise.