Applied Surface Science 271 (2013) 407–411

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

A study of copper oxide based resistive switching memory by conductive atom force microscope

Qianfei Zhou[a], Qian Lu[a], Xin Zhang[a], Yali Song[b], Yin Yin Lin[b], Xiaojing Wu[a,*]

[a] Department of Materials Science, Fudan University, No. 220 HanDan Road, Shanghai, 200433, PR China
[b] Department of Microelectronics, ASIC and System State Key Lab, Fudan University, Shanghai, 200433, PR China

ARTICLE INFO

Article history:
Received 26 June 2012
Received in revised form 24 January 2013
Accepted 31 January 2013
Available online 8 February 2013

Keywords:
Copper oxide
Resistive switching
Conductive atom force microscope

ABSTRACT

A copper oxide (Cu_xO) layer was formed by applying plasma oxidization on a copper film grown on a Si substrate. Pt deposited on this Cu_xO layer then function as the top electrode to form a Pt/Cu_xO/Cu structure. A device created with this structure exhibited a forming-free bipolar resistive switching property. Conductive atom force microscope (C-AFM) was employed to investigate the nanoscale electrical properties of the device. Based on *I*–*V* curve analysis, it was found that the Poole–Frankel and conducting filaments models were suitable for the present device. C-AFM analysis for the sample indicated that the random formation/rupture of conducting paths in the Cu_xO layer may play a key role for the device instability in high resistance state.

1. Introduction

Generally, copper oxide compounds include copper oxide (CuO) as well as cuprous oxide (Cu_2O) phases, which are conventional p-type semiconductors with an indirect band gap of 1.4 eV [1] and a direct band gap of 2.0 eV [2], respectively. The mixture of CuO and Cu_2O, denoted as Cu_xO ($2 \geq x \geq 1$), is widely used in fabricating solar cells [3]. Recently, this compound has received much attention due to it becoming an important material for the manufacturing of resistance-switching random access memory (RRAM).

The resistive switching property of Cu_xO films was initially reported by Chen et al. in 2005 [4]. Since then, Cu_xO-based RRAM devices have been widely studied. Kim et al. [5] prepared Cu_xO films by reactive magnetron sputtering, and found that it had unipolar resistive switching property. The origin of this property was attributed to the formation and rupture of conducting filaments under the external electrical field. Dong et al. [6] prepared Cu_xO by thermal oxidation and fabricated Cu_xO based RRAM device with Mo top electrode. They suggested that the space charge limited current (SCLC) model played a critical role for its resistive switching property. Yang et al. [7] came to the same conclusion in their study on the Cu_2O thin film prepared by radio-frequency sputtering using Cu_2O target. Hu et al. [8] grew Cu_2O/CuO thin film on Nb doped $SrTiO_3$ substrates by plasma assisted molecular beam epitaxy, and found that the resistive switching effect had a close relationship with the oxygen deficiency. Lv et al. [9,10] investigated the forming process and the endurance enhancement for the Cu_xO-based RRAM device and found that the forming process in Cu_xO originated from electrical-breakdown. Although much progress have been achieved for the Cu_xO based RRAM devices in recent years, some questions about the mechanism of its resistive switching property still remain. To further clarify this issue, some new techniques should be employed.

It is well known that the resistive switching property of oxides depend on the formation and rupture of nanoscale conducting filaments, while conductive atomic force microscope (C-AFM) is considered as one of the most powerful tools to study the material's nanoscale electrical property. Actually, in the study of $SrTiO_3$ single crystal by C-AFM, Szot et al. [11] found that the dislocations induced by the external electric field resulted in the formation of the conducting paths. In the study of TiO_2 film prepared by reactive magnetron sputtering by C-AFM, Hsiung et al. [12] found that the conducting paths may be formed by oxygen defects since the concentration of such defects controlled by oxygen flow during deposition and the density of conducting paths in 500 nm × 500 nm area are highly correlated. In another study on Cu/TiO_2/Pt structure device fabricated by atomic layer deposition (ALD), Yang et al. discussed the influence of Cu ion migration in the TiO_2-based RRAM device at SET and RESET voltage of ±4 V in an area of 500 nm × 500 nm by C-AFM [13].

In this work, the copper oxide layer formed by plasma oxidation on copper substrate is employed to fabricate Pt/Cu_xO/Cu RRAM device, which shows a forming-free bipolar resistive switching property. C-AFM is employed to study the nanoscale electrical property for the Pt/Cu_xO/Cu RRAM device. The working mechanism of Cu_xO is discussed based on this study.

---

[*] Corresponding author. Tel.: +86 021 65643258; fax: +86 021 65643258.
E-mail addresses: wuxj@fudan.edu.cn, 09110300003@fudan.edu.cn (X. Wu).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.01.217

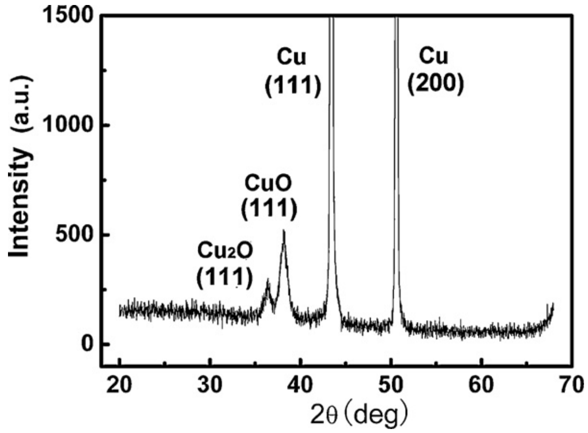

Fig. 1. XRD pattern from the Cu_xO layer.

2. Experimental

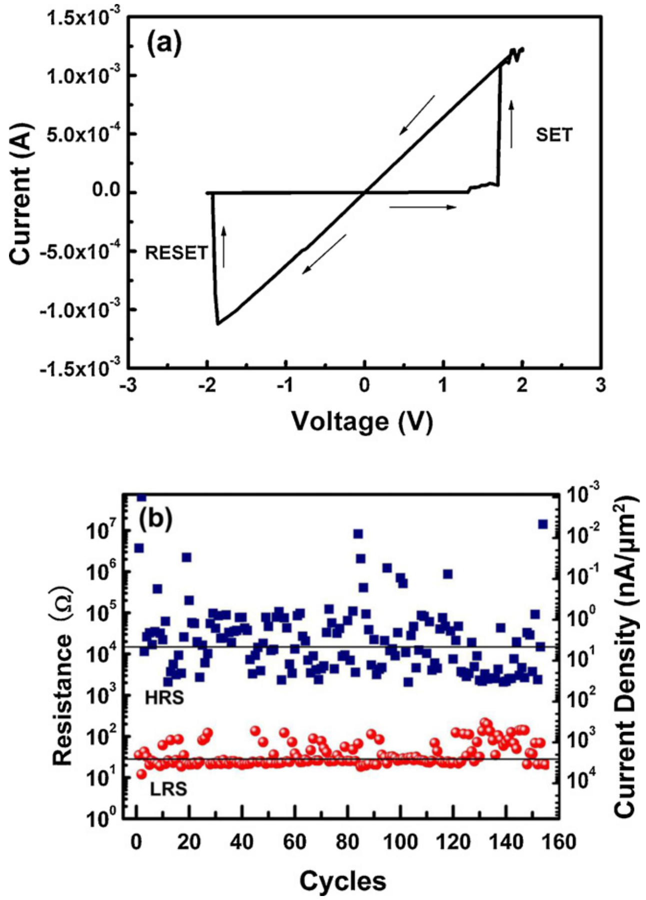

Fig. 2. (a) Typical *I*–*V* curve and (b) endurance analysis of Pt/Cu_xO/Cu RRAM cell. The RRAM device shows a bipolar resistive switching property with a resistance window of above 10 and an endurance of 160 cycles. Two solid lines illustrate the average resistance and current density of LRS and HRS, respectively. The SET and RESET voltages are not larger than ±2 V.

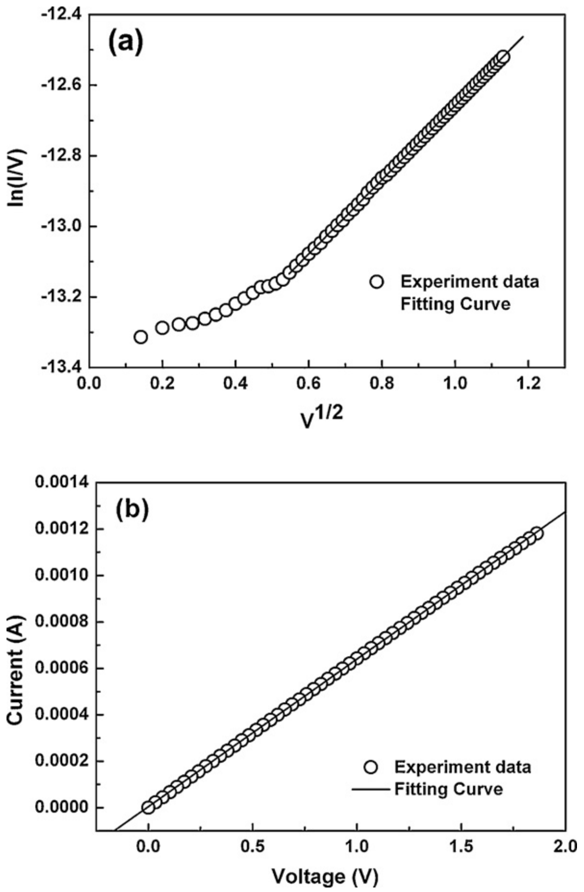

Fig. 3. Linear fitting of (a) HRS in higher electrical field and (b) LRS *I*–*V* curves for Pt/Cu_xO/Cu RRAM cell.

Cu film with thickness of 1 μm was deposited by standard electrochemistry plating process (Novellus ECP system) on Cu(seed layer:120 nm)/Ta(10 nm)/TaN(15 nm)/SiO_2(400 nm)/Si multilayer structural substrate. Subsequent plasma oxidation for the film was carried out in a reactive ion etching chamber with O_2 pressure of 6 Pa, O_2 flow rate of 30 SCCM and radio power of 300 W at room temperature for 20 min. The crystal structure of the film was examined by X-ray diffraction (XRD, BRUKER-D8 system).

The Cu_xO based RRAM devices were fabricated by physical vapor depositing (PVD) Pt as top electrodes with a thickness of 200 nm and a diameter of 100 μm on copper oxide film patterned by a shadow mask.

The resistive-switching and endurance properties of the RRAM cells were measured by Keithely 4200-SCS semiconductor parameter analyzer. The topography and nano-scale electrical properties of the RRAM cells were measured by C-AFM (Veeco Multimode Nanoscope V system).

3. Results and discussions

The XRD pattern for the Cu_xO film was shown in Fig. 1. The peaks of Cu(1 1 1) and Cu(2 0 0) came from the copper substrate, while two weak peaks at 36.28° and 38.21° came from Cu_2O(1 1 1) and CuO(1 1 1), respectively. Obviously, the copper oxide layer was a mixture of Cu_2O and CuO. On the other hand, the peaks from Cu_xO were rather broad with FWHM of 0.82° and 0.91° for Cu_2O(1 1 1) and CuO(1 1 1) respectively, indicating that the crystal structure of Cu_xO layer was far from perfect and contained a lot of structure defects.

The typical current–voltage curve and endurance properties of the device were taken with a dc voltage sweep measurement by applying a bias voltage on the bottom electrode. Fig. 2a shows a typical *I*–*V* curve for the Pt/Cu_xO/Cu memory cells. When the bias voltage was increased gradually, a sudden current jump occurred at 1.7 V, indicating that the film have changed from a high resistance state (HRS) to a low resistance state (LRS), which is well