Journal of Alloys and Compounds 709 (2017) 535–541

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Resistive switching behavior in copper doped zinc oxide (ZnO:Cu) thin films studied by using scanning probe microscopy techniques

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A R T I C L E I N F O

Article history:
Received 28 July 2016
Received in revised form
23 February 2017
Accepted 15 March 2017
Available online 18 March 2017

Keywords:
Resistive switching
Polarization switching
conductive Atomic Force Microscopy
Piezoresponse Force Microscopy
ZnO:Cu thin film

A B S T R A C T

The bipolar resistive switching (RS) behavior of Cu doped ZnO (ZnO:Cu) thin film samples is studied by using the conductive Atomic Force Microscopy (c-AFM) technique without an electroforming process. It is found that, comparing with the undoped ZnO, both "set" and "reset" voltages are increased in the ZnO:Cu (8 at.%) thin film. The "set" and "reset" voltage are slightly increased with the significantly increased built-in voltage. It is also found that the electroforming process has no influence on the retaining of the RS behavior. In addition, the results indicate that the RS behavior can only be retained on the control of scan rate and scan time. Furthermore, in the endurance tests by using the Piezoresponse Force Microscopy (PFM) in spectroscopy mode, the results suggest that the fatigue of polarization switching has a severely influence on the film endurance performance. The correlation of polarization switching and RS is further investigated by conducting PFM measurement on the same area where c-AFM measurement was performed. The results suggest that the polarization reversal occurs when samples are in the high resistance state (HRS). Hence, the coupling mechanisms between the polarization and RS behavior in ZnO:Cu thin film are studied.

1. Introduction

Resistance random access memory (RRAM) and ferroelectric random access memory (FRAM) have great potentials for next generation nonvolatile memory devices [1,2]. ZnO-based materials have been extensively studied in recent years due to their multi-functional properties, such as resistive switching (RS) [3,4], piezoelectric [5,6], ferroelectric-like [7], ferromagnetic properties [8], photoconductivity [9–12], photoelectrochemical properties [13,14] and easier fabrication characteristics [15]. In the previous studies, it was reported that the undoped ZnO has shown coexistence of the resistance switching (RS) and polarization rotation or "switching" behaviors [16–19]. Furthermore, both unipolar and bipolar resistive switching behaviors were reported in ZnO based thin films [20,21]. However, the factors affecting the RS behavior are still not fully understood. For example, it was found that the switching behavior could be improved by properly doping [22,23]. It was reported that Cu concentration could affect the RS behavior, as Cu could be the electron trap so that the resistivity was increased in Cu doped ZnO thin films (ZnO:Cu) [24,25]. In addition, the polarization rotation or "switching" (PS) has also been reported in the ZnO:Cu thin films [26,27]. Hence, in this study, the ZnO:Cu thin films with different Cu concentrations are studied. The correlations between the RS and polarization rotation or "switching" on the ZnO:Cu thin film samples are also studied in detail.

Generally-speaking, the resistive switching behavior can be studied at micro- to nanoscale by using conductive Atomic Force Microscopy (c-AFM) technique, whereas the corresponding polarization switching behavior can be investigated by applying Piezoresponse Force Microscopy (PFM) [28,29]. For memory application, the retention and reliability of devices are crucial issues. Therefore, in this work, the retention of the RS and PS behaviors are also studied. The possible factors affecting the RS and PS retention and relaxation in ZnO:Cu thin films, including the electroforming process, scan rate and scan time, are studied as well. Finally, the correlation between the polarization reversal and the resistance state are discussed.

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http://dx.doi.org/10.1016/j.jallcom.2017.03.169

2. Materials and experiments

2.1. Samples preparation

The ZnO:Cu thin film samples (with 2 at.% and 8 at.% Cu content respectively) were deposited by means of pulsed laser deposition (PLD) technique under oxygen partial pressure of 1×10^{-6} Torr. The nominal thickness of the film is approximately 240 nm. The parameters for the film deposition were the same as those used in the previous study [26]. The film was deposited on commercial available Pt-coated Si wafer (Addision Engineering, Inc, CA, USA) whereas the Pt coating acts as the bottom electrode for c-AFM and PFM measurements.

2.2. Characterization

The topography image of the ZnO:Cu thin film sample (8 at. % Cu) showed that the grains were distributed uniformly (Supplementary Information: Fig. S1). The average RMS roughness was measured to be around 16 nm from the AFM image on a scanning area of 2×2 μm^2. Uniformly distributed grains were also observed on the samples with other Cu concentrations. In addition, similar to the previous studies [26,27,30], the X-ray diffraction (XRD) patterns were confirmed that the ZnO:Cu film samples were fully crystalized and the ZnO crystals were oriented with the c-axis along the (002) direction. The Cu percentages in the films were also confirmed by energy dispersive spectroscopy (EDS) and X-ray photoemission spectroscopy (XPS) studies [26]. The relevance between the oxygen vacancy concentration and oxygen partial pressure during the deposition was reported previously by using the Raman spectra and X-ray absorption spectroscopy (XAS) analysis [8] and therefore not repeat here.

In this study, c-AFM measurements were conducted in several different experiments. First, the local I-V (current-voltage) curves were measured at single points, i.e., a voltage sweep from −10 V to +10 V was applied to the specific points on the sample surface with a triangle waveform and 1 Hz frequency in ambient air condition, whereas the current was measured at these points. To investigate the effects of moisture and oxygen on the I-V characteristics of ZnO:Cu thin film, the same experiments were also conducted in the slow-flowing synthetic air and Argon gas, respectively. The synthetic air contains less than 5 ppm water, whereas the Argon gas contains less than 0.02 ppm water and 0.01 ppm oxygen. Next, in the local area RS experiments, the “set” and “reset” experiments were conducted. In this test, swept biases (0 → 10 V→-10 V→10 V) were applied through the bottom electrode (Pt) and the current images were obtained at a selected area (1×1 μm^2). The current values on this area were then averaged to obtain the average I-V curve. The third experiment was to study the effects of electroforming, scan rate and the numbers of scan on the local area RS behavior.

In the Piezoresponse Force Microscopy (PFM) and the PFM in spectroscopy mode, i.e., Piezoresponse Force Spectroscopy or PFS measurements, the bias is applied to the conductive tip. For the PFM and PFS measurements, it was reported that electric screen effects in some non-ferroelectric/non-piezoelectric materials, such as glass plate, might also generate the responses similar to the ferroelectric hysteresis loop, and this was generally believed as PFM artefact [31]. In order to confirm the observed polarization switching behavior is intrinsic property of the ZnO:Cu films, rather than PFM artifact or from the SiO_2 substrate, the PFM measurements have been also conducted on SiO_2 wafer. The corresponding results of PFM in SiO_2 wafer show that there is no polarization switching signal observed in SiO_2 wafer, with only ~20° phase angle change and almost linear amplitude responses were observed with much higher applied voltage (Supplementary Information: Fig. S2). Therefore, it can be concluded that the PFM responses on Cu-doped ZnO are not artifact and it is real responses from the sample. In addition, to study the effects of RS on polarization switching characteristics, PFM was also conducted just after poling by −10 V sample bias on the specific locations. It should note that during c-AFM measurements, the bias was applied to the Pt layer under the sample, where the c-AFM tip is grounded. For the PFM measurements, on the other hands, the bias was applied through the PFM tip, whereas the bottom electrode (Pt layer on substrate) was grounded.

3. Results and discussion

3.1. Resistive switching characteristics

3.1.1. Local point I-V curve measurements

In the c-AFM experiments, the RS characteristics in the ZnO:Cu samples are first confirmed by local point I-V curve measurements. Bipolar resistance switching phenomena are found on both ZnO:Cu samples with 2 at.% and 8 at.% of Cu. These results are consistent with previous reported results for the undoped ZnO thin films [17,19]. Similar results for undoped ZnO thin film samples are shown in the Supplementary Information [Figs. S3(a) and S3(b)]. Fig. 1 shows the point I-V curves measured without a forming process. It is found that both “set” and “reset” voltages increase with the copper concentration. Compared with that of the ZnO:Cu (8 at.%) thin film sample [Fig. 1(a)], the values of the “set” voltage are fluctuated more for the ZnO:Cu (2 at.%) thin film sample [Fig. 1(b)]. However, for the ZnO:Cu (8 at.%) thin film sample, the currents for both the “set” and “reset” parts of the I-V curve are shifted along the bias axis [shown by the inset of Fig. 1(a)]. The shift of the current in the “set” part of the I-V curve is more significant than that in the “reset” part of the I-V curve, and this suggests the existing of the internal electric field as well as the non-uniform distributed space charges in the ZnO:Cu (8 at.%) thin film sample [32]. Generally-speaking, the mechanisms underlying the nonlinear I-V curves can be analyzed by Poole-Frenkel (PF) emission, or Schottky emission, or space-charge-limited current (SCLC),

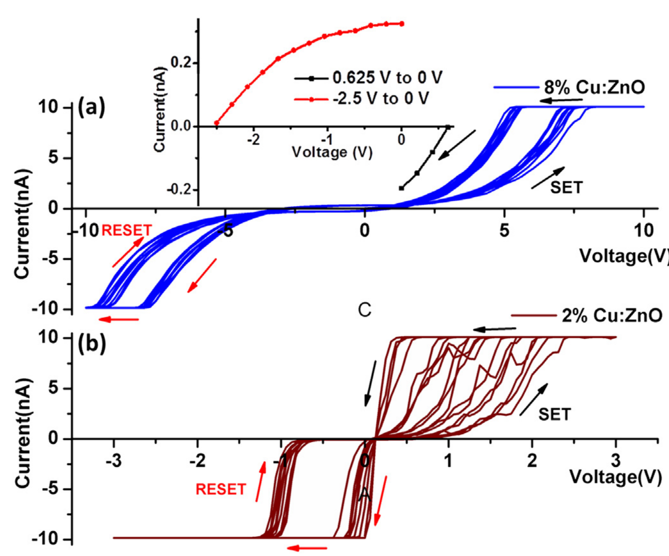

Fig. 1. Local I-V curves measurements on (a) ZnO:Cu (2 at.%); and (b) ZnO:Cu (8 at.%) thin film samples deposited under oxygen partial pressure of $P_{O_2} = 1 \times 10^{-6}$ Torr. The insert shows the shift of the current values at “set” and “reset” processes of the I-V curve for ZnO:Cu (8 at.%) sample.