Acta Materialia 123 (2017) 394–403

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Polarization rotation in copper doped zinc oxide (ZnO:Cu) thin films studied by Piezoresponse Force Microscopy (PFM) techniques

Juanxiu Xiao [a], Tun Seng Herng [b], Jun Ding [b], Kaiyang Zeng [a, *]

[a] Department of Mechanical Engineering, National University of Singapore, 9, Engineering Drive 1, 117576, Singapore
[b] Department of Materials Science and Engineering, National University of Singapore, 9, Engineering Drive 1, 117576, Singapore

ARTICLE INFO

Article history:
Received 25 April 2016
Received in revised form
18 October 2016
Accepted 21 October 2016
Available online 1 November 2016

Keywords:
ZnO:Cu thin films
Piezoresponse Force Microscopy
Polarization rotation
Copper concentration
Oxygen vacancy

ABSTRACT

In this study, the polarization rotation with approximately 180°, i.e., the phenomenon that polarization changes its angle by ~180°, in copper doped ZnO (ZnO:Cu) films under an applied electrical field are characterized by using Piezoresponse Force Microscopy (PFM) based techniques. First, the Band Excitation PFM (BE-PFM) measurements show that the polarizations in ZnO:Cu sample prefer the upward direction when the copper concentration is higher (above 8 at.%). Second, it is found that the piezoresponse property is enhanced with increasing the copper concentration. Third, by conducting PFM in spectroscopy mode (PFS), it reveals that the anomalous hysteresis loops occurs at certain locations and can be tuned to symmetry by increasing the bias window. Furthermore, it is found the built-in field during the DC poling processes are contributed by the oxygen vacancy in the films. The PFS results from as-grown sample and samples annealed in air and vacuum also verify that the oxygen vacancy plays an important role in the polarization rotation. Finally, by using the switching spectroscopy PFM (SS-PFM) technique, it is confirmed that the local polarization rotation is mediated by copper concentration. The parameters determined from the PFS measurements, including positive and negative coercive bias, V_p and V_n, coercive bias, E_c, maximum and remanent switchable responses, R_s and R_0, all increase with the copper concentration.

1. Introduction

Zinc oxide (ZnO) is a well-known semiconducting material with many promising properties and applications. Those properties include resistive switching [1], piezoelectric property [2], polarization switching [3] and magnetic property [4]. Recently, polarization switching properties has been studied in detail in ZnO doped with Li, Mg, or V [6–8], and this property suggests that ZnO based materials can be potentially used as memory devices, as the polarization switching refers to the 180° phase angle changes and this term is usually use to describe general behavior in traditional ferroelectric materials. However, ZnO based materials are generally not considered as ferroelectric materials, in order to avoid any confusion, in this paper, "polarization rotation" is used to describe the polarization phase angle changes and "180° polarization rotation" refers to that the phase angles have changed approximately 180° by this polarization rotation processes. Among the doped ZnO materials, copper-doped ZnO (ZnO:Cu) has been studied extensively because the Cu ions are electron traps in ZnO film and increase the resistivity so that the ZnO can be tuned from semiconductor to insulating-like material [5,6]. Furthermore, it was also observed the mutual coupling of the ferromagnetic and 180° polarization rotation in the ZnO:Cu film as well as Cu and Li codoped ZnO [7–10]. The large difference in ionic radii between the host Zn ions (0.74 Å) and dopants could increase the ionic bond and altered the lattice structure; and these might attribute to the polarization rotation behavior in the doped ZnO materials [7,11,12]. In addition, the intrinsic defects, such as oxygen vacancy (V_O) might play an important role for the polarization rotation behavior of the un-doped ZnO [13–15]. Theoretically, ZnO has non-centrosymmetric structure that consists of bilayers of alternating positively and negatively charged ions, in which can lead to a spontaneous polarization [13]. However, the origin of the polarization rotation behavior in ZnO based materials is still under vociferous debate. The relative high conductivity of these non-centrosymmetric compounds has hindered the macroscopic piezo-/ferro-electric measurements because the applied electric

* Corresponding author.
E-mail address: mpezk@nus.edu.sg (K. Zeng).

http://dx.doi.org/10.1016/j.actamat.2016.10.051
1359-6454/

field can be screened by electrons. It is also argued that the arising of the 180° polarization rotation or abnormal dielectric change was originated from the space charge or the presence of the moisture during the measurement [16–18].

Therefore, it urges to investigate the polarization rotation behavior and the underlying mechanisms in ZnO:Cu thin films. In this work, the Piezoresponse Force Microscopy (PFM) based techniques are used. PFM is a powerful technique to visualize the domain structure, measure the deformation under an external electric field, and detect the nanoscale polarization switching behavior in traditional piezo-/ferro-electric materials [19]. For this study, the ZnO:Cu thin films are prepared with Cu concentration from 0 to 12 at.% as the maximum Cu percentage in the ZnO:Cu thin films could be up to 12 at.% [7]. ZnO:Cu thin films with the content of ~2% V_O are prepared in an oxygen deficient environment according to our previous study [20]. It should be mentioned that, in the PFM-based measurements, the domain structure of the as-grown ZnO:Cu films are characterized by using the BE-PFM (Band-Excitation PFM) technique since this technique can measure the nanoscale amplitude, domain orientation, resonant frequency (contact stiffness), and the energy dissipative by tracking the resonance frequency in a pre-defined frequency range [21–23]. This method can systematically investigate the interplay between the domain structure, contact stiffness, and energy dissipation in the ZnO film, and it can open pathways to the ZnO-based device applications. Furthermore, the polarization rotation behaviors are studied by applying the DC poling processes in certain areas using the DART-PFM (Dual AC resonance tracking PFM) technique [24]. In the study of the V_O effects on the polarization rotation, PFM is further engaged in its spectroscopy mode (PFS) on the samples annealed in the ambient air and high vacuum conditions, respectively. In addition, Switching Spectroscopy PFM (SS-PFM) measurements are conducted on the samples with different Cu percentages to investigate the Cu concentration effects on the polarization rotation. The experiments in those optimized samples can clarify the concerns on the possible mechanisms of the 180° polarization rotation in ZnO based materials. This study can therefore provide the detail information on the application of doped ZnO as potential memory devices.

2. Materials and experiments

2.1. Samples preparation

Undoped ZnO and ZnO:Cu (2 at.%, 8 at.%, 12 at.%) thin film samples (with a nominal thickness of 240 nm) were deposited on commercial $Si/SiO_2/Ti/Pt$ substrate by pulsed-laser deposition (PLD) technique with a KrF excimer laser operating at 248 nm and a Florence of 1.8 J cm^{-2}. Optimized parameters were used to prepare the ZnO:Cu targets with different copper concentrations according to our previous study [7]. The oxygen partial pressure during film deposition was kept at 2×10^{-4} Torr. The deposition temperature was 600 °C. The substrate was commercial Si wafer with pre-deposited multilayers of 300 nm SiO_2 layer, 50 nm Ti layer and finally with 150 nm Pt layer (Addison Engineering, Inc. CA, USA). To confirm the macroscopic polarization rotation in ZnO:Cu films, one sample was also deposited with Pt top electrodes. The diameter of the Pt top electrodes was 150 μm. The schematic diagram of the film sample is presented in Fig. S1(a) (Supporting Information). The details sample preparation can be referred to the previous study [7]. To study the oxygen vacancy effects, samples were annealed in the ambient air and high vacuum respectively. The high vacuum was 1×10^{-5} mbar. All of the annealing temperature was at 650 °C. The annealing duration was 2 h.

2.2. Characterization

The X-ray diffraction (XRD) was used to characterize the structure of the ZnO:Cu films. The results confirmed that the crystals textures of ZnO:Cu (2 at.% and at.8%) films are fully crystallized and mainly oriented with (002) direction (Fig. S2, Support Information). The ZnO:Cu (12%) film also shows a fully crystallized structure. However, the limit of solid solubility of Cu has been exceeded and the peaks corresponding to CuO secondary phase can be observed (The inset of Fig. S2, Supporting Information). In addition, in order to determine the changes of the oxygen vacancies, the photoluminescence (PL) measurements were conducted with a laser excitation wavelength of 325 nm on ZnO:Cu films to determine the optical properties and native defects.

During the BE-PFM measurements, the dynamics of the AFM cantilever tip-sample interaction may be represented by damped simple harmonic oscillator (DSHO) model [25–27]. The parameters, including amplitude, A_0, resonant frequency, ω_0, quality-factor, Q of this model are expressed by the below equations:

$$A(\omega) = \frac{\omega_0^2 A_0}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \left(\omega_0 \omega / Q\right)^2}} \tag{1}$$

and

$$\varphi(\omega) = \tan^{-1} \frac{\omega_0 \omega}{Q\left(\omega_0^2 - \omega^2\right)} + \varphi_0 \tag{2}$$

By putting cantilever oscillation amplitudes and phases into these two equations, the parameters, such as piezoresponse, amplitude and phase, ($A_0 \varphi_0$), contact resonance frequency ω_0, and energy dissipation Q can be quantified and displayed by 2D images simultaneously. It should be noted that these parameters are independent. The resonance frequency is primarily determined by the tip-surface contact properties, i.e., it provides a measurement of conservative tip-surface interactions. The amplitude and phase depend on the driving force and the polarization state of the materials, whereas the Q-factor (or peak width) is a measurement of dissipative tip-surface interactions. During the BE-PFM measurements, the cantilever was excited and the responses were detected in a pre-defined band of continuous frequencies of 20 kHz, in which the resonant frequency was approximately in the middle of the frequency band. In this study, an AC drive voltage of 2.5 V was applied to the tip for the BE-PFM measurements.

In the study of the polarization rotation behavior, poling processes with bipolar DC biases (±15 V and ±18 V) were applied. The DC poling process was achieved by applying a bias to the conductive tip, and the bottom Pt electrode of the sample was grounded. DART-PFM was then conducted on the poled area to study the polarization rotation induced by the poling process.

To further study the polarization rotation, the PFM was conducted in its spectroscopy (PFS) mode, in which pulse square waves superimposed with triangular waveforms were applied to the tip at a frequency of 200 mHz (Fig. S3, Support Information). The duration of each square pulse was 25 ms. Using the PFS technique, the amplitude loop, A(E), and the phase loop, φ(E), were acquired at bias-off state. The piezoresponse hysteresis loop, P(E), was calculated with the formula of $PR(E) = A(E)^*\cos[\varphi(E)]$ (Fig. S4, Support Information). With the use of the high-voltage PFM module, the magnitude of the applied voltage was increased until the saturated hysteresis loops were obtained. By analysing the piezoresponse hysteresis loops, several parameters were obtained (Fig. S4, support information), including: the imprint bias, $E_{im}=(|V_p|-|V_n|)/2$; built-in field, $E_{built-in} = 2E_{im}$; coercive bias, $E_c=(|V_p|+|V_n|)/2$; remanent