Influence of annealing treatment on electric polarization behaviour of zinc oxide films grown by low-power dc-unbalanced magnetron sputtering

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Abstract. We study the annealing effect of highly oriented zinc oxide (ZnO) films grown by low-power dc-unbalanced magnetron sputtering (DC-UBMS). In this study, we compare the structural and electrical properties of thermal-annealed ZnO films (ann-ZnO) and as-growth ZnO films (ag-ZnO) by using x-ray diffraction (XRD), scanning electron microscopy (SEM) and RT66A standardized ferroelectric test system. We found that the ag-ZnO films and the ann-ZnO films show a high orientation in (101) plane. SEM images indicate that annealing treatment at 600°C in nitrogen ambient promote the surface atomics arrangement and convert a non-uniform ag-ZnO surface to relatively flat ann-ZnO film surface. Also confirm that the ag-ZnO and the ann-ZnO films have strong ferroelectric characteristics, while the values of remnant polarization and polarization saturation are almost similar. The electric coercivity ($E_c$) of the ann-ZnO film is larger than ag-ZnO films as an indication of structural defects elimination. Our results are beneficial for high energy electric-based storage devices with less depolarized structural systems.

1. Introduction

Ferroelectric materials were widely used for memory storage application and piezoelectric-based devices because it has a high electric polarization. The high electric polarization can be produced from a material that have non-centrosymmetric structure, such as Pb(Zr,Ti)O$_3$ (PZT) [1, 2], BiFeO$_3$ (BFO) [3, 4] and (Pb,La)(Zr,Ti)O$_3$ (PLZT) [5]. In memory storage application, electric polarization and electric coercivity were the important parameters to measure the quality of the storage devices. Non-volatile memory storage devices developed using material that has high electric coercivity value because it has a high electric energy storage and less depolarized [6]. Among the non-centrosymmetric material, the zinc oxide (ZnO) system was not widely used and still in the development of research for memory storage material systems because ZnO system has lower electric polarization and electric coercivity [7-11]. Many studies have been done to find out how the value of the electric coercivity can be improved, such as material structure modification [12], doping treatment [13], and arrangement of films growth [14].

Sputtering is one of many methods which were widely used for film fabrications. A high power deposition was required to produce high sputter yield and deposition rate [15]. In this work, as an attempt to increase the electric polarization and coercivity, we fabricated ZnO films by using a low-power sputtering deposition to provide a longer time for atomics arrangement on the substrate surface.
and promote a good orientation on a particular plane. Further studies of the polarization behavior of ZnO material will provide a good understanding of the utilization of this material for non-volatile memory storage devices and ferroelectric-based material application.

2. Experiment methods

Zinc oxide (ZnO) sputtering target was produced from pressed ZnO powder (99.99%, Sigma Aldrich) by using a mold with a diameter of 2.8 cm. Silicon (100) was used as the substrate which has been cleaned by using Radio Corporation of America (RCA) standard cleaning at 80°C. The ZnO films have been grown by using a dc-unbalanced magnetron sputtering (DC-UBMS) with following the parameters:

| Parameters                   | value | unit |
|------------------------------|-------|------|
| temperature                  | 300   | °C   |
| deposition power             | 4.5   | watt |
| chamber pressure             | $3 \times 10^{-2}$ | mbar |
| gas flow (argon)             | 100   | sccm |
| growth time                  | 1     | hour |

To study the annealing effect to the structural and electrical properties of the ZnO films, post-annealing treatment (600°C for 10 minutes) has been performed in a nitrogen ambient. In previous studies have been explained that the annealing temperature of 600°C films showed a high density and uniformity [16]. Annealing treatment was not performed with temperatures above 600°C to avoid the effects of deformation on the Si substrate [17]. The substrate deformation was avoided so that there is no involvement of the influence of the deformation on the properties of the ZnO films. The crystalline phase and the morphology of the ZnO films were characterized using x-ray diffraction (X-RD), analytical brand Bruker, tube anode: Cu, generator tension [kV]: 40, generator current [mA]: 30, alpha1 wavelength [Å]: 1.54060, alpha2 wavelength [Å]: 1.54439, and scanning electron microscopy (SEM), analytical brand JEOL JSM-6510, voltage [kV]: 15, magnification[x]: 20.000, respectively. The determination of the crystalline phase and the lattice parameter were performed with the help of software X’Pert Highscore Plus and PowderCell for Windows (PCW). Moreover, RT66A standardized ferroelectric test system, signal mode: single triangle wave, timing [ms/step]: 1.1, number of steps: 500, $V_{\text{max}}$ [V]: 5.00, was used to study the type of hysteresis curve and investigate behaviors of the electric polarization, including remnant polarization, polarization saturation, and electric coercivity of the ZnO films.

3. Results and discussions

As compared by inset in Figure 1, our ZnO films have a highly oriented wurtzite phase in the (101) plane. Another phase was found in the ag-growth ZnO film (ag-ZnO), where diffraction peak O$_2$ appears in the (012) plane. It showed that our system did not have a pure phase of the ZnO. Another treatment was performed on the ZnO film where the ZnO film was annealed at a temperature of 600°C for 10 minutes (ann-ZnO). The annealing treatment causes the crystallinity of the ZnO film enhanced, as indicated by O$_2$ peak vanishes and convert the multi-phase ZnO films to the single-phase ZnO films. We note that the crystallinity of the ZnO films increased due to the recrystallization process during annealing, as indicated by intensity of the diffraction peak increases. We report that the annealing treatment promotes a lattice strain in $a$-axis direction. The lattice parameters of the ZnO films was observed by using PowderCell software for Windows (PCW). The lattice parameters of the ag-ZnO film are $a = 3.2030\text{Å}$ and $c = 5.2510\text{Å}$, while the lattice parameters of the ag-ZnO film are $a = 3.2307\text{Å}$ and $c = 5.1010\text{Å}$. In the previous study, the lattice strain in the ZnO films promoted the polarization effect when the external field applied to the system. This polarization mechanism associated with the reduction of binding energy of the atoms so that the material easier polarized [18].
Figure 1. Diffraction pattern of the ZnO films on Si substrate with 1 hour deposition; as growth (red-line) and annealed (green-line). The inset figure shows diffraction pattern on multi-ordered ZnO films grown by dc-unbalanced magnetron sputtering with other parameters (power = 10 W).

Figure 2. (a)-(b) SEM image of the ag-ZnO and ann-ZnO films (c) the ferroelectric hysteresis curve of the ag-ZnO (red circle-line) and ann-ZnO (green rectangular-line) films.

The applied thermal energy contributed in reducing defect and internal stresses which drive diffusion mechanism and atoms rearrangement so that the ZnO progresses towards its equilibrium state. As shown in Figure 2(a)-(b), the ag-ZnO film has grain boundaries which act as a surface defects. It was showed that the grains were not uniformly distributed on the substrate. Otherwise, the ann-ZnO film has a flat profile with the absence of grain boundaries.

Further analysis was performed to investigated electric properties of the ZnO films by using RT66A standardized ferroelectric test systems that specifically characterize the hysteresis pattern of...
the materials. Figure 2(c) shows the hysteresis curves of the ag-ZnO and ann-ZnO films. We confirmed the ZnO films have a ferroelectric hysteresis curve profile, which was supported by the saturation curve and large electric coercivity value. The important point in this study is that our systems have a similar value between remanent polarization ($P_r$) and polarization saturation ($P_s$). This profile was contributed by high crystal orientation of the films, as reported in previous work. Similar hysteresis patterns are shown by other systems that also has a high orientation [19]. The annealing treatment on the ZnO films induced the increasing of electric coercivity ($E_c$). We have summarized $P_r$, $P_s$, and $E_c$ in Table 2.

| Samples  | $+P_r$ / $-P_r$ ($\times 10^4 \mu$ C/cm$^2$) | $+P_s$ / $-P_s$ ($\times 10^4 \mu$ C/cm$^2$) | $+E_c$ / $-E_c$ (kV/cm) |
|----------|------------------------------------------|------------------------------------------|-------------------------|
| ag-ZnO   | 11.77 / -11.85                           | 11.78 / -11.85                           | 1.36 / -1.34            |
| ann-ZnO  | 11.77 / -11.85                           | 11.78 / -11.85                           | 2.50 / -2.20            |

The annealing treatment contributes to the enhancement of the electric coercivity due to the absence of the grain boundaries, as reported in the previous discussion. The grain boundary is a low permittivity region [20]. The absence of the grain boundaries caused by densification during annealing which drive the interaction between atoms increases. As a result, when the film has polarized it will be more difficult depolarized. The behavior of the electric coercivity which was larger after the annealing showed that our systems have hard-ferroelectric properties. The enhancement of the electric coercivity was associated with an improvement ability of the ferroelectric material to store electrical energy which is required for non-volatile memory storage devices.

4. Conclusions
The annealing treatment causes the crystalline phase of the ZnO films containing $O_2$ and wurtzite ZnO phase to become single phase wurtzite ZnO. The films are highly oriented in (101) plane which contains the lattice strain in $a$-axis. In addition, the annealing treatment promotes flat profile on film accompanied by the absence of grain boundaries. We report that the absence of grain boundaries causes the ZnO films have a hard ferroelectric property, which indicated by the similar value between the $P_r$ and $P_s$ and enhancement of the $E_c$.

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