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Deposition of Polycrystalline ZnO Films by Two-Step Method and Characterization of Thermal Annealing Effects

Jin-Bock LEE, Myung-Ho LEE, Hye-Jung LEE, and Jin-Seok PARK
Department of Electrical Engineering, Hanyang University
1271 Sa 1-dong, Ansan, Kyonggi-do 425-791, South Korea

ABSTRACT

Polycrystalline ZnO thin films were deposited on SiO_2/Si(100) substrate using RF magnetron sputtering. The film deposition performed in this work was composed of following two procedures; the 1st-deposition for 30 min without oxygen at 100 W and the 2nd-deposition with oxygen in the range $O_2/(Ar+O_2) = 10\sim50$ %. Deposited ZnO films revealed a strongly c-axis preferred-orientation (the corresponding texture coefficient ~ 100 %) as well as a high resistivity ($> 10^7$ Ωcm). It was also observed that the crystallite size of ZnO was noticeably increased by thermal-annealing.

INTRODUCTION

With the rapid progress of communication technology, there has been an increasing interest in developing thin-film band-pass filters, including surface acoustic wave (SAW) filters and film bulk acoustic resonators (FBARs) [1,2]. These devices require the thin films to have c-axis preferred orientation, excellent crystallinity, and high electrical resistivity. Polycrystalline ZnO has been considered as one of promising materials for such device applications. The sputtering method has widely been used to obtain the c-axis oriented ZnO film. Very often the impurities (Li, Cu, etc.) and/or the oxygen have been injected during deposition to increase the resistivity of ZnO [2-4]. However, it seems that there is a trade off between the c-axis preferred orientation and the electrical resistivity of ZnO.

In the present study a new deposition technique for improving both the c-axis preferred orientation and the resistivity of ZnO film is proposed. In addition, the effect of thermal-annealing on the ZnO film is also discussed.

EXPERIMENTAL DETAILS

ZnO films were deposited on SiO_2/Si substrate using RF magnetron sputtering. During deposition the substrate was rotated at a low speed of 5 rpm to enhance the thickness uniformity of deposited films. The deposition method proposed in this work consisted of the 1st-step deposition without addition of oxygen and the 2nd-step deposition with addition of oxygen in the range $O_2/(Ar+O_2) = 10\sim50$ %. In addition, thermal treatment on deposited ZnO films was performed with varying the temperature from RT to 800 °C. Details of deposition and thermal-annealing conditions are summarized in Table 1.

Texture coefficient (TC) values for c-axis (002)-orientation and crystallite sizes of ZnO films were evaluated from the XRD (X-ray diffractometer, Bede D3 system) spectra. I-V characteristics were measured to calculate the resistivity of ZnO, in the voltage range 0 ~ 1 V with 0.01 V-step by using a pico-ampere meter/DC voltage source (HP 4140B). Raman spectra (Jobin Yvon T64000) were also monitored for all ZnO films to identify the oxygen-deficiency in the film.

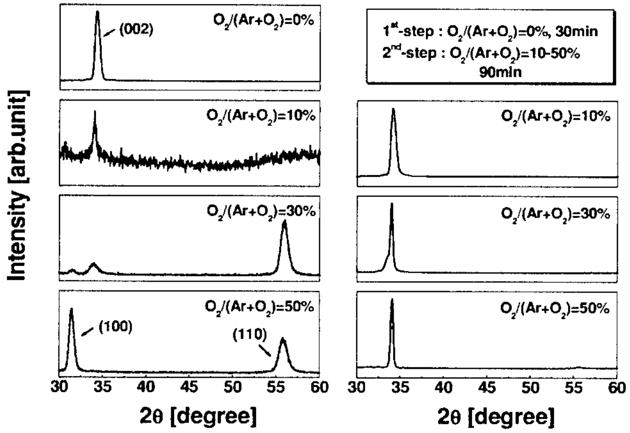
Table 1 Conditions for two-step deposition and thermal-annealing

	One-step method	Two-step method	
		1st-step	2nd-step
$O_2/(Ar+O_2)$ [%]	10~50	0	10~50
RF power [W]	100	100	100
Pressure [mTorr]	5	5	5
Sub-temp [°C]	200	200	200
Depo-time [min]	120	30	90

Thermal annealing	
Ann-temp [°C]	200, 400, 600, 800
Ann-time [min]	120
Ambient	Air

RESULTS AND DISCUSSION

Figure 1 (a) and (b) shows the XRD peak patterns measured from the ZnO films deposited by using the conventional one-step method and the proposed two-step method, respectively. In case of using the one-step deposition the (002)-orientation peak was relatively the most intense when the ZnO film was deposited without oxygen. However, as the amount of added oxygen was increased, the (002)-peak intensity was lessened and finally disappeared at $O_2/(Ar+O_2)$ = 50 %. It seemed that oxygen neutrals were embedded in lattice sites or interstitials during the growth of films, which caused a strain and change in the lattice constant and orientation of film [5].



(a) (b)

Figure 1. XRD peak patterns of deposited ZnO films; (a) films prepared by one-step deposition and (b) films prepared by two-step deposition, respectively

On the other hand, as shown in Figure 1 (b), the ZnO films deposited using the proposed method revealed a highly (002)-oriented growth nature, irrespective of $O_2/(Ar+O_2)$ ratio used in the 2nd-deposition step. It has generally been considered that the matching in the lattice parameter and crystal structure between the film and the substrate, on which the film is grown, may significantly affect the growth habit of the film [6]. It should be noted that in the 1st-deposition step of the proposed method the oxygen was not added. The 1st-deposited thin ZnO layer was expected to exhibit a highly (002)-oriented behavior and consequently act as a good substrate for the subsequently-grown 2nd-step ZnO film. This was believed to be one of important reasons why the ZnO films deposited using the two-step method revealed a (002)-preferred orientation with little affected by the oxygen.

The crystallite size estimated from the XRD results was depicted in Figure 2, as a function of $O_2/(Ar+O_2)$ ratio. When the same $O_2/(Ar+O_2)$ ratio was used, the crystallite size of ZnO films deposited by the two-step method was almost twice higher than that of films deposited by the one-step method. This was also attributed due to the reduction of mismatching between the film and the substrate, as already discussed in two-step deposition case. In addition, the crystallite size was observed to decrease with increasing $O_2/(Ar+O_2)$ ratio.

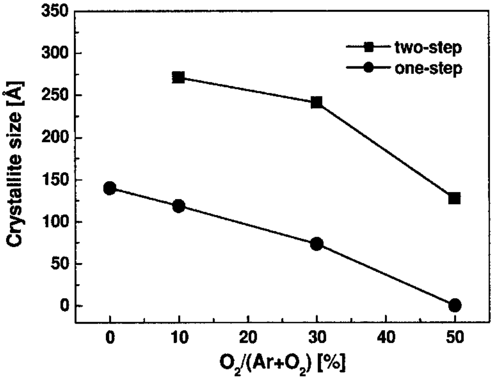


Figure 2. The crystallite size of ZnO films prepared by one-step (●) and two-step (■) method, respectively, as a function of $O_2/(Ar+O_2)$ ratio

Figure 3 shows the electrical resistivity measured for the ZnO films deposited by one-step and two-step method, along with the TC values for (002)-orientation estimated from the corresponding XRD peak patterns as shown in Figure 1. The film deposited using the one-step method without oxygen exhibited a low resistivity ($< 10^6$ Ωcm), while the TC value was almost 100 %. As the $O_2/(Ar+O_2)$ ratio increased, the resistivity rapidly increased, but the TC value significantly decreased. The similar trend regarding the effect of oxygen on the change of resistivity was also observed for the films deposited using the two-step method. However, it should be noted that the (002) TC value was not decreased and kept high, regardless of $O_2/(Ar+O_2)$ ratio. At a typical ratio of $O_2/(Ar+O_2) = 50$ %, the ZnO film deposited using the two-step method showed the resistivity as high as about 2.5×10^9 Ωcm and at the same time revealed a high TC value of about 100 %.

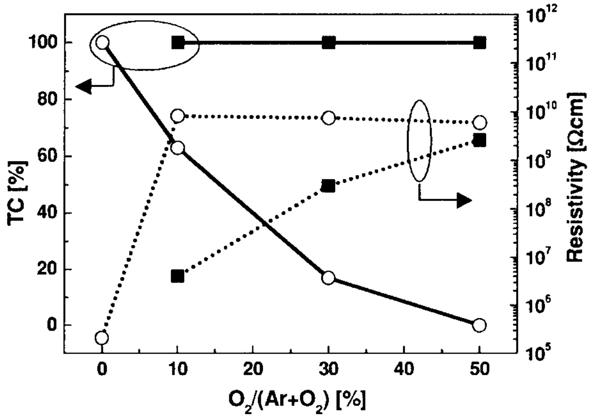


Figure 3. The changes of (002) TC value and resistivity of ZnO films, as a function of $O_2/(Ar+O_2)$ ratio (O: one-step deposition, ■: two-step deposition)

Figure 4 shows the Raman spectra of ZnO films deposited by one-step and two-step methods. It has been known that the peak at 430 cm^{-1} originates from E_2 mode of ZnO associated with wurtzite structure and the peak at 570 cm^{-1} is a contribution of $E_1(LO)$ mode of ZnO associated with oxygen deficiency [7,8]. At the $O_2/(Ar+O_2)$ ratio of 10 % (see Figure 4 (a)), the peak at 430 cm^{-1} was observed to be dominant for all the films. On the other hand, at the $O_2/(Ar+O_2)$ ratio of 50 % (see Figure 4 (b)) the peak at 430 cm^{-1} weaken for both films, but the peak at 570 cm^{-1} emerged very intense, especially for the film deposited by two-step. This indicated that a considerable amount of oxygen-vacancies were present in the ZnO film deposited by two-step.

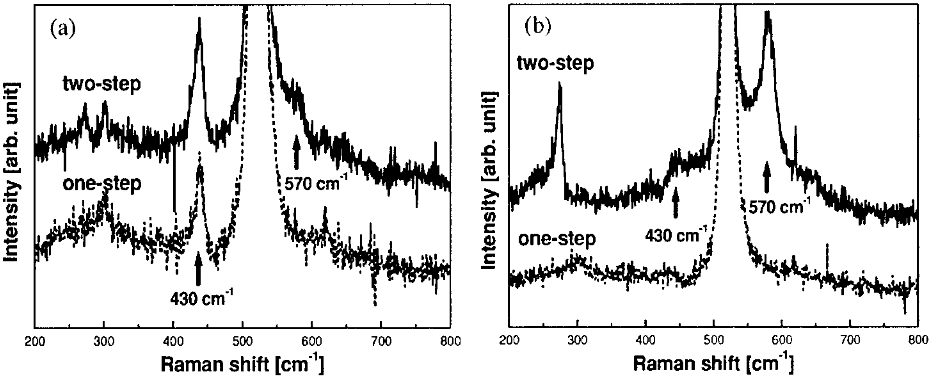


Figure 4. Raman spectra of ZnO films deposited using the one-step and two-step method : (a) $O_2/(Ar+O_2)$ = 10 % and (b) $O_2/(Ar+O_2)$ = 50 %, respectively

Thermal annealing on the deposited ZnO films was performed in air at 200 °C ~ 800 °C for 120 min. The changes of crystallite size and resistivity were measured as a function of annealing temperature. As shown in Figure 5 (a) and (b), with increasing the annealing temperature the crystallite size monotonically increased and the resistivity significantly decreased. This was ascribed due to the enhanced carrier mobility which was resulted from the reduction of grain boundary defects [9,10]. It may also be noted that the change in the crystallite size and resistivity was larger for the film deposited at $O_2/(Ar+O_2)$ = 10 % by using the two-step method, compared with the other films. This was explained by analyzing the Raman spectra obtained from those films. Figure 6 indicated that for the two-step deposited films the peak related to the oxygen-vacancy (at 570 cm^{-1}) noticeably decreased as the annealing temperature increased, while it rarely changed for the one-step deposited films. It was previously reported that the oxygen deficiency could be reduced by thermal annealing because some of oxygen atoms in air were combined with atomic Zinc in the ZnO film [11]. In addition, the (002) TC values of ZnO films were observed to be scarcely changed after thermal annealing.

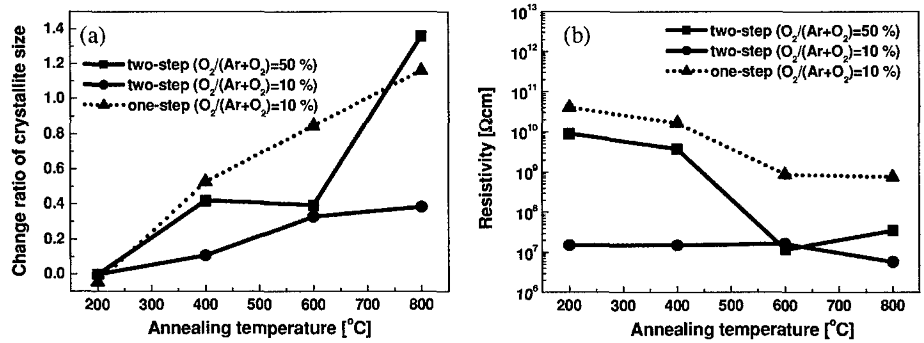


Figure 5. Effects of thermal annealing on the change of (a) crystallite size and (b) resistivity of ZnO films deposited by one-step and two-step methods

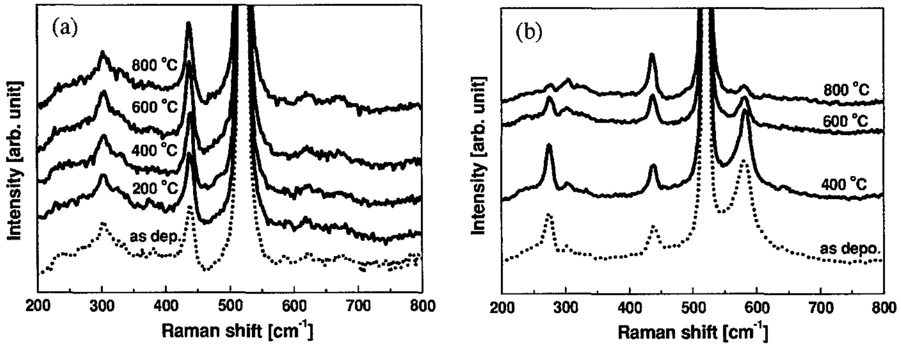


Figure 6. Effects of thermal annealing on the Raman spectra of ZnO films deposited by (a) one-step method and (b) two-step method

CONCLUSIONS

It was shown from this work that a highly resistive (> 10^9 Ωcm) and (002)-oriented (TC ~ 100 %) polycrystalline ZnO film could be achieved by using the proposed two-step deposition method. XRD peak patterns showed that, in contrast to the films deposited through the conventional one-step process, the films prepared using the two-step deposition method were grown along the (002) preferred-orientation even at a high $O_2/(Ar+O_2)$ ratio. It was also found from Raman spectra that the variations of crystallite size and electrical resistivity due to thermal annealing were closely related to the enhancement of crystallinity of ZnO films.

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