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Effect of thickness on properties of ZnO film prepared by direct current reactive magnetron sputtering method

C.-S. Baek[a,b], D. H. Kim[c], H. H. Kim[b] and K.-J. Lim[a,*]
[a]College of Electrical and Computer Engineering, Chungbuk National University, Cheongju, Chungbuk 361-763, Korea
[b]Department of Display Engineering Division, Doowon Technical University College, Paju, Kyonggi 413-861, Korea
[c]Department of Physics, Dongguk University, Seoul 100-715, Korea

Effect of thickness on ZnO properties including the compositional ratio and crystallinity has been systematically investigated using a variety of characterization tools of x-ray diffraction, field emission scanning electron microscopy, x-ray fluorescence and x-ray photoelectron spectroscopy. Interestingly, it was observed that ZnO films below 80 nm in thickness were in oxygen deficiency, while the oxygen ratio was increased in the films above the thickness, although the compositional ratio of ZnO film was not linearly varied with increasing film thickness. Also, ZnO crystallinity, which is characterized by (002) diffraction pattern, was clearly improved with increasing film thickness. The properties of ZnO film with different sputtering time and the nature of direct current reactive sputtering process were discussed in terms of compositional ratio, especially oxygen ratio in ZnO film.

Key words: ZnO, Crystallinity, Compositional ratio, Films.

Introduction

Zn-based oxides are a prospective semiconductor materials for a wide range of applications including thin film transistor in active matrix liquid crystal display and active matrix organic light emitting diode [1], highly transparent conductive oxides for organic solar cell and optoelectronic devices owing to their wide energy band gap (~ 3.3 eV) [2], large exciton binding energy (~ 60 meV) at room temperature, high transparency at visible light, abundant and non-toxic properties [3-5]. For this reasons, recently, Zn-based oxide semiconductors have been intensively investigated for various applications. The techniques such as metal organic chemical vapor deposition [6], direct current (dc) magnetron sputtering [7], radio frequency magnetron sputtering [8], spray pyrolysis deposition [9] and pulsed laser deposition (PLD) [10] have been developed to grow ZnO and Zn-related compound oxides with high film quality. Among these methods, dc reactive sputtering method has received much attention because high deposition rates can be obtained on large area substrates and the composition of the films can be easily controlled [11]. The detail behaviors, which are analyzed by using the compositional ratio of ZnO films, of dc reactive magnetron sputtering method with varied process duration have not been reported until now.

In this paper, the effect of thickness on ZnO properties, such as the compositional ratio and crystallinity, was investigated by various characterization techniques. The properties of ZnO film and the behavior of dc reactive sputtering process with different sputtering time were systematically discussed in terms of compositional ratio of ZnO film.

*Corresponding author:
Tel : +82-43-261-2424
Fax: +82-43-263-2419
E-mail: kjlim@chungbuk.ac.kr

Experimental

Films preparation

200 nm thick amorphous SiO_2 layer was deposited on n-type Si substrate by a plasma enhanced chemical vapor deposition method at 330 °C. Before deposition of ZnO thin film, the SiO_2 layers grown on Si substrates were ultrasonically cleaned with acetone, ethyl alcohol, and de-ionized water for 10 min, respectively. To deposit the ZnO films with different thickness, both Ar and O_2 gas were flowed into the sputtering chamber. The Zn metal target with purity of 99.9999% and 2 inch in diameter was used to sputter Zn ions. The total working pressure and power during sputtering process were kept at 40 mtorr and 50 W, respectively. Under these experimental conditions, ZnO films with thickness ranging from 30 nm to 130 nm were deposited by reactive method at room temperature. The sputtering time was varied between 10 min and 60 min. Above all, all of ZnO films did not experience any post annealing process for investigating the properties of ZnO prepared at room temperature.

Characterizations

The ZnO thicknesses were measured using a surface profiler meter (α-step, Ambios, XP-2) after patterning of ZnO . To examine the crystallinity of ZnO thin films with different thickness, x-ray diffraction (XRD, DIP-2020, MAC science) with a Cu Kα_1 source was performed at room temperature. Also, the size of grain formed on ZnO surface was evaluated from analysis of field emission scanning electron microscopy (FE-SEM, LEO-1530, Carl Zeiss) at an operating voltage of 30 KV. To investigate the compositional ratio of ZnO films with different thickness, x-ray fluorescence (XRF, S4, Bruker) was carried out. In order to study the relationship between oxygen vacancies and compositional ratio of the ZnO films, x-ray photoelectron spectroscopy (XPS, ESCALAB 210, VG Science) with a monochromatic Al Kα ($h\nu$ = 1486.6 eV) source was performed and O_{1s} spectra from ZnO films with different thickness were analyzed.

Results and discussion

Fig. 1 shows XRD (002) patterns for ZnO films with thickness ranging from 30 nm to 130 nm. The SiO_2/Si substrates, as starting materials, were used. The crystallinity of ZnO films prepared by dc reactive sputtering method was clearly improved with increasing film thickness. Therefore, thickness of ZnO film is an important parameter which affects on the crystallinity of ZnO. Interestingly, other patterns such as (100), (101), (103) and (112) from all ZnO films were obtained from XRD analysis as shown in inset of Fig. 1. However, only the intensity of (002) plane was increased as increasing film thickness, while there was no significant difference in intensity for other patterns, irrespective of film thickness. It is believed that thickness of ZnO prepared by dc reactive sputtering method can mainly affect only on the growth of (002) orientation which is the preferred growth plane.

Fig. 2 illustrates grains on ZnO surface obtained from FE-SEM measurements. The grain size was clearly increased as increasing film thickness as shown in Fig. 2(d). Average grain size of 30 nm thick ZnO film was about 28.4 nm. The grain size was extracted from SEM analysis. As increasing film thickness, 38.7 nm and 53.2 nm in grain size were estimated for 80 nm and 130 nm thick ZnO film, respectively. The increase of grain size indicates the improvement of crystallinity of the film [12]. Therefore, in terms of the crystallinity of ZnO, the SEM analysis is well consistent with that of XRD. As a result, thickness of ZnO film plays an important role in changing the crystallinity. So, it is necessary to consider the correlation between thickness of film and crystallinity in fabricating various ZnO-based devices.

Table 1 shows the compositional ratio of ZnO films with different thickness. These ratios were obtained from XRF analysis. The compositional ratio of ZnO was not linearly varied with increasing film thickness. However, it was found that ZnO films with thickness below 80 nm were in oxygen deficiency, while the oxygen ratio was increased to 0.92 at 130 nm thick ZnO film. This fact indicates that the contents of oxygen in dc reactive sputtering can be varied with the sputtering time. Therefore, the thickness of film can significantly affect on both the crystallinity and compositional ratio.

Fig. 3 shows XPS spectra for ZnO films with different thickness. The O_{1s} peaks from the films were analyzed by Gaussian fitting. The peak located at the

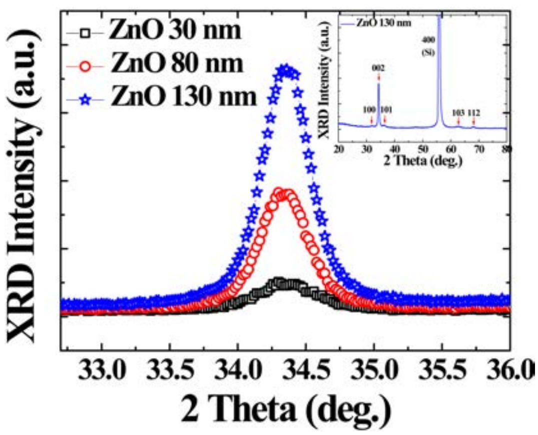

Fig. 1. XRD (002) patterns for ZnO films with different thickness. The inset shows the XRD patterns obtained in 2θ range from 20 to 80 ° of 130 nm thick ZnO film.

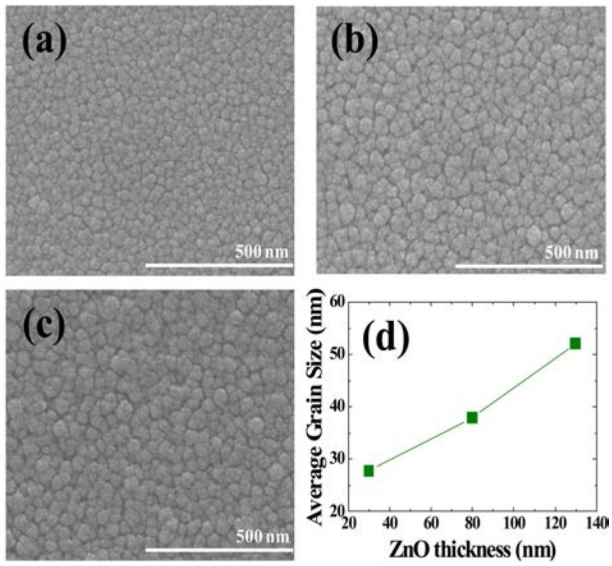

Fig. 2. FE-SEM images for (a) 30 nm (b) 80 nm, and (c) 130 nm thick ZnO film. (d) The variation of average grain size as a function of film thickness.

Table 1. The compositional ratio of ZnO films with different film thickness. The ratio was obtained from the XRF data.

ZnO thickness (nm)	Zn (%)	O (%)	Zn : 0
30	1	0.76	1 : 0.76
80	1	0.67	1 : 0.67
130	1	0.92	1 : 0.92

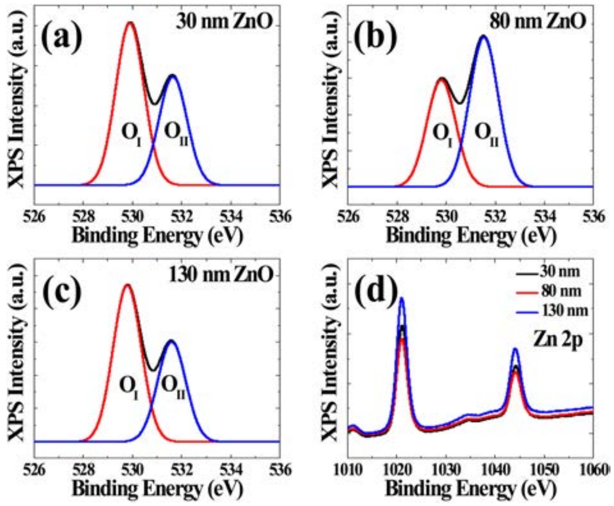

Fig. 3. XPS O_{1s} spectra for (a) 30 nm (b) 80 nm, and (c) 130 nm thick ZnO film. (d) Zn 2p spectra with different film thickness.

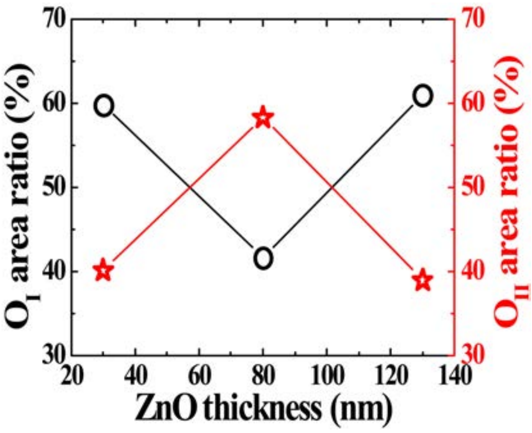

Fig. 4. The variation of O_I and O_{II} area ratio for ZnO films with different film thickness.

binding energy of ~ 529.0 eV (O_I) is due to oxygen ions in stable ZnO structure, while the peak located at ~ 531.9 eV (O_{II}) in binding energy is attributed to oxygen ions in oxygen deficient ZnO film [13]. Also, it was reported that the areal ratio of O_{II} peak (O_{II}/O_{Total}) indicates the relative quantity of oxygen vacancies in Zn based oxide film [14]. As a result, the ratio of O_{II} peak for 30 nm, 80 nm and 130 nm thick ZnO films was 40.2%, 58.3% and 39.0%, respectively, as shown in Fig. 4. 80 nm thick ZnO has larger oxygen vacancies compared with that of other ZnO films. This indicates that the 80 nm thick ZnO film has less oxygen content. This result is well matched with that of XRF. Therefore, the compositional ratio of the room temperature processed ZnO films with different thickness was clearly estimated by XRF and confirmed by XPS analysis. As shown in Fig. 4, the variation in ratio of O_I peak area was well consistent with that of O_{II} peak. The increase of oxygen vacancies induces the reduction of Zn-O bonding. The Zn 2p peaks from ZnO films with different thickness were exhibited as shown in Fig. 3(d).

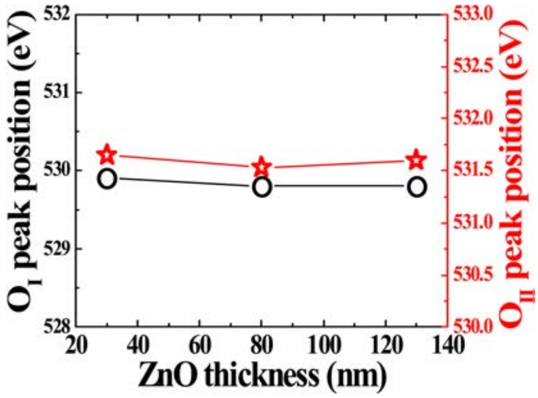

Fig. 5. The variation of O_I and O_{II} peak position for ZnO films with different film thickness.

Interestingly, the variation in intensity of Zn 2p peaks was well consistent with areal ratio of O_{II} peak.

Fig. 5 illustrates the variations of O_I and O_{II} peak position for ZnO films with different thickness. It was found that there was no significant difference in two kinds of peak position with increasing film thickness. The Zn 2p peaks with different thickness also had constant position in binding energy.

Conclusions

In this study, ZnO films with different thickness have prepared by a dc reactive magnetron sputtering method at room temperature. Thickness has a decisive effect on crystallinity and compositional ratio of ZnO film. Above all, the crystallinity of ZnO was clearly dependent on film thickness, while the compositional ratio was not linearly varied with film thickness. However, the compositional ratio of ZnO was distinctly affected on film thickness. Therefore, it is necessary to consider the relationship between film thickness and film properties, such as crystallinity and compositional ratio, in fabricating various devices using Zn-based oxide semiconductors.

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