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Research Paper

Effect of Heat Treatment Method on Properties of ZnO Thin Films Deposited by RF Magnetron Sputtering

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Abstract ZnO thin films which were deposited by RF magnetron sputtering system were annealed by furnace and in-situ heat treatment methods. We investigated the effect of heat treatment method on physical properties of ZnO thin films. The structural and optical properties of ZnO thin films were improved by heat treatment. Through the annealing treatment of ZnO film by furnace, the good crystallinity and ultraviolet emission were obtained. These results are attributed to the improved formation of Zn-O bond in ZnO thin film annealed at by furnace. We confirm that the formation of Zn-O bond plays an important role in obtaining the excellent structural and optical properties of ZnO thin films.

Keywords: ZnO, Heat Treatment, Crystal Structure, Optical properties, RF Magnetron Sputtering

I. Introduction

Recently, ZnO thin film has been increasing interest in the development of light emitting. ZnO, II-VI Type compound semiconductor, is a direct band gap semiconductor that has the crystal structure of wurzite, a hexagonal form, like GaN, and possesses a wide band gap of 3.37 eV at room temperature. Since it has structural and optical properties similar with GaN, which is currently the most used semiconductor in LED and LD of short wave-length region, numerous researches are being carried out on the development of more stable and economic ZnO based LED [1-3]. Generally, ZnO takes the form of nonstoichiometry compound with the occurrences of defects such as interstitial Zn ion (Zn_i^{2+}) and oxygen vacancy ion (V_O^{2+}) in the annealing and thin film processes due to the big difference of ionic radius between Zn ion and O ion, and the ions from such defects take on the role of donor ion within the crystals and display n-type conductivity [4]. The production of ZnO thin film that has minimal stress and superior stoichiometry is essential for the development and application of ZnO type LED and LD. The structural, electrical, and optical properties of ZnO thin films are readily modified by the addition of annealing. Kim et al have been reported the effect of in-situ annealing temperature on microstructural, elemental and emission properties of MgZnO thin films [5]. Tian et al have been reported the influences of annealing temperature on the structural and optical properties of the ZnO films annealed by furnace [6]. In this study, ZnO thin films were deposited by the RF magnetron sputtering method and annealed by furnace and in-situ heat treatment methods. We report the effect of heat treatment method on structural and optical properties of ZnO thin films.

II. Experimental Procedure

ZnO thin film sample used in this study was deposited in the thickness of about 1.6 μm using 2-inch ZnO target (99.999%) by the RF magnetron sputtering method. 2-inch (0001) sapphire substrate was used to deposit ZnO thin film. The deposition conditions of RF sputtering were base pressure 8.0×10^{-6} Torr, working pressure 15 mTorr, and RF power 210 W. Ambient gas was established with 32 sccm of argon and 8 sccm of oxygen. The deposited ZnO thin films were annealed by furnace heat treatment and in-situ heat treatment at 600°C in oxigen ambient. Both heat treatments were processed for 2 hours. Furnace heat treatment carries out in the external furnace tube, while In-situ heat treatment carries out in the same deposition chamber. The heat treatment temperature of 600°C was selected because the activation temperature of Zn was 430°C.

Atomic force microscope (AFM) was used to observe a surface morphology of ZnO thin film. The crystallinity of ZnO thin films was accomplished through X-ray diffraction (XRD) analysis method. The optical properties of ZnO thin films measured at 30 K by photoluminescence (PL). X-ray photoelectron spectrometer (XPS) was used for the quantitative analysis of Zn and O in ZnO thin films.

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III. Results and Discussions

Fig. 1 is AFM images of as-deposited ZnO thin film and ZnO thin film annealed by furnace and in-situ heat treatment methods. The image scale is 1 μm × 1 μm. The surface morphology and grain size of ZnO thin film annealed by in-situ is similar to that of as-deposited ZnO thin film. The grain size of ZnO thin film annealed by furnace is bigger than that for the other samples. The roughness of ZnO thin films changes by annealing method. The roughness of as-deposited ZnO thin film was 5.17 nm, while the roughness of ZnO thin films annealed by furnace and by in-situ was 4.63, 5.33 nm, respectively. The roughness of sample annealed by furnace displays a smaller value compared to the roughness of thin films with other heat treatment.

Fig. 2 displays the XRD pattern of as-deposited ZnO thin film and ZnO thin film treated by furnace and in-situ heat treatment methods. In all ZnO thin films, a strong peak which is related to the ZnO (002) plane is observed at about 34.4°. These results suggest that the ZnO thin films, without respect to heat treatment method, have a high preferred orientation (c plane) and a high quality. The peak position shift with annealing condition and this shift is due to strain change of ZnO thin films by heat treatment. We obtained the c crystal parameters of our samples using XRD data and calculated the out-plane strain using following equation [7]:

$$\varepsilon_{zz} = \frac{c - c_0}{c_0}$$

where c is the calculated value of the lattice constant and c0 is the bulk vale of the lattice constant (5.185 Å). The out-plane strain of as-deposited ZnO thin film exhibit a compressive strain, while the out-plane strain of ZnO thin films by heat treatment show a tensile strain. The out-plane strain of ZnO thin films is shifted from a compressive to a tensile by heat treatment. This phenomenon is due to compressive strain relaxation of ZnO thin films by heat treatment. In general, ZnO thin film on sapphire is placed under a tensile strain. The full width at half maximum (FWHM) of ZnO (002) peak was reduced after heat treatment. The sample annealed by in-situ has lower value compared to the other samples, and show good crystallinity. The crystallinity of ZnO thin film annealed by in-situ is superior to that of ZnO thin film annealed by furnace. We calculated the average crystallite size, which is the length of the crystal in the direction of the d spacing, using Scherrer's formula [8]:

$$D = \frac{0.9\lambda}{B\cos\theta}$$

where λ is the X-ray wavelength (1.5406 Å), B is the FWHM and θ is the Bragg diffraction angle. The average crystallite size of ZnO thin films increases by annealing process. The results related to XRD measurement are summarized in Table 1.

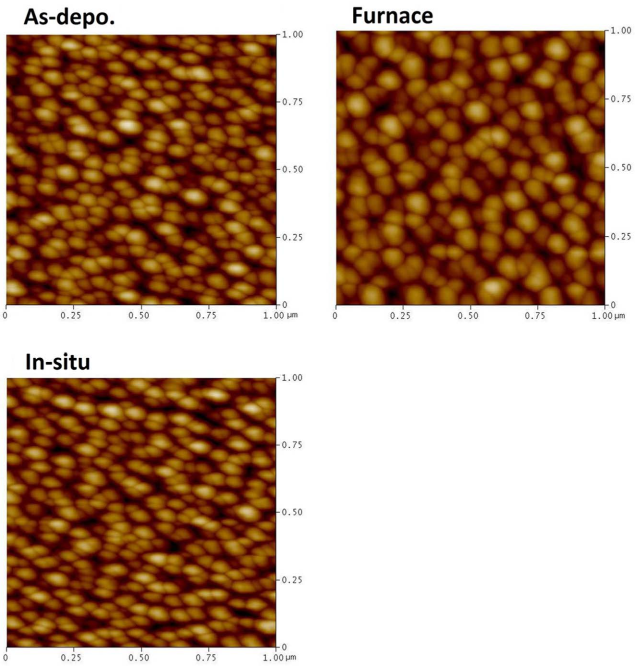

Figure. 1. AFM images of as-deposited ZnO thin film and ZnO thin films with furnace and in-situ heat treatment methods.

Fig. 3 illustrates the PL spectra of as-deposited ZnO thin film and ZnO thin film processed by furnace and in-situ heat treatment methods. The optical properties of ZnO thin films are seriously affected by annealing method. In all

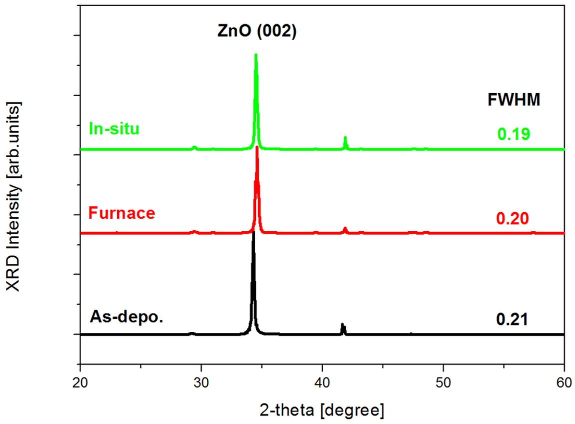

Figure. 2. XRD traces of as-deposited ZnO thin film and ZnO thin films with furnace and in-situ heat treatment methods.

Table 1. Summary of the structural parameters measured and calculated for as-deposited ZnO thin film and heat treated ZnO thin films.

Sample	Peak position [°]	FWHM [°]	c-axis lattice constant [Å]	Strain [10^{-3}]	Average crystallite size [nm]
As-depo.	34.3	0.21	5.225	3.6	39.7
Furnace	34.6	0.20	5.181	−4.9	41.2
In-situ	34.5	0.19	5.195	−2.1	43.7

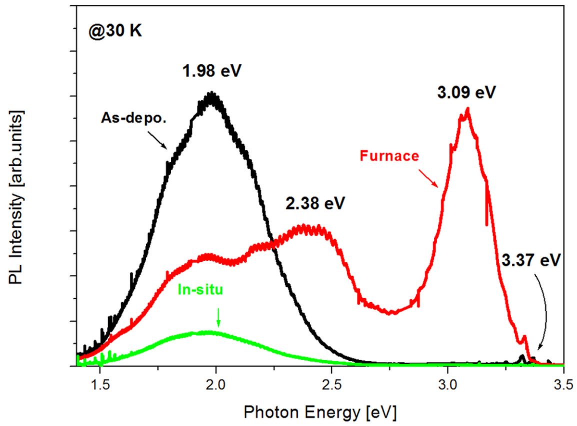

Figure. 3. Photoluminescence spectra of as-deposited ZnO thin film and ZnO thin films with furnace and in-situ heat treatment methods.

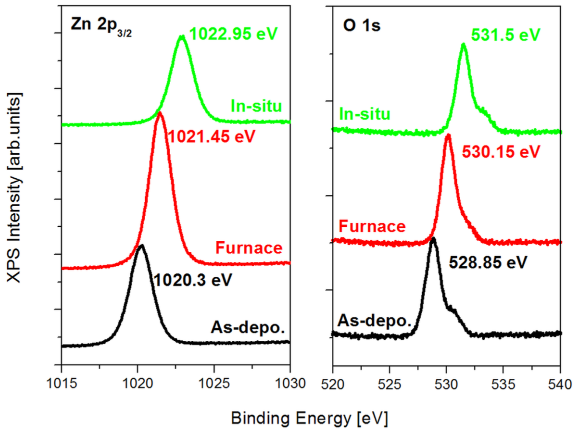

Figure. 4. XPS spectra of Zn $2p_{3/2}$ core levels and O 1s core levels of as-deposited ZnO thin film and ZnO thin films with furnace and in-situ heat treatment methods.

ZnO thin films, the broad red emission at 1.93 eV was observed, which could be related to the defects such as oxygen vacancy (V_O) and zinc anti-sites (Zn_O) [9]. Red luminescence shows a strong intensity at the as-deposited ZnO thin film, in particular, and reduces by annealing process. This result is coincided with the result of crystallinity in XRD. Also, the ultraviolet (UV) emission of the as-deposited ZnO thin film was located at 3.32 eV, which is concerned with near band edge (NBE) emission. In case of ZnO thin film annealed by furnace, the blue-green emission at 2.38 eV and the UV emission at 3.09 eV and at 3.37 eV were observed. The blue-green light may be due to the electron transition from the bottom of conduction band to oxygen anti-site (O_{Zn}) [10] and the UV emission at 3.09 eV is related to the Zn vacancy (V_{Zn}) [11]. The UV emission peak becomes a strong through heat treatment by furnace. In case of ZnO thin films annealed by in-situ, only the broad red emission at 1.93 eV was observed and the peak intensity showed a small value compared to as-deposited ZnO thin film. This result indicates that the furnace heat treatment is more powerful method in improvement of optical property.

Fig. 4 verifies the peak of peculiar binding energy of Zn $2p_{3/2}$ and O 1s of the ZnO thin films through the XPS analysis. The shift and the intensity of the peak of the binding energy displays the same form in the changes of Zn $2p_{3/2}$ and O 1s peak. The Zn $2p_{3/2}$ and O 1s of ZnO thin films shift toward a high energy by heat treatment. This phenomenon indicates that the binding force becomes a strong by annealing process. In all samples, the XPS spectra of Zn $2p_{3/2}$ core levels exhibit a symmetric shape centered at about 1020.3 eV, which corresponds to Zn-O bonds in ZnO [10]. The Zn-O bonds of the ZnO thin film annealed by furnace show stronger than that of the other samples. Also, the XPS spectra of O 1s exhibit component located at about 528.85 eV, which is related to O^{2-} ion in ZnO thin films surrounded by Zn atoms with full complement [12]. The O-Zn bonds in the ZnO thin film annealed by furnace show stronger than that of the other sample, same like the Zn $2p_{3/2}$. Therefore, ZnO thin film annealed by furnace can promote the formation of Zn-O bond, compared to ZnO thin film annealed by in-situ. This result explains that the furnace heat treatment is more effective than in-situ heat treatment in formation of Zn-O bonds. Thus, this reason leads to the outstanding optical property of ZnO thin film.

IV. Conclusions

In this study, the ZnO thin films deposited by RF magnetron sputtering have been processed with furnace and in-situ annealing methods. We confirmed that the structural and optical properties of ZnO thin film were seriously affected by heat treatments. For ZnO thin film annealed by furnace, the best properties were obtained. These results are attributed to the formation of Zn-O bond in ZnO thin film. Especially, the formation of Zn-O bond is the important factor in the production of high quality ZnO thin films.

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