Influence of anneal temperature in air on surface morphology and photoluminescence of ZnO thin films

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Abstract. The influence of anneal temperature in air ambient under atmospheric pressure on the surface morphology and photoluminescence of ZnO thin films grown on quartz substrate by RF sputtering has been investigated. The characterization of ZnO thin films was carried out by X-ray diffraction (XRD), atomic force microscope (AFM), DRUV-vis spectra (DRUV-vis), photoluminescence (PL), X-ray photoelectron spectroscopy (XPS). XRD analysis shows the crystal quality of ZnO thin films becomes better after annealing in air. AFM results shows that the influence of anneal temperature on surface morphology is obvious. DRUV-vis results reveal that the transmittance increases in the region from 400 nm to 500 nm after annealing, without affecting the band gap. PL spectra of ZnO thin films by annealed at various temperatures consists of a near band edge emission around 380 nm and visible emissions due to the electronic defects, which are related to deep level emissions, which are generated during annealing process. The evolution of defects is analysed by PL spectra based on the energy of the electronic transitions. XPS results hint that the obvious change of oxygen species on the surface of ZnO, especially the increased oxygen vacancies with increasing the anneal temperature.

1. Introduction
Zinc oxide (ZnO) has been well recognized as one of the most promising oxide semiconductor materials owing to its excellent optical, electrical and acoustic properties. Due to a direct band gap of 3.36 eV, ZnO has been found wider applications in recent years, such as light-emitting diodes (LEDs), solar cells, gas sensors, spintronics, transparent conductive contacts (TOCs) [1-3]. Nowadays, ZnO thin film and nanostructures can be fabricated by using many deposition techniques, such as molecular beam epitaxy (MBE), sputtering, pulsed laser deposition (PLD), chemical vapor deposition (CVD), sol-gel technique [4-8]. Among them, radio frequency (RF) magnetron sputtering method has many attractive advantages, which include better film growth control, repeatability, low temperature deposition, large scale stability and uniform film properties [7, 9]. It is well known that the properties of sputtered ZnO thin films are known to depend not only deposition parameters, but also on the post deposition processes, such as thermal anneal. However, the influence of anneal conditions on the ZnO
thin film fabricated by RF sputtering are still debatable. Meanwhile, some reports about the effects of the thermal anneal for ZnO thin films focus on the anneal temperature, anneal ambient, such as under a mixed gas under a contain vacuum pressure, or vacuum pressure, and so on [10-15]. However, these approaches require high vacuum and high temperature, and the harsh conditions inevitably result in a high cost. Therefore, it is necessary to develop an alternative method to prepare ZnO thin film with low-cost. In addition, when the anneal temperature up to 400 °C, the resistivity of annealed ZnO thin film becomes high, which would be suitable use as the TCO thin films [15, 16]. In this study, the influence of anneal temperature just in air ambient under atmospheric pressure at 350, 380 400 °C for 1 h, on the crystalline, surface, optical, and photoluminescence behaviour of ZnO thin films is investigated.

2. Experimental

2.1. Fabrication of ZnO thin films

Firstly, the ZnO thin films were deposited on quartz substrate by RF magnetron sputtering. The target is a high purity ZnO (99.99%). The sputtering chamber was initially evacuated down to a pressure of less than $5 \times 10^{-4}$ Pa. The depositing temperature, working pressure and sputtering power were kept for 30 min at room temperature (RT), 0.5 Pa and 75 W, while the Ar and O$_2$ flow rates were 0.2 and 29.8 sccm, respectively. Before films growth, the presputtering of the target surface was executed for 5 min to remove possible surface contamination. The ZnO films were deposited on quartz substrate at RT, named as "RT-ZnO". Then, the ZnO films were annealed in air ambient under atmospheric pressure, using muffle furnace (KDF S70) at 350, 380, 400 °C for 1 h, named as "Air-350", "Air-380", "Air-400", respectively.

2.2. Characterization

The crystal structure of the as-prepared samples was analysed by an X-ray diffraction (XRD, Rigaku Ultima IV) equipped with Cu-K$_\alpha$ radiation at 40 kV and 40 mA, employing a scanning rate of 0.01° s$^{-1}$. The surface morphology was examined by atomic force microscope (AFM, Seiko SPA3800N). Photoluminescence emission and excitation were obtained with a fluorometer (PL, iHR320) at room temperature with an excitation wavelength 325 nm. The ultraviolet-visible absorption spectra were measured with a scanning DRUV-vis spectrophotometer (DRUV-vis, Shimadzu SolidSpec-3700/3700DUV). The spectra of O 1s and Zn 2p were analysed by X-ray photoelectron spectroscopy (XPS, Jeol JPS-9010MC).

3. Results and Discussion

3.1. Crystal structure and surface morphology

XRD measurement has been carried out to investigate the crystalline property of the ZnO thin films and annealed ZnO thin films and the results are shown in Fig. 1. The crystal structure of ZnO thin films annealed at anneal temperatures of 350, 380 and 400 °C was identified to be c-axis oriented, which could be attributed to the (002) crystal plane of ZnO (JCPDS # 36-1451), corresponds to a wurtzite ZnO structure. The position of peak has been observed to increase consistently with increasing anneal temperature. The shift in the corresponding diffraction peak position for different anneal temperatures might have been caused due to stress changing in the films [16]. Assuming a homogeneous strain across the films, the crystallite size may be estimated from the full-width at half maximum (FWHM) of (002) diffraction peak using Scherer’s formula [17]:

$$D = \frac{0.9\lambda}{(A\cos\theta)}$$

(1)

where $\lambda$ is X-ray wavelength, $A$ the FWHM of the (002) diffraction peak in radians and $\theta$ the Bragg diffraction angle of the (002) peak. The results show that grain size of ZnO (Fig. 1b), is the minimum with a value of ~ 26 nm at RT and maximum with a value of ~ 57 nm at 400 °C. During anneal in air at low temperature, surface atoms had less relative energy, thus the surface mobility of atoms was low, resulting in generation of defects in ZnO thin films. With increasing the anneal temperature, those
atoms gained more energy and surface mobility to occupy stable positions inside ZnO crystals. It would help in enhancement of crystalline property of ZnO films [18]. Fig. 2 shows the surface morphology of the samples investigated by AFM measurement. The surface morphology of the RT-ZnO films shows a grain-like structure (Fig. 2a). After annealed at 350 °C, the grain-like structure substantially grows along vertical (Fig. 2b). While increasing the temperature up to 380 and 400 °C, the grain-like structure grows too large then becomes to partially fusion (Fig. 2c and 2d). In other words, with anneal in air, it shows an obvious increased size of the grain. The increased size in the surface morphology is matched with its grain size of ZnO crystals (Fig. 1b).

![Figure 1.](image1)

**Figure 1.** (a) XRD patterns and (b) the grain size of the films.

![Figure 2.](image2)

**Figure 2.** Surface morphology of the samples. (a) ZnO, (b) Air-350, (c) Air-380, (d) Air-400.
3.2. Optical properties

In order to use the TCO thin films in the applications as transparent electrodes for optoelectronic devices, ZnO thin film must be with high transparency in the visible region. DRUV-vis spectrum is used to investigate the light absorption property of the samples. As showed in Fig. 3a, all samples show good optical transmittance. With anneal in air, it is also observed that the transmittance of the annealed ZnO film increases in the region from 400 nm to 500 nm, but the transmittance slightly decreases in the region higher than 500 nm. While the corresponding Kubelka-Munk plots (Fig. 3b), it indicates that the change of band gap of the ZnO film is slight, after annealed in air. The slight change of band gap might be attributed to the formed defect during anneal in air at low temperature [18]. Moreover, the PL emission spectra has been widely used to study the fate of electron and hole in semiconductor [19-23]. Room temperature PL excitation and emission for all samples were measured in the wavelength range of 300-700 nm. PL spectra of ZnO film annealed at various temperatures are shown in Fig. 4a. For RT-ZnO film, the PL emissions show a typical luminescence behavior of a narrow near band edge (NBE) emission in the UV region and defect level (DL) emission in the visible region. The NBE emission could be attributed to the recombination of photoexcitation, while the band
emission existing in the visible region is due to the recombination of deep-level holes and electrons [19-23]. With increasing the anneal temperature from 350 to 400 °C, the UV emissions slightly increased, which may be ascribed to the oxidized layers formed on the surface and the grain boundary of ZnO film after annealing in air [24]. While the increase of the visible emissions of the annealed ZnO films could be due to the increase of the intrinsic defects and their concentrations [25].

To further investigate the intrinsic defects, the PL emission spectra of the Air-380 sample has been deconvoluted into five Gaussian components in Fig. 4b. The centre of each peak (A-E peak) is 380, 413, 449, 517, 631 nm, respectively. The peak in ultraviolet (peak A) is due to the recombination of photoexcitation. The peak B appearing through possible transition of electron of electrons trapped at Zn interstitial (Zn_i) defects to the valence band [22, 23]. The peak C is due to possible electron transition between extended states Zn_i (ex-Zn_i) defects level and the valence band [21, 22]. An emission band around 517 nm (peak D) occur through the photogenerated holes trapped in the deep level oxygen vacancy (V_O) recombine with the electrons trapped in a shallow level located just below the conduction band [21, 22]. The peak E could be attributed to possible electron transition between Zn_i defects level and the deep level [22, 23].

![Figure 5](image_url)

**Figure 5.** High resolution XPS spectra of O 1s core levels of the samples. (a) RT-ZnO, (b) Air-350, (c) Air-380, (d) Air-400. Peaks are deconvoluted into three components of oxygen, O_L (lattice oxygen), O_V (oxygen vacancy) and O_C (chemisorbed oxygen species), and the relative area ratios of the components evaluated from the fitted curves and plotted in (e).
3.3. Bonding environment

Furthermore, to gain insight into the surface/sub-surface components and oxidation states of the ZnO films has been investigated by with XPS spectra, as shown in Fig. 5. The O 1s peaks of the ZnO films are asymmetric and the deconvolution of the peaks yields three contributions attributable to different chemical states of oxygen using Gaussian fitting. For RT-ZnO film, the lowest peak at 540.6 eV is generally due to the O^{2-} ions, normally surrounded by the Zn ions in the ZnO structure (lattice oxygen, O_{l}) [26,27]. The higher peaks at 543.0 eV is due to the oxygen-deficient regions, such as oxygen vacancies (O_{v}). The highest peaks at 545.1 eV is due to the chemisorbed oxygens (O_{c}) on the film surface [26-28].

Moreover, the results of O 1s peaks of the ZnO films show shift to higher energy with increasing the anneal temperature in air, as shown in Fig. 5a-d. Also, the curve fitting for the O 1s core level peaks is conducted to confirm the relationship between the chemical states of oxygens in the films, and the relative area ratios (%) of the fitted curves are shown as Fig. 5e. Notably, with increasing the anneal temperature in air, it shows that the O_{v} peaks are enhanced and show highest of the Air-350 sample, which is matched with that of D peak in PL emission spectra. While the O_{c} peaks are significantly enhanced, which indicates that the loosely chemisorbed oxygen species on the surface increase during annealing in air.

4. Conclusion

In summary, the ZnO thin films were successfully fabricated on quartz substrate by RF magnetron sputtering and subsequent anneal in air ambient under atmospheric pressure. The influence of anneal temperature on crystal structure, surface morphology, optical properties was investigated. The ZnO thin films show a wurtzite ZnO structure. With increasing anneal temperature, the (002) crystal plane of ZnO thin films shift to higher and the grain size increase. The influence of anneal temperature on surface morphology of ZnO thin films is obvious, and the grain-like structure grows too large then becomes to partially fusion. The transmittance of the annealed ZnO thin films obviously increases in the region from 400 nm to 500 nm, without affecting the band gap. The influence of anneal temperature on photoluminescence of ZnO thin films is obvious, especially on the visible range. With the anneal temperature at 350 °C, the annealed ZnO thin films show highest, due to the relative concentration of oxygen vacancies, which is also confirmed by XPS results.

5. References

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