1. Introduction

Zinc oxide, as a low-voltage cathodoluminescent phosphor material, has been used in backlight for display and vacuum fluorescent display\cite{1-3}. Due to its promising electrical and optical properties of a wide bandgap semiconductor, zinc oxide thin film and nanostructures have been extensively investigated by many research groups in recent years, and have already been successfully applied in quantum dots, LEDs, nanolasers, solar cells, and, gas sensors, as well as in the biological applications such as cell labeling\cite{4-8}. However, the nano-sized phosphor fabrication is a very complex process and usually requires very high temperature\cite{9,10}. In order to improve the photoluminescence (PL) properties of ZnO nanostructures, the fabrication methods of ZnO nanostructures and its mechanism should be further investigated.

It is well-known that ZnO as the phosphor material usually has two well-established emission bands, the UV band edge emission and the green defect emission. In our previously research\cite{11-13}, we successfully obtained nanostructured ZnO thin film on quartz glass by a novel reducing annealing process at the low temperature of 450°C. In order to achieve the high quality ZnO nanostructures at low temperature, and meet the commercial application requirement, we have synthesized ZnO nanorods with both multi-annealing method in this research and low-temperature chemical bath deposition (CBD) method. The PL and structural properties of ZnO nanorods were compared. The emission mechanisms of ZnO nanorods by these two methods were investigated in detail.

2. Experiment

2.1 ZnO nanorods synthesized by CBD method

The conductive and transparent aluminum-doped ZnO (AZO) thin film with thickness of 300 nm were deposited on glass substrates by a conventional radio frequency (RF) (13.56 MHz) magnetron sputtering system using an AZO target (ZnO : Al2O3 = 98 : 2 wt%). As a reference, ZnO film with thickness of 300 nm on glass substrate was also deposited using a ZnO target (5N) by the same RF sputtering system, the deposition conditions were reported in previous papers\cite{13,14}. The obtained AZO film with thickness of 300 nm on glass substrate was also deposited using a ZnO target (5N) by the same RF sputtering system, the deposition conditions were reported in previous papers\cite{13,14}. The obtained AZO and ZnO films were used as substrates for ZnO nanorod growth in CBD method. The mixed solution consisting of 0.025 mol/L zinc nitrate hexahydrate (Zn(NO3)2•6H2O) and 0.0125 mol/L hexamethylenetetramine (HMTA) was prepared using ultrapure water as a solvent. The AZO and ZnO films were immersed into the solution with the growth temperature of 95 °C for 5 hours.
2.2 ZnO nanorods synthesized by CBD method

The 500 nm-thick ZnO film was deposited on 300 nm-thick AZO film by the same RF system and conditions as in 2.1. The obtained ZnO/AZO sample (sample 3) was put into a conventional annealing furnace. A multi-annealing process was carried out in forming gas (H₂ : N₂ = 2 : 98 %) firstly at 300 °C for 2 hours in order to increase the density of zinc seeds on the surface. Secondly, the temperature was increased to 450 °C and kept for 5 hours in forming gas ambient to produce the ZnO nanorods. Due to lack of oxygen during the reaction, the oxygen was introduced into the furnace for 1h before the second forming gas annealing process. For safety consideration, N₂ was introduced for 5 minutes between forming gas and oxygen annealing processes.

All of the as-deposition and annealing conditions were summarized in the table 1.

2.3 Characterization

The surface roughness of AZO and ZnO films was measured by an atomic force microscope (AFM) (Nanoscope II, Digital Instruments). Morphological properties of ZnO nanorods were examined using a field emission scanning electron microscope (FE-SEM) system (JEOL-JSM7400). The as-deposited films and ZnO nanorods were characterized using an X-ray diffraction system (Rigaku ATX-G diffractometer), employing a Cu Kα tube (λ = 0.154178 nm) radiation. The photoluminescence properties of ZnO nanorods were performed by an iHR320 Micro-PL/Raman spectroscope (Horiba Co.). A He-Cd laser with a wavelength of 325 nm was used as an excitation light source. The optical transmittance properties were analyzed using a spectrophotometer (Hitachi U-4100). All of measurements were carried out at room temperature.

3. Results and Discussion

3.1 Characterization of As-deposited Thin Films

Figure 1 showed the XRD measurement results for as-deposited ZnO/AZO, AZO and ZnO films. The XRD patterns showed that the only dominated (002) peak observed for three of as-deposited thin films, which indicated that as-deposited thin films had highly preferred orientation along (0001) direction. Comparing to ZnO film on glass, the (002) peak intensity of AZO film was much stronger and the full width at half maximum (FWHM) was much narrower, which meant the crystallinity of AZO film was better than that of ZnO film.

Based on the biaxial strain model, the compressive stress (σ) can be expressed as

![Fig. 1](image-url)
\[
\sigma = \frac{2C_{13}^2 - C_{33}(C_{11} + C_{12})}{2C_{13}^2} \times \frac{c_{film} - c_{bulk}}{c_{bulk}}
\]  

where \(C_{ij}\) is the elastic modulus of bulk ZnO, \(C_{11} = 208.8\) GPa, \(C_{12} = 119.7\) GPa, \(C_{13} = 104.2\) GPa, \(C_{33} = 213.8\) GPa; \(c_{film}\) and \(c_{bulk}\) represent the lattice constants of ZnO film and ZnO bulk respectively. Therefore, the compressive stresses were calculated as \(-0.28\), \(-0.51\) and \(-1.42\) GPa corresponding to the order of ZnO/AZO, AZO and ZnO films. As shown in Fig. 1 (b), the (002) peak position was shifted to higher angle with compressive stress decreased.

Figure 2 showed AFM images of the as-deposited ZnO, AZO and ZnO/AZO films. It was found that all as-deposited films showed uniform surface. The root-mean-square (rms) surface roughness was 7.74, 3.77, and 5.89 nm corresponding to ZnO/AZO, AZO and ZnO films.

Figure 3 showed the optical transmittance spectra obtained from three as-deposited films. It was observed that all films exhibited a transmittance higher than 70% in visible range. The highest transmittance of 80% was obtained from AZO film.

### 3.2 Characterization of ZnO Nanorods Synthesized by Two Different Methods

Figure 4 showed that SEM images of three different
kinds of ZnO nanorods obtained from both multi-annealing method and CBD method. Yellow dashed lines were made in the FE-SEM images to indicate the thicknesses of AZO and ZnO substrates (300 nm in thickness), as shown in the cross-section views of SEM images. From the top view of SEM images, it was clearly observed that ZnO nanorods on AZO thin films synthesized from both above methods showed the typical ZnO hexagonal wurtzite structure. However, the average diameters were 58.0 nm and 98.2 nm corresponding to ZnO nanorods obtained from multi-annealing method and CBD method. Except for the higher uniformity, the ZnO nanorods density of 103 /µm² obtained from multi-annealing was slightly lower than that of 152 /µm² obtained from CBD method. It was also found that the ZnO nanorods obtained from both methods showed very good alignment with vertical growth direction to AZO substrates. The average height of 1153 nm for ZnO nanorods by multi-annealing process was higher than that of 858 nm for ZnO nanorods by CBD method.

Compared to AZO substrate, it was found that the ZnO nanorods on 300 nm-thick ZnO film showed non-hexagonal structures and had a smaller diameter of 46.2 nm by CBD method. In addition, the average height of ZnO nanorods was 2063 nm but the growth direction was not so vertical to the substrates.

Figure 5 showed the XRD patterns of three different kinds of ZnO nanorods fabricated on the two different methods. It was found that the (002) peak was still dominated peak but getting much stronger than as-deposited samples. The peak position had much higher angle shifted with the narrowly FWHM value from ZnO nanorods compared to the as-deposited films. It was found that the crystallinity was much more improved from the ZnO nanorods/AZO by multi-annealing method compared to that from CBD method.

From the above SEM and XRD results, it was clear that well-aligned ZnO nanorods could be attributed to the good crystallinity of the AZO film. AZO film had much stronger (002) peak, lower compressive stress, which meant AZO film exhibited much better c-axis growth than ZnO film. During the CBD method, AZO and as-deposited ZnO served as seeds layer for ZnO nanorods growth. The growth direction of ZnO nanorods was dependent on the growth direction of seeds layer. Therefore, the ZnO nanorods grown vertically in the (0001) direction followed the AZO films because the lowest energy direction for ZnO growth is (0001) direction16). While the ZnO nanorods on ZnO film was not well-aligned due to the worse crystallinity of ZnO film. In the multi-annealing process, the alignment growth mechanism of ZnO nanorods was also followed the underneath AZO film. ZnO nanorods were fabricated by recrystallization of ZnO thin film during reducing annealing. It was noticed from the XRD results, the ZnO film (500 nm in thickness)/AZO film exhibited the very good crystallinity, which meant the as-deposited ZnO thin film followed the same growth direction as the AZO films. Due to the less lattice mismatching between ZnO and AZO films, the ZnO film was actually homoepitaxial growth from AZO film. During the reducing annealing process13), the initial formed ZnO nanorods would grow along the direction of

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**Fig. 5** XRD patterns of ZnO nanorods fabricated on AZO by multi-annealing, AZO by CBD and ZnO by CBD (The XRD pattern of ZnO NRs/ZnO was multiplied by 10 times for clear comparison).

**Fig. 6** Photoluminescence spectra of ZnO nanorods fabricated on AZO by multi-annealing, AZO by CBD and ZnO by CBD (PL spectra of bare glass was shown for excluding the influence of substrate).
The PL measurement results from ZnO nanorods were quite different from two different synthesis methods, as shown in Fig. 6. In order to exclude the influence of glass substrate, PL spectra of bare glass was shown in inserted image in Fig. 6, which indicated bare glass had no strong PL emissions. It was found that there were a strong visible emission peak and a suppressed UV band-edge emission for the ZnO nanorods/AZO substrate by both fabrication methods. The UV emission peak centered at 380 nm of ZnO nanorods obtained from multi-annealing was much stronger than those from CBD method due to the better optical crystallinity. However, the ZnO nanorods/AZO by multi-annealing process showed a strong deep level emission peak centered around 492 nm in the visible range which was attributed to the oxygen vacancies introduced during the reducing annealing process\(^{17}\). According to the mechanism of the ZnO nanorods synthesized by the reducing annealing method\(^{12,13}\), the as-deposited ZnO film was dissolved by the hydrogen, then recrystallized to form ZnO nanorods with the proper control of parameters during multi-annealing process. In the beginning, ZnO film was annealed in the forming gas at 300 °C for 2 hours resulting in controlling the density of zinc nuclei for further ZnO nanorods growth. Then the reducing annealing temperature was increased to 450 °C (greater than 419.6 °C, which is the melting point for zinc), ZnO nanorods would be recrystallized with controlling the rate of ZnO film reduction and the ZnO nanorods recrystallization. Due to lack of oxygen, the oxygen was supplied between two reducing annealing processes.

During ZnO nanorods growth, there were many oxygen vacancies introduced in the nanorods which contributed to the blue-green emission. As annealing time expanded, the size and height of ZnO nanorods were increased. Correspondingly, there were much more oxygen vacancies formed in the nanorods which contributed to the much intensive blue-green emission.

For the ZnO nanorods prepared by the CBD method, there were also two peaks: a very weak UV peak centered at 380 nm and a strong wide visible emission peak centered at 636 nm. In CBD method, the AZO or ZnO film served as the seeds layer to contribute to ZnO nanorods growth. According to the following chemical reaction equations\(^{14}\),

\[
\text{Zn(NO}_3\text{)}_2 \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^- \quad (2)
\]
\[
\text{C}_6\text{H}_{12}\text{N}_4 + \text{H}_2\text{O} \rightarrow 4\text{NH}_3 + 6\text{HCHO} \quad (3)
\]
\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (4)
\]
\[
\text{Zn}^{2+} + 4\text{NH}_3 \leftrightarrow \text{Zn(NH}_3)_4^{2+} \quad (5)
\]
\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (6)
\]
\[
\text{Zn(OH)}_2 \leftrightarrow \text{ZnO} + \text{H}_2\text{O} \quad (7)
\]

Because the concentration of Zn\(^{2+}\) source was twice higher than that of OH\(^{-}\) source, much more defects were easily to form during ZnO nanorods growth. The (orange-red) emission from ZnO nanorods might be attributed to much more Zn vacancies introduced during the fast reaction process in CBD except for the structural defects or impurities\(^{18}\).

Figure 7 showed transmittance spectra of ZnO nanorods obtained from both multi-annealing method and CBD method. Due to the vertical alignment of ZnO nanorods on the substrates, the high transmittance of about 75% in the visible range was obtained from ZnO nanorods/AZO films. However, ZnO nanorods fabricated on ZnO film showed low transmittance of 40% in visible range due to the poor alignment of ZnO nanorods.

4. Conclusions

Well-aligned ZnO nanorods were synthesized on AZO substrates by both chemical bath deposition method and multi-annealing method with the different growth mechanism. It was found that the vertical alignment of ZnO nanorods was dependent on the good crystallinity and c-axis growth direction of AZO film. ZnO nanorods/AZO films by both methods showed the higher transmittance of 75%. Comparing these two methods, it was found that ZnO nanorods obtained from multi-annealing showed better crystallinity, and better uniformity. PL spectra of ZnO nanorods fabricated by
multi-annealing showed a strong blue-green emission while a strong broad orange-red emission was found for ZnO nanorods by chemical bath deposition due to different growth mechanisms.

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