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Large Surface Nanostructured Zinc Oxide Thin Film Phosphor Fabrication on Different Conductive Substrates

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ABSTRACT

Zinc oxide thin film phosphor was fabricated on different conductive substrates. The uniformly and vertically aligned zinc oxide nanorods were formed on crystalline substrates by the reducing annealing process. The much intensive blue-green emission was observed from nanostructured zinc oxide on aluminum doped zinc oxide substrate.

1 Introduction

The wide band-gap semiconductor zinc oxide (ZnO) is one of the promising functional semiconductor materials which has been extensively applying for electrical and optical devices due to its unique properties. Particularly, as a full-fledged phosphor material, ZnO, which has various structural defects including oxygen or zinc vacancies and interstitials, is attracted much attention to be a low cost rare earth free phosphor material suitable for applying for LEDs, light waveguides optical device and vacuum fluorescent display, etc [1-3].

Up to date, the development of ZnO thin film phosphor is still a challenge due to the technical difficulty on defects controlling during the synthesis procedure at low temperature. There were some reported methods for fabrication of ZnO nanorods with solution or hydrothermal methods, etc. however, the reproducibility and stability of processes are still critical issues. In our previously research [4], we already obtained high blue-green emission from ZnO nanostructures by a novel annealing processes. However, the growth direction of ZnO nanostructures was hardly controlled well [5]. In this research, the three kinds of conductive substrates are used for investigating the substrates effect on forming the nanostructures and further influence their photoluminescence property.

2 Experiment

ITO and AZO (Al_2O_3 content of 2% wt) substrates with 300nm thickness were deposited by DC and RF magnetron sputtering. ZnO thin films with thicknesses 500 nm were deposited on ITO, AZO and silicon (p-type) substrates by RF (13.56 MHz) magnetron sputtering. The RF power, working pressure and the substrate temperature were respectively set 180W, 7 Pa and 150˚C with working gas of argon 30sccm. After deposition, the annealing process was carried out for three kinds of as-deposited samples in a conventional furnace. The annealing conditions were separated to reducing annealing processes with 5 hours and 2 hours at 450˚C in a forming gas (H_2:N_2 ratio 1.96%). Between the two reducing annealing processes, the oxygen annealing process was introduced for one hour at same temperature. For safety, nitrogen gas was introduced shortly to the furnace between every two steps.

The crystallinity of ZnO film and nanostructures was characterized using an X-ray diffraction system (Rigaku ATX-G diffractometer), employing a Cu Kα tube (λ = 0.154178 nm) radiation with a scan speed at 2°/min. The surface morphologies of the ZnO nanostructures were observed by a field emission scanning electron microscope (FE-SEM) system (Hitachi SU8020). The photoluminescence property was measured by PL measurement, which was performed on an iHR320 Micro-PL/Raman spectroscope (Horiba Co.). A He-Cd laser with a wavelength of 325 nm at a power of 20 mW was used as an excitation light source. All of measurements were carried out at room temperature.

3 Results

Figure 1 showed the SEM images of as-deposited ZnO films deposited on three different conductive substrates by RF magnetron sputtering. It was observed all of films are uniformly from top view, the average grain sizes were increased with the order of ZnO film on silicon, AZO and ITO substrates. From the cross-section views. it found the ZnO films with column structures growth vertically were observed obviously on AZO and silicon substrates.

From XRD patterns measurement results of ZnO films deposited on different substrates, as shown in Fig.2, there was only (002) diffraction peak observed from silicon and AZO substrates, there was no peak observed from ZnO thin film on ITO substrate. It revealed that the ZnO films on silicon and AZO substrates were preferentially oriented growth along c- axis perpendicular to substrates. Comparing to AZO, ZnO film on silicon substrate showed much high peak intensity and narrow FWHM value. After calculation, the results showed that

c-axis crystallite size and compressive stress was 35nm, -0.5GPa, and 26nm, -1.5GPa corresponding to ZnO films respectively on silicon and AZO substrates. The both lattice constant c was close to 0.52nm, which suggested that that the lattice distortion of constant c from ZnO films was less on the crystalline substrates of silicon and AZO resulting in the better crystallinity ZnO films.

Figure 3 showed the SEM images of the ZnO nanorods formed on three conductive different substrates after the annealing processes. It was found that ZnO nanorods with hexagonal symmetry were uniformly fabricated on the AZO and silicon substrates. The average diameters of the nanorods were around 75nm. Comparing to the silicon substrate, there was double density of ZnO nanorods formed on the AZO substrate. As well as, the well-aligned vertically growth of ZnO nanorods with length of 700nm were confirmed from cross-section view. Although the nanorods on ITO substrates were formed, the growth direction was not vertically controlled which might attribute to the amorphous phase of ITO. Therefore. this results indicated that vertically well-aligned ZnO nanorods were easily fabricated from ZnO film with high crystallinity which deposited on crystalline substrates.

Figure 4 showed the PL spectra of ZnO nanorods on different conductive substrates after annealing processes. There were two emission peaks observed, a UV peak and blue-green emission peak, from three kinds of substrates. Compared to the near-band edge (NBE) peak at 378 nm, the deep-level-emission (DLE) peak center at about 495 nm was the dominate one. It is well-accepted that the oxygen vacancies were responsible for the origin of green luminescence in ZnO film. During the reducing reaction of hydrogen and ZnO films at 450°C, the oxygen atoms were easily reduced from ZnO, there were much oxygen vacancies created and existed inside of the ZnO nanorods during reducing annealing processes.

The first reducing annealing process contributed to the density of nanorods which initial grew along to the lowest energy direction (0001) direction. The second reducing annealing process contributed the remarkable growth of nanorods because the recrystallized ZnO would prefer to grow along to the (0001) direction. According to the PL results, the blue-green visible emission peak was much stronger from ZnO nanorods on AZO substrate comparing to silicon and ITO substrates, which might attribute to the high density of nanorods which including much more oxygen vacancies comparing to the ones with lower density. According to the application of phosphor on the conductive substrate, as well as considering the cost of the manufacture process, the AZO substrate will be highly expected to replace ITO for applying for ZnO thin film fabrication.

4 Conclusions

The influence of different conductive substrates on fabricating ZnO thin films phosphor were evaluated. The results showed that the substrates had significant influence on the crystallinity of ZnO films. The good crystallinity of ZnO films with highly c-axis orientation growth could be achieved from the crystalline substrates, which contributed to well controlling of the vertical growth of ZnO naorods during annealing processes. Large density and uniform ZnO nanorods could be formed on the AZO substrate, from which the most intensive blue-green emission was obtained. Therefore, ZnO nanorods on the AZO substrate can be expected for phosphor application in the future.

References

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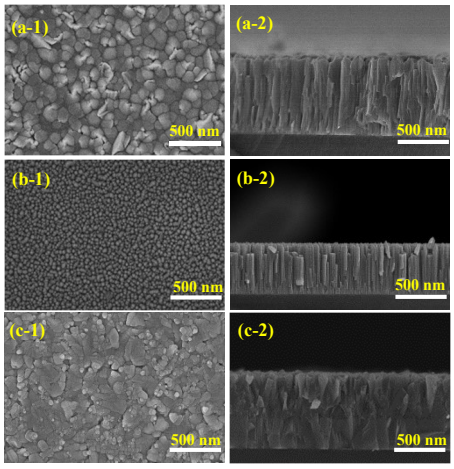

Fig.1 SEM images of ZnO films deposited on different substrates by RF magnetron sputtering. (a: AZO, b: silicon, c: ITO, (1) top view, (2) cross section view).

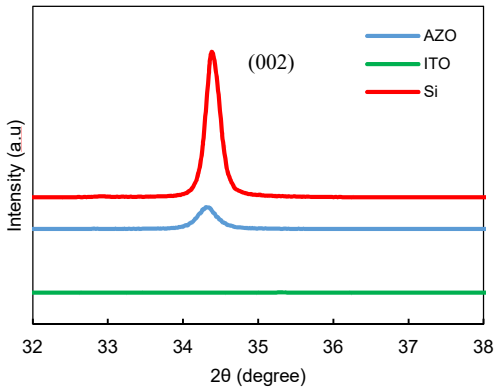

Fig. 2 X-ray diffraction patterns of as-deposited ZnO films deposited on different substrates.

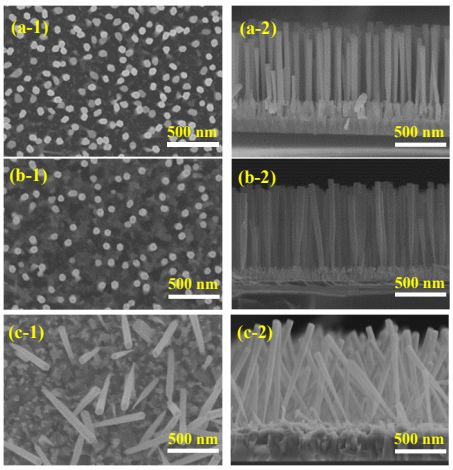

Fig.3 SEM images of ZnO rods obtained from ZnO films deposited on different substrates (a: AZO, b: silicon, c: ITO, (1) top view, (2) cross section view).

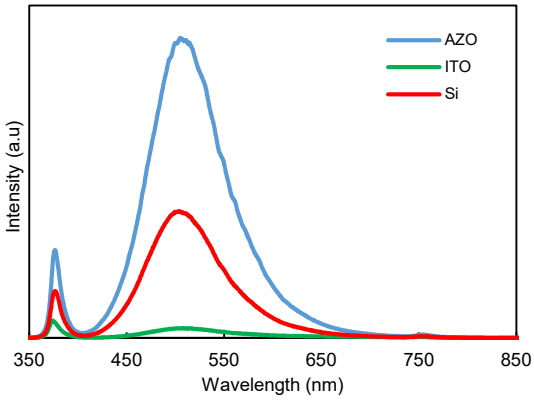

Fig. 4 Photoluminescence spectra measured at room temperature from ZnO nanorods prepared on different conductive substrates.