HYDROTHERMAL SYNTHESIZED ALUMINUM-DOPED ZINC OXIDE ON PLASTIC SUBSTRATE

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Introduction

Doping is an effective method to modify the physical properties of the base materials and this will extend the applications of the base materials. The Al-doped ZnO (ZnO:Al) nanowires are capable of reaching the highest conductivity without deterioration in optical transmission and crystallinity, and thus have been regarded as a potential alternative to the most accepted transparent conductive material [1]. Many research groups have prepared ZnO:Al by different methods (e.g. magnetron sputtering, sol-gel method and pulsed laser deposition) and investigated the effect of Al doping concentrations on the microstructure, optical property and electrical conductivity of ZnO:Al thin films [2,3]. However, these methods require complex procedures or rigid environmental conditions.
The hydrothermal zinc oxide (ZnO) nanowire synthesis method has been investigated by many researchers [4,5]. The problem associated with hydrothermal synthesis is the time required for the synthesis of nanowires, which ranges from several hours to several days.
In this paper, we report the synthesis of undoped ZnO nanowires and ZnO:Al nanostructures fabricated by the rapid microwave heating process. The formation of the ZnO:Al nanowires and nanosheets on the polyethylene terephthalate (PET) substrate by the rapid microwave heating process has not been reported yet. The influence of Al doping concentrations on the nanostructures and optical properties was investigated.

Experimental

The undoped ZnO and ZnO:Al nanostructures were grown using a two-step process: (a) preparation of the seed layer, and (b) growth of the nanostructures. In the first step, coating solutions (20 mM) were prepared by a zinc acetate dihydrate (98%, Aldrich) and 1-propanol (spectroscopic grade). The ZnO seed layers were produced by spinning the precursor solutions on a PET substrate. Among coatings, the ZnO seed layers were annealed at 100 °C for 5 minutes to ensure particle adhesion to the PET surface in air atmospheres. ZnO nanowires were then grown by dipping the substrates in a mixture of equimolar 25 mM zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Sigma Aldrich) and hexamethylenetetr-amine (HMTA, Sigma Aldrich) solution in deionized (DI) water. As the doping source, aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, 99.997%, Aldrich) powders were added in the solution. In the solutions, Al doping concentrations (the atom ratio of Al to Zn) were chosen to 0.5 at.%, 1.0 at.%, and 2.0 at.%, respectively. The hydrothermal process was carried out with a variable microwave sintering system (2.45 GHz) at 140 W power setting and atmospheric pressure as the optimal condition.
The morphology and size of the undoped ZnO and ZnO:Al nanostructures were investigated by field emission scanning electron microscopy (FESEM) (Hitachi S-4800S, operated at 10 kV). Energy dispersive X-ray (EDX, Inca Oxford) analysis was performed to determine the element composition. The optical characteristics of the as-grown nanostructures were investigated using photoluminescence (PL) measurements.

Results and Discussion

Fig.1 shows the SEM images of undoped ZnO and ZnO:Al nanostructures grown by the rapid microwave heating process at 140 W and 30 minutes. Fig.1(a) shows the top view image of undoped ZnO nanowire arrays. The SEM image of the ZnO nanowire arrays on the ZnO seed layer clearly shows a high density of vertically grown ZnO nanowire arrays with well-defined hexagonal facets (001). These nanowire arrays have a narrow size distribution centered of approximately 35 nm in diameter in Fig.1(a). The 45° tilted view (inset of Fig.1 (a)) of the ZnO nanowire arrays indicates that the ZnO nanowire arrays grew vertically with identical lengths of 310 nm. The well-defined crystallographic planes of the hexagonal-shaped nanowires can be clearly identified, providing strong evidence that the ZnO nanowire arrays orientate along the c-axis. The top view of ZnO doped with 2.0 at.% Al (Fig.1(b)) shows that the ZnO nanowire arrays are not well-aligned to the PET substrate. It can be found that there are the nanowire arrays companying with the nanosheets. Due to the doping of Al ions, the coexistence of the nanowires and nanosheets was observed. The number of nanosheets was increasing with the doping concentration.
Fig.2(a) shows the morphologies of the ZnO nanowire

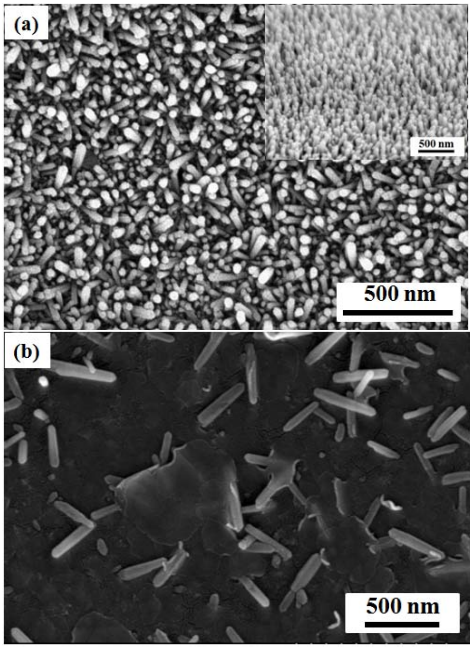

Fig. 1 SEM images of the undoped ZnO and ZnO:Al nanostructures.

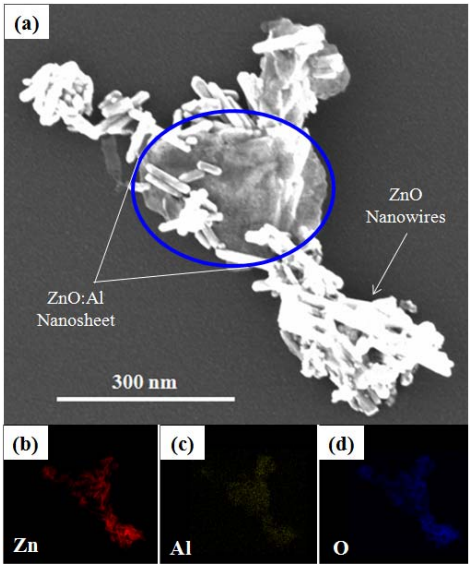

Fig. 2 (a) High magnification SEM image of the ZnO nanosheet doped with 1.0 at.% Al; (b)-(d) Elemental mapping of Zn, Al, and O in a ZnO:Al nanosheet.

arrays and ZnO:Al nanosheet. From the identification of chemical composition, as shown in Fig.2(b)-(d), Zn, Al, and O elements are distributed homogeneously through the entire ZnO:Al nanosheet.

Fig.3 shows the PL spectra for the undoped ZnO and ZnO:Al nanostructures. The peak due to the near band-edge emission of the wide band gap ZnO is centered at 387 nm. The undoped ZnO nanowire arrays exhibiting the strongest UV emission with a broad full width at half-maximum (FWHM) of 68 nm is observed from the PL spectra. When the Al concentration reaches 2.0 at%, the FWHM becomes 79 nm, as calculated from the PL spectra. The line was inhomogeneously broadened because those several lines were overlapped. As a result,

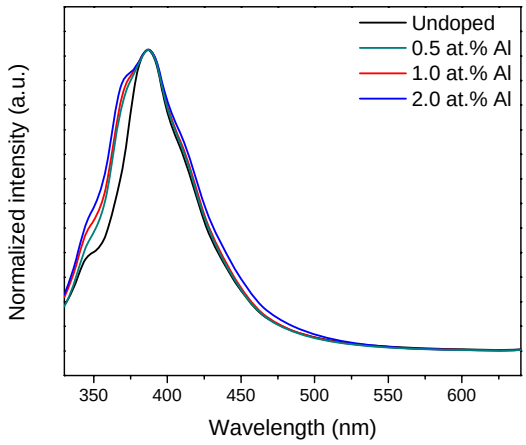

Fig. 3 Normalized room temperature PL spectra of the undoped ZnO and ZnO:Al nanostructures.

the PL spectra show a broad FWHM.

Conclusion

The undoped ZnO nanowire arrays and Al-doped ZnO nanostructures were successfully synthesized on a PET substrate using the rapid microwave heating process. The coexistence of the nanowires and nanosheets was observed as the introducing of Al ions. Room-temperature PL measurements show that the ZnO:Al nanostructures exhibit a strong UV emission and a broad FWHM. The ZnO:Al nanostructures created with the rapid microwave heating process show a great promise for use in flexible solar cells, flexible displays, and other flexible devices with low power, low growth temperature, short growth time, easy fabrication, and low cost.

References

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