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Growth and Structural Properties of ZnO and Zr Doped ZnO Nanostructures by Low Cost Spray Pyrolysis Technique†

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Semiconductor nanostructures have attracted increasing interest in the recent past due to their novel device applications. ZnO and Zr doped ZnO nanostructures with different morphologies were prepared by spray pyrolysis method on corning glass substrates and these nanostructures were characterized for their structural, surface morphological and optical properties. The XRD patterns show that Zr doped ZnO nanorods belong to the hexagonal wurtzite structure of ZnO.

Key Words: ZnO, Nanowires, Zr doping, Photoluminescence.

INTRODUCTION

Investigations on the low-cost and high performance optoelectronic materials have led to the development of transparent conducting oxide thin films with improved optical and electrical properties. Transparent conducting oxide thin films of In_2O_3, SnO_2, ZnO and their mixtures have been extensively used in optoelectronic applications such as transparent electrodes in touch panels and flat-panel displays[1-5]. Fabrication of silicon based thin film solar cells has encountered zinc oxide as one of the suitable options due to its high chemical stability[6]. Zinc oxide is a unique semiconductor material with a wide direct band gap of 3.37 eV and relatively large exciton binding energy of 60 meV at room temperature[1]. Zinc oxide films doped with boron, aluminum, gallium and zirconium have been actively studied as alternate materials to replace the indium tin oxide because they are nontoxic, inexpensive and abundant in nature[7].

Zirconium doped zinc oxide thin films belong to the group of wide band gap semiconductors, which shows lower electrical resistivity and high optical transmittance in visible region and becomes a promising substitute for indium tin oxide due to its stability at high temperature (>700 K)[8,9]. Nevertheless the understanding of Zr doping in ZnO film by spray pyrolysis will pave a way to prepare stable transparent conducting oxide with improved electrical properties without compromising optical transmittance. Zr is an *n*-type impurity and the ions Zr^{4+} and Zn^{2+} possess early equal ionic radius of *ca.* 0.72 Å. Zn^{2+} ions could easily be replaced by Zr^{4+} in crystal lattice. Hence, Zr is considered to an ideal dopant to improve the properties of ZnO towards stable transparent conducting oxide for photovoltaic applications.

Deposition of zirconium doped zinc oxide thin films have already been reported by sol-gel[10], RF sputtering[11], DC sputtering[12], pulsed laser deposition (ALD)[5] and spray pyrolysis[13] methods.

To the best of our knowledge, there is no report on the deposition of Zr doped ZnO nanowires by the chemical spray pyrolysis method. Hence we report the fabrication of ZnO and Zr doped ZnO nanostructures using simple spray pyrolysis method at 400 ºC and the effect of doping on the structural and optical properties of ZnO nanowires.

EXPERIMENTAL

Zinc oxide and Zr doped zinc oxide nanowires were grown on the corning 1737 glass substrates at 400 ºC by the chemical spray pyrolysis technique. The methodology of spray pyrolysis deposition technique has been reported elsewhere[3]. 0.1 M solution of zinc acetate was prepared in methanol and Zr doping was achieved from the source material of zirconium(IV) chloride. The required amount of Zr precursor was dissolved in methanol and then added to the zinc acetate-methanol

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solution to make up the final spray solution. The final solution was sprayed on the preheated corning 1737 glass substrates at 400 ºC. The structural properties of the nanowires were analyzed by the X-ray diffraction technique using a Philips X'pert pro diffractometer with CuK_α radiation (λ = 1.5406 Å). The surface morphology and elemental analysis were examined by field emission scanning electron microscope (FESEM) (ZEISS-SIGMA) equipped with energy dispersive X-ray analysis (EDAX, Oxford Instruments - INCAX-act).

RESULTS AND DISCUSSION

Fig. 1a and 1b show the XRD patterns of the ZnO and zirconium doped zinc oxide (4 at. % $ZrCl_4$) nanowires respectively. The peak position was indexed according to ICDD card no. 36-1451 and it is in good agreement with earlier report[4]. The XRD pattern indicates that ZnO and zirconium doped zinc oxide nanowires were preferentially oriented along (002) direction. Up to the detection limit of XRD, there were no secondary peaks in the XRD pattern. XRD peaks of (002) obtained for ZnO and zirconium doped zinc oxide are compared in Fig. 2. The (002) peak of the zirconium doped zinc oxide nanowires is shifted towards lower diffraction angle side compared that of ZnO nanowires. The decrease in intensity and full width half maximum(FWHM) of (002) peak in zirconium doped zinc oxide nanowires, as compared to that of pure ZnO nanowires, indicate the lattice distortion due to the introduction of Zr dopant[5].

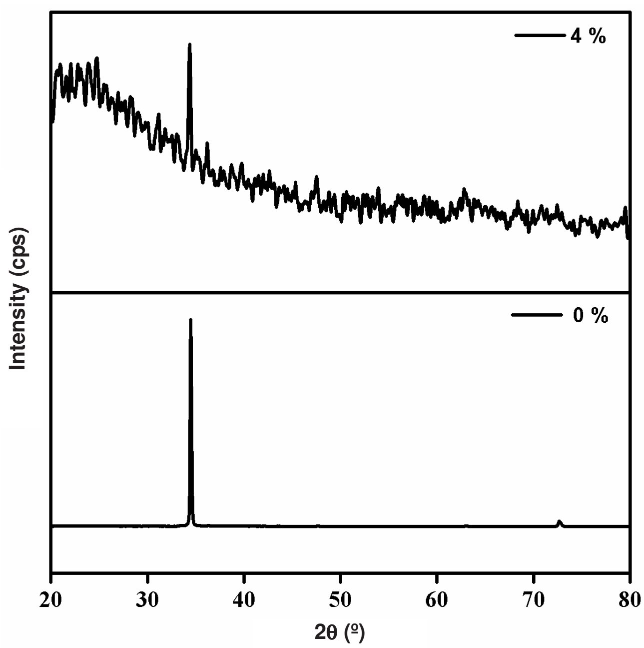

Fig. 1. XRD patterns of ZnO and ZZO films

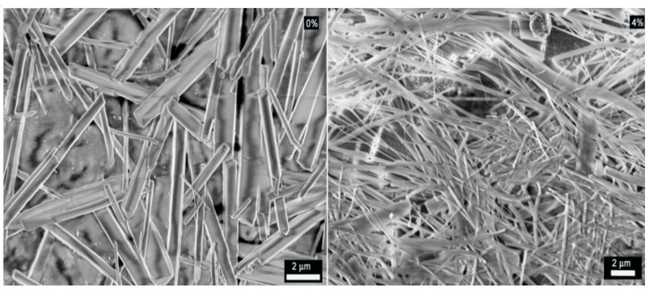

Fig. 2. SEM images of ZnO and ZZO films

Fig. 2 shows the FESEM images of the ZnO and zirconium doped zinc oxide nanowires grown on Corning 1737 glass substrates by the chemical spray pyrolysis method. Fig. 2 shows the pure and zirconium doped zinc oxide nanowires with different diameters ranging from ~50 to 300 nm and their lengths is up to several tens of micrometers[14-16]. Sprayed solution reaches the hot substrate, owing to the pyrolytic decomposition of the solution, in the presence of atmospheric oxygen, the ZnO nuclei is formed. The ZnO nuclei thus formed produce the grown in the form of nanowires. As the doping of Zr is added in the starting solution, the zirconium doped zinc oxide grows in different directions in the form nanowires.

Conclusion

The ZnO and Zr doped ZnO (ZZO) nanostructures have been grown on Corning 1737 glass substrates using spray pyrolysis method at 400 ºC. The effect of the dopant concentration and structural and surface morphology were studied. The broadened XRD peaks of the Zr doped ZnO nanostructures indicate the lattice distortion due to the doping.

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