Two Routes for Cobalt Doping in ZnO Nanostructures

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ABSTRACT

Controlled growth of ZnO nanorods on various substrates is of great importance in photonic and electronic devices. Also of interest is increasing the optical activity of zinc oxide nanorods in the visible spectrum. In this study, we report doping dependence on the morphology, optical, absorption, electrical conductivity and photoluminescence (PL) of aligned ZnO nanorods doped with cobalt from 5 % to 20% grown on glass substrates. The ZnO nanorods were grown by a chemical bath deposition (CBD) technique using equimolar ratios (selected at 0. 1M and 1 M) of zinc (II) nitrate and hexamethylenetetramine in solution at 95◦C. Doping is achieved by adding cobalt nitrate to the precursor solutions of the CBD in one set of samples and by adding cobalt chloride to the CBD precursor solutions in a second set of samples. We compared the doping efficiency in two sets of samples doped with cobalt via cobalt nitrate and cobalt chloride. Measurements of the cobalt incorporated in ZnO matrix were performed using atomic emission spectroscopy (AES). AES measurements show that cobalt incorporation is much more efficient at 1M concentration of the precursor solution using cobalt chloride than using cobalt nitrates for doping. Scanning Electron microscopy (SEM) images show that at 0.1 M ratio of the CBD precursor solutions, the morphology of ZnO deposited resulted in hexagonally shaped nanorods. The nanostructure morphology is maintained in 0.1 M cobalt doping, irrespective of the route (cobalt nitrate or cobalt chloride) taken to achieve the doping. At 1M ratio of the precursor solutions, SEM images show that the morphology revealed platelets at all doping levels, irrespective of the doping method used. Electrical conductivity measurements at 300K using Van der Pauw method show that ZnO nanorods doped with cobalt chloride yielded the lowest resistivity at 0.1 and 1 M. In addition, PL spectra of the doped samples show a peak shift to longer wavelengths in both cobalt nitrate and cobalt chloride samples. The near band edge in absorption measurements show a progressive shift in band gap to lower energies in both types of doping. However, the band edge shift was more pronounced in 0.1 M cobalt nitrate samples compared to other samples. Based on the cobalt incorporation efficiency, doping of ZnO by cobalt chloride may be a better method for achieving higher doping efficiency by chemical bath deposition.

Keywords: zno nanorods, cobalt doping, doping efficiency, photovoltaic cells, optoelectronic devices

1 INTRODUCTION

High efficiency photovoltaic (PV) cells use semiconductors to convert sunlight into electric power. Transparent semiconductors of conductive oxides can provide antireflection coatings to facilitate this effectively in PV cells. Currently various nanostructured materials are under study for manipulating light to increase absorption in PV cells. Our group has been working on ZnO nanostructures for the past 7 years. and has developed a scalable low temperature chemical bath deposition method by which the morphology and aspect ratio of the nanostructures can be easily controlled. ZnO is known to exhibit over 20 morphologies from nanorods to plate like structures [1]. Our group has also developed a solution based method to dope nanostructures with metallic dopants such cobalt, aluminum, cadmium and manganese to tune the index of refraction (and bandgap). Cobalt doping decreases the bandgap while aluminum doping increases the bandgap of ZnO [2, 3].

2 EXPERIMENTAL MEHODS

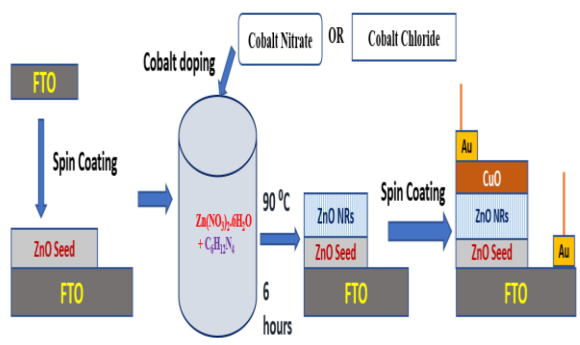

Figure 1: Experimental method and device design

Basic steps in fabricating ZnO nanostructutes using chemoical bath deposition are illustrated in Fig. 1. ZnO Nanowires (NW) arrays were grown on commercial Fluorine doped Tin Oxide (FTO) substrate using a chemical bath deposition process we developed in the lab. The substrate is dipped vertically in an equimolar (0.05M) solution of hydrated Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and Hexamethylenetetramine (HMT) used as precursor's reaction will carry out for 6 -8 hrs at 95ºC. The vertically grown NWs will be annealed at 300ºC for an hour. Finally, Gold (Au) top electrode will be deposited using dc sputtering process. To fabricate NWs doped with Co, either a chloride or nitrate based compound was be added to the chemical bath precursor solution for doping.

2.1 MORPHOLOGY

Figs 2-3 show the morphology of the thin films as the precursor solautions at avrious molarities are doped by either cobalt chloride or cobalt nitrate. As it is evident from these images, the doping via nirate presveres the nanorod structure at 0,1 M of the precursor solutions in CBD.

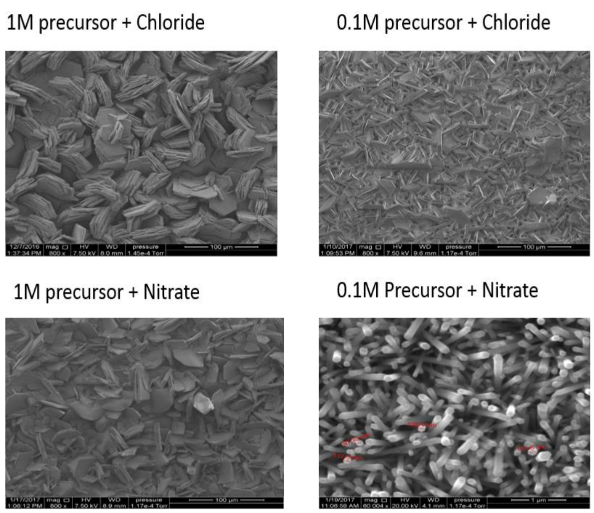

Figure 2: SEM images of cobalt doped ZnO via Cobalt chloride and Cobalt nitrate doping.

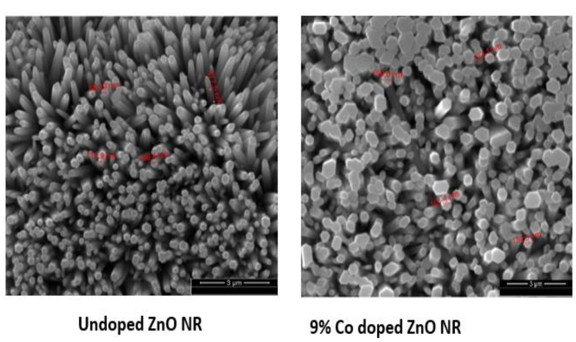

Figure 3: SEM images of nanorods at 0.1 M using cobalt nitrate as doping

2.2 OPTICAL STUDIES

As the doping is increases, we observe increase in ZnO nanorod size with doping in Cobalt doped via cobalt nirate at 0.1 M . This is shown in Fig. 4. One important result of our study is that regardless of the route taken to achieve doping, the bandgap in cobalt doped ZnO decreases with doping as shown in Fig. 5.

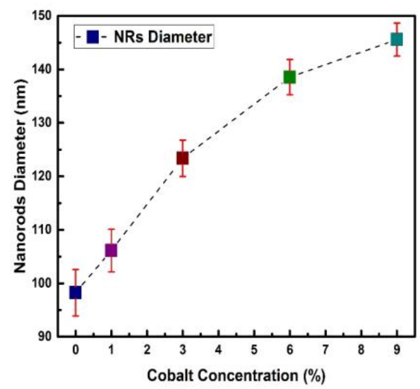

Figure 4: Variation in size of ZnO Nanorods with Co-doping

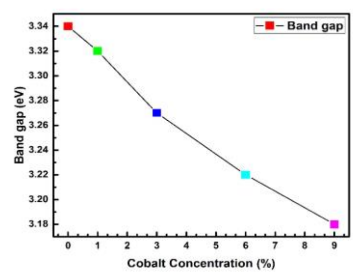

Figure 5: Changes in ZnO bandgap with cobalt doping

2.3 PHOTOLUMINESCENCE (PL)

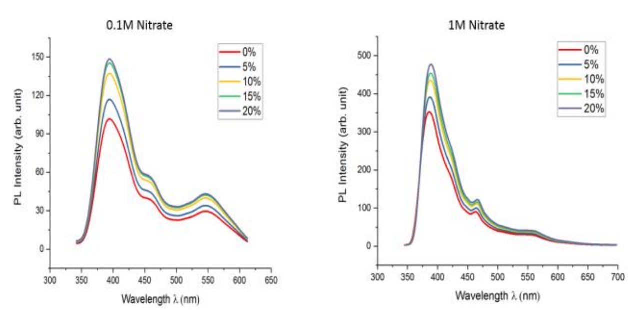

Figure 6: Photoluminescence spectra of doped samples

Fig. 6 shows the reults of photoluminescence (PL) measurenets on two sets of samples prepared at two diifferent molarities and doped with cobalt nirate. We compared the PL peakshift and intensity variation of the cobalt doped samples prepated by cobalt nirate and cobalt chloride as shiwn in Fig. 7.

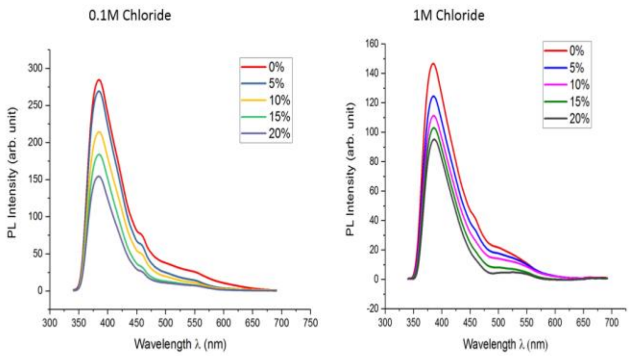

Figure 7: Photoluminescence spectra of doped samples

2.4 STRUCTURAL STUDIES

The actual percentage of cobalt incorporated into the doped sampels were measured using structural invasive measurments such as microwave-plasma coupled atomic emssion spectroscopy (MP-AES) and inductively coupled plasma-mass spectrsocopy (ICP-MS). Table 1 summarises the AES results.

Co %	MP-AES Measurement (Co%)		
	1M Chloride (%)	1M Nitrate (%)	0.1 M Nitrate (%)
5	7.37	2.50	0.35
10	12.04	5.23	3.43
15	16.33	6.05	6.74
20	16.33	10.03	9.13

Table 1: Comparision of MP-AES results of Co-doping

Co Doping Expected (%)	Doping observed from ICPMS	
	Co (%)	Zn (%)
5	1.07	98.93
10	3.13	96.87
15	6.18	93.82
20	9.08	90.92

Table 2: ICP-MS results of 0.1M Cobalt Nitrate

Table 2 summarizes theICP-MS results for a nitrate doped sample.

2.5 SOLAR CELL STUDIES

In order to test the doping efficiency in cobalt doped ZnO samples, we fabricated several photovoltaic cells (PV) using ZnO-CuO heterostructures. One interesting variation we tries was to use p-layer made of nanostructures CuO. We performed electrical measurments on the CuO-ZnO junction doped with cobalt via nirate and chloride. Samples doped with cobalt using cobalt cobalt chloride yielded porr results. Howver, we were able to measure current-voltage (I-V) cahacteristics of nirate based cobalt doped ZnO samples. Table 3 summarizes our results. There is a stead increase in efficiency with cobalt doping as we can see from Table 3.

Co (%)	Voc (V)	Jsc (mA/ cm2)	FF (%)	Eff (%)	Rs (Ω	Rsh (Ω)
0	0.52	4.78	55.82	1.85	67.34	389.54
1	0.53	5.73	56.20	2.27	54.64	467.09
3	0.53	6.58	56.58	2.61	47.53	498.76
6	0.53	8.02	56.70	3.03	38.06	540.79
9	0.54	8.72	57.23	3.18	31.85	595.00

Table 3: IV measurement power conversition efficiency

2.6 CONDUCTIVITY

In addition to I-V measurments, we also performed four point conductivity measurments on nirate based ZnO samples doped with cobalt.

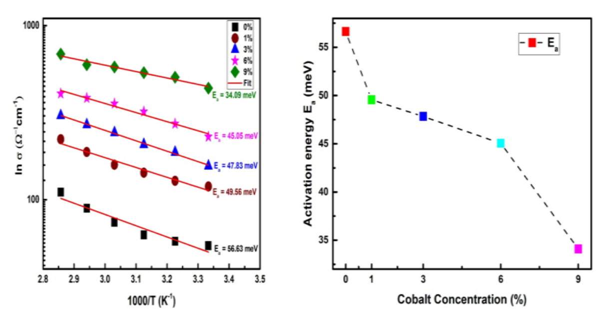

Figure 8: Conductivity Measurement 0.1 M Cobalt Nitrate

Fig. 8 summarizes the conductivity variation in doped ZnO samples doped with cobalt. As it is evident from the data, the conductivity increases with increase in doping concentarions. In addition, we also estimated several activation enegies indicative of the various conduction mechasims involved in the doped samples.

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