Structural, Morphological, And Gas Sensing Studies of Co-Doped ZnO Prepared by Simple Chemical Route

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Abstract- ***We report the synthesis of ZnO nanofibers doped with different amounts of Cobalt (Co) ions using the low-cost chemical technique, where the accumulation of doping material was initiated to affect the morphology of the composite material as well as the crystal structure of the annealed samples. As-prepared samples were annealed in air at 550 ºC for 2.5 h. Microstructural analysis of the X-ray diffraction (XRD) data shows that doping of Co ions in ZnO crystal structure has no sizeable influence because the atomic radius of Zn2+ and Co2+ are very close and they easily replace each other. Up to 5 % of Co doping could be accommodated in the single phase ZnO wurtzite structure as revealed by XRD data. Profile analysis of the XRD patterns reveals that the average crystallite size of CoO increases whereas micro strain decreases with an increase in dopant content. Morphology and microstructure of as-prepared and annealed nanostructures were characterized by Scanning electron microscopy (SEM) and a reduction in particle size was observed upon annealing as a result of the removal of organic components from the samples and conversion of ceramic precursors into ceramic nanomaterials. Their sensing ability is greatly affected by varying different parameters involved in the deposition process. The chemically synthesized Cobalt-doped ZnO nanostructures show that doping can enhance the sensitivity remarkably for LPG.***

I. INTRODUCTION

In modern-day, metal oxides-based nanostructured materials are very interesting because of their wide applications. Among them, zinc oxide (ZnO) is a wide band gap semiconductor with a direct band gap of ~3.36 eV and a large exciton binding energy of about 60 meV. Nanostructured ZnO has been extensively studied due to its intrinsic properties and application in devices like field effect transistors, solar cells, photocatalysts, piezoelectric devices, electro-optic devices, and gas sensors [1-4]. It is observed that tailoring the optical band gap of semiconductors by doping with other elements is preferred over varying the particle size of the semiconductor nanostructures from the viewpoint of applications [5-6]. In this regard, ZnO nanostructure doped with suitable elements is very effective for tuning its structural, optical, electrical, and magnetic properties. ZnO doped with Cd, Al, Mn, and Cr have been well studied [7-9]. Mg doping has been shown to enhance the band gap ZnO [10-11]. Synthesis routes such as hydrothermal [12], chemical vapor deposition [13], ball milling [14], electrospinning [15], and sputtering [16] have been used to prepare ZnO nanostructures. Chemical Bath Deposition is a convenient method to prepare well-adherent nanostructures and it has not been well explored to prepare optimized ZnO:Co nanostructures.

In our day-to-day life, liquefied petroleum gas (LPG) is an important material. It is also used for different industrial purposes. LPG can be termed as a potential explosive material due to its explosive nature and therefore detection of leakage for this gas is very important for preventing severe accidents [17]. Leakage of LPG during household use can make people victims severely. So, it is very much vital to have an efficient method for sensing at the trace level. The gas sensor based on semiconductor metal oxide (SMO) materials is becoming rampant due to its large application in different ecological and industrial sectors [18]. In this system, the specific target gas completely interacts with the surface of the metal oxide through the active participation of surface-adsorbed oxygen ions. As the surface-to-volume ratio of the thin film is larger for thin film, so surface morphology plays an important role here. Those interactions result in a change in the charge carrier concentration of that material which further changes its resistivity.

Here we report on the systematic study of structural, morphological, and gas-sensing properties of ZnO

nanostructures containing doped Co prepared by chemical technique.

II. PREPARATION METHOD

ZnO nanoparticles were synthesized by direct precipitation method using zinc nitrate and KOH as precursors. All the chemicals used were of analytical grade. In this work, the aqueous solution (0.2 M) of zinc nitrate (Zn(NO3)2.6H2O) and the solution (0.4 M) of KOH were prepared with deionized water, respectively. The KOH solution was slowly added to the zinc nitrate solution at room temperature under vigorous stirring, which resulted in the formation of a white suspension. The white product was centrifuged at 6000 rpm for 30 min, washed two times with distilled water, and washed with absolute alcohol at last. The obtained product was calcined at 450 °C in an air atmosphere for 4 hr. For doping, the same procedure was completed by adding 0.2 M Cobalt chloride ($CoCl_2.6H_2O$) with Zinc precursor maintaining a proper ratio.

III. CHARACTERIZATION DETAILS

The structural characterization was done by X-ray diffraction method. Structural characterization of the nanofibers was carried out by using a rotating anode-based powder X-ray diffractometer (Rigaku Ultima Diffractometer 1840) operating with Cu K_α radiation (λ = 0.1542 nm). The gas sensing property was measured using a simple homemade arrangement. The CdO thin film samples were electrodes using conducting silver (Ag) paste on a single side keeping an equal gap for all samples. The value of resistance was measured using a Keithley 6514 DMM electrometer. The amount of gas volume (V) for measurement of sensing properties in presence of 1000 ppm concentration (C_{ppm}) was calculated using the relation [18].

$$V = \frac{C_{ppm} V_T M}{24.5 \times 10^9 D} \qquad (1)$$

where V_T is the volume of the glass chamber, M is denoted for the molecular weight of the target gas, and D gives the density of the target gas. The percent sensitivity for the material can be expressed as

$$S\% = \frac{R_{air} - R_{gas}}{R_{air}} \times 100 \qquad (2)$$

In our work, we have done the sensing characteristic of Co-doped and undoped ZnO nanostructures for a fixed concentration of LPG gas.

IV. RESULTS AND DISCUSSIONS

The structural characterization was done using X-ray diffraction (XRD) patterns as shown in Figure 1. The planes present are (100), (002), (101), (102), (110), (103), (200), (112) and (201). The intensity of the main peaks increases with the doping of Cobalt but it has no or minimum effect on crystal phase formation. This confirms better crystallinity. It is observable from Fig. 1 that undoped ZnO shows a pure single-phase hexagonal wurtzite structure without any impurity phases and all the peaks could be indexed to the data in JCPDS file # 36-1451. The single-phase hexagonal structure was also observed in the samples containing up to 5 w/v.% Co^{2+} . However, the samples with 8 w/v.% Co^{2+} show two extra peaks at 42.72° and 62.07° which corresponds to the (200) and (220) peaks. This shows that up to Co substitutes for Zn up to 5 w/v.% of doping and beyond this amount, it precipitates as a secondary phase in the form of CoO. The average crystallite size (*D*) and micro strain (ε) present in the samples were estimated using the Williamson-Hall relation [20],

$$\beta_{\mathrm{hkl}} \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta$$

The relationship between the crystallite size and the broadening of the reflections was found using the formula where D is the volume-weighted crystallite size, k is the shape factor (0.9), λ is the wavelength of Cu Kα radiation, βhkl is the integral breadth (FWHM) of the reflection (in radians) located at 2θ, and θ is the Bragg angle (in degrees). The results are tallied in Table 1. The c-axis length falls for 5% doping and then increases, but the a-axis length progressively grows. However, there is little variation in the cell volume, which is consistent with the roughly equal ionic radii of Zn^{2+} and Co^{2+}.

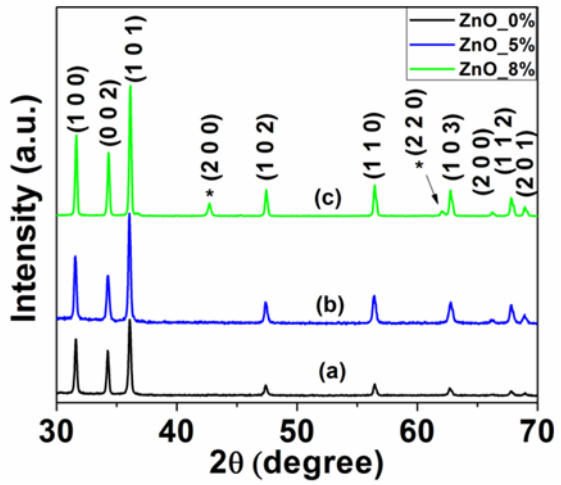

FIG.1. XRD patterns of undoped, 5 w/v% Co-doped, and 8 w/v% Co-doped ZnO annealed at 450 °C for 4 h.

Table: 1

Average crystallite size (d_{av}), microstrain (ε), lattice parameters (*a*, *c*) and unit cell volume (*V*) of ZnO.

Sample ID	*D* (nm)	ε (×10^{-3})	*a* (nm)	*c* (nm)	*V* (nm)^3
ZnO	108	1.75	0.3242	0.52153	0.04764
5% Co_ZnO	82	1.55	0. 32511	0.52018	0.04761
8%Co_ZnO	80	1.12	0. 32610	0.52133	0.04802

The SEM images shown in Figure 2 reveal the morphology of the samples. The doping of cobalt in ZnO increases the crystallinity of the nanomaterials. It also increases the surface roughness as shown in the image. The SEM images also show that the particle size is in the range of 140-160 nm. The surface roughness has impact on sensing abilities.

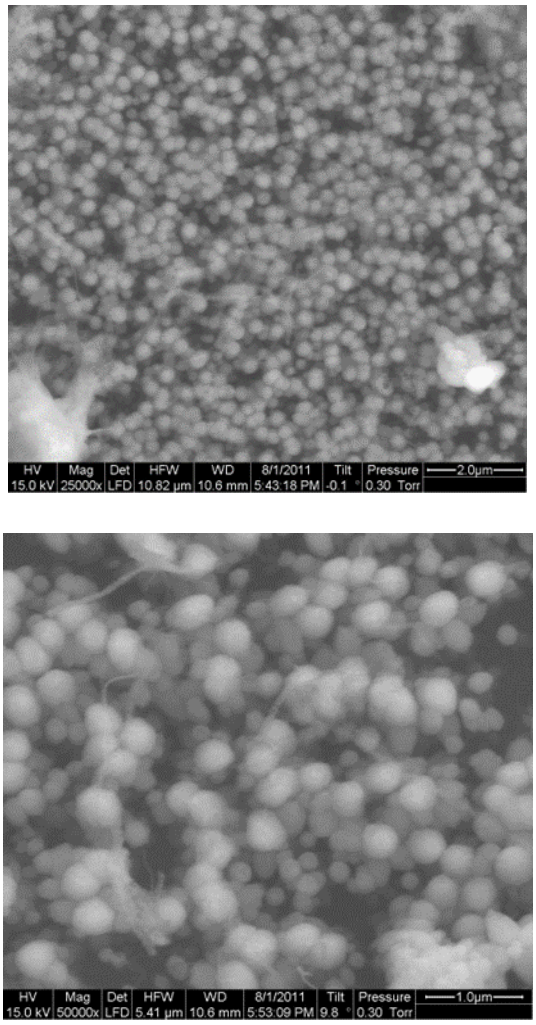

FIG.2. SEM images of undoped and Co-doped ZnO nanoparticles.

The gas-sensing characteristics of ZnO and Co-doped ZnO thin films were carried out for a fixed concentration of 300 ppm Liquified Petroleum Gas (LPG). The variation of percent sensitivity (S%) with operating temperature is shown in Figure 3. For all samples, the sensitivity increases with temperature up to 225^{o}C and decreases beyond this temperature. It is clear from Figure 3 that the percent sensitivity increases progressively with Co doping in ZnO for the total range of operating temperature. This might be due to enhanced surface roughness and porosity resulting from cobalt doping as observed from SEM images. An increase in surface roughness (porosity as well) increases the effective surface area for the reaction of target gas molecules with chemisorbed species [21].

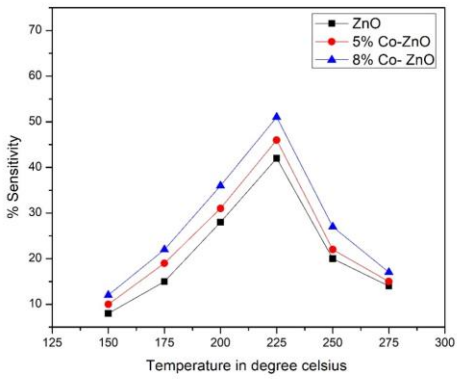

FIG 3. LPG Sensitivity vs operating temperature of ZnO and Co-doped ZnO

CONCLUSION

Cobalt doped ZnO nanomaterials with different concentrations were prepared by low-cost chemical method. XRD reveals formation of nanostructure and crystallinity increases with doping of cobalt on ZnO. SEM images show that Co substitution and annealing have a direct influence on surface morphology. Morphological studies from SEM show incorporation of nickel was found to enhance surface roughness and porosity apart from enhancing disorders in the samples. The LPG sensitivity of ZnO increases with cobalt doping for all operating temperatures. Such an increase in sensitivity from~ 42 % for pure ZnO to ~ 51% for 8%Co-doped ZnO at operating temperature 225ºC might be due to enhanced surface roughness and porosity resulting from cobalt doping. In the Future, a lot of work is required for the modification of these sensing materials.

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