Mg-doped and chemo-thermally treated ZnO nanoflowers for ethanol sensing

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Abstract

ZnO nanostructures are promising for a wide range of applications, including gas sensors. Ethanol sensing using ZnO remains unexplored though. In this paper, we report ethanol-sensing using un-doped ZnO nano flowers and Mg doped ZnO nano flowers. These are grown using a rather simple chemo-thermal process, making this a plausibly scalable technology. To study the structural and morphological properties of undoped ZnO and Mg doped ZnO nanoflowers, Raman spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), x-ray diffraction and Field Emission Scanning Electron Microscopy (FESEM) are carried out. Ethanol sensing properties of undoped ZnO and Mg doped ZnO nanoflower devices are investigated toward different ethanol concentration (concentration range of 1–600 ppm at 100°C–200°C). Our findings show that 15% Mg doped ZnO nano flower is better than ZnO nano flower for ethanol gas-sensing applications.

Introduction:

Zinc oxide (ZnO) has proven to be a rather versatile semiconductor material with several attractive properties such as direct and wide band gap (3.37 eV), non-toxicity and biocompatibility (hence eco-friendliness), and an exciton binding energy of ~60 meV [1-5]. ZnO, in its various morphologies offer different properties. For instance, wires, rods, tubes, nanocages, nanocombs, nanorings, nanosprings, nanobows, nanodiscs, and belts have been developed for a wide range of applications. These applications range is from water treatment [6-7], sensing, diode fabrication [8-9] etc). These nanostructures with improved surface-to-volume ratios and high one-dimensional electron mobility along growth directions, offer prospects for manufacturing advanced compound semiconductor devices [10-18]. Today ZnO is being deployed for applications such as gas sensors, solar cells, photodetectors, and liquid crystal displays [19-21]. Sensing, which is the target application in this study, has been one of the areas wherein ZnO has been found to be impactful [22-24]. However especially ethanol sensing using ZnO based nanostructures remains largely unexplored. It is in the context of this gap, that this work is carried out.

In this paper Mg doped and chemo-thermally treated zinc oxide (ZnO) nanoflowers are grown for ethanol sensing. Evaluation of the sample is carried out using techniques such as Raman spectroscopy, Fourier Transform Infrared Spectra (FTIR), x-ray diffraction, and scanning electron microscopy (SEM). It is also observed that ethanol sensing performance improves with increase of Mg doping percentage from 5% to 15%.

Fabrication Methods:

A p-type 2 inch diameter silicon wafer is treated through SC (standard cleaning)-I and SC-II to remove organic, ionic contaminants and thin oxide layer. Thin ZnO film (60nm) is deposited using a dielectric sputtering system with 100mm diameter and ~5mm thicker sputtering target. Radio-frequency for the sputtering is 13.56 MHz with 1.5×10^{-6} Torr vacuum, 99.9% pure Argon atmosphere and ~179W of RF

power. The deposition of ZnMgO using two different doping concentrations of 5% and 15% (using two different targets) is carried out using the same deposition technique. The RF power at the time of ZnMgO deposition is varied from 60W to 200 W. The oxygen and argon percentage are changed at the time of deposition to get better quality of film.

The deposition of gold (Au- 50 nm) and aluminium (Al-60nm) is carried out using a 4 target E-beam evaporator system. The photolithography step is carried out to form the contact and electrode using a double side aligner (DSA) with SPR 700-1.8 photo resist, 500rpm-3000rpm-500rpm rotational speed, and MF319 developer.

Growth of ZnO/ZnMgO nanoflower, on the sputter deposited ZnMgO film is carried out through chemo thermal method. This is done using a glass beaker, which contains a substrate holder. This holder is used to fix the patterned substrate, and a magnetic stirrer is used during the entire chemo-thermal process. Zinc acetate di-hydrate ($\text{Zn}(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_2$) and Hexamethamine ($\text{C}_6\text{H}_{12}\text{O}_4$) at molar ratio 15:10 is mixed in de ionized water (DI-water). The experiment is carried out for 4hr to 6hr at a constant temperature of 85 °C. Figure 1 represents the scanning electron microscopic image of ZnO/ZnMgO nano flower.

Result Analysis:

To confirm the formation of flower shaped nanostructures of ZnO, scanning electron micrography (SEM) is performed (Figure 1). It is clear that the ZnO/ZnMgO nano flower with 15:10 mM solution concentration and 4.50 hrs reaction time shows uniform nano structure formation on the sputter-deposited film (15% doped Mg:ZnO sample) (Figure 1(a)). Interestingly as doping concentration decreases, the uniformity of nano rods reduces (shown in Figure 1(b)). Also for the undoped sample, the uniformity and crystallinity is less than that of the sample with 5% and 15% Mg doped ZnO. This is evident from Figure 1(c), x-ray diffraction (XRD) and photo luminescence (PL) measurements. The crystallinity of all the samples is confirmed through x-ray diffraction (XRD) measurement.

Figure 2 shows the normalized XRD spectra of pure ZnO and Mg-doped ZnO nano flower at 5%, 15% doped and un-doped samples respectively. Figure 2 shows the High Resolution x-ray Diffraction (HRXRD) images of (a) pure ZnO (b) 15 mol% Mg-doped ZnO, (c) 5 mol% Mg-doped ZnO nano flower structures. the XRD pattern exhibit three major diffraction peaks which are assigned to (100), (002), and (101), respectively. These are consistent with the hexagonal wurtzite structure (JCPDS card No. 01-079-2205). It is observed from the XRD pattern that the position of XRD peaks shifted towards higher angle which indicates some lattice doping of the Mg atoms. With increasing Mg doping concentrations, shifts towards larger angles are observed; this is due to the smaller ionic radius of Mg^{2+} compared to Zn^{2+} [25-27].

In order to investigate the vibrational properties of the un-doped and 15% Mg doped ZnO nano flower structures, Raman spectroscopic analysis is carried out with the 514nm excitation wavelength. Figure 3 represents a Raman spectroscopic analysis of un-doped and 15% Mg doped sample. Raman peak shifts

occur for three reasons; first due to phonon confinement effects, [28] second due to lattice strain, [29] and third due to oxygen vacancies [30]. The 15% Mg doped ZnO nano flower shows the shift of the signals, when compared to the un-doped ZnO (which shows a rather weak Raman peak intensity). Also the Raman peak is broadened for the Mg doped ZnO. The peak at 587 cm^{-1} shows maximum shift (assigned to the E1 (LO) mode) due to the formation of defects like oxygen vacancies [31].

Also to confirm the Mg doped in ZnO sample the Fourier Transform Infrared Spectra (FTIR) is carried out (as shown in Figure 4). FTIR data for ZnO and 15% Mg doped ZnO sample is recorded in the wavelength region $4000\text{--}300\text{ cm}^{-1}$. The band stretches at $\sim 480\text{ cm}^{-1}$. This is due to the Zn–O stretching mode in the ZnO lattice [32]; the band at 1684 cm^{-1} is due to the first overtone of the crucial stretching mode of O–H [33–35]. The band stretches at $\sim 3316\text{ cm}^{-1}$ due to Mg–O stretching mode. A wide absorption band in the region of 3316 cm^{-1} is due to the stretching vibration mode of a hydroxyl group [36].

Figure 5 shows the response of un-doped ZnO at 180°C , and 15% Mg doped ZnO at 150°C . Ethanol is introduced in various concentrations. Sensing is carried out on ethanol gas molecules based on adsorption and desorption. It is clearly visible that the linear increase in the response is due to availability of active surface sites for the adsorption of ethanol molecules. In this case, the surface doping of Mg into the ZnO is most likely responsible for the enhanced sensing performance. Interestingly Mg doped ZnO also has enhanced recovery characteristics when compared with un-doped ZnO based samples (as shown in Figure 6). This indicates that the Mg doped system (likely containing MgO on the surface), in fact has rather shallow defect states.

It is evident that sensing response gets better with increasing temperatures. Figure 6 (b) shows that 15% Mg doped ZnO senses better than un-doped ZnO at low temperature (140°C). This is because of mainly two reasons. First, ZnO has larger (apparent) defect density when compared to ZnMgO. Furthermore, ZnMgO–ZnO results in p–n junction (heterojunction) diode and the built-in potential reduces the recombination at the defect states. Also, it is seen from Figure 6(b) that at low gas concentration, 15% Mg doped ZnO shows better performance than un-doped ZnO.

Conclusion:

To conclude, ZnO nano flowers are grown on sputter-deposited Mg doped ZnO. This material is found to be promising for ethanol sensing. Presence of Mg indeed improves the sensing performance. It is seen that 15% Mg doped ZnO shows faster sensing response than the rest.

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Figures

Figure 1

Scanning electron microscopic (SEM) image of the nano flower material, (a) ZnO/ZnMgO nano flower with 15:10 mM solution concentration and 4.50Hrs reaction time (15 % Mg doped), (b) ZnO/ZnMgO nano flower with 15:10 mM solution concentration and 4.50Hrs reaction time (5 % Mg doped), (c) ZnO nano flower with 15:10 mM solution concentration and 4.50Hrs reaction time (un doped), (d) ZnO/ZnMgO nano flower with 15:10 mM solution concentration and 5.50Hrs reaction time (15% Mg doped)

Figure 2

X-ray Diffraction (HRXRD) images of (a) un-doped ZnO (b) 15 mol% Mg-doped ZnO, (c) 5 mol% Mg-doped ZnO nano flower structures.

Figure 3

Raman spectra of undoped ZnO nano flower and 15% Mg doped ZnO nano flower samples.

Figure 4

Room temperature FTIR spectrum of un-doped ZnO sample and Mg doped ZnO sample

Figure 5

Response to ethanol of various concentrations by (a) 15% Mg doped ZnO at 150 oC (b) Un-doped ZnO at 180 oC. ZnMgO shows faster response rather than ZnO sample.

Figure 6

Sensing response of undoped ZnO sample and Mg doped ZnO sample (a) changing sensing response with the gas concentration, (b) changing sensing response with the temperature