Synthesis of ZnO/CuO Nanocomposite and Optical Study of Ammonia (NH_3) Gas Sensing

F. Z. Haque, Neha Singh, Pranjal Ranjan

Abstract. This article describes the synthesis of ZnO/CuO nanocomposite with the average crystallite size ~ 21nm through sol–gel and hydrothermal synthesis using Tetraethyl ammonium bromide (TEAB) as a surfactant. Crystallinity, average crystallite size were confirmed by X-ray diffraction analysis (Scherer's method), and morphology were confrmed by Scanning Electron Microscopy. Using the optical properties (PL) interaction between ammonia gas (25ppm) and ZnO/CuO nanocomposite nanostructures were also investigated.

Keywords: Ammonia gas, TEAB, ZnO/CuO nanocomposite.

1 INTRODUCTION

Ammonia (NH_3) is widely used in industry and the monitoring of its leakage has become an important task as it is toxic [1-6]. Metal-oxides (SnO_2, ZnO and TiO_2) based ammonia gas sensors are being developed extensively as they are more sensitive to NH_3 and also easy to fabricate. These sensors are, traditionally, of the electrical resistive-type whose resistance varies when they are exposed to the detecting gas. However, these sensors exhibit enhanced gas sensitivity only at high operating temperatures (above 200°C) and also respond to many gases (CO, methanol, NH_3 and CH_4) [7]. Hence, the gas sensitivity of metal oxide sensors are being improved by changing their physical properties by doping, annealing or changing their size (nanomaterials), to facilitate ambient temperature operation and improved gas selectivity. In the recent years, optical gas sensors based on metal oxides as the sensing medium have been reported for improving the gas sensitivity and selectivity and also for room temperature operation [8,9]. ZnO is an important wurtzite-type semiconductor with bandgap energy of 3.37 eV at room temperature and a very large excitation binding energy of about 60 meV[10,11]. It also has interesting chemical, acoustic, optical and electrical properties. Where as Copper (II) oxide (CuO) nanoparticles are also an important inorganic semiconductor with the direct band-gap value of 1.85 eV [12,13], By which ZnO & CuO can be used as emerging sensing material [14].

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This paper reports the results of a study on the characteristics of a optical ammonia sensor with as-prepared and annealed ZnO/CuO nanocomposite with TEAB (caping agent) as the sensing material. Results show the variation in PL spectra before and after the influence of ammonia gas. Other gases such as methanol and ethanol are used for studying the sensor's gas selectivity.

2. EXPERIMENTAL DETAILS

All chemicals were analytical grade and used without further purification. Zinc acetate dehydrate [$Zn(COOCH_3)_2.2H_2O$] and Copper acetate used as zinc and copper precursor material procured from Merck with 98% purity. 2Methoxy ethanol, Monoethylamine and Tetraethyl ammonium-bromide (TEAB) procured from Sigma Aldrich with 98% purity as solvent, stabilizer and surfactant respectively.

2.1 Synthesis of ZnO/CuO Nanocomposite

Sample A (Sol-gel synthesis of ZnO/CuO nanoseeds): Preparation of composite of nanoseeds ZnO/CuO has been done by using sol-gel method. ZnO and CuO sols were prepared separately by using Zinc acetate dihydrate and Copper acetate with 2Methoxy ethanol and Monoethylamine under constant stirring for 60mint. Both chemicals were mixed and stirred for 1hr. followed by the formation of gel. The as prepared sol was coated on glass slides and calcined it at 300°C with variation in heating time for different temperature (30 mints, 60 mints, 90 mints.).
Sample B (Hydrothermal synthesis of ZnO/CuO nanocomposite): An equimolar solution of $Zn(NO_3)_2.6H_2O$ and $Cu(NO)_3$ is prepared with the addition of TEAB as surfactant followed by NaOH as pH controller with pH 10. Seeded substrate of ZnO/CuO was kept up-side down within the solution for 30 mints. Finally the substrate were washed several times and calcined at 500°C for 2hrs.

2.2 Gas Detection

For optical gas sensing measurement the sample was excited by a Xenon laser as light source [F-7000 Hitachi] at 330 nm excitation wavelength. Sample was placed inside a quartz sample holder at room temperature, this sample holder was kept inside the spectrometer chamber for optical measurements, and then this sample holder was filled with ammonia gas. The data was recorded before and after the exposer of ammonia gas for comparison. The spectral response of the

sensor was recorded for ammonia at given concentration (25 ppm) after 20 min, & 40 min.

2.2 Characterizations

The synthesized powder was characterized by various techniques like X-Ray Diffraction, Scanning Electron Microscope, and PL spectroscopies. The crystallinity and phase identification of powder was investigated using X-ray powder diffraction, (X-ray powder diffractometer D8 Advance) in the scanning range of 20-80°θ using Cu Kα radiation having a wavelength of 1.5406Å at the scanning rate of 15.50sec with the measurement temperature 25°C, operating at 40 kV and 40 mA. The phase was identified using the standard JCPDS data files. The surface morphology was studied by scanning electron microscopy (JEOL-JSM-6390) with an accelerating voltage 10Kv, at operating potential of 15 kV. Optical analysis was determined from photolumineces Spectrophotometer (model: F-7000 FL Spectrophotometer) in region 350 to 700 nm.

3 Results and Discussion

3.1 X-ray Diffraction Analysis

Figure 1 shows XRD pattern of ZnO/CuO nanocomposite flower structures grown on Si substrate. The observed diffraction peaks in the recorded XRD pattern agrees well with the values available in the JCPDS card (JCPDS 36-1451 for ZnO and JCPDS 05-0661 for CuO). No other characteristics peaks were observed in XRD pattern, indicating the phase-purity and crystallinity ZnO has been obtained. The phase separation between ZnO and CuO is visible confirming the existence of both ZnO and CuO. Plane (100), (002) and (101) shown the differaction peak of ZnO, and CuO differaction peak obtaind at (-111) and (111) shown in figure 1, an very intense and sharp peaks appears at 2θ values around 31.31°, 33.96°, 35.79° for zinc oxide and 35.05°, 38.29° for copper oxideat 500 °C are in good agreement with the standard data. As shown XRD below there is some strain in material which have average value of 0.005428 for 500°C which are clearly describe through Williamson hall plot, and having the average crystalline size of 21.37 nm respectively (image not attech). The first two differaction peaks coming from Si substract shown in figure 1.

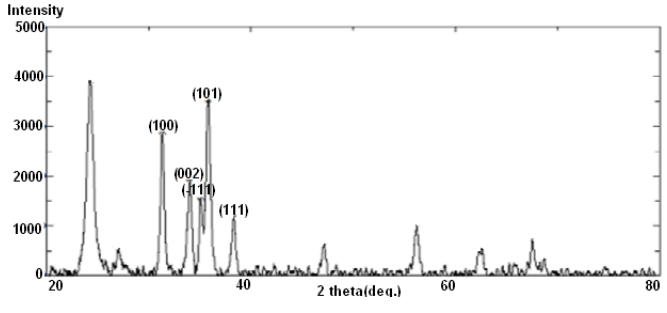

Figure 1: Shows XRD pattern of ZnO/CuO nanocomposite calcinated at 500°C

3.2 Morphology Using Scanning Electron Microscopy

Figure 2(a) shows the morphology of ZnO/CuO nanoseed synthesized by sol-gel method without post heating whereas Figure 2(b,c) shows the morphologies of ZnO/CuO nanocomposite grown on seeded substrate using hydrothermal method and calcined at 500°C which represents the formation of 3Dimension structures.

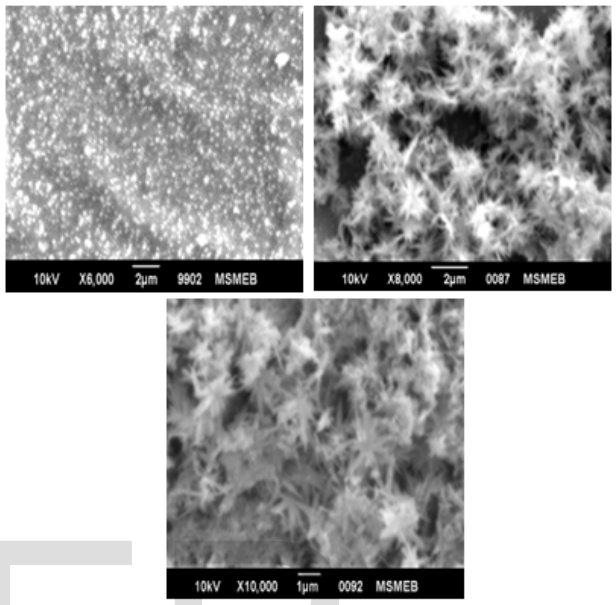

Figure 2: (a) shows nanoseeds and (b,c) nanoflower structure shown by ZnO/CuO composite using SEM.

3.3 Ammonia Detection

For optical characterization, sample was placed inside a sample holder which was inside a spectrometer chamber kept at room temperature, with quartz windows granting easy access for optical measurements. PL measurements were performed using a Xenon laser as light source at 330 nm. PL spectra were acquired perpendicular to the sample surface using a single spectrograph. A filter was used to get rid of secondary wavelength during the whole measurements, and for this reason only visible spectrum was acquired as a function of gas species. Figure3 shows the overlapped PL spectra of samples taken with and without the exposure of ammonia gas. The data was recorded in the presence of simple air in the chamber, and then the sample holder was filled with 25 ppm ammonia gas for comparison. To study the dynamic behaviour of PL with gaseous species we acquired PL spectra after 20 min & 40 min (with increase in influence of gas on nanocomposite) as shown in figure3. The PL spectrum of zinc oxide/copper oxide nanocomposite prepared at room temperature shown in figure3. A strong emission peak was observed around 406 nm and 410nm (violet emission). The enhancement of PL intensity

of the ZnO/CuO nanocomposite exposed to ammonia gas can be explained by an electron transfer mechanism as follows.

When ammonia gas (25 ppm) is exposed inside test chamber, we observed an increase in PL intensity, (see Figure 3), as well as we measure slightly shift of the peak. , the change in PL intensity is mainly caused by the absorption and desorption of oxygen on the surface of sensing materials. The overlapping of spectra with variation in time under the influence of gas is clearly shown in spectra.

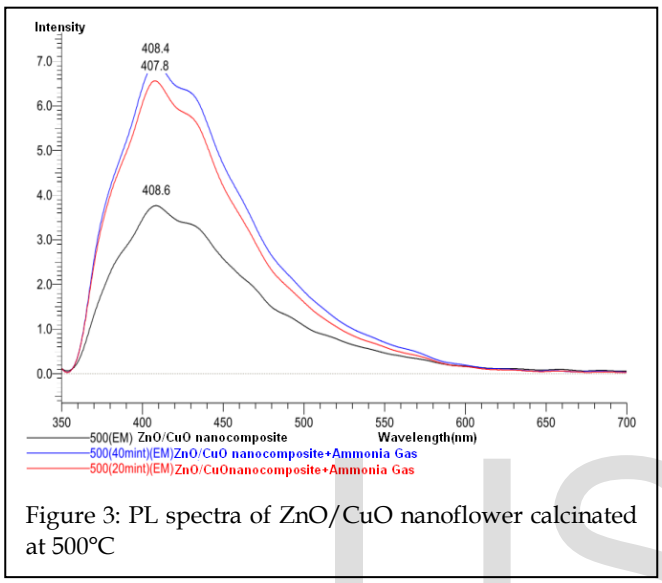

Figure 3: PL spectra of ZnO/CuO nanoflower calcinated at 500°C

ZnO is an n-type semiconductor where as CuO shows p-type. Due to this ZnO/CuO nanocomposite appeared as p-n hetrojunction. In case of ZnO material, Oxygen molecules are absorbed on the ZnO surface and capture free electron from them to form chemisorbed oxygen species which results high resistance and by which low conductivity hence low PL intensity. In similar fashion copper also results low intensity of PL. And when the ammonia gas is exposed on given composite, the reaction between NH_3 and oxygen species happens to release electron back to their respective oxides, which led increase in carrier concentration. By above procedure the named photo-excited ZnO/CuO nanocomposite promote the formation of excitons, thus reduce the tendency of non-radiative transition and consequently results in the PL intensity enhancement. There also very slight shifting in peaks is found due to presence of ammonia gas(25 ppm) when compared it with without influence of gas is because change in refractive index of the composite.

Conclusion

ZnO/CuO nanostructures prepared in a controlled manner, using sol–gel and hydrothermal synthesis with average crystallite size ~21 nm. TEAB is also efficient surfactant for the controlled fabrication of ZnO/CuO nanostructures with flower like shapes and size at 500°C. The optical properties with exposed to ammonia gas (25ppm) of ZnO/CuO nanostructures from using surfactant is systematically investigated in the present work.

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