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Pulse-like highly selective gas sensors based on ZnO nanostructures synthesized by a chemical route: Effect of in doping and Pd loading

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ABSTRACT

A low-temperature chemical route was used for the synthesis of hexagonal ZnO nanorods having an aspect ratio of ~10. The sensing properties of the thick films made from these nanorods were investigated. It was observed that the surface irregularities, calcination temperature and operating temperature altered the structure and thus the gas sensing properties. An effort was made to create surface misfits by doping indium into the zinc oxide and study the changes in the sensor performance. Effect of palladium loading on the selectivity was also investigated. It was observed that indium doping favors the ethanol sensing and palladium loading enhances the sensor response toward LPG. The quick response, high sensor response and selectivity are the main features of this work.

1. Introduction

Semiconductor metal oxides as a gas sensing materials have attracted great attention due to some advantageous features, such as; high sensor response, selectivity, low cost, simplicity in fabrication, fast response and recovery, non-toxicity and suitability to different doping [1]. ZnO has found to display good sensor response to many gases like; C_2H_5OH, NO_2, CO, etc. One-dimensional nanostructures, like nanorods and nanotubes have a high aspect ratio, and therefore, they are very attractive candidates for designing the next-generation gas sensors. The gas-sensing property of any material is related to the surface state and the morphology. Materials in bulk form have limited sensor response because they have a relatively low surface-to-volume ratio [2]. Yamazoe has demonstrated that reduction in crystal size would significantly increase the sensor performance because of increased surface area available for gas molecules. When the particle size is of the order of Debye length, whole grain becomes depleted of the charge carrier (as they get trapped in surface states), and they exhibit a poor conductivity in the ambient air. The target gas activates these carriers from trapped states in the conduction band resulting in change in drastic change in conductance [3]. There is a great demand for a highly selective gas sensor with good response, recovery time and low operating cost. Therefore, several metal oxide nanomaterials are being investigated.

Zinc oxide (ZnO) is an n-type direct band semiconductor having a wide-band gap (3.4 eV). It is known that by changing the stoichiometry and by doping; the conductivity can be altered. ZnO in the doped and undoped form are being studied intensively for gas sensing applications. In the presence of oxygen, a potential barrier (Schottky type) is formed at the inter grain boundaries of the film, which dominates the conductivity of the film. Depending upon the type of gas i.e. oxidizing or reducing, the potential barrier height changes, resulting in increase or decrease in the conductivity. It is well known that the sensing property depends highly on the grain size and porosity. Although, there are numerous reports on sensing properties of ZnO [4–7], there are few reports on the effect of indium doping and palladium loading in ZnO nanorods. Indium is chosen to decrease the resistance of the pure ZnO nanorods. Loading of noble metals increases the cost of the sensor but such modifications are necessary to monitor some explosive and toxic gases from a mixture of gases [8]. These additives act as catalysts for the reaction between gas molecules and film surface.

This paper describes a low-temperature chemical route for the synthesis of ZnO nanorods. The purpose of this investigation is to evaluate the sensing properties of thick-film gas sensors based on ZnO nanorods and to study the effect of indium doping and palladium loading on the sensor response and selectivity of the ZnO sensor.

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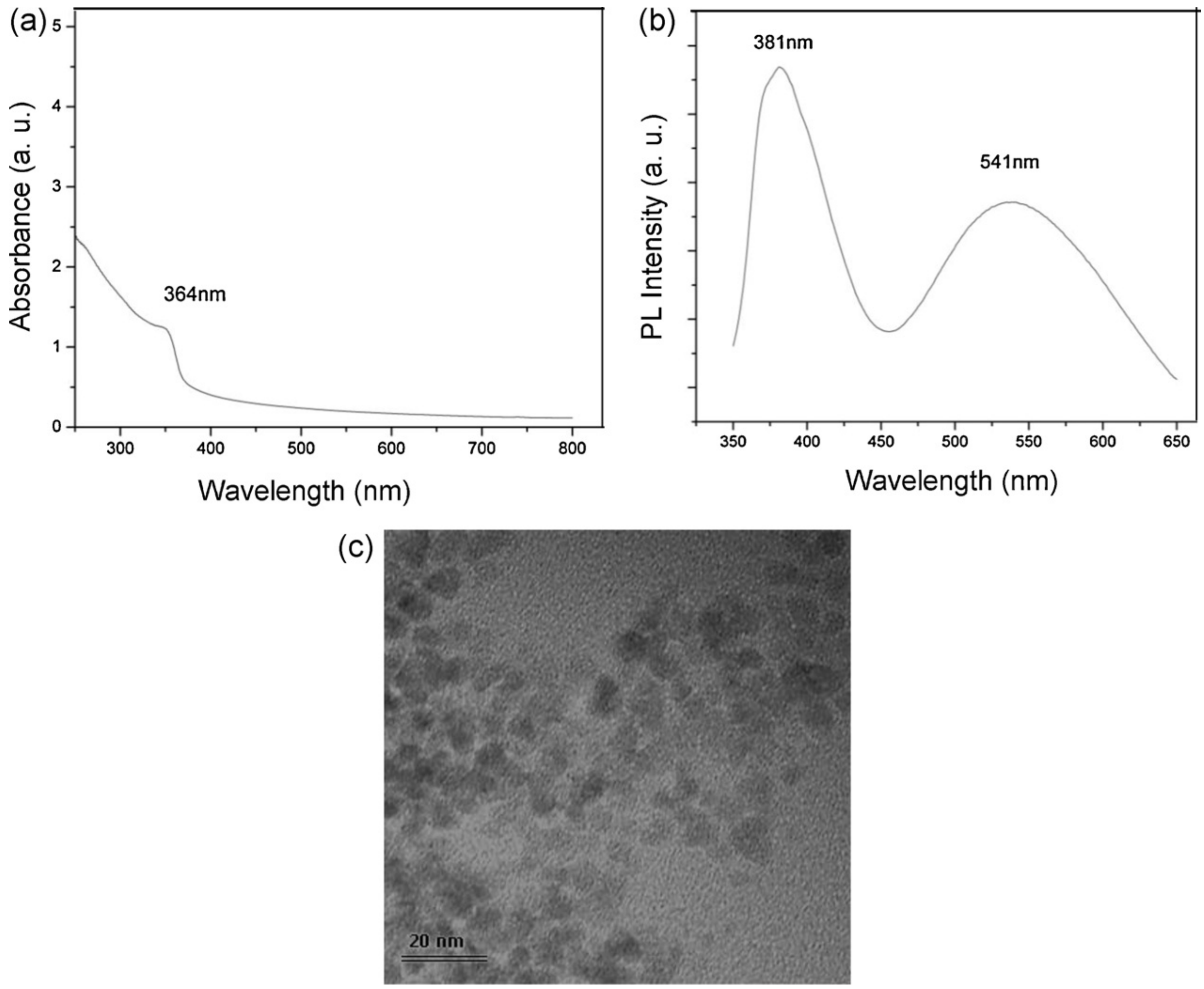

Fig. 1. (a) UV–vis spectra, (b) PL spectra, and (c) TEM images of synthesized ZnO seeds.

2. Experimental details

2.1. Synthesis of ZnO seeds

Precursor solutions of $Zn(CH_3COO)_2{\cdot}2H_2O$ and NaOH were made separately by dispersing them in 2-propanol under constant stirring at 50 °C. After mixing; solutions were cooled below 4 °C. In the next step, hydroxide solution was added drop wise to the zinc acetate solution under vigorous stirring. A transparent colloidal solution of ZnO nanoparticles was obtained when the mixture was aged at 60 °C for 2.5 h [9]. The seeds were used for synthesizing ZnO nanorods.

2.2. Synthesis of ZnO nanorods

For the synthesis of ZnO nanorods, 2.5 ml of 0.5 M hexamethylenetetramine (HMTA) was added to 32.5 ml water and heated to 70 °C. 5 ml seed solution was added to it [10]. The temperature was raised to 90 °C and 5 ml PEG (M_w = 10,000, 1 g dissolved in 10 ml water) and 5 ml zinc nitrate hydrate (0.25 M) solutions were added drop-wise into the flask simultaneously. The mixture was heated at 90 °C for 2 h while stirring. The solution was washed with hot distilled water several times in order to remove excess PEG. Powder was obtained by drying the solution at 80 °C.

For indium doping, 2 wt% of indium nitrate was added to the solution of zinc nitrate in water. 1 wt% Pd was loaded on the thick film sensors by dipping the film into the solution of $PdCl_2$ and then calcining it at 600 °C for an hour.

2.3. Fabrication of sensors

ZnO nanorods were mixed with ethyl cellulose (10:1 ratio) to make the paste and butyl-carbitol and terpineol were mixed to make the paste viscous. The paste was applied on the alumina substrates. The deposited film was dried at 100 °C for an hour and calcined at 600 °C for an hour. Ramp rate for calcinations was kept at 3 °C min^{-1} in order to avoid cracks in the deposited film. Sensor response characteristics were recorded using a Keithley Digital multimeter 6487 interfaced with a personal computer.

2.4. Sample characterization

The crystalline phase and crystallite orientation of the samples were characterized using Bruker D8-advance X-ray diffractometer with CuKα (λ = 1.5418 Å) incident radiation. The morphological and structural characteristics of ZnO nanorods were investigated by scanning electron microscope (SEM, LEO 440), and high-resolution transmission electron microscope (HRTEM, Technai G20-stwin). Chemical bonding of the sample was analyzed using X-ray photoelectron spectroscopy (XPS, Perkin-Elmer 1257) with a 279.4 mm diameter high resolution electron energy analyzer and Al Kα X-ray source.