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CO Gas Sensing Using Ga Doping ZnO Nanorods by Hydrothermal Method: Effects of Defects-Controlled

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Abstract

We report here the synthesis Ga-doped ZnO nanorods by hydrothermal (HT) method and investigate the effects of Ga-doping on their CO sensing properties. It is found that Ga doping cancel out oxygen-related defects (oxygen interstitial) based on the results of photoluminescence (PL) experiments and further confirmed by the CO sensing experiment. The defect-controlled, which are donor-(shallow donor and zinc interstitial) and acceptor-related (oxygen interstitial) ones, in ZnO nanorods were adjusted by Ga doping level. The CO sensing properties of ZnO nanorods are effectively improved by Ga doping. These can be explained in term of the removal excess oxygen in ZnO nanorods surface, increase shallow donor concentration and Ga-doped ZnO formed active component for CO absorption.

Key words: CO gas sensing, Ga doping, ZnO nanorods, Hydrothermal method, Defects-controlled

Introduction

Carbon monoxide (CO) is one of the most dangerous gases in air pollution and human life. CO is produced by incomplete combustion of fuels and commonly found in the emission of automobile exhaust, the burning of domestic fuels, etc. It is highly toxic and extremely dangerous because it is colorless and odorless [1]. Among several materials for CO sensing, ZnO nanostructures are considered as one of most potential candidates for gas sensor due to large specific surface area, good bio-compatibility and high electron mobility [2]. Doping with other element is effective way in order to improve gas sensing properties of ZnO nano-structure at low temperature. For example, Han et al. [3] evaluated the doping effect of Fe, Ti and Sn on gas sensing property of ZnO. Gaspera et al. [4] consider the effects of doping transition metal ions into ZnO, resulting in a lower detection limit of 1-2 ppm CO at 300 °C. However, the role of the dopants in the gas sensing process is however not well recognized, with presumption and discussion based on term of crystal structure, defects, surface area or active sensing component by doping.

The nonstoichiometry (crystal defects) of ZnO was a key factor determining the gas sensing properties [5-7]. These crystal defects such as oxygen vacancies [5-6] or shallow donor [7] play role as absorb site for gas molecules along ZnO nanostructures surface. The crystal defects can be controlled by doping [6] or post-annealing process [5, 7]. The ZnO nanostructures syntheses by physic vapor deposition (as vapor liquid solid or thermal evaporation) at high temperature usually possess oxygen vacancies defects [5-6] and inversely ZnO nanostructures synthesized by wet chemical method contain oxygen interstitial (excess oxygen) [7-9]. In comparison with physic vapor synthesis method, the chemical route, for example hydrothermal method has several advantages as low temperature, simple, cheap and easy for doping. Recently, Li et al. doped Co into ZnO nanorods to enhance CO sensing properties by electrochemical deposition, which is an economic, effective approach and suitable for large-scale production [9].

Among these metal dopants, the Ga doping seems to be the most successful and promising due to its advantages, such as the rather similar ionic radius and the covalent radius (0.62 and 1.26 Å), as compared to those of Zn (0.74 and 1.34 Å), respectively. Therefore, the Ga^{3+} can be substituted for Zn^{2+} without any lattice distortion and cause free-stress in ZnO materials. For the doping Ga into ZnO nanostructure, some typical growth techniques were used, such as the hydrothermal method [10], thermal evaporation [11] and pulsed laser deposition [12]. Among them, the hydrothermal method has distinct advantages of a large area film at a low cost, excellent compositional control, homogeneity on the molecular level due

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to the mixing of liquid precursors, and lower crystallization temperature [10]. In this work, we describe the synthesis and characterization of Ga-doped ZnO nanorods by hydrothermal method and investigate the effects Ga-doping on CO sensing properties of ZnO materials.

Experimental

The vertically aligned ZnO nanorods grow on p-type silicon (Si) to form p-n junction as a CO gas sensor. A template ZnO thin film was deposited as a seed layer on p-Si substrates by sol-gel technology before synthesizing the nanorods. The ZnO template, with a 200 nm thickness, was prepared by sol-gel method [13]. Next, ZnO nanorods were grown on ZnO seed layer coated p-Si substrates by hydrothermal method, which are 100 ml aqueous solution included 0.025M zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and 0.025M hexamethylene-tetramine ($C_6H_{12}N_4$) in sealed Teflon lined autoclave. To prepare the Ga-doped ZnO nanorods array, Ga concentration in the solution was varied from 0 at.% to 4 at.%. In detail, the different amounts of gallium nitride ($Ga(NO_3)_3.xH_2O$, 99.9%. Aldrich) were dissolved in a solution of zinc nitride hexahydrate and hexamethylenetetramine to fix its concentration at 0, 0.0125, 0.025, 0.05, 0.075 and 0.1 mM for undop, dop 0.5% to 4% Ga, respectively. The autoclave was kept in a laboratory oven at a constant temperature of 90 ^oC for 4 h.

The front contacts were deposited with gold (Au) on the top ZnO nanorods via metal mask using RF sputtering. The diameter of the contact was 1 mm. Ohmic contact was also made using thermal evaporator by depositing aluminum (Al) on the back of p-Si substrate. The ohmic contact was achieved by vacuum annealing structures at 400 ^oC for 3 min. The p-n junction samples with undop and Ga-doped ZnO nanorods grown on p-Si were assigned number from 1 to 6 as in Fig. 1. The cross-sectional structures of the n-type Ga:ZnO nanorods/ZnO seed layer/p-Si heterojunction for CO gas sensor was showed as Fig. 1. The I-V characteristics of the Au/n-ZnO/p-Si/Al diode were performed with KEITHLEY 4200 semiconductor characterization system. The surfaces of the thin films were characterized using a JSM-6500F field emission scanning electron microscope (FE-SEM). At.% (Atomic percent) of gallium in ZnO nanorods after synthesis was characterized by EDS (energy dispersive spectroscopy) equipped to FE-SEM. For optical characterization, photoluminescence (PL) measurements were obtained using a He-Cd laser operating at a wavelength of 325 nm and an excitation power of 15 mW.

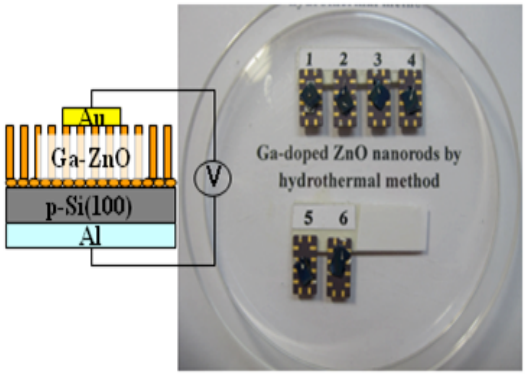
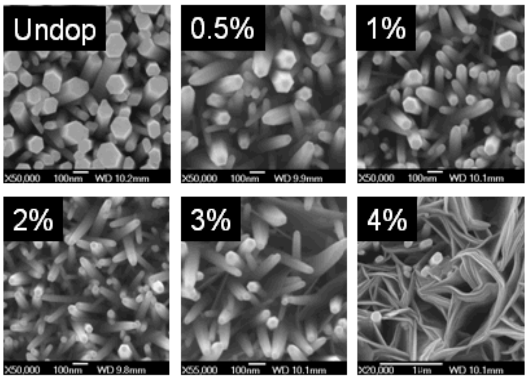


Fig. 1. The cross-sectional structures of the n-type Ga:ZnO nanorods/p-Si heterojunction (Sample 1 to 6 for undop, dop 0.5%, 1%, 2%, 3% and 4% Ga:ZnO).

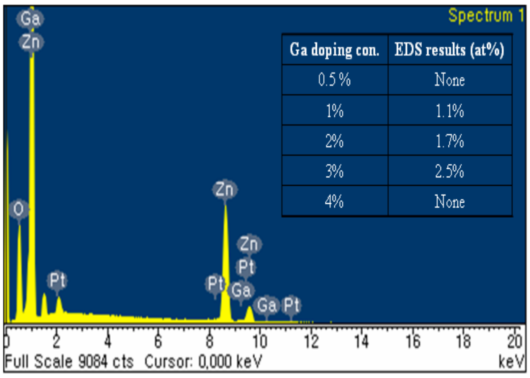
Results and Discussion

Fig. 2 (a) shows SEM images (top-view) of ZnO nanorods grown on p-Si substrate. The ZnO nanorods formed uniform rods in large area with average length is 750 nm (cross-view not show) and 100 nm in diameter. Fig. 2(a) show Ga-doping effects on ZnO nanorods morphology growth by hydrothermal method. In general, ZnO nanorods diameter became smaller with increasing doping concentration. At 2% Ga-doping, the ZnO nanorods diameter is the smallest and is more uniform rods in large area. When increasing to 3% Ga doping, ZnO nanoseeds appeared and mixed up with ZnO nanorods, which can be explained as large distortion and are affected on natural growth behavior of ZnO nanorods array. At 4% Ga-doping, the ZnO nanorods array were replaced by dense ZnO film comprise a lot of ZnO nanoseeds. The doped concentration was measured by EDS as shown in Fig. 2 (b) of 1 at.% Ga-doped ZnO. The table inserted in the figure shows the relationship between Ga concentrations in the solution an nanorods. Gallium ions in the precursor solution seem to be will incorporated into ZnO nanorods until 3% doping.

Fig. 3 shows the PL spectra of ZnO nanorods at room temperature growth by hydrothermal method with various Ga-doping concentrations consist of a UV emission at wavelength of 380 nm and a broad green emission band at 580 nm. The strong UV emission, which strongly relate to crystallite quality of ZnO, was contribute by conduction-valence band combination (~375 nm), shallow donor (~395 nm) and Zn interstitial (~420 nm) [5-7]. Fig. 3 shows an enhancement UV emission following to increase Ga-doping until 2% concentration. By doping suitable amount of Ga, the Ga atoms occupied at Zn vacancies defect position and increased donor-related defects (such as shallow donor and zinc interstitial) quantities in ZnO nanorods leading to strong UV emission in PL spectra [14]. With over doping, Ga atoms go into lattice sites substituting for Zn atom caused serious lattice distortion and leading to decrease UV emission peak at 3% and 4%. Especially, the broad green emission peak at 580 nm, which mainly contributed by oxygen rich in hydrothermal method [8], was disappeared by Ga-doping concentration higher 1 %. This phenomenon needed further study for fully explanation.



(a)



Ga doping con.	EDS results (at%)
0.5%	None
1%	1.1%
2%	1.7%
3%	2.5%
4%	None

(b)

Fig. 2. Effects of Ga-doping on (a) ZnO nanorods morphology and (b) EDS spectra of at.1% Ga doped ZnO nanorods.

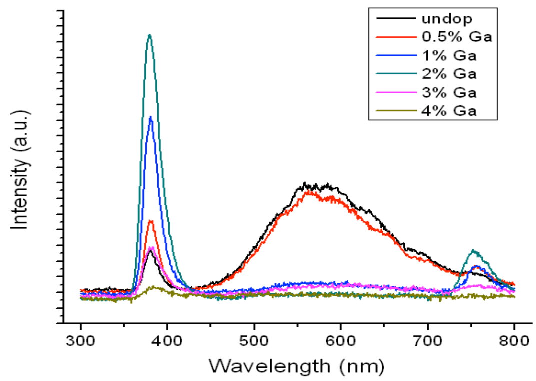
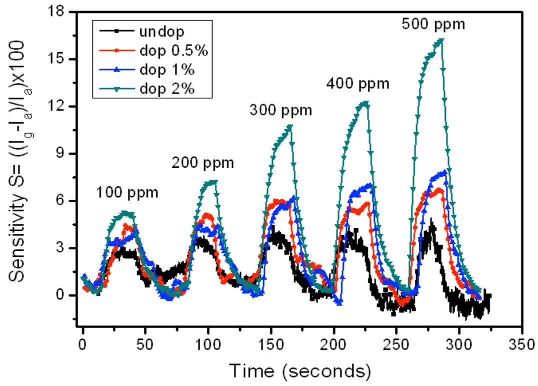
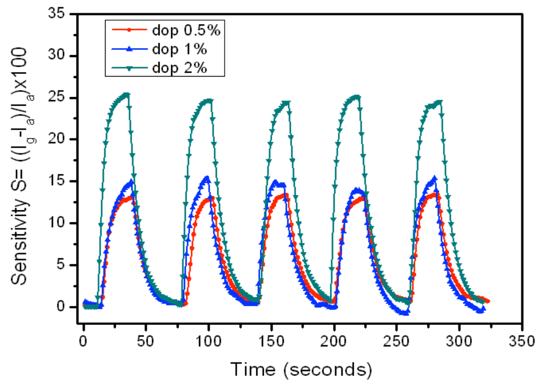


Fig. 3. PL spectra of Ga-doped ZnO nanorods.

Fig. 4 (a) shows linear response of Ga-doped ZnO nanorods at 75 °C with various CO concentrations, the increasing Ga concentration in ZnO nanorods yield more sensitivity with CO gas and obtained optimal doping value for CO gas sensing at 2%. Fig. 4 (b) shows repeatability of CO gas sensors at 1000 ppm concentration, the maximum sensitivity S is 25% for 2% Ga-doping sample. The response time and recovery time (τ_{90}) of sensor are 11 seconds and 21 seconds, respectively. The CO plays role as a reductive gas behavior with n-type semiconductor ZnO materials [2]. The reducing gas reacts with chemisorbed oxygen (O^-) on ZnO nanorods surface and released free electron back to conduction band ($CO+O^-$ -> CO_2+e^-); hence increased conductivity in ZnO nanorods. The high sensitivity in Ga-doping ZnO nanorods samples may be related to increasing donor-related (shallow donor) defects, reducing acceptor-related defects (oxygen interstitial) [5-7] and Ga:ZnO play role as active component for CO sensing [12].



(a)



(b)

Fig. 4. Current response of Ga:ZnO nanorods/p-Si as p-n junction for (a) various concentration CO and (b) repeatability in 1000 ppm CO at 75 °C, fixed bias of 2 V.

Conclusions

We illustrated Ga-doping into ZnO nanorods by hydrothermal method and investigate their CO gas sensing properties. We found that Ga atoms can be replaced Zn atoms without serious distortion until 2%. The Ga-doping ZnO nanorods at suitable doping concentration can improve conductivity, optical properties and cancel out acceptor-related defects (oxygen interstitial). Resulting in Ga:ZnO enhanced CO sensing property compare to pure ZnO nanorods. The CO gas sensing based p-n junctions have good response with sensitivity up to 25% in 1000 ppm CO at 75 °C with response time of few ten seconds.

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