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Sol-gel grown aluminum/gallium co-doped ZnO nanostructures: Hydrogen gas sensing attributes

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ABSTRACT

Aluminum (Al) and Gallium (Ga) co-doped ZnO nanostructures (AGZO NSs) were prepared on p-type Si(100) substrate using sol-gel united spin coating method. Ga contents were varied from 1 to 5 at% at fixed Al doping (1 at%). Synthesized samples were annealed at 500 °C for 3 h. The structural, morphological, and electrical property of the optimum sample (containing 3 at% of Ga) were determined. Optimum AGZO NSs enclosing highest density of nanorod (NR) arrays were selected to fabricate a hydrogen gas (H_2) sensor. As-grown AGZO NSs revealed hexagonal wurtzite structure with mean grain size ≈ 41.20 nm and resistivity ≈ 0.6475×10^{-2} Ω cm. The gas sensing attributes of the developed sensor was evaluated for two different temperatures (at 100 and 150 °C) under varying gas H_2 contents (from 250 to 1750 ppm). Furthermore, the selectivity of the AGZO NSs for three different gases such as H_2, CO and CH_4 were examined. The sensitivity of the sensor at 100 °C was augmented sharply from 60% to 385% with the increment of H_2 gas contents from 250 to 1750 ppm. This enhancement was attributed to the increases of hydrogen gas current (I_H) and good stability of the air atmosphere. The synthesized AGZO NSs have high potential for gas sensing, photovoltaic and field emission applications.

1. Introduction

Transparent metal oxide semiconductor nanostructures (NSs) became popular due to their exceptional chemical and physical properties. Transparent conducting oxide (TCO) thin films have been extensively studied and applied for various purposes as gas sensors, light emitting diodes (LEDs), transistors and solar cells [1]. Among all the direct bandgap semiconductors NSs, Zinc Oxide (ZnO) NS is greatly demanding due to its wide bandgap (≈ 3.37 eV) and large exciton binding energy (≈ 60 eV). ZnO is n-type intrinsic semiconductor due to the presence of native defects of Zn interstitials and oxygen vacancies that act as majority carriers (donor). In pertaining high efficient solar cells, transparent conducting electrodes required to have minimum resistance and maximum transmittance. Although indium tin oxide (ITO) is presently leading the transparent electrode with highest performance but its application is limited. This is subjected to its highly toxicity, low stability and high cost. Therefore, to resolve such drawbacks, alternative TCO needs to be considered.

It is well known that the optical and electrical properties of ZnO can be improved by doping it with elements of group III such as trivalent Al and Ga. Replacement of Zn atoms in the parent crystal structure via trivalent elements has been performed to modify the ZnO lattice to achieve ITO equivalent improved performance [2]. In the past, diverse techniques were developed to produce good quality doped ZnO films. These methods include chemical vapor deposition (CVD) [3], spray pyrolysis [4], magnetron sputtering [5], pulsed laser ablation [6], plasma-assisted molecular beam epitaxy [7], and sol-gel [8]. Among all, sol-gel technique was found to be beneficial due to its low cost, accuracy, easy processing, consistency, flexibility, wide area coating ability, and less time consumption. Besides, sol-gel synthesized materials showed high crystallinity and excellent NSs morphology [9].

Some related studies based on Al and Ga co-doped ZnO NSs film to modify their optical and electrical properties have been carried by Zhu et al., [10]. It was elucidated that significantly lower ionic radius of Al^{+3} (r_{Al} = 0.054 nm) compared to Zn^{+2} (r_{Zn} = 0.74 nm) is a major factor that responsible for the lattice deformation in Al substituted ZnO matrix (AZO film). Although the ionic radius of Ga (r_{Ga} = 0.062 nm) [11] is slightly greater than Al but the extent of lattice mismatch is less significant with Zn. Literature revealed that an additional doping of Ga in AZO structure could improve the optical and electrical attributes.

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Moreover, the effects of changing Al and Ga doping concentration on the ZnO thin films are still lacking [12]. Mamat et al., [13] deposited Al doped ZnO thin films on microscope glass substrate using sol-gel combined spin-coating method. Ebrahimifard et al., [11] had prepared AGZO thin films using the same method. Vishwas et al., [14] synthesized polycrystalline (hexagonal phase) Al doped ZnO NSs at deposition temperature of 400 °C.

Despite many efforts to produce trivalent metals doped ZnO nanofilm a reproducible method for solution preparation with controlled growth conditions are still deficient. The data on the influence of solution molarity, types of dopants and contents, heat treatment temperature and time, ageing time, substrate types, annealing temperature and time, and deposition speed and time on the growth morphology of such NSs are still inadequate. Moreover, the validity and the reproducibility of the results on the improvement of structural, physical, morphological, optical, gas sensing, and electrical properties reported by various researchers remain debatable. Very few studies compared the diverse properties of AZO and GZO films that were grown under identical conditions. Lee et al., [15] assessed the effects of annealing on the electronic and optical characteristics of AGZO thin films and achieved a resistivity as low as $4.5 \times 10^{-2}\,\Omega$ cm at an annealing temperature of 450 °C. X-ray photoelectron spectral analysis revealed a Fermi-level shift $\approx$ 0.6 eV and the optical bandgap was widened by an amount $\approx$ 0.3 eV.

In the absence of oxygen atmosphere and at room temperature, Kim et al., [16] synthesized AGZO thin films on fused quartz (FQ) and Cyclo-olefin Polymer (COP) substrates using radio frequency magnetron sputtering technique. The elemental distributions of Al, Ga, Zn and O were observed all over the film without any compositional change at working pressure. The resistivity of AGZO/FQ and AGZO/COP films were varied in the range of 0.03–4.07 Ω cm and 0.04–5.73 Ω cm, respectively. Meanwhile, a transmittance above 85% was obtained via the appropriate control of the working pressure. Using inexpensive sol-gel united spin coating method, Serrao et al. [17] prepared some transparent conducting ZnO films on the glass substrate by Al and Ga doping as well as Al/Ga (1:1) co-doping. Such thin films displayed very low resistivity ($2.54 \times 10^{-3}\,\Omega$ cm) and high visible transmittance (above 83%).

Considering the importance of Al/Ga co-doped ZnO NSs based films, AGZO films were deposited on Si substrate via sol-gel mediated spin-coating method. As-synthesized AGZO films containing aligned vertically nanorods were characterized. Furthermore, a H_2 gas sensor was fabricated using the best sample to determine its effective gas sensing property.

2. Experimental

Al/Ga co-doped ZnO (AGZO) films were grown by using analytical grade (Alfa Aesar, purity 99.999%) chemical compounds of zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), gallium nitrate nonahydrate ($Ga(NO_3)_3{\cdot}9H_2O$), 2-propanol and ethanolamine. Initially, $Al(NO_3)_3{\cdot}9H_2O$ was dissolved at room temperature in a solution made from 2-propanol and ethanolamine. The concentration of $Zn(CH_3COO)_2{\cdot}2H_2O$ was 0.1 M and the molar ratio of ethanolamine to zinc acetate was 1:1. The solution was magnetically stirred constantly for 30 min to get a homogeneous and clear mixture. Later, the resulting ZnO solution was doped with Al (1 at %) and Ga (3 at%). Next, the mixture was dissolved in methanol at 60 °C for 90 min and stirred continuously to obtain a transparent solution. Then, few drops of the solution were poured on a p-type Si(100) substrate before being spin coated for a duration of 30 s at the angular speed of 3000 rpm which was repeated for 10 times. The achieved uniform AGZO film was further dried for 20 min at 300 °C. Finally, the dried solid film was annealed for 3 h at 500 °C in atmospheric pressure.

The crystalline structure of as-synthesized sample was determined using X-ray diffraction (XRD, Bruker D8 Advance Diffractometer operated at 40 kV and 100 mA) analysis with Cu-Kα_1 radiations of wavelength 1.5406 Å in the scanning range 2θ = 20–80°. A slow speed of scanning $\approx$ 1.2°/min with a resolution of 0.01° was used. Elemental composition and surface morphology of the sample were analyzed using energy dispersive X-ray (EDX) spectroscopy and field emission scanning electron microscopy (FESEM, ZEISS SUPRA 35 VP), respectively. Four-point probe method was used to measure the resistivity of the annealed AGZO NSs sample.

The optimum AGZO NSs sample (3 at% of Ga) was used to design a hydrogen (H_2) gas sensor. A thin layer (thickness $\approx$ 250 nm) of silver (Ag) was deposited above the AGZO film via vacuum thermal evaporation method. Two planar Ag electrodes with a gap area of 2 cm × 2 cm were fabricated on the top of the AGZO film. The H_2 gas sensing performance of the designed sensor was measured using a self-designed test system adopted from previous researcher [18]. The temperature of the film-based sensor was varied from 100 to 150 °C using a heater made of Ni–Cr coil. A thermocouple was placed on the film surface to record the temperature. The concentrations of the inserted target H_2 gas within the glass chamber were varied (250, 500, 1250 and 1750 ppm) under a constant air flow rate. A high mega-ohm multi-meter was interfaced with a computer to measure the resistance of the AGZO NSs.

3. Results and discussion

Fig. 1 illustrates the XRD pattern of the optimum AGZO sample annealed at 500 °C in the air for 3 h duration. The observed XRD peaks were indicated to the hexagonal wurtzite structure of ZnO, which tallied from JCPDS Card No. 36-1451. The occurrences of sharp peaks at 2θ = 31.86°, 34.42°, 36.28°, 47.68°, 56.53°, 62.92° and 66.36° were assigned to Bragg's reflections from (100), (002), (101), (102), (110), (103) and (200) lattice planes. Secondary phases such as Al_2O_3, Ga_2O_3, $ZnAl_2O_4$ or $ZnGa_2O_4$ as well as the impurities were completely absent in the synthesized AGZO film. The appearance of most intense peak indicated the preferential growth of nanocrystallite (hexagonal wurtzite crystal structures) along the (101) lattice direction (crystallographic c-axis) which was consistent with earlier finding [19]. The emergence of intense peaks corresponding to the growth orientation along (100), (002), and (101) lattice planes were matched with the JCPDS 36-1451 standard. The preferred growth along (101) lattice direction compared to other crystallographic orientations was attributed to the lower surface energy of (101) plane [20].

The sharpness of the XRD peak indicated the good crystallinity of AGZO NSs and the associated broadening of the peak signified the quantum size effects of nanocrystallites. Most of the physical deposition methods for the synthesis of Al-doped ZnO film suffer from extrinsic residual stress generation in the film. The size of nanocrystallites (grain

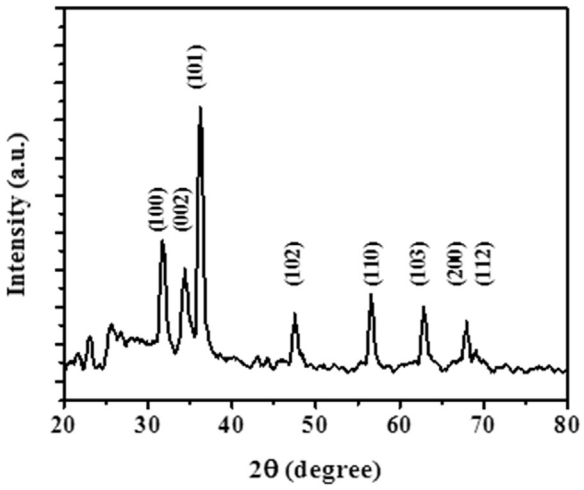

Fig. 1. XRD pattern of optimum AGZO NSs based film annealed in air at 500 °C for 3 h.