ZnO NANOWIRES GROWN BY CHEMICAL DEPOSITION AND RAPID PHOTOTHERMAL PROCESSING

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Abstract

Chemical deposition aqueous method has been developed to synthesize a new generation of smart and functional nanostructured zinc oxide thin films. This chemical process uses stable and inexpensive metal inorganic salts and solvents in a heterogeneous reaction, without additional template materials to obtain ZnO thin films with different morphologies. The nanosized structures of ZnO are obtained to analyze the physical and structural requirements of their applications in gas sensors. Post-growth photothermal annealing of nanostructured zinc oxide at 650ºC in N_2 leads to the suppression of deep-defect-level emission and improvement of near-band edge emission and is ascribed to the decrease in structure defects as compared to the initial nanostructure. The sensing behavior of the nanostructured elements to methanol is investigated.

Introduction

Wide band gap nanostructured materials, such as nanowires, nanobelts, and nanorods, have received high interest in the recent decade, due to their morphology-related properties, for their potential in building novel functional nanometer-scaled electronic, optoelectronic, electrochemical, and sensor nanodevices [1-3]. Recently, synthesis, research, and development of alternative energy technologies, such as low cost flat-panel solar cell thin film devices, solar cells based on semiconducting oxide nanowires and many other innovative concepts have increased. During the last few years ZnO has received considerable attention as an important multifunctional material due to its unique applications for nanoelectronic and optoelectronic devices and for self-assembled growth of three-dimensional nanoscale systems [4, 5].

Chemical deposition on a glass substrate is an emerging field of research in the nanostructured thin films. The physical properties of the nanostructured thin films can be explored by the optimization of the process parameters and post-deposition processing technique. It allows control of the size of nano and microparticles, their surface morphology, and arrangement on substrate. This technique allows the growth of functional metal oxide thin films at relatively low temperatures from aqueous solution without catalysts, at large scale and low-cost.

The post-growth annealing process is guided largely by the requirements of structure defect removal and electrical conductivity in zinc oxide films. Recently, lamp-based rapid photothermal processing (RPP) systems have been introduced as an alternative thermal an-

nealing equipment solution. The structural and electrical properties of nanostructured films can be improved by proper post-deposition rapid photothermal processing. This is based on rapid radiative heating by using halogen lamps followed by cooling of substrates in air, or vacuum, or in inert atmosphere. The RPP system's halogen lamps provide both heating and radiation effects due to the wide spectrum from 0.4 μm to 1 μm [6].

In this present work, a novel method combining the aqueous solution process under ultraviolet light with post-growth rapid processing is proposed to develop ZnO thin film nanowires. Optical properties of the as-grown and RPP nanostructures have been studied by photoluminescence measurements. We expected to obtain inexpensive nanostructured thin films for gas sensor applications. ZnO-based resistive type sensors have been developed for the detection of toxic gaseous compounds for environmental and industrial monitoring. The responses of the sensing elements exposed to 500 ppm methanol at temperatures between 20°C and 300°C have been assessed.

Experimental

Chemical deposition is a method of growing thin films on a substrate immersed in aqueous solutions containing appropriate reagents at relatively low temperatures (up to 98°C). In the present study, the nanostructured films were deposited on Corning glass and Si substrates using a beaker placed upon a heater during the growth process under ultraviolet (UV) light. Before the deposition, the substrates were cleaned in dilute HCl for 10 min, and then rinsed in de- ionized water (DI). Afterward, the glass slides were rinsed in ethanol:acetone (1:1) mixture, DI and dried in a nitrogen flux. The (100) silicon substrates were chemically cleaned using solution of sulfuric acid/hydrogen peroxide (Reagent grade CDA) in the proportion 1:4 for 5 min to remove any organic material. Then Si substrates were treated by nitric acid in order to eliminate the metallic impurities after re-distilled water cleaning for 5 min. The next step was cleaning in hydrofluoric acid ($HF:H_2O$=5:100) to remove chemical and native oxides. The cleaned substrates were immersed in an aqueous solution bath and the bath was heated with stirring for definite periods of time in order to fabricate nanostructures of desired size. Films of pure and Sn-doped ZnO were deposited on glass substrates from aqueous zinc-complex solution comprised of a mixture of $ZnCl_2 \cdot 2H_2O$, $ZnSO_4 \cdot 7\ H_2O$, NH_4OH, sodium stannate, and diethanolamine [DEN]. All the chemicals were analytic grade reagents without further purification. The concentration of complex solution was 0.05 and 0.1 M zinc concentration. Adding sodium stannate in the aqueous solution, 3-5 at % Sn concentration according to doping level the impurification was performed under a constant stirring at room temperature or at 80°C. The heterogeneous reaction and deposition of zinc oxide nanostructures took place on the substrate for 6-12 h or 0.1-0.3 h, respectively.

The as-deposited ZnO films were post-growth photothermally annealed at 300°C-650°C for 15-100 s. The optimum duration of annealing was determined to be 20 s for zinc oxide films.

Results and discussion

SEM images of the ZnO nanowires chemically deposited (a) from Zn:Sn:[DEN] (0.05 M:1 mM:0.02 M) aqueous bath: as grown without RPP (sample 1), and (b) from Zn:Sn:[DEN] (0.10 M:1 mM:0.01 M) (sample 2) are shown in Fig.1.

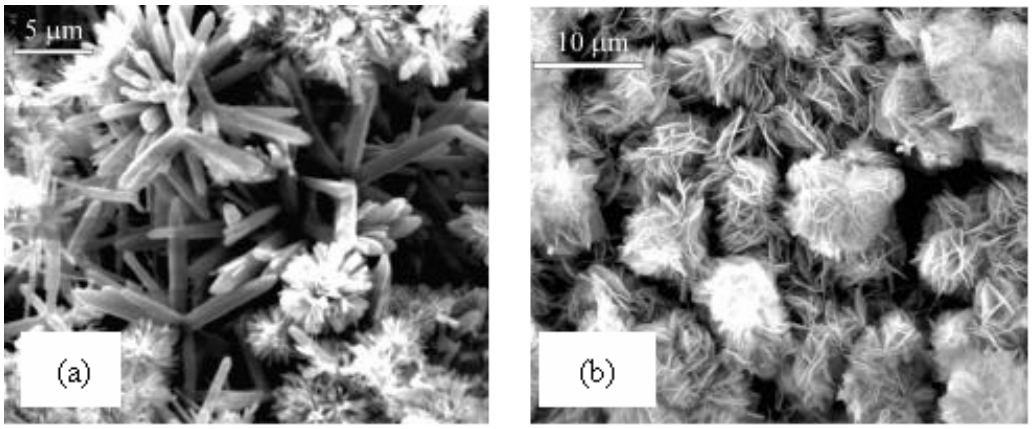

Fig. 1. SEM images of the zinc oxide nanowires chemically deposited from (a) Zn:Sn:[DEN] (0.05 M:0.001 M:0.02 M); (b) (0.10 M:0.001 M:0.01 M) on the glass substrate.

Figure 2 shows the low-temperature ultraviolet emission photoluminescence (PL) spectra of as-grown ZnO:Sn chemically deposited from a Zn:Sn:[DEN] (0.05 M:1 mM: 0.02 M) aqueous bath and RPP annealed at temperature of 650°C for 20 s.

The emission from the as-grown film represents a combination of luminescence dominated by a PL band associated with the recombination of excitons bound to a neutral donor (D^0X) and resonant Raman scattering (RRS).

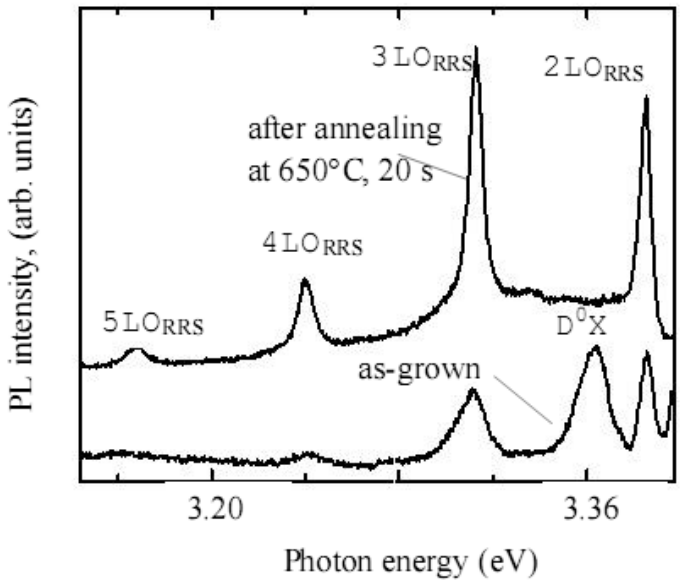

Fig. 2. Ultraviolet emission spectra of ZnO nanocomposites fabricated by chemical deposition and rapid photothermal processing at 650°C, 20 s measured at 10 K. The spectra are shifted Y-direction.

Photothermal annealing at 650°C for 20 s leads to the suppression of PL and the enhancement of multiphonon RRS labeled as $2LO_{RRS} - 5LO_{RRS}$ peaks. The difference between the position of the nLO_{RRS} peak and the excitation quanta energy (3.530 eV) is n times the energy of the A_1(LO) phonon in wurtzite-type ZnO (72 meV). This emission originates from the n-order Raman scattering.

The luminescence peak in the zinc oxide film (3.363 eV) is associated with excitons bound to a H-related neutral donor [7]. The D^0X PL band is related to an exciton bound to some structural defects. In such a case, the suppression of the D^0X PL band with photothermal processing is explained by the annealing of defects, which localize the excitons. The visible PL emission spectra of an as-grown and RPP at 650°C for 20 s are shown in Fig. 3. Two photoluminescence bands centered at 2.4 and 1.8 eV are present in the visible spectral range as illustrated in Fig. 3.

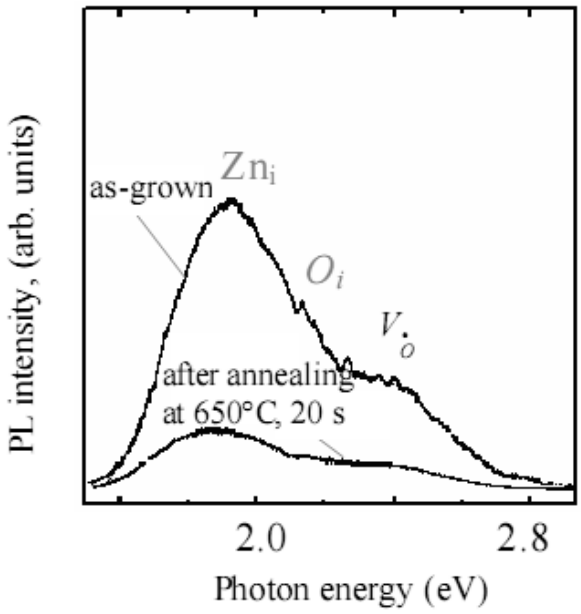

Fig. 3. Visible PL spectra of different ZnO nanostructured films as labeled: Initial is the as-grown film and second is treated by RPP at 650°C, 20 sec measured at T = 10 K.

The PL spectra of the as-grown zinc oxide nanostructure show a typical deep-defect level emission at 1.8 eV without near-band edge emission, but photothermal processing at 650°C for 20 s decreased the intensity of the red PL (1.8 eV) luminescence.

The emission from the initial zinc oxide sample represents a combination of luminescence dominated by a PL band associated with the recombination of excitons bound to a neutral donor (D^0X) and resonant Raman scattering (RRS). Deep-defect-level emission is reduced and newly emerging near-band edge emission is improved in the ZnO sample while underwent RPP at the 650ºC for 20 seconds. The ZnO annealed at 650ºC shows a near-band edge emission at 3.38eV and lower emission peaks related to the deep-defect-level. Deep-defect-level emission reduction in photothermal processed ZnO indicates that the concentration of defects responsible for this emission is reduced by RPP.

It was observed that irreversible changes in the PL occur when the zinc oxide films underwent RPP at temperatures higher than 300ºC for 20 s. Between 550°C and 650ºC, it was observed that improvement in the quality and stability of the ZnO samples occurred. Reliable ohmic contacts can be made to the ZnO by vacuum evaporation of Al.

Gas sensing characterization of nanostructure-based sensor elements (size 0.5×0.5 cm) was performed in a 1000 cc gas chamber. The undoped and tin doped zinc oxide nanostructured films (1 μm thickness) were tested to detect 500 ppm methanol at temperatures from 20 to 300°C. The readings were taken in 20 min after the sensor element and gases have been introduced to the test chamber.

It was found that resistance increased linearly with gas concentration and it was experimentally demonstrated that the ZnO nanomaterials present a fast response to a gas pulse at 100°C. The sensitivity of the sensor to gas was calculated [8]

$$S = \frac{100 \cdot \left(\left| R_{gas} - R_{air} \right| \right)}{C \cdot R_{air}}, \quad (1)$$

where R_{gas} and R_{air} are the electrical resistance in the presence of gas and in air, respectively; C is the gas concentration.

The methanol sensing characteristics of the sensors were studied at an operating temperature of 100°C, Figure 4.

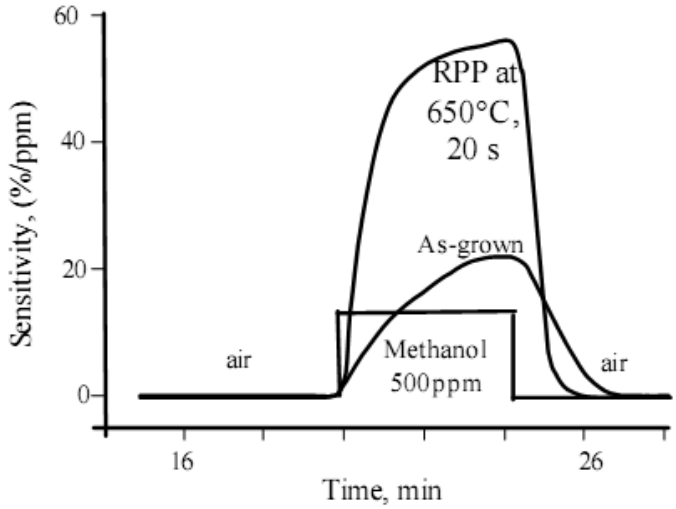

Fig. 4. The response of the zinc oxide nanostructured thin film sensor to methanol at 100°C operating temperature.

Figure 4 shows that sensor response and recovery time constants are of the order of 30 s, but there is a complete stabilization after 60 s. The conductivity decreased rapidly by exposing the sensor to methanol and recovered toward the original value after clean air was introduced. If the obtained sensors were to be operated in a ventilated chamber, or at a higher temperature the recovery characteristics could be enhanced. The results demonstrate a high potential for nanostructured zinc oxide sensors with superior sensitivity.

Conclusions

ZnO needle-like zinc oxide nanowires were synthesized by the chemical deposition process. These nanostructured zinc oxide films obtained by chemical deposition and rapid photothermal processing have shown high sensitivity, high long-term stability and fast response time to methanol.

It is possible to modify the sensing properties of the nanostructured films by controlling growth regimes and rapid photothermal processing conditions. This technique allows generation of, low-cost, large scale, advanced functional zinc oxide thin films from aqueous solution at low temperature. Our results indicate also that an important effect of rapid photothermal processing on photoluminescence properties is suppression of deep-defect-level emissions and improvement of near-band edge emission efficiency. We have demonstrated ZnO nanostructures are sensitive to methanol. The gas sensing characteristics of the ZnO films can be improved by modifying their nanostructures by tin impurity.

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