Applied Surface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Enhancement of gas sensor response of nanocrystalline zinc oxide for ammonia by plasma treatment

Yue Hou, Ahalapitiya H. Jayatissa*

Nanotechnology and MEMS Laboratory, Mechanical, Industrial and Manufacturing Engineering (MIME) Department, The University of Toledo, 2801 W. Bancroft, Toledo, OH 43607, USA

ARTICLE INFO

Article history:
Received 20 December 2013
Received in revised form 19 April 2014
Accepted 22 April 2014
Available online xxx

Keywords:
Zinc oxide
Oxygen plasma
Oxygen vacancies
Surface treatment
Gas sensing
Sol–gel

ABSTRACT

The effect of oxygen plasma treatment on nanocrystalline ZnO thin film based gas sensor was investigated. ZnO thin films were synthesized on alkali-free glass substrates by a sol–gel process. ZnO thin films were treated with oxygen plasma to change the number of vacancies/defects in ZnO. The effect of oxygen plasma on the structural, electrical, optical and gas sensing properties was investigated as a function of plasma treatment time. The results suggest that the microstructure and the surface morphology can be tuned by oxygen plasma treatment. The optical transmission in the visible range varies after the oxygen plasma treatment. Moreover, it is found that the oxygen plasma has significant impact on the electrical properties of ZnO thin films indicating a variation of resistivity. The oxygen plasma treated ZnO thin film exhibits an enhanced sensing response towards NH_3 in comparison with that of the as-deposited ZnO sensor. When compared with the as-deposited ZnO film, the sensing response was improved by 50% for the optimum oxygen plasma treatment time of 8 min. The selectivity of 8 min plasma treated ZnO sensor was also examined for an important industrial gas mixture of H_2, CH_4 and NH_3.

1. Introduction

Zinc oxide, as a well-known semiconducting material, has attracted extensive research interests mainly due to its wide direct band gap (3.3 eV) and large binding energy (60 meV). With these inherent properties, zinc oxide (ZnO) materials have been widely used in microelectronics, optoelectronics and information technology applications including light emitting diodes [1,2], transparent electrodes in solar cell [3], photo-detectors [4] and surface acoustic wave devices [5]. The ability of ZnO to detect chemical species at a low concentration (ppm level) in the atmosphere enables its applications of gas sensors in industrial emission control, environmental pollution monitoring, and medical diagnosis. ZnO is a promising material because it is inexpensive, nontoxic and easily producible. ZnO thin film based gas sensor can be prepared in a variety of nanostructures, such as nanoparticles, nanorods, and nanowires. Nanoparticles possess unique size-related properties, such as high surface-to-volume ratio, which is beneficial for the performance of gas sensors.

Many techniques can be used to synthesize ZnO thin films, such as molecular beam epeitaxy [6], pulsed laser deposition [7], radio-frequency (rf) magnetron sputtering [8], ion plating [9], and sol–gel process [10]. Amongst them, the sol–gel process is the most promising technique. The sol–gel process is known as a wet chemical deposition method, which is a powerful alternative to the vacuum deposition methods. The advantages of sol–gel process include easy handle process, large area deposition, economy and easy control of the final quality of the thin films [11,12].

ZnO usually contains a large number of defects, which are introduced during the synthesis process. The origin of intrinsic n-type electrical conductivity of ZnO is under debate. However, the oxygen vacancies (V_o) and Zn interstitials (Zn_i) have often been invoked as the most possible sources [13–16]. Therefore, the defects concentration in ZnO nanostructure and the existence of intrinsic or extrinsic defects directly affect the properties of ZnO films. For example, Kim et al. [17] fabricated the p-type ZnO films by reducing the oxygen vacancy concentration and facilitating the formation of arsenic As-related acceptors. The existence of such defects is prone to exert profound influence on the performance of electronic devices and as a result methods for their modification are of interest [18].

Plasma treatment is known as a useful method to adjust the charge carrier density and surface morphology because of the high reactivity of radical elements than gas phase. Moreover, it is found to be more suitable for the treatment of nanoparticles because of the large surface area than bulk materials. For example, Jiang

* Corresponding author. Tel.: +1 419 530 8245; fax: +1 419 530 8206.
E-mail address: ajayati@utnet.utoledo.edu (A.H. Jayatissa).

http://dx.doi.org/10.1016/j.apsusc.2014.04.158
0169-4332/

et al. [19] treated SnO*x* thin films with oxygen (O_2) plasma and investigated its effect on structural properties. It is known that gas response is a surface-controlled process. Therefore, this research proposes to apply O_2 plasma treatment as a surface modification technique to improve and control the sensing response of ZnO thin film gas sensors.

Herein, the effect of O_2 plasma treatment on nanocrystalline ZnO thin films and its impact on the performance of gas sensor were investigated. The ZnO thin films were treated with O_2 plasma by varying the exposure time (3–15 min). The sensing responses to different concentrations of NH_3 of O_2 plasma treated ZnO gas sensors were compared with the as-deposited ZnO gas sensor.

2. Experiments

ZnO thin films were prepared by sol–gel spin coating technique. The starting solution was prepared by dissolving zinc acetate dihydrate (ZnAc, $Zn(CH_3COO)_2{\cdot}2H_2O$, 99%) in isopropyl alcohol. Then, monoethanolamine (MEA) was added in the solution as a stabilizer. The molar ratio of zinc acetate and MEA was maintained at unity (1.0) and the solution concentration was kept at 0.25 M. The mixture was ultrasonically dissolved for 15 min to form a clear and homogenous solution. Before deposition, the solution was aged for 24 h at room temperature under magnet stirring. Alkali free glass was used as the substrates for deposition. In order to remove the organic residuals, the substrate was rinsed by detergent and deionized water, after which the substrate was cleaned ultrasonically for 10 min with acetone. The ZnO thin film was spin coated on the glass substrate at a speed of 3000 rpm for 30 s. After each coating, the film was pre-heated at 300 °C for 3 min on the hotplate to evaporate residual solvent. The process repeated 5 times to get a multilayered film. Finally, the film was annealed in a tube furnace at 550 °C for 3 h in the air to enhance the crystal growth. Two gold electrodes were fabricated on the surface of ZnO thin films by thermal evaporation followed by optical lithography. O_2 plasma treatment was applied to ZnO samples with the intention to reduce the intrinsic vacancies/defects (e.g. V_o) in ZnO thin films. The chamber was first evacuated and then purged with oxygen to 1.0 Torr. The applied rf power was 100 W. The ZnO samples were treated with different O_2 plasma treatment time varying from 3 to 15 min.

The structure of samples was examined by an X-ray diffractometer (PANalytical X'Pert Pro MPD) using Cu Kα radiation source. The scanning range was from $2\theta = 25°$ to 65° with $\lambda = 1.5418$ Å. Scherrer equation $D = K\lambda/\beta\cos\theta$ was used to estimate the average grain size from XRD data, where K is the shape factor which is 0.94 here. β Is the full width at half maximum (FWHM) of the XRD peak corresponding to 2θ. Optical transmittance was measured in the wavelength range between 300 and 1000 nm using an UV/Vis spectrophotometer (SHIMADZU UV-1650PC). The surface morphology was studied by atomic force microscopy (AFM, Nanoscope III, non contact mode) and scanning electron microscopy (Hitachi S-4800). The electrical property was investigated in vacuum environment. The resistance of samples was collected in the temperature range of 35–200 °C. The resistivity of the samples was measured by four-point probe method using Lucas Labs Pro4. The carrier concentration was calculated using the equation $\rho = 1/\mu ne$, where μ, n and e are the electron mobility, carrier concentration and charge of electron, respectively [20]. The gas sensing performance was studied in a homemade test system. The configuration of the system was described in a previous work [10]. The sensors were heated to 160 °C by a heater made of a Ni–Cr coil while the temperature was monitored by a thermocouple and controlled by the power supply (VIZATEK MPS-3003LK-2). The resistance of sensors was measured by a high mega-ohm multimeter (Keithly 2001) and collected by computer system. Different concentrations of mixture gases were introduced into the glass test chamber with a constant airflow of 100 ccm. The response of gas sensor is defined as $S = [(R_a - R_g)/R_a] \times 100\%$, where R_a is the resistance of the sensor measured in the air, while R_g is the resistance in the presence of both air and the target gas. Response time (T_{70}) was expressed as the time taken to achieve 70% of the saturation resistance for the target gas [21].

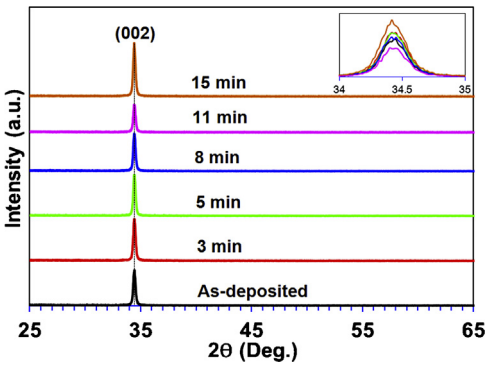

Fig. 1. The XRD patterns of as-deposited and O_2 plasma treated ZnO thin films.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the XRD spectra of as-deposited and O_2 plasma treated ZnO samples as a function of treatment time. All patterns show only a predominant peak at diffraction angle 2θ near 34.4°, which indicates a (0 0 2) preferential growth orientation along the *c*-axis for all the samples. The peak intensity of 3 and 5 min plasma treated ZnO samples increases slightly compared with that of the as-deposited sample, whereas it decreases with further increasing treatment time to 11 min. The increase in crystallinity of short time (3, 5 min) O_2 plasma treated samples can be attributed to the reduction of oxygen vacancies, whereas for long time (11 min) plasma treated sample, the Zn vacancies are likely generated by oxygen plasma because the Zn vacancies have a lower formation energy in an oxygen rich atmosphere than other possible defects [22], which in turn decreases the crystallinity of ZnO thin films. The average grain size (D) of samples can be estimated by Scherrer's formula. The variation of grain size estimated along the (0 0 2) peak is presented in Fig. 2. It is shown that the grain size is related to the O_2

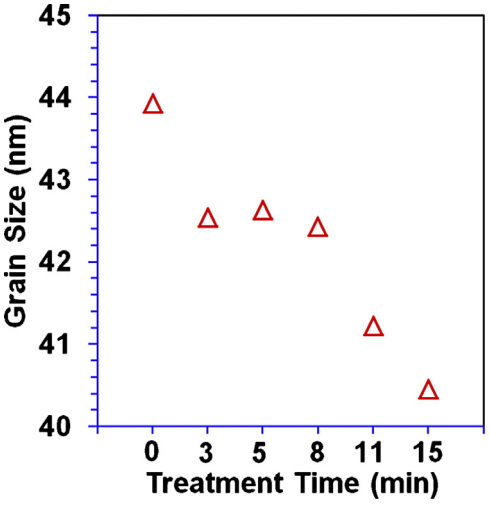

Fig. 2. Grain size of ZnO thin films as a function of O_2 plasma treatment time.

Please cite this article in press as: Y. Hou, A.H. Jayatissa, Enhancement of gas sensor response of nanocrystalline zinc oxide for ammonia by plasma treatment, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.04.158