STRUCTURAL DEGRADATION AND SENSING PROPERTIES OF ZNO NANO FILMS

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Introduction

Zinc oxide thin films have received considerable attention in the past several decades due to their high optical transmission and electrical conduction [1,2]. They have been used as transparent electrode in flat panel displays [3], solar cells [4], optoelectric devices, and sensors. Numerous low cost ZnO-based electronic devices are designed and fabricated. Nanocrystalline ZnO gas sensors have attracted more interest due to its good properties of detecting toxic gases and pollutants. Magnetron sputtering is considered to be a suitable technique to prepare ZnO nanostructures due to the fact that the deposition parameters can be easily controlled [5]. Si (100) is one of the most popular substrate to grow ZnO samples due to the reduced cost and possible integration with Si-based microelectromechanical and microelectronics systems.

In this work, the surface morphology and crystalline structure of ZnO nano films prepared by d.c magnetron sputtering have been investigated. The excellent properties of ZnO-based sensors such as high sensitivity, selectivity, reproducibility, and quick response time to different gases and temperature have been achieved.

Experimental

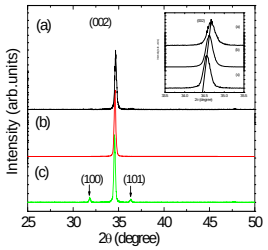
The ZnO films were deposited on Si (100) substrates under different deposition durations using d.c magnetron sputtering system. The target for the growth of ZnO films was sintered ZnO (99.9%, 2 in). The distance between the target and the substrate was kept around 7cm. D.C power was 200 W and the substrates were maintained at room temperature during the experiments. The base pressure of the chamber was 10^{-6} Torr and then argon was introduced by keeping the pressure at $8\sim10\times10^{-3}$ Torr. After depositions, the samples were transferred to a quartz tube furnace for annealing at 800℃ for 2 hours in an air atmosphere. The surfaces of the ZnO thin films were characterized using SEM. The crystal structure and phase formation were examined with the x-ray diffraction (XRD) technique. The micro-Raman measurements were performed in the backscattering geometry using high resolution Jobin-Yvon T-64000 Triple-mate instrument. The radiation of 514.5 nm from a coherent argon ion laser was focused to ~2*u*m in diameter on the samples. An LN_2 cooled charge-coupled device (CCD) system was used to collect and process the scattered data.

Characterizations of the sensing properties ZnO-based gas sensors were conducted in a home-made system where the ZnO sample is serially connected to a precise resistor and a battery to form a voltage-current-resistor (V-I-R) electrical circuit as a prototype sensor. Sensitive characters of the prototype were examined based on the measurement of the voltage drop across the precise resistor so that the variation of the electrical conductivity of the sensor at different environments such as temperature, types of the gases and their concentrations can be estimated.

Results and discussion

The thickness of the films almost linearly increases with deposition duration, measured as 180 ± 20, 400 ± 30 and 750 ± 45 nm for 5, 10 and 20 mins deposited samples, respectively and all the films mainly consist of a large amount of nanoparticles (not shown). The average grain size does not change by much but remarkable grains coalescences are observed with an increase of thickness.

Fig. 1 shows the XRD patterns of all the samples. Only peak corresponding to (002) has been identified in the patterns from the sample *a* and *b* as shown in Fig. 2, which suggests a monocrystalline structure in nature. Further increase of duration up to 20 minutes, this peak still dominates but two other weak peaks assigned as (100) and (101) can also be noticed, which suggests that the crystallization of ZnO turns worse. The overlay with deposition duration could damage the stable growth in the ZnO thin films and degrade the crystallinity of ZnO thin films.



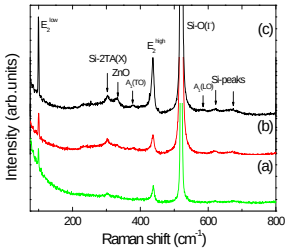
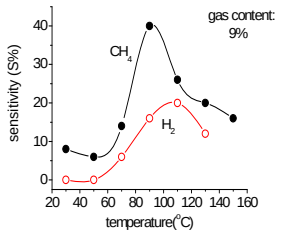


Fig.1 Fig.2

Fig. 1 XRD, Fig.2 Raman spectra of annealed films prepared for a) 5 (sample A), b) 10 (sample B), and c) 20 min (sample C) on Si (001)



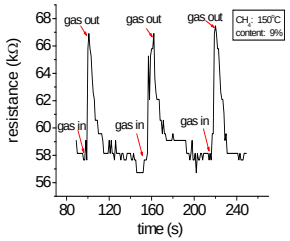


Fig. 3 Fig. 4

Fig. 3 Sensitivity of ZnO thin film to CH_4 and H_2 upon different operating temperature.

Fig. 4 Sensor dynamic sensitivity of ZnO to methane gas at operating temperature of 150 ºC.

In order to further understand the evolution of crystalline structures of ZnO films, micro-Raman measurements have been carried out and results are shown in Fig.2. Only two normal modes corresponding to polarization-allowed E_2^{low} and E_2^{high} phonon of ZnO are observed from the first two samples (Fig.2a and 2b), which is indicative of the wurtzite crystal structure and good epitaxial nature of films [6]. Three more low intensity peaks, $E_2^{high}-E_2^{low}$, $A_1(TO)$, and $A_1(LO)$ [7] appear in Fig. 2c, which confirms fatherly the degradation of crystalline structure, as proved by XRD. Significant variations of intensities and FWHM of E_2^{low} and E_2^{high} modes are also observed, which are probably caused by the relative disorientation of crystalline phases at nanoscale [8].

The sensitivity of the ZnO film-based prototypic gas sensor as a function of temperature to H_2 and CH_4 is shown in Fig.3. The sensitivity S of the sensor is defined as: $S(\%)=\frac{R_g-R_a}{R_a}\times 100\%$, where R_g and R_a represent the resistances of the sensor in the mixture gas and air atmosphere, respectively. The response of ZnO to CH_4 is much greater than that to H_2 gas.

The response behavior of the sensor in methane gas is depicted in Fig.4. Good repeatability, base line stability and quick response and recover time of the sensor have been obtained. Upon exposure to methane gas the sensor signal quickly increased as seen in Fig. 4. Response time and recover time are less than 1s and 10s, respectively. Actual response time and recover time should be shorter. This is because time delay in switching on or off the valves of gas inlet and outlet, as well as low pumping capacity ($7m^3/h$) would affect the measurement results.

Conclusion

In summary, the properties of nanostructured ZnO films have been investigated. The average grain sizes remained nearly unchanged with an increase of thickness. XRD and Raman measurements confirmed the structural degradation due to the structure disorder with an increase of film thickness. ZnO-based sensors with response and recover time less than 1 second and 10 seconds have been fabricated. The sensitivity of the newly designed sensor to CH_4 is greater than that to H_2 gas.

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