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Effect of Annealing on Conductivity Type of Nanocrystalline ZnO Films Fabricated by RF Magnetron Sputtering

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Abstract. Nanocrystalline ZnO films were deposited by rf reactive magnetron sputtering. The films were characterized by reflection high-energy electron diffraction, X-ray photoelectron spectroscopy and gas sensing measurements. It was found that annealing of the film enabled to invert its conductivity type. Thus, as-deposited ZnO film showed p-type conductivity while annealed film showed n-type conductivity behavior. The p- and n-type conductivities of the films obtained by gas sensing measurements have been confirmed by XPS results. The gas sensing properties of the films were investigated upon exposure to 10 ppm of NO_2 at 22ºC and exhibited good sensitivity with fast response and recovery times. The sensor response to NO_2 was found to be profoundly dependent on the conductivity behavior of the film.

Introduction

Zinc oxide is a promising multifunctional material for solar cell, optoelectronic, piezoelectric and sensor devices [1-10]. In recent years, ZnO has been found to play an important role in gas sensing application. In order to improve the gas sensing properties catalyst adding and high surface-volume ratio have been used [2]. Therefore, using the nanocrystalline ZnO films as a sensing layer for detecting gases is preferable [2-4]. Different deposition techniques have been used to prepare nanocrystalline ZnO films such as metallorganic chemical vapor deposition [5], sol-gel method [1], thermal evaporation [6], pulsed laser deposition [2-3] and magnetron sputtering [4,7-9]. Among them, the magnetron sputtering is considered to be suitable technique to prepare nanocrystalline ZnO films at wide variety of deposition parameters.

It has been proved that ZnO is an excellent gas sensitive material for detection reducing as well as oxidizing gases [1,4]. The gas sensing properties of ZnO films can be improved by controlling their electrophysical and structural properties which can be adjusted by the selection of the deposition parameters, such as the power, pressure of the oxygen, temperature of a substrate, type and concentration of the dopants, target-to-substrate distance and annealing conditions [7-9].

In this study, nanocrystalline ZnO films were deposited on polycor substrates by rf reactive magnetron sputtering and the effect post-deposition annealing on the crystalline phase formation and conductivity type have been investigated. In addition, the ZnO films were used to fabricate two-sensor elements for nitrogen dioxide detection at room temperatures.

Experimental methods

The ZnO films were formed on polycor substrate by rf magnetron sputtering using Auto 500 vacuum coating system (BOC Edwards, UK). The Zn of 99,999% purity with 3 in diameter (Kurt J. Lesker Company) was used as the target. The chamber was evacuated to residual pressure of 10^{-5} Torr. The

distance between the substrate and target was 15 cm. The target surface was cleaned for 10 min. ZnO film deposition was performed under room temperature. The chamber pressure and oxygen concentration in Ar/O_2 gas mixture were fixed at 5,6 mTorr and 80%, respectively. A film thickness was maintained at 60 nm. In order to increase the parameters stabilization and the resistivity of the as-deposited ZnO the films were annealed at 700 ºC for 1 h in ambient oxygen at 159 Torr.

The research of the structural parameters was carried out by reflection high-energy electron diffraction system (NANOFAB NTF-9, NT-MDT Co., Russia).

Composition analysis of the films was performed using the X-ray Photoelectron Spectroscopy (XPS, model: ESCALAB 250). XPS analysis was using a Mono AlKα (1486.6eV).

The 60 nm thick nanocryslalline ZnO film deposited on a polycor substrate with a dimension of 1.5 cm × 1.5 cm were used to fabricate the sensing elements. Metal electrodes were patterned after deposition of aluminium (thickness of 0.35 μm) using magnetron sputtering equipment (Auto 500, BOC Edwards, UK).

A home-made set-up equipped with a quartz chamber (around 700 cm^3), sensor heated holder, gas and purge lines was used to maintain the desired level of detected gas concentration. Resistance variation of the sensing element at 22 ºC to 10 ppm of NO_2 with air as the buffer gas was estimated.

The gas sensitivity was defined as the ratio of difference between resistance in the atmosphere of the detected gas and resistance in air to resistance in air. The response time and the recovery time of sensor were defined as the time taken for the sensor to reach 90 % of its total change in resistance after exposure to a detected and purge (dry air) gas, respectively [1].

Results and discussion

The research of the structural parameters was carried out by reflection high-energy electron diffraction system (RHEED). Analysis of RHEED-image (not shown here) of as-deposited ZnO film surface shown the film is nanocrystalline.

X-ray photoelectron spectroscopy was used to study the composition and to identify state of the species present in the films. XPS survey spectra of as-deposited and annealed nanocrystalline ZnO films after 5 minute etching are shown in Fig. 1. The peak positions of O1s and Zn2p are located at around 531 eV and 1021 eV. XPS signals of O1s and Zn2p confirm the well-known chemical structure of ZnO [2,3].The XPS spectrum in Fig. 1 is typical of that observed for the ZnO films.

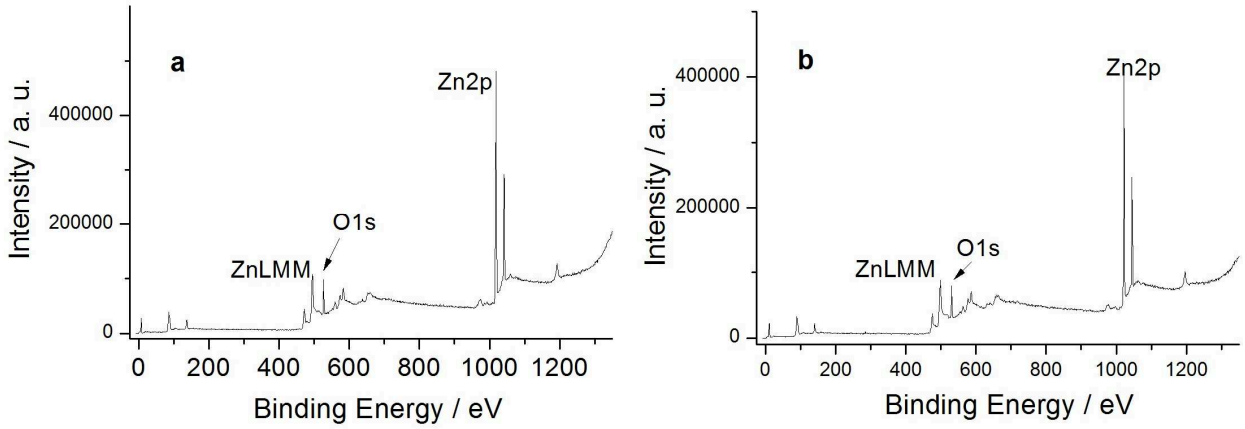

Fig. 1. XPS survey spectra of ZnO thin films: (a) as-deposited and (b) annealed film

Narrow scan XPS of Zn and O peaks of initial and 1 min etched surfaces are shown in Fig. 2. The components by peak fitting the Zn XPS data were identified. The Zn2p line exhibits a symmetric shape centered at 1021.7 eV and 1018.5 eV which can be assigned to oxidized Zn in ZnO of n- and p-type respectively [2,3,10]. There is the difference between XPS spectra of n-type and p-type ZnO on the films surface. The A_p line refers to $Zn2p_{3/2}$ signal of p-type ZnO and the A_n line – to n-type ZnO.

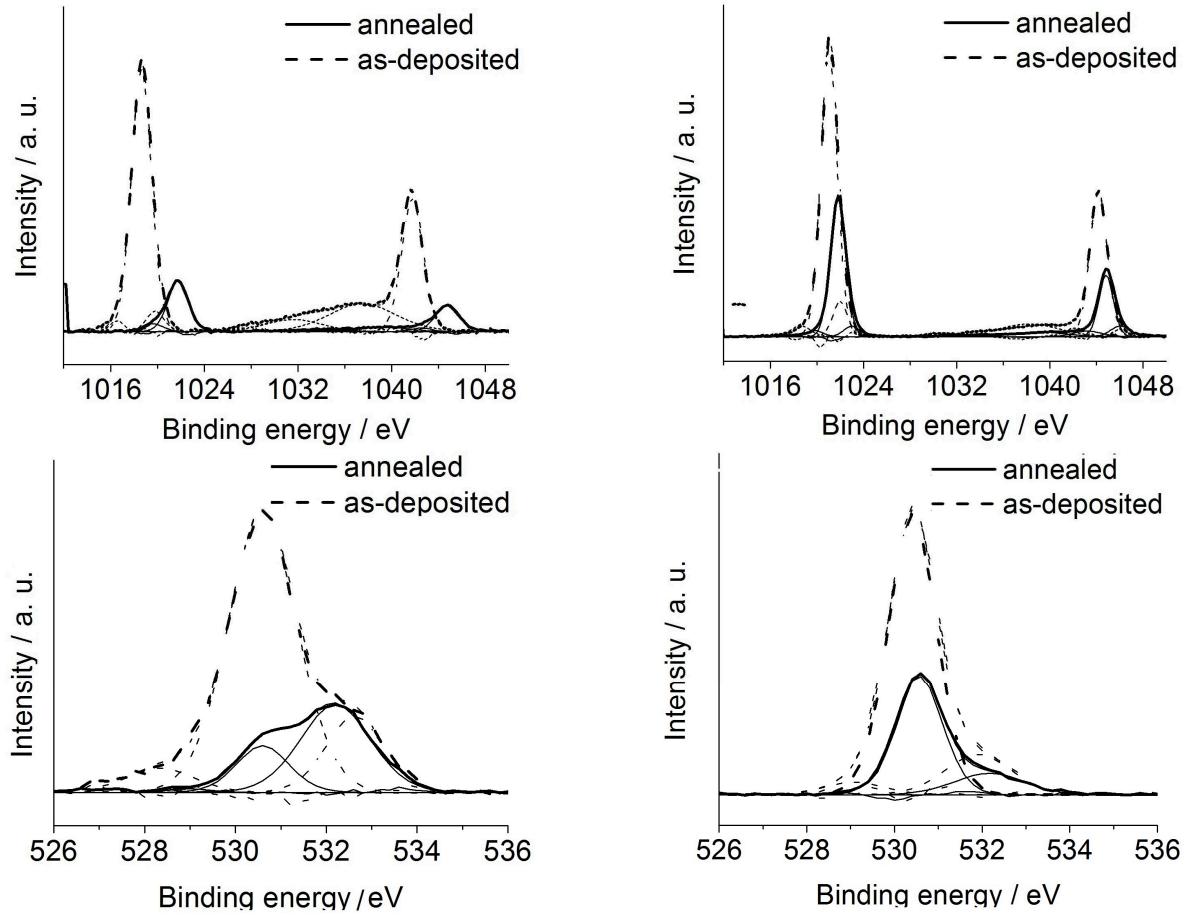

Fig. 2. XPS spectra of Zn2p (top) and O1s (bottom) corresponding to initial (left) and 1 min etched (right) surface of the ZnO films

The energy interval between A_p and A_n of 3.3 eV corresponds to the band of semiconductor ZnO. After etching the surface, the XPS spectra of the species are similar.

The peak-fit of the O1s core level reveals three binding energy states before etching the surface and two binding energy states after etching the surface (see Fig.2). The low-binding energy component at 530.6 eV and 529.8 eV is attributed to ZnO of n-type and p-type respectively. The high-binding energy component at 532,2 eV and 531.9 eV arises from absorbed carbon species combined with oxygen (C=O) or corresponds to O-H bonds in absorbed water molecules as reported elsewhere [2,3,10]. The lower energy line at 527.1 eV is from H–ZnO on (10$\bar{1}$0) surface [11].

Gas-sensing measurements were performed against room temperature in order to assess the sensing properties of the films for non-heated application. Before exposing to the gases, the ZnO film was allowed to be stable for electrical resistance for 30 min. The dynamic responses to 10 ppm of NO_2 at 22ºC are shown in Fig. 3. The resistance of the as-deposited film decreases while adsorbing the oxidizing NO_2 gas and opposite for annealed film as expected for p-type and n-type conductivity materials, respectively. The obtained results are in accordance with [1,4] and the XPS data.

It is observed that the sensitivity to NO_2 at 22 ºC is relatively high and equal of about 5.0 and 0.7, respectively. The response time is 1-2 s, while the recovery time is less than 10 s and 20 s for as-deposited and annealed film respectively.

Conclusions

Zinc oxide thin films were deposited onto polycor substrates by reactive sputtering. RHEED analysis revealed the films were nanocrystalline. XPS and gas sensing measurements showed the room temperature deposition resulted in p-type film while annealing at 700 ºC resulted in n-type film.

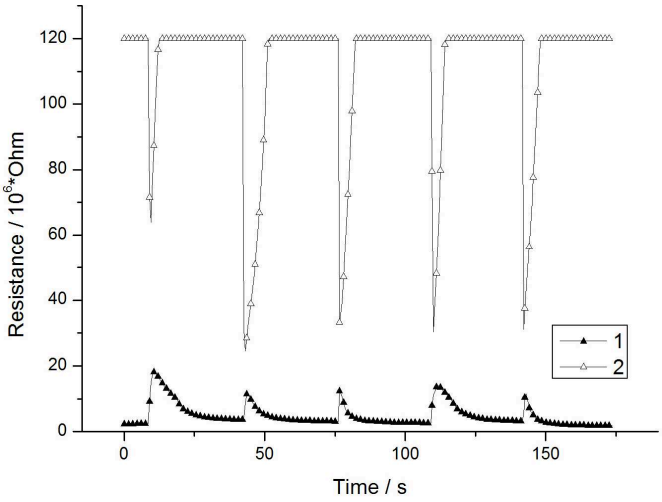

Fig. 3.The dynamic response of ZnO film to 10 ppm of NO_2 at RT: 1 – annealed, 2 – as-deposited

The obtained sensitivity to NO_2 was equal 0.7 and 5.0 for p- and n-type film respectively. Response and recovery time were less than 1-2 s and 10-20 s for both films. The gas sensing properties of the films were found to be strongly dependent on their conductivity type which was adjusted by annealing after deposition. The possibility to deposit films with p- and n-type conductivity behavior to NO_2 for non-heated sensor applications was demonstrated. The long term and temperature stability of the p- and n-type films, exposure to different gas environments and sensor arrays application with tunable selectivity should be further investigated.

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