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Nanocrystalline ZnO films grown by PLD for NO_2 and NH_3 sensor

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Abstract. Nanocrystalline ZnO thin films were grown by pulsed laser deposition technique on polycor substrates. The operation laser fluence of 2.0 $J \cdot cm^{-2}$ and film thickness of 60 nm were fixed while varying target-to-substrate distance (20–135 mm), substrate temperature (100–500 ºC) and annealing temperature (300–700 ºC). Structural and morphological investigations carried out by reflection high-energy electron diffraction, scanning electron and atomic force microcopies, have shown a strong influence of deposition technique parameters on grain size of the zinc oxide films. Atomic force microscopy showed the surface roughness decreasing and grain size increasing with the annealing treatment of the as-deposited films. The resistivity and Hall mobility of ZnO films were increased with substrate temperature and/or annealing temperature rise. The gas sensing characteristics of the films were investigated towards nitrogen dioxide and ammonia at a selected operating temperature (22 and 50 ºC).

Introduction

Nitrogen dioxide (NO_2) and ammonia (NH_3) are among the important industrial gases with high toxicity. NO_2 is emitted by internal combustion engines, thermal power station, heaters and furnaces, NH_3 is used in technological fields mainly [1,2]. Therefore NO_2 and NH_3 gas detecting in low concentration (few ppm) of environment and industries are challenging and improved reliability sensors are needed.

Semiconducting metal oxide sensors such as SnO_2, TiO_2, ZnO, In_2O_3, Fe_2O_3, WO_3 have been used to detect reducing (NH_3, CO, H_2, CH_4, C_3H_8) and oxidizing (NO_2) gasses [3]. Among them, zinc oxide (ZnO) is a very challenging one owing to its physical, chemical and thermal stability, its large bandgap and exciton binding energy, and owing to its high response to toxic (such as NO_2, NH_3) and inflammable gases [1]. Prior works have proven that ZnO films can be used as sensing elements for the detection of nitrogen dioxide and ammonia by measuring their electrophysical properties [1–5]. The sensor elements based on 5-10 at.% Sn in ZnO thin film used and gas sensitivity and response–recovery characteristics have been evaluated at room temperature, 100, 150 and 250 ºC for different NO_2 concentrations [4]. The films with 0.2–0.5 μm particle size showed a maximum sensitivity of about 6–11 %/ppm at 150 ºC and a sensitivity of 1.5–2 %/ppm at room temperature 25 ºC toward 1.5 ppm of NO_2 gas in air. The reaction time was 10–60 and 20 min, respectively. The dependences of the NO_2 and NH_3 responses on operation temperature, gas concentration were investigated [1–3]. The nanocrystalline ZnO films had the maximum NO_2 gas response of 37.2% with 78% stability upon of 100 ppm at the temperature of around 200°C [1]. The sensitivity of Pd impregnated nanocrystalline ZnO sensor to 100 ppm NH_3 was found to be 68% with response time and recovery time of 35 s at optimum operate temperature of 300 °C [2].

Therefore, using the nanocrystalline ZnO films as a sensing layer for detecting gases is preferable, since particle size reduction gives large ratio of surface area to bulk is one of the main factors enhancing gas-sensing properties [1,2,5,11,13]. Different deposition techniques are used to prepare nanocrystalline ZnO films such as sol-gel method [1–3], metalorganic chemical vapor deposition [6], thermal and electron beam evaporation [7,8], magnetron sputtering [5,9] and pulsed laser deposition [10–13]. Among them, the pulsed laser deposition is considered to be suitable technique to prepare nanocrystalline ZnO films at wide variety of deposition parameters [10–13].

It is obvious that the gas sensing characteristics of ZnO films can be improved by controlling the electrophysical and structural properties of the films. These properties of the films can be adjusted by the selection of the deposition parameters, such as the laser fluence, pressure of the oxygen, type and temperature of a substrate, type and concentration of the dopants, target-to-substrate distance and annealing conditions [10–13].

In this study, nanocrystalline ZnO films were deposited on polycor substrates by reactive pulsed laser deposition (PLD) and the effect of target-to-substrate distance, substrate temperature and post-deposition annealing on the films surface morphology, crystalline phase formation, and electrophysical properties have been investigated. In addition, the ZnO films were used to fabricate sensing elements for nitrogen dioxide and ammonia detection at different temperatures by recording the change in resistance of the film under the gas exposure.

Experimental methods

The ZnO films were formed on polycor substrate by pulsed laser deposition (NANOFAB NTF-9, NT-MDT Co., Russia). The ZnO of 99,99% purity with 2 in diameter (SCI Engineered Materials, USA) was used as the target. Laser ablation of the target was performed using an UV KrF excimer laser ($\lambda = 248$ nm, $\tau_{FWHW} \sim 10$ ns), operating at laser fluence of 2.0 J·cm^{-2}. Almost 50 000 laser pulses at 10 Hz pulse repetition rate were used for the ZnO film growth.

The chamber was evacuated to residual pressure of 10^{-6} Torr. The distance between the substrate and target was 11.5 cm. The target surface was cleaned by applying 5 000 laser pulses. The ZnO film deposition was performed for oxygen pressure (in flow) at 1 mTorr, measured by a Pirani gauge, respectively. A film thickness was maintained at 60 nm. 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). The morphologies were characterized by atomic force microscopy (Probe Nanolaboratory NTEGRA Vita, NT-MDT Co., Russia) as well as scanning electron microscopy (Nova Nanolab 600, FEI Company, Netherlands). Electrical parameters were measured by hall-effect measurements (HMS-3000, Ecopia Corp., Korea).

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 the deposition of nickel (thickness of 0.5 μm) on titanium (thickness of 0.04 μm).

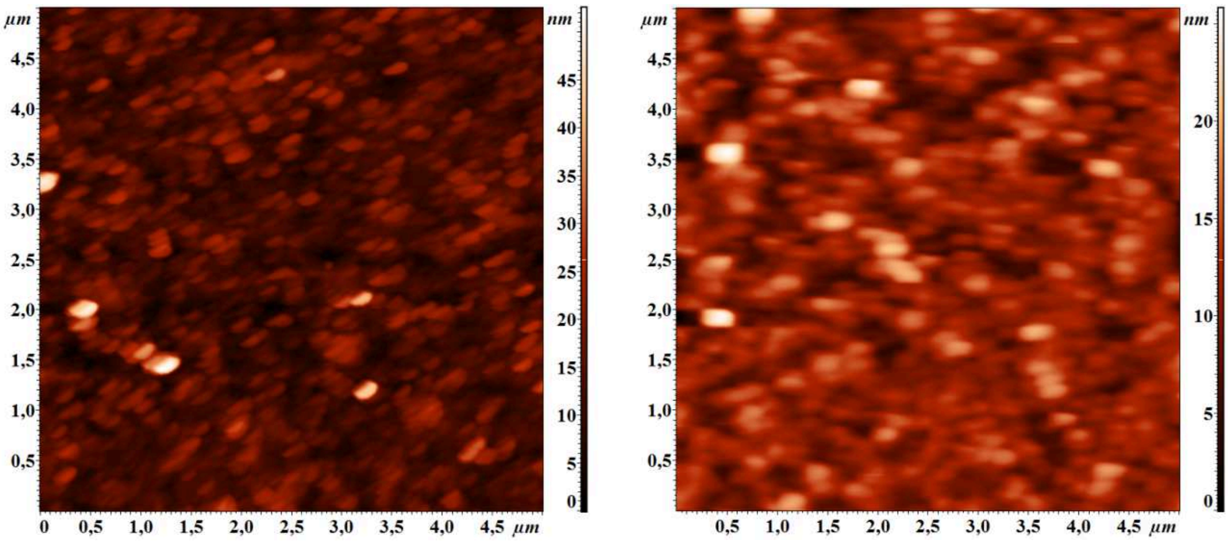
A home-made set-up equipped with a quartz chamber, sensor heated holder, gas/purge lines was used to maintain the desired level of detected gas concentration. The gas sensitivity was defined as the ratio of difference between resistance in the atmosphere of the detected gas and resistance in air to resistance in air. The response/recovery time of sensor were defined according to [1,2].

Results and discussion

Structural and surface analysis

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, since the reflections are of the form of semi rings. The lattice parameter of the nanocrystalline ZnO films was equal to 0.26 nm, measured using the program kSA-400 during the diffraction.

The morphology features of deposited ZnO films were examined by using atomic force microscopy (AFM) (Fig. 1). The as-deposited ZnO film is relatively dense with a rough surface. The images show a nanocrystalline morphology of the film with grain size about 90 nm (Fig. 1a).



a b

Fig. 1. AFM images of ZnO film surface obtained by PLD in 1 mTorr O_2 at 300 ºC: (a) as-deposited and (b) annealed film

The annealing treatment of the as-deposited films has effected on the surface roughness. The films were observed being denser, surface roughness decreasing and grain size increasing simultaneously (Fig. 1b). For the scanning area of 5 μm × 5 μm, the root mean square roughness value of the as-deposited and annealed ZnO films are 5.07 nm and 2.93 nm respectively. The distribution of grain sizes of annealed film seems to be more uniform with the average value of about 130 nm. It is also observed from cross-section profile variations that the surface morphology of the annealed film is smoother than that of the as-deposited. The behaviour upon annealing is in agreement with data reported by other authors [11,13]. Annealing temperature enhances the diffuse activation energy of the surface atoms. This has as a result the Zn and O atoms to occupy the correct site in the crystal lattice and grains with the lower surface energy will become larger at high temperature [13], and therefore the roughness decreases.

It was also found that as-deposited ZnO films demonstrated the strong dependence of the grain size on target-to-substrate distance (Fig. 2). The grain size varies between 55 and 610 nm, while the target-to-substrate distance is in the range from 20 to 135 mm. It can be explained by the non-uniformity of cross-beam laser power distribution along the laser beam axis.

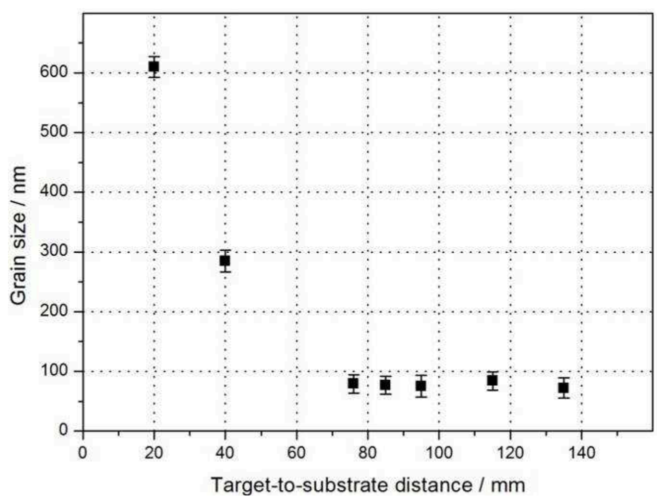
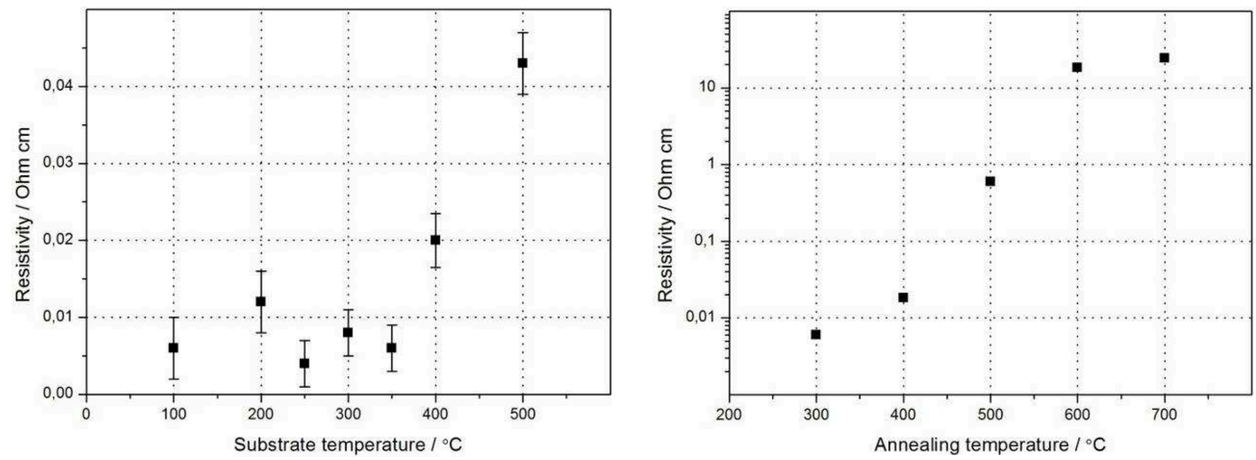


Fig. 2. Grain size vs. target-to-substrate distance for nanocrystalline ZnO structure obtained by PLD in 1 mTorr O_2 at 300 ºC

Electrical characterisation

The effect of substrate temperature and annealing temperature on the ZnO films resistivity have been performed by hall-effect measurements using a four-probe van der Pauw method. All deposited films were found to exhibit n-type conductivity, caused by intrinsic donor defects. The resistivity (Fig. 3) and Hall mobility (not shown here) of the obtained films were increased with substrate temperature and/or annealing temperature rise while the carrier concentration decreased (not shown here), that is in good agreement with [13]. This is because the intrinsic defects decreased, oxygen vacancies, responsible for the free carriers, decreased by oxygen diffusion into the films with the temperatures rise or the Zn interstitials decreased due to Zn [13].

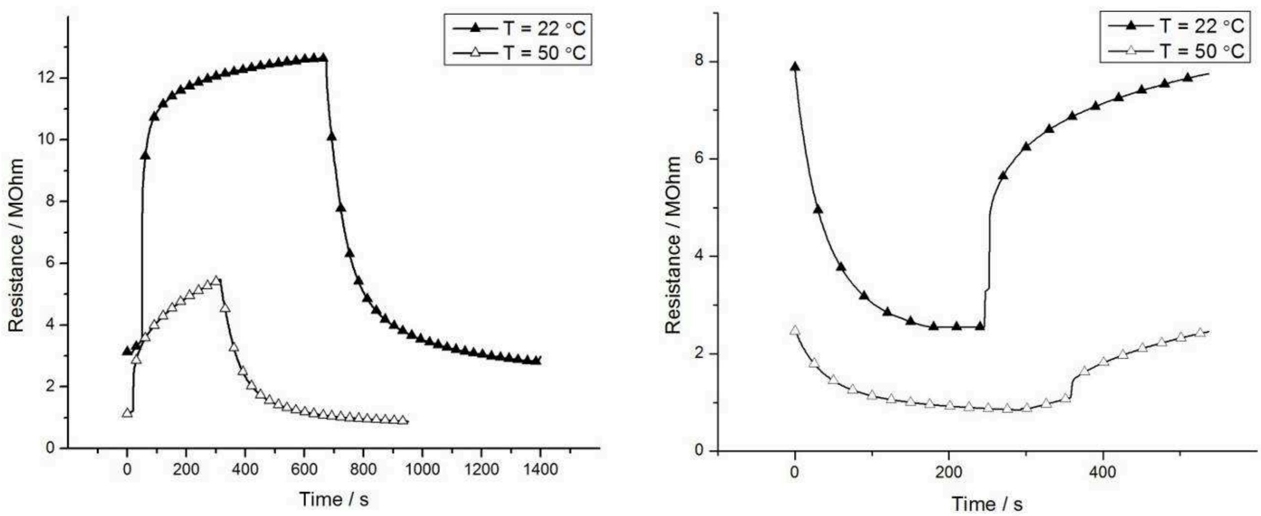


a b

Fig. 3. The effect of (a) substrate temperature and (b) annealing temperature on the resistivity of the ZnO film obtained by PLD in 1 mTorr O_2 and 11.5 cm target-to-substrate distance

Gas-sensing measurements

Gas-sensing measurements were performed against low 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 and NH_3 at different temperatures (22 and 50 ºC) are shown in Fig. 4. The resistance of the film increases while adsorbing the oxidizing NO_2 gas and opposite for reducing NH_3 gas as expected for n-type conductivity materials confirmed by hall-effect measurements.



a b

Fig. 4.The dynamic response of the annealed ZnO film to 10 ppm: (a) NO_2 and (b) NH_3

It is observed that the sensitivity to NO_2 and NH_3 at 22 ºC is relatively high and equal of about 3.3 and 0.67, respectively. The response time increases from 200 to 225 s (from 100 to 150 s) while the recovery time decreases from 210 to 170 s (from 250 to 200 s) for NO_2 (NH_3) with increasing work temperature from 22 to 50 ºC, that is not typically for ZnO films [13]. The obtained results of sensitive characteristics can be explained by interface modification of the ZnO films during first cycle measurements, resistance drop according to dependence of the film resistance on temperature and not enough temperature (of 50ºC) to recovery initial properties.

Conclusions

Zinc oxide thin films were deposited onto polycor substrates by pulsed laser deposition technique. RHEED analysis and AFM revealed the as-deposited films were nanocrystalline. The grain size and resistivity of the films have been adjusted by the selection of the target-to-substrate distance, substrate temperature and annealing temperature. The strong dependence of the grain size on target-to-substrate distance was observed in the range of 55 to 610 nm. The resistivity was increased with substrate temperature and/or annealing temperature, simultaneously.

The sensing elements based on the annealed ZnO films have been fabricated and used for detecting low concentration (10 ppm) of NO_2 and NH_3 against different work temperature (22 and 50 ºC). The obtained response and recovery time to NO_2 and NH_3 gases are less than 250 s and sensitivity are equal 3.3 and 0.67, respectively. Owing to low work temperature, the sensing elements are promising for non-heated sensor applications.

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