

Sensor properties of spray-pyrolysis deposited ZnO thin films*

N. STARBOV*, E. KRUMOV, D. KARASHANOVA, A. RACHKOVA, K. STARBOVA
*Central Laboratory of Photoprocesses "Acad. Jordan Malinowski", Bulgarian Academy of Sciences,
Acad. Georgi Bonchev Str., Block 109, 1113 Sofia, Bulgaria.*

Nano-sized ZnO thin films are prepared by spray-pyrolysis of Zn-acetate and Zn-nitrate onto glass substrates. Two different thermal post-processing – non-isothermal or laser annealing, are applied to improve the film microstructure and related properties. X-ray diffraction or scanning electron microscopy are used in order to identify the ZnO phase composition and film surface morphology respectively. DC-resistance measurements indicate that the electrical conductivity of the samples studied is sensitive to the presence of reactive compounds in the ambient gas atmosphere. The sensing efficiency of virgin, as well as annealed, ZnO films for the detection of ethanol, acetone, ammonia and dimethylamine is checked via resistance measurements at room temperature. The results obtained are used for calculation of the relative gas sensitivity of the samples studied. Finally, cyclic resistance measurements in a gas vapour/inert atmosphere show that either ammonia or dimethylamine vapors are simply physically adsorbed onto the ZnO film surface.

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1. Introduction

Recently, two post-deposition annealing methods have been applied for improvement of the microstructure and physical properties of spray-pyrolysis deposited ZnO thin films [1]. It was shown that excimer laser annealing of the as-deposited samples is more effective than conventional non-isothermal heating, thus leading to better film crystallinity, a three orders of magnitude higher DC-resistivity and a higher optical transmittance. Among these properties, the electrical conductivity is often very sensitive to the adsorption of different gases and vapors onto the ZnO surface. Therefore, the resistivity is a widely used characteristic of ZnO films in sensor technology [2-5]. In the present paper, the resistivity change of both virgin and annealed ZnO films is measured under different gas ambient conditions, in order to evaluate the sensor properties of the samples: the relative sensitivity, response time and recovery of the initial resistivity value after replacing the reagent vapours with an inert gas atmosphere.

2. Experimental

The samples studied are 200 nm thick ZnO films deposited onto pre-cleaned soda-lime glass plates. 0.1 Mol $Zn(CH_3COO)_2 \cdot 2H_2O$ or $Zn(NO_3)_2 \cdot 6H_2O$ solutions in ethanol are multiply sprayed on the substrates. The abbreviations ac-ZnO and ni-ZnO will be used below, as simple indications of films prepared via spray pyrolysis of zinc acetate or zinc nitrate respectively. During the sample preparation, the substrates are held at 350°C. At higher temperatures glass fracture occurs due to local thermal stress during the spraying procedure. Under these deposition conditions, the pyrolysis process is not completely finished. As a result, additional thermal annealing is necessary. For this reason, the ZnO films thus obtained are non-isothermally annealed for 16 hours in an inert atmosphere of pure dry nitrogen at 590°C, just under the soda lime glass softening temperature. In parallel, the ZnO samples deposited under the same spray-pyrolysis conditions are irradiated in air, by means of single excimer Ar*F pulses ($\lambda=193$ nm, $\tau=20$ ns, Lambda Physics – Germany) in the presence of a beam homogenizer. The laser energy density at the sample surface is 380 mJ/cm² for ac-ZnO and 690 mJ/cm² for ni-ZnO, the optimal values estimated previously for laser annealing of the ZnO films studied [1].

A vibrating capacitor electrometer (RFT Vakutronik VA-J-51 (Germany)) is used for DC-conductivity

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measurements. The experimental set-up is described in detail elsewhere [6]. Here it should be mentioned only that the resistance of the ZnO films is measured parallel to the substrate plane, with an accuracy of $\pm 2\%$ using 0.5 mm narrow strip gold electrodes, vacuum deposited onto the film surface. A specially designed thermostat allows us to maintain the sample temperature between 20° and 150°C, with an accuracy of $\pm 0.5^\circ\text{C}$. The conductivity of the samples, as dependent on temperature, is presented in Fig.1. It is obvious that the thermal annealing does not have a substantial influence on the ac-ZnO film conductivity, σ . However, the σ of annealed ni-ZnO films is about one order of magnitude higher than that of virgin ones. This increased conductivity is a result of the better crystallinity of non-isothermally treated ni-ZnO films as compared to the virgin samples, which is confirmed earlier by X-ray diffraction data [1].

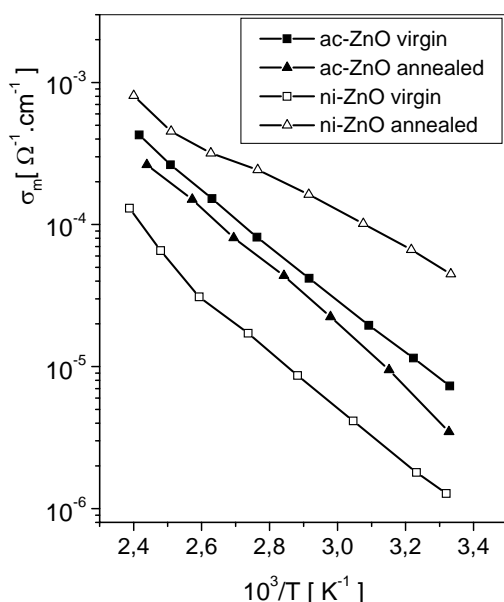


Fig.1. Temperature dependence of the ZnO thin films' conductivity

The sensing properties of the ZnO films are estimated as resistivity changes in different reagent gas ambients, at room temperature. For this purpose, saturated vapours of ethanol ($\text{C}_2\text{H}_5\text{OH}$), ammonia (NH_3), acetone (CH_3COCH_3) or dimethylamine ($(\text{CH}_3)_2\text{NH}$) (DMA) are leaked into the evacuated thermostat vessel. The data obtained are used for calculation of the relative sensitivity, using the equation [2,3]:

$$|S| = \frac{R_i - R_r}{R_r} \times 100\%,$$

where R_i and R_r are the ZnO film resistivity in an inert atmosphere, dry pure nitrogen, or reagent vapours respectively. Then, the sensing properties of the samples are evaluated for reagents selected as the most effective for changing the film resistivity. In this case, a mixture of reagent vapours and nitrogen as the transport gas is used, which allows one to dilute the reagent vapours down to several ppm. The ambient gas, either nitrogen or a reagent vapour/ N_2 mixture, is always dried by passing it into the thermostat vessel through a silicagel/zeolite filter.

3. Results

The relative sensitivity S obtained in saturated vapours of different reagent is presented in Fig. 2., as a bar-diagram for both virgin and annealed films. It is clearly seen that there is no dependence of the measured sensitivity upon the thermal pre-history of the ZnO films studied. For ac-ZnO films, conventional non-isothermal heating gives rise to a 4-5 times higher sensitivity in the presence of ammonia vapours, as compared to the virgin (ac-ZnO films) ones. Conventional thermal annealing is enormously effective for a DMA-vapour atmosphere, in which the virgin ac-ZnO films are not sensitive at all. At the same time, the sample's thermal pre-history has a minor or zero effect on S for ac-ZnO films in ethanol or acetone vapour atmosphere. The sensitivity dependence on the thermal pre-history of the ni-ZnO films is not very different. In this case, laser annealing is more effective than the non-isothermal treatment, increasing S by several tens of percent. Additionally, the sensitivity of the laser annealed samples, except for ethanol, never exceeds the values obtained for virgin ni-ZnO films. It is always higher than the sensitivity of conventional annealed films, reaching for an ammonia vapour atmosphere the highest S -value measured for ZnO films deposited from a nitrate precursor.

The results presented in Fig. 2. clearly demonstrate that the most intense response of the ZnO resistivity is observed in DMA (for non-isothermally annealed ac-ZnO films) and ammonia (virgin ni-ZnO films) vapour. Therefore, it is reasonable to evaluate the sensor properties of the films studied in both cases, which are more interesting for practical applications of the spray-pyrolysis deposited ZnO films. It is established that the response time τ of non-isothermally annealed ac-ZnO films in DMA vapour is about 15 minutes, while the τ value, measured for virgin ni-ZnO films in a NH_3 atmosphere is 5 min [7]. Also, the threshold ammonia concentration which could be identified with virgin ni-ZnO samples is about 3000 ppm, while for annealed ac-ZnO films this value is 4000 ppm. Substantially lower threshold concentrations - below 40 ppm for DMA vapour in the ambient could be detected with non-isothermally annealed ac-ZnO samples.

It should be mentioned here that the measured resistivity R_r rises when reagent vapours, either ammonia or DMA, are leaked into the thermostat vessel. The R_r value is not substantially changed when the thermostat is evacuated and filled with pure dry nitrogen thereafter. However, if this procedure is accompanied with an

increase in the sample temperature to above 100°C, the initial value R_i could be measured after sample cooling to room temperature. Thus, it is shown that the initial resistivity of the films studied could be recovered after

removing the reagent vapours from the ambient, followed by subsequent heating in an inert atmosphere.

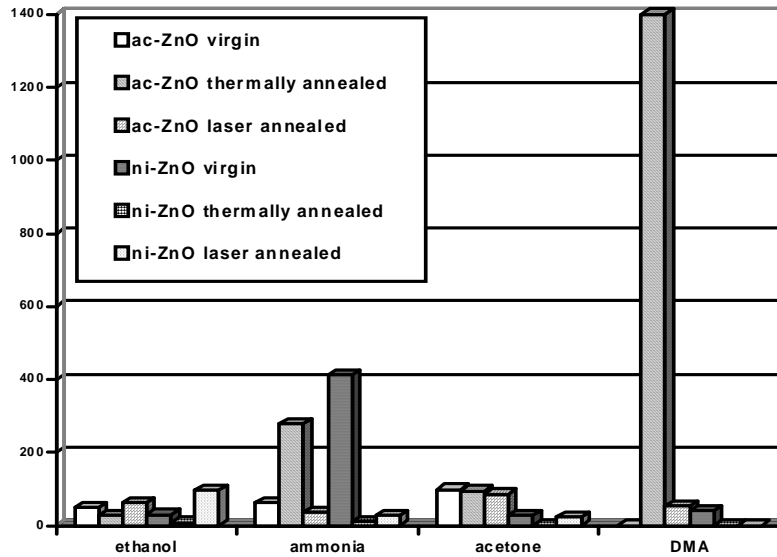
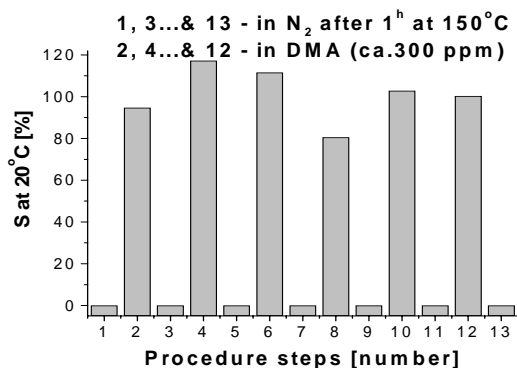


Fig.2. Effect of post-deposition annealing on the sensitivity |S| of ac-ZnO or ni-ZnO thin films in saturated vapours of different reagents

This procedure could be repeated many times, and Fig. 3. demonstrates the sensitivity measurements during periodical replacement of DMA vapours with dry pure nitrogen after sample heating at 150°C for 30 - 60 min. It is clear that the initial resistivity - R_i , is always recovered after a number of cycles “DMA/N₂ + 1^h heating”. Here, it should be noted that similar results for S are obtained for ni-ZnO samples during periodic replacement of ammonia vapours with dry pure nitrogen, after the same heating and cooling conditions.

Fig. 3. Sensitivity S of non-isothermally annealed ac-ZnO films vs. periodical replacement of DMA vapours with dry pure nitrogen.



4. Discussion

Looking at Fig. 2., it is obvious that the laser annealing does not influence substantially the sensitivity S , as compared to the conventional non-isothermal heating of ZnO films. The only exception from this conclusion is observed in ethanol vapours, for which S is about 30% higher for laser annealed than for conventional annealed ZnO samples. However, the threshold C₂H₅OH concentration is enormously high for the detection of this reagent with the ZnO-films studied. This sensitivity lack could be explained by the resistivity R_i of the laser annealed samples: $5 \cdot 10^8 - 1 \cdot 10^9$ ohm.cm. Obviously, this very high value could not be easily increased by the adsorption of the gas reagent, irrespective of its influence on the current carrier mobility or concentration. This means that the laser annealed ZnO films, which have excellent optical properties [1], are not suitable for application in the field of sensor technology.

Summarizing the results from the cyclic measurements of S in reagent/inert ambient it is clear that the influence of ammonia and DMA on the sample resistivity is simply due to physical adsorption of both

reagents on the ZnO surface. Thus, the ZnO films studied could be used as functional sensor materials for the multiple detection of NH₃ or dimethylamine. Obviously, it is necessary to improve the threshold sensitivity of ni-ZnO films, which is too low. One possible solution of this problem is to dope the ni-ZnO films with metals such as Al, In, etc. [8,9]. Additionally, the spray-pyrolysis deposited ZnO films have to satisfy a number of other important sensor properties, in order to be used for the fabrication of gas sensors: i.e. the accuracy, resolution, selectivity, nonlinearity etc. [10]. Related experiments on these objectives are in progress.

5. Conclusions

A substantial increase in the relative sensitivity of spray pyrolysis deposited ac-ZnO films for the detection of ammonia and dimethylamine vapors after non-isothermal annealing is established. The gas sensing properties of ZnO samples prepared from a nitrate precursor are found to remain unaffected by the same thermal processing. The results obtained are encouraging, and reveal opportunities for extending further the experiments on the modification of spray-pyrolysis deposited ZnO films, in order to satisfy the basic requirements for their application in the field of sensor technology.

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*Corresponding author: nstar@clf.bas.bg