Al doped ZnO thin films – microstructure, physical and sensor properties

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Abstract. Thin ZnO films doped with Al are deposited by spray pyrolysis onto glass substrates using starting solution of Zn-acetate + n.AlCl (where 0.1 < n < 30 at.%). The ZnO phase composition and surface morphology are revealed via X-ray diffraction or atomic force and scanning electron microscopy respectively. UV/VIS transmittance/reflectance, as well as DC-conductivity measurements are applied in order to reveal the influence of the Al doping on the optical and electrical transport properties of the films studied. The sensing efficiency of the pure as well as of doped ZnO films for detection of noxious gases is checked via resistivity measurements under saturated vapours of ethanol, acetone, ammonia, dimethylamine and formalin at room temperature. Finally the results obtained are discussed concerning the application of the ZnO:Al films studied in the field of sensor technique.

1. Introduction
It was demonstrated earlier that the electrical resistance of spray-pyrolysis deposited ZnO thin films is very sensitive to the surface adsorption of several noxious gases or vapours [1]. The films were prepared from different precursors - Zn-nitrate or Zn-acetate, and thermal post-deposition methods were applied for improvement of their microstructure and related physical properties [2]. It was shown that the ZnO films obtained via pyrolysis of Zn-acetate were more sensitive to the studied noxious gas ambient than those deposited from Zn-nitrate precursor. For further improvement of the gas sensing efficiency a doping of ZnO-films with Al, In etc. could be applied [3-5]. According to Vasanelly et al. [3] the incorporation of Al⁺³ ions in the crystal lattice of ZnO is accompanied with formation of strong local electrostatic field. Thus, an increased surface concentration of the adsorption sites number could be obtained. Therefore the present paper aims to check the sensing properties of Al-doped ZnO thin films deposited via spray-pyrolysis of Zn-acetate.

2. Experimental
The undoped ZnO thin films were prepared by spray pyrolysis of Zn(CH₃COOH)₂.H₂O ethanol solution onto pre-cleaned soda-lime glass substrates. The same precursor modified by adding of AlCl₃ to the starting solution was used to deposit the doped samples. Thus, ZnO films with different Al concentration as 0.1, 0.6, 3, 10 and 30 % were obtained. Following the procedure established earlier [1, 2] the films with thickness about 200 nm were prepared by multiple spraying on the substrates initially hold at 350°C since at elevated temperature a substrates fracture occurs due to the glass...
thermal stress during the spraying. Thereafter, the samples were non-isothermally annealed for 16 hours at 560°C for completely finishing of the pyrolysis process [1].

The surface morphology of the ZnO:Al films was investigated via AFM (Atomic Force Microscopy) measurements using a Multimode V Veeco. Imaging was performed in tapping mode and height, amplitude and phase images were recorded. Scan rate was 2 Hz, the images resolution is 512 lines per scan direction. At least two different points on the sample surface were explored. Silicon probes with cantilever length of 125 μm and Al reflective coating on the backside (RTESPA, Veeco probes) were used in these experiments. RTESPA probes have a nominal resonance frequency of ca. 300 kHz and a typical force constant of 40 N/m. The tip nominal radius for these probes is less than 10 nm. For comparison the surface microstructure of the films was visualized under scanning electron microscope Philips SEM 515, the samples preparation being described in details earlier [2]. The phase composition of the aluminium doped ZnO films was identified via WAXRD (Wide Angle X-Ray Diffraction) using Philips PW 1050 diffractometer.

The measurements of the optical transmittance and reflectance spectra were performed using double-beam spectrometer Shimadzu UV-190 in spectral range 250-650 nm. For calculation of the total reflectance the diffuse reflectance spectrum was measured with an attachment consisting of an integrating sphere with a photomultiplier R 446.

The samples resistance was measured parallel to the substrate plane with narrow gold strip electrodes at an accuracy of ± 2%. The DC-conductivity was obtained in the dark ambient conditions using special designed vacuum thermostat, the sample temperature being varied between 20° and 150°C with an accuracy of ± 0.5°C. More details related to the resistance evaluation are described elsewhere [2]. The relative sensitivity of the samples for detection of different gases or vapours was evaluated according to the equation [6, 7] as 

\[ S = \left( \frac{R_i - R_r}{R_i} \right) \times 100\% \]

where \( R_i \) and \( R_r \) are the ZnO film resistivity in inert atmosphere - dry pure nitrogen, or reagent gas respectively. For this purpose, saturated vapours of ethanol, ammonia, acetone, formalin or dimethylammine - DMA, were leaked in the evacuated thermostat vessel.

3. Results and Discussion

The surface morphology of the films studied is illustrated on figure 1. As seen, the undoped ZnO samples have granular microstructure, the mean grain size being between 50 and 150 nm. However, the doping with 3% Al is accompanied with distinct surface smoothing. These peculiarities were confirmed also at atomic scale resolution on AFM 3D images (figure 2).

![Figure 1. SEM micrographs (a-c) of spray pyrolysis deposited thin films of ZnO: undoped (a) or doped with 3% Al (b) and (c) - 30% Al](https://example.com/figure1.png)

The crystal structure of the films studied was identified from the WAXRD spectra presented on figure 3 for virgin samples, as well as for doped with 3% or 30% Al. The spectra are typical for textured ZnO films with wurtzite structure the most intensive peak being at 2θ = 34.5° which corresponds to [002] crystallographic axis. This peak slightly increases with Al concentration up to 3 %. This indicates a better crystallinity as compared to the undoped samples. However, the [002] peak reduces twice by further 30 % rise of Al content in the films, but new phases were not identified.
Figure 2. AFM maps of the samples studied. The symbols same as in figure 1

Figure 4 illustrates the DC-conductivity of ZnO films measured at room temperature for samples doped with different Al amount. The observed maximum conductivity at or above 1% Al content corresponds well to the results obtained by J. de Marchant and M. Cocivera [8], the maximal $\sigma$ in

Figure 3. XRD spectra of annealed ZnO films. The symbols same as in figure 1

Figure 4. DC-conductivity of ZnO:Al films as dependent on the doping concentration

these experiments being measured at Al concentration of 2%. Similar dependence was observed in implanted with C or Si materials [9, 10]. The optical properties of ZnO:Al samples are presented on figure 5. The transmittance decreases from 97% for undoped ZnO films down to 85% at 30% Al concentration in accordance with the results of Sato et al. [11]. The total reflectance changes more weakly in conformity with the surface modifications when Al content in the ZnO thin films increases.

Figure 5. Optical transmittance – a) and total reflectance - b) of doped ZnO thin films

The sensing efficiency of the Al doped samples studied could be evaluated from figure 6, which presents S vs. doping concentration for the different noxious agents. The data for the virgin samples are not included in this graph for simplicity since in this case S is below 20% with an exception of the
measured $S$ in DMA vapours ambient - 1400% [1]. Thus, the ZnO:Al thin films have an increased sensing efficiency as compared to the sensitivity of undoped samples. However, there is not any general dependence of $S$ on the Al content in the ZnO thin films studied.

![Figure 6](image_url)

**Figure 6.** Relative sensitivity $S$ of ZnO:Al films as measured for a number of hazardous agents

4. Conclusion
The results obtained in the present paper demonstrate that the Al doping has a noticeable effect on the sensing efficiency of ZnO thin films deposited via spray pyrolysis from acetate precursor. At the same time a definite general dependence of $S$ from Al content in the samples was not observed. This means that the proposed by Vasanelli et al. [3] increased surface concentration of the adsorption sites created from the incorporated Al atoms in the ZnO crystal lattice has not decisive role for detection of the noxious vapours studied. However, the observed specific sensing response - maximal sensitivity at content 0.6% Al for ammonia, 0.1% for acetone, 30% Al for formalin or the mentioned above for DMA in virgin samples, reveals a good prospective for preparation of selective chemical sensors based on ZnO thin films spray pyrolysis deposited from acetate precursor.

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