Al doped ZnO thin films for gas sensor application

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Abstract. Highly textured pure and Al doped ZnO thin films have been produced by pulsed laser deposition for optical gas sensor application. The influence of the processing parameters such as substrate temperature and oxygen pressure applied during depositions, and dopant concentration on the structural, morphological, and optical properties of the films were investigated. All deposited films are textured along the (002) direction. The substrate temperature and the oxygen pressure have stronger influence on the film crystallinity compared to the presence of the dopants. The grain size of the films prepared from 2 wt% Al2O3 doped ZnO target is approximately the same as the one produced from pure ZnO target. The increase in the dopant concentration into the ZnO target (to 5 wt% Al2O3) leads to an increase of the in-plane grain size of the as-deposited films which is well known to increase the gas sensitivity. At the same time, the use of doped targets increase the droplets on the film surface which deteriorates the optical detection of the gas sensing effect. The increase of the dopant concentration reduces the film transmission in the visible range and the transmission cut-off edge is shifted to the shorter wavelengths. The films deposited from 2 wt% Al2O3 doped ZnO target at oxygen pressure of 0.05 mbar and 300 °C substrate temperature have good mode properties which makes them good candidates for optical sensors.

1. Introduction

In contrast with the classical sensors where the detection is related to the variation of the sensor material’s electrical properties, the new class of miniaturized gas sensors is based on the reversible alterations of sensor material’s optical properties upon exposure to the gas environment. The main advantages of optical detection over the classical methods are very high accuracy, fast response time, advanced sensitivity, and possibility to operate at room temperature [1]. Optical sensors have been shown to be safe in explosive environment as well as being applicable even in unusual or extreme conditions. A potential type of optical sensors is the thin planar waveguide [2–4]. Usually, a prism coupling is applied in order to introduce the light into the planar waveguide. Recently, thin waveguide films working as optical hydrocarbon sensors were demonstrated [5,6]. For a characteristic incident angle, the resonant coupling of the laser beam into the waveguide can be observed by detecting one TE or TM mode line which appears in the reflected beam [5,6]. The physical or chemical interaction

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between the gas and the sensitive material leads to a variation in the refractive index of the waveguide film. This variation changes the position of the mode line, which is relatively easy to detect.

Various basic materials, such as ZnO, SnO2, In2O3, TiO2, SnO2/NiO, metal acetylacetonates etc. have been tested and studied as sensing media [7,8]. ZnO is a promising candidate for such application due to its high transparency in the visible wavelength range and low electric resistance [9-11]. The ZnO sensing media exhibit a strong response when reacting with reducing gas agents, such as H2, NOx, NH3, SOx and etc. At present, the efforts are mainly directed to the improvement of the selectivity of the sensing media to the gas components. Small concentration of dopants, such as Al, In, Cu, Sn, etc. are used for improvement of selectivity to different gases [11].

Various deposition techniques have been applied to the ZnO film synthesis. Pulsed laser deposition (PLD) was proven as a method for preparation of high-quality thin films with optical losses lower than 1 dB/cm, which are suitable for optical applications [12].

The aim of this work is to produce high-quality Al doped ZnO thin films for optical gas sensor application by PLD. Special attention was paid to the influence of the processing parameters, such as substrate temperature and oxygen pressure applied during depositions, as well as the dopant concentration into the targets on the structure, morphology, and optical properties of the films.

2. Experimental

The ZnO thin films preparation was carried out by using a standard on–axis PLD setup. The experiments were performed by a XeCl excimer laser (308 nm, pulse duration of 30 ns, repetition rate of 2 Hz). The laser fluence was kept at 2 J/cm2. Home–made pure and Al2O3 doped ceramic ZnO targets were used for ablation. Two ceramic targets with Al2O3 concentrations of 2 and 5 wt% were prepared and used. The targets were made from 99.99 % purity ZnO and Al2O3 powders which were mixed, homogenized, and pressed at 6 MPa. The as-prepared targets were calcified at 500 °C for 4 h and then sintered at 1150 °C for 12 h. The target-to-substrate distance was kept constant at 4 cm. (001) SiO2 was used for the substrates because of its low refractive index and high transparency in the visible and near infrared ranges. The lower refractive index of the substrate compared to ZnO allows us to obtain waveguide light propagation into the films and to ensure optical detection of gas molecules. All experiments were performed in oxygen atmosphere at pressure of 0.05 or 0.1 mbar. The films were grown at two different substrate temperatures: 150 and 300 °C. Our previous experiments have proven that such processing conditions are required for growing thin ZnO films that can be used as gas sensitive media [13].

The crystal structure of the films was analyzed by XRD measurements with Co Kα radiation in θ–2θ Bragg-Brentano geometry. The surface morphology of the films was studied by atomic force microscopy (AFM). The optical transmission spectra of the films were investigated by a CARY 5E spectrophotometer. The refractive index and the thickness of the as–deposited films were determined by m-line spectroscopy using a prism to couple the light of He–Ne laser.

3. Results and discussion

All deposited films (pure and Al doped) are textured along the (002) direction. The substrate temperature and the oxygen pressure maintained during deposition have stronger influence on the film crystallinity compared to the presence of the dopants. Our previous studies of the crystalline structure of pure ZnO films have shown that the increase of the substrate temperature enhances the diffraction peak intensity, which has mainly to do with mobility of the atoms in the films at different temperatures [13]. At the same time, the highest intensity peak along the (002) direction was obtained at oxygen pressure in the range of 0.05–0.1 mbar [13]. It is well known that the sensitivity of the sensor media strongly depends on the grain dimension of the sensing material. The grain size was calculated using the Scherrer’s equation and the estimated values are presented in table 1. As it is seen, the grain size is approximately the same for the samples prepared from a pure and from a 2 wt% Al2O3 doped ZnO target. The increase of the dopant concentration leads to a slight enlargement of the gain size. Table 1 presents the results obtained from the films deposited at 300 °C substrate temperature and 0.05 mbar.
O₂ pressure. The grain size increases with the temperature at each fixed dopant concentration. The O₂ pressure has a similar effect on the grains.

Table 1. Structural and morphological characteristics of the ZnO (undoped and Al₂O₃ doped) films deposited at 300 °C substrate temperature and 0.05 mbar oxygen pressure.

| Al₂O₃ dopant content in the target [wt%] | Out-of-plane grain size [nm] | In-plane grain size [nm] | RMS taken from 2×2 μm [nm] |
|-----------------------------------------|-----------------------------|-------------------------|---------------------------|
| 0 (pure)                                | 34                          | -                       | 5                         |
| 2                                       | 33                          | 125                     | 6-9                       |
| 5                                       | 40                          | 80                      | 23                        |

Figure 1. AFM images of ZnO films prepared at 300 °C substrate temperature and 0.05 mbar oxygen pressure from: (a) undoped, (b) 2 wt% Al₂O₃ doped, and (c) 5 wt% Al₂O₃ ZnO target.

The morphology of the sensing films is an important characteristic for optical gas detection. On the one hand, a porous surface with small grain size is recommended for better gas sensitivity [14]. On the other, a droplet free smooth surface is necessary to ensure optical detection. The AFM analyses show
that the use of doped targets leads to deposition of the thin films with droplets. The density and the size of the droplets increase with the dopant concentration into the targets. This result is probably due to the density of the sintered targets. 3D AFM images of the films prepared from different targets are presented in figure 1.

The RMS value of the roughness of the films deposited from a 2 wt% Al₂O₃ doped ZnO target is approximately the same as the one of the film deposited from pure ZnO target (see table 1). The increase of the dopant concentration increases the roughness of the films. The 2D AFM images taken from an area of 800×800 nm were used for estimation of the grain size on the film surface. The in-plane grain size of the films decreases as the dopant concentration is raised, as it is seen in table 1. This means that the increase of the dopant content into the targets leads to the production of ZnO films with more clearly expressed “column-like” growth structure (see table 1). Concerning the morphology characteristics, the ZnO target with the highest dopant concentration (5 wt% Al₂O₃) is not suitable for preparation of thin films for optical sensor application. Our previous investigation of the influence of the processing parameters on the morphology of the undoped ZnO films have shown that the increase of the substrate temperature leads to deposition of smoother films which is associated with the mobility of the atoms on the surface [13]. Moreover, the increase of the oxygen pressure at fixed temperature changes the film morphology as the porosity of the films rises with the O₂ pressure [13]. This tendency is preserved for the films prepared from doped targets.

As it was mentioned above, the optical properties of the sensing film are decisive when the working mechanism of the sensor is based on optical detection. All the films (pure and Al doped) are transparent in the visible (VIS) and near infrared (IR) ranges. The undoped ZnO films show 85-92 % optical transmission in the visible range [13,15]. It is worth pointing out that the substrate temperature applied during deposition has a positive effect on the film transparency. The optical transparency increases as the temperature is raised. As it was previously reported, this result is mainly connected to the better film crystallinity obtained by increasing the substrate temperature [13]. On the contrary, the optical transmission has a tendency to decrease with the increase of the O₂ pressure which is probably due to the higher roughness obtained when higher O₂ pressure is applied during deposition [13]. The optical transmission spectra of the ZnO films prepared from different targets are presented in figure 2.

As it is clearly seen, the transparency of the films decreases when the dopant content is raised. This is probably due to the increase of the surface roughness of the films, since the film crystallinity depends only slightly on the dopant concentration, as it was mentioned above. The result is in good agreement with previous investigations on the influence of the processing parameters on the optical properties of ZnO films [13,15].

![Figure 2. Transmission spectra of ZnO films produced at 300 °C substrate temperature and 0.05 mbar oxygen pressure from: (a) undoped, (b) 2 wt% Al₂O₃ doped, and (c) 5 wt% Al₂O₃ ZnO target.](image-url)
agreement with data reported previously [15]. The optical band gap ($E_g$) was calculated from the optical transmission spectra using the following relation:

$$E_g (eV) = \frac{1.24}{\lambda_c (\mu m)}$$

(1)

where $\lambda_c$ is the critical wavelength defined as the inflection point of the UV absorption edge. $\lambda_c$ was determined from the transmission curve’s second derivative [16]. The band gap energies of the Al doped ZnO films prepared at any temperature and O$_2$ pressure are larger than that of pure ZnO films. ZnO is naturally an n-type material and the Fermi level will fall in the conduction band when it is heavily doped. Since the states below are filled, the optical band gap should be increased to the higher energies [15]. This means that the absorption edge of the Al doped films will be shifted to the shorter wavelengths compared to that of pure ZnO films, as it is seen in figure 2. The optical band gaps of the Al doped films are estimated to range from 3.24 to 3.35 eV, while 3.20–3.22 eV are obtained for pure ZnO samples, which confirms the results previously reported [15].

As it was mentioned above, the working mechanism of optical sensors in thin-film configuration is based on detection of the shift in the position of a selected m-line [5-8]. For better sensitivity of the sensor element, thin contrast m-lines are necessary. Thin mode lines with good contrast were observed for most of the undoped ZnO films. The m-line spectra of the ZnO films produced from different targets are presented in figure 3.

As it is clearly seen, the increase of the dopants concentration leads to the deposition of films with thick and pale m-lines. No lines were observed from the sample with the highest dopant concentration. This result is a consequence of the rougher film surface obtained as the dopant concentration is raised, as it was discussed above.

The samples prepared from pure and 2 wt% Al$_2$O$_3$ doped ZnO targets were exposed to ammonia. For both samples a shift of the m-line position was observed. As it was expected, better ammonia sensitivity was obtained for the Al doped sample.

The films deposited from pure and 2 wt% Al$_2$O$_3$ doped ZnO targets at oxygen pressure of 0.05 mbar and 300 °C substrate temperature are good candidates for optical sensors.
4. Conclusion
Highly textured pure and Al doped ZnO films were prepared by PLD. The use of doped targets leads to the production of ZnO films with a clearly expressed “column-like” structure. The increase of the dopant concentration into the target increases the roughness of the as-deposited films. Moreover, the transparency of the films decreases with the raise of the dopant concentration. The dopants have also a negative effect on the m-line spectrum, which will decrease the accuracy of the optical sensors. The films deposited from pure and 2 wt% Al₂O₃ doped ZnO targets at oxygen pressure of 0.05 mbar and 300 °C substrate temperature are good candidates for optical sensors.

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