Microstructure and gas-sensing properties of sol–gel ZnO thin films

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Abstract

The paper presents the properties of zinc oxide thin films deposited on glass substrate via dip-coating technique. Zinc acetate dehydrate, ethanol and monoethanol amine were used as starting materials and N₂ gas was used as thermal annealing atmosphere for film crystallization. The effect of withdrawal speed on the crystalline structure, morphology, zinc and nitrogen chemical states, optical, electrical and gas-sensing properties of the thin films has been investigated using X-ray diffraction, atomic force microscopy, X-ray photoelectron spectroscopy, optical transmittance and photoreduction–ozone reoxidation data.

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1. Introduction

As an important semiconductor material, undoped and doped zinc oxide thin films have a wide range of applications such as solar cells, electrical, piezoelectric or luminescent devices and also as gas sensors and chemical sensors. As gas sensor material, ZnO can be used to detect reducing gases (CO and H₂) [1,2], O₂ [3], O₃ [4–6] or humidity [7]. Very recently, nanocrystalline ZnO gas sensors have attracted more interest due to their better properties of detecting pollutants, toxic gases, alcohols and food freshness, especially fish freshness [8], or as gas-sensing films integrated on one chip to make an “electronic nose” [9,10]. In₃O₅N₂ film with enhanced gas-sensitive properties has been reported [11]. These films have been prepared by various sputtering techniques [12], metalorganic chemical vapor deposition (MOCVD) [13], spray pyrolysis [14]. It is well known that the sensing mechanism of semiconducting oxide gas sensors is based on the surface reaction and a high surface–volume ratio. The grain size and the porosity of the sensing material are the most important factors for high sensitivity and short response time sensors.

This paper presents preliminary results on the crystalline structure, morphology, optical and gas-sensing properties of porous ZnO thin films prepared by sol–gel method. When dip-coating sol–gel technique is used, the withdrawal speed is the most important processing parameter affecting the porosity of the films. The results concerning the effect of withdrawal speed on the film morphology (pore size, grain size), crystalline structure, N-chemical states, optical and typical photoreduction–ozone reoxidation cycles of the films are presented.

2. Experimental

2.1. Films preparation

The sol was prepared by dissolution of zinc acetate dihydrate (99.5 %) in ethanol and monoethanol amine (MEA). The molar ratio of MEA to zinc acetate was 1.0 and the concentration of zinc acetate was 0.5 M. The thin films were deposited on glass (Corning 1737) substrates by dip-coating technique with different withdrawal speeds in the range 10–20 cm/min. After each layer deposition, the gel film was stabilized by pre-heating in air for 10 min at 400 °C. The procedure was repeated 4 times. The stabilized films were then crystallized by post-heating for 1 h in nitrogen at 500 °C. Final thickness of about 140, 160 and 190 nm was obtained for the crystallized films deposited at 10, 15 and 20 cm/min, respectively.

2.2. Film characterization

The thickness of the thin films was measured using a Sloan Dektak 3D surface profilometer. The X-ray diffraction (XRD)
patterns of the samples were recorded at room temperature using a Rigaku diffractometer (model RAD IIA), with CuKα radiation. The morphology on the surface and section of the films was analyzed using the atomic force microscopy (AFM). Tapping mode AFM experiments were performed in a Nanoscope IIIa Multimode AFM microscope (Digital Instruments, Veeco). Commercial etched silicon tips with typical resonance frequency of ca. 300 Hz (RTESP, Veeco) have been used as AFM probes. The chemical states (chemical environments) of the atomic species presented in the films have been investigated by X-ray photoelectron spectroscopy (XPS), using a Physical Electronics 5600 Photoemission System and ultrahigh vacuum. The electrical resistivity of the films was measured in the dark, using a Keithley 617 Model Programmable Electrometer. The optical transmittance was measured using a UV–VIS–NIR double beam spectrophotometer (Shimadzu, UV-3100 PC) in the wavelength range 200 to 2500 nm.

2.3. Sensing test

The gas (ozone) sensing properties were investigated by electrical measurements at room temperature, which were carried out in a special chamber presented elsewhere [4]. The conductivity value of ZnO film decreases when it is exposed to an oxidative (ozone) atmosphere. Because the films are resistive, first, its conductivity was increased by photoreduction, when the films are directly irradiated in vacuum by the UV light of a mercury pencil lamp. After that, the chamber was backfilled with oxygen at a pressure of 600 Torr and a UV lamp was used to produce ozone (the films are shielded from the lamp). The films were maintained for 40 min in this ozone atmosphere, when the reoxidation of zinc oxide crystallites results in a decrease of film conductivity. An electric field of 50 V/cm was applied to the film sample and the electrical current was measured.

3. Results and discussions

Figs. 1 and 2 show, respectively, the XRD patterns and AFM images of the films post-heat treated for 1 h at 500 °C in nitrogen. The XRD patterns of the film show a dominating (002) peak, indicating a high preferential c-axis orientated wurtzite type crystalline structure with grains uniformly perpendicular to the substrate surface. AFM images (Fig. 2) confirm this orientation and show porous, crack free film morphology with average grain size and pore size strongly depending on the withdrawal speed. The grain size and the pore size increase when the withdrawal speed increases. These films, deposited with high withdrawal speed at room temperature (RT) and room humidity (RH), have no very homogeneous microstructure. One can notice that the more the withdrawal speed rises, the more the tendency of grain agglomeration increases. The surface roughness mean square (rms) of the films estimated from AFM measurements rises from 15 nm to 30 nm, when the withdrawal speed increases from 10 to
20 cm/min, respectively. These roughness values derived from AFM measurements, however, are found to be large.

XPS survey spectra of the as-crystallized (non-cleaned) films showed the presence of zinc, oxygen, carbon and nitrogen. XPS spectra of Zn 2p\textsubscript{3/2} region showed a peak of about 1021.5 eV stemming from ZnO phase, for all the films. XPS data of the non-cleaned surface films indicate nitrogen surface composition in the range 0.7–1% for samples deposited at 10–20 cm/min, respectively. The N 1s XPS data (Fig. 3) showed two types of nitrogen species in these films, corresponding to ∼400 eV (cyclic amine) and ∼399 eV (linear amine). According to the literature data [13], these peaks correspond to C–N species, that have binding energies of 400 eV (cyclic amine) and 399–398 eV (linear amine). In these films, C–N species comes from monoethanol amine (MEA) used as sol stabilizer. The intensity of both peaks increases when the withdrawal speed increases (Fig. 3). In the same time, the ratio of the peaks intensity changes, while in the less porous film deposited at 10 cm/min the first peak (cyclic amine) is the most important, in the more porous film deposited at 20 cm/min the second peak (linear amine) becomes the most important. One can notice also a shift of the peaks at higher binding energy when the withdrawal speed decreases, and subsequently the porosity decreases. The chemical interactions of C–N species with the more electropositive zinc ions may account for the shift of the second peak to higher binding energy values in the less porous film deposited at lower withdrawal speed.

Electrical resistivity values between $6 \times 10^6$ and $7 \times 10^7 \, \Omega \cdot \text{cm}$ have been measured in air for ZnO thin films annealed in N\textsubscript{2}. These lower resistivity values, comparing with those ($6 \times 10^8$–$8 \times 10^9 \, \Omega \cdot \text{cm}$) of similar ZnO thin films deposited in the same conditions but annealed in air, are generated by a lower degree of zinc oxide crystallization and higher crystalline structure defects concentration, which contribute to the decrease in

![Fig. 3. XPS spectra of N 1s region of ZnO thin films deposited with different withdrawal speeds: 10 cm/min (a), 15 cm/min (b) and 20 cm/min (c).](image1)

![Fig. 4. Typical photoreduction–oxidation cycles (room temperature) of ZnO thin films deposited with different withdrawal speeds: 10 cm/min (a), 15 cm/min (b) and 20 cm/min (c).](image2)
resistivity of the films. Lowest resistivity values have been measured for higher grain size films deposited at 20 cm/min.

Fig. 4 shows typical photoreduction–oxidation cycles of the films. The photoreduction–ozone reoxidation behavior is reversible through many cyclic treatments. The shape of the cycles, showing the gas-sensing response, strongly depends on the porosity and the grain size of the polycrystalline films. From Fig. 4, one can notice that lower grain size films deposited at 10 cm/min showed significantly higher sensing response, than the films deposited at 20 cm/min. The gas sensitivity increases when the grain size decreases and when the number of smaller mesopores (10–20 nm) increases.

The optical transmittance of the thin films within the visible and the near infrared region was higher than 70% (Fig. 5). Surface morphology has an important influence on the optical properties of the film. Increasing porosity at higher withdrawal speed deposition, led to different variation of optical transmittance in the visible range: a decrease in 400–600 nm range and an increase in the 600–800 nm range (Fig. 5). The decrease in transmittance may be due to increasing optical scattering caused by increasing grain boundary density in the more porous films deposited with higher withdrawal speed.

4. Conclusions

Transparent porous ZnO thin films on glass substrate were prepared by dipping sol–gel method, using zinc acetate dihydrate and monoethanolamine for sol preparation, RT and RH conditions for films deposition and N2 gas atmosphere for thermal annealing. The withdrawal speed significantly affects the crystalline structure, morphology, optical and gas-sensing properties of the porous thin films.

ZnO porous thin films are polycrystalline with high preferred c-axis orientated hexagonal structure. The grain size and the pore size increase when the withdrawal speed increases. N 1s XPS spectra show two nitrogen states, stemming from C–N amine species, that have binding energies of 400 eV (cyclic amine) and 398–399 eV (linear amine). The withdrawal speed affects the amount and the ratio of these N-chemical states in the crystallized films. The chemical interactions of the second C–N specie with the zinc ions (more electropositive) may account for the shift of the second peak (linear amine) to lower binding energy values, when the withdrawal speed increases. All the films show good optical transmittance (between 70 and 90%) within the VIS and NIR wavelength region.

The investigated films reveal reversible room temperature change in electrical resistance during UV irradiation followed by reoxidation in ozone atmosphere. The shape of the photoreduction–reoxidation cycles, and subsequently the sensing response strongly depends on the grain size and on the porosity of the polycrystalline films. The gas sensitivity increases when the grain size and pore size decrease but the number of smaller pores (10–20 nm) increases. An optimization of the processing parameters for improving the morphology and sensing properties of the porous films will be presented in a future paper.

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References