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Annealing effects on the structural, electrical and H_2 sensing properties of transparent ZnO thin films, grown by pulsed laser deposition

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ABSTRACT

Transparent zinc oxide thin films were grown by reactive pulsed laser deposition on glass substrates. The substrates were kept at 200 °C constant temperature. Post-deposition heat treatment, applied to further promote crystallization and overcome any oxygen deficiency, yielded transparent thin films. Structural investigations carried out by atomic force microscopy (AFM) and X-ray diffraction (XRD), have shown a strong influence of deposition technique parameters and post-annealing on the crystallinity of the zinc oxide films. The gas sensing characteristics of these films were investigated towards different hydrogen concentrations (5000–30,000 ppm) at a selected operating temperature within the 150–230 °C range.

1. Introduction

Molecular hydrogen (H_2) is a combustible gas that is produced in large quantities by many industries and has a broad range of applications [1–4]. There is an emerging scientific interest to develop low-cost, lightweight, reliable hydrogen sensors for safety reasons, wherever hydrogen is produced, stored or used. Prior work has proven that ZnO thin films can be used as sensing elements for the detection of hydrogen by measuring physical properties of those films and monitoring their characteristics [5,6].

Since G. Heiland [7] who first reported in 1959 on the gas sensitive behaviour of zinc oxide (ZnO), it has been used as a sensing element, mainly due to its chemical sensitivity to volatile and other toxic gases, its high stability, suitability to doping, non-toxicity and low fabrication cost. Thus it can be integrated on cheaper and flexible substrates [8,9]. ZnO is an n-type semiconductor of wurtzite structure with a direct energy wide-bandgap of about 3.3 eV [10,11] at room temperature. Its gas sensing characteristics have been investigated in the form of bulk material, single crystal, thick film, and thin film. For example, Bott et al. [12] investigated the electrical conductivity changes of ZnO single crystals in H_2, in air mixture at 300–500 °C using a constant voltage source. The ZnO single crystals were sensitive to H_2 with maximum sensitivity at the temperature of around 400 °C. Mitra et al. [13] investigated the gas responses of chemically deposited thick films and Pd-sensitized ZnO films. A high sensitivity (approximately 99%) was observed for 3 vol.% H_2 at the temperature of 150 °C. Palladium sensitized ZnO thin films [14] exhibited a significant response for 2 vol.% H_2 at a minimum operating temperature of 150 °C. The sensitivity was found to be more than 99.8% with recovery time of 30 min. Kobrinsky et al. [15] employed n- and p-type ZnO films as hydrogen sensors. The gas sensing measurements were performed against 5 vol.% H_2 while the working temperature ranged from 100 to 300 °C. From the literature, it is obvious that the gas sensing characteristics of ZnO films can be improved by controlling the electronic and structural properties of the films. These properties of the films can be adjusted by the choice of the growth parameters, such as the pressure of the reactive gas (oxygen), the substrate and temperature, the dopants (type and concentration) used, and post-annealing conditions.

In the present work, good quality ZnO films were deposited on cheap microscope glass slides by reactive pulsed laser deposition (RPLD) and the influence of reactive oxygen pressure and post-deposition heat treatment on the films' surface morphology, crystalline phase formation, and electrical properties has been investigated. In addition, the ZnO films were used for hydrogen detection at different temperatures by recording the change in resistivity of the film in the presence of gas in air.

2. Experimental details

2.1. Films' preparation

The reactive pulsed laser depositions of ZnO films were performed inside a stainless-steel vacuum chamber which was evacuated down to a residual pressure of 6×10^{-4} Pa prior to the laser irradiation of the target. For the growth of ZnO thin films, a metallic Zn target (99,998% purity) was ablated by the focused beam of a Quantel YG851 laser ($\lambda = 355$ nm (THG),

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τ_{FWHM} ~ 10 ns) source at 10 Hz repetition rate. The laser fluence incident on the target surface was set at ~2 J/cm^2. The microscope glass slides were mounted on a stainless-steel oven, parallel to the target at a distance of 50 mm downstream, while the target was placed on a vacuum-compatible and computer-controlled XY table, to avoid fast drilling. An irradiation area of 10 × 10 mm^2 was uniformly scanned. The depositions were carried out at a constant substrate temperature of 200 °C for 146 min while the oxygen pressure ranged from 20 to 40 Pa. To study the annealing influence on the electrical and therefore sensing properties of the ZnO films, twin samples were prepared under identical experimental conditions. The preparation of one of the twin samples included a post-deposition annealing step, by heating it, for 70 min in air at 300 °C.

2.2. Films' characterization

The influence of the deposition parameters on the electrical and sensing properties of the grown ZnO films was evaluated by structural measurements [X-ray diffraction (XRD)], surface structure measurements [atomic force microscope (AFM)], electrical measurements (resistivity, Hall effect) and by dynamic response tests in a hydrogen/air gas mixture. XRD-scans of the grown ZnO films were recorded for values between 20° and 80° using the Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) for excitation. The surface morphology of the deposited thin films was investigated by atomic force microscopy (AFM) in contact mode with a Veeco CP-II instrument. Resistivity and Hall coefficient measurements, in a 0.5 T magnetic field, were performed, using the four-point van der Pauw technique in order to obtain the conductivity type of ZnO films, the carrier concentration and the mobility μ.

Optical transmittance measurements were carried out with a Perkin Elmer Lambda 19 spectrophotometer in the 300–1200 nm wavelength range. The thickness of the films was estimated from the transmittance spectra and ranged between 100 and 135 nm.

Dynamic sensor response measurements were performed against different hydrogen concentrations in air flow at operating temperatures between 150 °C and 230 °C in a stainless-steel tube. The gas mixture was introduced into the tube and as a consequence the resistance of the samples was changed. The relative response (sensitivity) to the gas was determined by the formula:

$$S = \frac{R_g - R_0}{R_0} \cdot 100\%. \tag{1}$$

where R_0 is the film resistance in air and R_g is the film resistance in gas mixture. The experimental set-up consisted of two calibrated flow-meters that controlled the gas flow, a sample holder with a copper heater resistance, capable of reaching temperatures up to 400 °C and a platinum resistor for the determination of temperature. The sample holder temperature was controlled by an ITC-502 (Oxford Instruments) controller with an accuracy of ± 1 °C while the film resistance versus time was recorded by a Keithley electrometer (model 617) for various operating temperatures.

3. Results and discussion

3.1. Morphological and structural characterization of ZnO thin films

XRD diffractograms of as-deposited ZnO thin films and annealed ones at 300 °C for 70 min are shown in Fig. 1. The polycrystalline hexagonal wurtzite structure was revealed, and a dominant peak positioned at 34.4° corresponding to the (002) direction was observed. With the annealing process the crystallinity and c-axis orientation of ZnO films exhibited an enhancement which was indicated by the increase of (002) peak strength and the decrease of full-width at half-maximum (FWHM) value of the peak for the ZnO films post-annealed up to 300 °C.

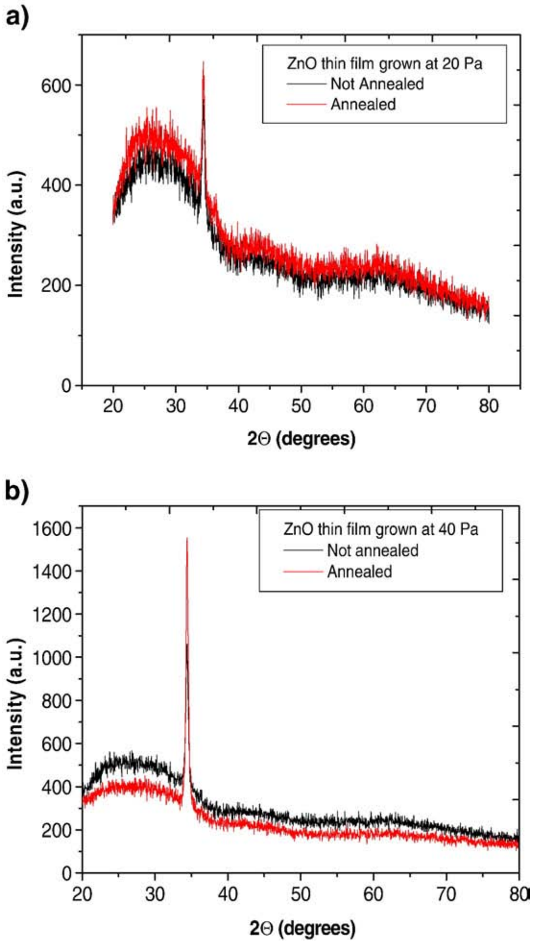

Fig. 1. XRD diffractograms of as-deposited and annealed ZnO thin films deposited at a) 20 Pa and b) 40 Pa oxygen pressure.

Atomic force microscopy (AFM) was used to investigate the surface morphology and surface roughness of the films over a cross-sectional area of 4 μm^2. Fig. 2 shows the AFM surface images of the as-grown sample at 20 Pa oxygen pressure (a) and of the sample post-annealed at 300 °C in air for 70 min (b). The root-mean square average surface roughness of the as-grown and the annealed ZnO samples, as determined from the AFM measurements is shown in Table 1.

The post-annealing treatment of the films had an effect on the surface roughness. It was also observed from surface profile variations that the local height was increased with post-annealing treatment (Fig. 2c and d). We noted that with post-annealing treatment, the surface morphology of the annealed sample was smoother than that of the as-deposited. This is consistent with the XRD measurements because high temperature could enhance 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 [16,17].

Three-dimensional AFM images of the ZnO thin films deposited at two different oxygen pressures and of the annealed films at 300 °C in air ambient are shown in Fig. 3.

3.2. Optical properties

Fig. 4(a) and (b) shows the optical transmittance spectra observed at room temperature of the ZnO films grown at 20 Pa and 40 Pa respectively. The as-deposited ZnO films were transparent to visible light and the average optical transmittance value of films was about 82% (Fig. 4a). Furthermore, the absorption edge of the ZnO film grown at 40 Pa oxygen pressure, appeared to shift towards the longer wavelength side.