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Thickness dependence of structural, electrical and optical behaviour of undoped ZnO thin films

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ABSTRACT

Undoped ZnO thin films of different thicknesses were prepared by r.f. sputtering in order to study the thickness effect upon their structural, morphological, electrical and optical properties. The results suggest that the film thickness seems to have no clear effect upon the orientation of the grains growth. Indeed, the analysis with X-ray diffraction show that the grains were always oriented according to the *c*(0 0 2)-axis perpendicular to substrate surface whatever the thickness is. However, the grain size was influenced enough by this parameter. An increase in the grain size versus the thickness was noted. For the electrical properties, measurements revealed behaviour very dependent upon thickness. The resistivity decreased from 25 to $1.5\times10^{-3}\,\Omega\,cm$ and the mobility increased from 2 to $37\,cm^2\,V^{-1}\,s^{-1}$ when the thickness increased from 70 to 1800 nm while the carrier concentration seems to be less affected by the film thickness and varied slightly remaining around $10^{20}\,cm^{-3}$. Nevertheless, a tendency to a decrease was noticed. This behaviour in electrical properties was explained by the crystallinity and the grain size evolution. The optical measurements showed that all the samples have a strong transmission higher than 80% in the visible range. A slight shift of the absorption edge towards the large wavelengths was observed as the thickness increased. This result shows that the band gap is slightly decreases from 3.37 to 3.32 eV with the film thickness vary from 0.32 to 0.88 μm.

1. Introduction

Metallic oxides like In_2O_3, SnO_2 and ZnO are largely used as transparent electrodes in solar cells. Their low electrical resistivity (10^{-5}–$10^{-3}\,\Omega\,cm$) and high transmittance (80–90%) in the visible range give them a particular importance in the field of photovoltaic conversion and optoelectronic devices. However, ZnO thin films can also have a high resistivity ($\sim10^{12}\,\Omega\,cm$) and a texture highly oriented according *c*(0 0 2)-axis. These two properties make ZnO a very interesting material in piezoelectricity. Currently, intense researches are focused on ZnO for several reasons: (i) the abundance of its components in nature (ii) its non-toxicity (iii) and the wide range of its electrical resistivity which can extend from 10^{-4} to $10^{12}\,\Omega\,cm$ according to the deposition conditions. ZnO is an n-type semiconductor of wide gap equal to 3.2 eV. It crystallizes in the wurtzite hexagonal structure. Some recent works have reported the preparation of p-type ZnO films obtained by suitable doping [1–3]. Its electrical conductivity comes, partly, from stoichiometric shift, mainly due to oxygen vacancies and/or zinc interstitials. Doping by trivalent or monovalent impurities, vacuum annealing in a reducing or oxidizing atmosphere, conditions and techniques of preparation are numerous means which make possible the control of its conductivity. In the case of polycrystalline films the microstructure plays a crucial role, in addition to the stoichiometry, in the conductivity behaviour.

The microstructure controls conductivity through the grain boundaries whose presence and density are closely related to the crystallites size and orientation. These two parameters could be affected by film thickness. Nowadays, most of the physical and chemical techniques of preparation were used to deposit ZnO thin films. We quote the various CVD techniques [4–6], spray [7–9], sputtering with its different forms [10–12], evaporation [13], laser ablation [14] and sol–gel [15]. Moreover, ZnO was the subject of several works [16] that studied the impact of deposition parameters and the needs of technological applications. Until now, ZnO is always under intensive research, as it can be seen in the literature, with the purpose to improve its electro-optical properties. Ebothe et al. [19] show that ZnO films have substantial photoinduced nonlinear optical effect which is very sensitive to the sample morphology. Recently, Ozga et al. [20] studied the photoinduced second harmonic generation (SHG) in Au nanoparticle-deposited ZnO nanocrystallite (NC) films was explored by applying bicolour coherent treatment of a Nd–YAG laser with

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wavelength 1.06 μm and its SHG. They have been established that coexistence of the ZnO and Au nanoparticles gives a substantially larger SHG output with respect to pure ZnO NC deposited on the glass substrate. It was established that the value of the second-order susceptibility is about 23 pm V^{-1}.

Due to its crucial role in controlling many properties, thickness dependence of structural, electrical and optical behaviour of undoped ZnO thin films was studied and reported in this paper. The main goal of this work is to study an influence of the nano-sized effects on the transport and optical properties of the investigated films.

2. Experimental details

The samples were prepared by r.f. sputtering. The preparation conditions are summarized in Table 1. Other details on the experimental procedure used to elaborate our samples were reported in a previous study [17].

The examination of the morphology of the deposited ZnO layer was undertaken using scanning electron microscope (SEM). This indicates, for the c(0 0 2)-axis orientation, the generation of uniform layer with a regular columnar growth; the columns being normal to the substrate. The surfaces, of such layers are relatively smooth. These observations confirmed the results obtained by X-ray diffraction (XRD). But the granular structure, which are visible on the surfaces, have not the same size as the ZnO crystallites, whose sizes are calculated from the following Sherrer formula: $D = (0.941)/[D(2q)\cos q]$.

The aim of the present work being the study of thickness effect, we varied only the deposition time in order to obtain different thicknesses. The studied thicknesses were as follows: 70, 170, 320, 440, 880 and 1800 nm. The layer thickness was measured by SEM observation of a cross-section. At the same time we observed the surface morphology of the coating. The crystallographic study was performed using XRD. The electrical behaviour of the layers was studied through the measurement of electrical resistivity (ρ) and Hall effect at room temperature. ρ was measured by the four square probes method and Hall effect by the potentiometric technique. The optical transmittance of the samples, measured using a double beam spectrophotometer, was carried out in the wavelength range of 300–900 nm.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows some typical XRD patterns of the investigated samples. We can deduce that the samples are of polycrystalline structure.

The investigated samples exhibit the same preferential texture according to c(0 0 2)-axis of ZnO hexagonal wurtzite structure perpendicular to the substrate surface. The effect of film thickness on the relative intensity of (0 0 2) peak is, therefore, obvious from these XRD spectra. Indeed, thicker films exhibit a (0 0 2) peak of a strong intensity and thin width, while in thinner ones, this peak is of lower intensity and thicker width. It is completely disappear in the films of the thickness smaller than ~70 nm.

This can be understood easily; in the samples which are sufficiently thick there is much more matter which can diffract X-rays and the peak is more intense. Whereas the less thickness samples diffract less and the noise in the recorded spectra is so important that it hides any form of growth orientation. This means that the crystallinity is improved when the film thickness increases. On the other hand, the existence of only one texture in all cases, namely the one according c(0 0 2)-axis, shows that the growth orientation of films is independent of their thickness; at least in the thickness range studied ~0.1–2.0 μm.

The average crystallite size has been estimated from the full width at half maximum (FWHM) of the (0 0 2) peak. These values are illustrated in Fig. 2.

This figure clearly shows that the thickness effect upon the crystallite size appears only in the thinnest films, the thickness of which is lower than approximately 600–800 nm. In this range the crystallinity is closely related to the film thickness. But a tendency to the saturation and independence versus film thickness was observed beyond that range.

Typical SEM micrographs are shown in Fig. 3. One can see the surface morphology (Fig. 3a) and the cross-section (Fig. 3b), of ZnO thin films.

This morphology contains grains whose average size increases as the film thickness increases. However, these grains have a very large average size (from ~200 to 600 nm in the same film) compared to that obtained by XRD analysis (from 10 to 15 nm depending on the film considered) in the present study. This observation suggests that the grains seen on the films surface are rather clusters of crystallites. Regular columns that are normal to the substrate surface can be seen in Fig. 3. This kind of texture and growth was found in all samples under investigation and confirms the analysis made using the XRD. It is more marked as the layer becomes thicker.

Due to specific features of the ZnO films with sizes below 300 nm principal roles begin to play nano-confined effect [21] which is very critical to the size dependence of the films and also to the substrate. This will cause substantial photoinduced effect. Additional role may give also specific electron–phonon interaction of the film.

Table 1
Deposition conditions of ZnO films

r.f. Power	200 W
Sputtering gas	Argon
Working pressure	25 mT
Substrate position versus target	Perpendicular
Substrate temperature	Ambient (140–160 °C)
Target–substrate distance	5 cm

3.2. Electrical properties

The electrical behaviour of ZnO samples with respect to their thickness was examined through measurements of the electrical resistivity ρ and Hall effect (carrier mobility μ and concentration N). The results are illustrated in Fig. 4.

The variations of ρ versus film thickness are shown in Fig. 4a. Examining this figure, one can notice that there are two ranges of thickness in which the resistivity exhibits two different behaviours. The first range (range I), which belongs to the low thicknesses, extends up to ~300 nm. In this area, a clear and unequivocal decrease of ρ was observed. Indeed, in a small interval of a few tens of nm, the resistivity falls by three orders of magnitude from 1 to $10^{-3}\,\Omega$ cm. In the second range (range II), which belongs to the thicknesses higher than ~300 nm, ρ becomes independent of thickness and remains constant and equal to $\sim 10^{-3}\,\Omega$ cm whatever the thickness. The resistivity is closely related to the carrier mobility and concentration by the following relation:

$$\rho = 1/Ne\mu$$

where e is the electron charge.

Thus it is useful, in this discussion on the variations of ρ, to examine the behaviour of μ and N. It can be seen from