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ScienceDirect
Applied Surface Science 254 (2007) 570–573
applied surface science
www.elsevier.com/locate/apsusc

Preparation and characterization of n-type conductive (Al, Co) co-doped ZnO thin films deposited by sputtering from aerogel nanopowders

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Received 6 June 2007; received in revised form 18 June 2007; accepted 19 June 2007
Available online 24 June 2007

Abstract

Highly transparent, n-type conducting ZnO thin films were obtained by low temperature magnetron sputtering of (Co, Al) co-doped ZnO nanocrystalline aerogels. The nanoparticles of ~30 nm size were synthesized by a sol–gel method using supercritical drying in ethyl alcohol. The structural, optical and electrical properties of the films were investigated. The ZnO films were polycrystalline textured, preferentially oriented with the (0 0 2) crystallographic direction normal to the film plane. The films show within the visible wavelength region an optical transmittance of more than 90% and a low electrical resistivity of 3.5×10^{-4} Ω cm at room temperature.

Keywords: Sputtering; Sol–gel method; Zinc oxide; Nanostructures; Transparent conductive oxide (TCO)

1. Introduction

Diluted magnetic semiconductors have initiated enormous scientific interest in the last few decades because of their potential applications in ferromagnetism [1–5], UV light emitting devices [6,7], solar cells [8–11], transparent electrodes [12] and others [13,14]. Aluminium-doped zinc oxide, ZnO:Al, has emerged as one of the most used transparent conducting film. Additional co-doping with Co seems very promising as it adds functionality, room temperature ferromagnetism, to these films [15]. In recent works, it has been shown that the presence of free charge carriers induced, for example, by interstitial zinc atoms, is a necessary condition for the appearance of ferromagnetism in ZnO:Co; as a mechanism exchange interaction between delocalized electrons and the localized d-spins of the Co ions have been proposed [16]. Based on first-principle calculations, Sluiter et al. [1] showed that both electron doping with zinc interstitials and hole doping with zinc vacancies (V_{Zn}) can make ZnO:Co strongly ferromagnetic. This should also explain why preparation methods involving high temperatures, where V_{Zn} are generally annealed and V_O are generated, fail to produce ferromagnetism.

In this work we report a synthesis protocol allowing the co-doping with both aluminium and cobalt and a thin film deposition technique; it is based on at room temperature radio frequency (rf) magnetron sputtering deposition of aerogel target materials. The influence of the Al doping level on the structural, optical and electrical properties, were equally investigated.

2. Experiment

2.1. Sample preparation

Co-doped ZnO:(Co, Al) nanopowders were first prepared by a sol–gel method using 16 g of zinc nitrate hexahydrate as a precursor in a 112 ml of methanol. After 10 min magnetic stirring at room temperature, 1.477 g of cobalt (II) acetylacetonate (Co/Zn correspond to 10 at%) and an adequate quantity of aluminium nitrate-9-hydrate (Al/Zn correspond to 1.0, 1.5, 2.0, 2.5 and 3 at%) were added. After 15 min magnetic stirring,

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doi:10.1016/j.apsusc.2007.06.028

the solution was placed in an autoclave and dried under supercritical conditions of ethyl alcohol. Then, thin films (thickness ~0.3 μm) were deposited on glass substrates by rf-magnetron sputtering. The r.f. generator operated at 13.56 MHz. The sputtering chamber was evacuated to a base pressure of 6×10^{-5} Pa before introducing the sputtering argon gas with 99.9999% purity without oxygen. The 5 cm in diameter sputtering targets were prepared from the aerogel powders, which had not been pressed nor sintered. 1 mm thick soda lime glass substrates, were ultrasonically cleaned in HCl, rinsed in deionized water, then subsquently in ethanol and rinsed again. During the sputtering process, the substrate temperature was set to room temperature, the r.f. power was maintained at 25 W and the target-to-substrate distance was 50 mm.

2.2. Characterization techniques

The X-ray diffraction (XRD) measurements were preformed with a Bruker D8 Advance spectrometer operating at 40 kV, 30 mA, using Co Kα radiation (λ = 1.789010 Å). The diffracted X-rays were collected by scanning between $2\theta = 20$ and 70° in 0.02° steps. The as-prepared nanopowders were also characterized by transmission electron microscopy (TEM). To examine the morphology and the thickness of the films, atomic force microscopy (AFM) measurements in the tapping mode and scanning electron microscopy (SEM) were made. The optical transmittance of the films in the 200–3000 nm range was measured with a UV–Vis–NIR scanning spectrophotometer (UV-3101PC; Shimadzu). For Hall effect and resistivity measurements, four probe indium contacts were used.

3. Results and discussion

Fig. 1 shows the XRD spectra of the as-prepared nanoparticles. Three pronounced diffraction peaks were observed at $2\theta = 37.07°$, 40.20° and 42.40°, respectively, and attributed to (1 0 0), (0 0 2) and (1 0 1) planes of ZnO [17]. This result shows that the nanocrystals have the ZnO hexagonal

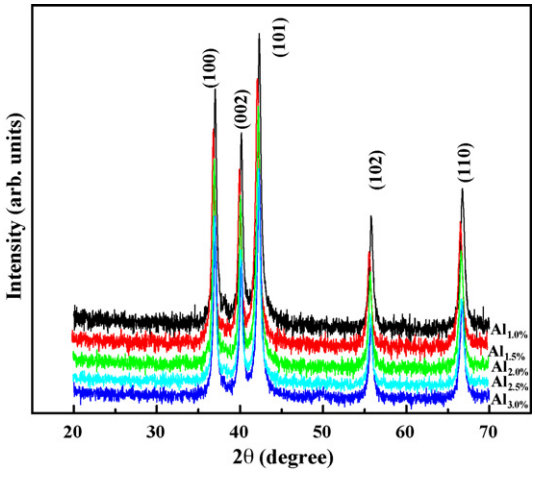

Fig. 1. X-ray diffraction of (Co, Al) co-doped ZnO aerogel nanoparticles.

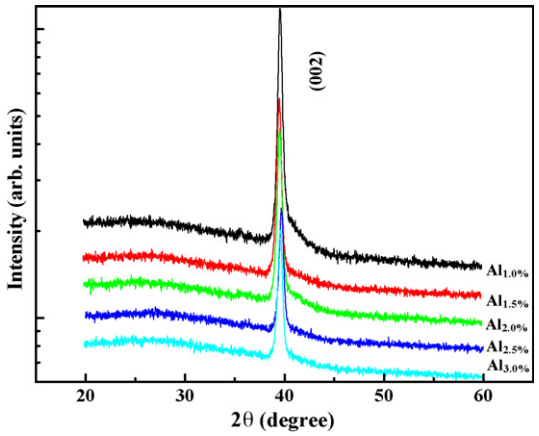

Fig. 2. X-ray diffraction of (Co, Al) co-doped ZnO thin films.

wurtzite structure. The diffraction lines are broad as compared to bulk crystals; the broadening was found to further depend on the Miller indices of the corresponding sets of crystal planes. For our nanoparticles, the (0 0 2) diffraction line was narrower than the (1 0 1) line and the latter one was narrower than the (1 0 0) line. This result indicates an asymmetry in the crystallite shape. Assuming that crystallites were in the form of cylinder (prism), having the height (direction of the crystal *c*-axis) bigger than the basal diameter (crystal axes *a* and *b*) an average grain size was calculated with Scherrer's equation [18]. After a correction for the instrumental broadening, an average value of the basal diameter of the cylinder-shape crystallites was found to be 15–20 nm, whereas the height of the crystallites was 22–30 nm. The sputtered thin films were polycrystalline, preferentially oriented in the (0 0 2) crystallographic direction (Fig. 2). The preferential (0 0 2) orientation is a result of a self-texturing which can be explained in terms of surface energy minimization. Indeed, it has been established that the preferred orientation is a result of self-ordering caused by the minimization of the crystal surface force energy [19]. On the other hand, Fujimura et al. [20] suggested that the surface energy density of the (0 0 2) planes is the lowest in the ZnO crystal system. The XRD results show also that the film properties are strongly dependent on the Al concentration. The 1 at% Al-doped ZnO thin films show the highest diffraction peak intensity. This peak intensity decreases when the Al concentration is increased. This means that the crystalline quality degrades with the increase of the Al concentration. Such behaviour has been reported before by Xu et al. [21] and was interpreted as being due to stresses arising from the difference in the Zn and the Al ion size, and the segregation of dopants in grain boundaries for high doping concentrations.

The TEM measurements (Fig. 3) show that very small ZnO particles are present in the as-prepared aerogel powder. The size of the ZnO particles varies between 20 and 30 nm. Taking into account the results of crystallite size measurements by XRD, it can be concluded that the crystallite size is approximately equal to the particle size in the ZnO powder.

Fig. 4 shows cross-sectional SEM (a) and AFM images (b) of (Co, Al) co-doped ZnO film obtained from aerogel nanopowder target with Al dopant concentrations of 1.0 at%,