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Sol-gel synthesis and nanostructured semiconductor analysis of undoped and Cd-doped ZnO thin films

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ABSTRACT

The semiconductor thin films of undoped and cadmium (Cd) doped zinc oxide (ZnO) via different concentrations (Cd: 2, 5 and 10 wt.%) were prepared by sol-gel route technique using a dip-coating method onto glass and silicon substrates. The Zinc acetate dehydrate (ZnAc), the Cadmium acetate dehydrate (CdAc), the 2-Methoxyethanol and the Ethanolamine were used as a starting material, doping, solvent and stabilizer, respectively. All films were annealed for 120 min at 500 °C. The samples were characterized by different analysis techniques to understand their structural, morphological and optical properties and its components such as the thin films surface are a nanometric crystallite size with a ganglia-like structure as observed by Environmental Scanning Electron Microscopy. The films were characterized by X-ray diffraction, it was crystallized in a hexagonal crystal structure with a highly c-axis preferred (002) orientation, and the crystallites size decrease from 30 to 23 nm with the increasing of cadmium doping. The Rutherford Backscattering Spectrometry and the Auger Electron Spectroscopy spectra given an idea in the thickness of the film by simulation and relation to the etching time respectively, where did the two agree that the film of ZnO doped 10 wt.% Cd is the thickest. All films exhibit an optical transmittance above 75 to 85% nm and a sharp absorption onset about 375 nm corresponding to the fundamental absorption edge 3.08 to 3.21 eV. The room-temperature luminescence emission spectra of these films were excited under the same conditions with 250 nm Xenon lamp excitation, showed an ultraviolet and visible emissions.

1. Introduction

Over the last decade, zinc oxide (ZnO) has been the subject of intense research. It is a semiconductor oxide that has very interesting properties. The use of zinc oxide as a semiconductor material allows applications ranging from electronics, photovoltaic cells, optoelectronic components, Piezotronic and piezophototronic, gas sensors, photoprotective as well as optical devices … etc [1–5]. This material has a large band gap (3.37 eV) of the family of transparent conductive oxides (TCO) type II−VI with a natural conductivity of type n, a high exciton bond energy at room temperature (60 meV) which is much higher than other semiconductor materials. In addition, the zinc oxide is a nontoxic material [6–9]. It has excellent chemical and thermal stability. Therefore, the form of the nanostructures of ZnO with different morphologies and sizes is of great importance both for basic research and for the development of new devices on an industrial scale [10,11].

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Doping is a process where impurities are added to the semiconductor structure to improve its properties. The band gap of the semiconductor can be modified by the doping and the excitation of the electrons from the valence band to the conduction band can be easier due to this induction.

It has been found that the Cd-doping ZnO conferred stability and moreover, Cd doped ZnO films are useful humidity sensors [9]. The formation of $Zn_{1-x}Cd_xO$ alloys of ZnO and Cd (CdO: a semiconductor material of type II−VI belongs to the cubic system, toxic and has a band gap of 2.3 eV [9]) can provoke the ZnO band gap. Proper incorporation of Cd allows tuning the band gap for various potential applications [12]. Otherwise, the lattice shift between ZnO and a $Zn_{1-x}Cd_xO$ alloy with a lower Cd content is low and this feature allows the preparation of $Zn_{1-x}Cd_xO$ / ZnO heterojunctions [13–16].

The objective of this work is to develop and characterize the thin films of undoped and cadmium-doped ZnO semiconductor (Cd: 2, 5 and 10 wt.%) in order to ameliorate the structural and optical properties. The thin films of zinc oxide were prepared by Sol-gel method, deposited on glass and silicon substrates using the Dip-coating technique.

2. Experimental

Undoped and Cd-doped ZnO (Cd: 2, 5 and 10 wt.%) semiconductor thin films were deposited by sol-gel process, dip-coating method onto glass and silicon substrates. The preparation of the solutions and the deposition of the films are given step by step in detail below. The zinc acetate dehydrate [$Zn(CH_3CO_2)_2{\cdot}2H_2O$;ZnAc] and the cadmium acetate dehydrate [$Cd(CH_3CO_2)_2{\cdot}2H_2O$;CdAc] as a starting material and doping source respectively, this powders were mixed with cadmium mass concentrations being CdAc/ZnAc = 0, 2, 5 and 10 wt.%. They are dissolved in 30 ml of 2-Methoxyethanol by intensively magnetic stirring. We followed by drop-wise addition 0.6 ml of Ethanolamine; the obtained precursor was stirred 60 min at 60 °C. After the heat treatment, we let it overnight at room temperature where the quality of our final solutions products was homogeneous, clear and transparent. The precursor solution was deposited on to glass and silicon substrates by dip-coating method with fixed the dipping speed controller at 10 s/mer. The two types of substrates were rinsed with water, ethanol and acetone, more with diluted HF (5%) for the silicon substrate. The doping solution was then deposited by dip-coating method onto clean substrates.

The preheat temperature of the thin films is taken at 100 °C for 10 min repeated for ten times, is the number of sub-films of our samples. While the heat treatment was carried out at 500 °C for 120 min, during this time, the evaporation of solvent occurs, in order to promote the thermal decomposition of zinc acetate and the crystallization of the ZnO phase.

The crystalline structure was analyzed by X-ray diffraction (XRD) using X'Pert Pro of Philips diffractometer (X-ray tube Cu: $\lambda = 1.54059$ Å and generator settings: 45 Kv, 40 mA). The morphology of the films surfaces was observed by environmental scanning electronic microscope type (ESEM) XL 30 FEG Philips. The thickness and the compositional were studied by Rutherford Backscattering Spectrometry (RBS) with 2 MeV energy and $^4He^+$ ion beam using the accelerator Van De Graaf. The backscattered ions were recorded by a surface barrier detector, placed at 165° with respect to the beam. The recorded RBS spectra were processed by the RUMP simulation computer program [17]. The Auger electron spectroscopy (AES) measurements performed on our films have been executed with a Perkin Elmer PHI 600 sound. The electron acceleration voltage and intensity were fixed at 3 kV and 1 μA respectively. In order to obtain a deep profile and a maximum spray efficiency. During the analysis, the sample is stripped with the argon gun (Ar^+, 4 keV) fixed at 15° to the sample surface with an argon beam forming an angle 75° with the sample normal located in the analysis chamber. The AES allows identifying the nature of the chemical elements present in the first plus the sub-films of the samples and gives an idea about its thickness. The optical properties were measured by UV–vis spectrophotometer using Shimadzu, UV-3101, while photoluminescence (PL) measurements were carried out by a Perkin-Elmer LS 50B luminescence spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The diffractograms of undoped and Cd doped ZnO (Cd: 2, 5 and 10 wt.%) semiconductor thin films deposited by sol-gel route technique using a dip-coating method onto glass substrates at 500 °C are shown in Fig. 1. Our samples were analyzed in the angular range of [20°–80°] with 0.33°/min scanning speed.

The two peaks located about the angles of 34.50° and 72.50° correspond respectively to the (002) and its harmonic (004) peaks of hexagonal crystal structure 'wurtzite' of the ZnO (JCPDS card N° 00-036-1451). All films are the c-axis preferential orientation (002), moreover an increase in the intensity and in the width of this intense peak (002) were observed with increasing of Cd doping concentration up to 5 wt. %. Where we can say that the increasing of Cd concentration lead to ameliorate the crystallization of zinc oxide phase, after decreasing for 10 wt.% (see Fig. 2) without detected a formation of the CdO secondary phase as before was founded by another search in our work [5]. Otherwise a decrease in the crystallites size was observed with the increasing of Cd up to 5 wt.%, to resume a little increase at the sample doped 10 wt.% Cd. It was noted too that the peak (002) of the films shifted toward low angles as the Cd concentration increase, confirmed the increases of the lattices parameters a(Å) and c(Å) with increasing of Cd doping concentration [5], it was summarized in the Table 1.

Because the (002) diffraction dominates plan in all diffractograms, suggests that the most oriented crystallographic growth of ZnO thin films with c-axis perpendicular to the substrate, which is an essential condition for the ZnO film to have a high piezoelectric quality. So generally when we observed the (002) orientation of ZnO wurtzite structure is preferential, suggesting that the surface free energy of (002) plane is the lowest in our samples of ZnO doped via different Cd concentrations (Cd: 0, 2, 5 and 10 wt.%) thin films [18–20].