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ZnO based transparent conductive oxide films with controlled type of conduction

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ABSTRACT

The transparent conductive oxide films with controlled type of conduction are of great importance and their preparation is intensively studied. In our work, the preparation of such films based on doped ZnO was realized in order to achieve controlled type of conduction and high concentration of the charge carriers. Sol–gel method was used for films preparation and several dopants were tested (Sn, Li, Ni). Multilayer deposition was performed on several substrates: SiO_2/Si wafers, silica-soda-lime and/or silica glasses. The structural and morphological characterization of the obtained films were done by scanning electron microscopy, X-ray diffraction, X-ray fluorescence, X-ray photoelectron spectroscopy and atomic force microscopy respectively, while spectroscopic ellipsometry and transmittance measurements were done for determination of optical properties. The selected samples with the best structural, morphological and optical properties were subjected to electrical measurement (Hall and Seebeck effect). In all studied cases, samples with good adherence and homogeneous morphology as well as monophasic wurtzite type structure were obtained. The optical constants (refractive index and extinction coefficient) were calculated from spectroscopic ellipsometry data using Cauchy model. Films with n- or p-type conduction were obtained depending on the composition, number of deposition and thermal treatment temperature.

1. Introduction

ZnO has attracted much attention as a promising material for the transparent conductive oxide (TCO) coatings [1], electrodes for dye-sensitized solar cells [2], gas sensors [3], and field emission materials [4] due to its wide band gap of 3.37 eV, large excitation binding energy (60 meV) and high optical gain (320 cm^{-1}) at room temperature [5]. ZnO is easy to be doped as an n-type semiconductor [6,7], but for most optoelectronic devices such as solid state light emitting diodes or lasers made of ZnO [8,9], it is also necessary to have p-type ZnO, which is difficult to be obtained because of low solubility of the dopants in the ZnO matrix. Growth of p-type ZnO is a highly challenging problem because of the self compensating native donor defects such as oxygen vacancies (O_v) and zinc interstitials (Z_{ni}) in the system. In principle, p-type conductivity can be realized in ZnO by doping either with group-I and IB elements [Li, Na, K, Ag, Cu] in the place of Zn or by doping with group-V elements [N, P, As, Sb] in the place of oxygen [10–13]. Controlled doping is one of the most important problems in semiconductor physics, because for a specific application it is often desirable to introduce a specific dopant at a particular site to generate required carriers. Literature data reported that group-I elements are better dopant materials than group-V elements in terms of the shallowness of the accepter level [14]. Among group I elements, theoretically Li is the best candidate in producing p-type ZnO in regard to strain effects and energy levels by substituting at the Zn site Li_{Zn} [15]. ZnO has been also doped with magnetic metals, such as Mn, Co and Ni, in order to form diluted magnetic semiconductors for spintronic device applications [16–18]. The oxygen vacancies play a key role in controlling p-type conductivity and ferromagnetism in ZnO.

Several groups of researchers have tried to prepare p-type ZnO thin films by employing different methods such us: RF/DC magnetic sputtering deposition [19,20], pulsed laser deposition [21], spray pyrolysis technique [22,23] etc. Studies regarding the preparation of p-type ZnO thin films by the sol–gel method are much less reported in the research literature.

The un-doped, Sn, Li, Ni, doped ZnO and Li-Ni co-doped ZnO thin films were prepared by the sol–gel method. The films were realized by multilayer deposition on several substrates as: SiO_2/Si wafers, silica-soda-lime and/or silica glasses. This paper aims to study the

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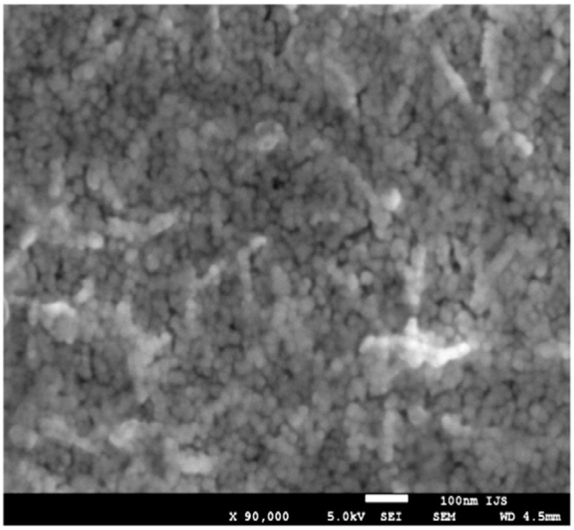

Fig. 1. SEM micrograph of the ZnO film.

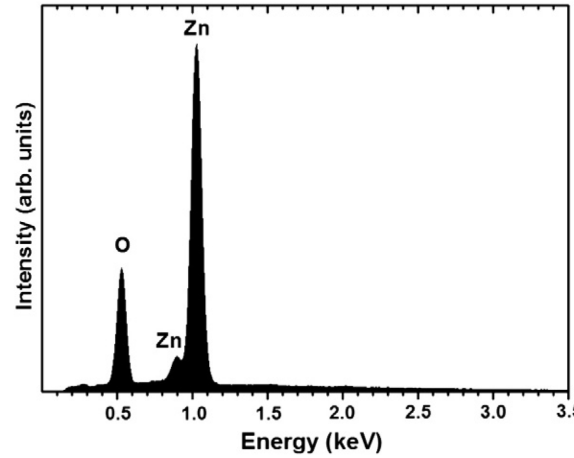

Fig. 3. EDX spectrum of the ZnO film.

influence of doping elements and of the substrate on the structural, optical and electrical properties of ZnO thin films. The results could lead to a better understanding of the behavior of such materials as

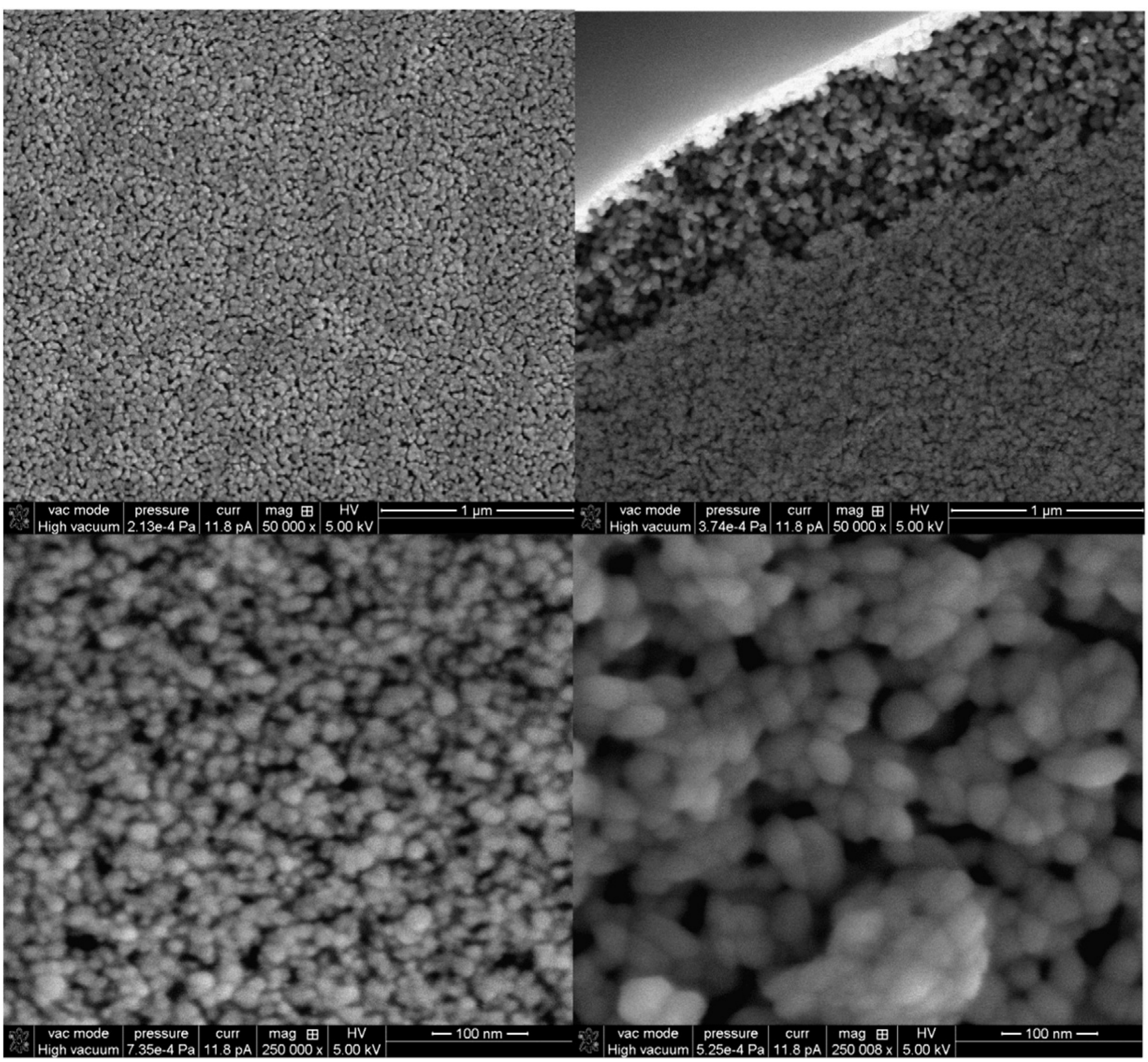

Fig. 2. SEM micrographs showing the typical microstructure of undoped ZnO films: (top left) surface morphology showing the micro-scale porosity; (top right) cross section, showing the internal microstructure of the nanoparticulate porous films; (bottom left) detail of the outer surface morphology showing the particle size and interparticle porosity; and (bottom right) detail of the microstructure inside the film.

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