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Effect of tin doping on optical properties of nanostructured ZnO thin films grown by spray pyrolysis technique

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ABSTRACT

Sn-doped ZnO thin films with 0%, 0.5%, 1%, 1.5% and 2% Sn were grown by spray pyrolysis method on glass substrates under optimized conditions. High resolution Field Effect Scanning Electron Microscopy characterization showed that the films consist of hexagonal-like grains. A comprehensive study of the optical properties was performed and the dispersion constants were determined. The effect of Sn content on the optical band gap and the optical constants (refractive index, extinction coefficient, dielectric constants, and dispersion parameters) was studied. These Sn-doped ZnO thin films are highly transparent (73–93%) in the visible region. A blue shift of the optical band gap, attributed to the Burstein Moss effect, was observed for the Sn-doped films. All the optical dispersion parameters depend on the Sn content of the films, but were found to reach threshold values at a Sn content of 0.5%. These optical parameters are discussed in terms of the single oscillator model. This study demonstrated that this 0.5% Sn-doped ZnO thin film has enhanced physical properties, allowing its better integration in optoelectronic devices.

1. Introduction

ZnO has potential applications for a variety of optoelectronic devices because of its unique combination of physical properties. Compared to other II–VI semiconductors such as ZnSe and ZnS or to III–V compounds such as GaN, ZnO combines many advantages: (1) ZnO is a n type semiconductor with a direct wide band gap of 3.37 eV; (2) ZnO possesses a large exciton binding energy of 60 meV (compared to GaN: 25 meV, ZnSe: 22 meV, ZnS: 40 meV); (3) ZnO is non-toxic; (4) ZnO occurs in many forms such as bulk single crystal, powder, thin film, nanowires, nanotubes, etc.. Furthermore, ZnO thin films are widely studied because they can be grown on different substrates at low temperature. These films are optically transparent in the visible spectrum. Depending on the specific process used for their growth, ZnO films can have widely varying electrical resistivity from 10^{-4} to 10^{12} Ω cm [1,2]. To optimize their electrical and optical properties for specific applications, ZnO thin films are often deliberately doped with group III elements (B, Al, In, Ga) and/or group IV elements (Pb, Sn). Paraguay et al. [3] studied the relationships between microstructure and a variety of dopants (Al, Cu, Fe, In and Sn) in ZnO films grown by spray pyrolysis. Further studies by Han et al. [4] examined the functional properties of undoped, and Al, Fe, Ni, and Sn-doped ZnO films prepared by co-precipitation method.

Sn is considered one of the most promising of these dopants because Sn can easily substitute for Zn due to their similar ionic radii (0.074 nm for Zn^{2+} and 0.069 nm for Sn^{4+}), resulting in a small lattice distortion [5]. The substitution of Zn with Sn results in a large increase in the electrical conductivity due to the presence of additional free electrons. At present, Sn has proven to be the best n type dopant for high quality ZnO thin films [6,7]. For these reasons Sn-doped ZnO films possess excellent sensing properties, making them ideal candidates for gas sensor devices [8–10]. Additionally these Sn-doped ZnO films have applications as dye sensitized solar cells (DSSC), as reported by Ameen et al. [11] and Ye et al. [12]. These films can also be used as transparent electrode materials [6] or anti-reflecting coatings (ARC) in semiconductor solar cells [13].

Since the first studies by Bougrine et al. [14] in 2003, many reports dealing with the deposition parameters of transparent and conductive Sn-doped ZnO thin films have been published. Numerous techniques can be used for the deposition of Sn-doped ZnO films on glass substrates such as the sol–gel processes

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[6,13,15], the hydrothermal method [11,12,16], the SILAR technique and the rapid photothermal processing (RPP) [10], the thermal evaporation method [8,17], the pulsed laser deposition (PLD) [18], the chemical vapor deposition (CVD) [19], and the spray pyrolysis method [14,20–22]. Compared to other techniques, the spray pyrolysis method, which was initially developed for conductive oxide deposition on solar cells applications, has several advantages: the spray pyrolysis method allows large area deposition; it is flexible for process modifications; it is simple and non-expensive. Furthermore, to optimize the physical properties requested by the large panel of applications, the ZnO thin films produced with this technique can be doped with a great variety of elements.

The influence of the concentration of dopants, such as Ni, Mo, V, F, Cu, on the structure and/or the optical constants of ZnO thin films has been studied by various research groups [7,23–26]. The refractive index, the absorption index, and the dielectric constant were analyzed from the transmittance spectra [26]. The effect of doping with Sn on the structure and optical and electrical properties of relatively thick Sn-doped ZnO films, over 600 nm, has been studied by a number of researchers. Ajili et al. [20] found that films doped from 0% to 1% Sn have a constant optical band gap of 3.25 eV, while Vasanthi et al. [27] found an optical band gap varying from 3.18 to 3.24 eV for films doped from 0% to 10% of Sn.

While Sn-doped ZnO films have received extensive attention, many aspects of the material behavior have not been well characterized. In particular, the effect of Sn-dopants on the optical constants of thin ZnO films have not been evaluated. Furthermore, the role of processing by spray pyrolysis on these optical constants has not been studied in relation to doping levels and microstructure. In this work, Sn-doped ZnO thin films were grown on glass substrates by the spray pyrolysis method. The microstructure of these films was characterized by high resolution scanning electron

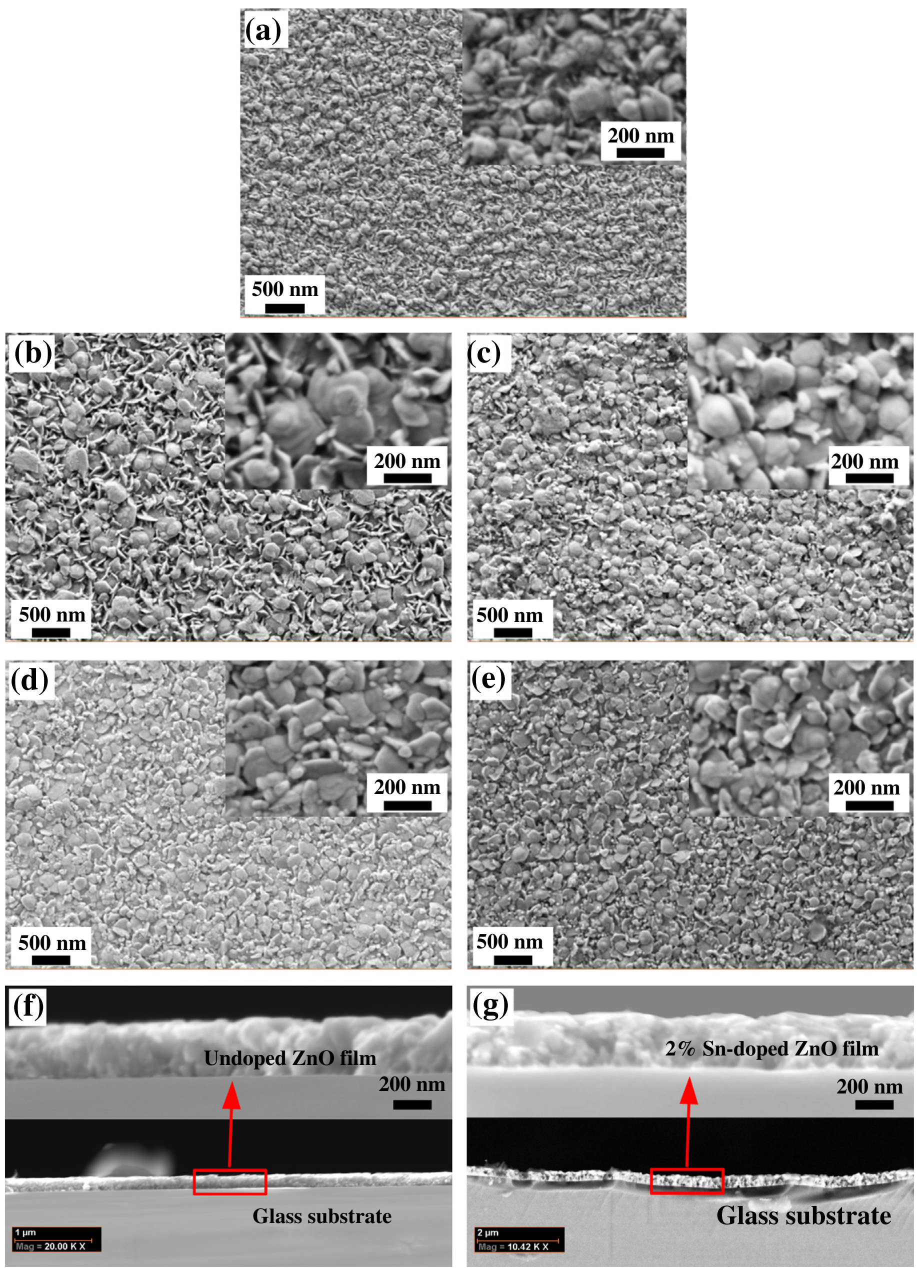

Fig. 1. High resolution SEM micrographs of undoped and Sn-doped ZnO thin films. (a–e) show the surface morphology of the films for different Sn contents: (a) 0%, (b) 0.5%, (c) 1%, (d) 1.5%, (e) 2%. (f) and (g) are the cross-sectional micrographs of the undoped and 2% Sn-doped ZnO thin films respectively. High magnification SEM images are shown in the insets.