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Effect of Sn-doped on microstructural and optical properties of ZnO thin films deposited by sol–gel method

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Abstract

In this study, transparent thin films of Sn-doped ZnO (ZnO:Sn) were deposited onto alkali-free glass substrates by a sol–gel method; the effect of Sn doping on crystallinity, microstructural and optical properties was investigated. The atomic percentages of dopant in ZnO-based sols were Sn/Zn = 0, 1, 2, 3, and 5 at.%. The as-deposited films were pre-heated at 300 °C for 10 min and then annealed in air at 500 °C for 1 h. The results show that Sn-doped ZnO thin films demonstrate obviously improved surface roughness, enhanced transmittance in the 400–600 nm wavelength range and reduced average crystallite size. Among all of the annealed ZnO-based films in this study, films doped with 2 at.% Sn concentration exhibited the best properties, namely an average transmittance of 90%, an RMS roughness value of 1.92 nm and a resistivity of 9.3×10^2 Ω-cm.

Keywords: Transparent oxide semiconductors; ZnO thin films; Sn doping; Sol–gel method

1. Introduction

Wide bandgap (>3 eV) transparent oxides have been extensively used for photovoltaic devices and optical–electrical devices. Among these materials, zinc oxide (ZnO) is a promising candidate for novel device applications, such as transparent electronics [1–3] and flexible displays [4,5]. ZnO exhibits non-toxicity, high transparency, a wide range of conductivity from metallic to insulating, and high crystallinity. Its unique electrical and optical properties have made it popular in piezoelectric transducers, surface acoustic wave (SAW) devices, laser diodes, photoconductive UV detectors and gas sensors, etc. Recently, interest in ZnO-based thin films has focused on flat-panel displays (FPDs) and photovoltaic applications, such as the anodic electrode of organic light-emitting device (OLED) displays [6,7], the active channel layer of thin-film transistors (TFTs) [8–10] and the transparent electrode/window layer of thin-film solar cells [11,12].

ZnO is an n-type oxide semiconductor material with a direct wide bandgap of 3.3 eV. Its electrical characteristics can be controlled by doping with ternary elements or adjusted process conditions [13,14]. The carrier mobility of the pure ZnO exceeds the field effect mobility of hydrogenated amorphous silicon (a-Si:H), which serves as the active channel layer in typical TFT arrays. In addition, polycrystalline ZnO films can be prepared in a normal atmosphere and possess low photosensitivity. Therefore, ZnO may replace a-Si:H as an active layer; for this reason, the subject presently attracts much attention.

ZnO-based thin films have been prepared by various thin-film deposition techniques, such as RF/DC magnetic sputtering deposition, pulsed laser deposition, chemical vapor deposition, chemical bath deposition, spray pyrolysis, sol–gel method, etc. The solution-based process offers a simple, low cost and large area thin-film coating method as an alternative to vacuum deposition techniques (PVD or CVD). Use of the solution process to form oxide semiconductors may improve the manufacturing throughput of microelectrical devices since it enables maskless processes, including inkjet printing [15] and selective electroless plating [16], etc. The sol–gel method is one of the common solution processes; it is popularly used for polycrystalline oxide thin-film deposition [17,18]. ZnO-based semiconductor films have served as active channel layers in

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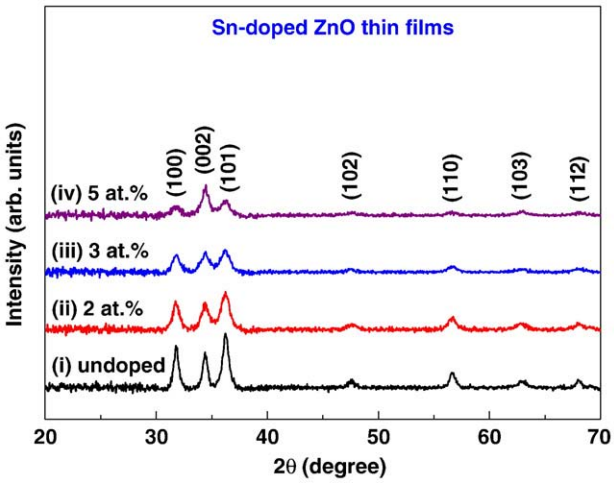

Fig. 1. X-ray diffraction patterns of undoped and Sn-doped ZnO thin films annealed at 500 °C for 1 h.

TFTs. Kwon et al. [19] have indicated that controlling the carrier density of the active layer is a challenge in ZnO-based TFTs, since the active layer supplies high carrier density that will conduct when an applied gate voltage is absent.

Lee et al. [20] have reported on TFTs with spin-coated $Zn_{1-x}Zr_xO$ thin films (ZnO doped with a group IV group element) as active channel layers. However, transparent oxide semiconductors of Sn-doped ZnO thin films prepared by a solution-based process or a vacuum deposition technique have not been reported. The ionic radius of Sn^{4+} (0.69 Å) is smaller than Zn^{2+} (0.74 Å), and thus Sn^{4+} ions can replace Zn^{2+} ions in substitutional sites [13]. The present study used a sol–gel method to prepare transparent oxide semiconductors with Sn-doped ZnO thin films; it investigated the effects of Sn concentration on crystallinity, microstructure and optical properties.

2. Experimental

Sn-doped ZnO (ZnO:Sn) thin films were prepared on glass substrates by a sol–gel method. Zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and tin tetrachloride ($SnCl_4$) were dissolved in 2-methoxyethanol, and then monoethanolamine (MEA) was added to the solution as a stabilizer. The concentration of metal ions in ZnO:Sn sols was controlled at 0.35 M and Sn/Zn ratios varied from 0 to 5 at.%. Each complex solution was stirred for 2 h at 60 °C until a transparent and homogenous sol was obtained. All ZnO:Sn gel films were coated onto alkali-free glass (Corning 1737, with dimension 5×5 cm^2) using spin coating at a speed of 1000 rpm for 30 s. These as-coated films were pre-heated at 300 °C for 10 min immediately after coating. After repeating the coating procedure three times, the films were annealed in air at 500 °C for 1 h.

The crystallinity levels of Sn-doped ZnO thin films after annealing were determined by glancing angle X-ray diffraction (GAXRD). These diffracted patterns were examined on a MAC Science MAXP3 diffractometer with a glancing incident angle of 1°. Surface morphology and microstructure of each ZnO:Sn film were observed using a field-emission scanning electron microscope (FE-SEM, HITACHI S-4800, Japan). A scanning probe microscope (SPM, Digital Instrument NS4/D3100CL, Germany) was used to analyze the films' surface roughness levels. The resistivities were measured at room temperature by a high resistivity meter (MCP-HT450, DIA INSTRUMENTS CO., LTD, Japan). A spectrophotometer (Mini-D2T, Ocean Optics Inc., USA) was used to measure optical transmittance spectra in the visible ranges of these films.

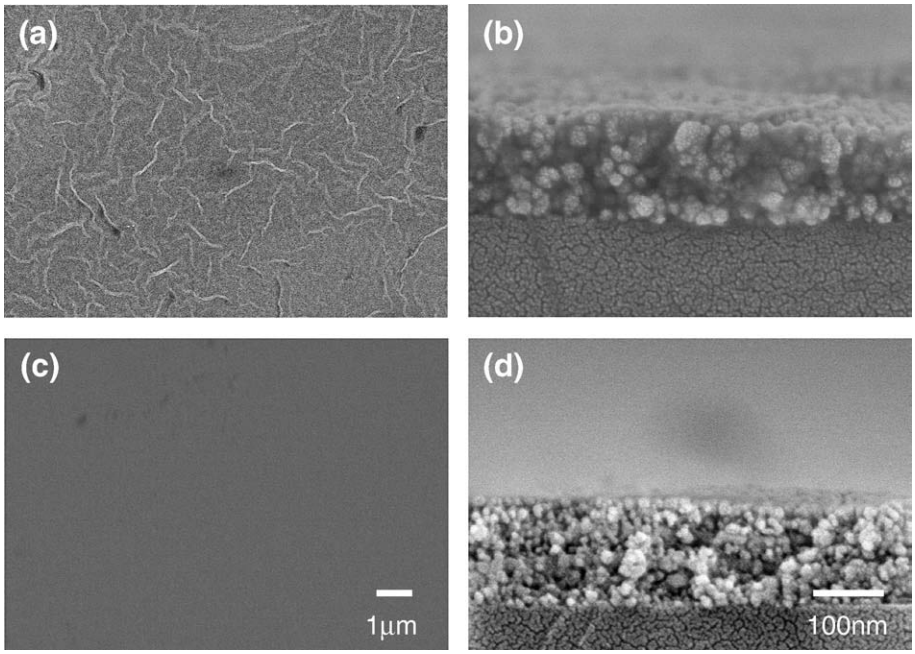

Fig. 2. SEM micrographs of plane view and cross-section of Sn-doped ZnO thin films: (a), (b) undoped sample and (c), (d) 2 at.% Sn-doped sample.