Materials Science in Semiconductor Processing 41 (2016) 323–334

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Effects of lanthanum and sodium on the structural, optical and hydrophilic properties of sol–gel derived ZnO films: A comparative study

Mohamed Shaban [a], A.M. El Sayed [b,c,*]

[a] Nanophotonics and Applications (NPA) Lab, Department of Physics, Faculty of Science, Beni-Suef University, Beni-Suef 62514, Egypt
[b] Department of Physics, Faculty of Science, Fayoum University, Fayoum 63514, Egypt
[c] Department of Physics, Faculty of Science, Northern Border University, Arar 91431, Kingdom of Saudia Arabia

ARTICLE INFO

Article history:
Received 22 May 2015
Received in revised form
20 August 2015
Accepted 1 September 2015

Keywords:
ZnO films
Wettability
Wrinkle nanostructure
Refractive index

ABSTRACT

The technological applications of the transparent ZnO films could be broadened via incorporation of small amounts of some special elements. In this work, the optical and surface properties of the spin coated $Zn_{1-x}M_xO$ films (M=Na or La and $x \leq 0.075$) grown on glass substrates, are reported. According to X-ray diffraction (XRD) results, all films consist of a single phase with a hexagonal structure and the ZnO crystallites are preferentially oriented towards (002) direction. The plane surface of the pure ZnO film turned to be wrinkle network structure after Na and La addition. The reflectance (R%) of the films decreased after Na doping and significantly increased with increasing La content. The optical band gap of pure ZnO is 3.26 eV and red-shifted after Na and La incorporation. The dependence of the refractive index and film's wettability on the structural and morphological changes are reported. The obtained results of these two systems are compared with those of similar materials and some expected applications are explored.

1. Introduction

The distinctive physicochemical and optoelectronic properties of the transparent ZnO semiconductor material still stimulate enormous interest for use in a variety of industrial and technological applications. ZnO has the strongest piezoelectric response among the tetrahedrally bonded semiconductors and this property can be exploited in actuators and surface acoustic wave (SAW) devices [1,2]. ZnO films have thermal diffusivity in the range of $(4.35–5.03)x10^{-2}$ cm^2/s and electrical resistivity varying from 10^{-4} to 10^{12} Ω cm [3]. Then, these films are suitable for monitoring of some gasses like CO and H_2S and CH_4 [4]. The free exciton binding energy of ZnO at room temperature (RT) can be increased from 60 meV to over 100 meV in superlattices [5]. Therefore, high-efficiency blue/UV light emitting diodes and lasers can be fabricated to exploit this property [2,6,7]. Moreover, the ZnO surface is, generally, known to be hydrophilic and ZnO nanostructures could be applied for dew-harvesting systems [8], the effective control of micro or nanofluid motion and in the construction of self-cleaning surfaces [9].

Lanthanum is a rare earth element with electronic configuration [Xe] $5d^1$ $6s^2$. Tang et al. [10] reported that $Zn_{0.99}La_{0.01}O$ film is appropriate as a switching layer for resistive random access memory (RRAM) applications. The wide energy gap of ZnO offers a large spectral area for La [7] and the *4f–4f* intra-shell transitions in La give very intense emission peaks in the visible and near-IR regions. This makes La a good dopant for enhancing the ZnO photoluminescence (PL) properties [11]. Also, La can trap the electrons and reduce the recombination of photogenerated electron–hole pairs and hence enhance the photocatalytic activity of ZnO [12–15]. La-doped ZnO nanostructures have been prepared via different methods such as chemical precipitation [11] and microwave assisted method [13]. La-doped ZnO thin films have been prepared by chemical solution deposition (CSD) [10], RF magnetron sputtering [16], spray pyrolysis [17], and sol–gel spin coating [18].

On the other hand, sodium (Na), the group I element with electronic configuration [Ne] $3s^1$, is a good acceptor having a shallow acceptor level between 164 and 170 meV and provides a high hole concentration up to 3×10^{18} cm^{-3}. Thus, Na is a good substitute for Zn to achieve stable *p*-type conductivity [19–21]. Na can enter the ZnO lattice interstitially in combination with a neighboring oxygen vacancy [22,23]. Na-doped ZnO materials are a candidate for self-cleaning coatings [24] and were reported as

* Corresponding author at: Department of Physics, Faculty of Science, Fayoum University, Fayoum 63514, Egypt.
E-mail addresses: ams06@fayoum.edu.eg, adel_sayed_2020@yahoo.com (A.M. El Sayed).

http://dx.doi.org/10.1016/j.mssp.2015.09.002
1369-8001/

good blue emission materials with excellent photocatalytic activity for organic pollutants in water [25]. Various Na-doped ZnO nanostructures such as microwires [21], nanowires [23,25], and thin films [18,20,26–28] have been prepared by chemical vapor deposition (CVD) [21], thermal decomposition [25], RF-sputtering [23], sol–gel [24,26–28], pulsed laser deposition (PLD) [19,29], and metal–organic chemical vapor deposition (MOCVD) [20].

In the literature, very few reports on La-doped ZnO films prepared via spin coating method [18]. This work is, thus, devoted to making comparisons between the effect of La and Na on the structural, morphological, optical properties as well as the wettability of sol–gel spin coated ZnO films.

2. Materials preparation and measuring techniques

To prepare pure, La- and Na-doped ZnO films, the required amounts of the source material [$Zn(CH_3COO)_2.2H_2O$, M_W=219.49, Panreac] and the dopant materials [$LaCl_3.7H_2O$, M_W=371.37, Schorlau, Spin, and $CH_3COONa.3H_2O$, M_W=136.08, Sigma-Aldrich] were dissolved in 7 ml 2-Methoxyethanol [$C_3H_8O_2$, M_W=76.1]. Ethanolamine (ME) [C_2H_7NO, M_W=61.08, Scharlab S.L., Spain] was added to the solution as a stabilizing agent. The concentration of zinc acetate was 0.5 mol/l and the molar ratio of ME to zinc acetate was maintained at 1:1. The prepared mixtures were magnetically stirred at 60 °C for 2 h to obtain a clear homogeneous solution and then aged for 24 h prior to film deposition. The additives were controlled to obtain the following film's compositions; ZnO, $Zn_{0.975}La_{0.025}O$, $Zn_{0.95}La_{0.05}O$, $Zn_{0.925}La_{0.075}O$, $Zn_{0.975}Na_{0.025}O$, $Zn_{0.95}Na_{0.05}O$, and $Zn_{0.925}La_{0.075}O$. For simplicity, these compositions are named: pure ZnO, 2.5% La, 5.0% La, 7.5% La, 2.5% Na, 5.0% Na, and 7.5% Na, respectively. Before the spin coating process, glass substrates of thickness 1.3 mm, were cleaned by sonication in acetone, ethanol, and deionized water for 10 min each. Then, the substrates were dried using an air gun and baked at 100 °C for 20 min to remove any residual moisture. The thin films were obtained by a spin coating method at 2000 rpm for 30 s. Then, the gel thin films were dried at 180 °C for 20 min, and this procedure was repeated six times for all films. After that, the as-prepared films were annealed at 500 °C for 120 min in an air furnace and then cooled to *RT*.

High-resolution X-ray diffraction (XRD, Philips X'PertPro MRD) was used for crystallographic properties identification of the prepared oxide films using Cu K_α radiation (λ=1.5418 Å) with a step 0.021. The chemical compositional analysis was studied using energy dispersive X-ray (EDX; Oxford Link ISIS 300 EDX). Morphological studies of the fabricated nanostructured films were carried out using field emission-scanning electron microscopy, FE-SEM (model: ZEISS SUPRA 55 VP and ZEISS LEO, Gemini Column). Optical spectra (reflectance and transmittance) in the spectral range from 300–1000 nm were measured using UV/VIS/NIR 3700 double beam Shimadzu spectrophotometer at *RT*. Barium sulfonate was used as a reference to provide a nominal 100% reflectance measurement. The surface wettability of ZnO thin films was characterized via measuring water contact angle, WCA (Θ) using a CAM 200 Optical Contact Angle Meter (KSV Instruments), using the sessile drop method. A 5 μl droplet of distilled, deionized water was positioned on the surface via a microsyringe and images were captured to measure the angle that formed at the liquid/solid interface.

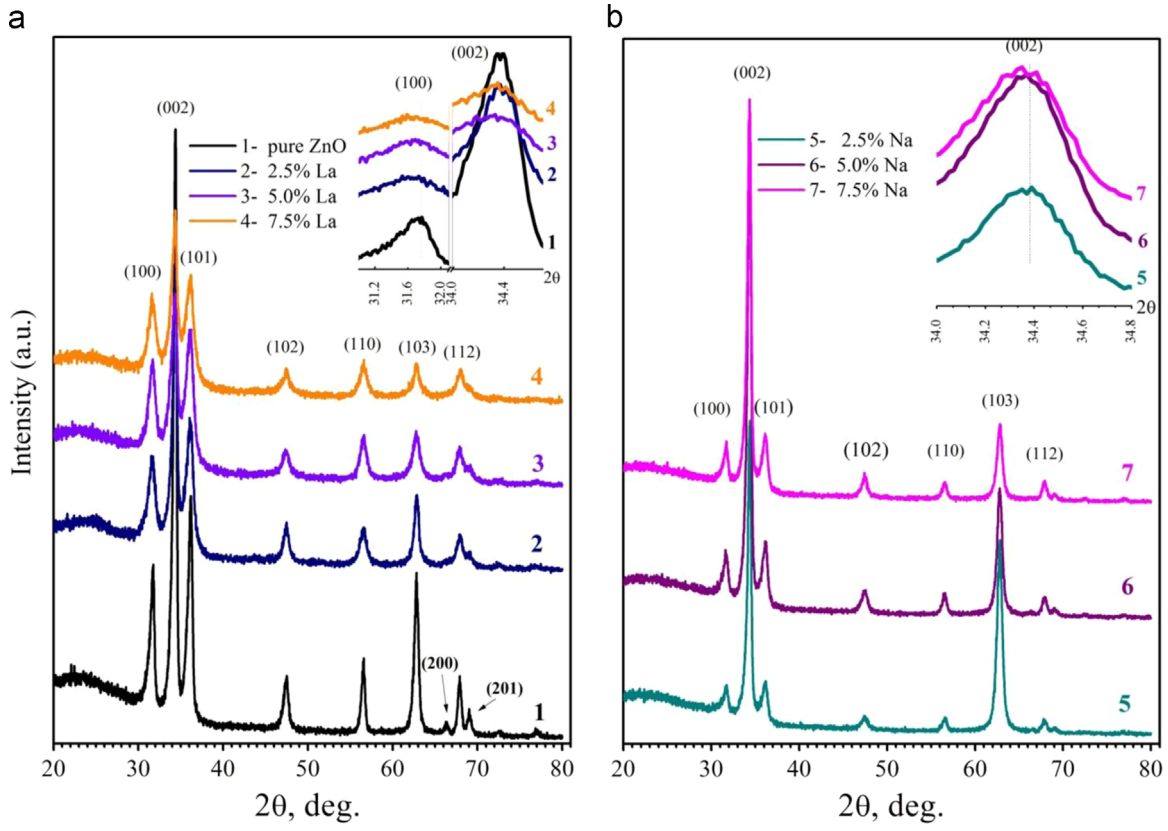

Fig. 1. XRD patterns of (a) ZnO and La-doped ZnO and (the inset shows the (100) peak shift to lower 2θ values) and (b) Na-doped ZnO films (the inset shows the (002) peak shift to lower 2θ values).