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Structural and optical properties of Na-doped ZnO films

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ABSTRACT

$Zn_{1-x}Na_xO$ (x = 0.0–0.05) solutions have been synthesized by the sol-gel technique using Zinc acetate dihydrate and Sodium acetate which were dissolved into solvent and chelating agent. Na-doped ZnO nanoparticles were obtained from solutions to find phase and crystal structure. Na-doped ZnO films have been deposited onto glass substrate by using sol-gel dip coating system. The effects of dopant concentration on the structure, morphology, and optical properties of Na-doped ZnO thin films deposited on glass substrate are investigated. Characterization of $Zn_{1-x}Na_xO$ nanoparticles and thin films are examined using differential thermal analysis (DTA)/thermogravimetric analysis (TGA), Scanning electron microscope (SEM) and X-Ray diffractometer (XRD). Optical properties of $Zn_{1-x}Na_xO$ thin films were obtained by using PG Instruments UV–Vis–NIR spectrophotometer in 190–1100 nm range. The structure, morphology, and optical properties of thin films are presented.

1. Introduction

ZnO is pointed for many potential applications such as gas sensors, field-effect transistors, light emitting diode, photodiode, and solar cell in many geometries like thin films, nanobelts, nanowires, nanoparticles etc. due to its superior properties, like wide direct band gap, 60 meV exciton binding energy, high electron concentration, high transparency in optical region, and a large conductivity range from 10^4 to 10^{-12} Ωcm [1–6].

There's an intense study to improve p-type electrical characteristics by implanting various dopants mainly the group-V elements such as N, P, As, and Sb [7]. Na doping attracted more attention due to possible shallow acceptor production by replacing ZnO and Na is proved to be a good candidate for the production of various p-n junction devices [8]. Na also reported for decreasing oxygen vacancy density which is also an important step for achieving stable p-type conduction [9]. Besides introducing p-type properties to ZnO, it's shown that Na substitution ZnO lattice improved conversion efficiency in dye-sensitized solar cells (DSSCs) when ZnO based nanostructures are used as photo-anode [10].

Currently, studies are also very intensely focused on the production of ZnO based films in a cost-effective way by various techniques such as electrodeposition, spray pyrolysis, sol-gel, chemical bath deposition, and metal organic chemical vapor deposition [11–14]. Among these studies sol-gel route is very frequently followed for advantages like low investment costs, non-vacuum application, ease in the arrangement in stoichiometry [15–20].

The aims of this study are; to investigate characterization and processing parameters of $Zn_{1-x}Na_xO$ ($x = 0.01, 0.02, 0.03, 0.04$ and 0.05) thin films, to growth high quality c-axis oriented and single phase $Zn_{1-x}Na_xO$ thin films, and to investigate doping effect on the structural and optical properties of c-axis oriented $Zn_{1-x}Na_xO$ thin films.

2. Experimental

The mixed oxides $Zn_{1-x}Na_xO$ solutions were prepared with different compositions (0.0, 0.01, 0.02, 0.03, 0.04 and 0.05) using sol-gel technique. Zinc Acetate Dihydrate (Merck, ACS grade) and Sodium Acetate Hydrate (Merck, ACS grade) were used as precursor materials and Methanol (Merck, HPLC grade) was a solvent. All chemicals are used as received. Precursors are weighed using precision balance according to molar ratios in the film structure. Prepared solutions are stirred and aged for 8 h. The solution concentration was 0.25 M. $Zn_{1-x}Na_xO$ thin films are coated with sol-gel dip coating method. Before depositing the thin films, the cleaning process was applied using methanol in an ultrasonic bath

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for 5 min each and deionized water. Then glass substrates were immersed in precursor solutions then preheated at 300 °C and this process is repeated 10 times till desired thickness is reached. Once coating process ended films are heat-treated at 600 °C in the box furnace for crystal orientation. Optical properties are measured by PG Instruments UV–Vis–NIR spectrophotometer. Incoming light spectrum was arranged to 190 nm–1100 nm interval. The crystal structure was examined by Bruker X-ray diffractometer (XRD) and Microstructure properties of prepared samples were observed using SEM analysis (JEOL, JSM-5910LV).

3. Results and discussion

3.1. Structural properties of ZnNaO thin films

The heat treatment conditions of ZnNaO nanoparticles synthesized by sol-gel method were perfectly clarified by Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TG) in 0 and 900 °C temperature range in Fig. 1. In the DTA curve, (at almost 90 °C) a sharp endothermic peak and the first 25% weight decreasing were observed because of solvent removal and evaporation of the volatile organic component in ZnNaO samples. The second weight decrease (50%) was monitored in TG curve in the region of 130 and 300 °C in which, a wide exothermic and two slight endothermic interval peaks in DTA were also examined. 15% lost weight was observed by burning Carbon-based materials in the range of 300 and 570 °C in which the lost weight corresponding to a shallow and wide exothermic peak in DTA curve.

$Zn_{1-x}Na_xO$ (0.0, 0.01, 0.02, 0.03, 0.04 and 0.05) thin films are coated onto glass substrate by using sol-gel dip coating system. Then, coated glass substrate annealed at 600 °C for 30 min which was found optimum annealing temperature from DTA and TG as shown in Fig. 1.

X-ray diffraction (XRD) analysis has been executed by means of Bruker D8 Advance model diffractometer. Fig. 2a illustrates XRD of ZnNaO thin films annealing at 600 °C. As shown in Fig. 2a, all $Zn_{1-x}Na_xO$ (0.0, 0.01, 0.02, 0.03, 0.04 and 0.05) films are oriented along the (002) plane which is the conformation of well crystallized ZnO structure. ZnNaO thin films are the single phase with ZnO wurtzite hexagonal structure and there is no indication of secondary phase. This means that the Na ions incorporated substitutionally in the ZnO lattice replacing the Zn ions.

Incorporation of Na ions in ZnO lattice is intensely studied

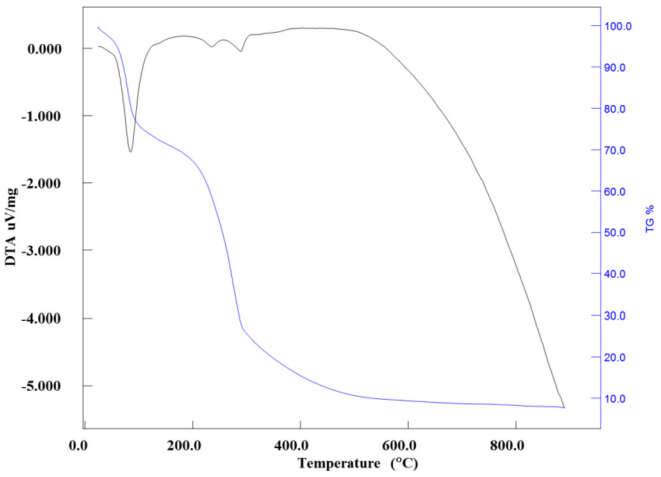

Fig. 1. DTA and TG behaviors of $Zn_{0.99}Na_{0.01}O$ samples synthesized by the sol-gel technique.

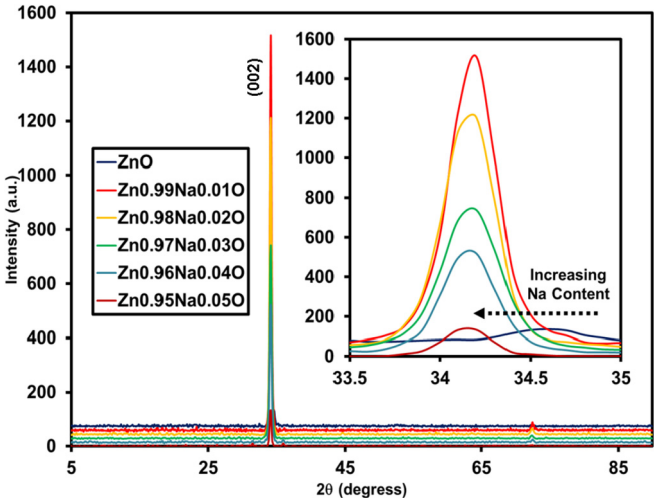

Fig. 2a. The X-ray diffraction patterns of the $Zn_{1-x}Na_xO$ thin films (x = 0.00, 0.01, 0.02, 0.03, 0.04, and 0.05), The inset shows enlarged view of XRD patterns around (002) peak.

employing a variety of methods such as pulsed laser deposition (PLD), thermal evaporation, and hydrothermal. All these studies have common outputs as result of implantation of Na. Replacement of Zn ions with Na ions generally causes a shift in (002) peak of XRD spectrum to lower 2θ direction (Fig. 2a) which is caused by substitution of Na^+ ions with larger ionic radius (0.099 nm) replacing Zn^{2+} ions with smaller ionic radius (0.060 nm) [21–24]. As seen in Fig. 2a, Na doping affects the peak intensity. Strongest intensity is observed at x = 0.01 doping concentration which gives the higher preferential c-axis orientation and better crystal quality. When the Na-doping concentration is increased from x = 0.01 to x = 0.05, the (002) peak intensity decreases.

The width of lines of XRD spectrum and Sherrer equation the crystallite size (d) of ZnNaO thin films were found.

$$d = \frac{K\lambda}{\beta Cos\theta} \tag{1}$$

Where β is the full width at the half-maximum (FWHM) intensity of line and taken from XRD pattern, λ is the well-known X-ray wavelength (0.15406 nm), and K is a constant taken as 0.9. The calculated crystallite sizes and FWHM are presented in Table 1. Concentration-dependent crystallite size and FWHM variation in ZnNaO films are shown in Fig 2b. As seen in Fig 2b, when the Na concentration is increased, the crystallite size increases and FWHM decreases.

Using, XRD pattern and Eq. (2), the lattice parameter c of the hexagonal structure was calculated and presented in Table 1.

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{2}$$

Table 1
Doping effect-dependent particle sizes, lattice parameter c, micro starin and stress.

Samples	D (nm)	FWHM	c(Å)	α (°)	β (°)	ε	$\sigma^{*}10^9$ (N/m^2)
ZnO	33.43	0.1975	5.1843	90	120	0.01337	37.6
$Zn_{0.99}Na_{0.01}O$	33.51	0.1968	5.1843	90	120	0.01337	37.6
$Zn_{0.98}Na_{0.02}O$	36.16	0.1733	5.1740	90	120	0.01339	35.6
$Zn_{0.97}Na_{0.03}O$	36.49	0.1706	5.1945	90	120	0.01334	40
$Zn_{0.96}Na_{0.04}O$	38.07	0.1576	5.1843	90	120	0.01337	37.6
$Zn_{0.95}Na_{0.05}O$	39.35	0.1476	5.1843	90	120	0.01337	37.6