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Effect of precursor solvent on the opto-electrical properties of spin coated transparent conducting ZnO: Ga thin films

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HIGHLIGHTS

- *c*-axis preferred orientation of spin coated Ga-doped ZnO thin films.
- Selection of solvents for preparation of precursor solutions.
- Alternative transparent conducting oxide thin films.
- Low cost method.

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ABSTRACT

ZnO: Ga thin films have been prepared by spin coating on glass substrate using solutions of zinc acetate dihydrate and gallium nitrate hydrate precursors in methanol, ethanol and 2-methoxyethanol with mono-ethanolamine as complexing agent to examine the effect of solvent on their opto-electrical characteristics. The selection of the solvent involves factors like toxicity, sol stability and the film properties. Accordingly, ethanol is shown to be suitable for yielding a stable sol to produce low cost 1 at% Ga–ZnO thin films useful for photovoltaic applications. These films exhibit hexagonal structure with (0001) preferred orientation, optical transmittance of ~75–96% in wavelength range 400–900 nm, electrical resistivity of ~ 3×10^{-2} Ω-cm and electron mobility of ~24 cm^2/ V. s.

1. Introduction

Transparent conducting oxide (TCO) thin films exhibit high optical transparency (>80% in the visible wavelength) as well as low electrical resistivity (<10^{-2} Ω-cm) [1] and so are of immense interest for applications in emissivity windows, gas sensors, flat panel displays, thin film transistors, and light emitting diodes [1–4]. ZnO has shown promise as it is cheaper, easier to etch, and possesses high mechanical strength besides exhibiting high transparency in the visible range (energy band gap E_g being 3.30 eV). However, its electrical resistivity is too high (~10^3 Ω-cm) to be used as TCO [5]. So, group III elements such as aluminum (Al), boron (B), indium (In) or gallium (Ga) are used as dopant to make ZnO a n-type semiconductor and competitive TCO material. Further, thin films of metal-doped ZnO have been realized by a number of sophisticated techniques, namely atomic layer deposition, sputtering, chemical vapor deposition and pulsed laser deposition on different substrates (glass, quartz, Si-wafer and sapphire) with optical transmittance of ~70–95% and electrical resistivity of ~10^{-1}–10^{-4} Ω-cm [6–9]. Sol-based spin coating technique has now-a-days become attractive because of its simplicity and low cost [10–13]. For this, zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and gallium nitrate nonahydrate [$Ga(NO_3)_3 \cdot 9H_2O$] have been used as precursors with methanol, ethanol and 2-methoxyethanol as solvents and mono-ethanolamine (MEA) as a complexing/stabilizing agent. Hosono et al. [14] synthesized zinc oxide nano-particles by using zinc acetate dihydrate precursor with the three solvents (viz., methanol, ethanol and 2-methoxyethanol) but without a base such as NaOH, LiOH or NH_4OH at 60 °C for a comparative study of the reactions involved. Accordingly, a layered hydroxide zinc

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acetate [$Zn_5(OH)_8(Ac)_2 \cdot 2H_2O$; LHZA] was formed as an intermediate phase to yield zinc oxide through a process depending on the nature of sol, e.g., (i) hydrolysis and deprotonation if non-aqueous, (ii) polymerization leading to Zn–(OH)–Zn bridges in absence of basic $(OH)^-$ ions and (iii) oxolation reaction giving Zn–O–Zn network under strong basic conditions. Also, the precursor was found to dissolve easily in methanol in comparison to ethanol or 2-methoxyethanol due to its high dielectric constant; the values being 32.3–32.6, 24.3–25 and 16.9 for methanol, ethanol and 2-methoxyethanol, respectively [14–16]. Moreover, the reflux time necessary for obtaining ZnO (displaying green photoluminescence with ultraviolet excitation) was reported as 12 h for methanol, 48 h for ethanol and 72 h for 2-methoxyethanol. While zinc ions assume octahedral coordination and forms $[Zn(MeOH)_6]^{2+}$ spheres in methanol (MeOH), water molecules are additionally associated in cases of ethanol (EtOH) and 2-methoxyethanol (2-ME) solvents. Nevertheless, the zinc coordination sphere of charge (2^+) and acetate ion of charge (1^-) form a pair complex of hydroxyl and acetate groups. Znaidi et al. [17] adopted dip-/spin coating using aged solution of zinc acetate dihydrate in ethanol with MEA as complexing agent in mild alkaline media and obtained highly oriented optical quality ZnO thin films. Moreover, the degree of preferred orientation is reported to depend on factors like precursor, stabilizer, sol molarity, solution aging, substrate, pre- and post-annealing temperature and thickness [18–25]. The opto-electrical data reported in the literature on gallium doped zinc oxide thin films, prepared by different deposition techniques on varieties of substrates have been summarized in Table 1 for the sake of comparison. The motivation of work is to find out a suitable solvent for precursors for making spin coating solution to produce ZnO: Ga films for photovoltaic application. The criteria have been i) solution stability and toxicity and ii) film structural morphology, high optical transmission, and low electrical resistivity. Gallium (Ga) is chosen as substitute because of its size being comparable to zinc and expected to cause little structural deformation besides having poor oxidation characteristics vis-a-vis aluminum. The covalent bond lengths of Ga–O and Zn–O are 1.92 Å and 1.97 Å, respectively [11, 26–42].

2. Experimental procedures

Thin films of 1 at% Ga–ZnO (ZnO: Ga) were prepared by spin coating using three different unit molarity solutions (termed as S_M, S_E and S_{2M}) of precursor(s) in methanol, ethanol and 2-methoxyethanol, respectively. A mixture of zinc acetate dihydrate and gallium nitrate nonahydrate in appropriate amounts was dissolved in each solvent separately with addition of monoethanolamine as a stabilizer and heated at 80 °C for 1 h under vigorous stirring to obtain a clear sol. The doping concentration of 1 at% was ensured by (Ga)/(Zn + Ga) atomic ratio of precursors at the stage of solution preparation itself and maintained in all the cases. Gallium concentration of films was not measured and hence the figure pertains to the solution used. Thin film was cast by dropping the sol on a clean glass substrate ($10 \times 10 \times 1$ mm^3), spinning at 4000 rpm for 30s and heating subsequently at 400 °C for 10 min in air. After repeating this process several times the resulting film was vacuum annealed at ~10^{-3} mbar by raising the temperature to 500 °C, holding there for 30 min, and finally cooling in the furnace itself. While an x-ray powder diffractometer (Panalytical X'Pert PRO) with the CuKα_1 radiation was used for phase identification and determining the average grain size, a double beam spectrophotometer (Hitachi Model U-3310) was engaged for recording the optical transmittance in the wavelength range of 300–900 nm, and a Fourier transform infrared spectrometer (Tensor 27- Bruker) was employed for gathering information about the bands and chemical groups present. Moreover, the electrical parameters such as sheet resistance (R_s), carrier concentration (n) and mobility (μ) of ZnO:Ga thin films were determined from the measurements carried out in the Van der Pauw configuration [43].

3. Results and discussion

Fig. 1 shows the x-ray diffraction (XRD) patterns of various ZnO: Ga thin films. All these correspond to a wurtzite-type hexagonal structure similar to ZnO but with parameters $a = 3.254 \pm 0.002$ Å, $c = 5.208 \pm 0.002$ Å and (0001) preferred orientation. The average crystallite size determined from the Scherrer's formula [44] for films cast with all the precursor sols is found to be ~30 nm. The degree of preferred orientation data as deduced from the 0002 diffraction peak are 0.73, 0.64, and 0.46 for 1 at% Ga–ZnO prepared with sols S_M, S_E and S_{2M}, respectively [11]. The nature of preferred orientation of films is better understood in terms of texture coefficient Φ_C, defined by [45],

$$\Phi_C = [I(hkil)/I_o(hkil)] \Big/ \left[(1/m)\sum_m [I(h_m k_m i_m l_m)/I_o(h_m k_m i_m l_m)\right] \quad (1)$$

where I/I_o refers to the intensity ratio of the observed hkil reflection and standard polycrystalline sample and Σ_m $[I(h_m k_m i_m l_m)/I_o(h_m k_m i_m l_m)]$ is the sum of the intensity ratio of all the 'm' peaks present

Table 1
Summary of the optical transmittance (T%) and electrical resistivity (ρ) data on Ga–ZnO thin films, prepared by different methods on various substrates.

Method	Composition	Substrate (s)	T (%)	ρ (Ω-cm)
Pulsed laser deposition	2 wt% Ga_2O_3:ZnO [28]	Borosilicate glass	~84	3.90×10^{-4}
	5 wt% Ga_2O_3:ZnO [29]	Silica glass	~81–87	1.40×10^{-3}
Sputtering	4 at% Ga_2O_3:ZnO [30]	Polycarbonate	~80	7.80×10^{-4}
	2wt% Ga_2O_3:ZnO [31]	Si and amorphous silica	~85	9.85×10^{-4}
e-beam deposition	0.9–9.3 at% Ga–ZnO [32]	Sapphire	~80–90	2.48×10^{-4}
	2.5 at% Ga–ZnO [33]	Glass	~75	1.62×10^{-2}
Spray pyrolysis	3 at% Ga–ZnO [34]	Glass	~80	4.21×10^{-3}
	3 at% Ga–ZnO [35]	Glass	~90	6.80×10^{-3}
Atomic layer deposition	2.9 at% Ga–ZnO [36]	Sodalime glass	~80	2.30×10^{-4}
Chemical vapor deposition	Ga–ZnO [37]	Corning Glass	~93	7.50×10^{-4}
	Ga–ZnO [38]	Glass	~75–85	3.60×10^{-4}
Dip coating	3%wt Ga_2O_3:ZnO [39]	Corning Glass	~80	1.90×10^{-2}
	1 at% Ga–ZnO [40]	Glass	~72–82	5.12×10^{-1}
Spin coating	2 at% Ga–ZnO [41]	Glass	~91.5	2.80×10^{2}
	1.5 mol% Ga–ZnO [12]	Glass	~85	4.95×10^{-2}
	2 at% Ga–ZnO [42]	Alkali-free glass	~91	1.41×10^{2}
	1 at% Ga–ZnO [11]	Quartz	~75–80	9.00×10^{-3}