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Intermittent spray pyrolytic growth of nanocrystalline and highly oriented transparent conducting ZnO thin films: Effect of solution spray rate

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ABSTRACT

Uniformly distributed jet of fine droplets was created with control of spray rate (S_f) to deposit nanocrystalline ZnO thin films by spray pyrolysis technique. X-ray diffraction analysis indicated the polycrystalline film growth with most preferred orientation along *c*-axis [002] direction for $S_f \leqslant 4.5$ ml/min, above which films favored [101] direction. FE-SEM and AFM analysis revealed the uniform vertical growth of ZnO nano-rods for $S_f = 2.5$ ml/min and the film exhibited highest transmittance (95%) with lowest dark resistivity ($\sim 10^{-2}$ Ω-cm). The deposition rate increased due to rise in S_f. Alteration of crystallinity, grain size and film thickness with variation in S_f lead to variation of band-gap energy from 3.198 eV to 3.302 eV. ZnO film deposited at optimal $S_f = 2.5$ ml/min exhibited maximum electrical conductivity $\sigma = 78.8\ \Omega^{-1}\text{-cm}^{-1}$, minimum sheet resistance $R_s = 2.04 \times 10^2\ \Omega/\square$ and highest figure of merit $\Phi_{TC} = 2.93 \times 10^{-3}\ \Omega^{-1}$.

1. Introduction

Zinc Oxide (ZnO) is n-type, wide, direct band gap (E_g –3.27 eV), II–VI semiconductor materials with potential for optoelectronic, spintronics and photonics applications. It has high chemical and mechanical stability in hydrogen plasma, high optical transparency in the visible and near-infrared region with non toxicity and low cost of synthesis. These unique properties make ZnO an ideal transparent conducting oxide (TCO) substitute for SnO_2:In (indium tin oxide-ITO) and SnO_2:F (fluorine tin oxide – FTO). ZnO films are adaptable for a variety of potential applications such as sensors (chemical, optical and gas), photodetectors, liquid crystal displays, light-emitting diodes, ultraviolet laser, heat mirrors, optical modulators, surface acoustics wave filters and spintronics devices [1–12]. Moreover, ZnO films are used as an active channel material in high performance thin film transistors [12–15]. ZnO based TCO thin films form an integral part of low cost thin film solar cell (TFSC) technology. It can function as antireflection coating, window material, transparent electrode and active layer in heterojunction solar cells [15–20].

Various techniques have been used for synthesis of ZnO nanostructures, which include chemical vapor deposition (CVD) [21–23], sol–gel method [24], electrochemical deposition [25,26], sputter deposition [27,28], hydrothermal technique [29] and spray pyrolysis [30–43]. However; the chemical spray pyrolysis (CSP) technique has acquired considerable attention because it is simple, inexpensive, non vacuum, easy to commercialize and further capable to have large area deposition. The important CSP process parameters; which influence the film growth viz. deposition temperature (T_s), precursor composition and concentration etc. have been investigated and published [30–36]; however, there are very few reports on the effect of solution spray rate [38–40]. In CSP technique, spray rate (S_f) optimization is crucial step because it governs the preferred orientation, structural, optical and electrical properties [38].

In this study, we report spray rate (S_f) optimization to synthesize better quality nanocrystalline ZnO thin films by the pyrolytic decomposition of zinc acetate solution. S_f control achieved with peristaltic syringe pump provides sufficient time to enhance nucleation and re-crystallization, which is an important criterion for growth of device quality TCO films. The effect of S_f on the structural, optical and electrical properties of the deposited films was investigated. The crystal structure, orientation, surface morphology, optical and electrical properties of the deposited films were analyzed by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), ultraviolet–visible (UV–VIS) spectroscopy and Van der Pauw Hall measurement techniques. The variation of texture coefficient TC (hkl) and standard deviation (σ_g) was also studied in order to

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understand effect of S_f on growth mechanism. The transparency and conductivity of the ZnO thin films are the characteristics to be optimized for a transparent electrode. Moreover, the dependence of sheet resistance (R_s) and figure of merit (Φ_{TC}) on different S_f have also been investigated for possible applications of ZnO films such as TCO coatings and window layers in photovoltaic devices.

2. Experimental details

2.1. Film synthesis

The success of spray coating application depends on evenly distributing the spray's volume flux over the substrate area. The volume flux distribution can be described as the variation of spray density over a spray area. The solution spray rate S_f and air flow rate A_f, together decides the volume flux distribution and size of the spray droplet. In case of conventional spray guns with spray nozzle and solution reservoir, S_f depends on the air flow rate (A_f). In such reservoir based air driven spray guns, S_f increases with increase in A_f, which causes the large solution quantities to be sprayed in a short time. This hampers the nucleation process because of incomplete pyrolysis. Furthermore, higher spray rates (S_f) lead to decrease in T_s which influences the growth mechanism of ZnO thin films resulting in deposition of non-uniform and powdery films. However, higher A_f is essential for the formation of fine droplets which leads to synthesis of nanocrystalline thin films. In order to improve the atomization of precursor jet avoiding the formation of powdery films, we replaced conventional reservoir based spray gun with just a spray nozzle. The precursor solution was externally and intermittently fed to this nozzle using peristaltic syringe pump.

The Fig. 1(a)–(d) shows (a) the photograph of conventional glass spray gun with precursor reservoir, (b) schematic of new spray nozzle, (c) photograph of new spray gun and (d) its spray distribution. The new nozzle is an external-mix two fluid atomizer which features coaxial liquid (inner) and air (outer) inlets. The liquid directed through a nozzle during exit makes contact with the atomizing air initiating primary breakup. This new nozzle due to better control over spray rate (S_f) facilitated the formation of a solid conical spray pattern of small droplet size. It also enabled us to reduce drop down in T_s to a magnitude less than 1% and thus provided sufficient time for nucleation avoiding the formation of powdery thin films. However, the films deposited for higher spray rates ($S_f \geqslant 4.5$ ml/min) observed to have a propensity of powdery formation. Hence, the S_f was fine tuned with small steps in the range 1.5–3.5 ml/min.

ZnO films were synthesized by spray pyrolysis of 0.4 M, 50 ml solution of (A.R. grade) zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) in ethanol on soda lime glass substrates for different S_f. The 0.4 M concentration allows higher deposition rates during CSP deposition. Water is the best oxidizing agent, however it was not used as a solvent because (at $T_s = 450$ °C) evaporation of water of crystallization from zinc acetate dihydrate results in complete oxidation [44]. On the other hand ethanol due to its high volatility facilitates fast conversion of precursor mist into vapor during spray pyrolytic deposition. The solution was pumped to spray nozzle with fine flow adjustment at a desired rate, using peristaltic syringe pump (Make: Universal, Model: UM05). This was done to avoid control of A_f on S_f and both A_f as well as S_f were optimized independently [37]. The soda lime glass substrates (size: 25 mm × 75 mm) were chemically and ultrasonically cleaned before deposition. In all depositions the precursor solution was sprayed onto the hot substrate ($T_s = 450$ °C optimized [37,43]) which was at a distance of 30 cm from the spray nozzle. The substrate heater used was 1.5 cm thick stainless steel (SUS 316L grade) plate with 3 kW heater (Make: Baker, UK) attached at its base. The T_s was maintained constant using an electronic temperature controller unit outfitted with Cromel–Alumel thermocouple located under the substrate. Properly insulated housing was used around the substrate to ensure that the deposition temperature remained constant during film synthesis. Ultra filtered compressed air was used as a carrier gas at a constant air pressure (8 kg/cm^2) at nozzle during all depositions. The air flow rate was kept constant (15 m^3/min – optimized [37]) for all depositions. At the end of deposition process films were kept on the heater at the deposition temperature for 10 min in order to provide sufficient time and temperature for recrystallization. The films were then allowed to cool to ambient temperature before they were taken off for further characterization.

2.2. Film characterization

The Bruker make (Model D8 – Advanced) low grazing angle XRD system was used to study the structural properties of the ZnO thin films. Surface morphology was investigated using FE-SEM and AFM technique. The spectral transmittance and absorbance were measured with a Shimadzu spectrophotometer (model UV-1650 – PC) in the wavelength range of 350–1100 nm. The thickness of the films was calculated from the interference observed in the visible region using the method developed by Manifacier et al. [45]. The electrical properties of the film were measured by Hall Effect arrangement with the Van der Pauw's four point probe geometry at room temperature and atmospheric pressure assuming homogenous conduction throughout the depth of the film. The four ohmic contacts for Hall electrical measurements were made using the commercially available silver conductive paint (Make: RS Components, UK).

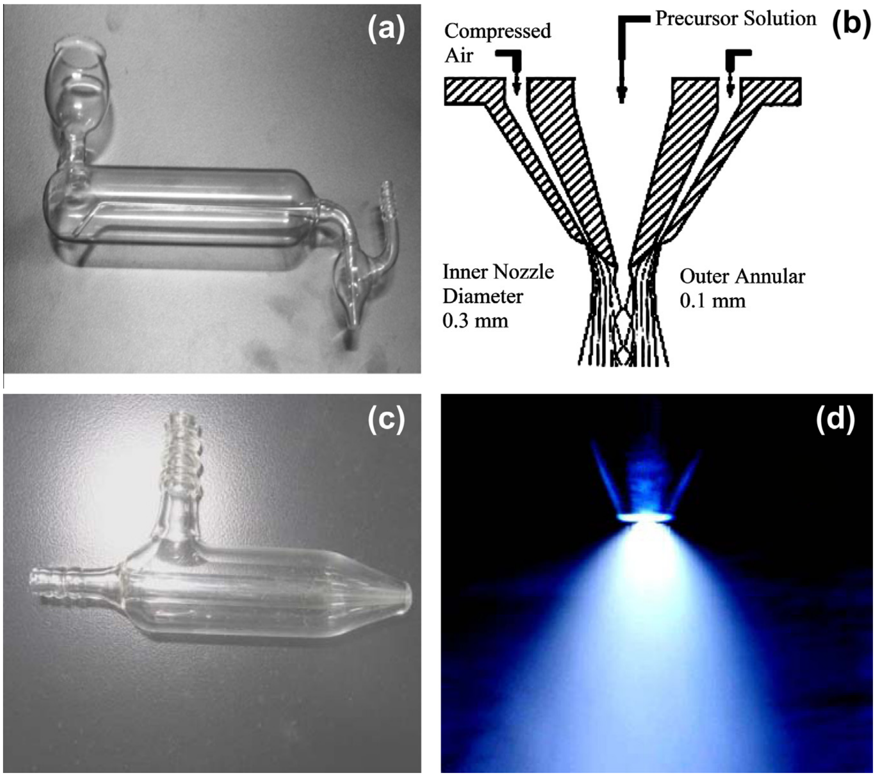

Fig. 1. (a) Photograph of conventional spray gun with precursor reservoir, (b) schematic of new spray nozzle, (c) photograph of new spray gun and (d) photograph of spray distribution of new spray nozzle.