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Effect of zinc nitrate concentration on structural and optical properties of ZnO thin films deposited by Spray Plasma device

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ABSTRACT

ZnO thin films were deposited on glass substrate at 200 °C by Spray Plasma device using an aqueous solution of zinc nitrate. In this technique, the energy required for chemical transformations of precursors to zinc oxide is provided by plasma electrons rather than heat transfer. The effect of solution concentration on the structural and optical properties of the deposited films was investigated. X-ray diffraction results show that nanostructured polycrystalline films are formed with the typical wurtzite structure. The c-axis orientation growth depends highly on the initial concentration of precursor. Williamson–Hall calculations, atomic force and transmission electron microscopy images show an increase of grain size with an increase in molar concentration from 0.1 to 0.4 M. The transmittance decreases from 85 to 50% with an increase of the molar concentration.

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1. Introduction

Because of its excellent physical properties and potential technological applications [1], zinc oxide (ZnO) has recently attracted a lot of attention. ZnO is a semiconductor with a wide and direct band gap (~3.3 eV at room temperature), which covers the insufficiently explored UV region of the optical spectrum, similarly to ZnS (~3.6 eV) and GaN (~3.42 eV). It has a wurtzite crystal structure and a high exciton binding energy (~60 meV). Improvement of its electrical and optical properties can be achieved by n-type doping with group III dopants [2] such as B, Ga, Al or In, which can be promising for solar cells [3], light emitting diodes [4,5], touchscreen [6] applications, etc.

Synthesis methods, like sputtering [2,7], pulsed laser deposition [8,9], metal organic chemical vapor deposition [10,11], and spray pyrolysis [12,13], have been extensively used to obtain high quality ZnO thin films. Among these methods, the spray techniques, like spray pyrolysis or spray chemical vapor deposition [14–16], have several advantages, such as simplicity, safety and low cost. Zinc acetate [17], zinc chloride [18] and zinc nitrate [19] – dissolved in water or alcohols – are mostly used as precursors in spray techniques. Many authors [19,20] have described the preparation and characterization of ZnO thin films by spray techniques. The influence of operating parameters, such as the substrate temperature [20,21] and the nature of the precursor solution [18,22], on the properties of the deposited films has been widely investigated, but few studies on the effect of the precursor solution concentration (especially zinc nitrate concentration) on the structural and the optical properties of ZnO thin films have been carried out.

We have demonstrated in previous works the advantages of Spray Plasma technique, which combines the advantages of spray techniques and the reactivity of a non-thermal plasma atmosphere in Ar/O_2 [23]. The role of reactive plasma species, i.e. O and OH radicals in the transformation of nitrates to perovskite oxide in this technique has been investigated [23]. A global (volume-averaged) model of the $Ar–O_2$ low-pressure radio-frequency (RF) inductive discharge used for the plasma spray deposition has been developed to estimate the equilibrium discharge parameters, such as the electron temperature, the species densities and fluxes [24]. The atomic oxygen density is around 10^{19} m^{-3} and the dominant ion is Ar^+ in the pressure and O_2 fraction ranges investigated. The electron temperature is around 2.8 eV and the corresponding electronegativity is very low (a few percent) under our typical conditions. The model shows that the ratio of the reactive species flux (Γ_O) to the total positive ion flux ($\Gamma_{Ar^+} + \Gamma_{O^+} + \Gamma_{O_2^+}$) decreases with plasma power while it increases with O_2 fraction and pressure [24].

In this paper, we report the effect of zinc nitrate precursor solution concentration on the structural and optical properties of ZnO thin films deposited on glass substrate at 200 °C, under non-equilibrium plasma conditions. Structural and morphological properties were investigated with X-ray diffraction (XRD), atomic force microscopy (AFM) and transmission electron microscopy (TEM). Optical properties were analyzed using UV–Vis spectroscopy.

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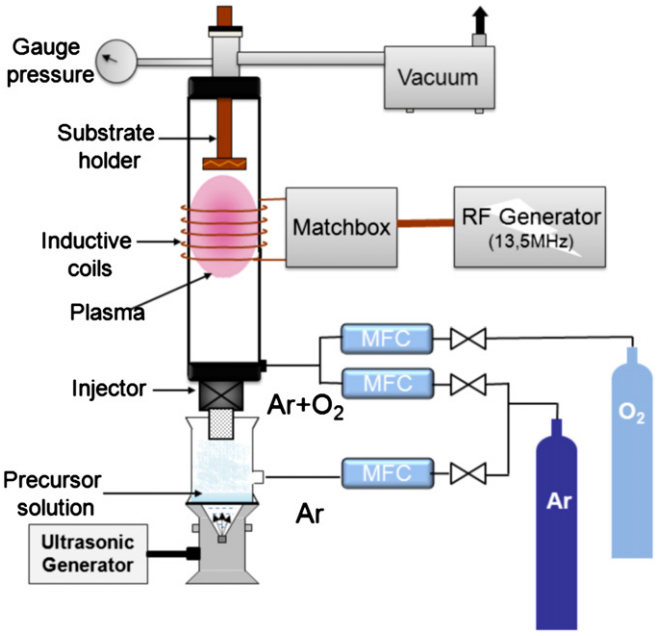

Fig. 1. Experimental setup.

2. Experimental details

ZnO thin films were deposited on glass substrate by Spray Plasma process using an aqueous solution of $Zn(NO_3)_2$ (Sigma-Aldrich, 99.999%) dissolved in bi-distilled water. Fine droplets of the starting solution are produced using an ultrasonic aerosol generator and then are injected in a quartz tubular low pressure plasma reactor using argon as a carrier gas. The experimental setup is presented in Fig. 1. As mentioned in the introduction, the discharge is a RF inductively coupled argon/oxygen plasma (13.56 MHz) and the droplets undergo both the reactivity and the rapid evaporation of water. The reactive plasma species and the OH and O radicals formed by inelastic collisions of water with electrons generated in the plasma, lead to the transformation of nitrates to oxide on the surface of the substrate.

The plasma gas flow was fixed at 200 mL/min, the RF power at 300 W and the substrate temperature at 200 °C. The experimental setup and the other experimental details are explained elsewhere [25,26]. In order to investigate the effect of zinc nitrate molarity on structural and optical properties of the deposited films, we use four starting solution concentrations: 0.1, 0.2, 0.3 and 0.4 M. All other parameters are kept constant. The crystalline structure properties of ZnO films are characterized by X-ray diffraction (XRD) measurement (Inel XRG 3000) using CuKα radiation. The surface morphology of the grown films is analyzed by AFM in tapping mode (Nanoscope III from Digital Instruments). The average size of the crystalline grains and strain in the films are estimated using the Williamson–Hall method [27]:

$$\beta\cos\theta = \frac{k\lambda}{D} + 4\varepsilon\sin\theta \quad (1)$$

where D is the actual particle size, ε is the strain (or micro strain), k is the spherical factor ($k = 0.9$), β is the full width at half maximum (FWHM) in radians, λ is the diffraction angle and θ is the peak position.

The strain in the films can be calculated from the slope of ($\beta\cos\theta$) versus ($\sin\theta$) plot and the particle size in the film can be estimated from the y-intercept of the plot. An example of this kind of plot is presented in Fig. 2. We also use high resolution transmission electron microscopy (HR-TEM) to estimate grain size by image analysis done with

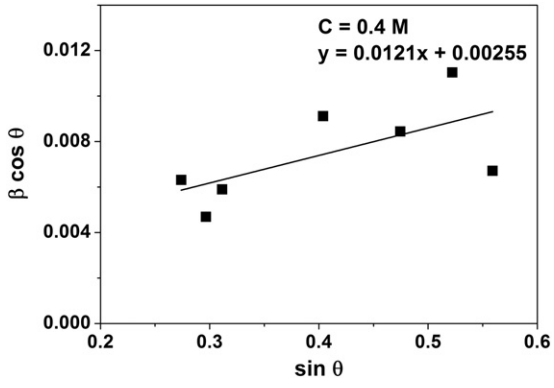

Fig. 2. Williamson–Hall plot for the ZnO film deposited with 0.4 M $Zn(NO_3)_2$ solution concentration. The strain is extracted from the slope and the crystallite size is extracted from the y-intercept of the fit.

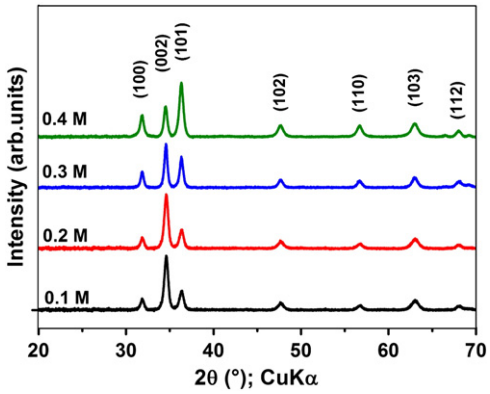

Fig. 3. XRD patterns of ZnO films prepared using various $Zn(NO_3)_2$ solution concentrations, under an argon plasma (Ar flux = 200 mL/min, RF power = 300 W) and a substrate temperature of 200 °C.

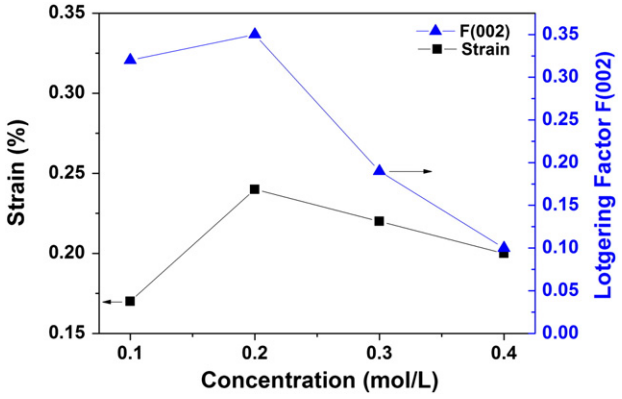

Fig. 4. (002) orientation degree $F(002)$ and strain of ZnO films as a function of the $Zn(NO_3)_2$ solution concentration.

Table 1
Average crystallite size from XRD (D), FWHM of the (002) peak, strain (ε), Lotgering factor for the 002 orientation, Rms, thickness and average crystallite size from TEM images of the deposited films as a function of the zinc nitrate solution concentration.

C (mol/L)	D (nm) XRD	FWHM (°)	Strain ε (%)	$F(002)$	Rms (nm)	Thickness (μm)	TEM average grain size (nm)
0.1	29.7	0.4415	0.17	0.10	12.7	0.896	8
0.2	35.4	0.4083	0.24	0.23	27.8	1.099	–
0.3	54.0	0.3499	0.22	0.16	23.4	1.381	–
0.4	56.1	0.3446	0.20	0.06	16.1	2.957	32

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