Influence of Deposition Parameters on the Optical and Morphological Properties of ZnO Thin Films Deposited by the Electrospray Method

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Abstract. Electrospray method with vertical set-up is used for deposition of ZnO films with thicknesses in the range 100 – 300 nm. Substrate temperature is varied from 150 ^{o}C to 250^{o}C with home-made heating plate enabling annealing in controlled manner. The emitter-collector distance is kept constant (6 cm) while the voltage is set to 16.5, 18 and 20 keV. Two types of substrates are used – semiconducting (silicon wafer) and conducting one (chromium film deposited on glass substrate) and two emitters with different diameters are implemented. The topography, roughness and optical quality of deposited films are monitored through optical profiling and atomic force microscope measurements; the structure is studied by X-ray diffraction, while optical properties are evaluated by ellipsometric and photoluminescence measurements. The relationship between deposition parameters and films properties is revealed and discussed.

Keywords: ZnO films, electrospray, sol-gel, optical properties.

1. INTRODUCTION

ZnO is a wide band semiconductor with large exciton binding energy, transparency in VIS and NIR ranges, low resistivity, biocompatibility, low cost and long-term stability. Due to its properties, ZnO gains increasing interest and has been already used in the field of biosensors, optical gas sensors, optoelectronics, transducers and resonators, integrated optical devices (Dikovska et al. 2007; Sun et al., 2006; Klingshirn, 2007) etc. Besides, ZnO thin films are regarded as a cheaper alternative to the widely used ITO for optically transparent electrodes in flat panel displays or solar cells (Hirao et al., 2007).

Different physical and chemical methods of ZnO films deposition have already been implemented such as rf sputtering, pulsed laser deposition, plasma enhanced chemical vapor deposition, spray pyrolysis, atomic layer deposition etc. (Dikovska et al., 2007; Kitova et al., 2010; Dimitrov et al., 2014; Blagoev et al., 2016),

Sol–gel method is an efficient method for preparation of ZnO where molecular precursors are transformed into oxide networks by polycondensation and hydrolysis processes. Thin films are prepared by spin or dip-coating and annealed at high temperatures (usually more than 400 ^{o}C) in order extra constituents to be removed.

Besides, sol-gel method could be successfully combined with electrospray method for film deposition having advantages of simple setup, low cost and easy control of morphology and stoichiometry. Electrostatic set-ups with horizontal (Hosseinmardi et al., 2012) and vertical configurations (Hwang et al., 2007) have already been used and amorphous or crystalline films with diverse properties have been deposited using different deposition parameters. Recently we have demonstrated successful application of ZnO films using electrospray deposition method (Marinov et al., 2016). It was shown that the refractive index of the films increases with the

voltage in the range 9-14 kV, while the roughness of the films and the surface morphology are slightly influenced. Besides after high temperature postannealing (550 ^{o}C, 2h) a lot of defects are generated in the films (Marinov et al., 2016).

In this paper we studied ZnO thin films with thicknesses in the range 100 – 300 nm deposited by electrospraying at voltages of 16.5, 18 and 20 kV, substrate temperature of 150, 200 and 250 ^{o}C and two types of substrates – conductive (Cr film) and semi-conductive (Si-substrate). The relationship between deposition parameters and films properties is revealed and discussed.

2. EXPERIMENTAL DETAILS

The solution for electrospraying was prepared by dissolving of 0.115 g of zinc acetate dehydrate in 4 ml mixture of ethanol and deionized H_2O with volume ratios of 4.4 and 7. Two drops of acetic acid were added as stabilizer and the solution was stirred for 2 hours and aged for 24 h at room temperature. All chemicals (Sigma Aldrich) were of analytical reagent grades and used without further purification.

Thin ZnO films with thickness in the range 100 – 300 nm were deposited using an electrostatic set-up presented in (Fig. 1). The emitter of the electrospraying set-up was a 5 ml syringe with stainless steel needles of outer to inner diameters of 508 to 241 microns and 406 to 191 microns and the collector is a stainless steel-duralumin plate put on the heater with thermo-controller and grounded in a save way. The distance between the emitter and collector was kept at 6 cm and a high voltage of 16.5, 18 and 20 kV was applied via a DC power supply (Applied Kilovolts, UK). The substrate temperature was varied from 150 to 250 ^{o}C, while the flow rate is fixed at 0.013 ml.min^{-1}.

The surface morphology and roughness of the films were characterized by Atomic Force Microscopy (MFP-3D, Asylum Research, Oxford Instruments), optical profiler (Zeta-20, Zeta Instruments) and scanning electron microscope (Philips 515, 30 kV accelerating voltage). The crystal status of the films was confirmed by X-ray diffraction measurements (Philips 1710).

The optical properties (refractive index (*n*) and extinction coefficient (*k*)) and photoluminescence spectra of the films at room temperature were determined using ellipsometric measurements (UVISEL 2, Horiba JobinYvon) and spectrofluorometer FluoroLog3-22 (Horiba JobinYvon), respectively.

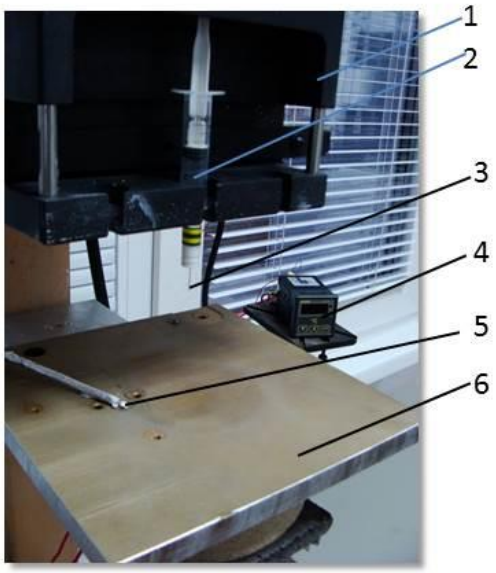

Fig. 1 Electrospraying set-up with vertical configuration consisting of syringe pump (1), 5 ml syringe with ZnO precursor (2), emitter (3), temperature control (4), thermo coupler (5) and collector with heater (6).

3. RESULTS AND DISCUSSIONS

The influence of voltage polarity is demonstrated in Fig. 2. From the pictures of ZnO films deposited onto silicon substrate using 18 kV and both type of polarity is seen that in the case of negative polarity the thickness distribution is more symmetrical as compared to positive polarity, but the gradient in thickness is stronger. For the films deposited with positive polarity the film thickness varies in the range 120 -320 nm, while in the opposite case the variations are substantially higher – from 120 to 540 nm

(Figs. 2c and 2d). The reason is the poorer spraying in the former case that might be due to the predominantly positively charged ions in the solution. As a result the surface of the films deposited by negative voltage contains a lot of traces of droplets that increase the surface roughness. Because of the strong inhomogeneity in the thickness across the surface and increased roughness of the film deposited at negative voltages in our further experiments we use only positive polarity for electrospraying.

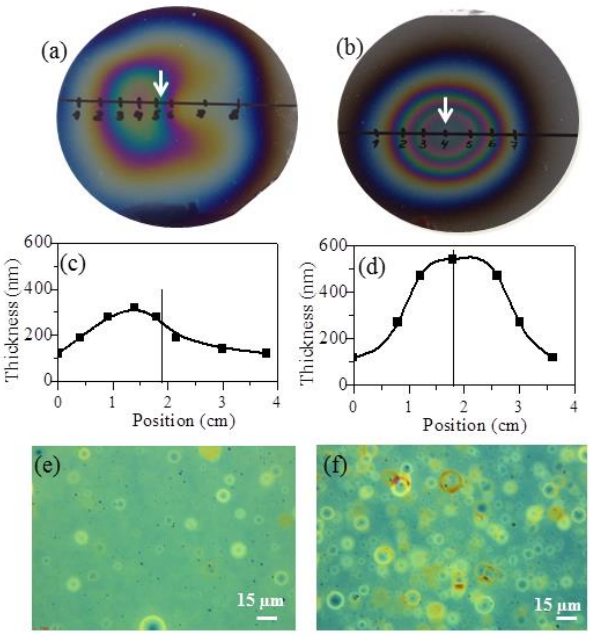

Fig. 2 Pictures of ZnO films deposited on silicon substrate at 6 cm (a, b), the thickness distribution along the substrate (c, d) and surface morphology of the films (e, f) when voltage of 18 kV with positive (a, c, e) and negative (b, d, f) polarity is used. The arrows spot the position of the emitter.

Our additional studies (not shown here) have shown that smoother films are obtained when using emitter with higher diameter. Thus, for emitter with inner diameter of 241 microns the rms roughness of the films with thickness of 250 nm is 35 nm, while if 191 microns emitter is used the rms roughness is 45 nm. The possible reason of increased roughness could be the higher flow rate when thinner emitter is used that may lead to poorer spraying.

In order to study the influence of the conductivity of the substrate on the film properties we used two types of substrates - semiconductive Si-substrate and conductive chromium film. Fig. 3 presents the optical micrographs of ZnO film with thickness of 200 nm electrosprayed at 18 kV on both types of substrates. All other parameters are kept the same: distance between emitter and collector is 6 cm and substrate temperature is 200 ^{o}C.

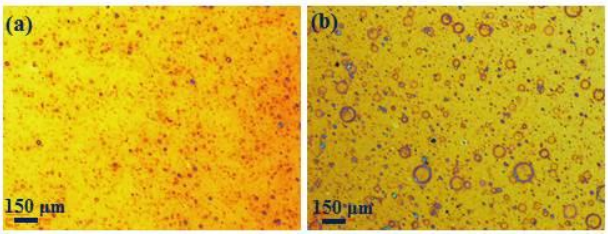

Fig. 3 Optical profiler pictures of ZnO with thickness of 200 nm deposited at 18 kV, 6 cm on silicon (a) and chromium (b) substrates.

The different surface morphology is well seen from fig. 3. In the case of conductive substrate (fig. 3(b)) a lot of formations with donut shape and different diameters from 30 to 120 microns are formed on the surface. In the case of silicon substrate similar formations also exist but their number and diameters are considerably smaller – the size varies from 7 to 30 microns. In the case of a conductive substrate, the electrical charge of the drops is neutralized and uncharged "drops" remain on the surface. In the case of silicon, the charge neutralization is embarrassed due to low conductivity and the drop stay charged on the surface for much longer time. When a new drop comes from the gas phase a repulsion will occur and the drop will not land on top of the previous drop. In this way smoother films are obtained in the case of silicon substrate.

The next step of our investigation concerns the substrate temperature during electrospray deposition. Our experiments related to deposition on unheated substrates have shown that non-transparent and heavily scattered films consisting of isolated islands with sizes in the micrometric range are formed. Two

possible reasons exists for explanation: i) the mobility of species on cold substrate surface is significantly lower as compared to the one on hot substrate where the species probably have enough energy to move across the surface and build continuous films; ii) the low substrate temperature does not allow the decomposition of metal organic salt to take place and the formed film contains residues that deteriorate its optical quality.

The surface morphology and X-ray diffraction spectra of ZnO films with thickness of 170 nm are shown in Fig. 4. The films are deposited on silicon substrate at a voltage of 18 kV and different substrate temperatures (150, 200 and 250 ^{o}C).

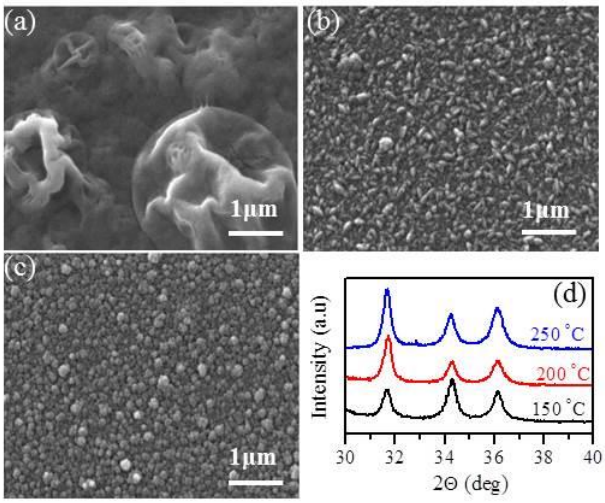

Fig. 4 SEM images of ZnO thin film with thickness of 170 nm deposited by electrospray method (18 keV, 6 cm) at substrate temperature of 150 ^{o}C (a), 200 ^{o}C (b) and 250 ^{o}C (c); XRD spectra of films deposited at different substrate temperatures (d).

It is seen that the surface morphology of films deposited at 150^{o}C differ significantly from the two others: they comprise circular formations with sizes from 1 to 3 microns and worm-like interior, while the films at higher substrate temperature consist of small grains with sizes in the range 70 – 170 nm. With increasing the substrate temperature from 200 ^{o}C to 250 ^{o}C the shape of the grains slightly changes from elongated to oval. XRD spectra of the films show three prominent peaks at 31.8^{o}, 34.43^{o} and 36.3^{o} and also few peaks with low intensities (not shown in the figure). At all studied substrate temperatures the ZnO films are polycrystalline in nature and exhibit hexagonal wurtzite structure (Komaraiah et al., 2016). The crystallite size has been calculated to be 13 nm for films deposited at 150 ^{o}C and 12 nm for films at higher substrate temperature. The size was evaluated from full width at half maximum (FWHM) of the strongest diffraction peak using Debye-Scherrer's formula (Komaraiah et al., 2016). It is interesting to note that if we used Zn sol with increased amount of water, for example ethanol to water ratio of 4.4 instead of 7, an additional peak in XRD spectra appears at 32.85^{o} that cannot be identified as ZnO. The possible reason is formation of zinc hydroxides but additional measurements have to be performed for confirmation.

The next step of our investigation concerns the properties dependence on film thickness. Fig. 5 (a) presents a comparison of photo-luminescence spectra at room temperature and excitation wavelength of 335 nm of ZnO films with thicknesses in the range 70-240 nm. Two emission peaks are observed in the spectra: a relatively narrow UV peak centered at 377 nm which is ascribed to the inter-band radiation recombination of photo-generated electrons and holes (Kim et al., 2005) and a broad green emission peak corresponding to the transition between band edges and the local levels in the bandgap. The last are formed by some defects in ZnO (Lin et al., 2001), for example zinc and oxygen vacancies, interstitial zinc, interstitial oxygen, etc. (Vanheusden et al., 2010; Kim et al., 2005). The relative intensity of both peaks as a function of film thickness is presented as an inset in Fig. 5 (a). It is seen that the intensity ratio of UV and VIS peaks increases with thickness indicating a decrease of number of the defects in the crystal structure of the films.

AFM measurements of ZnO films with different thicknesses have revealed similar surface morphology of the films. Fig. 5(b) presents a typical example of the surface. It

comprises small grains with approximate size between 50 and 350 nm and height between 15 and 60 nm, homogeneously dispersed across the surface.

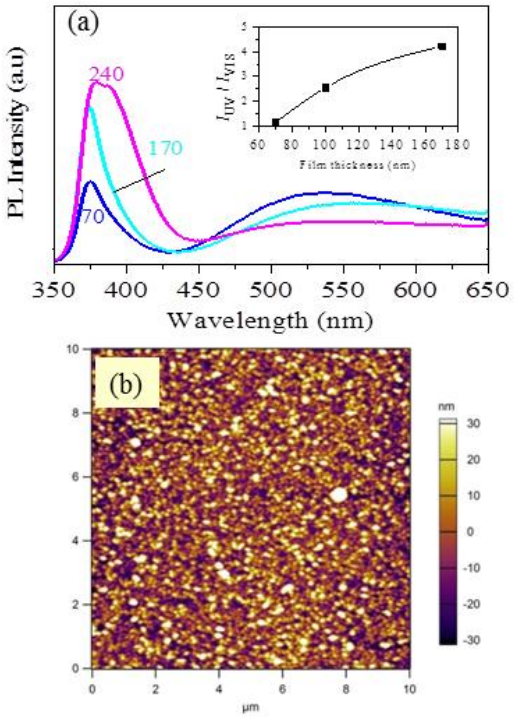

Fig. 5 Photoluminescence spectra of ZnO films with different thickness and intensity ratio of the peaks in the UV and VIS range as an inset (a); AFM picture of the surface of ZnO film with thickness of 170 nm (b).

Refractive index (n) and extinction coefficient (k) (the so called optical constants) along with film thickness (d) of ZnO thin films were determined through ellipsometric measurements and consequent modelling using DeltaPsi2 commercial software (Horiba-Jobin Yvon). The measured parameters are the ellipsometric angles Ψ and Δ that are defined as:

$$\tan(\Psi) = \frac{|r_p|}{|r_s|},\ 0^o \le \Psi \le 90^o \qquad (1)$$

$$\Delta = \delta_p - \delta_s,\ 0^o \le \Delta \le 360^o \qquad (2)$$

where r_p, r_s and δ_p, δ_s are the amplitude and phases of reflection coefficient for p- and s-polarized light, respectively. The measurements were performed at incident angle 70° in the spectral range from 200 nm to 800 nm and increment of 1 nm.

To extract the parameters of interest (n, k and d) a physical model of the studied film has to be set up that allows a theoretical calculation of Ψ and Δ. The unknown parameters are derived by non-linear minimization of the difference between the measured and calculated ellipsometric functions. In our studies we use three-layered model that comprises thin (3 nm) native oxide on the silicon substrate, ZnO film and top layer consisting 50 % voids.

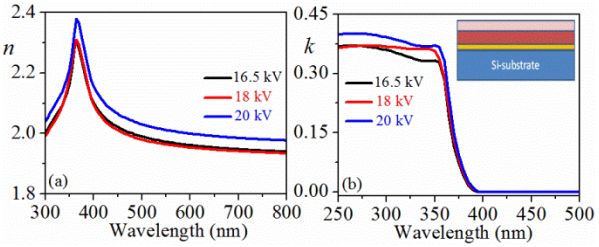

Fig. 6 Dispersion curves of refractive index (n) and extinction coefficient (k) of ZnO thin films with thickness of 190 nm deposited at different voltages denoted on the figure. As an inset - three-layered model used for modelling of measured ellipsometric data.

The calculated dispersion curves of n and k as a function of voltage applied during film deposition are shown in Fig. 6. For wavelength higher than 400 nm all films are transparent (k=0) and refractive index exhibit normal dispersion (n decreases with wavelength). At higher energies the absorption in the film substantially increases reaching the highest value of k for the film deposited at 20 kV. Refractive index for films at 16.5 and 18 kV are almost the same (n at 600 nm is 1.961 and 1.954, respectively) and increases to 2.000 for 20 kV indicating a densification of the film at higher deposition voltage. It is interesting to note that the calculated thickness of the top layer is 30 nm that matches the rms roughness of the films measured by the optical profiler. The calculated optical band gap is 3.31 eV and is independent of applied voltage.

CONCLUSIONS

The successful deposition of polycrystalline ZnO films using electrospray method is demonstrated. It is revealed that in order to obtain films with smaller rms roughness it is preferable to apply voltage with positive polarity, use emitter with bigger inner diameter and substrate with lower conductivity. Besides, films with smaller grain size are obtained at substrate temperature of 200 and 250 ^{o}C as compared to the case of films at 150 ^{o}C, but the crystallites size (around 12 nm) is independent of substrate temperature. Photoluminescence measurements indicate an enhancement of the crystal structure of the films and a decrease in the grating defects for thicker films, while optical measurements show a densification of the films with applied voltage.

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