Solution deposition of ZnO thin films

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Abstract. A solution deposition technique is investigated as an approach for formation of nanostructured ZnO films with tailored geometric shape and aspect ratio, electrical conductivity, and high optical transmittance. Having in mind thermodynamic particulars of ZnO precipitation from aqueous solutions, we show deposition of thin films of intrinsic ZnO with well-defined hexagonal wurtzite structure and with high optical transmission in the visible region. Deposition of doped layers of Al:ZnO with aluminium concentration up to 3 wt% does not cause degradation of the wurtzite structure and sheet resistance of the films is near 8.0*10² Ω/□. After applying thermal annealing, the absorption edge gets sharper and optical band gap is found to be near 3.26 eV for direct transitions. Addition of the ethanol in the aqueous deposition solution leads to formation of ZnO nanostructured films with trigonal configuration.

1. Introduction

ZnO is a popular material with wide applications depending on the structure, composition, and specific shape orientation [1]. It is a wide bandgap semiconductor with near 3.40 eV direct bandgap crystallizing typically in cubic (Zincblende) or hexagonal (Wurtzite) forms. The last one poses near ideal value of crystal parameters for hexagonal cell and because of its higher stability, ZnO crystallizes preferentially in Wurtzite rather than Zincblende structure [2]. The ZnO can form ordered nanostructures of nanowires or nanoplates in preferential crystallization along the c-axis or along the a-axis [3]. The ZnO arrays are used in numerous technologically important devices such as gas sensors [4], catalysts [5] and solar cells [6]. In photovoltaics, they can be used as passive, surface light trapping elements in Si-based solar cells [7], buffered or active transparent n-type electrode [8] or as mesomeric Electron-Transporting Material (ETM) in Organic Solar Cells (OSC) [9]. There are numerous chemical approaches to form ZnO thin films with specific composition, structure and orientation, including hydrothermal [10], electrodeposition [11] and a few efforts on Chemical Bath Deposition (CBD) [12]. Formation of ZnO in aqueous solutions passes through intermediate Zn(OH)₂, known in several different forms and only ε – phase (Wulfingite) is recognized as stable mineral in nature [13]. The overall reaction of formation of the compound is:

\[ \text{Zn(OH)}_2 \rightarrow \text{ZnO + H}_2\text{O}. \]  (1)
The Free energy of formation of the ZnO by reaction 1 is as low as $\Delta G_{298}^{\circ} = -1.13$ kJ/mol [13] and reaction can go on further at standard conditions, but very small deviations in temperature or the activity of water can change the reaction route. Addition of ions of III group metals, such as $\text{Al}^{3+}$, $\text{Ga}^{3+}$ or $\text{In}^{3+}$ to the solution places them in the crystal cell as dopants and improves the conductivity and optical properties [14].

In this work, based on deductions for reaction 1 we present solution process for formation of thin films ZnO and approaches for modification of the composition and shape of the deposited nanoparticles.

2. Experimental

Solution was composed by precursors without additional treatments – $\text{Zn(CH}_3\text{COO)}_2$, 30 % $\text{NH}_3$, $\text{Al(NO}_3)_3$ and $\text{NaOH}$. Thin films ZnO were deposited in 100 ml solution of $\text{Zn(CH}_3\text{COO)}_2$ and $\text{NH}_3$ in controlled temperature. In order to get deposition of doped Al:ZnO layers, stock solution of 0.1 M $\text{Al(NO}_3)_3$ was added to it. Additionally, stock of 96 % ethanol was added in concentration of 25 w% to modify the water activity. The ZnO layers were deposited on soda lime glass substrates in size of 25 x 25 mm or mono – Si. The thickness is measured by profilometer TelyStep and by ellipsometry. Optic properties were measured by UV-Vis-NIR spectrophotometer Cary 5E (VARIAN). X-ray Diffractometer XRD Brucker D8 advance spectrometer with Cu Kα radiation was used for thin films ZnO structural characterization in the interval 10 – 80° $\theta / 2\theta$ in steps of 0.02° $2\theta$ with 8s step time. Routine scanning electron microscopy and energy dispersive X-ray analysis (EDAX) was performed on Hitachi TM 1000. Fine film morphology was examined by Zeiss ULTRA 55 at an accelerating voltage 1.74 kV.

3. Results and discussion

Chemical bath deposition process was investigated in different concentrations of zinc ions $[\text{Zn}^{2+}]$ – (0.1 M, 0.075 M and 0.05 M). At constant deposition temperature the decrease of $[\text{Zn}^{2+}]$ results in formation of more uniform and transparent ZnO layers. The concentration of 0.075 M $\text{Zn}^{2+}$ was found to be optimal regarding overall time of deposition about 10 – 100 min and temperatures 50 – 80°C.

Figure 1 presents the dependences of thickness of the deposited films on time in solution of 0.075 M $[\text{Zn}^{2+}]$ in aqueous solution and modified solvent of water with 25 wt% Ethanol. As seen from the picture, dependences are linear and speed of deposition of ZnO films in solution with Ethanol is slower than the deposition speed in plain aqueous solution.

Figure 2 shows dependence in logarithmic scale of deposition rate of ZnO films on temperature $1/T$. Reaction of deposition is thermally activated and in the interval of 55 – 85 °C follows the Arrhenius equation. At higher temperature, near 95 °C, the dependence is not followed due to the volatility of

![Figure 1](image1.png)  
**Figure 1.** Dependence of the thickness of ZnO films on deposition time in aqueous – a and in 25 % Ethanol solvent, 75 mM $[\text{Zn}^{2+}]$.

![Figure 2](image2.png)  
**Figure 2.** Temperature dependence of CBD rate of ZnO thin films on soda lime glass substrates.
ammonia at elevated temperatures aqueous solutions. Value of activation energy \( E_a = 90.8 \) J/mol is determined from the linear slope.

![Figure 3](image)

**Figure 3.** X-ray spectra of: a) pure ZnO and b) Al:ZnO layers.

Addition of aluminium ions to the solution for deposition of ZnO resulted in incorporation of Al in the deposits. The set of experiments showed that uniform and dense layers could be deposited at comparatively low temperatures near and under 50 °C. X-ray diffractometry was used to investigate the structural properties of CBD ZnO thin films deposited on In-SnO\(_2\) (ITO) covered glass substrates. On Figure 3 are shown diffractograms of ZnO (Figure 3.a) and Al:ZnO (Figure 3.b) obtained in the experiments. In the X-ray spectra presented, characteristic reflections for ZnO and other compounds are not identified. The most remarkable peaks for diffraction by faces \([100]\), \([002]\) and \([101]\), typical for Wurtzite structure of ZnO are manifested at 32°, 34.2° and 36° 2\(\Theta\) (CCPDPDF 00-005-0664). In addition to this, minorities at 47.5° – [102]; 56.5° – [110]; 63° – [103]; 66° – [200], 68° – [112], 69° – [201] are seen respectively. With asterisks (*) are marked reflexes from substrate. It can be inferred that the doped Al:ZnO layers crystallize in the same orientation as undoped. The incorporation of Aluminum near 3 wt% does not influence remarkably the structure of the Wurtzite which is not the case for concentrations of Al over 7 wt%, which is in agreement with [15]. Sheet resistance of the Al:ZnO layers with 2.5 wt% Al, proportional value of the [Al\(^{3+}\)] in deposition solution, measured by the four – point method, is about 8*10\(^2\) \(\Omega/\square\).

![Figure 4](image)

**Figure 4.** Optical spectra of doped films Al:ZnO

![Figure 5](image)

**Figure 5.** Scheme for calculation of bandgap
The optical spectra of transmission and reflection of thin films ZnO were investigated for determination of the absorption coefficient $\alpha$. Linear extrapolation of curve $\alpha^2$ against photon energy $h\nu$ (assuming direct transitions) allows to define the bandgap (Eg) of the ZnO thin films. Figure 4 presents sample of transmittance spectra of doped Al:ZnO thin films and Figure 5 presents the correlation to determine the energy band gap - Eg.

Deposition at lower temperatures layers (50 °C) shows wider bandgap, typical for doped samples. At higher deposition temperatures (80 °C) the calculated bandgap of Al:ZnO thin films leans towards the value of pure ZnO. All data is summarized in Table.1.

Table.1. Optical bandgap of as-deposited ZnO and Al:ZnO films deposited at different temperatures and annealed at 400 °C for 1 hour.

| Temp | 50 | 60 | 70 | 80 |
|------|----|----|----|----|
| Eg - ZnO | 3.7 eV | 3.45 | 3.38 | 3.3 eV |
| Eg – Al:ZnO | 3.6 | 3.50 | 3.50 | 3.48 |

As-deposited layers were annealed for dehydration and recrystalization. After thermal treatments, as is shown in Figure 6, the region of strong absorption gets steeper which could be interpreted as an indication of improving the structural arrangement. Similar effects were presented in previous investigations [16].

Figure 6. Transmittance spectra of CBD Al:ZnO thin films before and after annealing in air at 150 °C and 400 °C.

Figure 7. Transmittance spectra of ZnO thin films, deposited at 0.05 M and 0.075 M [Zn2+] in aqueous and modified with 25 wt% Ethanol solvent.

When Ethanol is added to the deposition solution, the rate of deposition decreases as seen in (Figure 1). Figure 7 presents transmittance spectra of ZnO layers deposited in aqueous solution of 0.05 M and 0.075 M [Zn2+]. There the ZnO layers deposited in solution of 0.05 [Zn2+] are the most transparent (about 80 %) in the vis – IR area most probably due to the lower thickness, whereas the ZnO layers, deposited in 0.075 M [Zn2+] aqueous solution transmits near and below 60 %. The layers of ZnO deposited at the same conditions but in modified solvent, composed of water and 25 wt% Ethanol presents transmittance spectra close to ZnO sample, deposited in diluted solutions.

In the next Figure 8 are presented HD SEM pictures of ZnO thin films in different stages of growth – 5 min plating time (a) and 60 min (b) at 60°C temperature of the solution. The presented pictures illustrate the fine structure of the ZnO layers in high resolution. The nanoparticles’ length is about 250 – 300 nm in both cases, however, after 5 min of plating time their thickness is near 10 nm, whereas after 60 min of deposition, well-defined triangles in cross-section nanorods with thickness of about 60 -70 nm are formed.
Figure 8. High definition (HD) SEM pictures of ZnO thin films deposited in aqueous 0.075 M [Zn$^{2+}$] solution modified with 25 wt% Ethanol in different stages of growth – 5 min plating time (a) and 60 min (b) at 60 °C temperature of the solution. Scale bars are 200 nm.

In both cases, the structure of nanoparticles forming the films are in trigonal configuration in contrast to the typical hexagonal Wurtzite structure of ZnO. Similar effects are identified in several investigations of how additives influence the solution of chemical bath deposition of ZnO thin films. In presence of polyglyceryl groups [17], the additive interacts selectively with (0100) surface and blocks growth in this direction, but facilitates growth on (0010), (1000), (0001) faces. To a large extent, there is a detailed investigation on the influence of various types of additives on the shape of anisotropy and selective growth of ZnO nanoparticles [18].

4. Conclusion
In this work we presented a solution-based method for deposition of thin films ZnO. The ZnO layers are crystallized after thermal annealing in open air atmosphere in hexagonal Wurtzite configuration. The doping with aluminum does not influence remarkably the structure up to 3 % contain. The determined band gap is larger for as deposited ZnO layers and approaches the parameter for bulk material after thermal treatment in temperatures of 150 – 400 °C. Addition of Ethanol in the rate of 25 wt% in aqueous deposition solution leads to formation of ZnO layer consisting of trigonal nanoprisms.

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