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Zno Nanostructures Via Hydrothermal Synthesis on Atomic Layer Deposited Seed-Layers

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***Abstrac t*— The original results of two different types of ZnO nanostructures grown via hydrothermal synthesis on ZnO seed-layers coated by atomic layer deposition process on Si substrates were presented. Scanning electron microscopy and X-ray diffractometry were used for the analysis of resulting nanostructured ZnO samples. The influence of annealing on crystal properties of the ZnO nanostructures was shown. It was ascertained that solution composition had a significant influence on the morphology of nanostructures and post-growth annealing modified the crystal properties of nanostructures.**

Keywords — seed-layer, ZnO nanostructures, atomic layer deposition, hydrothermal synthesis, zinc acetate, zinc nitrate

I. INTRODUCTION

Nanostructured ZnO is a promising material for the novel electronic devices development due to its wurtzite crystal structure, wide direct band gap and high exciton binding energy. ZnO can be manufactured in a controlled manner to produce nanostructures with a uniform size, distribution and orientation by vapor-phase synthesis [1], pulsed laser deposition method [2], electrochemical method [3], hydrothermal method [4-5] etc. Hydrothermal method has many advantages when compare to the most common vapor-phase synthesis, such as low-cost, low temperature, scalability and ease handling.

Generally, there are two main steps in nanostructured ZnO growth by hydrothermal method: (1) preparation of a seed-textured ZnO thin layer and (2) the nanostructured ZnO array growth. For the first step magnetron sputtering [6], sol-gel method [7], atomic layer deposition (ALD) [8] can be applied. Sol-gel technique is attractive due to the ability to conveniently synthesize the films with required properties for a given application almost on all types of substrates. The length and diameter of the nanowires are highly dependent on the crystalline properties (i.e., grain size) of the seed-layer films. Typical pre-seeding sol-gel method includes thermal decomposition of the precursor; spin coating of sol-gel solution and annealing at certain temperature to improve ZnO particles adhesion to the substrate [7]. The type and concentration of precursor, annealing temperature have an obvious influence on the surface structure of ZnO films. On the other hand, ALD technique is known to be unique in terms of sub-nm thickness control and uniformity and provides an ideal performance for seed-layer growth.

The current study is aimed to the ascertainment of the most suitable process parameters for obtaining of ZnO nanorods with certain morphometric characteristics which define physicochemical properties of the material. This research was devoted to the investigation of solution type and post-growth annealing influence on ZnO nanostructures synthesized via hydrothermal method on ZnO seed-layers formed by ALD process.

II. MATERIALS AND METHODS

ZnO seed-layer deposition on pre-cleaned Si (100) wafers was carried out at ~200°C in a Savannah S100 ALD reactor (Ultratech/CambridgeNanotech Inc.). Diethylzinc (DEZn) and water (H_2O) were utilized as Zn and O precursors, respectively. N_2 was used as the carrier/purge gas at a flow rate of ~20 sccm. One ALD cycle consisted of the following steps: H_2O pulse (0.015 s)/N_2 purge (20 sccm, 10 s)/DEZn pulse (0.015 s)/N_2 purge (20 sccm, 10 s). 400 cycles were applied to achieve a ZnO seed-layer thickness of ~45 nm, which was confirmed through spectroscopic ellipsometer measurements.

Two types of starting materials were used to determine the solution composition for growing perfectly aligned and uniform ZnO nanostructures. The equimolar (1:1) mixed solution of analytically pure zinc acetate ($Zn(COOH_3)_2$) for the first group of samples and zinc nitrate ($Zn(NO_3)_2$ for the second group and hexamethylenetetramine (HMT) $C_6H_{12}N_4$ for both were used to perform the hydrothermal synthesis. The chemicals were solved in deionized water, resulting in a transparent solution under magnet stirring for 5 min at room temperature. As-pretreated Si substrates were immersed and suspended in the mixed solution. The growth of ZnO nanorods was carried out by heating the reaction solution from room temperature to 90°C and then kept for 90 min for the first group and for 120 min for the second without any stirring. The as-grown samples were rinsed with deionized water for several times and dried in air at room temperature before characterization. The resulting samples were annealed at 350°C in air for 60 min to study the influence of annealing on the crystal structure.

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Scanning electron microscopy (SEM, Hitachi S4800) was used to examine the morphology. The structural properties of the as-prepared ZnO nanorods were characterized by X-ray diffractometry (XRD, Rigaku ULTIMA IV) before and after annealing in asymmetric mode, which allows obtaining information about the crystalline phase of the surface layer, substrate in this measurement mode makes a minimum contribution to the resulting X-ray spectrum.

III. Results And Discussion

Process parameters of the chemical materials synthesis, substrate preconditioning and seed-layer growth significantly affect the quality and the shape of the obtained structures. The seed-layer deposition was carried out to provide the growing centers and bonding interface with substrates.

The characterization of the deposited ZnO seed-layer on Si substrate by ALD technique is presented in the Fig. 1 and 2. The SEM image of seed-layer (Fig. 1, a) illustrates high quality regular smooth ZnO seed-layer, the thickness of the layer is about 45 nm.

The crystalline phase of the seed-layer was assessed by X-ray diffractometry in asymmetric mode (Fig.2). The intensive diffraction peaks corresponded to the (100), (002) and (101) planes of ZnO, which clearly indicates the polycrystalline form of the thin ZnO seed-layer.

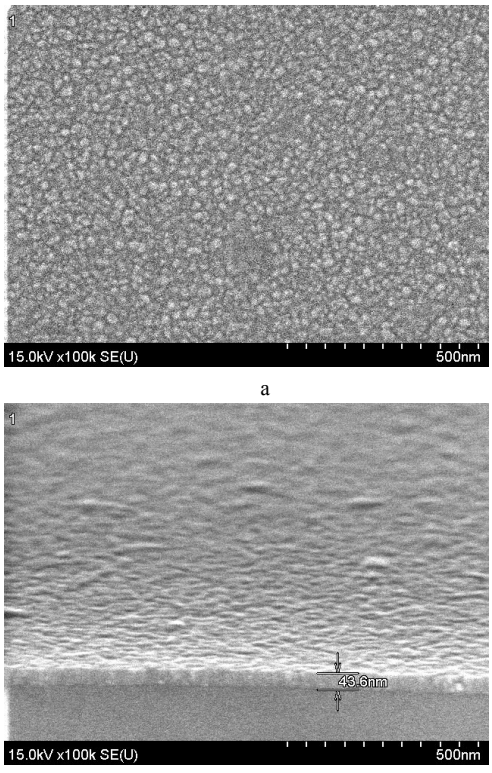


Fig. 1. Top-view (a) and cross-sectional (b) SEM images of ZnO seed-layer formed byALD process.

The shape and geometric characteristics of synthesized structures were studied by SEM analysis. The results of SEM for the first group of samples (Fig. 3) show that synthesized in zinc acetate/hexamethylenetetramine solution at 90°C on ZnO seed-layer consisted of densely packed flake-shape particles; the thickness of the film was about 460 nm. From the SEM for the second group of samples (Fig. 4) it can be seen that nanorod structures with diameters of about 60-80 nm and length of about 550 nm were formed in zinc nitrate/ hexamethylenetetramine solution at 90°C on ZnO seed-layer.

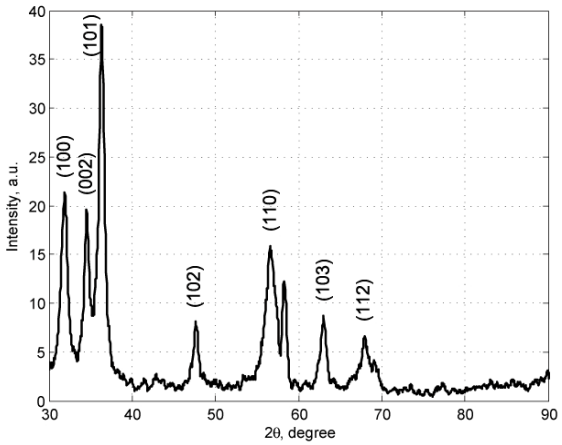


Fig. 2. XRD patterns of ZnO seed-layer formed by ALD process.

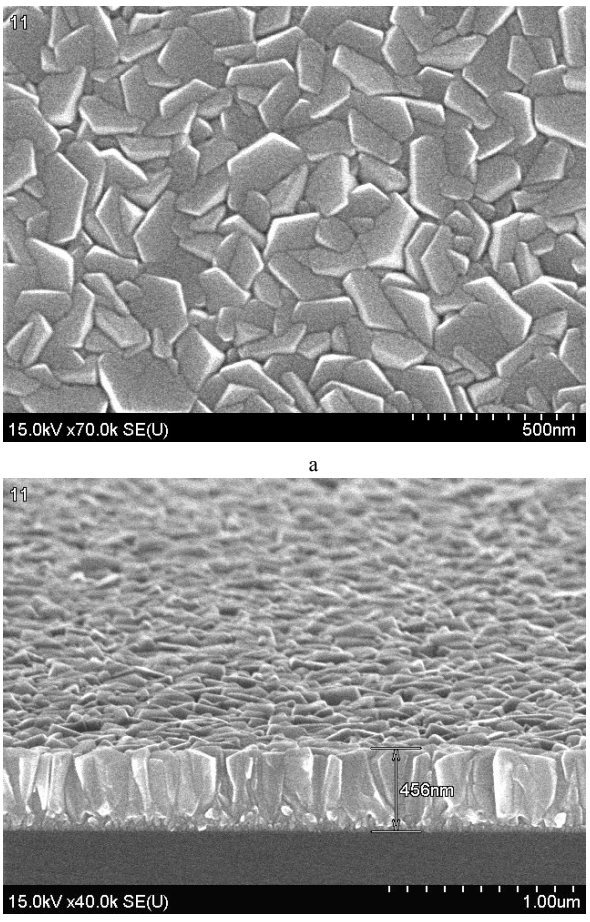
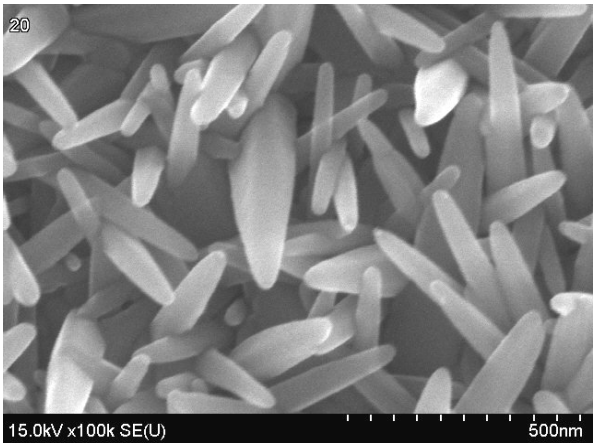


Fig. 3. Top-view (a) and cross-sectional (b) SEM images of ZnO nanostructured film obtained from zinc acetate based solution.



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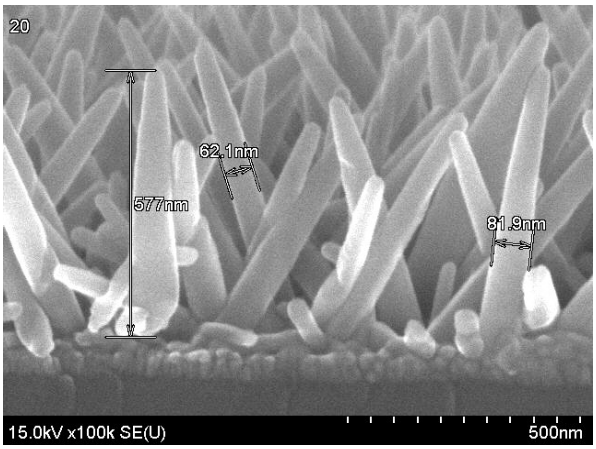


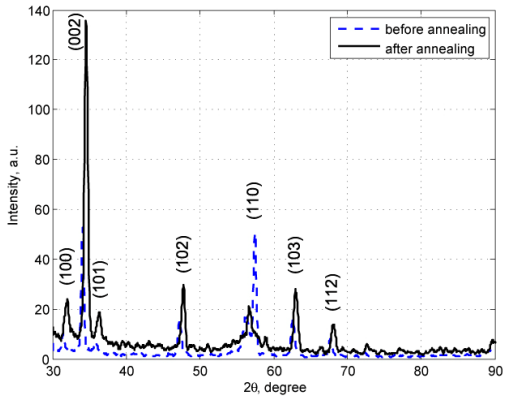
b

Fig. 4. Top-view (a) and cross-sectional (b) SEM images of ZnO nanostructured film obtained from zinc nitrate based solution.

The crystalline phase of the flake-shape particles before and after annealing was assessed by X-ray diffractometry in asymmetric mode as well as the crystalline phase of the ZnO nanorods (Fig. 5). The most intensive diffraction peak corresponds to the (002) plane of wurtzite ZnO, other peaks corresponding to (100), (101), (102), (103) and (112) planes are pronounced with relatively lower intensities.

After annealing process, the diffraction peaks are sharpened and enhanced for both samples. The intensity of the reflexes increased twice after annealing, suggesting that the thermal treatment improved the crystallization of the ZnO nanoparticles.

It was found that XRD patterns of ZnO nanostructures before and after annealing showed the same form. This indicates that ZnO films prepared by hydrothermal method showed a good c-axis orientation perpendicular to the substrate and also means that orientation of prepared ZnO films was not destroyed after annealing. The demonstrated diffraction peaks are in good agreement with standard diffraction peaks of hexagonal wurtzite phase ZnO (PDF Card No.: 01-075-6445) for both samples. The diffraction angle of diffraction peak corresponding to the planes of hexagonal ZnO for both groups after annealing became closer to standard XRD spectrum (Tables I and II).



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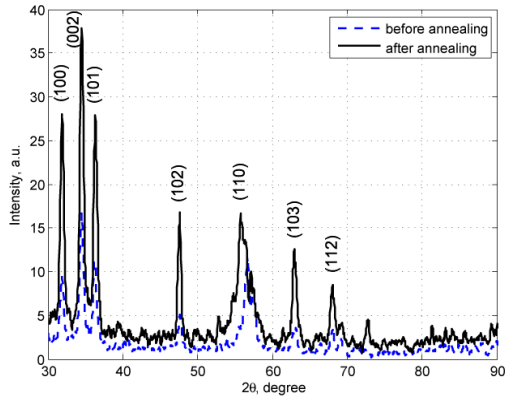

b

Fig. 5. XRD patterns of ZnO nanostructured film obtained from zinc acetate (a) and zinc nitrate (b) based solution before and after annealing.

TABLE I. PEAK LIST OF THE XRD PATTERNS OF ZNO NANORODS FROM THE FIRST GROUP

2θ, degree			**Miller indices**		
Card No.: 01-075-6445	***before annealing***	***after annealing***	***h***	***k***	***l***
31.8193	31.36	31.99	1	0	0
34.4664	34.05	34.54	0	0	2
36.1904	36.12	36.33	1	0	1
47.5678	47.33	47.79	1	0	2
56.7814	56.21	56.60	1	1	0
62.7262	62.54	62.95	1	0	3
67.8592	67.69	68.08	1	1	2

Calculated lattice constants of the synthesized ZnO nanostructures samples before and after annealing and standard values are presented in the Tables III and IV.

From the analysis of obtained results it could be seen that after annealing lattice constants became closer to the standard values.

Crystallite sizes calculated by Williamson-Hall method increased from 15.9 nm to 19.2 nm for the first group and from 10.2 nm to 16.2 nm for the second. This can be viewed as the merging process of ZnO nanoparticles induced from thermal

annealing. In the case of ZnO nanostructures, at high temperature the merging process of the zinc or oxygen defects occurred at the grain boundaries by stimulating the coalescence of more grains during annealing.

TABLE II. PEAK LIST OF THE XRD PATTERNS OF ZNO NANORODS FROM THE SECOND GROUP

2θ, degree			**Miller indices**		
Card No.: 01-075-6445	***before annealing***	***after annealing***	***h***	***k***	***l***
31.8193	31.94	31.82	1	0	0
34.4664	34.48	34.48	0	0	2
36.1904	36.16	36.32	1	0	1
47.5678	48.02	47.58	1	0	2
56.7814	56.65	56.36	1	1	0
62.7262	63.27	62.86	1	0	3
67.8592	68.02	68.10	1	1	2

TABLE III. LATTICE CONSTANTS OF THE SYNTHESIZED SAMPLES FROM THE FIRST GROUP

	a	**b**	**c**
Card No.: 01-075-6445	3.2494	3.2494	5.2038
before annealing	3.271396	3.271396	5.231784
after annealing	3.243334	3.243334	5.189394

TABLE IV. LATTICE CONSTANTS OF THE SYNTHESIZED SAMPLES FROM THE SECOND GROUP

	a	**b**	**c**
Card No.: 01-075-6445	3.2494	3.2494	5.2038
before annealing	3.244255	3.244255	5.181704
after annealing	3.253413	3.25413	5.196336

CONCLUSION

The original results of ZnO nanostructures hydrothermal synthesis from two different solutions on ZnO seed-layer obtained by ALD process on Si substrates were presented. The type of starting material for the solution preparation defined the morphology of the formed structures.

Thus, zinc acetate based solution allowed obtaining of dense nanostructured film composed of flake-shape particles, while nanorods structures were formed from the zinc nitrate based solution. The influence of annealing process on crystal properties of the ZnO nanostructures was shown.

Post-growth thermal treatment at relatively low temperature could be the main approach to further improvement of the ZnO nanostructured films crystal properties due to the decrease of the defects. From XRD spectrum of the samples the lattice constants and crystallite sizes of ZnO were verified.

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