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Influence of Li-nitrate doping on the hydrothermally grown ZnO nanorods

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Abstract: *Large-scale, dense ZnO nanorods(NRs) are grown on Si(100)/SiO_2 substrates with the assistance of a sol-gel nucleation layer. In this study ZnO NRs are hydrothermally grown by a simple aqueous solution route of Zinc Nitrate Hexahydrate with the addition of lithium nitrate as dopant reagent. The influence of doping concentration and growth duration on the NR morphology was studied in comparison to undoped ZnO NRs grown under the same experimental conditions. It was found that the Li-doped ZnO NRs approached the crystal structure of wurtzite ZnO with well-defined diffraction peaks. The addition of the lithium dopant at 0.5:1, 1:1 and 2:1 ratio to Zinc Nitrate Hexahydrate resulted in an increase of the growth rate (nm/min) in comparison to the undoped NRs.*

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I. Introduction

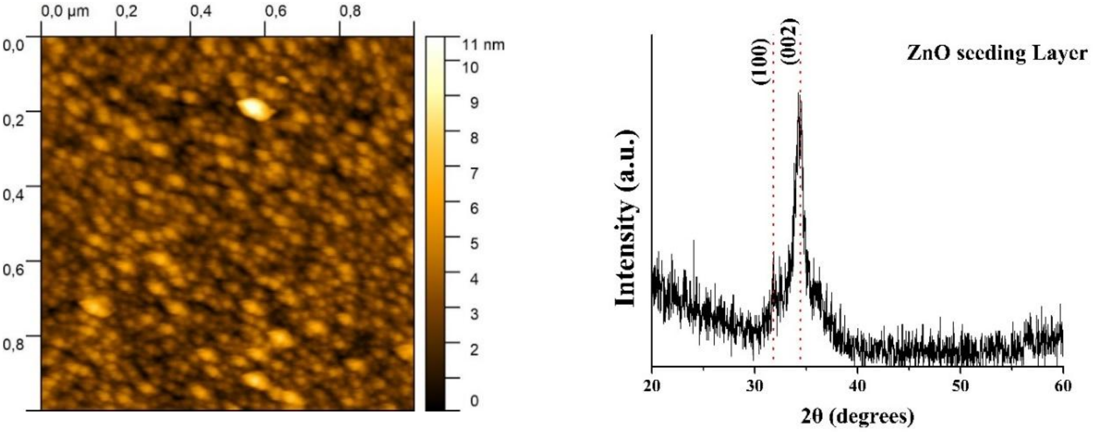
Zinc oxide (ZnO) (3.37 eV) a representative II–VI compound semiconductor has attracted considerable scientific and technological attention due to its excellent semiconducting, piezoelectric kai pyroelectric [1, 2, 3]properties. It is well known that ZnO is a commonly-used, low-cost, antibacterial [4] material that forms various nanostructures depending on the growth process conditions [5, 6, 7]that can act as building blocks in many applications [8, 9]. Different methods that can be applied in order to synthesize ZnO nanorods (NRs) are chemical vaporand metal organic vapor deposition [10, 11, 12], thermal evaporation [13, 14], electrochemical deposition [15]and the hydrothermal method [1, 16, 17]. The hydrothermal synthesis method, received increased attention for ZnO NRs due to its non-toxic nature, low temperature requirements, low operating cost as also its capability to grow ZnO NRs of various morphologies and dimensions on various substrates [18, 19, 20]. Furthermore, the variations of the process parameters (range of precursors, concentration of reactants, temperature, time etc.) leads to morphological differences in size and shapes for the resulted nanorods [18, 21].The hydrothermal method used to form ZnO NRs,also facilitates the doping (n or p-type) of semiconductor NRswhich is necessary for functional electronic and optoelectronic devices. The doping process of semiconductors with a range of elements is well known to significantly affect their electrical, optical, and magnetic properties [22, 23]. Numerous studies with different kind of doping materials as a donor (to obtain high quality n-type ZnO) or as an acceptor in order to fabricate p-type ZnO, emphasizing the important challenges for ZnO based devices have been reported in the literature [24, 25, 26, 28].The present work reports the synthesis of vertically aligned Li-doped ZnO NRs utilizing hydrothermal growth with lithium nitrate as the dopant source. The influence of Li doping on the growth rate of ZnO nanowires is investigated for various Li to Zn ratios.

II. Material and Methods

The hydrothermal method applied in this study is solution-basedand consists of a two-step process. The first step is the formation of a nucleation or seeding layer on the substrate surface, and the second step is the hydrothermal growth of the ZnO NRs. The seeding layer can be applied onthe substrate surface, by various film deposition methods [29, 30] or through the coating of the substrate with ZnO nanoparticles. In this study the seeding layer was prepared from a zinc acetate solution and was deposited using spin coating. In particular, zinc acetate solution of 40 mM concentration was prepared by dissolving zinc acetate dihydrate (98%, Aldrich) in ethanol. The prepared mixture was magnetically stirred at 60 ^oC for 60 minutes to obtain a clear homogeneous solution and left to cool down to room temperature and age for 24 hr. Prior to the spin coating process, Si/SiO_2 (100 nm) substrates were etched by piranha solution (1:1 mixture of concentrated H_2SO_4 / 30 % H_2O_2) for 20 min, rinsed with deionized (DI) water and dried under N_2 atmosphere. Finally, the prepared solution was spin coated on the Si/SiO_2 substrates at 1000 rpm for 30 s and baked at 500 ^oC in atmospheric air for 10 min. This coating step has been repeated ten (10) times in order to form the requiredseeding layer. The seeded, with ZnO crystallites, Si/SiO_2 substrates were placed upside down into the growth solution. The growth solution consisted of an equimolar aqueous growth solution of 40 mM zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, ZNH) and hexamethylene tetramine ($C_6H_{12}N_4$, HMTA) for the un-doped ZnONRs. For Li doped ZnO NRs lithium nitrate ($LiNO_3$, Aldrich) was added to the growth solution with a molar ratio to ZNH (0.5:1), (1:1) and (2:1). The growth duration ranged from 60 to 180 minutes at a temperature range of 87 ± 3^oC. After the growth process, the samples were rinsed with deionized (DI) water and dried in N_2 atmosphere. Surface roughness surveys of the seeding layer were performed using an Atomic Force Microscope (AFM, Veeco CP-II) and the surface morphologies of the grown NRs were studied using a Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM-7401F). The crystallinity, for undoped and Li-doped ZnO NRs was determined by X-Ray Diffraction (XRD) measurements using a D500 SIEMENS diffractometer (Cu Kα radiation; λ =1.5418 Å, 40 kV, 35 mA) for both seeding layer and grown NRs.

III. Results

The process applied for the preparation of the seeding layer, driven from the decomposition of 40 mM zinc acetate dihydrate in ethanol at 60 ^oC, resulted into a □ 30 nm-thick film of textured ZnO nanocrystals. The prepared film had a smooth surface with a Root Mean Square (RMS) roughness of 1.03 nm, measured by the AFM as shown in Fig. 1(a). The surface of the film is covered by nanosized ZnO grains. The XRD analysis revealed that the as prepared seeding layer is polycrystalline with ac-axis preferred orientation that is perpendicular to the substrate surface. The diffraction peaks are matched with the standard diffraction pattern of wurtzite ZnO (JCPDS 036-1451).



(a) **(b)**

Figure 1. (a) Surface morphology and **(b)** XRD spectra of the seeding layer film formed after 10 spin-coating cycles.

The growth mechanism for the formation of ZnO NRs can be summarized by the following chemical reactions[1]:

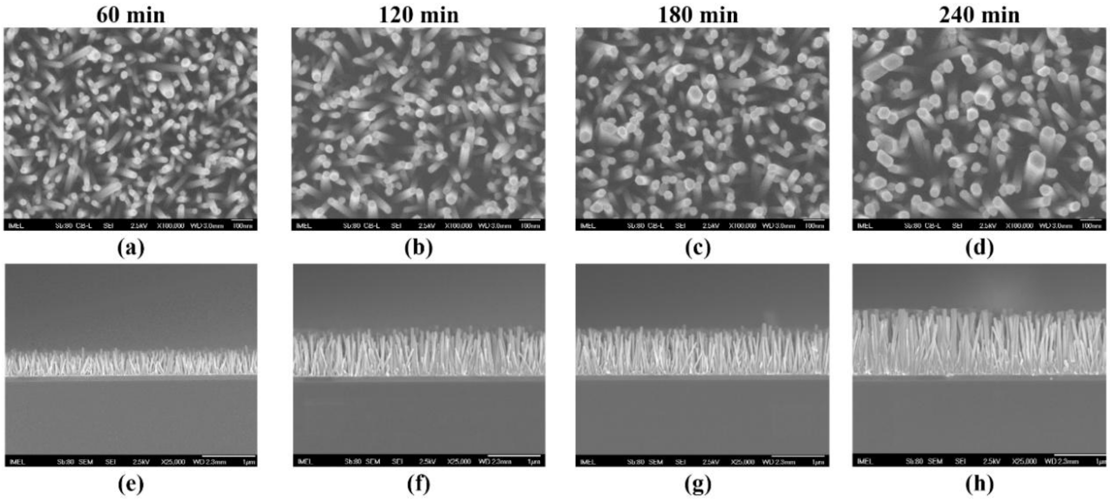
Decomposition reaction $$(CH_2)_6N_4 + 6H_2O \xrightarrow{\text{heat}} 6HCHO + 4NH_3$$

Hydroxyl supply reaction $$NH_3 + H_2O \leftrightarrow {NH_4}^+ + OH^-$$

Supersaturation reaction $$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$$

Formation of ZnO nanorods reaction: $$Zn(OH)_2 \xrightarrow{\text{heat}} ZnO + H_2O$$

Previously reported studies of hydrothermally grown ZnO NRs have shown that precursor concentration determines the NR density, while growth time and temperature controls the ZnO NR morphology and aspect ratio [31]. The NRs morphology evaluation was conducted by FE-SEM. Images at different locations across each sample were capturedin order to confirmtheoverall morphology of the grown NRs. In Fig. 2, FE-SEM micrographs (top and cross section view) are presented for NRs grown in an equimolar ZNH:HMTA growth solution of 40mM, for growth duration ranging between60 and240 minutes. It can be observed that under the applied hydrothermal conditions, the ZnO NRs have ahexagonal crystal morphologygrown in c-axis direction with a uniform diameter along their axisandflat-top termination.The flat-top termination indicates that the growth rate of the polar [002] planes is faster than the nonpolar surfaces [32]. The increase of the growth duration results into a length and diameter increase, showing that even after 4 hours the growth solution has not been depleted of reactants.



(a) (b) (c) (d)

(e) (f) (g) (h)

Figure 2. Top and cross section SEM micrographs for undoped ZnO NRs with growth duration of (a-e) 60, (b-f) 120, (c-g)180 and (d-h) 240 min at 2.5kV and for x100.000 and x25.000 magnification respectively.

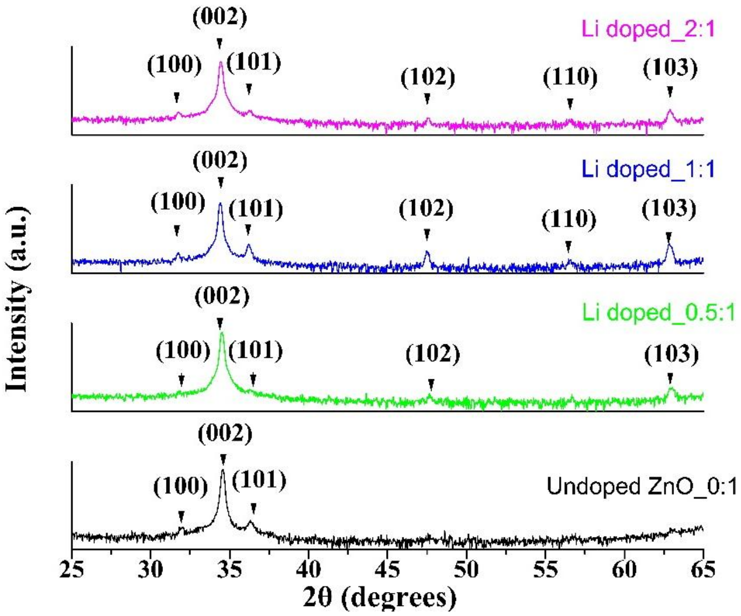
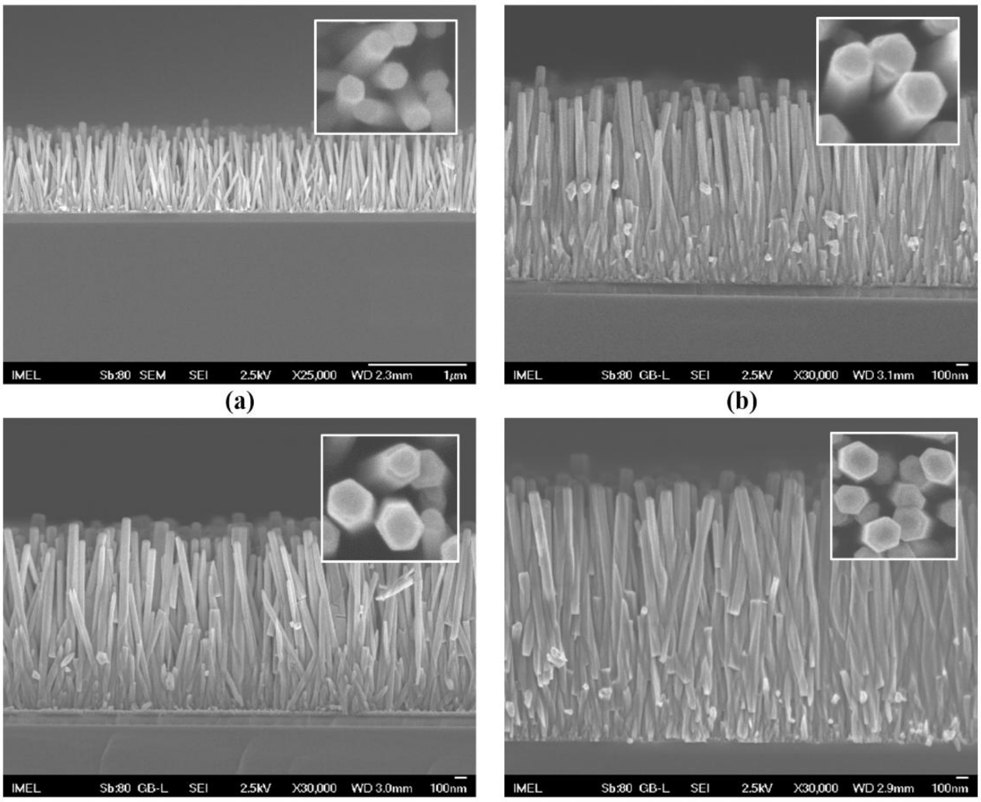


Figure 4.XRD spectra of grown NRs for pure (undoped ZnO_0:1) and Li-doped (Li:ZNH ratio 0.5:1, 1:1 and 2:1)(growth duration 180 min)

XRD results for 180 min grown NRs are shown in Fig. 4 for pure (undoped) and Li-doped ZnO NRs for the different dopant concentrations. The diffraction peaks for all studied samples are well matched with the pure hexagonal phase of wurtzite structure. As it can be observed, the crystallographic phase remains unaltered with the increase in dopant concentration. When Li doping reagent is introduced into the growth solution, a partial replacement of Zn^{2+} ions by Li^{+} ions takes place in the ZnO lattice since their ionic radii are comparable [33]. Li can occupy interstitial and substitutional sites in the lattice structure of ZnO, leading to improved crystallinity of respective phases [25, 33]. Therefore, the crystal structure and growth direction of the Li-doped NRs are similar to the un-doped one. The growth direction for all ZnO NRs is along [002] direction with clearly defined (102), (110) and (103) diffractive peaks at higher angles for the Li-doped NRs.In Fig. 5, representative FE-SEM images for Li-doped grown NRs are shown in comparison to the undoped NRs, for the case of 180 mingrowth duration.As it can be observed in all cases the NRs are grown in the [002] crystal direction. Li-doped NRs are found to have a flat-top termination in agreementto the undoped NRs with improved diameter uniformity.For the same growth duration NRs grown at 2:1 Li to ZNH (Fig. 5 (d)) are found to be the longest in comparison to 0.5:1 and 1:1 ratio, with all Li-doped NRs being highly aligned, perpendicular to the substrate.

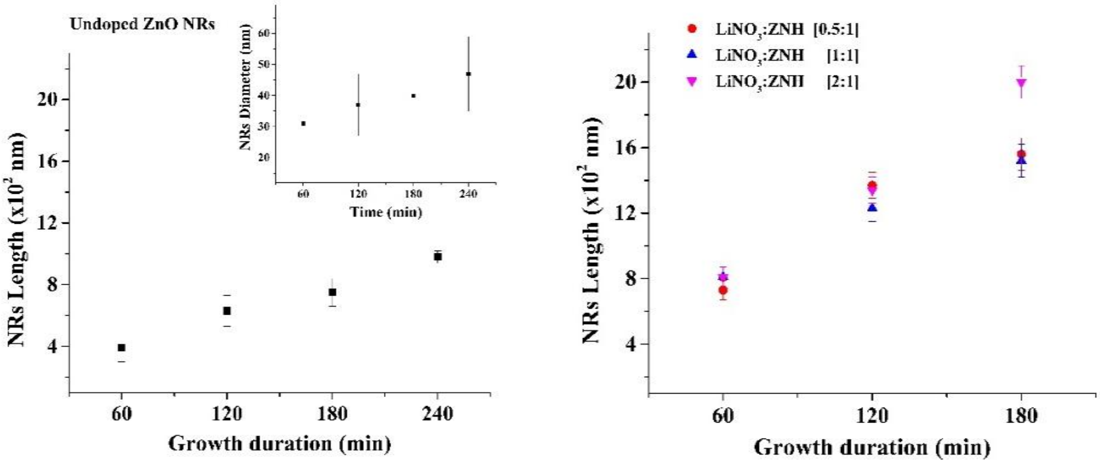


(a) **(b)**

(c) **(d)**

Figure 5. Cross section SEM micrographs at 2.5 kV for (a) undoped and (b) 0.5:1, (c) 1:1 and (d) 2:1 Li-doped NRs hydrothermally grown for 180 min (inset shows the correspontinng top view FE-SEM micrographs at x100.000 magnification)

ImageJ software was utilized in order to measure the NRs length and diameter as a function of the growth duration.The obtained results are presented in Fig. 6. The NRs growth rate in (002) direction was found to be highly linear in all examined cases. The growth rate for the undoped NRs was found to be inthe order of (4.0 ± 0.5) nm/min and their average diameter increase was up to 50% in 240 min compared to 60 min (inset of Fig. 6 (a)).For Li-doped NRs a higher growth rate in the c-axis direction is obtained compared to undoped NRs.Specifically, the growth rate in the cases of 0.5:1 and 1:1 was found the same and of the order of (10±1) nm/min while it increased to (12±1) nm/min in the case of 2:1Li to ZNH ratio. As a result, Li-doped NRs length was greater than the undoped ones for all Li to ZNH ratios.



(a) **(b)**

Figure 6. Length as a function of the growth duration (a) for undoped NRs (inset: NRs diameter as a function of the growth duration) and (b) for Li-doped NRs at various Li to Zn ratios

IV. Conclusions

In this study, the influence of growth duration on the structure of hydrothermally grown Li-doped NRs was investigated. ZnO NRs were hydrothermally grown on seeded Si/SiO2 substrates at a constant temperature using a zinc nitrate/HMTA nutrient solution with the addition of lithium nitrate as a dopant. The resulted NRs had a hexagonal crystalline structure coinciding with the standard diffraction pattern of wurtzite ZnO (JCPDS 036-1451) with a preferential growth orientation along the c-axis. It was identified that the addition of the Li dopant intensified the diffraction pattern of the NRs at higher angles corresponding to (102), (110) and (103) planes. From the FE-SEM analysis, undoped NRs were grown at a linear rate, with increasing length and diameter as a function of time. The Li-doped NRs showed an increase of the growth rate in comparison to the undoped case, with NRs grown at 2:1 Li to ZNH showing the highest growth rate value.

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