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ВЕСТНИК

КАЗАХСКОГО НАЦИОНАЛЬНОГО
ТЕХНИЧЕСКОГО УНИВЕРСИТЕТА
ИМЕНИ К.И. САТПАЕВА

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INFLUENCE OF AQOUES SOLUTIONS ON MORPHOLOGY AND PROPERTIES OF ZINC OXIDE NANORODS

Abstract. Uniform layers of zinc oxide nanorods (NRs) were synthesized on F-doped SnO_2 (FTO) coated glass substrates by hydrothermal route using two different water solutions. The first aqueous solution contained zinc nitrate hexahydrate and hexamethylenetetramine (HMTA). The second one was obtained by adding to the previous components ammonium hydroxide and polyethylenimine to favour the formation of ZnO nanorods and nanorods on the substrate surface. Before the nanorods growth, the FTO slides were covered with a ZnO seed layer deposited by spin-coating techniques.

Keywords. ZnO nanorods, hydrothermal synthesis, different growth solutions, X-ray spectrum.

Introduction

Zinc oxide is a commercially important material used in paints, protective coatings for metals, rubber processing, and sunscreens because it is abundant and nontoxic. Last time ZnO nanostructures and thin films have become promising materials for emerging electronic applications. ZnO is a wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV). ZnO nanorods are important due to own structural one-dimensionality and possible quantum effects in two dimensions [1]. They can possess novel electronic and optical properties with uses as room-temperature ultraviolet (UV) lasers [2], field-effect transistors [3], photodetectors [4], gas sensors [5], and solar cells [6]. In addition, magnetic and electrical properties can be modified by intentionally introducing impurities into the lattice. Transition-metal-doped ZnO wires are a model material system for dilute magnetic semiconductors [7].

The {0001} planes of wurtzite ZnO crystal have the highest energy of the low-index surfaces [8]. So the one-dimensional ZnO nanostructures are easily synthesized due to *preferred growth* orientation of ZnO in the c-axis which is the fastest growing direction. The growth rates of various surfaces can be increased or decreased by using additives preferentially adsorb to specific crystal faces in the case of solution-phase syntheses [1].

ZnO nanorods are most commonly synthesized by gas phase synthesis such as metal-organic chemical vapor deposition [9, 10], chemical vapor transport [11, 12] and laser deposition [13]. These methods can produce high-quality, single crystalline nanostructures. However, these processes require elevated temperatures of 450-900 °C and often face other limitations in terms of sample uniformity, substrate choice, and low product yield. In contrast, hydrothermal synthesis is appealing because of the low temperatures of growth (less than 350°C), it is useful for producing of high-density arrays [14].

Experimental part

F-doped SnO_2 (FTO) coated glass and n-type silicon (100) wafers were used as substrates. Before NRs growth, Si substrates were ultrasonically cleaned in acetone and ethanol for 15 min respectively. FTO substrates were also cleaned in ultrasonic bath with acetone and ethanol and then treated in piranha solution ((H_2O_2 35%):(H_2SO_4 96%)=3:7) followed with plasma cleaning to create hydrophilic surface. These substrates were masked by Scotch tape in order to maintain a conductive electrode.

ZnO seed-layers were prepared according to sol-gel spin coating method [15]. 10 mM zinc acetate $Zn(CH_3COO)_2$ (purity 98%, Sigma-Aldrich) in ethanol was spincoated on the cleaned substrates at 1000 rpm for 20s and at 3000 rpm for 30s. After spinning substrates were washed for few seconds in ethanol and dried by nitrogen flow. This process was repeated 5 times. Then the substrates were calcined in air at 250^{o}C (Si) and 350^{o}C (FTO) for 20 min (heating rate 5°C/min) to obtain the oriented seed layers.

Hydrothermal synthesis of ZnO NRs was performed according to simple low temperature technique [16–17]. Vertically oriented zinc oxide nanorods were synthesized on FTO substrates by hydrothermal route using two different water solutions.

<u>Solution A:</u>

The growth solution A was prepared by dissolving 15 mM zinc nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$ (purity 98 %, Sigma-Aldrich) and 30 mM hexamethylenetetramine (HMTA) $C_6H_{12}N_4$ (HMTA, purity 98

%, Sigma-Aldrich) in bi-distilled water. Synthesis occurs for 2-6 hours under slight magnetic stirring at 80^{0}C.

Solution B:

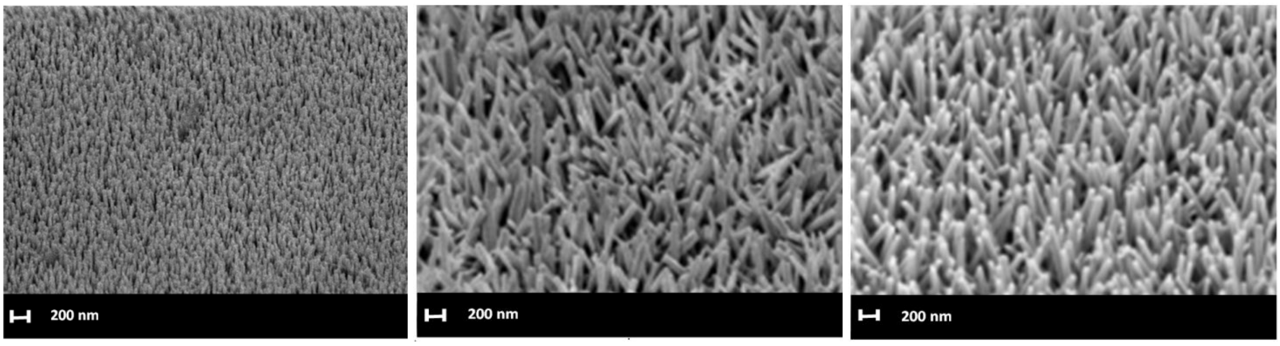
Another growth solution B was prepared by dissolving 25 mM zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ (purity 98 %, Sigma-Aldrich) and 12.5 mM hexamethylenetetramine $(CH_2)_6N_4$ (HMTA, purity 98 %, Sigma-Aldrich) in bi-distilled water. 5 mM water solution of polyethylenimine $(C_2H_5N)_n$ (PEI, average M_w~800 by LS, average M_n~600 by GPC, Sigma-Aldrich) was added as capping agent and 320 mM ammonium hydroxide NH_4OH (28%, Sigma - Aldrich) was added to adjust the pH of the solutions to about 9. Substrates were located vertically in the beaker using a Teflon sample holder. Synthesis occurs for 2-6 hours under slight magnetic stirring at 88^{o}C.

After growth the samples were washed with bi-distilled water to remove any residual impurity from the surface and dried in nitrogen flow.

Morphology and structure of obtained samples were studied by Field Emission Scanning Electron Microscope (FESEM) *coupled with* Focused Ion Beam (*Auriga, Karl Zeiss) and by Philips X'pert diffractometer respectively.*

Results and Discussion

Fig. 1 shows morphology of the samples obtained in Solution A. Dependence of the average length of obtained NRs and they diameter on time of growth in solution A is represented in Table 1.



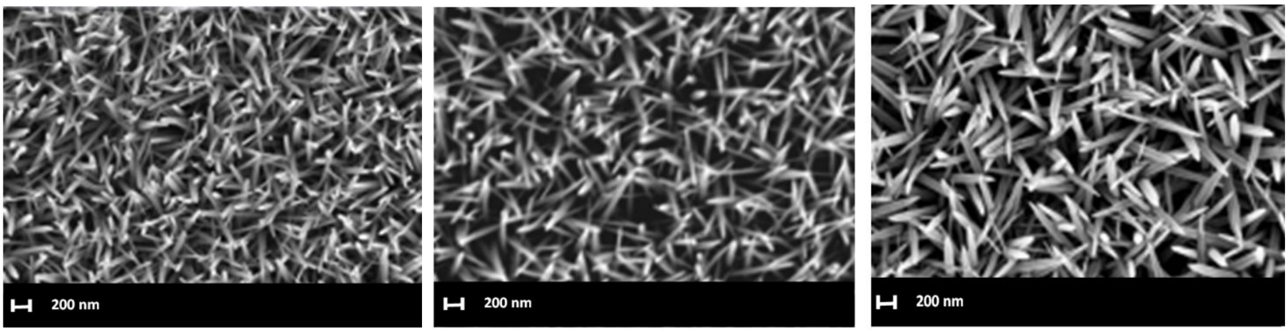
a b c

Figure 1. Morphology of ZnO NRs grown on FTO coated glass slides in 10 mM water solution of zinc nitrate hydrate and HMTA for a - 2, b – 4, c – 6 hours.

Table 1. **Dependence of the average length of obtained NRs and they diameter on time of growth in solution A**

Time, hours	Length, μm	Diameter, nm	Length/Diameter ratio	Description
2	0.31	35	8.85	Short, mainly vertically oriented
4	0.67	40	16.75	
6	0.82	54	15.18	

Fig. 2 shows morphology of the samples obtained in Solution B and Table 2 represents the average length and diameter of NRs grown in solution B during 2, 4 and 6 hours. Fig. 3 shows the *XRD* patterns of the ZnO layers grown on FTO coated glass slides using water solution A (a, b, c) and B (d, e, f). The SEM (Fig. 1 and 2) and XRD data (Fig. 3) demonstrate that a well-*aligned* growth of nanorods with a [*002*] *preferred orientation* was observed in ZnO synthesized by a simple hydrothermal method.



a b c

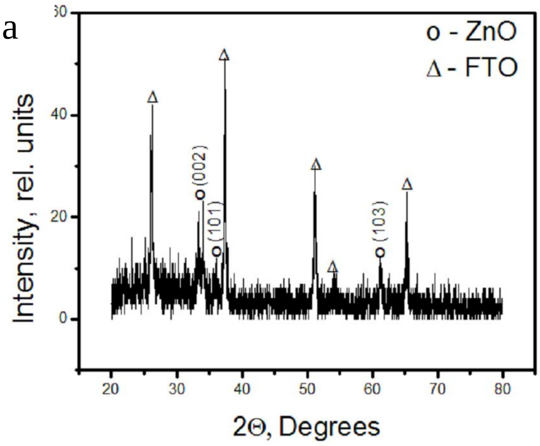
Figure 2. Morphology of ZnO NRs grown on FTO coated glass slides in 10 mM water solution of zinc nitrate hydrate, HMTA, PEI for a - 2, b – 4, c – 6 hours

Table 2. **Dependence of the average length of obtained NRs and they diameter on time of growth in solution B**

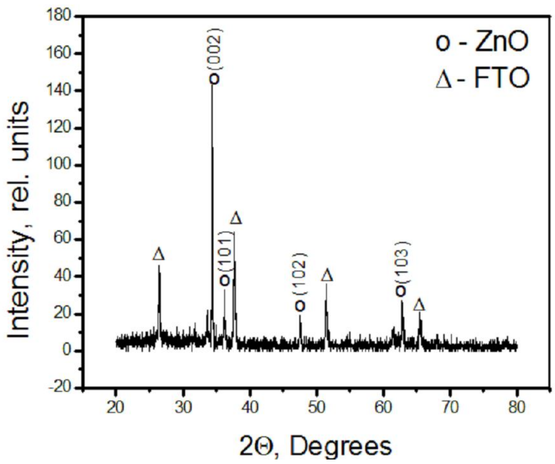
Time, hours	Length, μm	Diameter, nm	Length/Diameter ratio	Description
2	1.7	38	44	Long
4	1.67	75	24	Long, a little tilted
6	2	80	25	Long, ever more tilted

As it can be seen from the comparison of the Tables 1 and 2 the addition of PEI in the grown solution leads to increase of the length and diameter of ZnO NRs. The aqueous solution synthesis provides a ready means to tune the wire diameter, length, and aspect ratio.

a

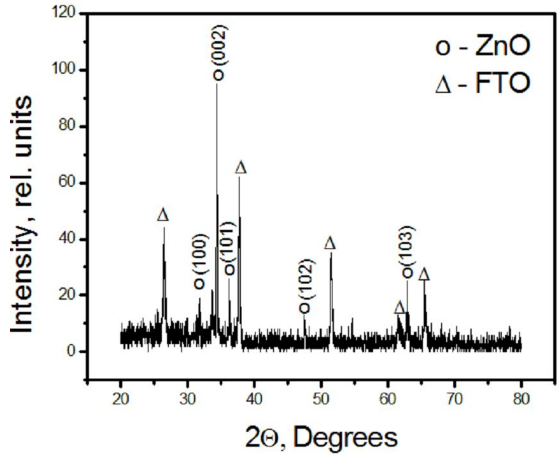


d

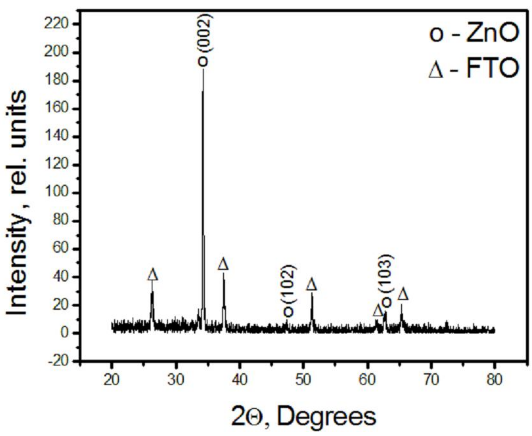


2 hours

b

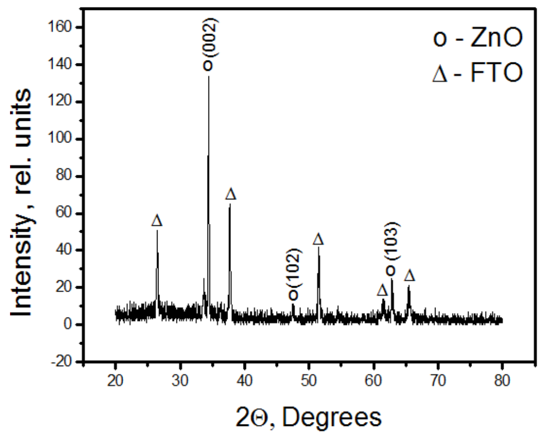


e

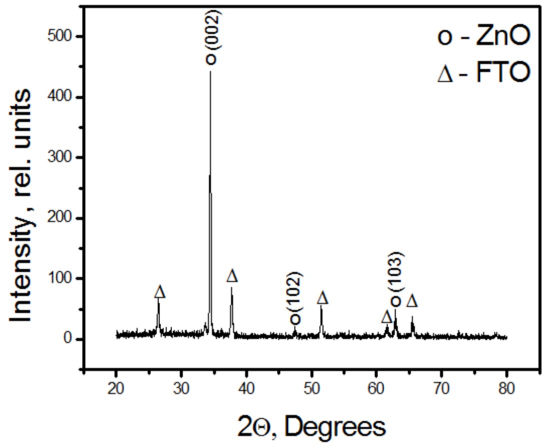


4 hours

c



f



6 hours

Figure 3. XRD data of ZnO NRs on FTO coated glass slides grown in water solution A (a, b, c) and B (d, e, f).

Conclusions

In this work the influence of process parameters, such as seed layer formation, growth time and temperature on morphology of ZnO nanorods, was studied. The optimal growth regimes for both solutions to obtain aligned nanorods were found: successful growth occurred during 2 hours at temperature 80^{o}C (solution A) or at 88^{o}C (solution B). Both growth solutions provide a cost-effective approach to fabricate aligned nanowire arrays with controllable sizes and lengths on FTO conductive substrates. The growth in solution A results to shorter nanorods of 0.5-0.7 μm in length. The nanorods are more vertically oriented, that is useful for some applications, such as gaseous sensors and piezoelectric devices. Synthesis in solution B allows growth of long ZnO nanorods from 1.7 to 2 μm without the formation of contaminating ZnO structures in the bulk solution. However long tilted nanorods are obtained that sometimes stick together. ZnO nanorods obtained from solution B could be used for photovoltaic applications and dye sensitised solar cells (DSSC), where it is necessary to have high surface area.

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Подрезова Л.В., Кауда В., Чичеро Дж., Абдуллин Х.А.

Сулы ерітінділердің мырыш оксиді наностержендерінің қасиеті мен морфологиясына әсері

Түйіндеме. Гидротермалды синтезде жабынды қабат концентрациясының, синтез ұзақтығы мен температураның синтез параметрлеріне әсері зерттелді. Вертикал бағытталған мырыш оксиді наностержендерін өсіру мақсатында екі сулы ерітінді үшін оптималды режим анықталды.

Түйін сөздер - Zno нанобілекшелері, гидротермалды синтез, өсіруге арналған әртүрлі ерітінділер, рентгенқұрылымдық сараптама.

Подрезова Л.В., Кауда В., Чичеро Дж., Абдуллин Х.А.

Влияние водных растворов на морфологию и свойства наностержней оксида цинка

Резюме. Изучено влияние таких параметров гидротермального синтеза, как концентрация затравочного слоя, продолжительность синтеза и температура. Найдены оптимальные режимы роста для двух водных растворов с целью получения вертикально ориентированных наностержней оксида цинка.

Ключевые слова – наностержни ZnO, гидротермальный синтез, различные растворы для роста, рентгеноструктурный анализ.

Podrezova L.V., Cauda V., Cicero G., Abdullin Kh.A.

Influence of aqoues solutions on morphology and properties of zinc oxide nanorods

Summary. The influence of process parameters (i.e. seed layer concentration, growth time and temperature) was studied and optimal growth regimes for both solutions to obtain vertically aligned zinc oxide nanorods were found.

Keywords – ZnO nanorods, hydrothermal synthesis, different growth solutions, X-ray spectrum.