LATVIAN JOURNAL OF PHYSICS AND TECHNICAL SCIENCES
2015, N 5

DOI: 10.1515/LPTS-2015-0026

OBTAINING A WELL-ALIGNED ZnO NANOTUBE ARRAY USING THE HYDROTHERMAL GROWTH METHOD

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Optimal growing parameters have been found using the hydrothermal method to obtain well-aligned vertical ZnO nanorod and nanotube arrays. The influence of different growing factors (such as temperature, growing solution concentration, method of obtaining seed layer and condition) on nanotube morphology and size is described in the paper.

Well-structured ZnO nanotubes have been obtained by using a self-selective etching method with lowering temperatures of growth during the hydrothermal process.

It is shown that the optical properties of the nanostructure arrays obtained are sensitive to the medium in which they are placed, which is why they can be used as sensors for pure substance detection and in different solutions for impurity determination.

Keywords: *hydrothermal growth, nanotubes, nanotubes-based sensor, self-selective etching, ZnO nanostructures.*

1. INTRODUCTION

Zinc oxide is a promising material for application in several areas: nanogenerators [1], [2], piezoelectric devices [8], photo conductors [3], [5], biochemical and biological processes [9], [12], [13] and various sensors [6], [9]–[14]. It is very sensitive to changes in growing conditions, and so by changing the growth parameters it is possible to obtain different ZnO morphologies: 1D nanostructures (rods, needles, tubes) [2], [8], [11], [15], 2D (plates, ribbons, walls) [1], [3], and 3D ("trees", "moss", "flowers", "urchins") [2], [5], [6], [7].

Of all ZnO morphologies nanorods have been researched most intensively [1]–[4], [19], but in recent years nanotubes have attracted the attention of scientists due to their larger surface area compared to other ZnO morphologies [3], [4], [8], which is why ZnO nanotubes are a potential material for sensing applications [8], [10].

ZnO nanotubes can be obtained using several methods: by the chemical etching of previously obtained ZnO nanorods in a weak alkaline or acidic solution (*chemical etching (CE))* [3], [16], [17], [18], lowering the temperature during the growing process using the hydrothermal method (*self-selecting etching (SSE*)) [4], [8], [15], and using forms and templates (*template assisted growing (TAG*)) to define complicated or multi-compositional shapes [1]–[2] etc.

In the present research we have used the hydrothermal ZnO nanostructure growing: this method is environmentally friendly, simple and cheap, and it does not require complicated equipment or growing conditions, such as vacuum, high temperatures or specially prepared surfaces, because the process takes place in the aqueous solution at temperatures lower than 100 °C on glass substrate, allowing the use on an industrial scale.

In comparison with other methods, SSE has a number of advantages for obtaining ZnO nanotubes: during the growing process there is no need to take the sample out of the oven and the growth solution; additional chemical substances for etching are not required, which increases the purity and the quality of nanostructure shape because the etching process occurs in a less aggressive chemical environment compared with alkali and acidic solutions and affects only certain ZnO planes; and no special templates are needed, which accelerates the growing process and makes it cheaper and easier.

2. EXPERIMENT

2.1 SEED LAYER GROWING

Seed layers have been obtained in two different ways: electrodeposition (ED) and by using colloidal zinc acetate solution in ethanol (AD). In both cases, the samples have been obtained on glass pre-cleaned with acetone.

In the first case, the samples have been obtained by electrodeposition on 26x76 mm glass plates, which have been pre-cleaned and covered with ITO and then annealed at 500 °C in the air. The electrodes have been immersed in a cuvette containing aqueous solution of zinc nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$ with concentration varying from 3.4 mM to 50 mM, to which a current density of 25 to 75 µA/cm^2 has been applied. The period of electrolysis varies from 2 to 20 minutes. After disconnecting the voltage, the samples covered with Zn have been rinsed with DI water to wash away traces of the growth solution, and then they have been dried and annealed in the air at 500 °C to transform Zn into ZnO, and finally slowly cooled to room temperature.

In the second case, the seed layer has been obtained by covering pre-cleaned glass with the zinc acetate $Zn(CH_3COOH)_2{\cdot}2H_2O$ 5 mM solution in ethanol.

The pre-cleaned glass has been immersed in acetate, rinsed with pure ethanol and dried using a nitrogen gun. The procedure has been repeated for three times, and then the samples have been annealed in the air at a temperature of 250 °C for 30 minutes to transform $Zn(CH_3COOH)_2{\cdot}2H_2O$ into ZnO, and slowly cooled to room temperature.

2.2. GROWING OF ZnO NANOTUBE ARRAYS

ZnO nanorods and nanotubes have been grown by applying a hydrothermal method and using 0.1M equimolar zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$) aqueous solution.

Growth solution has been poured into a glass vessel with a glass lid and the samples have been dipped in the solution with the pre-seeded ZnO layer downwards to separate them from sediment created during the chemical reaction.

The vessel with the samples has been placed in a programmed LINN HIGH THERM oven preheated to 90 °C.

The growth process takes place in two phases:

a) A temperature of 90 °C is maintained for 3 h;

b) The temperature is lowered to 50–60 °C and maintained at this level for 18–20 h.

A sample with nanorods obtained in the growing process of 90 °C for 3 h is considered the control sample.

2.3. ANALYSIS

To determine the crystalline structure and phase composition of the obtained sample, XRD analysis has been carried out using a diffractometer RIGAKU Smart Lab Cu-Kα (λ=1.543 Å) with high resolution parallel beam scanning geometry and additional Ge(220)x2 monochromator. The obtained XRD pattern has been analysed by PDXL software.

The surface morphology has been determined by using a scanning electron microscope (SEM, TESCAN-VEGA LMU II).

Optical spectra have been taken by Shimatzu spectrophotometer.

3. RESULTS AND DISCUSSION

During the process of growth, the following reactions take place:

$$C_6H_{12}N_4+6H_2O \rightarrow 6HCHO+4NH_3 \quad (1)$$

$$NH_3+H_2O \rightarrow NH_4^{+}+OH^{-} \quad (2)$$

$$2OH^{-}+Zn^{2+} \leftrightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 \leftrightarrow ZnO+H_2O \quad (4)$$

These reactions are in equilibrium and can be shifted from this equilibrium by changing physical parameters, such as temperature, precursor concentration, pH and the growing time. According to [19], precursor concentration determines the density of rod distribution, but the time of growth, temperature and pH determine the morphology and aspect ratio of facets.

HMTA is a slowly decomposing weak base, which creates a weak alkaline environment in the solution and provides Zn^{2+} ions with OH^- ions (see eqs. (2), (3)) [2], [4], [8].

At high temperatures, HMTA decomposes rapidly; therefore, in a short period of time it produces many OH^- ions that are enough for the complete growth process of nanostructures: that is why at high temperatures the base diameter of the rod is greater than at low temperatures: at first, both the lateral growth and axial growth occur extremely rapidly; however, in the case of a high-speed chemical reaction at high temperatures by increasing growth time, the Zn^+ precursor concentration is exhausted rapidly and, as a result, incomplete rods with pointed tops (pyramids, needle-like shapes) are formed [8], [19].

In our experiment, we have performed two previously described full hydrothermal cycles for obtaining nanotubes, which differ only in the initial temperature of the first hours of growth. As Fig. 1 shows, when increasing the temperature in the first phase from 90 °C to 105 °C, and in both cases maintaining the temperature in the second phase at 50 °C, incomplete rods with pointed tops are formed instead of nanotubes in Case b.

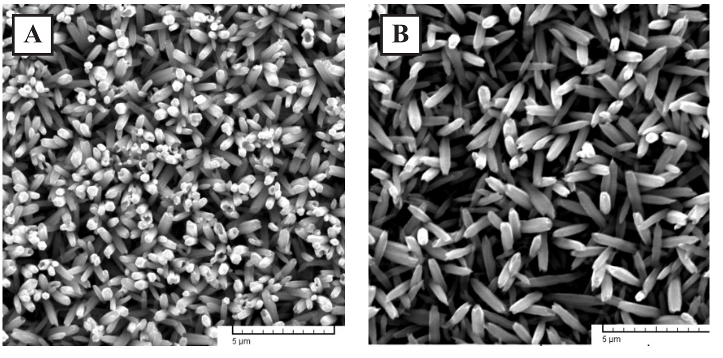

Fig. 1. SEM image of hydrothermally grown ZnO nanostructures at 0.1 M solution on ED seed layer; *a*) 90 °C 3 h, 50 20 h; *b*) 105 °C 3 h, 50 20 h.

When choosing the optimal temperature of growth, it is necessary to take into consideration that at significantly lower temperatures the reaction is slower, but the mobility of atoms is low, the length of diffusion is small and, therefore, the density of the rods is also low, which is why the optimal temperature of growth should be between 70–90 °C [4], [8], [19].

When choosing the period of growth, it should be taken into account that within the 30-minute time interval lateral growth dominates: the needles grow in width. After this interval expires, the diameter of needles no longer changes. Within a 30 min – 6h period of time axial growth dominates: the rods grow in length. Within the 30 min – 6h period of time, both lateral growth and axial growth take place [19].

During this period, the length and diameter of needles double, and the aspect ratio of sides is close to the constant value [19].

In our experiment, 3h has been chosen as the optimum for supporting the sample, where the rods have completely been formed but have not grown fully together yet to form a solid film.

Another important growth parameter is the pH level of the solution. Commonly the growth solution is slightly alkaline, but it is possible to change it in acid or alkaline solutions of small concentrations.

As shown in [3], changing the solution pH morphology of ZnO nanostructures also radically changes other elements: the increasing pH level of the growth solution significantly reduces rod diameter, but length increases, and instead of vertically arranged nanorods and nanotubes arrays, there are one-point-centred 3D "flower-like", "sea-urchin-like" structures.

It is possible to change the solution pH not only by adding an acid or alkali, but also by modifying the concentration of the growing solution [4], [8]. As the experiment demonstrates, the pH of equimolar Zn $(NO_3)_2$ and HMTA solution increases from 5.41 to 6.31 when the concentration decreases from 0.1 M to 0.0025 M (see Fig. 2), which causes the morphology to change from rods at a lower pH level to 3D "urchin-like" structures at higher pH values.

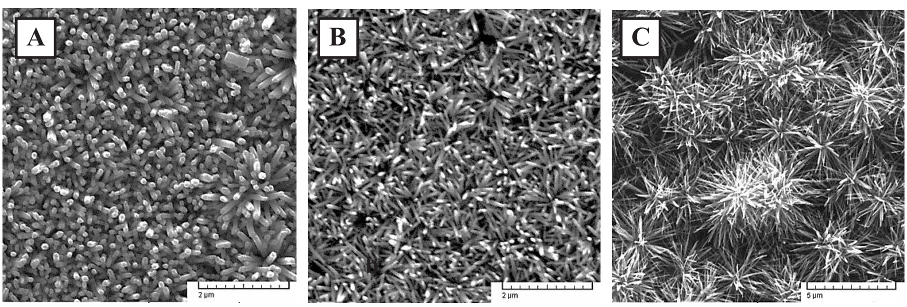

Fig. 2. SEM image of hydrothermally grown ZnO nanostructures using equimolar growing solution concentration; *a*) 0.1 M, pH (90 °C)=5.41; *b*) 0.05 M, pH (90 °C)=5.92; *c*) 0.0025 M, pH (90 °C)=6.31 on ED seed layer t= 15 min, q=40 $\mu A/cm^2$.

It is possible to change the pH level not only by adding specific chemical substances or changing the solution concentration, but also by changing the temperature of the solution: as known [4], decreasing temperature causes an increase in OH^- ion concentration and pH level. This underlies the SSE method of growing nanotubes.

The SSE method of tube formation may be explained as follows.

As we know [4], [8], a hexagonal ZnO has polar and non-polar faces. O-terminated (0001) and Zn-terminated (0001) are typical polar faces, they have a charge and they are metastable: they tend to participate in different chemical reactions with higher probability.

Zn-terminated surfaces are more active than O-terminated, which causes a growth of rods in the c-axis direction.

Non-polar facets are composed of low index faces (parallel to c-axis), such as {1010} and {1120}; they are electrically neutral, contain both Zn and O, and are chemically stable.

Due to the high activity of metastable faces during the growth period, both processes occur: both growing and aging or etching processes.

In the first phase, when a temperature is high (90 °C) and the concentration of Zn adatoms is high too, the growing processes dominate.

In the second phase when reducing the temperature, the pH level of the solution grows from 5.4 at 90 °C to 5.9 at 50 °C and the mobility of adatoms decreases. The major part of the precursor has been used in the first phase (Zn^{+} concentration is exhausted and precipitation rate is limited); therefore, the intensity of the growing process decreases. The aging processes begin to dominate: polar faces start reacting with other substances in the solution and are intensively etched.

An essential role in the nanotube growing process and morphology is played by the obtaining of parameters and quality of seed layer.

3.1. ELECTROLYSIS

In order to determine how the thickness of a seed layer affects nanostructure morphology when maintaining another constantly growing parameter, a series of samples has been prepared using the ED method, which differ only in the density of the electrical current of electrolysis (namely, in thickness of a sedimentary Zn layer per time unit).

The nanostructure arrays have been obtained using the hydrothermal method described above, by lowering the temperature (90 °C 3 h, 50 °C 20 h) and with a 0.1 M equimolar growing solution concentration.

5 minutes have been chosen as the optimal time, at which the seeds have not grown together yet in a solid layer.

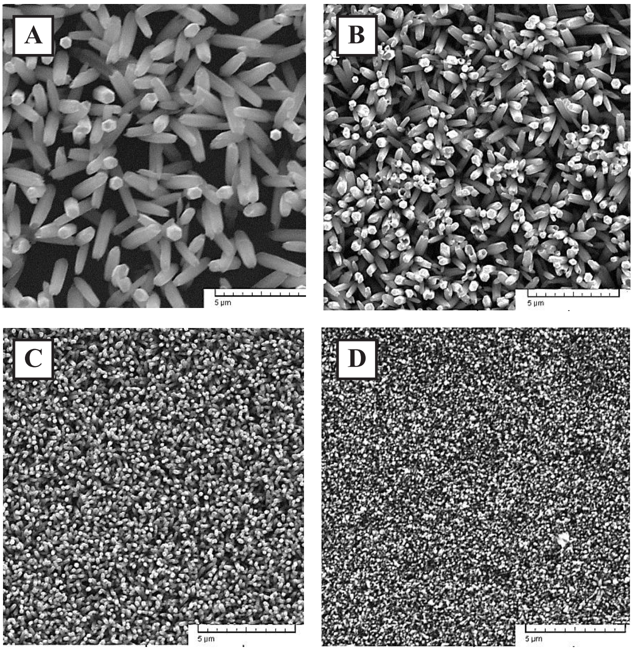

Fig. 3. SEM image of ZnO nanostructure arrays hydrothermally grown on a seed layer obtained at different ED current density; *a*) q=25 µA/cm², *b*) q=40 µA/cm², *c*) q=50 µA/cm², *d*) q=75 µA/cm², and ED time t=5 min, and further hydrothermal growth process at 90 °C 3 h and 50 °C 20 h.

Figure 3 shows that increasing the current density causes an increase in nanostructure arrangement and density, and when the value q=40 μA/cm^2 is exceeded, the dimensions of the nanostructures rapidly decrease, until tubes are no longer observable. The key role of the primary size of the nanorods in the nanotube formation process is also underlined [4], [18].

In a further experiment, the current density q=40 μA/cm^2 has been chosen as the optimum because at this density the array of nanostructures is sufficiently aligned and the dimension of nanorods still allows them to transform into nanotubes.

A series of experiments with the concentration of the electrolyte solution has been carried out to improve the dimension and form of the tubes, and it has been established that the optimal result can be achieved when the seed layer is obtained at the concentration of 50 mmol, current density of 40μA/cm^2 and at the time period of 5 minutes. The results are shown in Fig. 4.

The XRD pattern shows that arrays of nanorods and nanotubes obtained under these conditions are textured and well-aligned in the vertical direction (major peak corresponds to (002) plane); there is a high degree of crystallinity and a homogenous chemical composition, because all the peaks correspond to ZnO and ITO.

For tubes the {002} plane corresponding to peak intensity is twice as low as in the case of rods. This leads to the conclusion that the surface parallel, metastable ZnO faces are indeed being etched.

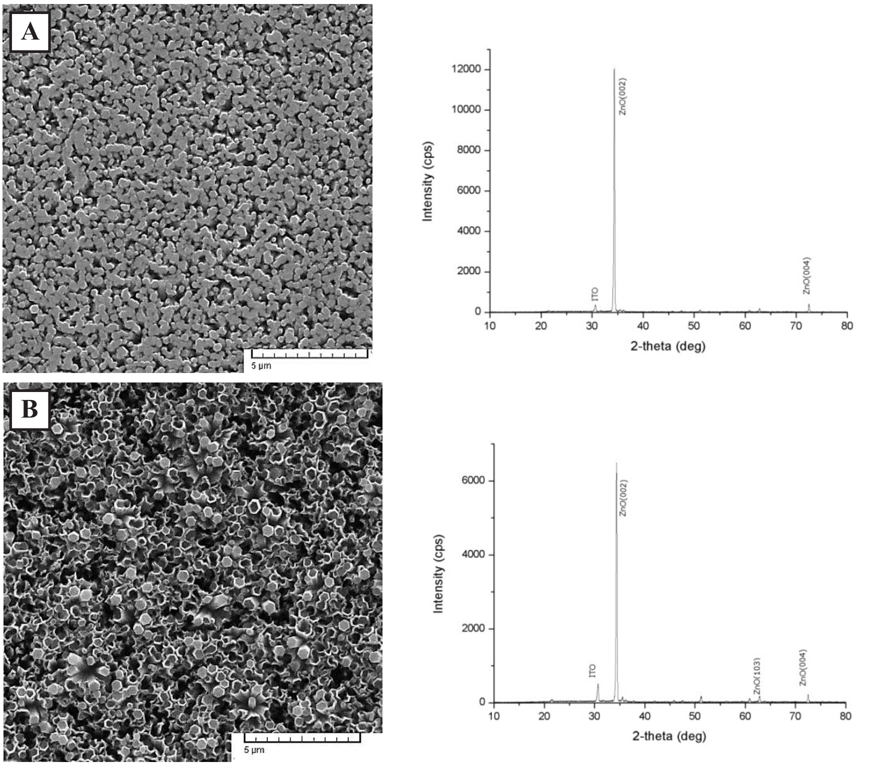

Fig. 4. SEM image of hydrothermally grown ZnO nanostructures using ED seed layer obtained in optimal conditions t=5 min, q=40 μA/cm^2 and their XRD patterns. Solution concentration 0.1 M, reaction time *a*) 3 h 90 °C (reference sample), *b*) 3 h 90 °C, 18 h 50 °C.

3.2. OBTAINING FROM ACETATE SOLUTION

Another method of obtaining a ZnO seed layer is using a Zn acetate ethanol solution [3], [22]–[28].

In comparison with the ED seed layer method, the AD method has a number of advantages: it is not necessary to use an additional conductivity layer such as ITO (which is why there is no influence of this layer on the nanostructure morphology or further analysis and measurements), and there are no limits in coating surface size, quality, and shape.

As [3], [26] show, the optimal concentration is 5 mmol, which allows obtaining well-aligned nanorod arrays with a diameter of 500–700 mm, which is ideal for growing nanotubes.

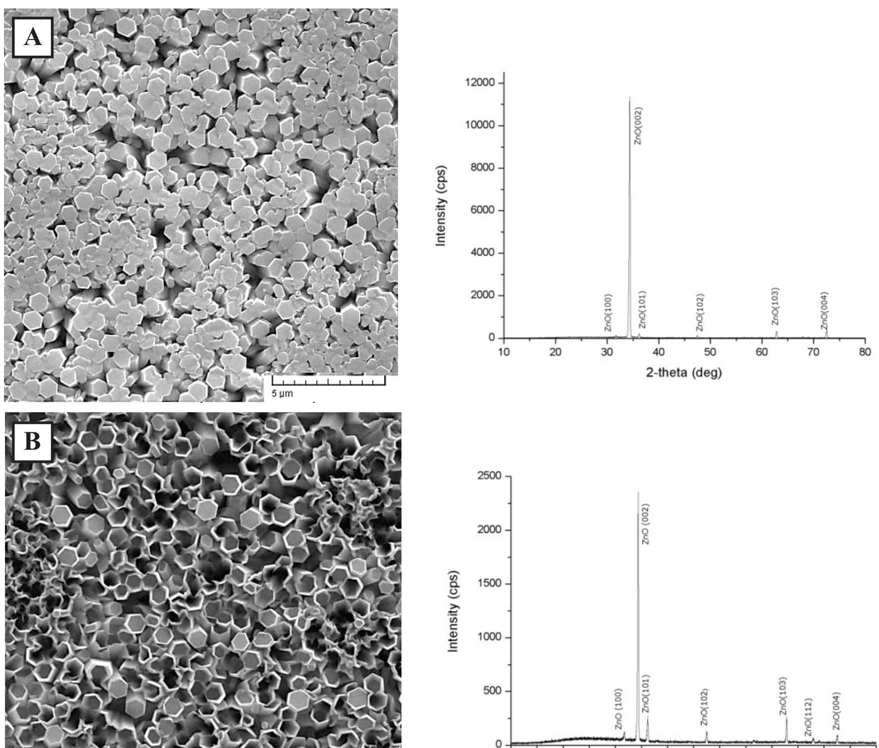

Fig. 5. SEM image of hydrothermally grown ZnO nanostructures using the acetate derived seed layer and their XRD patterns. Solution concentration 0.1 M, reaction time *a*) 90 °C 3 h (reference sample), *b*) 90 °C 3 h, 50 °C 18 h.

Figure 5 shows that after hydrothermal growing cycle of 3 h at 90 °C well-aligned nanorod arrays with 700nm-size crystallites are formed and they have a bigger diameter than those grown on ED seeds, which is why they can be easily transformed into nanotubes during the second growing phase at a lower temperature (18 h 50 °C).

For reference rod samples no difference in crystallinity or alignment occurs for both ED and AD seed layer obtaining methods, which is indicated by the close values of peak intensities of the respective face (002) in XRD patterns.

The dimension of nanotubes grown on AD seeds (3 h 90 °C, 18 h 50 °C) is larger than of those grown on ED layer in the same growth conditions.

For tubes {002} plane corresponding peak intensity is about 5 times lower than in the case of rods and more than 2 times lower than the intensity of tubes grown on ED seeds and it is in agreement with the fact that in the aging process with higher probability of etching there are ZnO metastable planes and {002} plane, in particular: the growth of tube dimension also provokes the growth in the dimensions of metastable areas as well as in the total area of the etched surfaces.

3.3. OPTICAL MEASUREMENTS

To evaluate the optical properties of ZnO nanorods and nanotube coating for further practical applications for detecting different impurities in the solutions, the following experiment has been carried out.

One side of a glass substrate has been coated with a ZnO nanotube/nanorod layer and fixed to a cuvette face, where the other side is without nanostructures. The experiment setup is demonstrated in Fig. 6.

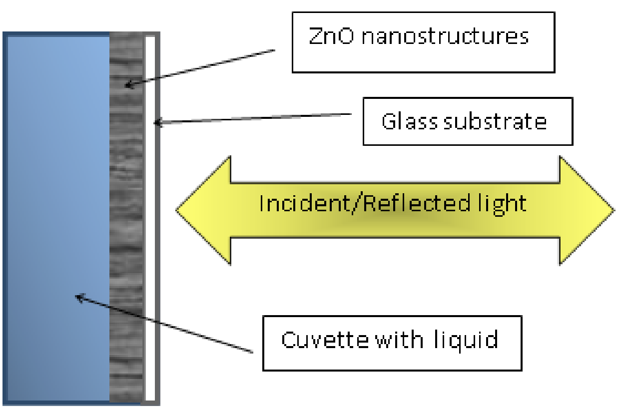

Fig. 6. The measurement setup of ZnO nanostructure array reflection spectra.

The reflection spectra of the samples with ZnO nanotubes (a), and with ZnO nanorods (b), and that of a bare glass substrate are seen in Fig. 7.

As Fig. 7a shows, nanotubes are markedly sensitive to both pure substances (air, ethanol, water) and solutions (e.g., if the spectra of distilled water and tap water or sugar aqueous solutions are compared) in all wavelength ranges: all spectra are parallel.

The degree of nanorod sensitivity is considerably low (see Fig. 7b): it distinguishes pure substances (water, ethanol) but is almost unable to distinguish impurities in water: slight differences can be seen only in the short wave area.

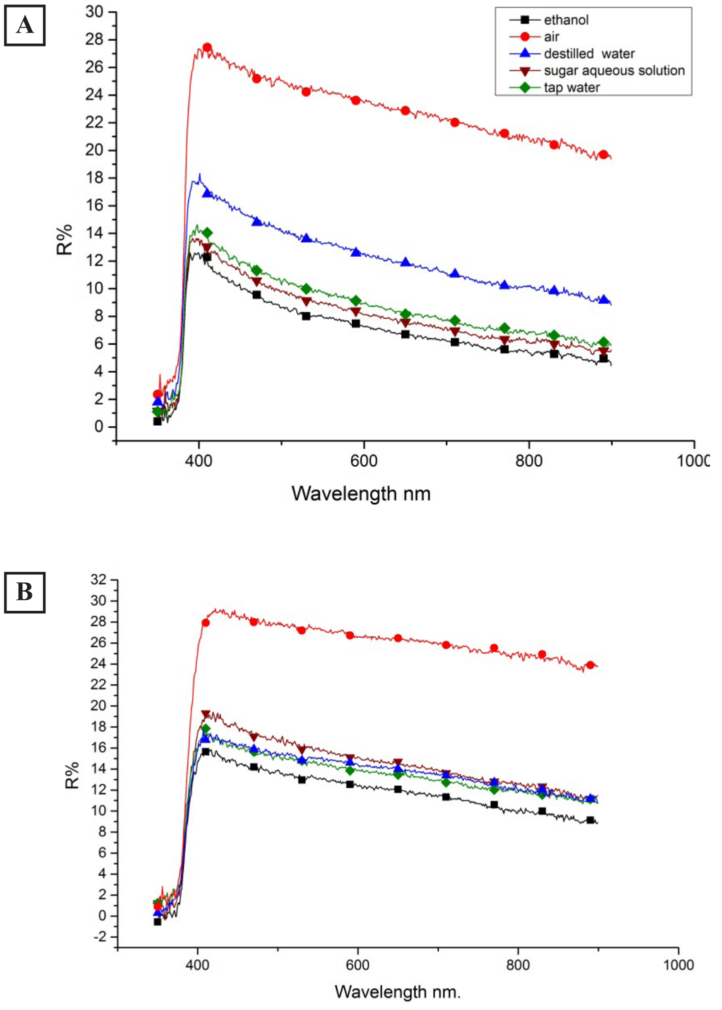

Fig. 7. Sensing properties of ZnO nanotubes (a) and nanorods (b) for different pure substances and aqueous solutions.

The most likely explanation for this phenomenon is a significantly bigger surface area of the nanotubes compared to the nanorods and, consequently, an increasing number of adsorbed molecules of liquid and additives on the surface during physical immobilisation, which causes changes in the ZnO nanostructure array refractive index.

4. CONCLUSIONS

The experiment has demonstrated that ZnO nanostructures are sensitive to their growing conditions and that by varying the growth parameters it is possible to obtain a nanostructure array with a predictable morphology. The method of obtaining ZnO seed layers plays an essential role in their size, morphology and the quality of the nanostructure arrays obtained.

It has been established that most optimal nanotubes appear using the self-selective etching hydrothermal method on pre-seeded glass obtained at a current density q=40 μA/cm^2, time t=5 min, concentration 0.1 M, $Zn(NO_3)_2$ with the ED method or AD method, using 5 mM zinc acetate colloidal ethanol solution. These parameters provide the optimal thickness of a seed layer and, as a result, an optimal rod diameter for further obtaining of nanotubes: if the layer is thicker, needles of a smaller diameter are obtained and nanotubes do not form on them.

Well-aligned arrays of ZnO nanotubes with high crystallinity have been obtained. It has been established that the optical properties of ZnO nanotubes allow for their practical application to detect different impurities in aqueous solutions.

ACKNOWLEDGEMENTS

The present research has been supported by ESF Project No. 2013/0029/1DP/1.1.1.2.0/13/APIA/VIAA/029.

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LABI SAKĀRTOTU ZnO NANOCAURUĻU KOPU IEGŪŠANA, IZMANTOJOT HIDROTERMĀLO METODI

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K o p s a v i l k u m s

Dotajā darbā tika noteikti optimāli parametri labi sakārtotu ZnO nanocaurulīšu kopu iegūšanai, izmantojot hidrotermālo metodi ar temperatūras pazemināšanu, jeb t.s. selektīvu paškodināšanas metodi (self-selective etching), ir uzsvērtas šās metodes priekšrocības salīdzinājumā ar ķīmiskās kodināšanas metodi, kā arī tika aprakstīta dažādu augšanas faktoru (tādu, ka darba šķīduma koncentrācija, augšanas temperatūra un laiks, iedīgļu slāņa iegūšanas veids un iegūšanas parametri) ietekme uz iegūtu nanostruktūru morfoloģiju.

Tika konstatēts, ka noteicošu lomu ZnO nanocaurulīšu audzēšanas procesā spēlē iedīgļu slāņa graudu izmēri, kas savā starpā nosaka augošu nanostieņu izmērus un to tendenci pie paškodināšanas.

Rentgenogrammas parāda, ka iegūtām pie noteiktiem parametriem ZnO nanostruktūrām piemīt augsta kristāliskuma pakāpe un sakārtotība vertikālā virzienā.

Optiskie mērījumi parāda, ka ZnO nanocaurulītes ir jutīgas gan pret tīrām vielām (ūdens, spirts), gan pret dažādiem šķīdumiem, kas ļauj izmantot tos kā piejaukumu sensoru.

Salīdzinājumā ar ZnO nanostieņiem caurulīšu jūtība pieaug, jo pieaug nanostruktūru kopas efektīvā virsma.

11.08.2015.