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Formation of ZnO Nanostructured Thin Film by Hydrothermal Method

V.O. Ulianova[1,*], A.T. Orlov[1,†], O.V. Bogdan[2,‡]

[1] *National Technical University of Ukraine "KPI", 37, Peremogy Ave., 03056 Kyiv, Ukraine*
[2] *Research Institute "Applied Electronics" National Technical University of Ukraine "KPI", 16, Polytechnique Str., 03056 Kyiv, Ukraine*

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Formation of zinc oxide nanostructured thin films at different temperatures on Al-coated silicon and lithium niobate substrates by hydrothermal method was presented. The comparison of morphology of nanostructured thin films formed by hydrothermal and electrodeposition method was carried out. The opportunity to use the hydrothermal method instead electrodeposition to obtain nanostructured films on a conductive layer was shown. The dependence of morphology and crystallinity from growth temperature was established using scanning electron microscopy and X-ray diffractometry. The application of synthesized films as sensing layer of acoustic wave based and electrochemical sensors could enhance its sensitivity to pollutants in gas or liquid phases by an active area increasing.

Keywords: ZnO nanostructured film, Flake-shape particle, Hydrothermal method, Electodeposition, Sol-gel, Sensing element.

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1. INTRODUCTION

Zinc oxide (ZnO) is an attractive material for electronics, photonics and sensing due to having mechanical, piezoelectric, optical and electrical properties, biocompatibility, nontoxicity, chemical and photochemical stability, high specific surface area, optical transparency, electrochemical activities and so on [1]. This wide band gap semiconductor (of 3.37 eV at room temperature) may have numerous possible applications, particularly in the form of thin films, nanowires, nanorods, or nanoparticles [2]. ZnO nanorods could be used as active element of acoustic wave based sensors [3], while ZnO nanostructured films could be used as sensing element of electrochemical enzyme biosensors [4] or as photocatalytic degradation material for environmental pollutants [5].

Various fabrication techniques such as VLS [6], MOCVD [7], and laser ablation [8] have been established for the formation of ZnO nanostructures and films. Due to the disadvantageous of these methods, low-temperature approaches such as hydrothermal techniques [9] and electrochemical growth [3] become more accepted. The electrodeposition method requires voltage applying to the surface for the film formation. It is not always possible, especially when the manufacturing of the sensors array on the single wafer is carried out. The hydrothermal method could be used for the formation of nanostructures or nanostructured films almost on all substrates, but it requires a preparation of a seed layer. The hydrothermal method has following advantages: low-cost, ease handling, scalability, opportunity to form various structures depending on process parameters and it can be integrated with other classical technologies such as lithography, epitaxy or diffusion.

In this paper we proposed the formation of ZnO porous thin film at different temperatures on Al-coated silicon (Si) and lithium niobate ($LiNbO_3$) substrates by hydrothermal method and on Al-coated Si substrates by electrodeposition method for application as sensing layer of acoustic wave based and electrochemical sensors. Scanning electron microscopy and X-ray diffractometry were used to examine the morphology and crystallinity of fabricated ZnO nanostructured thin films.

2. MATERIALS AND METHODS

There were two main steps in ZnO nanostructured film hydrothetmal growing: (1) preparation of a ZnO seed-layer by sol-gel method and (2) nanostructured thin film growing by hydrothermal method. We used the technic similar for the synthesis of ZnO nanorods described in [10].

Initially the Al thin film was deposited on the $LiNbO_3$ and Si substrates by magnetron sputtering. Al-coated substrates were cleaned with hydrogen peroxide at 30 °C for 30 min. For the first step zinc acetate dihydrate (ZnAc) $Zn(COOCH_3)_2 \cdot 2H_2O$ was used as the starting salt material to prepare ZnO thin films by sol-gel method. The ZnAc was dissolved in isopropanol ($(CH_3)_2CHOH$). Then monoethanolamine (MEA) $HOCH_2CH_2NH_2$ solution was added at room temperature. The concentration of ZnAc was 0,8 mol/l and molar ratio of MEA to ZnAc was kept to 1,0. The mixture was stirred by a magnetic agitator at 65 °C until the clear and homogeneous solution formed. Prepared sol-gel was cooled to room temperature and filtered with 0,22 μm membrane filter. Film deposition was carried out in air at room temperature. The precursor solution was spin coated at 3000 rpm for 30 s on the substrate.

* v.ulianova@gmail.com
† atorlov@rambler.ru
‡ bogdan@ee.ntu-kpi.kiev.ua

After each coating the obtained film was dried at 100 °C for 30 min at the sintering furnace. The pre-heat-treatment temperature at 100 °C is required for the complete evaporation of organics and the initiation of formation and crystallization of the ZnO film. After the deposition of the fifth layer, the resulting thin films were annealed at 400 °C in air for 1 h to obtain the homogeneous and stable film.

The equimolar (1 : 1) mixed solution of analytically pure ZnAc and hexamethylenetetramine (HMT) $C_6H_{12}N_4$ was used for the second step. The chemicals were solved in deionized water, resulting in a transparent solution under magnet stirring for 5 min at room temperature. The as-pretreated substrates were immersed and suspended in the mixed solution and the growth of ZnO was carried out by heating the reaction solution from room temperature to 60 °C for the first experiment and to the 80 °C for the second one and then stayed for 1.5 h without any stirring. The as-grown pattern was rinsed with deionized water for several times and dried in air at room temperature before characterization. The electodeposition were carried out in the same solution at temperature of 60 °C at applying 1.5V DC between neighboring conducting lines for a deposition time of 40 min, a stainless steel sheet acts as a counter electrode. The spacing between both electrodes was about 2 cm.

Scanning electron microscopy (JEOL Ltd., NeoScope JCM-5000) was used to examine the morphology of the films. The structural properties of the as-prepared ZnO nanostructured films were characterized by Rigaku X-ray diffractometer ULTIMA IV in asymmetric mode.

3. RESULTS AND DISCUSSION

ZnO porous thin film which consists of flake-shape particles was synthesized by the combined with sol-gel technique hydrothermal method on Al-coated Si and $LiNbO_3$ substrates at different temperatures. The seed layer deposition was carried out to provide the growing centers and bonding interface with substrates.

The temperature of the hydrothermal synthesis have affected on morphology and crystallinity of the structures. From SEM images (Fig. 1) it could be noticed that all the patterns demonstrated good regularity overall observed surface (about 10 × 9 μm). ZnO thin film gown at 60 °C was more regular than the thin film gown at 80 °C. The distance between flake-shape particles made pores on the thin film. For the patterns synthesized at 80 °C the distance between flake-shape particles were larger, but the particles became thicker or grown together.

The nanostructured thin film obtained by electrodeposition method consists of the same flake-shape particles. The distances between them were larger than between particles synthesized at 60 °C by hydrothermal method, and the density of the film was lower. It could be caused by growing time or applying of a voltage.

The crystalline phase of the flake-shape particles was assessed by conducting XDR measurements (Fig. 2). It was carried out 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. It could be seen that synthesized nanostructured film demonstrated diffraction

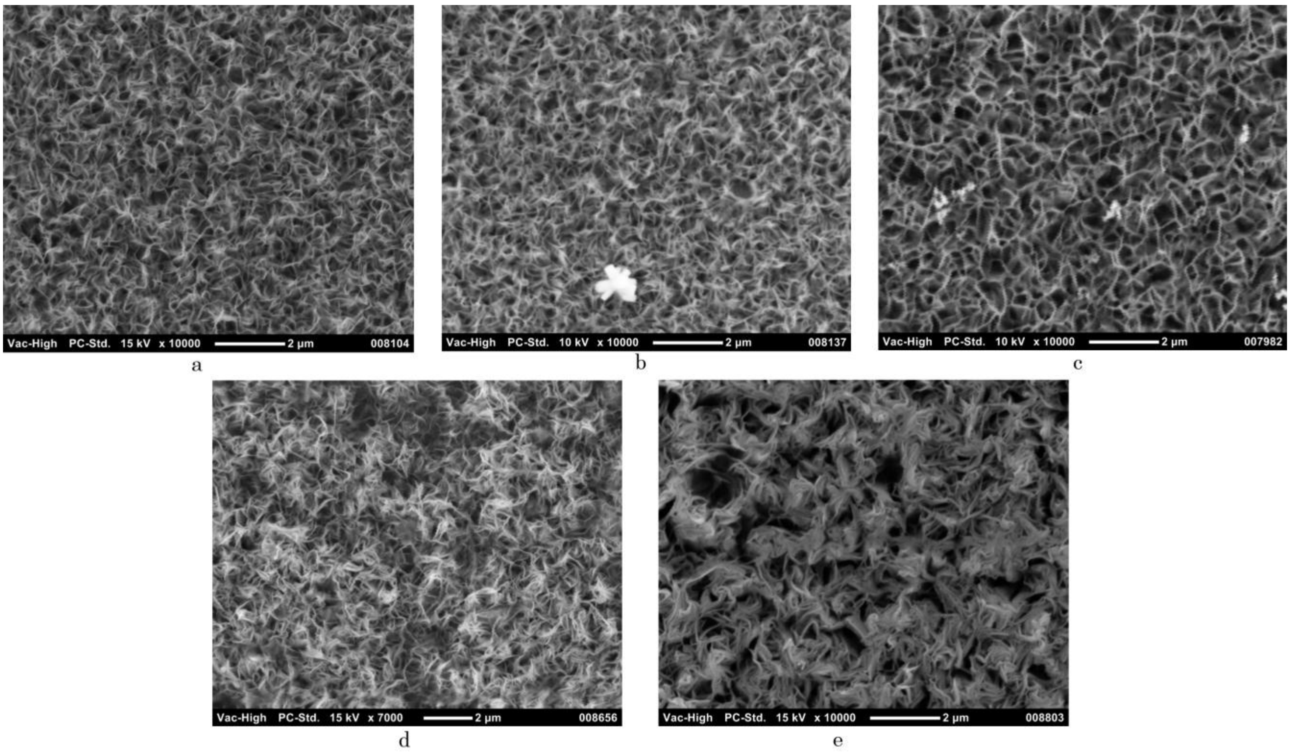

Fig. 1 – SEM images of ZnO nanostructured film deposited at 60 °C (a-c) and at 80 °C (d, e) on the Al-coated Si (a, c, d) and Al-coated $LiNbO_3$ (b, e) substrates by hydrothermal method (a,b,d,e) and electrochemical growth (c)

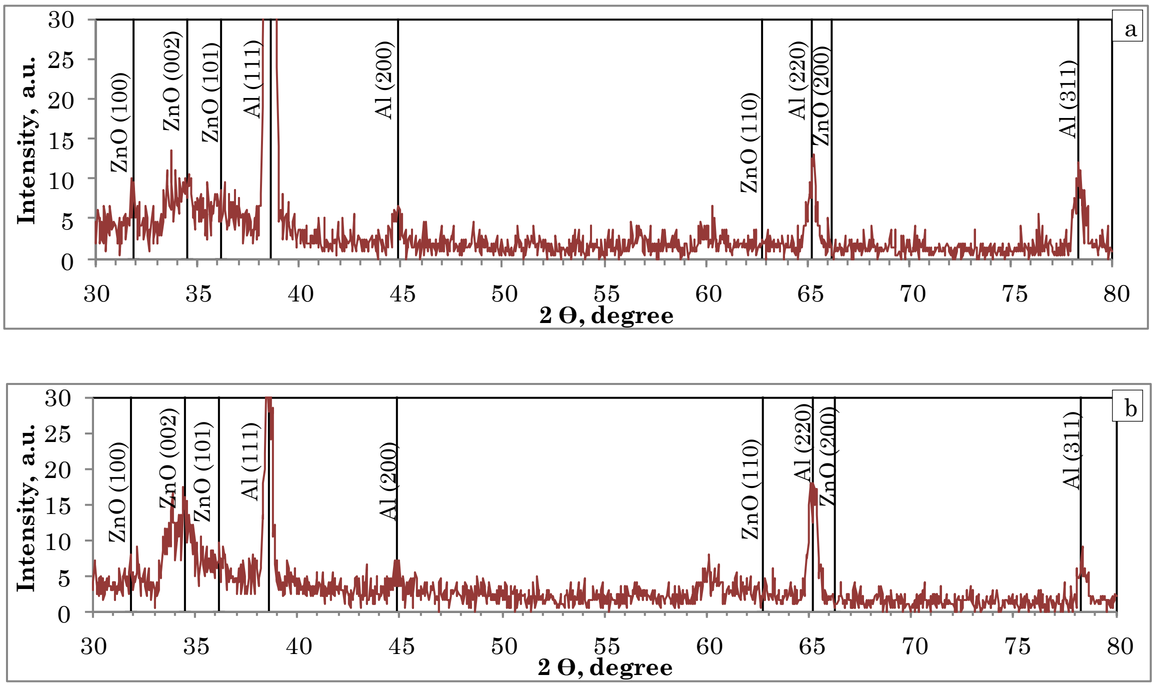

Fig. 2 – XRD patterns of the ZnO nanostructured thin film grown on $LiNbO_3$ substrates at 60 °C (a) and 80 °C (b)

peaks corresponding to the (100), (002), (101) and (200) planes of hexagonal ZnO. Others peaks corresponded to Al-coating. It was shown that reflexes corresponding to the plane (002) were the most intensive. This implied that atoms were arrangement in c-axis which was perpendicular with the substrate.

4. CONCLUSION

ZnO nanostructured thin films were formed by hydrothermal and electrodeposition methods on Al-coated Si and $LiNbO_3$ substrates at 60 °C and 80 °C. It was shown that films obtained by hydrothermal and electrodeposition methods had the same morphology. This result allows the use of hydrothermal method instead of electrodeposition for the high quality nanostructured ZnO thin films formation as sensing element of any configuration of sensors or sensors array including planar electrodes of electrochemical sensors.

The hydrothermal method was ease handling and the morphology of the obtained structures depended from such process parameter as temperature. It was established that regularity of the synthesized at lower temperature film was better, but crystallinity of the flake-shape particles was more pronounced for the synthesized at higher temperature film.

Presented structures could significantly increase an active area of sensing devises, this way enhance their sensitivity to pollutants in gas or liquid phases.

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