Formation of ZnO nanorods on seed layers for piezoelectric nanogenerators

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Abstract. The influence of zinc oxide seed layers on morphological and electrophysical properties of ZnO nanorods was studied. Sublayers were obtained via spin-coating and magnetron sputtering methods. Nanorods were produces via low-temperature hydrothermal synthesis in the presence of anionic and zwitterionic surface-active substances. Characterization of the obtained coatings was carried out using scanning electron microscopy and atomic-force microscopy methods.

1. Introduction

In the 21st century, the development of nanoelectronics sets special terms for the elemental base of energy sources. Piezoelectric nanogenerators (PENG), which are devices that convert scattered mechanical energy in the pulses of electric current [1], are promising for powering medical devices inside a human body (e.g. pacemakers) and for a vehicles pressure conversion on the roads. Such devices are sources of renewable energy, furthermore, PENGs open-circuit voltage can reach 30 V [2].

Piezoelectric crystals – dielectric and semiconductor materials with a lack of a symmetry center in a crystal structure - are used as an active part of the PENG. Inorganic materials are mainly used because of rapid thermal and mechanical degradation of the organic one.

Among the wide variety of materials (PZT, GaN, CdS etc.) for formation of the active part of the PENG one of the most promising is zinc oxide ZnO – wide bandgap semiconductor ($E_g = 3.36$ eV), which has a $n$-type conductivity [3]. The advantages of this material are high values of piezocoefficients in the direction of the 6th order axis, high chemical resistance, technological ease of preparation, possibility to use this material at the high and ultra-high frequencies. Materials based on low-dimension ZnO structures are being applied in gas sensors [4, 5], photocatalytic systems and new generation solar cells.
ZnO one-dimensional (1D) nanostructures (nanorods) form an active part of PENGs [6]. In comparison with bulk materials using 1D-nanostructures allows to increase the output signal due to their parallel connection between the electrodes, to improve the mass-dimensional characteristics and effectively change the properties of an active layer. To obtain highly oriented nanorods it is necessary to ensure their growth from the seed layer. In this paper, the formation of sublayers was carried out by spin-coating and magnetron sputtering methods because of their efficiency and the possibility to obtain thin films with a small size of crystallites.

2. Experiment

Spin-coating is the method of applying thin films based on the coating a substrate with an agent solution with the further rapid rotation leading to the removal of a solvent and formation of a thin film. 10 mM ethanol solution of chemically pure zinc acetate Zn(CH$_3$COO)$_2$ was used as the source of the zinc oxide in this method. Spin-coating was carried out for 60 s at the rate of 3000 revs per min. Annealing of samples on Si-(100) substrates was held at 350°C, and for samples on PET-substrates (polyethylene terephthalate) with ITO (60 Ohm/cm) layer (Sigma Aldrich) – at 120°C.

Also sublayers were made by magnetron sputtering. Deposition of ZnO and ITO thin films was carried out using RF magnetron sputtering setup (BOC EDWARDS Auto 500RF) from ZnO and In$_2$O$_3$ (90%) SnO$_2$ (10%) sintered targets, respectively. Deposition of thin films performed at room temperature. Pure argon (99.999%) and oxygen (99.999%) were used as working gases.

Finally, ZnO nanorods were produced on the obtained thin films via low-temperature ($T = 85°C$) hydrothermal synthesis. The solution of Zn(NO$_3$)$_2$ 25 mM was used as a Zn$^{2+}$ precursor. As the result of two-stage hydrolysis reaction unstable zinc hydroxide is formed:

$$
\text{Zn(NO}_3\text{)}_2 + \text{H}_2\text{O} \leftrightarrow \text{Zn(OH)NO}_3 + \text{HNO}_3 \quad (1)
$$

$$
\text{Zn(OH)NO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Zn(OH)}_2 + \text{HNO}_3 \quad (2),
$$

which converts by the reaction $\text{Zn(OH)}_2 \rightarrow \text{ZnO}_{\text{solid}} + \text{H}_2\text{O}$ into zinc oxide.

Hexamethylenetetramine was used (HMTA) C$_6$H$_{12}$N$_4$ for the creation of a buffer solution and consequently providing the possibility of carrying out synthesis at the low (less than 100°C) temperature [7] due to its slow two-step OH$^-$ groups release:

$$
\text{C}_6\text{H}_8\text{N}_4 + 6\text{H}_2\text{O} \leftrightarrow 6\text{HCHO} + 4\text{NH}_3 \uparrow \quad (3)
$$

$$
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (4)
$$

Formed in the process of the hydrolysis zinc cations Zn$^{2+}$ react with anions of alkali OH$^-$ with various hydroxides formation: ZnOH$^-$ (aqueous), Zn(OH)$_2$ (aqueous), [Zn(OH)$_3$]$^-$ (aqueous) and [Zn(OH)$_4$]$^{2-}$:

$$
\text{Zn}^{2+} + \text{OH}^- \leftrightarrow [\text{Zn(OH)}]^+ \quad (5)
$$

$$
\text{Zn}^{2+} + 2\text{OH}^- \leftrightarrow \text{Zn(OH)}_2 \quad (6)
$$

$$
\text{Zn}^{2+} + 3\text{OH}^- \leftrightarrow [\text{Zn(OH)}_3]^- \quad (7)
$$

$$
\text{Zn}^{2+} + 4\text{OH}^- \leftrightarrow [\text{Zn(OH)}_4]^{2-} \quad (8)
$$

Charged hydroxocomplexes of zinc are adsorbed on the respective surfaces of oxygen O$_2^-$ and the zinc Zn$^{2+}$ due to the presence of the pyroelectric effect in seed ZnO crystallites with a further condensation in the oxide form. Zinc hydroxide Zn(OH)$_2$ (6) is not involved in the process of growth 1D-nanostructures ZnO because of an absence of charge. One of the possible ways of hydroxide – oxide conversion is the process (9):

$$
[Zn(OH)]^{2-} \leftrightarrow \text{ZnO} + 2\text{H}_2\text{O} + 2\text{OH}^- \quad (9)
$$

Overall, the chemical reaction can be written as:

$$
\text{Zn}^{2+} + 2\text{OH}^- \leftrightarrow \text{ZnO} + \text{H}_2\text{O} \quad (10)
$$

Reactions take place in the solution lead to minimization of the free energy of the entire system. As the polar planes (0001) have the highest energy, an adsorption of occurred during reactions (1)-(4) molecules happens on these polar planes with the further nanostructures growth in the c axis direction. In particular, the adsorption of molecules occurs due to formation of a monolayer which has an opposite polarity to the existing (0001) plane. Thus, on the surface of Zn$^{2+}$ atoms, the precipitate
hydroxides are formed in (7) and (8), then, according to reaction (9), ZnO is formed. At the end, the plane (0001) ends again with Zn$^{2+}$ ions.

Dielectric insulation of the nanorods, as well as control of the morphology of the obtained structures was achieved by addition to stock solution anionic (sodium lauryl sulfate C_{12}H_{25}SO_{4}Na, SLS) and zwitterionic (cysteine C_{3}H_{7}NO_{2}S, Cys) surface-active substances (surfactants) with concentrations 1 surfactant molecule per 10 Zn$^{2+}$ cations. Using SLS reduces the rate of growth of zinc faces due to the adsorption of C_{12}H_{25}SO_{4}-. The use of Cys moreover leads to the diminution of O$_{2}^-$ edges growth rate, in addition to zinc one, due to the partial hydrogen sulphide release and C_{3}H_{6}NO_{2}+ formation.

3. Results and discussion

Obtained structures were investigated using scanning electron microscope (SEM Seron Technology AIS 2300C, TESCAN MIRA LMU with an energy dispersion spectrometer EDX). Morphological and electrophysical characteristics of ZnO layers were studied using atomic force microscopy (AFM Therma NTEGRA NT-MDT).

In the case of the seed layers obtained via spin-coating method and annealed at temperatures less than 330°C the formation of zinc oxoacetate crystallites takes place:

$$4\text{Zn(CH}_3\text{COO)}_2 \rightarrow \text{Zn}_4 \text{O(CH}_3\text{COO)}_6 + (\text{CH}_3)_2\text{CO} + \text{CO}_2$$

For a sample obtained on Si-substrate and annealed at $T_{an}=120°C$ elemental composition analysis was carried out by electron probe micro analysis method (EPMA) (figure1).

![Figure 1. EPMA-data of ZnO seed layers obtained via spin-coating method on Si-substrate at an annealing temperature $T_{an}=120°C$.](image)

Peak corresponding to carbon indicates the zinc oxoacetate crystallites formation at low temperatures of the synthesis. These coatings cannot be used as the seed layers for the formation of ZnO nanorods due to the absence of a pyroelectric effect in the material.

The optimal samples annealing temperature for the ZnO solid phase formation is 350°C, herewith the reaction proceeds on a substrate surface with the formation of homogeneous layers:

$$\text{Zn(CH}_3\text{COO)}_2 + 4\text{O}_2 \rightarrow \text{ZnO} + 4\text{CO}_2↑ + 3\text{H}_2\text{O}$$

The average size of obtained on Si-substrates at $T_{an}=350°C$ zinc oxide crystallites is 50 nm (figure 2).
Figure 2. AFM-data of ZnO thin film (5 layers): a - topography, b – phase contrast.

With spin rate increasing a porosity of the layers decreases, however, at speeds above 5000 rpm is the uneven distribution profile of the film along the radius of the sample is observed.

ZnO 1D-nanostructures were produced on the obtained sublayers via low-temperature hydrothermal synthesis. The best ratio of a diameter to length $X$ was achieved using cysteine as the surfactant (table 1). This effect may be associated with the possibility of zwitterionic surfactants adsorption on both sublattices, while anionic surfactants can be adsorbed only on the zinc one. As the growth of ZnO nanorods in the $c$ axis direction ends by ions Zn$^{2+}$, the presence of anionic surfactants in solution reduces the rate of growth in this direction.

Table 1. The dependence of the ZnO nanorods aspect ratio obtained on spin-coating seed layers (5 layers) on the nature of the surfactant.

| Surfactant                  | The dimensions of nanorods | $D$ = 30 nm, $L$=600 nm, $X$=0.05 |
|----------------------------|---------------------------|-----------------------------------|
| Cysteine                   | Sodium LAryl sulfate      | $D$ = 60 nm, $L$= 630 nm, $X$=0.09 |

Changing pH by adding an aqueous solution of ammonia leads to a uniform one-dimensional arrays of ZnO nanorods formation, moreover, their average diameter increases (figure 3). 

Figure 3. SEM-data of ZnO nanorods (5 seed layers obtained with the spin rate 3000 revs per min on Si-substrates): a – pH=10, b – pH=13.5.

In the absence of NH$_4$OH addition solution become depleted during the process of growth, whereby the geometrical parameters of the nanorods depend on the size of the sublayers crystallites, moreover, increase in time of synthesis does not change the sample structure. With increasing in the concentration of OH$^-$ groups the solution is less depleted in the synthesis process, therefore, the size of the nanorods is mainly determined by the time of synthesis.
For the creation of a seed layers on flexible PET-substrates magnetron sputtering method was used. The deposition of thin films was carried out at room temperature. Thickness of obtained layers reached 10, 20, 30 nm.

The dependence of the nanorods sizes obtained on 20 nm seed layers (via magnetron sputtering method) on the nature of the surfactant is presented in the table 2. The best aspect ratio (as in the case of layers obtained by spin-coating method) refers to the 1D-nanostructures formed in the presence of Cys.

**Table 2.** The dependence of the ZnO nanorods aspect ratio obtained on magnetron sputtering seed layers (20 nm) on the nature of the surfactant.

| Surfactant                 | The dimensions of nanorods                                      |
|----------------------------|-----------------------------------------------------------------|
| Cysteine                   | $D=25$ нм, $L=390$ нм, $X=0.06$                                 |
| Sodium lauryl sulfate      | $D=40$ нм, $L=350$ нм, $X=0.11$                                 |

According to SEM-data disordered growth of nanorods with increasing thickness of seed layers was found (figure 4).

**Figure 4.** SEM-data of ZnO nanorods, obtained on PET-substrates in the presence of SLS with a seed layers thickness: $a$ – 10 nm, $b$ – 30 nm.

This effect occurs due to increased probability of seed crystallites formation in different crystallographic directions, beside this increases thickness of nanorods and their length.

Electrophysical parameters of the structures obtained in the initial stages of growth with using SLS as surfactant were investigated using piezo-response force microscopy PFM (figure 5). Probes NSG10 were used in this paper (tip curvature radius 10 nm, resonant frequency 240 kHz, force constant 11.8 N/m, cantilever length 95 мkm, cantilever width 30 мkm, cantilever thickness 2 мkm):

**Figure 5.** PFM-data of ZnO nanorods, obtained on PET-substrates in the presence of SLS: $a$ – topography, $b$ – amplitude, $c$ – phase.
The piezoelectric response was registered on nanostructured coatings; moreover, its maximum value reached 350 pA. Detailed piezo-response force microscopy data analysis allows concluding that the main directions of the piezoelectric response in the initial stages of nanorods formation are directions along the surface of the substrate. The emerging crystallites are polarized in lateral directions. This conclusion is confirmed by increase in the number of disordered ZnO nanorods formed in these conditions in the later stages of hydrothermal synthesis (figure 4).

4. Conclusion

In this paper, arrays of ZnO nanorods were obtained via soft hydrothermal synthesis in the presence of different surfactants (cysteine, sodium lauryl sulfate) on the seed layers obtained by spin-coating and magnetron sputtering methods. These methods allow forming thin films with high homogeneity of the crystallites.

The using of zinc acetate as the source of zinc cations for the seed layers formation via spin-coating method is not possible on PET substrates due to the low melting temperature of the polymer.

The optimal thickness of the sublayer, is obtained by magnetron sputtering is 10 nm. With appropriate thickness of ZnO sublayer increases the probability of tunneling of charge carriers in the lower electrode increases, growth oriented nanorods perpendicular to the substrate.

Thus, the most optimal method of the seed layers formation is the method of magnetron sputtering, which provides the possibility of ZnO films deposition at low temperatures.

The best aspect ratio X=0.05-0.06 independent of the thickness of the nucleation layer was achieved using cysteine as the surfactant. The increase in the concentration of OH- groups leads to the formation of nanorods with an equal length. These nanostructured coatings can be used as an active part of piezoelectric nanogenerators.

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