Formation of an active part of inertial mass based piezoelectric nanogenerator

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Abstract. Zinc oxide piezoelectric nanostructured coatings were formed on tantalum and aluminum substrates by the chemical solution methods. The methods mentioned above are suitable for formation of active parts of inertial mass based piezoelectric nanogenerator (PENG). This PENGs design using leads to an enhanced output due to the increased effective active parts area. Obtained nanostructured ZnO coatings were investigated by scanning electron microscopy and atomic force microscopy.

1. Introduction

In accordance with the increasing energy demands a large number of alternative energy converters are being developed. Recently, converters of mechanical impact pulses energy into electrical current – piezoelectric nanogenerators (PENG) – are widely disseminated [1, 2].

One of the most prospective materials for a PENGs active parts formation is zinc oxide ZnO – wide bandgap \(E_g = 3.36 \text{ eV at } T = 300 \text{ K}\) semiconductor compound of \(\text{A}_2\text{B}_6\) group, which crystallizes in wurzite modification under normal conditions [3]. Zinc oxide has piezoelectric properties due to the lack of the inversion center and to the partially ionic nature of the relationship between the cations \(\text{Zn}^{2+}\) and anions \(\text{O}^{2-}\).

In most papers [4, 5] for the ZnO nanorods (NR) based PENG is used a construction in which the nanorods are vertically oriented to a stiff substrate and upper electrode. During the deformation of 1D-nanostructures in the 6th order axis direction the electrical signal is formed. The main disadvantage of this design is the applications constraint due to the required horizontal devices position and a uniform mechanical loads distribution on upper electrode surface.

Flexible substrates application narrows the range of methods suitable for the active part formation due to low temperature resistance. However, with the using of PENGs in a flexible manner the possibility of uneven vibration impact appears, as well as the implementation of the nanogenerator with a partially suspended fixed design [6, 7].

Among a wide variety of methods for a ZnO based PENGs active part formation chemical bath deposition was used [8] because of the low synthesis temperatures and the possibility of nanostructures formation on both sides of a substrate in a single technological cycle.

2. Piezoelectric nanogenerator design
The structure of the piezoelectric generator created in this work is shown in figure 1. PENG is performed on a flexible dielectric substrate (marker 1) with lowers electrodes coated sides. The necessity of their separation is caused by opposite polarities of the voltage generated by the upper and lower (marker 2) active parts of the nanogenerator.

![Figure 1. The ZnO nanorods based piezoelectric nanogenerator scheme.](image)

One of the parts is rigidly fixed in the wall, located in the vertical plane (marker 3). Vibration impact is transmitted through the wall on the fixed part of the PENG. Increasing the nanogenerator sensitivity to a mechanical impact is achieved by the inertial mass application (marker 4) made of a dielectric polymeric material.

Lower electrodes terminals are located behind the wall (marker 5, a and b). The opposite contact to the active parts is carried out using flat electrodes (marker 6, a and b) fixed in the inertial mass.

The equivalent circuit diagram of the considered device is presented in figure 2. Terminals 1 and 2 (figure 2) correspond to the markers 6, a and 5, a (figure 1), respectively (contacts to the "top" active part of the PENG). Terminals 3 and 4 (figure 2) correspond to the markers 5, b and 6, b (figure 1).

![Fig. 2. The equivalent electrical circuit of ZnO nanorods based piezoelectric nanogenerator.](image)

The main difference between the construction mentioned above and a one active part based PENG consists of increased parasitic capacitances $C_{im}$, corresponded to the inertial mass, and $C_{sub}$, corresponded to the substrate capacitance. The capacitance reduction is achieved by applying materials with a low dielectric permeability $\varepsilon$ at high frequencies and decreasing of electrodes unused area (5, a and b in figure 1).

During substrate selection penetration of the material is also needed to be taken into account (due to the high voltages (up to 200 V) supplied to the generator).

3. **Experimental**

The PENGs active part formation was carried out in two stages: seed layers deposition via liquid phase ionic layering (SILAR) and nanorods synthesis by chemical solution deposition. Seed layers
application is necessary for higher nanorods orientation achievement, as well as improving their adhesion to a substrate.

In the paper tantalum and aluminum substrates were used as the bottom electrode.

3.1. Deposition of ZnO seed layers
SILAR method (liquid phase ionic layering, «Successive Ionic Layer Adsorption and Reaction») [9] consists of the sequential immersion of a substrate into appropriate solutions and proceeds of the following stages:

- creation of the initial solution containing synthesized substances ions;
- ions adsorption on a substrate during solution immersion;
- rinsing the substrate for excess ions removing from the surface;
- reaction in the interaction of adsorbed ions with an aqueous agent;
- drying process for a film securing on a substrate surface.

Zinc nitrate hexahydrate \[ \text{Zn(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O} \] with the 0.1 M concentration and 4.4% aqueous solution of ammonia were used for the solution creation with zinc-ammonium complexes $\text{[Zn(NH}_3\text{)}_4\text{]}^{2+}$:

\[
\text{Zn(NO}_3\text{)}_2 + \text{NH}_4\text{OH} \rightarrow \text{[Zn(NH}_3\text{)}_4\text{]}^{2+} + n\text{H}_2\text{O} + 2\text{NO}_3^- (1)
\]

Within washing in aqueous solution at low temperature (20°C) absorbed complexes $\text{[Zn(NH}_3\text{)}_4\text{]}^{2+}$ partially react with zinc hydroxide formation:

\[
\text{[Zn(NH}_3\text{)}_4\text{]}^{2+} + 4\text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 4\text{NH}_4^+ + 4\text{OH}^- (2)
\]

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 (3)
\]

Increased (more than 900°C) temperature is used for zinc oxide synthesis:

\[
\text{Zn(OH)}_2 + \text{O}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} + \text{O}_2 (4)
\]

Zinc nitrate hexahydrate \[ \text{Zn(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O} \] don't participate in 1D-nanostructures growth, because as a result of its flow the uncharged zinc hydroxide is formed.

Dielectric insulation of the nanorods, as well as control of the morphology of the obtained structures was achieved by addition to stock solution \( L-\text{Cysteine (C}_3\text{H}_7\text{NO}_2\text{S)} \) used as the zwitterionic surface-active substance (surfactant) with concentration 1 surfactant molecule per 10 Zn\(^{2+}\) cations. \( \text{C}_3\text{H}_6\text{NO}_2^+ \) adsorption mainly on ZnO nanorods lateral surfaces leads to an increase in 1D-nanostructures growth rate in the \text{c-axis} direction. Also surfactant hydrophobic parts eliminate adsorbed water layer appearance on the ZnO crystal surfaces, thereby preventing electrostatic leakage on the lateral faces of the nanorods.

Investigation of obtained nanostructures was carried out using atomic force microscopy (AFM Therma NTEGRA NT-MDT) and scanning electron microscopy (SEM Seron Technology AIS 2300C).

4. Results and discussion
Investigation of zinc oxide seed layers via AFM revealed a large roughness of the crystallites (figure 3), meanwhile a large contribution to the structures morphology is made by the relief of the substrate. Deposition of crystallites occurs mainly between the rolling stripes.

![Figure 3. AFM-data of ZnO thin film (1 layer): a - topography, b – phase contrast.](image)

A further number of cycles increasing leads to the formation of uniformly distributed ZnO crystallites.

On the obtained seed layers were formed zinc oxide 1D-nanostructures (figure 4). Usage of tantalum substrates (figure 4, a), in comparison with aluminum, does not lead to the porous structures formation. This effect is explained due to the high inertia of Ta and its oxides formed via heating SILAR layers.

Obtained on Ta substrates ZnO 1D-nanostructures have a hexagonal cut and the average aspect ratio of nanorods $X$ (the ratio of the diameter to the length) is 0.12. Thickness increasing of the seed layer leads to a probable mechanical stresses rising resulting to delamination of zinc oxide nanostructures.

![Figure 4. SEM-data of ZnO nanostructures on substrates (3 seed layers): a - Ta, b – Al.](image)

During the process of chemical deposition the etching of aluminum oxide takes place (figure 4, b). Thus, the etching of the $\text{Al}_2\text{O}_3$ layer occurs via the reaction with the formation of ammonium tetrahydroaluminate:

$$\text{Al}_2\text{O}_3 + 2\text{NH}_4\text{OH} + 3\text{H}_2\text{O} \leftrightarrow 2\text{NH}_4[\text{Al(OH)}_4] \quad (6)$$

$$\text{NH}_4[\text{Al(OH)}_4] \leftrightarrow \text{Al(OH)}_3 \downarrow + \text{NH}_4\text{OH} \quad (7)$$

passing by the reaction (7) in aluminium hydroxide in an aqueous solution during heating with time.

On substrate areas near aluminum plates in the cavities of the porous layer the formation of tetrahydroaluminate ammonium takes place according to reaction (6). This process is parallel to the
surface passivation with the further Al₂O₃ layer formation at the interface solution-aluminum in accordance with the processes:

\[
\begin{align*}
2\text{Al} + 6\text{H}_2\text{O} &\rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2 \\
2\text{Al(OH)}_3 &\rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}
\end{align*}
\]  
(8)  
(9)

It must also be noted that aluminum substrates application leads to the ZnO nanostructures Al³⁺ cations doping, further carrier concentration increasing and reduction of piezoelectric signal time formation. By contrast, due to the high inertia Ta substrates doesn’t significantly impact on the zinc oxide crystallite nanostructures properties.

**Conclusion**

The ZnO based PENG construction mentioned in the paper can improve output characteristics due to the two-layer structure of an active part. Such zinc oxide nanostructured coatings can be obtained within a single technological cycle with the methods of a liquid phase ionic layering and a chemical bath deposition.

In comparison with aluminum substrates, tantalum wafers application allows obtaining zinc oxide NR uniform arrays all over the substrates surface and thus reducing the parasitic capacitance \(C_{\text{sub}}\).

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