Formation of one-dimensional ZnO structures on flexible substrates

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Abstract. Within the frames of the research described in the paper, 1D ZnO nanostructures on flexible substrates were synthesized by the hydrothermal method. The paper describes technological features of obtaining oxide nanorods using low-temperature synthesis. Morphological properties of obtained structures were investigated.

1. Introduction
Zinc oxide ZnO is one of the most promising materials for formation of piezoelectric nanogenerators [1]. It is a wide band-gap ($E_g = 3.36$ eV) piezoelectric semiconductor, which has a $n$-type conductivity and is crystallized in a wurtzite type structure. The advantages of using this material are an environmental safety and ease of preparation as well as a possibility to use this material at high and ultra-high frequencies [2, 3].

The hydrothermal method [4, 5] is one of the simplest and most available methods suitable for synthesis of ZnO nanorods on polymeric substrates.

2. Experiment
The hydrothermal method is based on dissolving of substances, which are insoluble under normal conditions in water or aqueous solutions, at high temperatures and pressures. Main parameters of the hydrothermal synthesis, which determine the properties of the formed products, are the initial value of the solution pH, duration and temperature of synthesis.

In present work, zinc nitrate $\text{Zn(NO}_3\text{)}_2$ was used. Zinc nitrate is a salt of a strong acid and a weak alkali, so the hydrolysis reaction proceeds in two steps:

\begin{align}
1) & \ \text{Zn(NO}_3\text{)}_2 + \text{H}_2\text{O} \leftrightarrow \text{Zn(OH)}\text{NO}_3 + \text{HNO}_3 \\
2) & \ \text{Zn(OH)}\text{NO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Zn(OH)}_2 + \text{HNO}_3
\end{align}

In this case, zinc ions are formed; its interaction with hydroxide ions results in formation of unstable $\text{Zn(OH)}_2$ converted into zinc oxide by the reaction $\text{Zn(OH)}_2 \rightarrow \text{ZnO}_{\text{solid}} + \text{H}_2\text{O}$.

Usually, NaOH, KOH, ammonium hydroxide NH$_4$OH or hexamethylenetetramine C$_6$H$_{12}$N$_4$ are used as an alkali. During the reaction, a zinc precursor is hydrolyzed, and, as a result, $\text{Zn}^{2+}$ ions appear and react with the anions of alkali OH$. During the reaction, various hydroxides can be formed: $\text{ZnOH}^-$ (aqueous), $\text{Zn(OH)}_2$ (aqueous), $\text{Zn(OH)}_3^-$ (aqueous) and $[\text{Zn(OH)}_4]^{2-}$.

$$\text{Zn}^{2+} + \text{OH}^- \leftrightarrow [\text{Zn(OH)}]^+,$$ (1)
Zn\(^{2+}\) + 2OH\(^-\) ⇌ Zn(OH)\(_2\), \((2)\)

Zn\(^{2+}\) + 3OH\(^-\) ⇌ [Zn(OH)\(_3\)]\(^-\), \((3)\)

Zn\(^{2+}\) + 4OH\(^-\) ⇌ [Zn(OH)\(_4\)]\(^{2-}\). \((4)\)

Interim hydroxides condense as oxides. One of the possible ways of hydroxide – oxide conversion is the process:

[Zn(OH)\(_4\)]\(^{2-}\) ⇌ ZnO + H\(_2\)O + 2OH\(^-\). \((5)\)

Overall, the chemical reaction can be written as:

Zn\(^{2+}\) + 2OH\(^-\) ⇌ ZnO + H\(_2\)O. \((6)\)

It should be noted that in terms of the formation of one-dimensional structures based on ZnO, equation (2) with Zn(OH)\(_2\) formation cannot be used because, as a result of the corresponding reaction, the uncharged zinc hydroxide is formed. The charged reaction products may be adsorbed on different charged crystal faces of growing structures or nucleation layer crystallites.

These chemical reactions are usually equilibrium reactions in aqueous solutions and proceed in the direction of minimizing the free energy of the entire system. The most high-energy surfaces of zinc oxide are the polar planes (0001), which end with Zn\(^{2+}\) or O\(^{2-}\) ions. Therefore, adsorption of new molecules, formed by the precursor hydrolysis, occurs on the polar planes in order to minimize the surface energy. 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 (3) and (4), then, according to reaction (5), ZnO is formed. At the end, the plane (0001) ends again with Zn\(^{2+}\) ions. Therefore, the growth of zinc oxide micro- and nanostructures occurs in the direction of c-axis, resulting in formation of an anisotropic structure.

In this work, hexamethylenetetramine (HMTA, (CH\(_2\))\(_6\)N\(_4\)) was used for ZnO nanorods growth. In the work [5], it was discovered that HMTA molecules are a constant source of OH\(^-\) groups due to their slow release. At high concentrations of hydroxyl, the rate of nanorods growth increases and the solution is depleted of Zn\(^{2+}\) ions rapidly. This leads to the formation of tapered crystallites. Concentrations of reagents in the solution, used for growth of nanorods, were 25 mmol/l.

The samples were placed in the solution and incubated at 85°C for various times. After the nanorods synthesis, samples were washed with distilled water and dried in air.

Obtained structures were investigated using TESCAN MIRA (a scanning electron microscope (SEM) with an electron gun through a field-emission cathode (Schottky cathode)) and Seron Technology AIS 2300C.

Polyethylene terephthalate (PET) with ITO (60 Ohm/□) layer (Sigma Aldrich) was used to form ZnO nanostructures on flexible substrates.

3. Results and discussion

Experimental results are shown in figure 1. Figure 1 (a) shows formation of arrays and individual nanorods with a length of ≈ 500 nm and a diameter of ≈ 50 nm. In the synthesis of ZnO nanorods by the hydrothermal method on polymeric substrates, the cubic nanostructures grow in size from 50 nm to 150 nm uniformly over the entire surface of the substrate (figure 1 (b)).

In order to create a more uniform nanostructured ZnO coating on flexible substrates, 0.1 ml of NH\(_3\)-H\(_2\)O was added to the initial solution (figure 2).

The change of pH during the synthesis of ZnO nanorods on polymeric substrates leads to a uniform coating of the individual zinc oxide nanorods (figure 2) with a length of up to 1 μm. In this case, the ammonia solution acts as an activator of the substrate surface formed by a conductive layer of ITO. Alongside this, the activation occurs due to formation of an adsorption layer consisting of hydroxyl groups (OH\(^-\) ), which are the centers of zinc hydroxide adsorption (equation 1).
To limit the growth of anisotropic crystalline properties in some dimensions, the surface-active substances (surfactants) are often used. The use of surfactants during hydrothermal synthesis of ZnO leads to significant changes in the crystals’ morphology.

In the experiments, for synthesis in alkaline medium (5 ml of NH₃·H₂O) on polymeric substrates, polyvinylpyrrolidone (PVP) was used. The experiments led to formation of needle-like crystals collected on the single growth center (figure 3).

As can be seen in figure 3, the average size of the needle structure is about 3 µm and individual nanoobjects have a hexagonal cut and taper in the direction of the growth center.
4. Conclusions
Thereby, in this paper, 1D nanostructures based on zinc oxide were formed on flexible conductive substrates via low temperature hydrothermal synthesis. Due to changes of pH, the individual nanorods and arrays of nanoobjects can be formed as well as the needle-like crystals collected on the single growth center.

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