

Short Communication

Optically Stimulated Piezoelectric Effects in the Electrochemically Synthesized ZnO Nanoparticles

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ZnO nanoparticles were synthesized by the electrochemical method. The samples were synthesized at different electrochemical conditions, i.e. time and the voltages. The different topologies were obtained. The photo induced piezoelectricity was studied during illumination by the 10 ns nitrogen laser at wavelength 371 nm. The strong dependence on the topology was observed. Crystallochemical aspects of the observed IV-laser piezoelectricity is discussed.

Keywords: electrochemical synthesis. Piezoelectricity, ZnO nanoparticles

1. INTRODUCTION

ZnO nanoparticles (NP) are very promising materials for the piezoelectricity [1]. The coexistence of piezoelectric and semiconducting features in ZnO NP creates a strain field and aligned charge separation across the nanoparticles. The efficiency of the such prepared piezoelectric power generator was equal to about 17 ... 30%. Analyzing the crystalline structure of ZnO, it is necessary to

emphasize the second coordination environment (SCO) [2] for the oxygen atoms in a form of hexagonal cubo-octahedral.

One of the important aspect for the use of the ZnO low-dimensional structure is a possibility to vary their nonlinear optical properties versus the external light [3] which opens a rare possibility of their use for the optical triggers. Particular role here may also play the morphology and size dispersion. As a consequence in the present work we will explore the changes of the piezoelectric features under influence of the external laser light near the fundamental laser beam

In the present work for the first time were explored their piezoelectric properties under influence of the external UV laser light.

2. CRYSTALLOCHEMISTRY ASPECT

For the latter the Zn atoms are situated opposite to the triangle faces. So formally they are situated in the tetrahedral voids as shown in the Fig. 1. Within a framework of SCE there remains free the same number of tetrahedral voids in the site position $2b$ possessing $1/3 \ 2/3 \ z$ ($z=0.625$) with the same distances to the oxygen atoms as to the Zn ones. Their space arrangement is presented in the Fig. 2. Within a framework of $P6_3mc$ for this structure are available yet six octahedral voids in the sites $2a$ with coordinates $0 \ 0 \ 3/4$, geometry of which is shown in the Fig. 3. The shortest distance to the oxygen atoms from the octahedral voids is equal to 2.28 Å. Concerning the size factor following the Fig. 4 the chemical bonds to the centers of the voids are substantially pronged. So the structure may include a hug number of atoms with the possibility to choose the coordination – oxygen tetrahedral or octahedral. During the synthesis of the ZnO NP, there exists a possibility to occupation of the additional number of atoms in the available voids which are able to form the local charge density non-centrosymmetry responsible for the effects like piezeoelctricity.

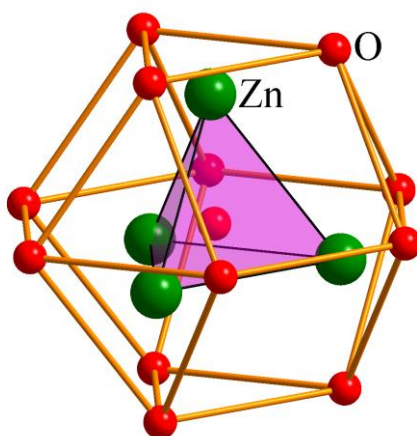


Figure 1. First and the second coordination environment of oxygen atoms in the ZnO.

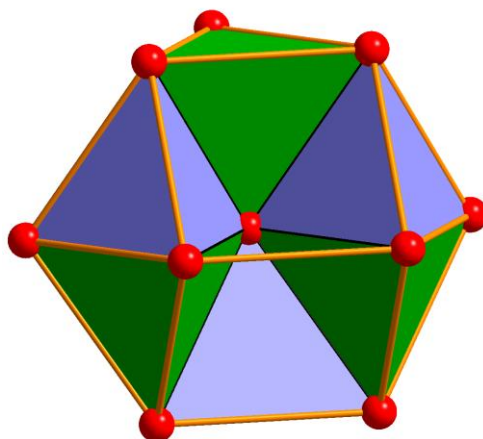


Figure 2. Space situation of the tetrahedral voids (blue) with respect to the occupied by Zn atoms (green) for the structure ZnO.

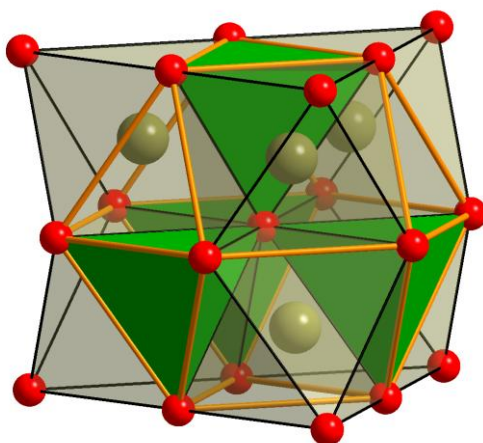


Figure 3. Space architecture of the octahedral voids for the ZnO.

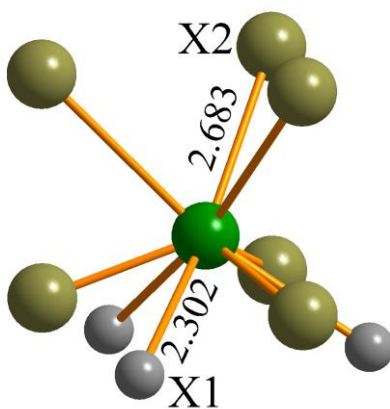


Figure 4. Inter-center distances to Zn atoms for X1 (tetrahedral) and X2 (octahedral) voids.

So varying the conditions of the electrochemical synthesis of the ZnO NP one can achieve the different morphological topography for the ZnO NP [3]. Varying the such parameters as the deposition time and the current one can achieve the changes of the ZnO nanorods.

3. EXPERIMENTAL SECTION

Weighed amount of sodium chloride is placed into a 500 ml graduated flask and dissolved in distilled water. Obtained solution is transferred to a 600 ml electrolyzer, and previously weighed zinc metal electrodes are immersed and connected to the power source – V-24 M AC/DC converter. The electrolyzer with the immersed electrodes and a contact and a common thermometer are placed into a thermostat. After heating to the desired temperature, the timer and the power source are switched on, setting the current and the voltage. As anode is dissolved, white particles immediately begin to form around it. After the synthesis time is reached, the electrolyzer is removed from the thermostat and left to cool. After cooling, the solution is decanted, and the precipitate is washed three times with distilled water. The precipitate is transferred to a Petri dish and dried at 50°C. Zinc electrodes are washed with distilled water, air-dried and weighed. Specific synthesis conditions for zinc oxide nanoparticles by electrochemical deposition are listed in Table 1. And their XRD diffractograms are presented in Fig.5.

Table 1. Conditions of the electrochemical synthesis of zinc oxide nanoparticles.

| Sample № | [NaCl], mmol/l | T, °C | I, A | U, V | τ , min |
|----------|----------------|-------|------|------|--------------|
| 340 | 855 | 99 | 4 | 7 | 5 |
| 342 | 855 | 99 | 2 | 4.3 | 5 |
| 343 | 855 | 99 | 1 | 2.5 | 5 |
| 346 | 855 | 99 | 4 | 7.5 | 10 |
| 353 | 855 | 94 | 4 | 8 | 5 |

Diffraction pattern of zinc oxide sample 340 is presented in Fig. 5 (red line is the experimental powder pattern, black line is the theoretical pattern for the space group $P6_3mc$. The product has clearly defined crystalline cubic structure, of $P6_3mc$ type. Their principal topologies are given in the Fig. 6. One can see substantial difference of the effective nanorod sizes for the title samples. Following the Fig. 6 the dispersion of the sample's sizes did not exceed the 7 %. Their topology is substantially different, however the main difference consists in the differences of their efficient surface sizes. So varying the electrochemical technology one can achieve the changes of the sizes in the desired directions.

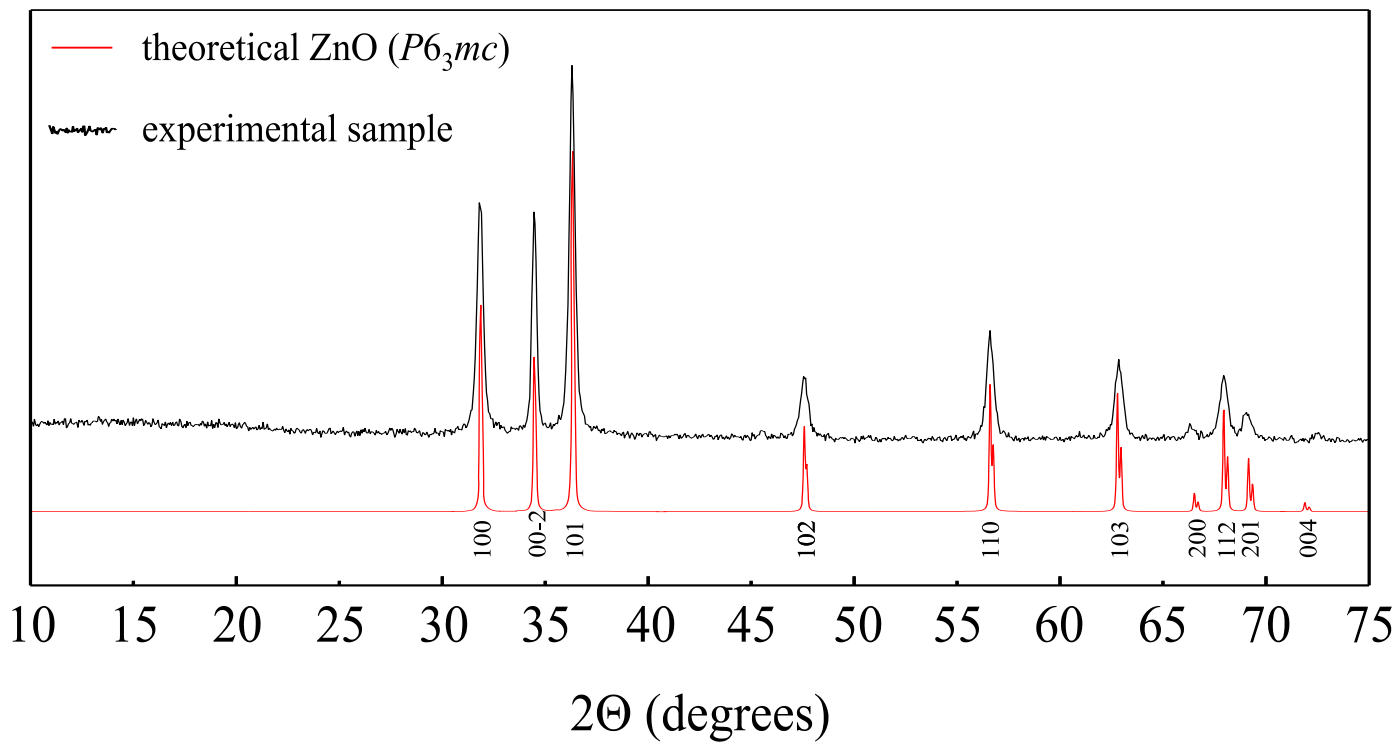
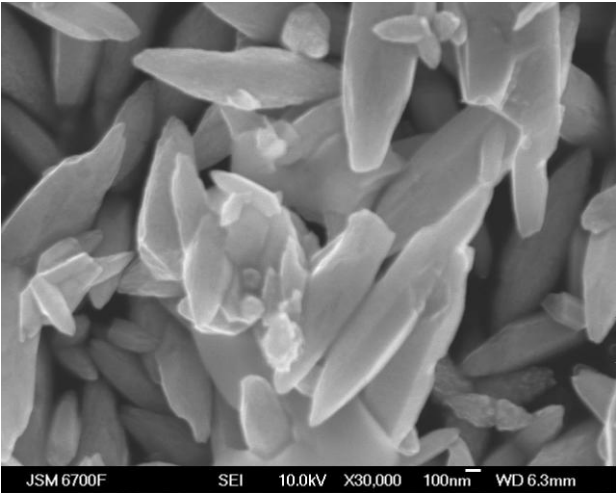

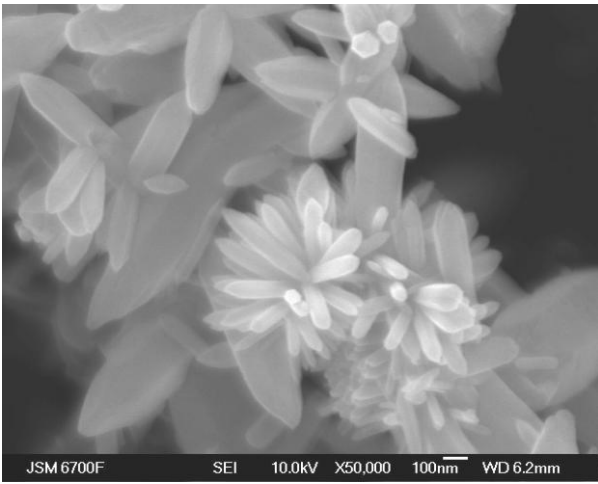


Figure 5. X-ray diffraction behaviour of the ZnO : * theoretical – [4]

| № | T, °C | I, A | τ, min | U, V | SEM images |
|-----|-------|------|--------|------|------------|
| 340 | 99 | 4 | 5 | 7 | |

| | | | | | |
|-----|----|---|----|-----|--|
| 342 | 99 | 2 | 5 | 4,3 |  |
| 343 | 99 | 1 | 5 | 2,5 |  |
| 346 | 99 | 4 | 10 | 7,5 |  |

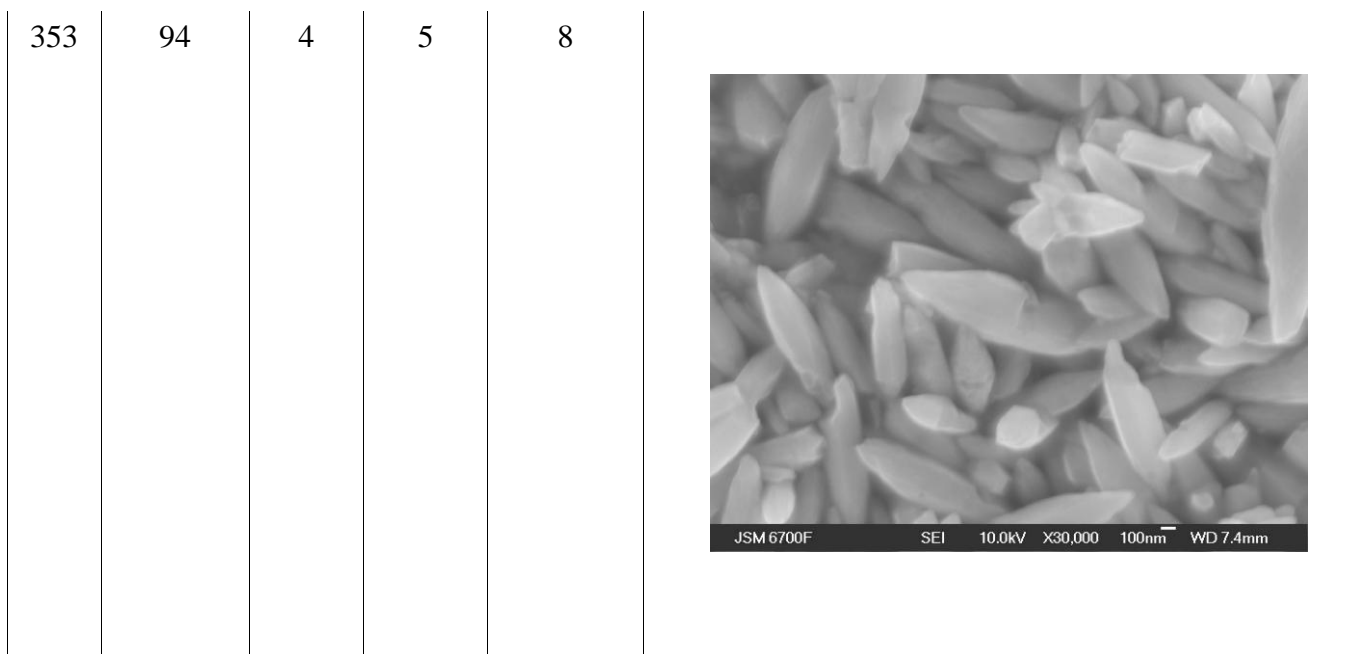


Figure 6. The TEM images of the ZnO NP.

The photoinduced piezoelectric measurements were performed similarly to the described in the ref.5. As a photoinduced source was used the illumination of the nitrogen laser with the wavelength 337 nm and time duration about 7 ns. which illuminates the samples oriented due to use of the mica substrates. The degree of orientation was equal to about 85 %. The piezoelectric response was measured with precision up to 0.2 pm/V.

4. RESULTS AND DISCUSSION

The principal results of the measurements for the effective piezoelectric constants versus the power density of the incident lasers are given in the Fig. 7. Following the fig. 7, one can clearly see that the effective piezoelectric coefficients are nonlinear by dependent versus the external light of the UV-nanosecond laser at wavelength 371 nm. This may be a consequence of strong interactions of ZnO NP with mechanical stress [6]. It is clear that the maximal changes of the piezoelectric coefficients were achieved for the samples possessing the flower-like form [7]. This confirms a principal role of the interface trapping levels [8]. These levels possess high dispersion of the living times [9]. Particularly important these levels are to the external light illumination. This may be a huge applications like piezoelectric LED [10]. Another important factor is a contribution of electron-phonon anharmonicity [11-13] which give very strong contributions.

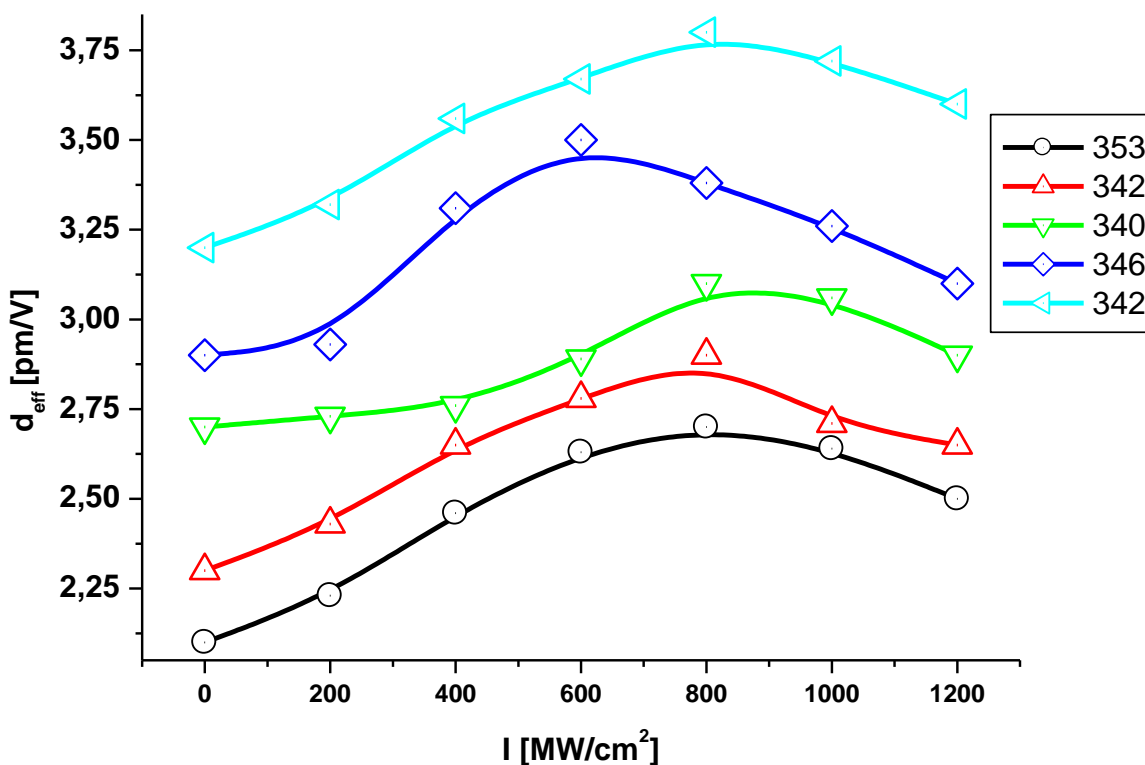


Figure 7. Photoinduced dependence of the effective piezoelectric coefficients versus the nitrogen laser power density.

Following the presented figures one can clearly see that with the increasing of the effective nanorod surfaces there is observed an enhancement of the piezoelectric coefficients. This reflects a principal role of the trapping levels on the interfaces which give substantial contribution to the output piezoelectricity.

5. CONCLUSION

We have observed dependence of the photoinduced piezoelectricity under influence of the UV-nitrogen nanosecond laser. It was found that maximal effect exists for the samples possessing the flower-like topology. This fact indicates on a principal role of such complicated topology in the observed effects. The dependence versus the power density is substantially asymmetric. This fact may indicate on existence of a large number of nano-trapping levels. The existence of the maximum may indicate on the existence of some competition processes during the photo-excitation. It is crucial that increasing of the effective nanorod surfaces leads to an enhancement of the piezoelectric coefficients. This reflects a principal role of the trapping levels on the interfaces which give substantial contribution to the output piezoelectricity.

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