Optical SHG for ZnO films with different morphology stimulated by UV-laser thermotreatment

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Abstract. We have discovered a strong influence of the ZnO grain sizes on the output second harmonic generation stimulated by nanosecond pulses of 371 nm nitrogen laser during simultaneous superposition of the electrostatic electric field with electric strength about 2 kV/cm. To explore an influence of film morphology on the second order optical susceptibility we have explored the films prepared by electron sputtering with averaged grain sizes about 1000 nm and films synthesized by rf-magnetron sputtering on the two different substrates – glass and amorphous quartz with average grain sizes about 137 nm and 29 nm, respectively. Comparing the UV-induced optical second harmonic generation for the ZnO films with different grain sizes we have concluded that the samples with nanorods are characterized by considerably larger second order susceptibility (up to 5.7 pm/V at 1064 nm fundamental wavelength) compared to those for the films with smaller grain sizes (1.5 pm/V). This may be caused by a fact that UV-illumination deals only effectively with simultaneous electric field treatment enhancing the second order optical susceptibility. A correlation between the temperature of local laser thermo-heating and the output optical second harmonic generation may indicate on principal role of the local thermal expansion in the observed output second harmonic generation.

1. Introduction
The modern development of the quantum electronics requires search and design of nonlinear optical materials which may be used as nonlinear optical waveguides, laser modulators, deflectors etc. Due to miniaturization of the devices it is necessary to retreat from the traditional bulk nonlinear crystals like LiNbO₃, LiTaO₃, BiB₃O₆ [1-4]. Besides this the technology of the bulk materials synthesis is relatively expensive since it requires highly developed technology for crystal growth methods and long processing time. The fabrication of the thin films instead of the bulk materials is now a promising route for the search and design of the new nonlinear optical materials [5-6]. Among the dozens of nonlinear optical materials [7] ZnO seems to be the most promising

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due to its excellent optical and photomechanical properties, and ability to deposit the layers on different kinds of substrates [8]. Moreover, measurements performed for the thin ZnO films of different crystallinity [9] have shown a relevant second order susceptibility (up to 10 pm/V) at 1064 nm wavelength. It was shown that this parameter is strongly dependent on degree of the film crystallinity and the grain boundaries, and interfaces play in this case a main role. It is interesting to note that the moderate SHG signals were obtained even for the films deposited by a simplified and chip spray technology [10]. The first experiments were performed for the case when the wurtzite-like c-axis was oriented perpendicularly to the substrate plane [11-13]. There were different efforts to achieve the enhancement of the second order susceptibilities. In particular, one of the approaches involve in the deposition of the hexagonal films with c axis orientation lying intra the substrate plane [14] that allowed enhancement of corresponding susceptibility up to 30 pm/V. Another method [15] has applied critical resonance frequencies approaching the energy gap. The maximal value of the second order susceptibility was found to be equal to about 83 pm/V that is 14 times larger than in the bulk materials and is the highest among the reported ones for today. Another approach involved a doping of the ZnO film by the highly polarized F ions [16] that allowed to receive the value of the linear electrooptic coefficient equal to about 17 pm/V in the blue spectral range. In the Ref. 17 it was established that decreasing film thickness favors substantial enhancement of the SHG independently on the technology. However it is incompatible with the data of other researchers showing that the use of the rf-magnetron sputtering or plasma-enhanced chemical vapor deposition also may influence considerably the SHG values. Moreover, using the bicolor optical treatment [18], the strongly influence of the substrate on the induced optical susceptibilities was shown. In the present work we apply UV-induced SHG to explore SHG behavior. In order to enhance additionally the stimulated non-centrosymmetry we apply simultaneously electric field along the film surface. The main goal of this work is the exploration of the ZnO morphology and parameters of second order optical susceptibilities. To obtain the film of different morphology we apply two different methods - RF-magnetron sputtering and electron sputtering. The Section 2 presents experimental methods including sample preparation. Section 3 describes results of the photoinduced SHG and discussion concerning the relation between the output SHG and the grain morphology of the ZnO films.

2. Experimental

2.1. Sample preparation

The sample I has been fabricated by a simple two-step approach, i.e. preparing Zn polycrystalline film by electron sputtering of the metallic zinc in vacuum (10^{-4} Torr) and then oxidizing it to ZnO polycrystalline film in air [20]. The substrate temperature for preparation of Zn film was ~200°C, and that for the oxidation step was 850°C. In this case the structure with long nanorods is obtained [21].

The thin films II and III were deposited on the glass and the amorphous quartz substrates, respectively by the standard RF-magnetron sputtering using ZnO targets in the argon atmosphere at a gas pressure of 10^{-3} Torr. The substrate temperature and RF-power were fixed at 300 °C and 100 W, respectively. The target-to-substrate distance was 60 mm, the magnetic field strength was about 0.1 T. Prior to deposition the target was pre-sputtered for 10 min in order to remove any contamination. The surface morphology of ZnO films was monitored by atomic force microscope (AFM) (Digital Instruments - USA with Nanoscope E controller), working in the contact mode and equipped with OTR8 probe (Veeco NanoProbe™). The length and the spring constant of the applied V-shaped cantilever were 200 mm and 0.15 N/m, respectively. The used constant forces were about 10 nN. All the measurements were performed in air. Some of the samples were studied using the scanning electron microscope (SEM) REMMA-102-02.
2.2. The principal optical set-up
The 5 ns Q-switched Nd-YAG laser with averaged 1 MW pump power was used as a fundamental laser beam for investigation of the second order susceptibility by measurements of optical second harmonic generation (see Fig. 1). The 3 ns nitrogen laser with wavelength about 371 nm was used for photoinduction. Operating by $\lambda/2$ wavelength plate and polarizers P we were able to change polarization and power densities of the photo inducing laser beams. The apparatus allowed to vary continuously the power density of the photo inducing UV-laser beam up to 0.9 GW/cm$^2$ with the beam diameter of Gaussian shape varying within 0.5 - 0.9 mm.

![Figure 1. Principal scheme of the UV-induced SHG set-up.](image)

The fundamental Nd:YAG laser beam was completely overlapped with the UV photo inducing ones on the sample surface. The sample was rotated relatively to the incident beam axis and green filter has cut spectrally the output optical second harmonic generation at 530 nm. To have a reference we replaced the sample S by the KDP crystal to determine the values of the second order optical susceptibility. Fast response photo detector (PD) registered the changes of the output SHG versus the applied UV laser beam power density. The illuminated ZnO samples were under applied electrostatic field with electric strength up to 2 kV/cm directed perpendicularly to the laser beam propagation.

3. Results and discussion
The micrograph of the surface of the sample I obtained using the scanning electron microscope is presented in Fig. 2.
The surface morphology of ZnO samples II and III was monitored by AFM (Fig. 3a) and (Fig. 3b), respectively.

The dependence of crystallinity and crystallite sizes on the film thickness was revealed by their micrographs. The root mean square (RMS) roughness and average grain size were measured on 5 µm×5 µm area. The principal parameters of the mentioned samples obtained on the basis of SEM and AFM studies are presented in Table 1.
Table 1. The RMS roughness and average grain size in the zinc oxide thin films

| Sample | Structure       | Film thickness, nm | Production                                                   | RMS roughness, nm | Average grain size (rod diameter), nm |
|--------|-----------------|--------------------|-------------------------------------------------------------|-------------------|--------------------------------------|
| I      | ZnO/sapphire    | 3000               | Oxidation of the Zn film in air at T = 850 ºC               | 1000              |                                      |
| II     | ZnO/quartz      | 250                | RF-magnetron sputtering                                    | 21                | 140                                  |
| III    | ZnO/glass       | 450                | RF-magnetron sputtering                                    | 12.2              | 30                                   |

We have found that without the additional UV inducing beam the maximal second order optical susceptibility was achieved for the sample I and was equal to about 2.4 pm/V. This is a consequence of partial z-axis orientation of the hexagonal ZnO crystallites along the substrate surface. Following the Fig. 3 one can see that it is almost twice larger than for the samples II and III with lower sizes. One can suggest that such a situation is connected with a much larger grain (rod) sizes which give higher crystalline ordering within the particular crystallites. As a consequence the output second order optical susceptibility is for such samples larger. The maximal output intensity was obtained for the p-polarized input and output fundamental beams. The measurements have shown that the output SHG achieves maximum during the 1.5 – 3 min of the laser treatment, and then the output SHG begins to decrease. Moreover without the applying of the electrostatic electric field the output SHG is changed only slightly (not exceeding 5-7 %). So only simultaneous applying of the photo inducing polarized nitrogen laser and the electrostatic field allows to achieve a considerable enhancement of second order optical susceptibility. This may be caused by local thermo-heating forming the local non-centrosymmetry and additional photo-polarization of the excited states. Usual thermo-heating did not give any substantial enhancement of the SHG. The recent factor is crucial for obtaining of more photo-operated near-the-surface states due to high inter-grain gradients. The mechanical rigidity will be substantially larger intra the grains as compared to the inter-grain space. So the corresponding structural fragments may be slightly photo-oriented, in particular during the light illumination near the energy band gap. The temperature changes of the surfaces confirm this prediction. The signal is clearly observed only at the applied electrostatic field with the strength about 2 kV/cm applied in direction parallel to the ZnO surface. Comparing the Figs. 4 and 5 one can clearly see that for the ZnO films with larger nanorods we have substantially higher increase of local temperature compared to the low-sized samples. One can expect that due to lower sizes the UV-induced scattering would be larger leading to lower thermo-heating, and more long-range ordering would be difficult to achieve. For the ZnO crystallites with larger sizes the process of carrier thermo-diffusion may be more important due to larger participation of interfaces between crystallites and surrounding disordered background. Indeed the total values of surface gradients will be larger forming both additional local heating as well as larger charge density non-centrosymmetry detected by the SHG. Without the applied electric field an increase of the SHG output larger than 5-7 % was not observed. Removal of the applied electrostatic field leads to decrease of the SHG signal for about 12-15 % during 3-4 hours. Occurrence of the SHG maximum confirms an enhancement of the disordering between the excited dipole moments due to thermal reorientation.
Figure 4. Pump power dependences of the effective second order optical susceptibility $d$ versus the intensity of the UV-induced field at applied static electric field about 2 kV/cm.

Figure 5. The sample’s temperature during the UV-treatment corresponding to the maximal.

Therefore, after applying of the UV-induced field at fixed electrostatic field we observe substantial increase of the second order optical susceptibility for all the samples, however higher morphology grain sizes favour enhanced output.
Table 2. Principal parameters of the ZnO AFM self-faces

| Sample | RMS roughnes | Average height | FFT 1/k (grain size) |
|--------|--------------|----------------|---------------------|
| II     | 6.5299 nm    | 33.7244 nm     | 28.6 nm             |
| III    | 4.7291 nm    | 28.2732 nm     | 137 nm              |

It is crucial that the value of the second order optical susceptibilities is increased for the sample I by about 2.3 times achieving 5.7 pm/V. At the same time the two other samples (with lower grain sizes) have demonstrated an increase only about 1.3 times. To exclude bothering factors caused by multi-photon fluorescence we have measured additionally the pump-power SHG dependences for the several fixed UV inducing powers and at fixed electrostatic field. Dependence of the output SHG intensity versus the fundamental beam power had a power-like feature with power coefficient about 1.92.

The obtained results unambiguously show that for the sample with comparatively large nanorods and grains the photo induced SHG signals are larger as compared to the sample with smaller grains. It is out of accordance with the general assumption that the less grains should give the larger effect due to the nano-confined large local dielectric fields. However, correlation of the output SHG with the local thermo-heating may indicate on substantial role of the photo-thermal expansion in the observed dependences.

4. Conclusions

We have found that for the UV-stimulated second harmonic generation of the ZnO films at fixed electrostatic electric field the inter-grain sizes play a crucial role. It was revealed that for the three different ZnO films obtained by different methods the maximal SHG output was achieved for the films with nanorods of the averaged sizes about 1000 nm. The two other films prepared by RF-magnetron sputtering on the two different substrates – glass and amorphous quartz with average grain sizes about 140 nm and 30 nm have shown substantially lower signal. The samples with nanorods have a considerably larger second order susceptibility (up to 5.7 pm/V at 1060 nm fundamental wavelength) compared to those for the films with smaller grain sizes (1.5 pm/V). A correlation between the output SHG and the local UV-stimulated thermo-heating was established.

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