High-temperature annealing effect on photoluminescence of ZnO nanoparticles produced by laser ablation in hydrogen peroxide

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Abstract. Zinc oxide nanoparticles were for the first time produced by laser ablation of a solid zinc target in 35% liquid hydrogen peroxide. As-produced nanoparticle-based films on Si substrates were visualized by scanning electron microscopy (SEM) and energy-dispersion x-ray micro-spectroscopy (EDX) as amorphous, containing highly defective mixed oxide/hydroxide structures and crystallization-water molecules. Specific structural defects, damping the photoluminescence band of the nanoparticles peaked near 550 nm for the 488 nm pump laser wavelength, were annealed in air at temperatures 200-400 °C over 1-2 hours, with the accompanying strong photoluminescence yield and the appearance of the absorption cut-off near 350 nm. However, the following annealing at higher temperatures up to 1200 °C for time periods variable in the range of 1-3 hours, resulted in the damping of the photoluminescence. According to x-ray diffraction (XRD) characterization of the nanoparticle-based films on fluorite substrates, high-temperature annealing at 800 °C for 1 hour induce crystallization of the common hexagonal ZnO phase (wurzite structure) via loss of peroxide bridges, crystallization water molecules and other structural defects. Meanwhile, annealing at 1200 °C yields in another distinct crystalline phase of ZnO, which appears to be a sphalerite.

1. Introduction
Zinc oxide (ZnO) attracts much attention due to its exceptional properties: direct band gap with energy value of 3.4 eV, high exciton energy of 60 meV and antibacterial properties [1-3]. High exciton energy means that zinc oxide can provide bright emission at room temperature. At room temperature zinc oxide has strong luminescence in the blue region. Also nanoparticles of zinc oxide can luminesce in a wider range due to defects in the internal structure [4,5]. These defects can be impurities and molecular groups embedded in ZnO structure, e.g., extra peroxide (-O-) or hydroxide (-OH) groups, or other structural defects. Defects are related to additional energy levels in the band gap, called “defect states”. Defects in the ZnO band gap appear during preparation of nanoparticles via laser ablation in liquid. Nanoparticles of zinc monoxide and zinc peroxide are formed by laser ablation of a zinc target in hydrogen peroxide. Conversion of zinc peroxide to zinc monoxide can be carried out by their annealing in the air[6, 7].

In this study, laser ablation of a solid zinc target was performed not in water, but, for the first time, in a 35% hydrogen peroxide solution, providing colloidal zinc oxide nanoparticles. As-
prepared nanoparticles were annealed at various temperatures in air for 1, 2 or 3 hours. Both as-prepared and annealed nanoparticles were characterized by SEM, EDX, broadband optical transmittance (200-1100 nm) spectrum, XRD and visible photoluminescence. The effects of annealing temperature and time on the photoluminescence of the nanoparticle-based films were examined.

2. Experiments
A galvoscanning system HTF Mark (Bulat) was used to obtain nanoparticles by laser ablation in liquid. It is based on a fiber Yb laser with a wavelength $\lambda = 1064 \text{ nm}$, a pulse duration $\tau = 120 \text{ ns}$, a pulse repetition rate $\nu = 20 \text{ kHz}$ and an energy $\varepsilon = 0,8 \text{ mJ per pulse}$. This system is equipped by a galvomirror to raster-scan the laser beam in two dimensions and protected output lens F-theta with a focal length $F = 160 \text{ mm}$. Scanning of the zinc target was carried out in a cuvette with 35 % water solution of hydrogen peroxide $\text{H}_2\text{O}_2$ for three minutes. Then, the resulting colloidal solution of nanoparticles was deposited on a Si substrate. Nanoparticle precipitation occurred from colloidal solution, which led to irregular allocation of nanoparticles on the substrate surface. Then Si substrate with ZnO nanoparticles were placed in an electric furnace SNOL-12/6 for annealing in ambient air atmosphere. The electric furnace was gradually heated and kept temperature at the specified value from 200 to 1200 $^\circ\text{C}$ for 1, 2 or 3 hours.

Nanoparticles were characterized by SEM visualization (JEOL7001F), chemical EDX microanalysis (INCA), broadband optical transmittance, X-ray diffraction PanExpert and photoluminescence techniques. The transmittance spectra were recorded in the spectral region of 200-1100 nm by a spectrophotometer SF-2000 (OKB SPECTR LLC). The transmittance was measured by nanoparticles deposited on a $\text{CaF}_2$ substrate. The photoluminescence of ZnO nanoparticles was observed by means of a Raman microscope U-1000 (Jobyin Yvon) with the pump radiation wavelength at 488 nm focused into the focal area of 1-2 mm. Nanoparticles were deposited on a Si substrate to measure photoluminescence in the range of 450 - 850 nm. Crystalline order of as-produced and annealed nanoparticles were characterized by x-ray diffraction acquisition, using a Panalytical X’Pert Pro MRD Extended diffractometer with a Cu-Kα1 source, 4+Ge(220) Bartels monochromator (divergence - 12”) combined with a x-ray parabolic mirror.

3. Results
SEM images in Fig. 1 show morphology of as-produced and annealed zinc oxide nanoparticles on the silicon substrate and their chemical composition according to EDX analysis. The as-produced nanoparticles appear rather small and amorphous, while the annealed ones at 400 $^\circ\text{C}$ for 2 hours look like much more aggregated. Moreover, in the as-produced nanoparticles one can see O/Zn atomic ratio more 38/13 = 3, comparing to its value of 1 in pure ZnO substance. This potentially indicates the presence of extra oxygen atoms in the nanoparticle structure peroxide bridges (-O-O-), hydroxyl groups (-OH), crystallization water molecules in complexes $[\text{Zn(H}_2\text{O)_6}]^{2+}$. Furthermore, such annealing in the air makes the micron-thick nanoparticle-based films much less scattering and broadly absorbing, but more transparent in the optical range even beyond the fundamental cut-off wavelength about 350 nm for interband transitions in ZnO [8]. In fact, such interband absorption appears for the annealed nanoparticles as very minor drop in transmittance below 400 nm (Fig.2).

The other important and very useful indicator of crystalline quality in the ZnO nanoparticles is their photoluminescence yield. In this study, upon 488-nm pumping the acquired nanoparticle photoluminescence spectra revealed their annealing details in terms of annealing temperature and its duration (Fig. 3). Regarding the photoluminescence yield, for 1-hour annealing the most efficient annealing occurs at the temperature of 200 $^\circ\text{C}$ (Fig. 3 a), while temperature of 400 $^\circ\text{C}$ is more effective for annealing during 2 hours. If temperature is increased to 800 $^\circ\text{C}$ and 1200 $^\circ\text{C}$
Figure 1. SEM image of as-produced (a) and annealed (400 °C, 2 hours) (b) nanoparticles, with their EDX-acquired chemical composition in the insets (label 1 µm).

Figure 2. Optical transmittance spectra of as-produced and annealed nanoparticles, exhibiting the cut-off wavelength for the interband transitions.

for 2 hours, photoluminescence of the samples in the visible spectral region yield considerably decreases (Fig. 3 c).

Figure 3. Photoluminescence yield of as-produced and annealed ZnO nanoparticles in the visible spectral range for different annealing conditions.

XRD analysis provides the additional enlightening justification of the tendencies in nanoparticle morphology and chemical composition, optical transmittance spectra, and photoluminescence yield, caused by our annealing studies. Specifically, the diffractograms of the nanoparticle-based films demonstrate in the range 2θ from 30° to 60° an amorphous phase at 400 °C, converting to the wurzite phase at 800 °C and then to sphalerite phase at 1200 °C [9] (Fig. 4). These high-temperature structural transformations in ZnO explain the decreased photoluminescence yield upon annealing of the nanoparticle-based film at high temperatures.
4. Conclusion

In our study, nanosecond laser ablation of solid Zn was for the first time performed in 35% hydrogen peroxide solution in water to ensure complete Zn oxidation without core-shell metal-dielectric composite nanoparticles. However, the resulting colloidal nanoparticles were present in both oxide and peroxide forms, with some crystallization water molecules in the structure. Their minor annealing for 1 hour at 200 or 400 °C resulted in the appearance of the absorption cut-off for band-band transitions and enhanced visible (greenish) photoluminescence. Meanwhile, the following annealing at higher temperatures or for longer times yielded in strongly reduced and slightly displaced photoluminescence peak. These tendencies were enlightened by x-ray diffraction studies, showing the crystallization of the wurzite ZnO phase at 800 °C and sphalerite phase at 1200 °C.

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