MASS PRODUCTION OF HYDROGENATED ZnO NANORODS

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Abstract

We have developed an inexpensive and efficient technology of hydrothermal growth of ZnO nanorods from zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), as a precursor and hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$), as a surfactant followed by plasma hydrogenation in a novel inductively coupled plasma (ICP) quartz reactor and equipped with the rotary sample holder to stir powder during plasma treatment. We have optimized the photoluminescence spectroscopy for measuring optical scattering samples with the high sensitivity, precise sample positioning and very low influence of the scattered excitation light. Here we present the latest results on the enhancement of the UV photoluminescence of the ZnO nanorods after plasma hydrogenation. The exciton-related photoluminescence has been significantly enhanced whereas the deep defect related yellow photoluminescence has been significantly decreased.

Keywords: Nanomaterials, ZnO, photoluminescence, excitons, inductively coupled plasma, hydrogenation

1. INTRODUCTION

Zinc oxide is one of the most popular II-VI semiconductors, because of its low-cost, non-toxicity, wide band gap of 3.36 eV and big exciton energy of 60 meV. Additionally, ZnO is a material with a great diversity of morphologies. Due to a high surface-to-volume ratio and related size effects, ZnO nanorods (NRs) are a perspective for energy conversion or sensing applications such as solar cells, light emitting diodes [1], high performance electrochemical capacitors [2], biosensors [3], gas sensors [4] or highly efficient scintillators [5]. The surface composition of the ZnO NRs drastically changes upon the exposure to hydrogen and oxygen plasma treatments affecting the defects creation processes [6]. The first-principles studies of the native point defects in ZnO have been reported previously [7]. However, the role of native defects in ZnO nanorods is still not fully understood [8]. The synthesis of ZnO NRs has been performed through complex methodologies, most of them starting with a seed layer followed by NRs growth. Nanopowders tend to form agglomerates due to different reasons that include electrostatic and Van der Waals forces or because they are interlaced by different geometry of the nanoparticles. Sonication is a powerful tool for the treatment of dispersing nanoparticles; it is easy to use, inexpensive and efficient. We have developed the technology of hydrothermal growth of ZnO NRs powder from zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$) and shown that the surface composition drastically changes upon the exposure to plasma treatments [9-11].

2. EXPERIMENTAL

2.1. Growth of ZnO nanorods

Zinc nitrate hexahydrate p.a. ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$) p.a. was purchased from Slavus. Deionized water was purified with a So-Safe Water Technologies, having a conductivity 0.20 $\mu S \cdot cm^{-1}$ (25 °C). The chemicals were used in ambient conditions and without further

purification. The reaction conditions were 25 mM aqueous solutions $Zn(NO_3)_2 \cdot 6H_2O$ and HMTA at 90 °C for 3 h. The precursor salt residue was removed from the sample by washing 3-times with deionized water followed by centrifugation at 18,000 rpm (RCF: 23542g) for 20 min. Finally, the ZnO NRs were dried by lyophilization, see **Figure 1**.

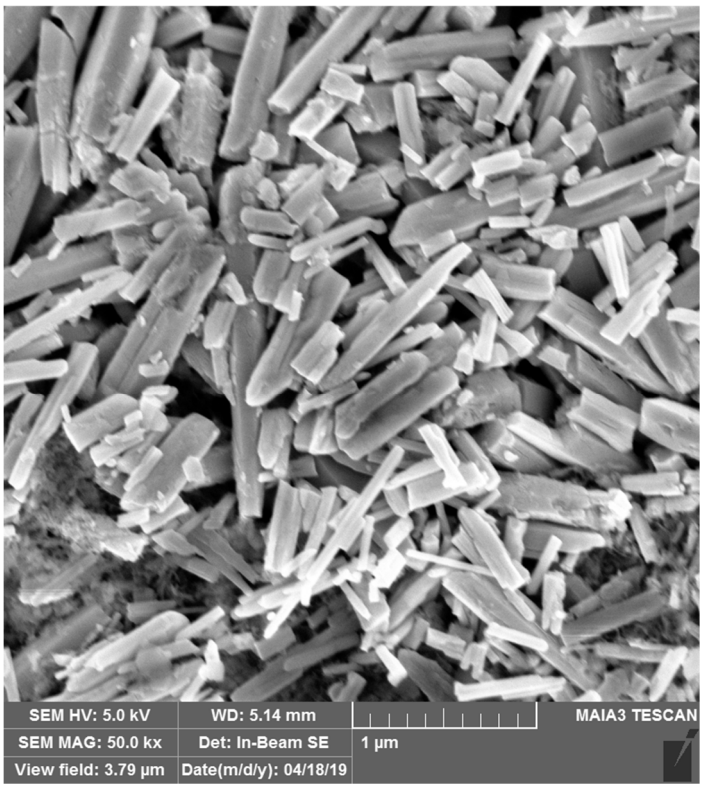

Figure 1 SEM image of ZnO NRs by MAIA3, TESCAN with the In-beam SE detector placed in objective lens. The electron beam had an energy 5 keV.

2.2. Inductive plasma reactor

The plasma oxidation and hydrogenation of ZnO NRs was done in a novel inductively coupled plasma (ICP) quartz reactor developed in the cooperation with SVCS Process Innovation, s.r.o. The reactor operates at 13.56 MHz, 10-200 W discharge power, pressure 1-100 Pa and gas flow 1-100 sccm: hydrogen (purity 99.999 %), oxygen (purity 99.995 %), argon (purity 99.998 %) and nitrogen (purity 99.999 %). Prior the plasma treatment, the chamber was evacuated below 1 Pa and flushed by process gas to reduce residual gas contamination. To achieve good homogeneity, the powder was stirred during the plasma treatment using motorized cradle-like rotary quartz holder controlled by Arduino microcontroller, see **Figure 2**. Prior the material characterization, the ZnO powder was sintered at room temperature to compact 0.5 mm thick pellets with diameter 3 mm.

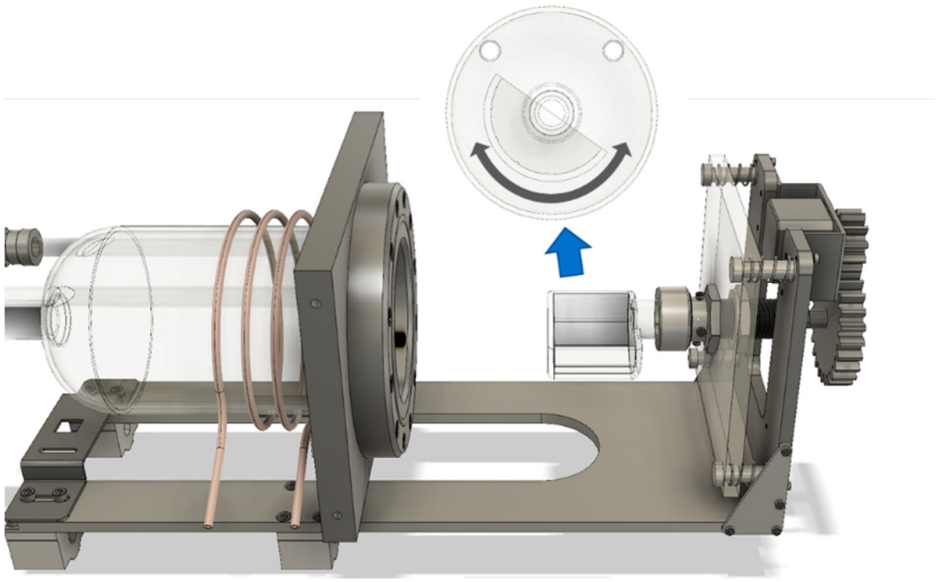

Figure 2 Rotary holder for ICP reactor swinging ±60 degrees to achieve good homogeneity of plasma treatment

2.3. Photoluminescence spectroscopy

The schema of photoluminescence spectrometer is shown in **Figure 3.** The photo-excitation is provided by the fiber-coupled pulsed UV LED (Thorlabs #M340F3) optically filtered by narrow band pass optical filter featuring 90% transmission at 340 nm and blocking wavelengths in the spectral range 250-310 nm and 370-450 nm by more than 10 orders and in 450 - 750 nm by 6 orders (EdmundOptics fluorescence filter #84-092). The sample holder is positioned by two perpendicularly oriented translation stages manually driven by adjuster screws for precision motion. The emitted and scattered light is collected and focused onto the monochromator input slit by two 90° off-axis mirrors coated by UV enhanced aluminum. The scattered UV light is filtered at the monochromator input slit by the fluorescence long pass filter EdmundOptics #34-302 (UV grade fused silica substrate, the cut-on wavelength 375 nm). The f/4 double gratings monochromator SPEX 1672 operating in the spectral range 300 - 900 nm is equipped with 1200 grooves/mm gratings blazed at 500 nm with less than 10^{-9} scattered light. The spectral resolution is 2 nm with 1 mm slits. The monochromatic light intensity is detected at the monochromator output slit by the Peltier cooled multi-dynode multi-alkali red sensitive photomultiplier (Photonis XP2203B, the spectral range 300 - 700 nm) biased to a high voltage by the Stanford Research Systems PS325/2500V-25W high voltage power supply. The photomultiplier current output is connected via coaxial cable to Stanford Research Systems SR570 low-noise current preamplifier followed by the Signal Recovery 5105 lock-in amplifier referenced to LED frequency.

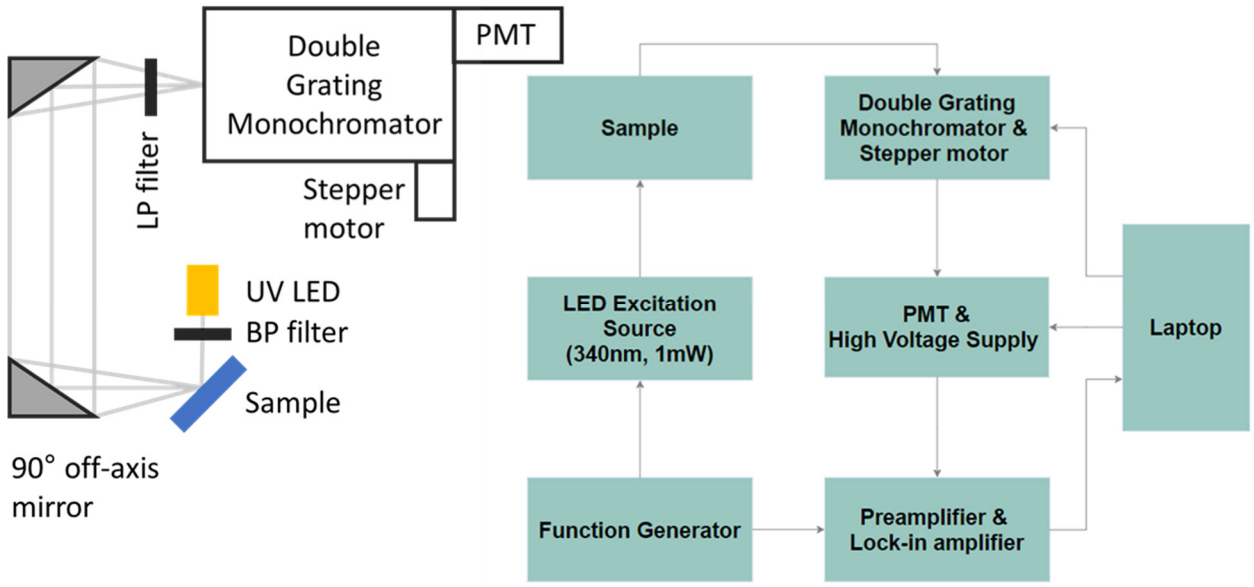

Figure 3 The schema of photoluminescence spectrometer with pulsed UV LED as a light source, band pass (BP) and long pass (LP) filters, focusing off-axis mirrors, double grating monochromator SPEX 1672 controlled by a stepper motor and a photomultiplier (PMT)

3. RESULTS AND DISCUSSION

Figure 4 compares PL spectra of as grown ZnO NRs powder with PL spectra of ZnO NRs after plasma oxidation or hydrogenation. The excitation UV LED was operating at the wavelength 340 nm in pulse mode with the repetition rate 600 Hz and 50% duty cycle. The PL emission spectra were measured in the spectral range 370 - 670 nm. The photomultiplier was biased by the cathode voltage -1600 V. The anode dark dc current as measured by pico-ammeter decreased from 2.8 nA at 20 °C to 0.2 nA at -15 °C while the dc noise was reduced from 300 pA to 50 pA. Since the ac current preamplifier gain was fixed to 10 μA/V and the input

voltage range of lock-in amplifier is 1μV - 1V, the maximum measurable ac photocurrent was 10 μA and the minimum measurable ac photocurrent as well as the ac noise level was 10 pA providing the dynamic range of 6 orders of magnitude. We have chosen the arbitrary units of PL intensity in such a way that 1 a.u. corresponds to 10 pA photocurrent.

The as grown ZnO NRs pellets show measurable PL, but excitation peaks in near UV at 380 nm have lower intensity then the defect-related yellow PL (broad band 550 - 600 nm). The oxygen plasma treatment has no effect on the observed PL emission spectra. However, the PL emission in near UV region has been significantly enhanced after ICP plasma hydrogenation whereas the deep defect related yellow PL (broad band 550 - 600 nm) has been significantly decreased. We explain the observed phenomena by passivation of defects at grain boundaries that significantly prolongs the lifetime of excitons.

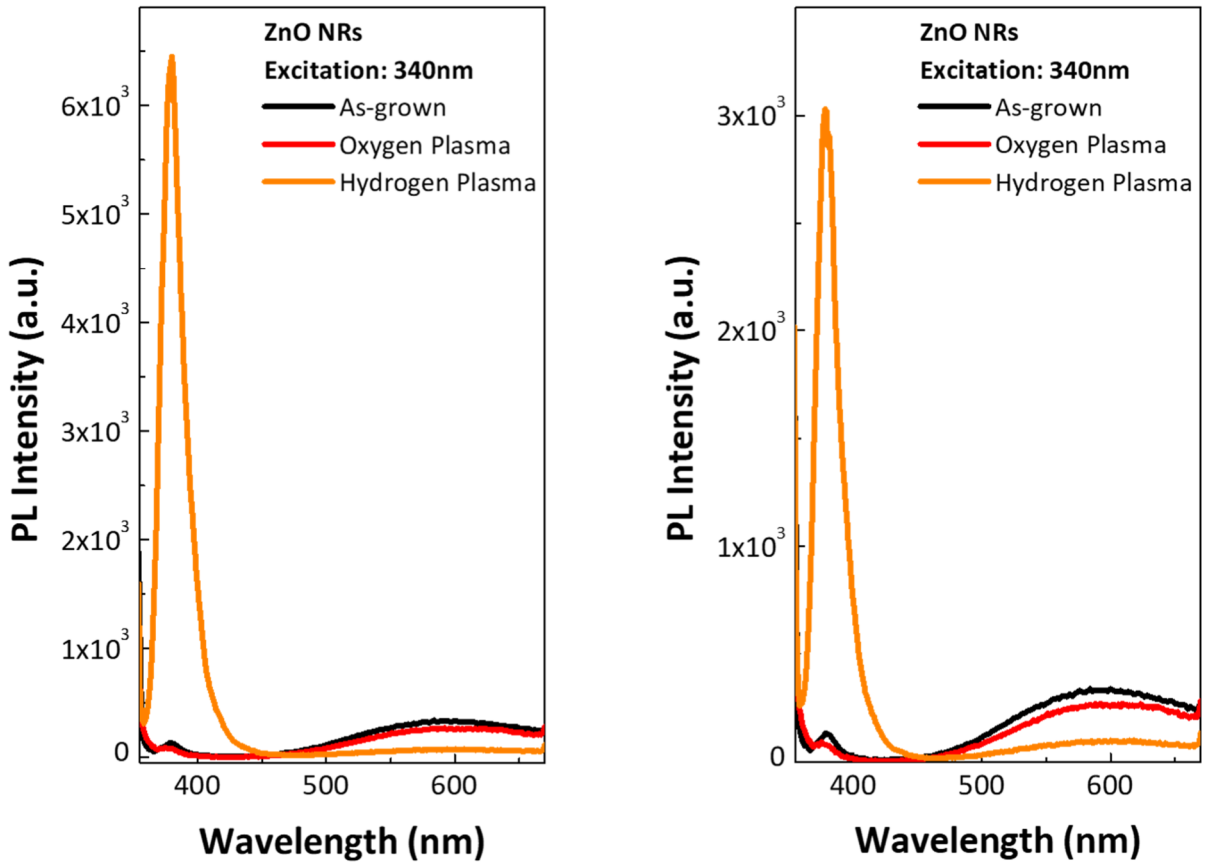

Figure 4 The photoluminescence emission spectra of two pellets prepared independently from ZnO NRs before (as-grown) and after exposition to oxygen or hydrogen plasma in ICP reactor. The excitation wavelength was 340 nm.

4. CONCLUSIONS

We have developed an inexpensive and efficient the technology of hydrothermal growth of ZnO NRs powder from zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$). The plasma oxidation and hydrogenation were done in a novel inductively coupled plasma (ICP) quartz reactor equipped with the rotary sample holder to stir powder during plasma treatment. We have shown that the photoluminescence drastically changes upon the exposure to hydrogen plasma treatments.

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REFERENCES

[1] HSIEH, Ya-Ping, CHEN, Hsin-Yi, LIN, Ming-Zhang, SHIU, Shu-Chia, HOFMANN, Mario, CHERN, Ming-Yau, JIA, Xiaoting, YANG, Ying-Jay, CHANG, Hsiu-Ju, HUANG, Hsuan-Ming, TSENG, Shao-Chin, CHEN, Li-Chyong, CHEN, Kuei-Hsien, LIN, Ching-Fuh, LIANG, Chi-Te and CHEN, Yang-Fang. Electroluminescence from ZnO/Si-Nanotips Light-Emitting Diodes. *Nano Letters*. 2009. vol. 9, no. 5, pp. 1839-1843. Available from: https://doi.org/10.1021/nl803804a.

[2] YU, Guihua, XIE, Xing, PAN, Lijia, BAO, Zhenan and CUI, Yi. Hybrid nanostructured materials for high-performance electrochemical capacitors. *Nano Energy*. 2013. vol. 2, no. 2, pp. 213-234. Available from: https://doi.org/10.1016/j.nanoen.2012.10.006.

[3] TERESHCHENKO, Alla, BECHELANY, Mikhael, VITER, Roman, KHRANOVSKYY, Volodymyr, SMYNTYNA, Valentyn, STARODUB, Nikolay and YAKIMOVA, Rositza. Optical biosensors based on ZnO nanostructures: advantages and perspectives. A review. *Sensors and Actuators B: Chemical*. 2016. vol. 229, pp. 664-677. Available from: https://doi.org/10.1016/j.snb.2016.01.099.

[4] DAVYDOVA, Marina, LAPOSA, Alexandr, SMARHAK, Jiri, KROMKA, Alexander, NEYKOVA, Neda, NAHLIK, Josef, KROUTIL, Jiri, DRAHOKOUPIL, Jan and VOVES, Jan. Gas-sensing behaviour of ZnO/diamond nanostructures. *Beilstein Journal of Nanotechnology*. 2018. vol. 9, pp. 22-29. Available from: https://doi.org/10.3762/bjnano.9.4.

[5] PROCHÁZKOVÁ, Lenka, GBUR, Tomáš, ČUBA, Václav, JARÝ, Vítězslav and NIKL, Martin. Fabrication of highly efficient ZnO nanoscintillators. *Optical Materials*. 2015. vol. 47, pp. 67-71. Available from: https://doi.org/10.1016/j.optmat.2015.07.001.

[6] NEYKOVA, Neda, STUCHLIK, Jiri, HRUSKA, Karel, PORUBA, Ales, REMES, Zdenek and POP-GEORGIEVSKI, Ognen. Study of the surface properties of ZnO nanocolumns used for thin-film solar cells. *Beilstein Journal of Nanotechnology*. 2017. vol. 8, pp. 446-451. Available from: https://doi.org/10.3762/bjnano.8.48.

[7] JANOTTI, Anderson and VAN DE WALLE, Chris G. Native point defects in ZnO. *Physical Review B*. 2007. vol. 76, no. 16. p. 165202. Available from: https://doi.org/10.1103/PhysRevB.76.165202.

[8] JANOTTI, Anderson and VAN DE WALLE, Chris G. Fundamentals of zinc oxide as a semiconductor. *Reports on Progress in Physics*. 2009. vol. 72, no. 12, p. 126501. Available from: https://doi.org/10.1088/0034-4885/72/12/126501.

[9] NEYKOVA, Neda, CHANG, Yu-Ying, BURYI, Maksym, DAVYDOVA, Marina, KUCERKOVA, Romana, SIMEK, Daniel, REMES, Zdenek and POP-GEORGIEVSKI, Ognen. Study of ZnO nanorods grown under UV irradiation. *Applied Surface Science*. 2019. vol. 472, pp. 105-111. Available from: https://doi.org/10.1016/j.apsusc.2018.03.173.

[10] CHANG, Yu-Ying, STUCHLÍK, Jiří, NEYKOVA, Neda, SOUČEK, Josef and REMEŠ, Zdeněk. Optical properties of the plasma hydrogenated ZnO thin films. *Journal of Electrical Engineering*. 2017. vol. 68, no. 7, pp. 70-73. Available from: https://doi.org/10.1515/jee-2017-0060.

[11] MIČOVÁ, Júlia, BURYI, Maksym, ŠIMEK, Daniel, DRAHOKOUPIL, Jan, NEYKOVA, Neda, CHANG, Yu-Ying, REMEŠ, Zdeněk, POP-GEORGIEVSKI, Ognen, SVOBODA, Jan and IM, Chan. Synthesis of zinc oxide nanostructures and comparison of their crystal quality. *Applied Surface Science*. 2018. vol. 461, pp. 190-195. Available from: https://doi.org/10.1016/j.apsusc.2018.05.176.