

# GROWTH, PROPERTIES AND SENSOR APPLICATIONS OF LOW TEMPERATURE GROWN ZnO NANORODS

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Received 28 October 2011; accepted 1 December 2011

ZnO nanorods with the average diameter of about 60–300 nm have been grown by the low temperature aqueous chemical growth technique. The impact of growth time and reactant concentration on the morphology on ZnO structures was tested by scanning electron microscopy and photoluminescence spectroscopy. High optical quality of obtained ZnO nanorod films was evidenced by dominating free exciton transitions. The reduction of surface to volume ratio by increasing the diameter of ZnO nanorods resulted in a linear increase of excitonic luminescence intensity with respect to the defect related emission. Excellent photoluminescence properties and high surface area of ZnO nanorods can be used for the detection of organic contaminants dissolved in water. The quenching of both excitonic and defect luminescence was observed upon exposure of ZnO nanorod films to various organic contaminants.

**Keywords:** ZnO, nanorods, low temperature growth, fluorescence sensor

**PACS:** 78.55.Cr, 78.67.Lt, 61.46.Km

## 1. Introduction

Zinc oxide is an attractive wide-bandgap semiconductor showing large exciton binding energy and enabling simple fabrication of variously shaped nanostructures [1]. Nanostructured ZnO offers some additional features, like quantum confinement, large surface area and waveguide behaviour that can be applied for ZnO based LEDs, solar cells, sensors and photocatalytic applications [2].

The low-temperature aqueous chemical growth (ACG) technique is very promising since it allows one to obtain well-oriented ZnO nanorods (NRs), it is of low cost and can be easily integrated with large-area low-cost organic semiconductor device technologies. In this letter we report on the growth and optical properties research of ZnO NR films by the low temperature ACG technique. The sensing ability of the ZnO NR films of organic contaminants in water is tested.

## 2. Experimental procedure

Two sets of ZnO NRs on pre-treated glass substrates were prepared by the low temperature ACG

technique. The details of the method and substrate pre-treatment can be found in [3]. In the first set, reactant concentration was varied from 0.05 M to 0.175 M while growth time was kept constant (5 h). Reactant concentration was constant (0.1 M) and growth time was being increased from 3 to 7 h for the second set of samples. Growth temperature was 95 °C in both cases.

The structure of ZnO NRs was analysed utilising the Oxford *Apollo 300* scanning electron microscope (SEM). Luminescence properties were studied for low and high intensity excitation conditions. Low intensity excitation conditions were fulfilled by using a low power ( $\sim\mu\text{W}$ ) light emitting diode as an excitation source. Luminescence spectra were detected by CCD camera. High intensity excitation spectra were measured by using picosecond laser ( $\tau = 25$  ps,  $h\nu = 4.66$  eV, excitation energy density  $5$  mJ/cm<sup>2</sup>) and photomultiplier detection. The sensing properties of ZnO NRs were tested by comparing luminescence spectra of ZnO in distilled water and in 1% solution of methanol, dimethylsulfoxide and chloroform. In this case,  $\lambda = 310$  nm wavelength dispersed by monochromator from a xenon lamp was used as an excitation source.

### 3. Experimental results and discussion

Figure 1 shows SEM images of two sets of ZnO NRs grown with different duration (Fig. 1 (a, b)) and with different reactant concentration (Fig. 1 (c, d)).

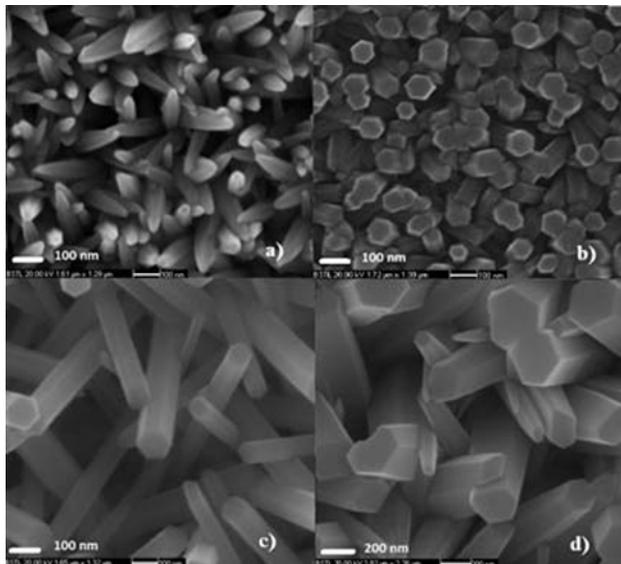


Fig. 1. Scanning electron microscope images of ZnO NRs grown in different conditions: (a)  $t = 3$  h,  $n = 0.1$  M; (b)  $t = 7$  h,  $n = 0.1$  M; (c)  $t = 5$  h,  $n = 0.05$  M; (d)  $t = 5$  h,  $n = 0.175$  M, where  $t$  is growth time,  $n$  is equimolar concentration of reagents. Growth temperature is  $95$  °C.

SEM pictures of prepared films show a nearly uniform layer of hexagonal ZnO nanorods (Fig. 1). The average diameter of NRs increases from 60 to 110 nm, when the growth time is increased from 3 to 7 h. The average diameter of ZnO NRs also increases from 60 to 300 nm with the increase of reactant concentration from 0.05 to 0.175 M. The length of NRs is about  $2.5 \mu\text{m}$ . Since the density of NRs is almost uniform, thin nanorods are not perfectly aligned. The alignment increases for thick NRs due to higher density, which limits the possibility to grow in unparallel directions. However, a variation of NR alignment is still present in the same sample, though this variation is remarkably lower for NRs of a larger thickness. The density of ZnO NRs can be controlled by growth time alteration, while the diameter is more sensitive to variation in reactant concentration. The coalescence of neighbouring NRs was observed for the films with

the average diameter of NRs exceeding the average value of 160 nm. This effect was observed in both sets of samples.

The emission spectrum of ZnO NRs obtained at low intensity excitation is shown in Fig. 2. Two luminescence bands typical of high purity ZnO are observed: free exciton recombination band at 3.195 eV and defect band at 2.35 eV. The origin of “green” defect band can be related to zinc vacancy states [4]. The spectral structure of luminescence spectra of all studied samples is almost the same. The only difference is the intensity ratio of excitonic and defect PL bands in samples of different NR diameter (see inset in Fig. 2). Free exciton luminescence intensity increases more rapidly than defect luminescence in accordance with the reduction of surface recombination. Excellent optical quality of the obtained ZnO NRs films is confirmed by similar results of the exciton and defect luminescence intensities observed in ZnO films deposited by molecular beam epitaxy [5].

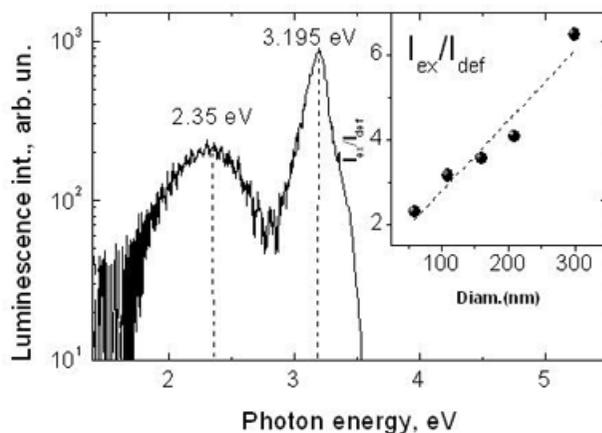


Fig. 2. Luminescence spectrum of ZnO NRs ( $t_{\text{growth}} = 5$  h,  $n_{\text{reactants}} = 0.125$  M,  $T_{\text{growth}} = 95$  °C). Inset depicts luminescence intensity ratio (exciton to defect) dependence on average NR diameter.

The latter trend was observed for the set of samples grown by varying the reactant concentration. The opposite trend was observed for the set of samples grown at various growth time. A decrease of exciton luminescence in comparison with defect emission was observed when the average diameter of NRs was increased and can be tentatively attributed to the emergence of non-radiative defect states under variation of growth time.

Shallow and deep defect states are saturated at high excitation conditions, thus information about dominating near band-edge recombination mechanisms can be obtained. Luminescence spectrum at high excitation conditions shows a sole exciton luminescence band at 3.19 eV. The luminescence intensity dependence on excitation density is linear, which is typical of free exciton recombination. Free exciton luminescence intensity increases linearly together with increasing NR diameter up to 160 nm. Further increase of ZnO NR diameter leads to a decrease of PL intensity. It can be attributed to the emergence of non-radiative structural defect states, which occurs due to coalescence of NRs. This effect was observed in both sets of the samples.

The luminescence intensity of ZnO NR films embedded in a clean ambient is governed by intrinsic recombination processes. When ZnO NRs are in a polluted ambient, e. g. in water with organic contaminants, these molecules adsorb on NR surface and start to capture photoexcited holes [6]. This causes a pronounced emission quenching phenomenon which can be applied for detection of contaminants in water. The nanostructured profile enhances the surface area of the films exposed to the quencher. The fluorescence quenching of ZnO NRs was tested by three organic solvents dissolved in distilled water (adding 1% of organic solvent). The sample exposed to pure distilled water was used as a reference. All three solvents caused quenching of both excitonic and defect luminescence. The strongest quenching was observed for dimethylsulfoxide (94% for the UV band and 85.6% for the green band). The presence of chloroform decreased emission by 64.9% (UV band) and 35.5% (green band), and the presence of methanol by 52% (UV band) and by 48.7% (green band).

#### 4. Conclusions

In conclusion, films containing ZnO NRs with a controllable diameter (60–300 nm) have been grown by the ACG technique. The obtained ZnO NRs showed efficient excitonic emission indicating high optical quality of the films. Optimal conditions for the growth of size-controllable ZnO NRs were elucidated. Excellent photoluminescence properties and high surface area of ZnO NR films enable their application for detection of organic contaminants in water.

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## ŽEMATEMPERATŪRIU BŪDU UŽAUGINTŲ ZnO NANOSTRYPELIŲ SAVYBĖS BEI TAIKYMAS JUTIKLIAMS

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### Santrauka

Cheminio auginimo iš tirpalo metodu buvo gauti ZnO nanostrypelių sluoksniai su valdomomis morfologinėmis savybėmis, auginimo metu keičiant auginimo trukmę bei reagentų koncentraciją. Užauginti sluoksniai buvo tirti taikant nuskaitymo elektronų mikroskopo bei fotoluminescencijos metodus. Tyrimai nuskaitymo elektronų mikroskopu parodė, jog ZnO nanostrypeliai yra 2–2,5  $\mu\text{m}$  aukščio ir 60–300 nm skersmens. ZnO nanostrypelių fotoluminescencijos spektre stebimos dvi juostos: laisvųjų eksitonų bei žalioji – defektų. Mažo intensyvumo sužadavimo atveju spektre vyraujanti laisvųjų eksitonų liuminescencijos juosta rodo aukštą nano-

struktūrų optinę kokybę, palyginamą su ZnO epitaksiniu sluoksniu. Didelio intensyvumo fotosužadavimo atveju pastebėta, kad eksitonų liuminescencijos intensyvumas nanostrypeliuose, storesniuose nei 160 nm, pradeda mažėti, veikiausiai dėl gretimų nanorypelių suaugimo. Dėl didelio paviršiaus ploto ZnO nanostrypelių sluoksnių liuminescencijos intensyvumas yra jautrus aplinkos poveikiui. Liuminescencijos gesimas iširtas į vandenį įpylus nedaug organinių tirpiklių. Labiausiai ZnO nanostrypelių liuminescenciją gesino 1 % dimetilsulfoksido tirpalas (apie 90 %). Toks didelis jautris organiniams teršalams leidžia panaudoti ZnO nanostruktūras organinių tirpiklių detekcijai.