INFLUENCE OF H_2O_2 TREATMENT ON MORPHOLOGICAL AND PHOTOLUMINESCENCE PROPERTIES OF HYDROTHERMALLY GROWN ZNO NANORODS

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Abstract

We report photoluminescence properties of hydrothermally grown ZnO nanorods (NRs) before and after hydrogen peroxide (H_2O_2) treatment. The H_2O_2 treatment introduces oxygen related defects and thus enhances chemisorption processes in ZnO NRs. These effects amplify interactions between the gas species and adsorbed oxygen and thus can influence sensing properties of ZnO NRs.

Keywords: ZnO nanorods, photoluminescence, H_2O_2 treatment

1. INTRODUCTION

Nanostructures such as nanorods and nanotubes show interesting physical properties and are promising for the next generation of electronic and photonic devices. ZnO nanorods with a large band gap of 3.37 eV at room temperature, an exciton binding energy of 60 meV, and a large surface-to-volume ratio show great potential for optoelectronic applications [1]. To grow high quality of ZnO nanorods gas phase methods are often used [2]. However, these techniques require high temperatures, sophisticated equipment, and a catalyst, which is a potential source of impurities. Solution-based methods, in contrast, use low growth temperatures and allow for the large scale production. However, the low temperature growth results in a high density of native defects, which strongly affect physical and optical properties of ZnO nanorods. Photoluminescence spectroscopy (PL) is commonly used to evaluate the optical quality of semiconductor materials. A typical PL spectrum of ZnO nanorods contains excitonic lines in the UV region and a broad band in the visible region. The red, orange, yellow, and green broad bands are attributed to a variety of native defects such as oxygen vacancies (V_O), zinc vacancies (V_{Zn}), oxygen interstitials (O_i), zinc interstitials (Zn_i), and clusters formed by two point defects [3]. Nevertheless, a controlled introduction of defects can be useful for specific applications such as gas sensors or UV photodetectors [4, 5]. In this work we demonstrate that both the excitonic line and the visible broad band of the ZnO NRs can be easily tuned by applying hydrogen peroxide (H_2O_2) treatment. The H_2O_2 treatment introduces more oxygen-related defects and thus enhances chemisorption processes in ZnO nanorods.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Vertical arrays of ZnO nanorods were grown on a seed layer, consisting of electrophoretically deposited ZnO nanoparticles, by low temperature hydrothermal method. Details of the ZnO nanorod growth and of the seed layer preparation were described in our previous work [6]. The PL spectra of the ZnO NRs were measured with a set-up comprising a He-Cd laser (325 nm) as an excitation source, a grating monochromator Jobin Yvon THR 1000, a closed cycle He optical cryostat, and a GaAs photomultiplier detection system. The PL spectra were recorded at 4 K and room temperature (RT). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were applied to study morphological and structural properties of the ZnO NRs, respectively. The ZnO NRs grew preferentially along the c-axis with the length of 1.5 μm and diameter of 30-70 nm [4,6]. The as grown ZnO NRs were treated by dipping in boiling 5%,10%, and 20% H_2O_2 for less than 30 s. After the treatment, the samples were immediately rinsed with deionized water and dried with argon. **Fig. 1** shows the morphology of ZnO NRs before and after the H_2O_2 treatment. The morphology of the ZnO NRs does not change at low H_2O_2 concentrations below 5%. Larger concentrations result in the etching of the NRs, and above 10% the morphology of the NRs is significantly affected.

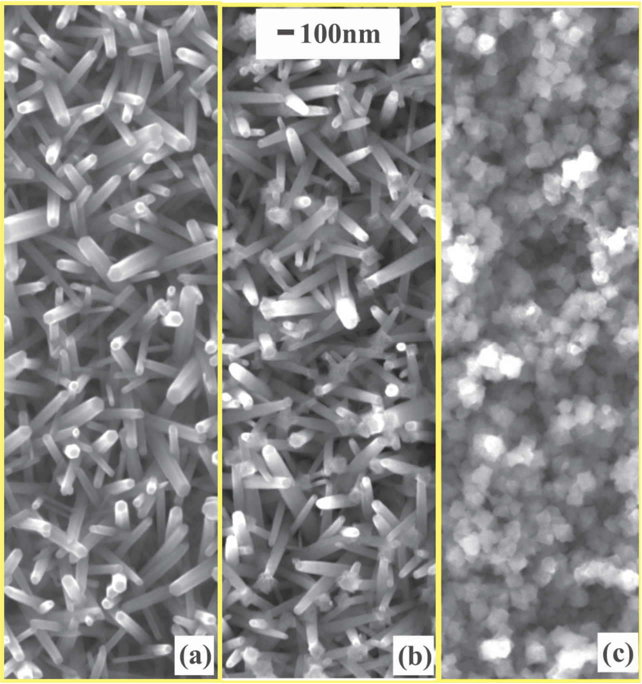

Fig. 1 SEM images of the as grown ZnO NRs (a); and after 10% (b), and 20% (c) H_2O_2 treatment

The room temperature PL spectra from the as grown ZnO NRs consisted of the excitonic emission band with the maximum at 3.24 eV and of the broad composite band consisting of three sub-bands peaked at 2.2 eV, 2.06 eV, and 1.8 eV. The origin of the yellow emission band (2.2 eV) in the hydrothermally grown samples at low temperature was attributed to oxygen interstitials or the presence of Li impurities [3], or due to $Zn(OH)_2$ groups attached to the surface of ZnO NRs [7]. To verify the origin of the yellow band we annealed the ZnO NRs in air (red line in **Fig. 2**). After annealing the yellow band was strongly suppressed due to the desorption of hydroxyl groups from the NR surface. At the same time the intensity of the red band luminescence (1.8 eV) was increased. The increase of the red band emission can be explained by the lattice disorder along the c-axis of the ZnO NRs [8]. The emission at 2.06 eV is probably due to the transition from the conduction band to a specific defect level (oxygen vacancy **-** zinc interstitial cluster). The peak at 1.68 eV is related to the second order diffraction of the near band-gap emission.

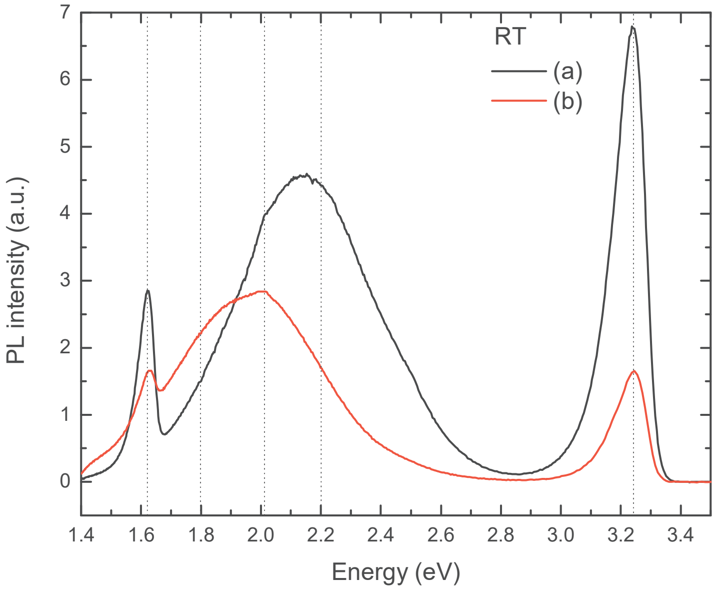

Fig. 2 RT PL spectra from the ZnO NRs: (a) as grown, (b) annealed in air at 500°C for 1 hour

The excitonic luminescence at low temperature was dominated by two peaks; the first peak at 3.36 eV is attributed to an exiton bound to a shallow donor, and the second peak at 3.24 eV is associated with a shallow donor-shallow acceptor transition (nitrogen compounds present in the growth solution are most likely the source of shallow acceptors) [3]. As presented in **Fig. 3**, after the H_2O_2 treatment, we observed the intensity decrease of the excitonic line and the intensity increase of the broad composite band. The ratio between the intensity of the excitonic line (NBE -near-band edge emission) and the broad composite band (DLE - deep level emission) is frequently used as an indication of the optical quality of ZnO NRs.

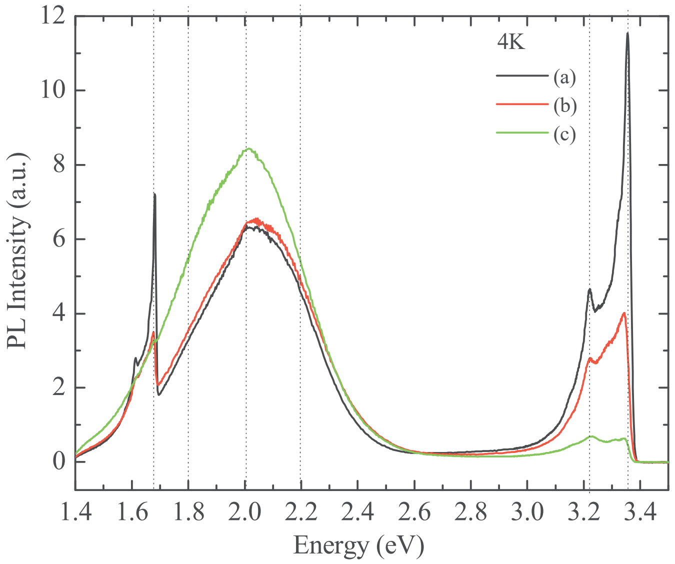

Fig. 3 4K PL spectra obtained from ZnO NRs: as grown (a); after 10% H_2O_2 treatment (b); and after 20% H_2O_2 treatment (c)

As shown in **Fig. 4**, after the H_2O_2 treatment the $I_{(NBE)}/I_{(DLE)}$ ratio significantly decreases. This decrease is related to the generation of more oxygen related defects in ZnO NRs. In our previous paper we demonstrated a strong correlation between the concentration of oxygen related defects (related to the morphology variation of the ZnO NRs) and the sensitivity of the graphite/ZnO NR hydrogen sensor [9]. More oxygen related defects enhanced the chemisorption processes in ZnO nanorods and therefore yielded improved sensing properties of the gas sensor. The H_2O_2 treatment is an alternative way of tuning the gas sensor properties.

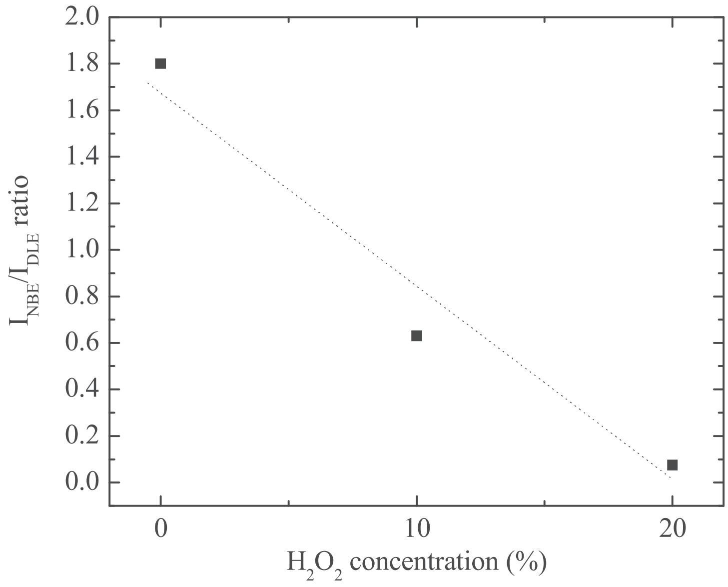

Fig. 4 The I_{NBE}/I_{DLE} ratio as a function of the H_2O_2 concentration

3. CONCLUSION

The effect of hydrogen peroxide treatment on the optical properties of ZnO NRs was investigated by PL spectroscopy. The room-temperature emission spectra of as grown ZnO NRs comprised an excitonic emission band with the maximum at 3.24 eV and a broad composite band consisting of three sub-bands peaked at 2.2 eV, 2.06 eV, and 1.8 eV. The yellow emission at 2.2 eV was shown to be given by the $Zn(OH)_2$ group attached to the surface of ZnO NRs. At 4 K the yellow emission is quenched and the spectra in the visible region are dominated by the orange emission (2.06 eV). The H_2O_2 treatment resulted in the etching of the ZnO NRs when the concentration of H_2O_2 was larger than 5%. The H_2O_2 treatment increases the concentration of oxygen-related defects on the NR surface. A strong correlation between the NBE-to-DLE intensity ratio in the 4K PL spectra and the H_2O_2 treatment was found. With increasing H_2O_2 concentration the DLE band dominates at the expense of the NBE emission. Oxygen-related defects enhance the chemisorption processes on the surface of semiconductor oxides and are responsible for their high sensitivity towards various gases. The H_2O_2 treatment thus enables to tune the gas sensing properties.

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