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Enhanced room temperature exciton photoluminescence of plasma hydrogenated ZnO nanocolumns

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Abstract. Zinc oxide (ZnO) nanocolumns have interesting material properties such as the direct band gap, tunable electrical conductivity, high optical transparency, high thermal conductivity, and large surface to volume ratio. Here we present the latest results on the enhancement of the infrared optical absorptance and ultraviolet photoluminescence in ZnO nanocolumns after hydrogen plasma treatment. The photoluminescence in near UV region at 378 nm has been significantly enhanced by hydrogen plasma treatment at room temperature whereas the defect related yellow photoluminescence (broad band 550–650 nm) decreased.

1. Introduction

ZnO is a direct band gap semi-conductor with optical transparency in the visible spectral range, large exciton binding energy and related room temperature photoluminescence, tunable electrical conductivity and high thermal conductivity [1]. The native point defects [2] and oxygen vacancies [3] have been studied including their sensitivity to hydrogen. Hydrogen works as a shallow donor as shown by photoluminescence and photoconductivity measurements [4]. The hydrogen plasma treatment of single crystal ZnO passivates deep defects and enhances the band edge luminescence [5].

The layers of vertically aligned ZnO nanocolumns can be grown on glass substrate coated by thin polycrystalline films [6]. The nanostructure ZnO is attractive for applications in sensors and energy converters such as gas sensors [7] and biosensors [8] as they possess useful electrical and optical properties such as tunable electrical conductivity, low optical absorbance and room temperature luminescence [9]. The annealing in H₂ atmosphere at temperature above 800°C enhances significantly excitonic emission in ZnO nanoparticles [10]. The experimental results indicate that the OH and H bonds play the dominant role in facilitating surface recombination [11].

In our technology, the seeding layer is deposited by DC reactive magnetron sputtering of Zn target in the gas mixture of argon and oxygen plasma followed by the hydrothermal growth of ZnO nanocolumns. We have shown that the lack of the seeding layer leads to random growth of low quality nanocrystals [12]. We have found that the oxidation by the thermal annealing in air significantly reduces the near infrared optical absorption as well as the electrical conductivity in correlation with the increased presence of non-lattice oxygen in the form of Zn–O–H and Zn–O–Zn [13]. On the contrary, the increase of the infrared optical absorption and the electrical conductivity related to free carrier concentration was detected below the optical absorption edge after hydrogen plasma treatment



[14]. Our latest results showed a significant increase in the length of the ZnO nanocolumns grown under UV irradiation, as well as the improvement in their uniformity [15].

2. Experimental

2.1. Sample preparation

The seeding layers were prepared by reactive magnetron sputtering in the stainless-steel vacuum chamber using a Zn target and O₂ plasma. The Zn target was sputtered in a capacitive coupled dc glow discharge plasma (grounded substrate holder at temperature 400°C, constant potential of +400 V on the target, DC current of 0.13 A) of a reactive mixture of argon (purity 99.99%, flow rate 2.0 sccm) and oxygen (purity 99.95%, flow rate 0.5 sccm) under pressure of 1 Pa [16].

The ZnO nanorods grew on nucleated fused silica glass substrates by hydrothermal process in an oil bath containing a flask with ZnO nutrient solution that contained a mixture of two equimolar aqueous solutions of 25 mM zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and hexamethylenetetramine (C₆H₁₂N₄). The resulting solution was preliminary stirred at 60°C for 1 h and then filtered using a polytetrafluoroethylene (PTFE) filter with a pore size of 0.45 µm. Finally, the samples were carefully washed in deionized water and purged in nitrogen. During the ZnO nanostructural growth, the substrates were mounted upside-down on a flat bottom quartz tube with an optical fiber placed inside the tube. The UV LED light source operating at power 1 W and the wavelength 365 nm was turned on to perform the UV-assisted growth. The average height of ZnO nanorods was 1250 nm and the diameter 200 nm.

The plasma hydrogenation was done in the stainless-steel vacuum chamber at room temperature using 9 W rf discharge at 13.56 MHz, hydrogen flow 50 sccm and pressure 70 Pa. Prior the plasma hydrogenation, the vacuum chamber had been evacuated down to the pressure vacuum 10⁻⁷ Pa.

2.2. Photoluminescence spectroscopy

The steady state photoluminescence spectra (PL) of the highly scattering thin films were measured in the 360–660 nm spectral range using the f/4 double gratings monochromator SPEX equipped with two 1200 grooves/mm gratings blazed at 500 nm. The photoexcitation was provided by the 1 mW LEDs at the wavelength 340 nm and optically filtered by narrow band pass optical filter featuring 90% transmission and OD 6 blocking outside of the 20 nm passband. The sample holder was positioned by two perpendicularly oriented translation stages manually driven by adjuster screws for precision motion. The emitted light was collected and focused onto the 1 mm wide monochromator input slit by two 90° off-axis mirrors coated by UV enhanced aluminum. The signal was detected by the multi-dynode multi-alkali red sensitive photomultiplier (Photonis XP2203B) cooled to -12°C as the dc anode current from 1 pA up to 1 µA, coaxial cables and the electrometer Keithley 6517. The dark anode current at 1000 V was 2 pA and the noise 0.5 pA. The voltage was provided by the electrometer via coaxial cables. The PL spectra were measured at room temperature and calibrated on the spectral efficiency of the spectrofluorometer [17].

2.3. Photothermal deflection spectroscopy

The photothermal deflection spectroscopy (PDS) measures directly the optical absorption of thin films with sensitivity of four orders of magnitude [18]. The PDS spectrophotometer used the 150 W Xe lamp as a light source and the monochromator equipped with three gratings blazed at 300, 750, 1250 nm operating in a broad spectral range from ultraviolet to infrared region 250–1700 nm. The measured sample was immersed in transparent liquid with the probe laser beam passing parallel to the sample surface. The sample was illuminated by the monochromatic light. The heat absorbed in the sample deflected the probe laser beam detected by the position detector. Since the amplitude of the probe beam deflection was proportional to the optical absorption, the optical absorbance was measured by normalizing the signal on the deflection of the black sample.

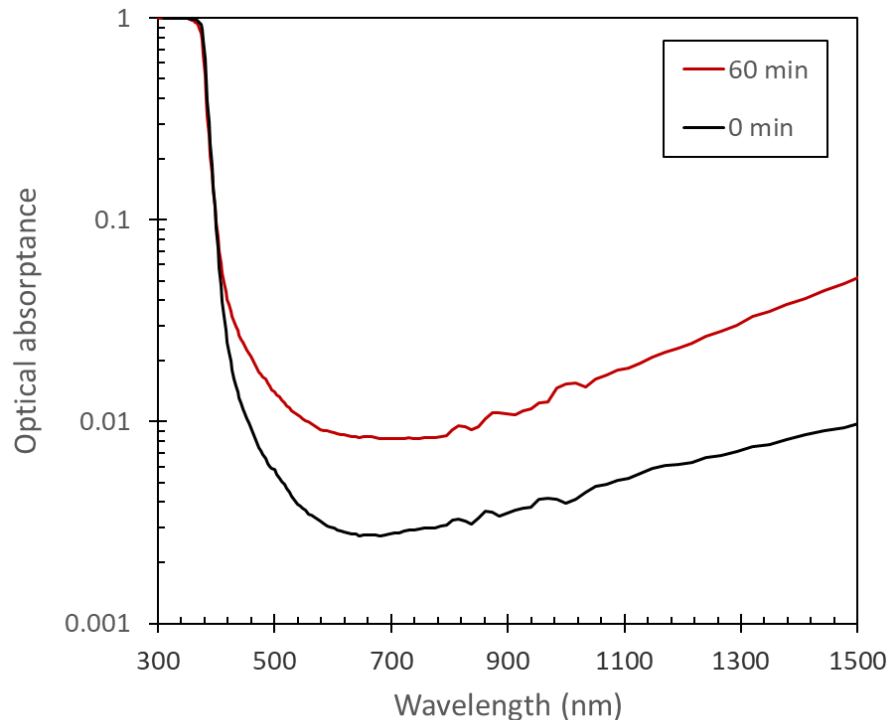


Figure 1. Optical absorbance spectra of ZnO nanocolumns before (0 min) and after plasma hydrogenation (60 min)

3. Results and discussion

Figure 1 shows the optical absorbance spectra of ZnO nanocolumns measured by the photothermal deflection before and after plasma hydrogenation. The optical absorption edge related to the ZnO band gap appears at wavelengths below 380 nm in both samples. The region of the free carrier absorbance appears in the near infrared region [19]. The infrared optical absorbance increased after hydrogen plasma treatment whereas the optical absorption edge has not been effected by plasma hydrogenation.

Figure 2 shows the photoluminescence emission spectra (PL) of the as grown and plasma hydrogenated fused silica glass substrate coated by the very thin nanocrystalline ZnO thin film by reactive magnetron sputtering. Since at 680 nm would appear the second harmonic of the excitation wavelength 340 nm, the emission spectra were measured only at wavelengths below 660 nm. On the other hand, the emission spectra were not measured at wavelengths below 360 nm because of the scattered excitation light. Figure 2 shows that the PL signal of the substrate is very low in the visible region above 400 nm being comparable with the background noise level. The signal increases in UV below 400 nm probably due to the scattered excitation light. However, there is a detectable weak emission peak at 378 nm that has been related to the indirect annihilation of intrinsic excitons with the simultaneous emission of one LO phonon [20]. Moreover, the emission related to deep defect states is visible in dark room by eye as a weak yellow luminescence in the spectral range 550–650 nm [21].

Figure 3 shows the enhanced photoluminescence emission spectra of the plasma hydrogenated ZnO nanocolumns compared to the as grown samples before the plasma hydrogenation. The strong emission peak appears centered at 378 nm. The broad defect related emission band in the spectral range 550–650 nm is reduced. The exciton-related emission increased by two orders of magnitude after plasma hydrogenation while the defect related emission band significantly decreased. The optimal plasma hydrogenation has been found to be about 30 min.

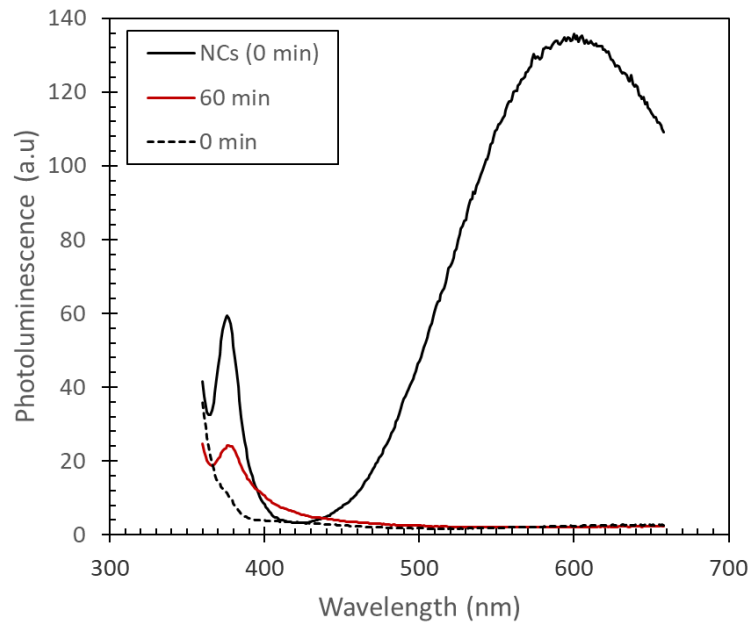


Figure 2. Photoluminescence spectra of the nucleated substrate before (0 min) and after plasma hydrogenation (60 min). The PL spectra of ZnO nanocolumns before the plasma hydrogenation (NCs 0 min) has been added for comparison and they are also shown in figure 3.

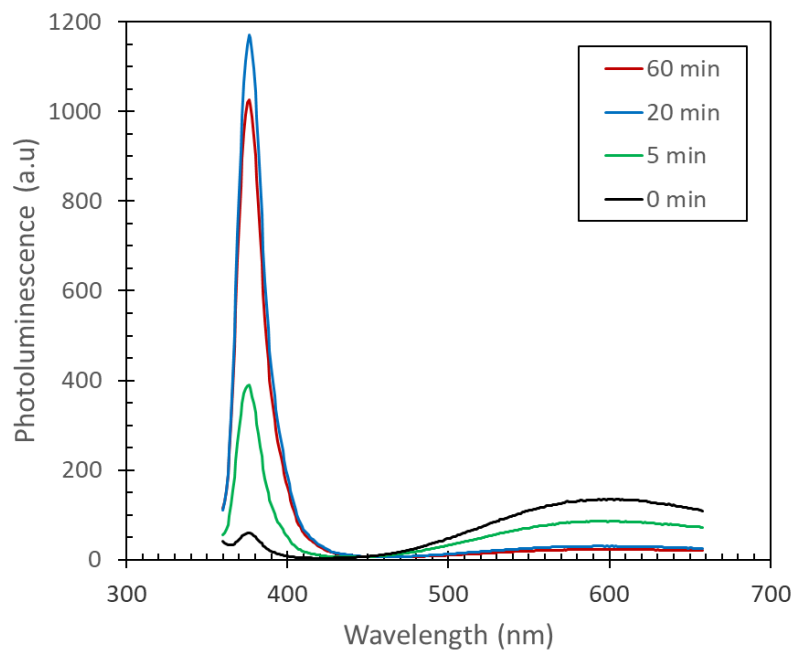


Figure 3. The enhanced photoluminescence emission spectra of the plasma hydrogenated ZnO nanocolumns compared to the as grown samples before the plasma hydrogenation.

Figure 4 compares the optical absorptance and photoluminescence spectra of the hydrogenated ZnO nanocolumns (UV enhanced growth, 60 min plasma hydrogenation). The horizontal axis has been recalculated to energy expressed in eV. Since the photoluminescence measurements has been done with constant spectral resolution 2 nm, the photoluminescence spectra expressed as a function of the energy needs to be normalized by multiplying with factor E^{-2} , where E is energy in eV [22]. This correction in conjunction with the conversion to line shape provides the properly treated emission data for quantitative analysis. Figure 4 shows that the photoluminescence peak has maximum at 3.3 eV just below the optical absorption edge.

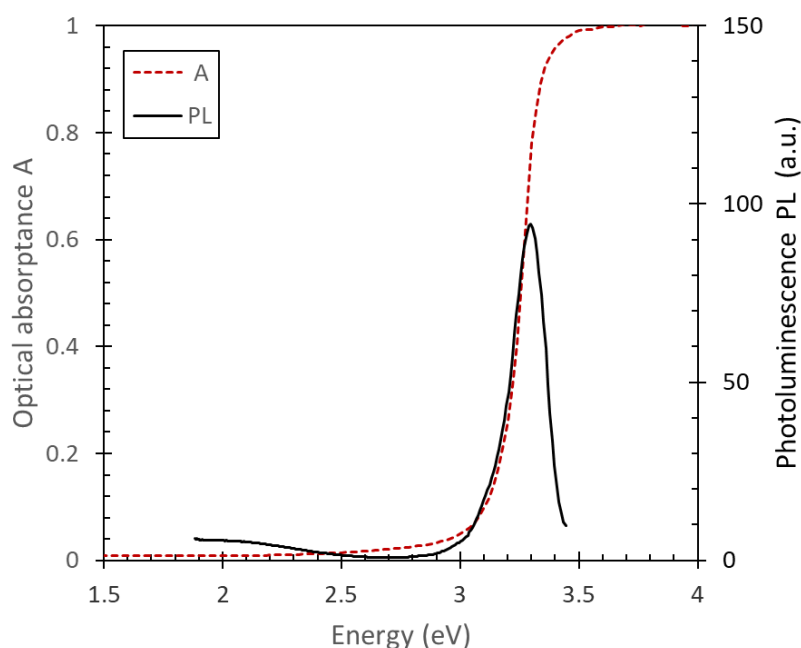


Figure 4. Comparison of the optical absorptance (A) and photoluminescence (PL) spectra of the hydrogenated ZnO nanocolumns (UV enhanced growth, 60 min plasma hydrogenation).

4. Conclusion

The optical absorption and photoluminescence emission spectra of thin films of the ZnO nanocolumns were measured using optical methods optimized for optically scattering samples. These methods include photothermal deflection spectroscopy and the photoluminescence spectroscopy measured using the double grating spectrofluorometer with very low background scattered light. The main advantages of our methods are the precise sample positioning of thin films, the high sensitivity and very low influence of the scattered light. This is very important for the highly scattering samples such as nanostructured thin films. We have observed that the exciton related emission band of ZnO nanocolumns centered at the wavelength 378 nm increased significantly after the hydrogen plasma treatment, whereas the defect related emission band at wavelengths 550–650 nm significantly decreased. These effects correlate with the increase of the infrared absorption. The optimal plasma hydrogenation has been found to be about 30 min.

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