THE PHOTOLUMINESCENCE AND OPTICAL ABSORPTANCE OF PLASMA HYDROGENATED NANOCRYSTALLINE ZNO THIN FILMS

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Abstract

We have developed the technology of the deposition of the nominally undoped ZnO nanocrystalline thin films by DC reactive magnetron sputtering of Zn target in the gas mixture of argon and oxygen plasma. We have optimized the photoluminescence spectroscopy for measuring optically scattering thin layers 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 photoluminescence of the nanocrystalline ZnO thin films after plasma hydrogenation. The photoluminescence in near UV region has been enhanced whereas the deep defect related photoluminescence has been significantly decreased. We found good room temperature stability of the plasma hydrogenated ZnO nanocrystals in air, but fast degradation at elevated temperature.

Keywords: Nanomaterials, ZnO, photoluminescence, magnetron sputtering

1. INTRODUCTION

The high electron mobility, high thermal conductivity and tunable electrical conductivity make ZnO suitable for a wide range of devices, including transparent thin-film transistors, photodetectors, light-emitting diodes and laser diodes that operate in the blue and ultraviolet region of the spectrum. ZnO is a semi-conductor with optical transparency in the visible spectral range, large exciton binding energy and strong room temperature photoluminescence [1]. The native point defects [2] and oxygen vacancies [3] have been studied including their sensitivity to hydrogen. The experimental results indicate that the OH and H bonds play the dominant role in facilitating surface recombination [4]. Moreover, hydrogen works as a shallow donor as shown by photoluminescence and photoconductivity measurements [5]. The hydrogen plasma treatment passivates deep defects [6] and it influences the relative luminescence intensities of bound excitons, in particular, the PL intensity at 3.363 eV (369 nm) [7]. The annealing in H_2 atmosphere at temperature above 800°C enhanced significantly excitonic emission in ZnO nanoparticles [8].

The RF sputtering technique has drawn considerable attention since the films properties can be controlled by changing the sputtering conditions. In our previous paper we have shown the effect of hydrogen plasma treatment on the nominally undoped ZnO thin film deposited by DC reactive magnetron sputtering of Zn target in the gas mixture of argon and oxygen plasma [9]. After oxidation due to thermal annealing in air, the optical absorption was significantly reduced in the infrared region and the electrical resistivity increased. After hydrogen plasma treatment, the increase of the infrared optical absorption, related to free carrier concentration, was detected below the optical absorption edge [10]. The increase of the optical absorption goes with the increase of the electrical conductivity related to the increase of the free carrier concentration. Moreover, we have developed the software based on the contactless reflectance interferometry as the fast method of the thin film thickness evaluation from the optical interference fringes [11].

In this paper we show how the photoluminescence of the plasma hydrogenated nanocrystalline ZnO layer correlates with optical absorption edge. Moreover, we study the stability of the plasma hydrogenated nanocrystalline ZnO layer upon exposition to air at room and elevated temperature.

2. EXPERIMENTAL

2.1. Reactive magnetron sputtering

The 450 nm thick ZnO layer was deposited on fused silica glass substrate by reactive magnetron sputtering in the stainless-steel vacuum chamber using a Zn target and O_2 plasma. The Zn target was sputtered in a DC capacitive couple 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 [12].

2.2. Plasma hydrogenation

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.

2.3. Photothermal deflection spectroscopy

The photothermal deflection spectroscopy (PDS) measures directly the optical absorption of thin films with sensitivity of four orders of magnitude [13]. The measured sample is immersed in transparent liquid with the probe laser beam passing parallel to the sample surface. The sample is illuminated by the monochromatic light and the heat absorbed in the sample deflects the probe laser beam with the amplitude of the deflection being proportional to the optical absorption. Thus, the optical absorptance is detected by the position detector normalized on the deflection measured using black sample [14].

2.4. Photoluminescence spectroscopy

The steady state photoluminescence (PL) spectra of the highly scattering ZnO thin films were measured in the 360–660 nm spectral range using the f/4 double gratings monochromator SPEX 1672 equipped with two 1200 grooves/mm gratings blazed at 500 nm with less than 10-9 scattered light. The photoexcitation was provided by the 1 mW LEDs with maximum intensity centered at the wavelength 340 nm and optically filtered by narrow band pass optical filter featuring 90 % transmission and OD 6 blocking outside of the 330–350 nm passband. The sample holder was positioned by two perpendicularly oriented translation stages manually driven by adjuster screws for precision motion, see **Figure 1**. The scattered and emitted light was collected and focused onto the monochromator input slit by two 90° off-axis mirrors coated by UV enhanced aluminium. The PL signal was

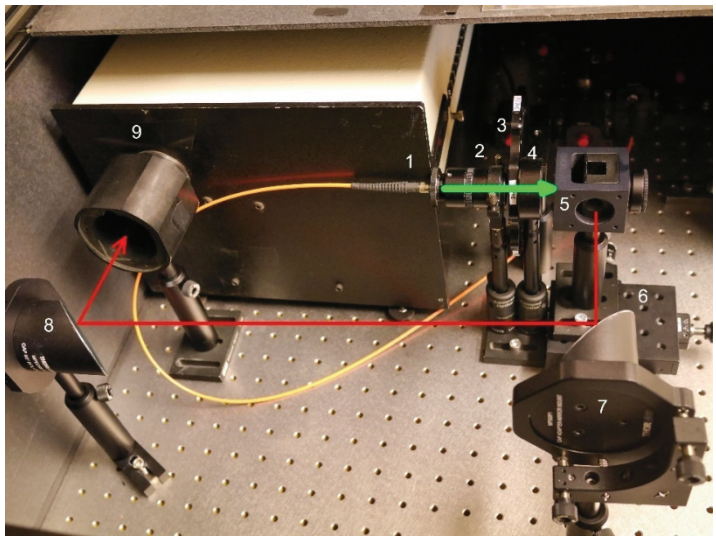

Figure 1 The detail of the photoluminescence setup: (1) optical fiber, (2) collimator, (3) bandpass filter, (4) focusing lens, (5) sample holder, (6) XY stage, (7-8) 90° off axis mirrors, (9) monochromator entrance slit

detected in dc mode by the cooled multi-dynode multi-alkali red sensitive photomultiplier (Photonis XP2203B) and the electrometer Keithley 6517A providing a high voltage for photomultiplier. The dark anode current was 2 pA, maximum photocurrent 1 μA and the noise 0.5 pA

3. RESULTS AND DISCUSSION

Figure 2 compares the photoluminescence (PL) emission and optical absorptance (A) spectra of the as grown and plasma hydrogenated ZnO thin film grown on fused silica glass substrate by reactive magnetron sputtering. Both the PL as well as A spectra were measured at room temperature. The A spectra show the optical absorption edge below 400 nm. The band gap of a single crystal ZnO 3.37 eV at room temperature corresponds to the wavelength 368 nm and the free-exciton binding energy in ZnO is 60 meV [15]. This large exciton binding energy indicates that efficient excitonic emission in ZnO can persist at room temperature. Indeed, **Figure 2** shows the exciton-related peak at 372 nm (3.33 eV) in the A spectrum of the hydrogenated nanocrystalline ZnO [16]. It should be noted that various authors report lower band gap values for the polycrystalline ZnO depending on the deposition conditions [17]. **Figure 2** shows that the PL signal is very low in the as grown sample. The PL signal strongly increases after plasma hydrogenation. The emission peak at 380 nm has been contributed to the indirect annihilation of intrinsic excitons with the simultaneous emission of one LO phonon [18].

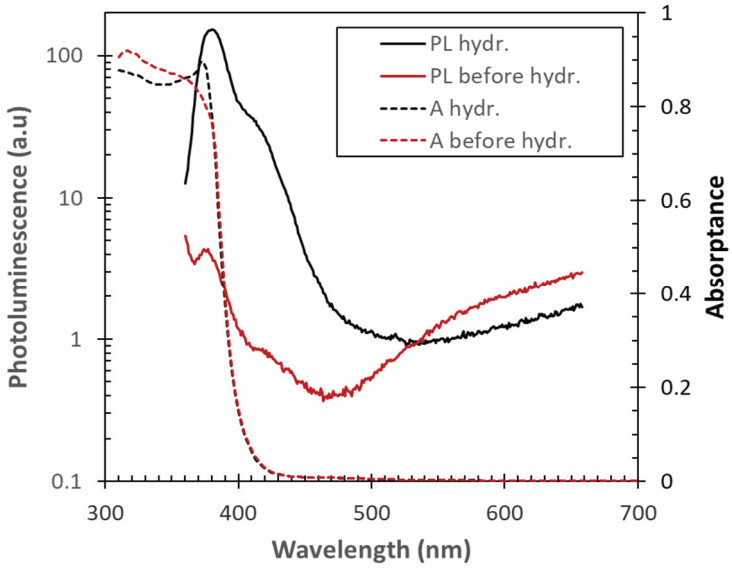

Figure 2 The comparison of the photoluminescence (PL) emission and optical absorptance (A) spectra of the as grown (PL before hydr.) and plasma hydrogenated 450 nm thick nanocrystalline ZnO layer grown on fused silica glass substrate by reactive magnetron sputtering

The photoluminescence of the hydrogenated nanocrystalline ZnO layer slightly decreased after several weeks in air, see **Figure 3**. This indicate good room temperature stability of the plasma hydrogenated ZnO nanocrystals in air. However, the degradation of the UV PL intensity is much faster at elevated temperatures. **Figure 3** shows that the significant deterioration occurs at 150°C in air within 1 h. Since our sample has been deposited in O_2 rich environment at 400°C, the ZnO nanocrystals should be stable in air at 150 °C. In general, the annealing in air atmosphere improves the crystal structure and optical properties of ZnO nanocrystals [19]. Thus, the observed degradation of the exciton-related PL intensity indicates that the involved processes are related to the surface oxidation. This hypothesis needs to be proved by further XPS and FTIR measurements that we plan in near future. However, our previous results on ZnO nanorods have shown that the surface composition drastically changes upon the exposure to O-plasma. The plasma treatments increased the presence of non-lattice oxygen in the form of Zn-O-H and Zn-O−Zn [20].

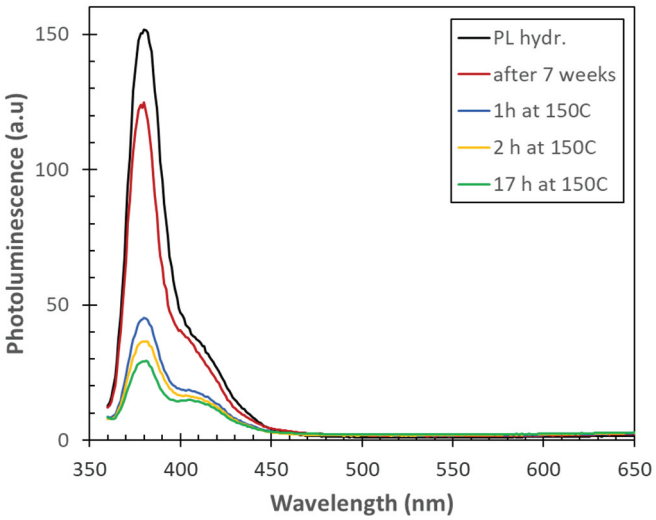

Figure 3 The degradation of the photoluminescence intensity of the plasma hydrogenated nanocrystalline ZnO layer after 7 weeks in air at room temperature followed by annealing in air for 1, 2 and 17 hours at 150°C

4. CONCLUSION

The nanocrystalline ZnO thin films were deposited by DC reactive magnetron sputtering of Zn target in the gas mixture of argon and oxygen plasma followed by hydrogen plasma treatment. The optical properties of the optically scattering were measured using the optimized spectrophotometer based on the double grating monochromator equipped with the fiber coupled LEDs as the excitation light sources. We have observed that the exciton related emission band centered at the wavelength 380 nm is influenced significantly by the plasma treatment and it correlates with the peak in the optical absorption spectra. In general, hydrogenation enhances the UV luminescence and passivates the visible emission. Our results indicate good room temperature stability of the exciton-related photoluminescence of the plasma hydrogenated ZnO nanocrystals in air, but the fast degradation at elevated temperatures.

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