Enhanced photoluminescence from polycrystalline ZnO films resulting from oxygen processing

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Abstract

We report studies of photoluminescence from polycrystalline ZnO films deposited on sapphire as a function of the \textit{in situ} oxygen pressure during growth and \textit{ex situ} annealing. The ultraviolet photoluminescence was observed to increase by more than two orders of magnitude as a result of the annealing treatment. Enhanced cathodoluminescence was observed from the same films. The role of oxygen defects is discussed.

Keywords: Photoluminescence; Oxygen partial pressure; ZnO films

1. Introduction

ZnO has been targeted as an attractive material for potential ultraviolet (UV) laser emission (lasing) applications due to its large room-temperature band gap combined with a high excitonic gain and a large exciton binding energy \[1,2\]. Spontaneous lasing at 3.3 eV has been reported in ZnO single crystals, thin films, and powders at room temperature \[3–7\]. Photoluminescence (PL) has been widely studied as a prelude to possible lasing applications. However, a relative high lasing threshold and a weak PL response was observed in previous studies which herald the importance of further enhancing ZnO luminescence. ZnO films have been prepared by sputtering [8], reactive thermal evaporation [9], metallic oxidation [10], pulsed laser deposition [11], plasmon enhanced chemical vapor deposition [12], and molecular beam epitaxy [13] for this purpose. In this work, we investigated the \textit{ex situ} processing of sputtered ZnO films and the effects of oxygen defects on photoluminescence.

2. Experimental details

We prepared our polycrystalline ZnO thin films on fused silica and [0001] sapphire substrates by reactive, pulsed-direct-current, sputtering at a temperature of 523 K from a 99.99% pure zinc target (purchased from Goodfellow Co., PA). The chamber gas environment during sputtering consisted of argon and oxygen with the partial pressure of the latter controlled by a residual gas analyzer. The substrates were radiantly heated from the backside. The resulting films were all \((0001)\) oriented (with the \(c\)-axis perpendicular to the film surface), as determined by X-ray \(\theta/2\theta\) diffraction (XRD). The widths of the rocking curves were \(<0.5^\circ\). These samples were also examined with a scanning electronic microscope (SEM). The SEM images show that the grains are randomly distributed in size and roughly hexagonal in shape. Details of the deposition were reported elsewhere [14].

The experimental setup used to study the PL is shown in Fig. 1. We used the third harmonic output from an active–passive mode-locked Nd:YAG laser as the pump-
Fig. 1. Schematic experimental setup of the PL measurements. F, Filter; L, Converging Lens.

The laser has an average energy output of 8 mJ/pulse with a pulse width of 35 ps; the repetition rate was 10 Hz. After passing through the filter, which eliminates the fundamental and second harmonic frequencies emerging from the laser, the 355 nm laser beam was focused using a biconvex lens onto the sample. The PL signal could be measured in either a transmission or reflection geometry. We chose to measure in the reflection mode to avoid the influence of the substrate. Some substrates we used were opaque or strongly absorbing at 385 nm, the ZnO lasing wavelength. The PL signal was collected by another converging lens, with a large solid angle acceptance, and was coupled into the spectrometer through an optical fiber bundle.

3. Results and discussion

At different levels of the pumping, it was observed that the PL spectrum changes significantly. When pumped over some threshold, lasing lines appear which are seen as sharp peaks over the broad PL background [14]. At higher pumping power, more than one lasing mode could be excited. The peak position and full width at half maximum (FWHM) of a 200 nm thick ZnO film on a sapphire substrate deposited with an argon pressure of 1.07 kPa and oxygen partial pressure of 107 Pa is shown in Fig. 2. The PL spectra curves (from bottom to top) arise from pumping at relative intensities of 1, 2, 4, 8, 16, 32, 64, 72, respectively. The peak associated with the highest pumping power is red-shifted to 3.163 eV and has a FWHM of 0.039 eV.

Fig. 3 shows the PL spectra of ZnO thin films deposited at different oxygen partial pressures; the four curves from top to bottom represent O\textsubscript{2} partial pressures of 40 Pa, 120 Pa, 240 Pa, and 360 Pa, respectively; the
argon partial pressure was fixed at 1.2 kPa throughout these depositions. The film thicknesses were controlled by the deposition time and were later measured using an Alpha-Step film profiler to be 298 ± 18 nm, except for the one deposited with an oxygen partial pressure of 40 Pa. Due to the extremely small oxygen partial pressure used for this particular sample, the deposition rate was much faster than for any of the other samples in the group. (The XRD measurement showed that the film contained both ZnO and metallic Zn.) The thickness of this sample was twice that of the others. Hence the strong PL signal in this particular sample is due to the combined effects of the deposition conditions and the film thickness.

From these control experiments, we find that the PL signal strongly depends on the oxygen partial pressure during growth. Consistent behaviors were observed on both sapphire and silica substrates: films grown under higher oxygen partial pressures showed lower photoluminescence at the same pumping level. It has been reported that changes in the partial pressure of any gas component induce various defects in the film [15]. It is natural to expect that more oxygen-deficiency defects will be generated in films grown at a lower oxygen pressure. It has been shown that Schottky defects are intimately involved in the generation of some of the PL emissions in ZnO [16]. Although a quantitative correlation of the oxygen partial pressure and the oxygen deficiency has not been reported, our study of the pressure dependant PL spectrum provides direct evidence of such a connection.

Ex situ processing was also used to enhance the PL response. We annealed our ZnO films (deposited on both sapphire and fused silica substrates) in air. Oxidation during the annealing changed the concentration of oxygen-deficiency defects or slightly doped with nitrogen acceptors [17]. Various recipes were tested to search for the best PL response. The best recipe found in this study was to anneal sputtered ZnO in air at 1073 K for 10 h, including a 1-h temperature ramp-up from room temperature but excluding self cooling in air back to room temperature, which took approximately 3 h.

The experimental results from the same ZnO film on sapphire, plotted in Fig. 2, show that the annealing processing increased the PL intensity by two to three orders of magnitude, as seen in Fig. 4, and hence yields a lower lasing threshold. Absorption spectra of the film are shown in Fig. 5. After annealing, a sharper absorption edge was observed. This observation is consistent with our finding that annealing narrows the lasing and...
PL peak in ZnO. The cathodoluminescence (CL) measurement shown in Fig. 6, though preliminary, indicates a strong correlation between annealing treatment and CL. The luminescence from the sample before annealing was uniform across the film and no CL was observed, as shown in Fig. 6a. In the annealed sample, some part of the film crystallized into large, approximately 10 μm crystals. These crystals showed an easily detectable CL signal, shown in Fig. 6b. However, the ZnO thin films on the fused silica substrate prepared and annealed with same recipe did not show an observable change in the PL spectrum.

It is generally accepted that the green and red emissions from ZnO (520 and 650 nm) are associated with the oxygen defects [18]. However, the correlation of UV emission from ZnO has not been confirmed. The correlation between the PL spectra and the in situ oxygen partial pressure are consistent for ZnO films on both sapphire and fused silica substrates. However, the difference in the annealing process indicates that the presence of oxygen vacancies is not the only factor affecting the PL response. Another important factor may be the different in-plane strain in the films. Sapphire has a 16.7% lattice constant mismatch with ZnO. However, (0001) oriented ZnO grows epitaxially on c-axis sapphire with a 30° in-plane rotation [19]; i.e. with the (1010) axis of ZnO parallel to the (1120) of sapphire, which represents a 1% mismatch. Studies have shown that ZnO films deposited on sapphire have much better crystallinity than those on fused silica [20]. The XRD measurement showed that the ZnO film deposited on sapphire was highly c-axis oriented with an o-rocking curve smaller than 0.15° [21]. The increase of the PL signal after annealing, observed in the films on sapphire substrates, validates this hypothesis because the heat treatment partially eliminated the strain in the films on sapphire while the same treatment had a much smaller effect for the films deposited on fused silica. Note that the intensity of the PL peak in Fig. 7 is much stronger and spectrally sharper for the film deposited on the sapphire. The pumping power used for the sample on fused silica, in the spectrum measurement shown Fig. 7, was 10 times higher than that for the sample on sapphire. This also gives direct evidence that the film with less strain has a stronger PL response and a lower lasing threshold.

4. Conclusion

In conclusion, we studied the effects of ex situ annealing and in situ control of the oxygen partial pressure during growth, on ZnO thin films using UV photoluminescence and cathodoluminescence. The correlation between these procedures, which are tied to the oxygen defect structure, and the PL response is demonstrated. Defects are not the only factor affecting the UV emission; strain also plays an important role.

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