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Ultraviolet Lasing of Sol-Gel Derived Zinc Oxide Polycrystalline Films

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1. Introduction

Zinc oxide (ZnO) is a wide band gap II-VI semiconductor having very attractive properties such as high transparency in the 0.4~2 μm optical wavelength range, high piezoelectric constant, large electro-optic coefficient and large exciton binding energy of ~60 meV at room temperature. This large exciton binding energy provides excitonic emission more efficiently even at high temperature. In recent years, the fabrication of zinc oxide-based films has attracted a considerable amount of interest due to their potential application in solar cells, gas sensor, optical waveguides, surface acoustic devices, piezoelectric transducers and varistors. In this work, we deal with structural and optical properties of sol-gel derived ZnO thin films. As a consequence, the influence of post-thermal treatments on the degree of crystalline orientation and microstructure properties will also be investigated. In the room temperature PL spectra, we have observed a strong 380 nm near-band-edge emission with accompanying deep-level emission. We also report the observation of laser emission from our polycrystalline ZnO thin films.

2. Experimental procedure

Zinc acetate-2-hydrate [$Zn(CH_3COO)_2 \cdot H_2O$] was chosen as the starting materials, and alcoholic solution were used as solvent. The details of the preparation method are similar to those described in earlier literatures. The concentration of zinc acetate was chosen to be 1 mol l^{-1}, and the precursor solution has been mixed thoroughly on a magnetic stirrer. The resultant solution was stirred at 80 ^oC for 2 hours to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating was usually made 3 days after the solution was prepared. Both x-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements were carried out for structural and morphological characterization. A He-Cd laser with a wavelength 325 nm was used for as the excitation source for photoluminescence (PL) measurement and a photomultiplier tube was used to detect emission from samples. For high excitation measurements we used a pulse-type diode pump solid state (DPSS) system operated at 355 nm output.

Fig. 1 shows X-ray diffraction patterns for ZnO/Si(100) films formed by a six-cycle spin-coating of zinc acetate films followed by various post-thermal treatments. It is obvious that only the (002) peak was observed in XRD patterns, indicates that all the ZnO films prepared by sol-gel method have preferential orientation along (002) plane under suitable thermal treatment. Shown in Fig. 1(e) is the XRD pattern of ZnO film annealed at 750 ^oC with a heating rate of 10 ^oC/min. The spectrum of Fig. 1(e) reveals well defined diffraction peaks with with hexagonal wurtzite type, and the crystallites are randomly orientated.

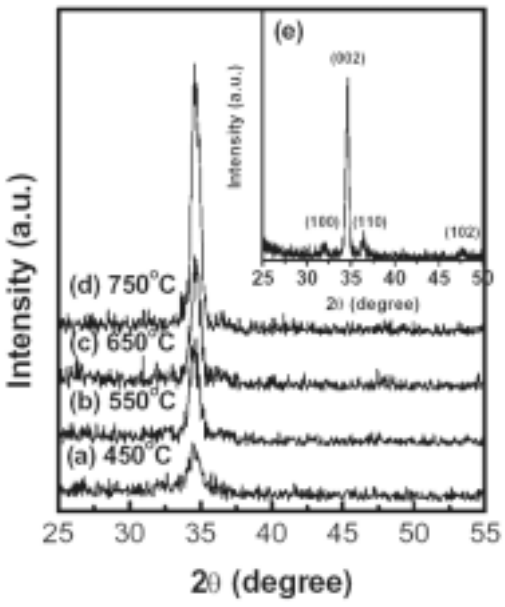

Fig. 1 XRD patterns of ZnO films annealed under different thermal treatments. Typical diffraction pattern of random-oriented ZnO film, annealed at higher heating rate, is shown in figure 1(e).

Fig. 2 shows the PL spectra of ZnO films heated at different temperatures are displayed. We can observe that the PL peak intensity increase with increasing the annealing temperature from 650 ^oC to 950 ^oC. An evident ultraviolet (UV) emission peak is observed near 380 nm from the ZnO films deposited at 950 ^oC. The film deposited at 950 ^oC shows the strongest peak. In addition, the intensities of the UV emission can be used as a standard for the crystalline and stoichiometric quality of the ZnO semiconductor films.

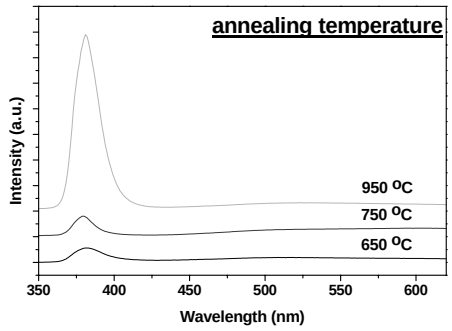

Fig. 2 PL spectra of ZnO films annealed at different temperature.

Fig. 3 shows the SEM images of ZnO thin films annealed at various temperatures. The surface morphologies of the ZnO films change greatly with an increase in annealing temperature. At the lowest annealing temperature of 450 ^{o}C, the film contains fine grains and the grains agglomerate together so that grain boundaries cannot be distinguished easily. For films annealed at higher temperatures, the grain boundaries can be distinguished clearly. It is clear that the grain size increased with increased annealing temperature.

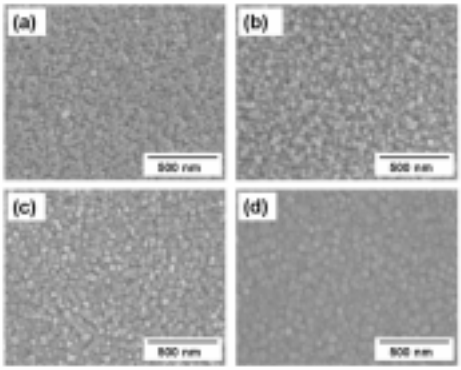

Fig. 3 SEM images of ZnO films annealed at (a) 450 ^{o}C , (b) 550 ^{o}C, (c) 650 ^{o}C and (d) 750 ^{o}C. The grain sizes become larger and denser with increasing annealing temperatures.

We have also performed optical pumped-lasing experiments at room temperature. The beam from the earlier mentioned DPSS system was focused to a spot on the surface of a 950 °C annealed film at normal incidence. At low pumping intensity, we observed a single broad spontaneous-emission peak. As the pumping intensity was increased, the peak became sharper. When the excitation intensity exceeded a threshold, the emission spectra consisted of a large number of narrow peaks, as shown in Fig. 4, indicating the onset of laser action in our polycrystalline films. The threshold intensity (I_{th}) for the lasing was ~100KW/cm^2, determined from superlinear behavior on optical power versus luminescence intensity.[5]

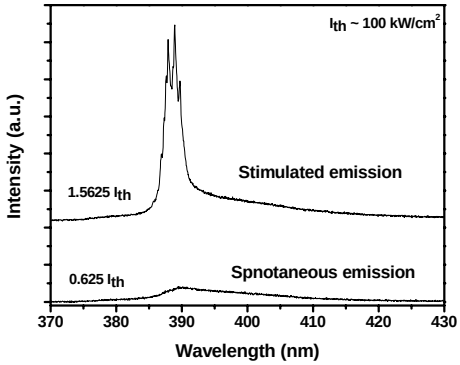

Fig. 4. Spontaneous and stimulated emission spectra under pumping intensities of 0.625I_{th} and 1.5625I_{th}.

3. Conclusions

Highly c-axis oriented ZnO thin films were prepared on glass and Si substrates by the well-established sol-gel technique under suitable thermal treatment. The impacts of the heat-treatment condition on the structural optical properties of the films were studied in detail. Furthermore, we have observed good luminescent properties with this simple method. PL spectra showed a strong single peak around 380 nm at room temperature, corresponding to the ZnO free exciton emission. We have also observed optical pumped lasing action in our ZnO polycrystalline films. The threshold intensity for the lasing was 100 KW/cm^2. These results indicate that polycrystalline ZnO thin films prepared by sol-gel technique may be a promising material for further photonic devices.

References

[1] C. Guille´n, J. Herrero, Thin Solid Films **480–481** (2005) 129.
[2] M. Emziane, K. Durose, N. Romeo, A. Bosio, D. P. Halliday, Thin Solid Films **480-481** (2005) 377.
[3] Das, Rajesh; Jan, Tapati; Ray, Swati, Sol. Energy Mat. Sol. Cells **86** (2005) 207.
[4] P. B. Kirby; M.D.G. Potter, C.P. Williams, M.Y. Lim, J. Europ. Ceram. Soc. **23** (2003) 2689.
[5] X. Q. Zhang, I. Suemune, H. Kumano, J. Wang and S. H. Huang, J. Appl. Phys. **96** (2004) 3733.