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Lasing action of high quality ZnO thin film deposited by radio-frequency magnetron sputtering*

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ZnO thin films are deposited on SiO_2 substrates by radio-frequency magnetron sputtering. The A and B excitons are observed from the absorption spectra at room temperature. The A, B and C excitons are observed from the reflectance spectra at 19K. These results indicate that the obtained ZnO films have a good wurtzite structure. We obtain the stimulated emission resulting from electron-hole plasma. The laser spectrum is observed, which consists of a large number of narrow peaks with an around 0.5nm spacing in between, corresponding to a self-formed cavity length of around 31.5μm. The self-formation of laser cavity in the ZnO thin film is closely related to its hexagon structure.

Keywords: ZnO thin films, stimulated emission, absorption
PACC: 7135, 7845, 4255

1. Introduction

In the last decade, much attention has been paid to wide band-gap semiconductor materials because short-wavelength optical devices are highly desired for applications in future optoelectronic technical industries. Compared with other wide band-gap materials that have been studied very extensively before, ZnO has some advantages such as large excitonic binding energy of 60meV, stable chemical property, large excitonic laser gain, low optical loss and low power threshold for optically pumped lasing action at room temperature and so on.[1−3] Owing to its unique properties, ZnO has become an attractive candidate for ultraviolet laser diodes, ultraviolet-blue light emitting diodes, piezoelectric transducers, window material for flat-panel displays, and more efficient solar cells.

Several groups have already done much research on ZnO-based materials by use of various film-growth technologies such as metal organic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE), chemical vapour deposition (CVD), pulsed laser deposition (PLD), atomic layer deposition (ALD) and radio-frequency (RF) sputtering. Stimulated emission and optically pumped lasing action in ZnO epitaxial films were observed.[4−6] The structural characterization, excitonic optical properties of the ZnO thin films and epitaxial layers were reported.[7−11]

According to the previous reports about lasing action of ZnO films, the random laser was believed to be due to scattering in highly disordered gain media,[10,11] while the formation of the resonant cavity laser was attributed to resonance in natural cavity or self-formed cavity. However, how the self-formed laser cavity formes in the ZnO film has not reached a recognizable conclusion so far. In order to understand it, we deposit ZnO films on SiO_2 substrates by RF-magnetron sputtering and study their lasing characteristics at room temperature. And finally we come to a conclusion that the self-formation of laser cavity is closely related to the hexagon structure of the ZnO.

2. Experiment

The ZnO films used in this study were deposited on SiO_2 substrates by RF-magnetron sputtering in an Ar and O_2 mixed gas discharge. The ratio of Ar

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to O_2 was about 7:2 with a total gas pressure being 0.4Pa. The substrate temperature was about 230°C. To achieve better crystal structure and higher quality, the annealing of the as-deposited films was performed. The annealing lasted 1.5h at a temperature of 550°C. X-ray diffraction measurement revealed that the ZnO thin films had high crystallinity with c-axis orientation and high quality. The detailed description of structural characterization can be found elsewhere.[12]

Stimulated emission and lasing action were obtained in the edge emission geometry. The sample was pumped by the frequency-tripled output of a Q-switched, Nd:YAG laser with a pulse duration of 4.5ns and a repetition rate of 10Hz at a wavelength of 355nm. The excitation power was controlled by a neutral density filter. The excited laser beam was focused on the sample surface by a cylindrical lens to form an excitation stripe. This edge emission was then focused into a monochromator. In stimulated emission spectra, the signal was detected by a photomultiplier tube, amplified by a BOXCAR and then recorded by a computer. In laser spectra, the sample was pumped by single pulse, which was a way different from that in the previous work where a multi-pulse was used.[8,9] The laser signal was detected by an intensified charge-coupled device (ICCD) and then recorded by a computer.

3. Results and discussion

The wurtzite crystal with three valence bands allows three exciton transitions to be labelled as "A", "B", and "C" which correspond to transitions from the s-like (Γ_{7c}) conduction band to the three p-like ($\Gamma_{7\nu}^{u}$, $\Gamma_{9\nu}$ and $\Gamma_{7\nu}^{l}$) valence bands.[13,14] In order to illustrate the existence of excitons in our ZnO thin film, absorption and reflectance spectra were measured respectively at room temperature and low temperatures. Figure 1 shows the absorption spectrum of ZnO thin film at room temperature. A steep absorption edge can be seen in the absorption spectrum. Two distinct absorption peaks labelled by A and B are observed respectively at 374nm and 368nm in the near band-edge. The origins of the two peaks are attributed to the A and B excitons.[4,15] The well-resolved A and B excitons observed from the absorption spectra at room temperature indicate that the ZnO thin films have high quality, a low density of defects and little strain.

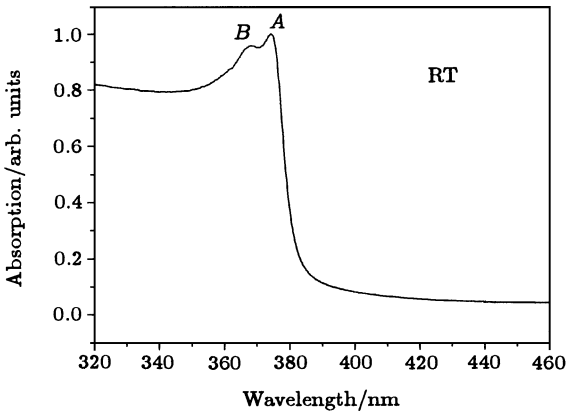


Fig.1. Absorption spectrum of ZnO thin film at room temperature.

Figure 2 shows the reflectance spectrum of ZnO thin film measured at 19K. The A, B, and C excitons are clearly observed. In the case of ZnO, the selection rule for optical transitions is that the A and B transitions are allowed for light polarization perpendicular to the c axis, while the C transition is essentially allowed for polarization parallel to the c axis. Since the incident light is unpolarized and the sample is c-axis oriented, the intensity of the C exciton is far lower than that of the A as well as B exciton. In the absorption spectrum, the C exciton is not observed at room temperature. We consider that this might come from two reasons: the temperature is so high that thermal effect makes the C exciton disappear; the small but finite incident angle in our experimental configuration prevents the C exciton from appearing. Excitons provide a sensitive indicator for material quality and crystal structure. The more perfect the crystal is, the more possible the observation of exciton will be. The A, B, C excitons observed from the reflectance spectra indicate that the ZnO thin films have an excellent wurtzite crystal structure.

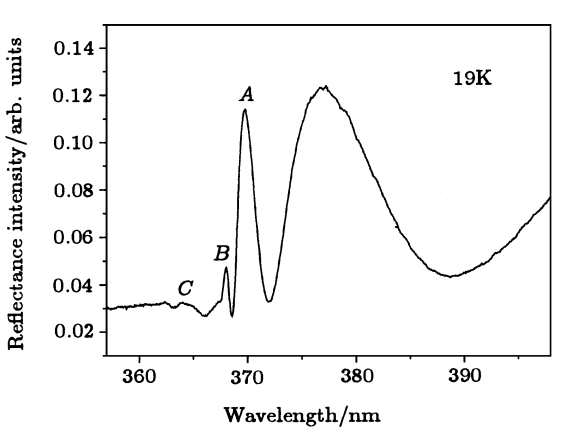


Fig.2. Reflectance spectrum of ZnO thin film at 19K.

Stimulated emission spectra of the ZnO thin film, measured at room temperature under various excitation densities, are shown in Fig.3, in which a peak labelled by FE appears at 381nm at a lower excitation intensity of 528kW·cm^{-2}. Compared with the absorption spectrum, the peak is mainly due to a radiative recombination of free excitons (FE) at room temperature. As the excitation intensity increases, the FE peak gradually reduces in its relative intensity. Meanwhile, a narrow peak as a mark of electron-hole plasma (EHP) emerges on the lower energy side of the FE peak and gradually dominates in the emission spectra. The EHP peak shifts towards lower energies and is broadened as the excitation intensity increases. The EHP peak will be reasonably attributed to the EHP radiative recombination and the relevant band-gap renormalization effect in the EHP regime.

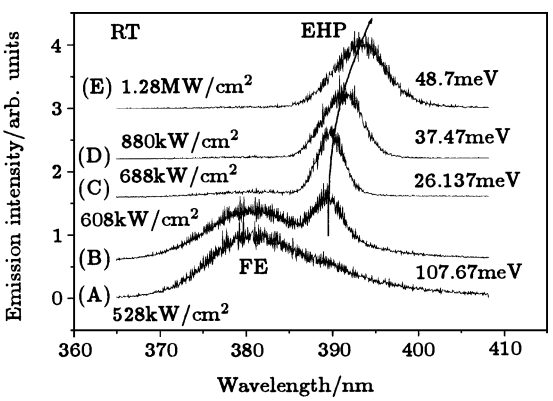


Fig.3. Stimulated emission spectra of ZnO thin film under various excitation intensities at room temperature.

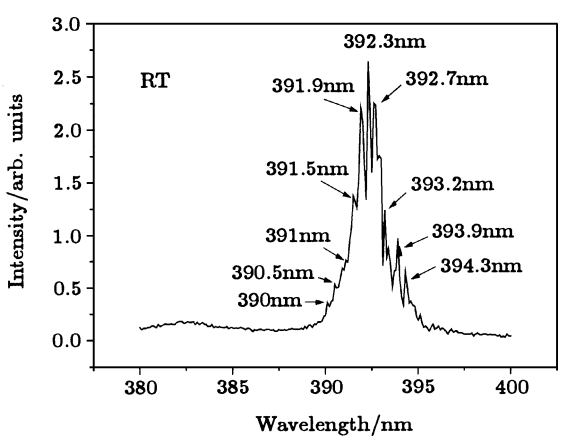


Fig.4. Laser spectrum of ZnO thin film at room temperature. The spacing between the narrow peaks is around 0.5nm.

We study lasing action in ZnO thin film in the absence of any fabricated mirror at room temperature. Figure 4 shows longitudinal cavity modes at room temperature. As the excitation intensity exceeds a level (laser threshold), we can see the laser spectrum consisting of a large number of narrow peaks. The spacings between these narrow peaks are almost the same, being a value of around 0.5 nm. These indicate the lasing action occurring in our ZnO thin film. The lasing action obtained may be attributed to self-formed cavity. According to the equation

$$L = \frac{\lambda_0^2}{2\Delta\lambda[n - (\mathrm{d}n/\mathrm{d}\lambda)\lambda_0]}, \qquad (1)$$

the mode spacing of 0.5nm corresponds to a cavity length of 31.5μm, which is different from the cavity length of 70μm reported by Bagnall *et al.*[16] Therefore we conclude that self-formation of laser cavity should be closely related to the hexagon structure of ZnO. The facets belonging to different hexagon ZnO grain boundaries might serve as cavity mirrors and generate the resonant cavity.

4. Conclusion

ZnO thin films have been deposited on SiO_2 substrates by RF-magnetron sputtering. The A and B excitons from the absorption spectra at room temperature and the A, the B and the C exciton from the reflectance spectra at 19 K have been clearly observed. These results indicate that ZnO thin films have a good wurtzite crystal structure. The stimulated emission which results from the electron-hole plasma, has been measured at room temperature under various excitation intensities. The emission peak red-shifting and linewidth broadening augment as the excitation intensity increases. We have observed laser spectra consisting of a large number of narrow peaks. The spacing between these narrow peaks is around 0.5nm corresponding to the self-formed cavity length of around 31.5μm. We conclude that the self-formation of laser cavity is closely related to the hexagon structure of ZnO thin film.

References

[1] Zhang X Q, Tang Z K, Kawasaki M, Ohtomo A and Koinuma H 2003 *J. Cryst. Growth* **259** 286

[2] Zhang X Q, Tang Z K, Kawasaki M, Ohtomo A and Koinuma H 2003 *J. Phys.: Condens. Matter* **15** 5191

[3] Zhang X Q, Tang Z K, Kawasaki M, Ohtomo A and Koinuma H 2004 *Thin Solid Films* **450** 320

[4] Zhang X Q, Suemune Ikuo, Kumano H, Wang J and Huang S H 2004 *J. Appl. Phys.* **96** 3733
[5] Bagnall D M, Chen Y F, Zhu Z, Yao T, Koyama S, Shen M Y and Goto T 1997 *Appl. Phys. Lett.* **70** 2230
[6] Zu P, Tang Z K, Wong G K L, Kawasaki M, Ohtomo A, Koinuma H and Segawa Y 1997 *Solid State Commun.* **103** 459
[7] Muth J F, Kolbas R M, Sharma A K, Oktyabrsky S and Narayan J 1999 *J. Appl. Phys.* **85** 7884
[8] Tang Z K, Wong G K L, Yu P, Kawasaki M, Ohtomo A, Koinuma H and Segawa Y, 1998 *Appl. Phys. Lett.* **72** 3270
[9] Bagnall D M, Chen Y F, Zhu Z, Yao T, Shen M Y and Goto T 1998 *Appl. Phys. Lett.* **73** 1038
[10] Cao H, Zhao Y G, Ong H C, Ho S T, Dai J Y, Wu J Y and Chang R P H 1998 *Appl. Phys. Lett.* **73** 3656
[11] Cao H, Zhao Y G, Ho S T, Seelig E W, Wang Q H and Chang R P H 1999 *Phys. Rev. Lett.* **82** 2278
[12] Xiong D P and Zhang X Q 2004 *Chin Opt. Lett.* **2** 179
[13] Thomas D G 1960 *J. Phys. Chem. Solids* **15** 86
[14] Hopfield J J 1960 *J. Phys. Chem. Solids* **15** 97
[15] Srikant V and Clarke D R 1997 *J. Appl. Phys.* **81** 6357
[16] Bagnall D M, Chen Y F, Shen M Y, Zhu Z, Goto T and Yao T 1998 *J. Cryst. Growth* **184/185** 605