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2002 Chinese Phys. Lett. 19 127

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CHIN.PHYS.LETT. Vol. 19, No. 1 (2002) 127

Photoluminescence and Optically Pumped Ultraviolet Lasing from Nanocrystalline ZnO Thin Films Prepared by Thermal Oxidation of High-Quality ZnS Thin Films *

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(Received 3 July 2001)

We present a simple and useful method for preparing high-quality nanocrystalline ZnO thin films, i.e. the thermal oxidation of high-quality ZnS films prepared by the low-pressure metal–organic chemical vapour deposition technique. The x-ray diffraction measurements reveal that the nanocrystalline ZnO has a hexagonal wurtzite structure. Raman spectra show that the longitudinal optical phonon with the E_1-mode appears at 578 cm^{-1}. The multiple phonon scattering process is also observed, indicating the formation of a high-quality nanocrystalline ZnO thin film. The photoluminescence spectrum has a single emission peak at 3.264 eV from the free-exciton mission, under the condition of low excitation power at room temperature. However, when excitation intensities exceed the threshold of 150 kW/cm^2, a new and narrow peak emerges at lower energies, which are attributed to exciton–exciton collisions, and is called the P line. The intensity of this peak increases superlinearly with the pumping power over a threshold value. This supplies strong evidence of stimulated emission. The multiple longitudinal cavity modes observed in the stimulated emission spectrum indicate the successful realization of optically pumped lasing from nanocrystalline ZnO films at room temperature.

PACS: 78. 55. Et, 48. 55. Sa, 79. 60. Jv, 78. 30. Fs

As a wide bandgap (E_g = 3.37 eV) semiconductor, ZnO has attracted considerable attention due to its potential applications,[1] such as ultraviolet light-emitting devices and laser devices. Compared to other wide bandgap materials, ZnO has a larger exciton binding energy (60 meV),[2] which ensures more efficient exciton emissions at room temperature. In fact, ultraviolet (UV) stimulated emission and lasing have been observed in bulk ZnO crystals at cryogenic temperatures.[3–6] However, a rapid quenching of emission intensity with increasing temperature prevented a demonstration of room-temperature stimulated emission until recently, when the UV lasing from ZnO films was observed.[7] Meanwhile, innovative techniques have allowed the growth of high-quality ZnO films and the observation of stimulated emission[8] and lasing[9] from ZnO films at room temperature.

In recent years, there have been many reports on UV stimulated emission and lasing.[8–16] There are three interesting findings concerning this phenomenon. Firstly, under a moderate pumping intensity, the stimulated emission process was caused by exciton–exciton collisions even at room temperature (RT) because of the very large exciton binding energy (60 meV).[2] Secondly, the threshold of this excitonic process was very low when the nanocrystalline size in ZnO films was controlled at about 50 nm. Lastly, a longitudinal cavity was automatically formed by the grain boundaries between hexagonal nanocrystals acting as mirrors. In other words, the hexagonal facets of nanocrystallites formed natural Fabry–Pérot lasing cavities. Hence, for the lasing of ZnO films, it is necessary to prepare high-quality ZnO films with a nanocrystalline size less than 50 nm with a low pumping intensity.

In this letter, we present a simple and useful method for preparing high-quality ZnO thin films with an intense UV luminescence and report RT optically pumped lasing from nanocrystalline ZnO films prepared by the thermal oxidation of ZnS films grown by the low-pressure metal–organic chemical vapour deposition (LP-MOCVD) technique.

The ZnO films used in this study were prepared by thermal oxidation of high-quality ZnS films grown on quartz glass substrates using dimethyl zinc (DMZn) and hydrogen sulphide (H_2S) by the LP-MOCVD technique. The flow rates of DMZn and H_2S were fixed at 28.65×10^{-6} mol/min and 4.00×10^{-4} mol/min, respectively. Hydrogen (H_2) was used as the carrier gas to transport the reactant, and the total flow rate was kept at 1.3 LMP/min. The pressure of the

*Supported by the Hundred Talents Programme of the Chinese Academy of Sciences, the National Fundamental Applied Research Project, the Key Project of the National Natural Science Foundation of China under Grant No. 69896260, the Innovation Foundation of CIOFP, Excellent Young Teacher Foundation of Ministry of Education of China, and Jilin Distinguished Young Scholar Programme.

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growth chamber was 300 Torr. The films were deposited on quartz glass substrates which were maintained at 320°C. The thickness of the deposited ZnS thin films was about 500 nm. After deposition, thermal oxidation of the films was carried out in an oxygen ambient at 900°C for 2 h. In order to characterize the film structure, x-ray diffraction (XRD) and atomic force microscopy (AFM) studies were performed. Micro-Raman spectral experiments were carried out in a backscattering geometry configuration using a He–Cd laser as an excitation resource. The optically pumped lasing experiments were performed using the laser output (320 nm, 200 fs) of optical parametric amplifier (OPA) in an active passive mode-locked femtosecond Ti:sapphire laser operated at a repetition rate of 1000 Hz. The output of laser was focused onto the sample surface with normal incidence by using a cylindrical lens to form a rectangular stripe of $300 \times 800\,\mu m^2$. When the excitation stripe was moved, a speckled light was observed in high-intensity regions. This emission from the edge of the sample was then focused into a monochromator with 0.5 m focal length allowing detection by a CCD camera with the choice of high resolution or wide spectral range.

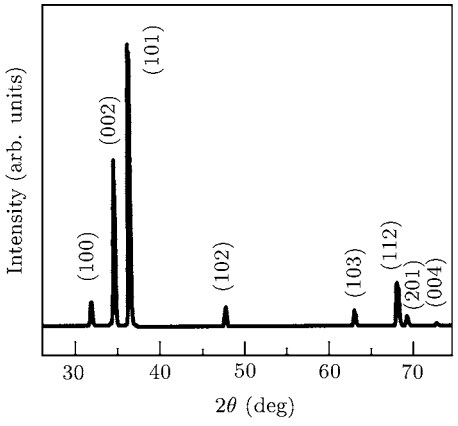


Fig. 1. XRD pattern of ZnS thin films annealed at 900°C.

The ZnO film structure annealed at 900°C was examined by $\theta - 2\theta$ XRD measurements. Three pronounced peaks (100), (002) and (101) appear at $2\theta = 31.91°$, 34.66° and 36.35°, respectively, as shown in Fig. 1. The lattice constants calculated from the XRD pattern are $a = 3.235$ Å, $c = 5.170$ Å, and were very close to those of wurtzite ZnO, i.e. $a = 3.249$ Å, $c = 5.205$ Å.[17] This result indicates that ZnO has a polycrystalline hexagonal wurtzite structure. In order to evaluate the average grain size of the films, the Scherrer equation[18] was adopted. The average grain size of all the films annealed at 900°C was about 38 nm. Polycrystalline dimensions determined by AFM were consistent with the XRD results, indicating that high-quality nanocrystalline ZnO thin films have been obtained.

Figure 2 shows a typical Raman spectrum of a sample annealed at 900°C. The Raman spectrum consists of five sharp lines at frequency shifts which were multiples of the 1-LO (mode E_1) zone-centre frequency of 578 cm^{-1}. This result indicates a resonant Raman scattering of the ZnO E_1-LO phonon. The number of multiple phonon scattering processes observed in a semiconductor varies monotonically with the polaron coupling coefficient.[19] ZnO crystalline material has a large polaron coupling coefficient and large phonon frequency. Therefore, enormous frequency shifts are observed. Just as n-(LO) can be compared with the polaron coefficient α, the maximum frequency shift n-(LO)$\times\omega_{LO}$ can be compared with the deformation energy, which is equal to $\alpha\hbar\omega_{LO}/2$. Hence, the large 5-LO Raman shift indicates that ZnO has a large deformation energy. To our knowledge, multiple phonon scattering processes have previously been observed in a ZnO bulk crystallline material.[20] For ZnO thin films, multiple phonon resonant Raman scattering has not yet been reported in the literature. Intense 2-LO scattering was observed in all the samples annealed at different temperatures, indicating a resonant enhancement effect.[21,22] The intensity of n-LO ($n > 2$) scattering was also enhanced by the same factor, which is in agreement with the theory of multi-LO Raman scattering.[23]

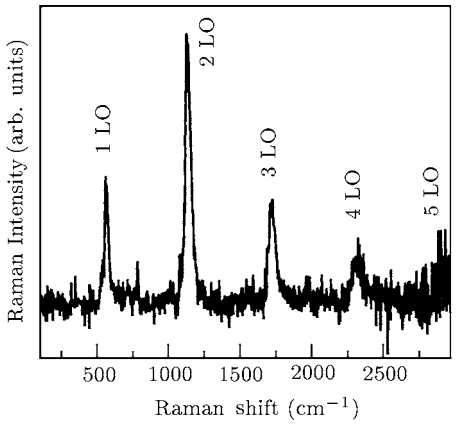


Fig. 2. Representative Raman spectrum of ZnS thin films annealed at 900°C.

II–VI semiconductors have larger polarization than III–V, which will cause stronger exciton–phonon coupling correlated with the deformation potential (LO and TO phonons). The ratio of the FrÖhlich (F) interaction to the deformation potential (DP) interaction in II–VI semiconductors is larger than in III–V semiconductors, i.e. [F/DP(II–VI)>F/DP(III–V)].[24,25] In our experiment, multi-phonon processes might result from the strong Fröhlich interaction and large deformation energy.[26]

For comparison to photoluminescence (PL) line shapes, Fig. 3(a) shows the normalized RT emission spectra from the edge of the nanocrystalline ZnO films at below, near and above the threshold $I_{th} = 150\,kW/cm^2$. As a reference, Fig. 3(b) shows the lu-

minescence spectrum excited by the 325 nm line of a He–Cd laser in a backscattering configuration. An intense free-exciton emission ($E_{\rm ex}$) is seen at around 3.264 eV, however the light emissions related to deep-level defects are barely observed.

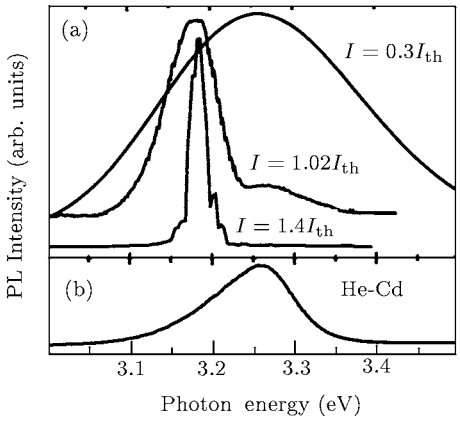


Fig. 3. NBE PL spectra of ZnS thin films annealed at 900°C. (a) NBE PL spectra at below, near and above threshold, $I = 150\,{\rm kW/cm^2}$, excited by using the laser output (320 nm, pulse width 200 fs) of the OPA in an active passive mode-locked femtosecond Ti:sapphire laser operated at a repetition rate of 1000 Hz. (b) PL spectrum excited by a 325 nm line of a He–Cd laser.

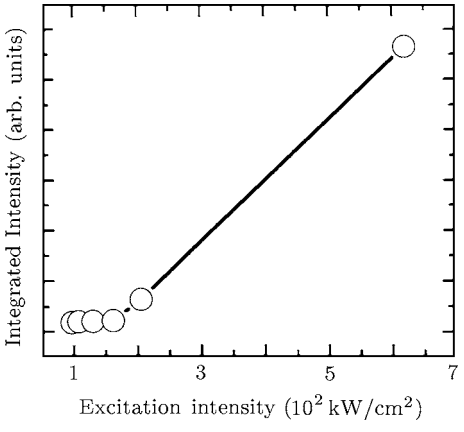


Fig. 4. NBE PL integrated intensity of ZnS thin films annealed at 900°C as a function of the excitation intensity.

At low pumping intensities, i.e. $I = 0.3I_{\rm th}$, a broad emission band is observed at around 3.264 eV with a full width at half maximum (FWHM) of 243 meV. This is the near band edge (NBE) emission. As expected for spontaneous emission, the intensity of this emission band increases linearly with the increase of the pumping intensity below $I_{\rm th} = 150\,{\rm kW/cm^2}$, as shown in Fig. 3(a). When the ZnO film is pumped at an intensity near the threshold $I_{\rm th}$, $I = 1.02I_{\rm th}$, a new and narrow emission peak p emerges directly from the low-energy shoulder of the broad spontaneous spectrum at around 3.178 eV. At this point emission, the intensity of the P band increases superlinearly with pumping intensity with an unchanged peak position. When the ZnO thin films are excited at $I = 1.4I_{\rm th}$, there is a super-intense emission peak in the spectrum with an FWHM of 21 meV, in contrast to the linear increase in the free-exciton emission intensity. Figure 4 shows the dependence of UV emission integrated intensity on excitation intensity at room temperature. The linewidth narrowing from 243 meV to 21 meV, the superlinear increase of the p band intensity as well as the total suppression of the broad spontaneous emission background indicate that stimulated emissions have occurred.[17]

Compared to previous reports on stimulated emissions from ZnO films at RT, the position of our sharp emission peak is found to be in agreement with that expected from an inelastic collision between excitons,[4,8] in which one of the two excitons obtains energy from the other and scatters into a higher exciton state with a quantum number $n = 2$, while the other recombines radiatively. The photons emitted in this process have the energies of P_n given by[4]

$$P_n = E_{\rm ex} - E_b^{\rm ex}(1 - \frac{1}{n^2}) - \frac{3kT}{2} \quad (n = 2, 3, 4, \cdots, \infty), \qquad (1)$$

where P_n is the emitted photon energy, $E_{\rm ex}$ is the free-exciton emission energy, $E_b^{\rm ex}$ is the binding energy of the exciton, n is the quantum number of the envelope function, and kT is the thermal energy. At RT, Eq. (1) gives 84 meV as the energy difference between the free-exciton peak and the exciton–exciton peak. In our experiment, the position of the stimulated emission peak at 3.178 eV is about 86 meV below the free-exciton emission. This calculated value is in good agreement with our experimental result. Because the peak position of the P band is independent of the pumping intensity, we believe that it also has an excitonic origin.[13]

However, it should be noted that the equally-spaced sharp lines of the stimulated emission spectrum are attributed to the multiple longitudinal modes of an optical cavity having a cavity length equal to the entire excitation stripe,[16] indicating the onset of laser action in our nanocrystalline ZnO thin films. The line spacing is calculated for a Fabry–Pérot resonant cavity with length L, using equation $\Delta E = (\pi ch/L)(n + E{\rm d}n/{\rm d}E)^{-1}$, where $E({\rm d}n/{\rm d}E)$ is the variation of the refractive index n with photon energy E. The data of the refractive index $n(E)$ are obtained from Ref. [26]. The good agreement between the calculated values and the measured line spacing between the cavity modes strongly proves that. The natural optical cavity was formed by the microcrystalline facets in the sample.

RT optically pumped lasing of nanocrystalline ZnO is observed in our experiment. The mean grain size of our films is about 38 nm. When the microcrystalline size is much larger than the excitonic Bohr ra-

dius but smaller than the excitonic coherence length, an excitonic wavefunction can coherently extend over the microcrystal. This can lead to a large enhancement in the exciton oscillator strength.[13] The ZnO microcrystals in our films are spheres with a diameter $d = 38$ nm, from the result determined by AFM (not shown). The enhancement factor of the oscillator strength f is expected to be $f/f_{\rm ex} = d^3/\pi^2\alpha_{\rm B}^3 \approx 2 \times 10^3$, where $f_{\rm ex}$ is the exciton oscillator strength in bulk crystal and $\alpha_{\rm B}$ is the exciton Bohr radius ($\alpha_B = 1.8\,$nm). This huge enhancement of oscillator strength may be responsible for the stronger RT optically pumped lasing observed in our samples.

In summary, we have observed lasing and Raman multi-phonon scattering processes in nanocrystalline ZnO films. These results show the effectiveness of the thermal oxidation method in preparing ZnO films. The mechanism of laser emission is believed to be exciton–exciton scattering at moderate excitation intensities. It is expected that devices with much lower thresholds can be produced by further optimizing annealing conditions, and improving growth technique conditions.

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