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High-Temperature Lasing Characteristics of ZnO Epilayers**

By Hong Dong Li, Siu Fung Yu,* Shu Ping Lau, Eunice S. P. Leong, Hui Ying Yang, Tu Pei Chen, Agus Putu Abiyasa, and Chi Yung Ng

ZnO thin films deposited on sapphire, silicon, and fused silica substrates have demonstrated UV excitonic lasing at room temperature (RT) under optical excitation.^[1–5] Because of the large binding energy (~60 meV) of ZnO, it is also expected that the ZnO films can sustain excitonic lasing at high temperature. Recent studies of ZnO epilayers have observed spontaneous emission from free-exciton (FE) radiative recombination as well as stimulated emission from exciton–exciton scattering (EES) and electron–hole-plasma (EHP) radiative recombination at temperatures up to ~550 K.^[2] ZnO nano-sheets can also sustain photoluminescence (PL) at ~870 K.^[6] These studies have suggested the potential of using ZnO to fabricate high-temperature UV excitonic lasers. However, investigations on the temperature dependence of stimulated excitonic emission from ZnO films and ZnO/ZnMgO superlattices have shown that the corresponding characteristic temperature, which reflects the quality of the high-temperature performance of the lasers, is less than 90 K in a narrow range of temperature between 294 and 377 K.^[7] In order to obtain high-quality excitonic lasing at high temperature, it is necessary to improve the characteristic temperature of the ZnO lasers. In this communication, strained ZnO epilayers with nanostructures are proposed to sustain coherent random lasing at high temperature. It is found that the ZnO epilayers can achieve lasing up to 570 K, and the corresponding characteristic temperature can be as high as 127 K. This is because i) the formation of ZnO nanostructures prevents the spreading of excited carriers over the pumped region and ii) the closed-loop path of light by random laser action allows the size variation of random cavities. Therefore, lasing can be obtained from the ZnO epilayers at high temperature.

Two ZnO epilayers, sample A (ZnO(100 nm)/SiO₂(400 nm)/Si (substrate)) and sample B (ZnO(100 nm)/MgO(200 nm)/ZnO(100 nm)/SiO₂(400 nm)/Si (substrate)), were fabricated by the filtered cathodic vacuum arc technique and thermal annealing.^[4,5] It is shown that the top (002)-ori-

ented ZnO active layer of sample A (sample B) experiences tensile (compressive) strain along the *c*-axis.^[5] Figure 1 shows the lasing spectra versus temperature, *T*, for the two samples under optical excitation at ~2 × *I*_{th}, where *I*_{th} is the pump

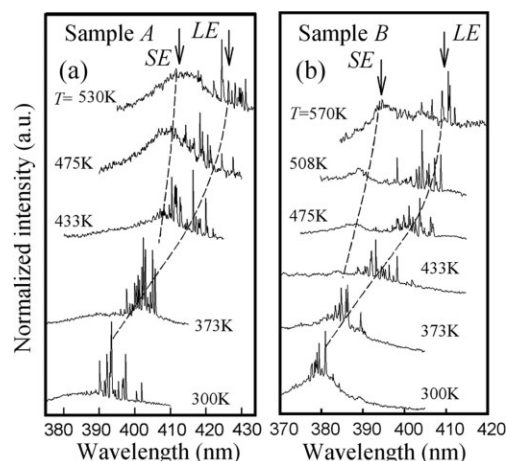


Figure 1. Lasing spectra for a) sample A and b) sample B at different temperatures, *T*, taken under the excitation intensity of 2 × *I*_{th}, where *I*_{th} is the pump threshold intensity at *T*. ‘LE’ and ‘SE’ refer to lasing and spontaneous emission, respectively.

ent threshold intensity at the corresponding *T*. It can be shown that sample A (sample B) demonstrates RT EHP (FE) radiative recombination with discrete peaks at ~393 nm (~380 nm), and the corresponding lasing mechanism is attributed to random laser action.^[5] With the increase of temperature, the shrinkage of the bandgap red-shifts the lasing peaks. Furthermore, it is observed that the full width at half maximum of the lasing peaks for both samples remains less than 0.4 nm for *T* up to 570 K. Hence, it is shown that coherent random lasing, which arises from the formation of closed-loop paths of light,^[8] can be sustained inside the annealed ZnO epilayers with nanostructures at high *T*.

Figure 2 plots the peak energy of lasing and spontaneous emission (LE and SE, respectively) versus *T* for both samples. The data^[2] for temperature-dependent stimulated emission of the ZnO film deposited on sapphire is also plotted in Figure 2 for comparison. It is observed that the LE of sample A (▲) is red-shifted with *T* at a rate of –1.03 meV K^{–1} for the whole range of *T* and coincides with that of the EHP emission (○) observed from the ZnO/sapphire film. Hence, it is shown that EHP lasing is sustained in sample A at high *T*. On the other

[*] Prof. S. F. Yu, Dr. H. D. Li, Prof. S. P. Lau, E. S. P. Leong, H. Y. Yang, Prof. T. P. Chen, A. P. Abiyasa, C. Y. Ng
School of Electrical & Electronic Engineering
Nanyang Technological University
Block S2, Nanyang Avenue, Singapore 639798 (Singapore)
E-mail: esfy@ntu.edu.sg

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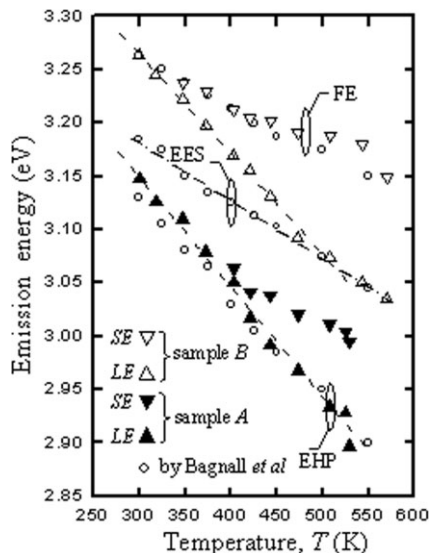


Figure 2. Energy positions of LE and SE as a function of T for samples A and B. The dashed lines represent linear fits of the experimental data. The data from Bagnall et al. [2] is also plotted for comparison.

hand, the LE of sample B (Δ) is red-shifted at a rate of -0.94 meV K^{-1} for T varying between 300 and 510 K. However, the slope of the LE increases to -0.53 meV K^{-1} for T larger than 510 K. When comparing with the FE and EES emissions of the ZnO/sapphire film, it is noted that LE overlaps with FE (EES) emission for $T < 320 \text{ K}$ ($> 500 \text{ K}$). This implies that sample B underwent a transition from FE to EES lasing on increasing T from 320 to 500 K. This is because the probability of collision (scattering) between excitons is proportional to $T^{1/2}$, and therefore the amount of transition from FE to EES radiative recombination is also increased with T . Hence, the corresponding recombination process for T varying between 320 and 510 K is a mixture of FE and EES radiative recombination. The transition from FE to EHP lasing, however, has not been observed from sample B. This is because the density of excitons is less than the Mott density at $T < 570 \text{ K}$ (i.e., although the density of excitons is increased with T , the corresponding Mott density is also increased^[9]). Figure 3 plots the high- T emission spectra of samples A and B versus excitation intensity. As the center lasing wavelength of sample A is red-shifted with the increase of optical excitation, EHP emission should be the dominant process. However, the lasing wavelength of sample B remains unchanged with the increase of excitation intensity, so that the corresponding dominant process is excitonic recombination. Hence, the recombination processes of samples A and B at high T have been clarified.

Figure 1 also shows the appearance of broad emission spectra on the shorter wavelength side of the lasing peaks at T greater than 400 K (also labeled in Fig. 2 as SE of sample A (\blacktriangledown) and SE of sample B (∇)). The broad emission of sample B is attributed to FE recombination in ZnO films. The overlapping of the energy with that of the FE emission (\circ) as

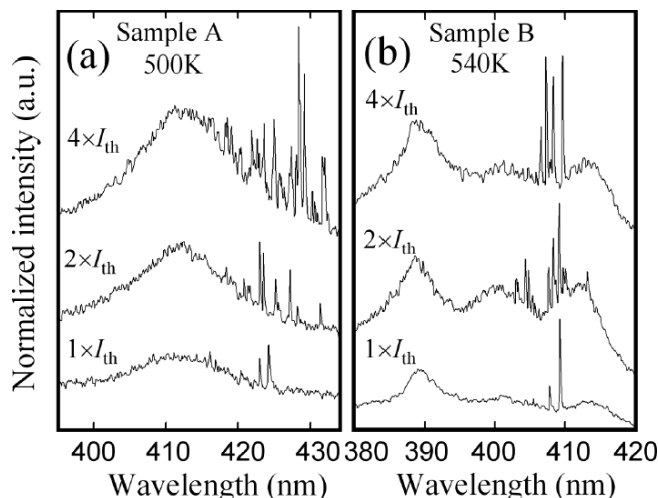


Figure 3. Lasing spectra for a) sample A and b) sample B at temperatures of 500 and 540 K, respectively, versus different excitation intensities.

shown in Figure 2 supports our claim. On the other hand, the origin of the SE of sample A is still not clear, though its features are similar to that of EES emission, except it has a corresponding lower emission energy.

Figure 4a shows I_{th} of the two samples versus T . It is expected that the value of I_{th} for sample A is slightly higher than that of sample B from RT to 400 K. This is because the optical gain of EHP radiative recombination is lower than that of the FE radiative recombination near RT.^[5] For T higher than 450 K, I_{th} of sample A increases more rapidly than that of sample B. Nevertheless, the variation of I_{th} with T for both samples followed an exponential dependence. The solid lines plotted in Figure 4a represent the best fit of the experimental data with an empirical formula $I_{\text{th}}(T) = I_0 \exp(T/T_c)$, where I_0 and T_c are the threshold current at $T = 0 \text{ K}$ and the characteristic temperature, respectively. T_c of sample A (sample B) was estimated to be 95 K (127 K). This implies that sample B has lower temperature sensitivity than sample A, and hence random laser actions supported by excitonic recombination are more effective than those supported by EHP recombination at high T .

Investigations of the temperature dependence of stimulated EES emission of the ZnO films on sapphire and the ZnO/(Mg,Zn)O superlattices on ScAlMgO_4 have found that the corresponding T_c values are 67 and 87 K, respectively.^[7] These samples (i.e., without grain boundaries) show smaller values of T_c (i.e., poorer high- T performance) than those of our ZnO epilayers. This is because the increase in T causes the spreading of excited carriers over the nonuniformly pumped region,^[10] which leads to the reduction of optical gain, and hence the corresponding value of T_c is small. In contrast, the formation of ZnO grains inside our ZnO epilayers (Fig. 4a, inset) confines the excited carriers over the pumped region so that the optical gain can be maintained at high T , and hence the value of T_c is higher. This is because the potential barrier appearing at the grain boundaries^[11] blocks the

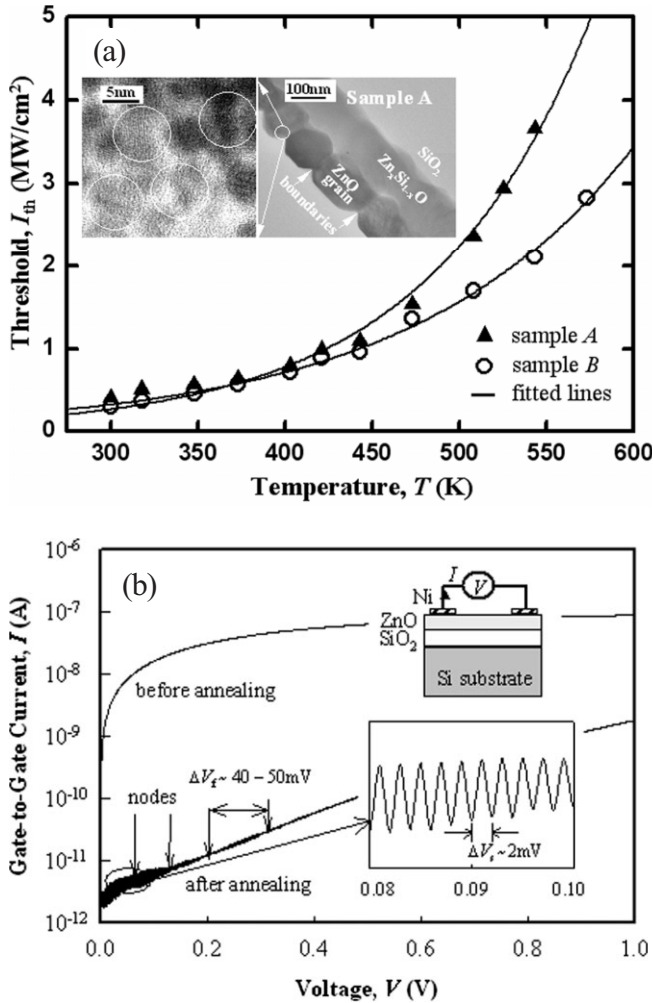


Figure 4. a) Plot of I_{th} versus T for samples A and B. The insets give the cross-sectional transmission electron microscopy (TEM) image of sample A (right) and the high-resolution TEM image of the ZnO grain (left). Circles show the location of the nanocrystals. b) RT current–voltage (I – V) characteristics of sample A before and after annealing. The insets show the schematic diagram of sample A (top) and the enlargement of the I – V curve at low bias voltage for the annealed sample (bottom).

diffusion of optically excited carriers/excitons across the pumped region. On the other hand, the presence of nanocrystals inside the ZnO grains could also contribute to the capture of carriers/excitons.

The above confinement of carriers/excitons can be verified by measuring the current–voltage (I – V) characteristics of sample A. This is possible because if the external injection of carriers can be trapped inside the ZnO grains, similar confinement of optically generated carriers/excitons should occur. Figure 4b shows the RT gate-to-gate I – V curves of sample A before and after annealing. The I – V curve of sample A before annealing (i.e., with very small and closely packed grains^[4]) exhibits a linear I – V relationship. However, the I – V curve of sample A after annealing exhibits fast (slow) oscillation with a period of ~ 2 mV (~ 40 – 50 mV), which indicates there is

charging and discharging of injected carriers^[12] inside the ZnO grains (ZnO nanocrystals inside the grains). The occurrence of oscillations is due to the Coulomb blockade from the nanostructures, and the corresponding Coulomb energy, E_c , can be calculated from $E_c = e^2/2C$, where e is the electron charge and C is the capacitance. The capacitance of ZnO grains and nanocrystals (i.e., assuming that they work like spherical capacitors) can be expressed as $C \approx 4\pi\epsilon_0\epsilon_r r/a$,^[13] where ϵ_0 is the permittivity of free space, ϵ_r (≈ 7.4) is the relative permittivity, r is the radius of the nanostructures, and a is the correction factor. If $r \approx 60$ nm ($r \approx 4$ nm) and $a = 1$ ($a = 1.54$) are used to calculate the capacitance of ZnO grains (nanocrystals), the corresponding value of E_c is found to be ~ 1.6 mV (~ 38 meV), which is close to V_f (V_s), where V_f and V_s are the oscillation potentials due to the presence of nanocrystals and grains, respectively, measured from the I – V curve. Hence, we can conclude that the confinement of injected carriers is mainly due to the presence of nanostructural ZnO grains. This also implies that the confinement of optically excited carriers/excitons at high T can be achieved.

Nonradiative recombination, which is caused by the trapping of carriers/excitons (i.e., by defects, such as grain boundaries, surface, vacancies/interstitials, etc.) inside the ZnO nanostructures, can also affect the UV lasing of the ZnO epilayers. This is because at elevated temperatures the increase in the number of nonradiative recombination centers further reduces the intensity of radiative recombination so that UV lasing will be suppressed. However, higher pump intensity can generate more excited carriers to compensate the loss due to the nonradiative recombination. As a result, high-temperature UV lasing can still be observed from the ZnO epilayer at the expense of a higher pump threshold.

Random laser action can also play an important role in maintaining the optical gain of the random cavities inside the ZnO epilayers at high T . This can be demonstrated by investigating the length of the random cavities, L_c (i.e., length of the closed-loop paths of light), of the ZnO epilayers under the influence of T . L_c can be obtained by applying a Fourier transform (FT) to the lasing spectra as given in Figure 1.^[14] Figure 5a plots the corresponding values of L_c (i.e., the fundamental resonator of random lasing) for samples A and B versus T . As an example, the FT distribution of the lasing spectra of sample B at $T = RT$ and 475 K is shown in Figure 5a. It is found that the value of L_c decreases from ~ 6 – 8 μm at RT to ~ 2 – 4 μm at high T . Figure 5b explains the reason for the dependence of L_c on T . As the optical excitation has a Gaussian profile (i.e., high gain at the middle of the pump stripe), random cavities with short L_c will only experience high average optical gain at the region near the middle of the pump stripe to sustain lasing at high T . For regions away from the middle of the pump stripe, the average optical gain at high T is not large enough to overcome the scattering loss of long random cavities (i.e., long L_c). On the other hand, the average optical gain at low T is still sufficient to support random cavities with long L_c to achieve coherent lasing. This phenomenon of self-compensation maintains the optical gain

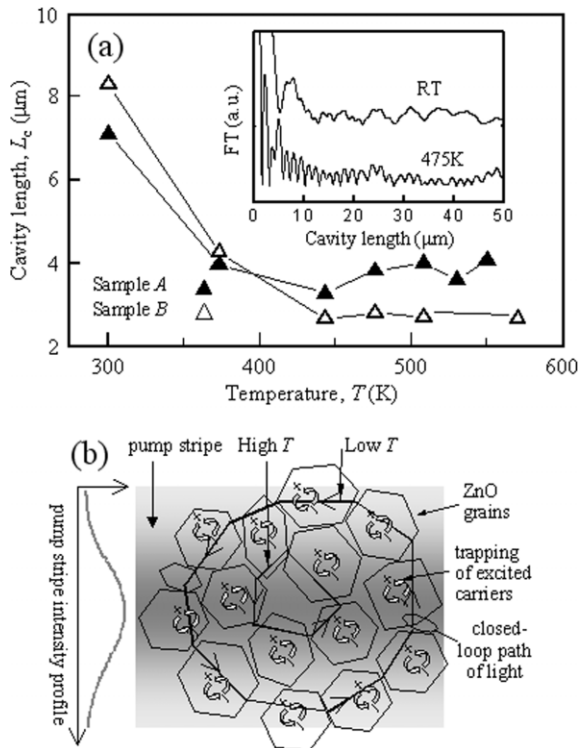


Figure 5. a) Plot of L_c versus T for samples A and B. The inset shows the FT spectra of the LE spectra of sample B taken at RT and 475 K. b) The formation of closed-loop random cavities inside the ZnO epilayers at low and high T .

of the random cavities and hence short (long) L_c is observed from the samples operating at high (low) T .

Our investigation has also shown that the ZnO epilayers can allow “temperature tuning” of the lasing wavelength from ultraviolet to purple (red-shifted by more than 30 nm), and the process is reversible and repetitious. Therefore, this unique behavior of the proposed ZnO epilayers will lead to the development of novel ZnO UV lasers, tunable over a wide range, by controlling the substrate temperature. In summary, we have studied the influence of temperature on the lasing characteristics of ZnO epilayers with nanostructures. It is found that the characteristic temperature of the annealed ZnO epilayers can be as high as 127 K, which is almost double that of the ZnO films on a sapphire substrate without nanostructures.^[7] We have shown that the improvement of the characteristic temperature is due to i) the confinement of excited carriers inside the ZnO grains (i.e., related to the potential barrier formed at grain boundaries), so that the spreading of excited carriers can be minimized, and ii) the size flexibility of the random cavities, so that the optimum gain for the closed-loop path of light can be obtained. As a result, lasing can be maintained in the ZnO epilayers at high T .

Experimental

ZnO epilayers were deposited on a Si substrate with a ~ 400 nm thick SiO_2 buffer layer by the filtered cathodic vacuum arc technique. During the deposition, the substrate temperature and chamber pressure were set to 230°C and 9×10^{-4} Torr (1×10^{-3} Torr = 133 Pa), respectively. These as-grown samples were then annealed in air (900°C , 2 h) in a standard Lindberg-type furnace using a quartz tube reactor. After annealing, highly disordered loss-packed ZnO grains (with size varying between 100 and 150 nm) were formed in the top ZnO active layer of both samples.

The optical characteristics of these samples were studied under optical excitation by a frequency-tripled Nd:YAG laser (at 355 nm; YAG = yttrium aluminum garnet) at pulsed operation (6 ns, 10 Hz). The laser beam has a Gaussian profile with a beam width of ~ 4 mm. A pump stripe was formed on the sample surface by focusing the laser beam through a cylindrical lens. The pump stripe also has a Gaussian shape with a beam width of ~ 18 μm . The laser emission was measured from the edge of the samples. For the heating experiments, the samples were mounted on an electrical ceramic heater of size 1 cm \times 1 cm, and the temperature was allowed to vary between 300 and 600 K.

The RT I - V characteristics of sample A before and after annealing were measured by deposition of Ni gate contacts (with a thickness of ~ 100 nm and an area of ~ 100 $\mu\text{m} \times 100$ μm) on the top ZnO layer of the sample. The side-to-side separation of the gate contacts is ~ 200 μm . The contacts underwent rapid thermal annealing at $\sim 500^\circ\text{C}$ for 2 min to achieve ohmic behavior.

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