

# High temperature excitonic lasing characteristics of randomly assembled SnO<sub>2</sub> nanowires

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(Received 18 June 2009; accepted 8 September 2009; published online 28 September 2009)

The lasing characteristics of randomly assembled SnO<sub>2</sub> nanowires, whose excitonic gain is attributed to the exciton states bounded to the surface defects, are studied from room temperature up to 500 K. It is found that the amount of excited carriers under the lasing conditions is well below the Mott density of SnO<sub>2</sub> so that high pumping intensities have less influence on the radiative recombination mechanism and wavelength of the lasing peaks. Furthermore, the redshift of lasing peaks is mainly due to the reduction of bandgap energy of SnO<sub>2</sub> with the increase of temperature.

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SnO<sub>2</sub>, which is a wide bandgap semiconductor material with bandgap energy of 3.6 eV, has been used as a functional material to realize solid-state gas sensors and transparent electrodes.<sup>1,2</sup> This is because SnO<sub>2</sub> has high intrinsic conductivity and transparency in the visible spectrum. However, due to the dipole-forbidden nature of SnO<sub>2</sub>, intrinsic bandedge transition is not allowed. Ultraviolet emission at around 3.2 eV observed from SnO<sub>2</sub> is mostly related to excitonic recombination from the shallow trap state induced by defects or impurities within the bandgap.<sup>3–5</sup> Recently, efficient ultraviolet luminescence has been observed from the nanostructured SnO<sub>2</sub>, such as nanowires and nanobelts, due to the abundance of surface states. Room temperature ultraviolet stimulated emission<sup>6</sup> and random lasing<sup>7</sup> have been realized from SnO<sub>2</sub> nanowires with suitable control of surface states and excitation conditions. On the other hand, as SnO<sub>2</sub> has a large exciton binding energy of 130 meV, it is believed that the excitonic radiative recombination should survive well above room temperature. Hence, the high temperature lasing characteristics of randomly assembled SnO<sub>2</sub> nanowires are investigated in this letter.

The randomly assembled SnO<sub>2</sub> nanowires were grown on Si substrate by a vapor transport method. Detailed fabrication procedures of the SnO<sub>2</sub> nanowires have been described elsewhere.<sup>7</sup> The sample, which was explored to the open air during the experiment, was optically excited by a frequency-triple 355 nm pulsed neodymium doped yttrium aluminum garnet laser with 120 ps pulsewidth and 10 Hz repetition rate. A spherical lens was used to focus a pump beam of 1 mm in diameter onto the sample. The sample was mounted on an electrical ceramic heater of size 1 × 1 cm<sup>2</sup>, and the temperature was allowed to vary between 300 and 500 K. Figure 1 plots the light-light curve and emission spectra of the sample at *T* equal to 350 K. A kink (i.e., excitation threshold) at ~0.4 MW/cm<sup>2</sup> is observed from the light-light curve indicated that the sample exhibits lasing action. Furthermore, lasing peaks start to emerge from the emission spectra at around 391 nm for pumping intensities above

threshold. The wavelength of lasing peaks maintains at 391 nm even at high pump intensities. On the other hand, lasing peaks at around 387 nm are also emerged from the spectra at high pumping intensities. However, as (1) the wavelength of the two set of lasing peaks are separated by less than 4 nm and (2) the lasing peaks with shorter wavelength (i.e., at 387 nm) are only emerged at high pumping intensities, the excitation of 387 nm lasing peaks is not related to electron-hole plasma emission. These imply that the mechanism of radiative excitonic recombination remains unchanged inside the SnO<sub>2</sub> nanowires. The excitation of electron-hole-plasma emission (i.e., its wavelength should longer than 387 nm), which is used to be observed in ZnO material at high temperature,<sup>8</sup> has not been observed at high pumping intensities. On the other hand, lasing peaks at 387 nm were observed from randomly assembled SnO<sub>2</sub> nanowires under room-temperature excitation.<sup>7</sup> Hence, the excitation of lasing peaks at both 387 and 391 nm from the SnO<sub>2</sub> nanowires at

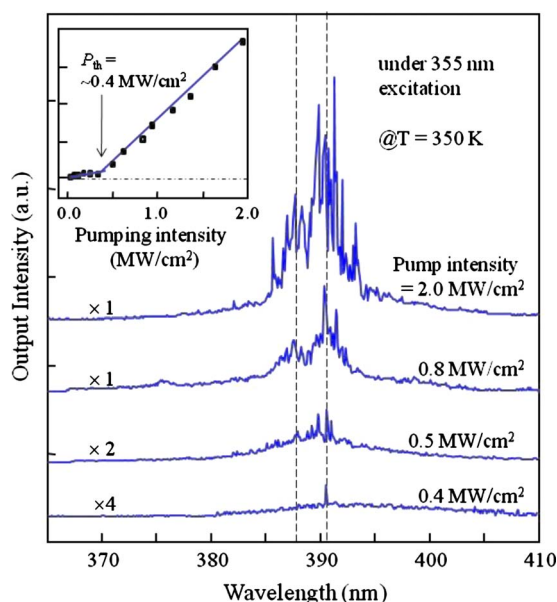


FIG. 1. (Color online) Lasing spectra and light-light curve of the randomly assembled SnO<sub>2</sub> nanowires with substrate temperature of 350 K.

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$T=350$  K is mainly due to the broadening of excitonic gain.

For the sample under lasing operation, the excited carriers will be clamped at the laser threshold,  $N_{th}$ , which can be estimated from

$$N_{th} \approx \frac{1}{dh} \frac{\lambda T_{FWHM}}{c} P_{th}, \quad (1)$$

where  $T_{FWHM}$  ( $=120$  ps) is the pulsedwidth of pumped pulses,  $P_{th}$  ( $=0.28$  MW/cm<sup>2</sup>) is the pump threshold at room temperature,  $d$  ( $=2$   $\mu$ m) is the thickness of the randomly assembled SnO<sub>2</sub> nanowires,  $h$  is Plank's constant,  $c$  is light velocity in free space, and  $\lambda$  ( $=387$  nm) is the lasing wavelength. Hence, the corresponding value of  $N_{th}$  can be calculated and is found to be  $1.86 \times 10^{17}$  cm<sup>-3</sup>. On the other hand, Mott density,  $N_M$ , of SnO<sub>2</sub> at and above room temperature can be approximated by<sup>9</sup>

$$N_M \approx (a_B l_c^{-1})^2 \frac{k_B T}{2a_B^3 E_{ex}}, \quad (2)$$

where  $a_B$  ( $\sim 2.7$  nm) is the Bohr radius,<sup>10</sup>  $a_B l_c^{-1} = 1.19$ ,<sup>9</sup>  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $E_{ex}$  ( $\sim 130$  meV) is the exciton binding energy. Equation (2), which is deduced under the assumption of classical Boltzmann statistics, is valid for nondegenerate electron-hole plasma. As degeneration of electron-hole plasma is likely to occur at low temperature (i.e.,  $\ll 300$  K), it is reasonable to use Eq. (2) to estimate the Mott density of SnO<sub>2</sub> nanowires in this study. Hence,  $N_M$  of SnO<sub>2</sub> nanowires at  $T=300$  K can be found to be  $7.2 \times 10^{18}$  cm<sup>-3</sup> which is much higher than that of  $N_{th}$ . This verifies the observation given in Fig. 1 that the excitation of electron-hole-plasma emission will not be supported so that the wavelength of lasing peaks, which is of an excitonic origin, is independent on the pumping intensities.

Lasing characteristics of the randomly assembled SnO<sub>2</sub> nanowires at  $T=350$  K can be attributed to random lasing action. The increase of number of lasing peaks with pump intensity as shown in Fig. 1 is one of the strong evidences of random lasing action. There are two more observations that can verify the presence of random lasing action: (1) Emission spectra are different at different observation angle and (2) plot of  $A_{th}^{2/3}$  versus  $P_{th}^{-1}$  exhibits a linear relationship where  $A_{th}$  is threshold excitation area and  $P_{th}$  threshold pump intensity.<sup>11</sup> Figure 2 plots the emission spectra of the randomly assembled SnO<sub>2</sub> nanowires measured at different observation angles. It is noted that different observed directions give different emission spectra. This is because different laser cavities formed by multiple scattering can have different output different output directions. The inset of Fig. 2 plots  $A_{th}^{2/3}$  versus  $P_{th}^{-1}$ , which shows a linear relationship, for a constant pump intensity of  $1.0$  MW/cm<sup>2</sup>. Hence, it can be concluded that random lasing action is the lasing mechanism of the randomly assembled SnO<sub>2</sub> nanowires at  $T=350$  K.

Figure 3 shows the change of lasing spectra for  $T$  varied between 300 and 500 K. The sample was pumped at about  $2 \times P_{th}$  where  $P_{th}$  increases with the increase of  $T$ . It was observed that the dominant lasing peaks are shifted to the longer wavelength with the increase of  $T$ . In fact, it can be shown that for  $T$  equal to 500 K, the large value of  $P_{th}$  will still be insufficient to cause the excitation of electron-hole plasma emission as the corresponding  $N_{th}$  remains well below  $N_M$ . The lasing mechanism should be mainly related to

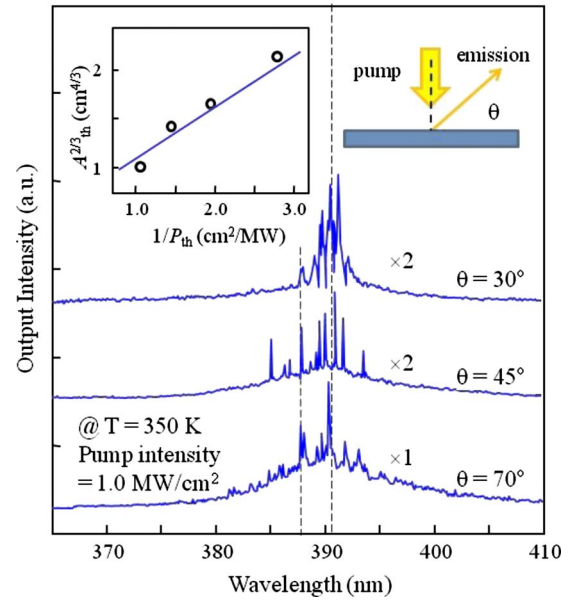


FIG. 2. (Color online) Emission spectra measured from different observation angles from the randomly assembled SnO<sub>2</sub> nanowires. The insert shows the relation between  $A_{th}^{2/3}$  and  $P_{th}^{-1}$  of the sample.

the recombination of exciton states. Furthermore, it was estimated that the trapping potential of excitons at the surface defects is about 50 meV,<sup>6</sup> the thermal energy at 500 K is about 43 meV so that the amount of excitons as well as the excitonic gain of SnO<sub>2</sub> nanowires are significantly reduced with the increase of  $T$ . Therefore, the intensity of lasing spectra reduces with the increase of  $T$ .

Figure 4 plots the dominant lasing energies and  $P_{th}$  of the sample versus  $T$ . The emission energies can be linearly fitted with the change of  $T$  and the corresponding slope is found to be about 0.5 meV/K. The linear dependence of lasing wavelength on  $T$  can be attributed to the reduction of

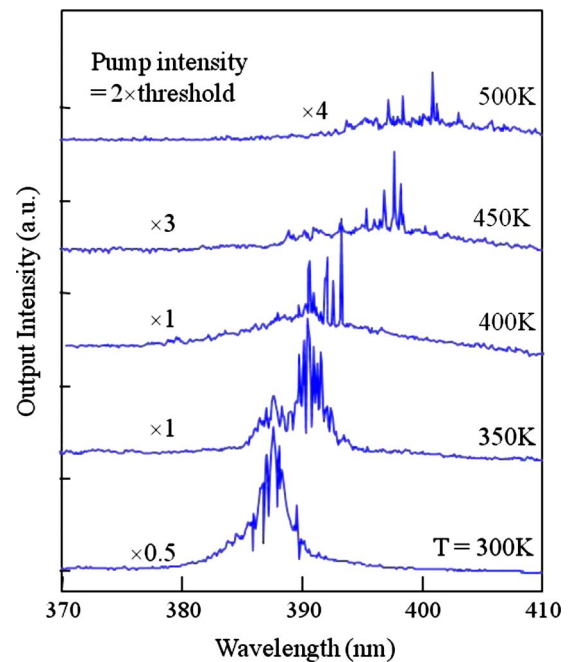


FIG. 3. (Color online) Lasing spectra of the randomly assembled SnO<sub>2</sub> nanowires vs  $T$ . The sample was pumped at  $2 \times P_{th}$ .

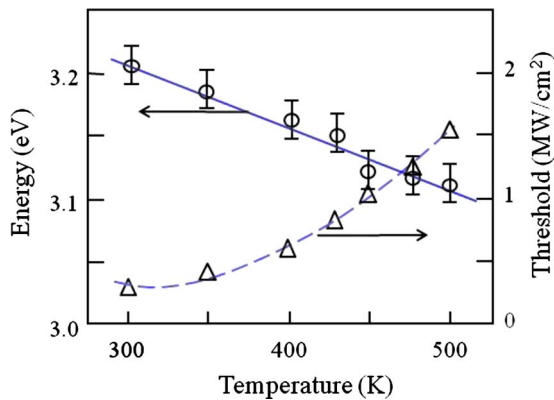


FIG. 4. (Color online) Plots of lasing energy and  $P_{\text{th}}$  vs  $T$ .

bandgap energy.<sup>12</sup> In addition, the variation of  $P_{\text{th}}$  versus  $T$  is also fitted with an empirical formula,

$$P_{\text{th}}(T) = P_0 \exp(T/T_c), \quad (3)$$

where  $P_0$  and  $T_c$  are the threshold pump intensity at  $T = 0$  K and the characteristic temperature, respectively.  $T_c$  is a parameter which reflects the quality of the high- $T$  performance of lasers. It is found that  $T_c$  of the randomly assembled  $\text{SnO}_2$  nanowires is about 92 K. Investigations on the  $T$  dependence of stimulated excitonic emission from ZnO films and ZnO/ZnMgO superlattices have shown that the corresponding  $T_c$  is less than 90 K in a narrow range of  $T$  between 294 and 377 K.<sup>13</sup> Hence, the excitonic gain of  $\text{SnO}_2$  nanowires obtained from the recombination of exciton states at the surface defects is compatible to that of ZnO films related to the direct bandgap recombination at high  $T$ .

It has been shown that thermal annealing at 500 K in  $\text{O}_2$  rich condition will significantly reduce the ultraviolet emission intensities of  $\text{SnO}_2$  nanowires. This is because the amorphous layer can be crystallized so that the available surface defects as well as the exciton states will be removed after the thermal annealing process.<sup>7</sup> However, for the sample operating at or below 500 K in open air, the crystallization of amorphous layer is suppressed due to insufficient  $\text{O}_2$ . It was observed that after the sample was heated up to  $T = 500$  K

for 30 min in open air, the corresponding room temperature lasing characteristics remained unchanged.

In conclusion, the high- $T$  lasing characteristics of randomly assembled  $\text{SnO}_2$  nanowires were studied. It was found that the radiative recombination of exciton states bounded to the surface defects of  $\text{SnO}_2$  can survive at high  $T$ . As a result, ultraviolet lasing observed from the randomly assembled  $\text{SnO}_2$  nanowires is sustained up to 500 K. The redshift of lasing wavelength with  $T$  was found to be mainly due to the reduction of the bandgap energy of  $\text{SnO}_2$ . Furthermore, we have shown that the high- $T$  lasing characteristics of randomly assembled  $\text{SnO}_2$  nanowires are compatible to that of ZnO films. This implies that the excitonic gain obtained from the surface defects of  $\text{SnO}_2$  is as good as that supported by the direct bandgap of ZnO. Such a discovery of high- $T$  radiative recombination mechanism in nanostructured  $\text{SnO}_2$  may lead to the development of optoelectronic devices.

This work was supported by LKY PDF 2/08 startup grant.

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