

High-temperature random lasing in ZnO nanoneedles

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We report the high-temperature ultraviolet random laser action in ZnO nanoneedles. The characteristic temperature of the ZnO nanoneedle lasers was derived to be 138 K in the temperature range from 300 to 615 K. The cavity length of the random lasers as a function of temperature was determined by Fourier transform spectroscopy. The cavity length decreased with an increase in temperature from $\sim 14 \mu\text{m}$ at 300 K to $\sim 2 \mu\text{m}$ at 550 K. The optical gain of the ZnO nanoneedle lasers at high temperature is attributed to a self-compensation mechanism in the cavity length.

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Since the demonstration of ultraviolet lasing emission from ZnO nanowires by Huang *et al.*,¹ one-dimensional (1D) ZnO has stimulated great deal of interests due to its potential technological applications. The performance of 1D ZnO based photonic devices is expected to be highly efficient and robust at high temperature as the exciton oscillator strength is highly enhanced in nanostructure.² The later remains poorly understood and studied. Although the photoluminescence of ZnO nanosheets has been demonstrated up to 850 K,³ high-temperature lasing from 1D ZnO has not been reported. In this letter, we demonstrate high-temperature ultraviolet random laser action in ZnO nanoneedles. The characteristic temperature (T_c) of ZnO nanoneedles was derived to be 138 K from the temperature dependence of the lasing emission threshold in the temperature range of 300–615 K, which is significantly higher than ZnO thin films (87 K) and ZnO/ZnMgO superlattices (67 K).⁴

ZnO nanoneedles were fabricated using an ion-beam technique.⁵ ZnO thin films were first grown by the filtered cathodic vacuum arc (FCVA) technique at 300 °C on a silicon substrate with a 400 nm thick SiO₂ layer acted as a buffer layer to confine light scattering. This was followed by sputtering carried out in an ultrahigh vacuum scanning electron microscopy (SEM) system, with a differentially pumped microbeam ion gun (JEOL; MIED). An Ar⁺ ions beam with 3 keV was focused into a microbeam of 380 μm in diameter. The samples were irradiated for 30 min at room temperature.

Figure 1(a) shows the field emission scanning electron microscopy (FESEM) image of the ZnO nanoneedle arrays. The lengths of the cone structure were ranging from 400 to 700 nm. The diameter of the nanoneedles in the stem part was around 100 nm, where some of the nanoneedles tend to form in a cluster with similar sharpness at the tip. It can be seen that the separation between the nanoneedles was irregular and ranged from a few nanometers to tens of nanometers. As the ZnO thin film was only 300 nm thick, the upper part of the cone was ZnO (white contrast) and the lower part of the stem was SiO₂ (dark contrast). Figure 1(b)

shows the TEM image of an individual nanoneedle, which exhibits sharp-tip morphology. The high-resolution TEM image of the ZnO nanoneedle and the corresponding selective area electron diffraction (SAED) pattern are shown in Figs. 1(c) and 1(d), respectively, which illustrate the high crystal quality and wurtzite structure of the ZnO nanoneedles. The nanoneedles fabricated by this method have a unique characteristic to maintain the high crystal quality of bulk material and retain its superior optical properties.

Optical characteristics of the samples were investigated under an optical excitation by a 355 nm frequency-tripled Nd:YAG (yttrium aluminum garnet) pulse laser. The optical pumping was achieved by using a cylindrical lens to focus a pump stripe of ~ 2 mm in length and $\sim 40 \mu\text{m}$ in width onto the sample. It is remarkable to find that laser action in ZnO nanoneedles can be observed at a temperature up to 615 K. Figure 2(a) shows the lasing spectra of the ZnO nanoneedles as a function of temperature T under optical excitation of $\sim 2 \times I_{\text{th}}$, where I_{th} represents the pump threshold at the corresponding T . When the pump power reached I_{th} , a dramatic emission oscillation in a linewidth as narrow as 0.4 nm emerged from the single-broad-emission spectra at room temperature. This phenomenon of emission spectra was attributed to random lasing with coherent feedback.^{5–7} It should be noted that no lasing can be observed from the ZnO thin films without nanostructures. The linewidth of the lasing peaks remained less than 0.4 nm for T up to 615 K. The peak lasing wavelength was redshifted from 394 to 435 nm as the temperature increased from 300 to 615 K. It is due to the reduction of band gap as temperature increases. Moreover, a broad emission band in the shorter wavelength side of the lasing peaks becomes apparent when temperature is higher than 450 K [as labeled by the arrows in Fig. 2(a)]. The origin of this broad emission band was not clear, though its features are similar to that of exciton-exciton scattering emission as reported by Bagnall *et al.*,⁸ except it has a corresponding lower emission energy. Figure 2(b) shows the typical light-light curve of the ZnO nanoneedles at various temperatures. The spectra showed a “kink” in the light-light curves which was the characteristic of laser action. The lasing threshold at 300 K was $\sim 0.25 \text{ MW/cm}^2$ and it increased to $\sim 2.05 \text{ MW/cm}^2$ at 615 K. The coherent random lasing de-

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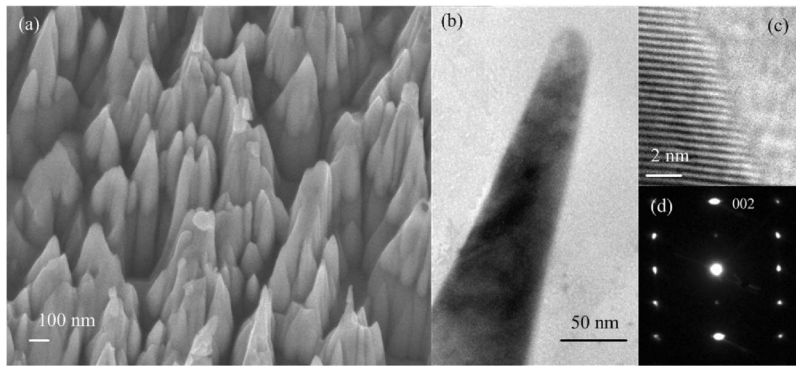


FIG. 1. (a) FESEM image of the ZnO nanoneedles. (b) TEM image of a single ZnO nanoneedle. (c) High-resolution TEM image of the nanoneedle and (d) the corresponding selected area electron diffraction pattern.

duced by the formation of closed-loop paths of light scattering was sustained inside the ZnO nanoneedles at high temperature.

Figure 3 plots the peak energy of lasing emission in ZnO nanoneedles as a function of temperature. The emission peak of the ZnO nanoneedles at room temperature is 3.15 eV. It was redshifted with increasing temperature at a rate of -0.97 meV/K for the entire temperature range. The observed linear relationship between the emission peak energy and temperature of our ZnO nanoneedles is in good agreement with the electron-hole plasma stimulated emission observed from ZnO thin film on sapphire substrate.⁸ The lasing threshold of ZnO nanoneedles as a function of temperature is also shown in Fig. 3. It was found that the I_{th} of the ZnO nanoneedles is increased exponential with temperature. The solid line represents the best fit using least-squares fitting of the experimental data to the empirical formula: $I_{th}(T) = I_0 \exp(T/T_c)$, where I_0 is the threshold pump intensity at $T=0$ K and T_c is the characteristic temperature. The T_c of the ZnO, was determined to be 138 K. The T_c of the ZnO nanoneedles was significantly higher than that of ZnO/sapphire (67 K) and ZnO/Zn_{0.74}Mg_{0.26}O superlattice on ScAlMgO₄ (87 K).⁴ Most importantly, the T_c of the ZnO nanoneedles on Si was comparable to the value (162 K) reported for laser structure based on InGaN/GaN multiquantum well in the temperature range of 175–575 K.⁹ The high operating temperature of our lasers is evident of the high quality of the structures. In this case, the internal loss of the laser should be very low. The optical gain is increased due to the enhancement of oscillator strength in 1D nanostructure. This modified density of states should results in a narrower spread of carriers in energy, a higher peak gain, and thus better temperature stability. The relatively high values of lasing thresholds in the temperature range effectively eliminate exciton-related effects from consideration of laser mechanisms. Electron-hole plasma is believed to be the dominant lasing mechanism in ZnO nanoneedles for temperature above 300 K.

To further investigate the closed-loop random laser cavities at high temperature, Fourier transform (FT) of the lasing spectrum is used to determine the change of cavities length L_c (i.e., length of the closed-loop paths of light),¹⁰ which is also an important factor in retaining the optical gain of the ZnO nanoneedles at high T . The FT distribution of the lasing spectra of ZnO nanoneedles at 300, 400, and 550 K under an excitation density of $2I_{th}$ are shown in Fig. 4(a). A series of broad peaks of the harmonics in each of the FT transform is observed and the fundamental resonator at each of these three temperatures was determined to be ~ 14 , ~ 8 , and

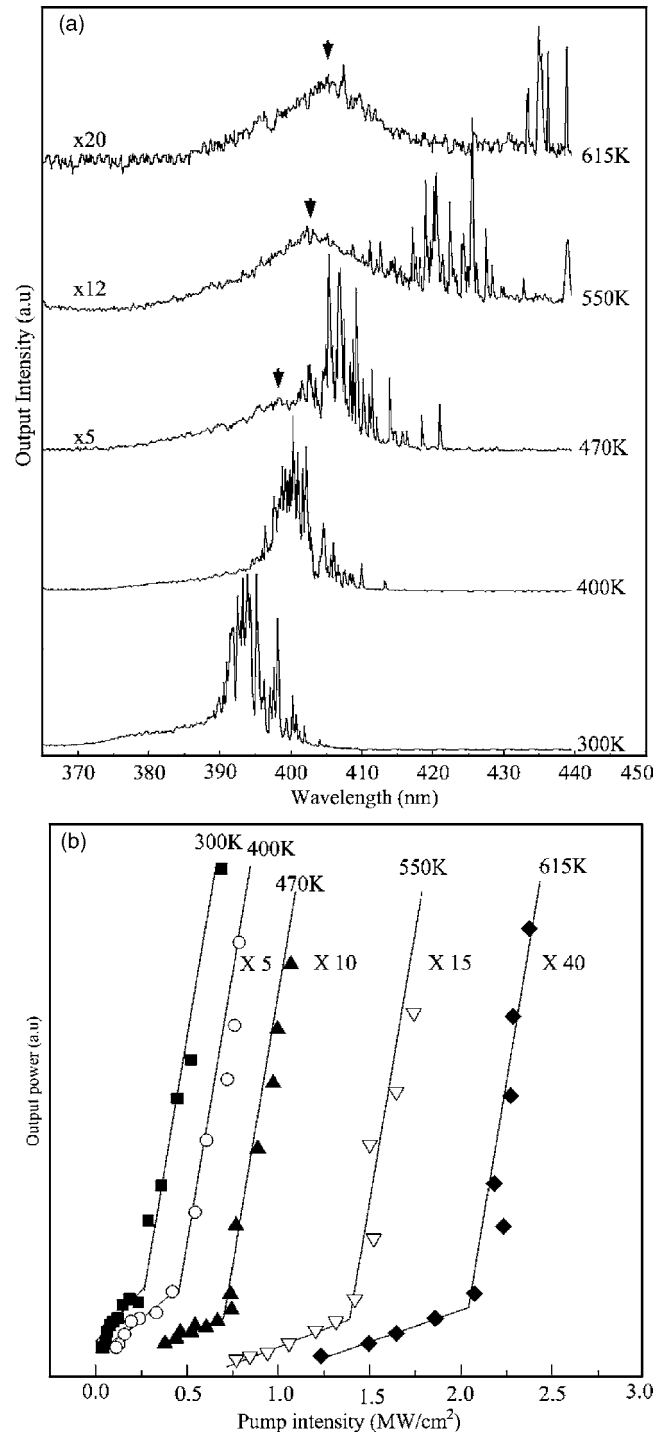


FIG. 2. (a) Lasing emission spectra at different temperatures from ZnO the nanoneedles; the emission spectra were obtained under an excitation density of $2I_{th}$. (b) Light-light curves of the ZnO nanoneedles at different temperatures.

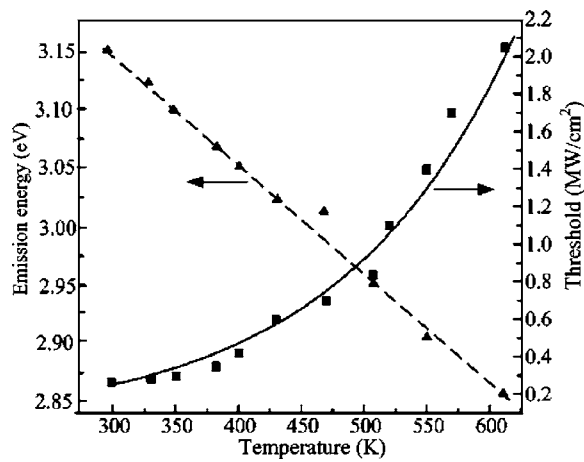


FIG. 3. Temperature dependence of lasing peak emission (▲) and lasing threshold (■) in the ZnO nanoneedles. The solid line represents the best result of the least-squares fit to the experimental data.

$\sim 2 \mu\text{m}$, respectively. It is found that the length of the cavities reduced as temperature increases. All the estimated values of L_c are much smaller than the spot size of the pumping laser beam on the samples. Figure 4(b) is the schematic diagram of the dependence of L_c on T . The optical excitation has a Gaussian profile, which has a high gain at the middle of the pump stripe. According to Yu *et al.*,¹¹ random cavities with a short L_c will only experience a high optical gain near the middle of pump stripe at high temperature. At low temperature, the long L_c provides a high average optical gain to sustain coherent random lasing.⁶ When T increases, the L_c decreases which reduces the average optical gain and a higher pump power is needed to sustain the lasing. When T is above 615 K, the optical gain is not sufficient to overcome the scattering loss, therefore, lasing ceases. This self-compensation mechanism of random laser cavities maintains the optical gain for lasing emissions at high temperature.

It should also be noted that the changing temperature allows “tuning” of the lasing peak energy of ZnO nanoneedles from UV to the blue spectral region for up to ~ 300 meV. Remarkably, the high-temperature lasing process of the ZnO nanoneedles is reversible and repetitious, even operated in air. In conclusion, the T_c of the ZnO nanoneedle random lasers was determined to be 138 K. The optical gain is increased due to the enhancement of oscillator strength in 1D nanostructure. In addition, the optical gain of the ZnO nanoneedles at high temperature was attributed to a self-compensation mechanism in the random cavities, where the cavity length decreases with an increase in temperature.

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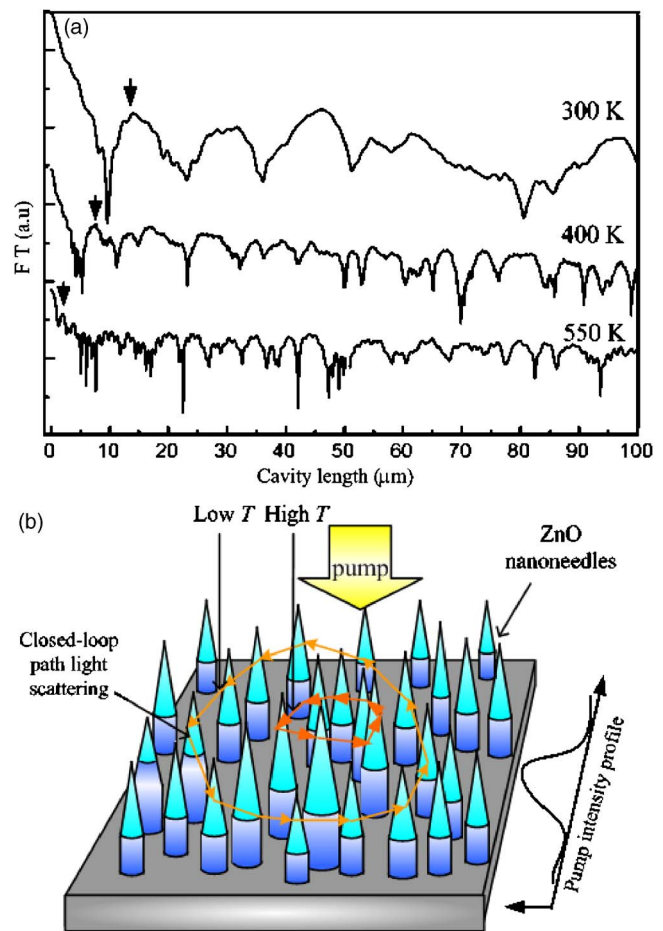


FIG. 4. (Color online) (a) Fourier transform of lasing spectra of the ZnO nanoneedles taken at 300, 400, and 550 K as given in Fig. 2(a). The arrow indicates the cavity length of the fundamental resonator. (b) Schematic diagram of the formation of closed-loop laser cavities at low and high temperature.

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