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High-temperature lasing characteristics of randomly assembled SnO$_2$ backbone nanowires coated with ZnO nanofins


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Lasing characteristics of randomly assembled SnO$_2$ backbone nanowires coated with ZnO nanofins are investigated. It is shown that the hierarchical nanostructures can sustain ultraviolet random lasing action even at substrate temperature higher than 700 K and the corresponding characteristic temperature is found to be about 390 K. This is because the presence of ZnO nanofins improves heat transfer from the SnO$_2$ backbone nanowires to the surrounding. Hence, some portion of the hierarchical nanostructures can be cooled down and the corresponding optical gain can be maintained even at high substrate temperature. © 2009 American Institute of Physics. [doi:10.1063/1.3273390]

I. INTRODUCTION

ZnO has attracted considerable attention to realize ultraviolet (UV) lasers for high-temperature operation due to its wide bandgap and high excitonic binding energies.$^{1,2}$ UV lasing has been observed from ZnO epilayers up to 570 K and the corresponding characteristic temperature, which reflects the quality of the high-temperature performance of the lasers, can be as high as 127 K.$^3$ This is because the formation of ZnO grains confines the excited carriers over the pump region of the ZnO epilayers so that the corresponding optical gain can be maintained at high operating temperature. Furthermore, the use of ridge waveguide, which confines the closed-loop path of optical light, improves the characteristic temperature of randomly assembled ZnO nanowires lasers by 10 K.$^4$ However, further optimization on the electrical and optical confinement of the random media cannot substantial improve the high-temperature performance of the UV ZnO lasers.

An effective method to advance the high-temperature performance of lasers is to improve heat dissipation of the lasers’ gain media. In this paper, we proposed to realize ZnO nanofins, which provide optical gain to amplify spontaneous emission as well as act as heat spreaders to improve heat convection to the surrounding, on randomly assembled SnO$_2$ backbone nanowires to support UV random lasing action at high temperatures. It is found that these hierarchical nanostructures can sustain UV lasing even at substrate temperature higher than 700 K and the corresponding characteristic temperature can be as large as 390 K. This paper is organized as follows. In Sec. II, the fabrication processes of SnO$_2$ backbone nanowires coated with ZnO nanofins as well as its physical properties are discussed. High-temperature UV lasing characteristics of the randomly assembled hierarchical nanostructures at different ambient temperature and pressure are investigated in Sec. III. It is intended to show that the high heat transfer rate of ZnO nanofins coating contributes to the high-temperature lasing performance of the hierarchical nanostructures. In Sec. IV, the thermal characteristics of a SnO$_2$ backbone nanowire coated with ZnO nanofins are studied by a simplified heat transfer equation to review the conditions for better heat transfer. A conclusion is given in Sec. V.

II. FABRICATION AND STRUCTURE OF THE RANDOMLY ASSEMBLED SnO$_2$ BACKBONE NANOWIRES COATED WITH ZnO NANOFINS

The SnO$_2$ nanowires were fabricated by the vapor transport method in a horizontal tube furnace.$^5$ The growth was taken place in a horizontal tube furnace. A mixture of SnO$_2$ and graphite (weight ratio 1:1) was used as the source powder located at the center of the furnace. A clean Si wafer, which had been coated with a 2 nm thick Au film, was used as the growth substrate. The substrate was place at the center of a quartz tube. The quartz tube was then inserted into the horizontal tube furnace. A mixture of Ar with 0.1% of O$_2$ was used as the carry gas and the pressure inside the quartz tube was maintained at 20 mbar. The temperature of the substrate was calibrated to about 900 °C. After the growth of 1 h, a ∼2 μm thick of white film was formed on the Si substrate.

The average length and thickness of nanowires are determined from the transmission electron microscopy (TEM) image [e.g., see Fig. 1(a)] to be ∼15 μm and ∼80 nm,
respectively. It is observed that the nanowire has good crystallinity of tetragonal rutile SnO₂ structure with lattice constants of $a$ and $c$ equal to 4.72 and 3.17 Å, respectively. Furthermore, the surface of the nanowire is very smooth and the thickness of an amorphous layer is less than 1 nm, as seen in Fig. 1(b). It is believed that the stoichiometry of the amorphous layer is SnO. This is because during the vapor-solid process, SnO₂ powder will first be reduced by active carbon to SnO and CO gas. The remaining SnO₂ powder will be further reduced to SnO by the presence of CO gas. Finally, the metastable SnO will be oxidized by O₂ from the carrying gas to form SnO₂ nanowires on the Si substrate. However, if the surface temperature of the SnO₂ nanowires is reduced to less than 900 °C, the formation of SnO on the surface of SnO₂ nanowires is possible due to the incomplete oxidation of SnO. Figure 1(c) shows the photoluminescence (PL) of our SnO₂ nanowires under excitation by a frequency-tripled 355 nm pulsed Nd:YAG laser with intensity of ~0.8 MW/cm². An Oriel MS257 monochromator, which consists of a grating with primary wavelength region between 250 and 1300 nm, was used to measure the lasing spectra of the sample. A weak emission peak at about 380 nm was observed from the surface of the sample. The low emission intensity of the SnO₂ nanowires is expected as the amorphous SnO layer is not thick enough to capture a large amount of free excitons for the generation of UV emission. In addition, no lasing action was observed from the pristine SnO₂ nanowires even at higher excitation intensity.

The as-obtained SnO₂ nanowires were then coated with a layer of ZnO nanoparticles, which were then used as seed for subsequent growth of ZnO nanorods in a hydrothermal condition. This was done by baking the passivated SnO₂ nanowires into an aqueous solution of equimolar zinc nitrate [Zn(NO₃)₂·6H₂O] and hexamethylenetetramine (C₆H₁₂N₄) 95 °C for 8 h. Figure 2(a) shows the scanning electron microscopy (SEM) images at different scales of the randomly assembled SnO₂ backbone nanowires coated with ZnO nanofins. It is observed that all the pristine SnO₂ nanowires are coated with short ZnO nanorods. Figure 2(b) gives the x-ray diffraction (XRD) spectrum of the entire nanostructures. The peaks are indexed to the tetragonal rutile SnO₂ and wurtzite ZnO. Based on TEM observation (data not shown), the average diameter and length of the ZnO nanorods are 10 and 100 nm, respectively. A high resolution TEM (HRTEM) image of the interface between ZnO nanorod and SnO₂ nanowire is shown in Fig. 3(a). A distinct boundary is visible and no transitional layer is found. This indicated that the ZnO nanorods were fused together with a SnO₂ nanowire to form a single structure in the deposition process. As expected, the ZnO nanorods have a hexagonal wurtzite structure with lattice constants $a$ and $c$ equal to 3.25 and 5.2 Å, respectively, and the growth direction is along (002), as revealed by Fig. 3(b).

### III. HIGH-TEMPERATURE LASING CHARACTERISTICS OF THE RANDOMLY ASSEMBLED SnO₂ BACKBONE NANOWIRES COATED WITH ZnO NANOFINS

Emission characteristics of the randomly assembled SnO₂ backbone nanowires coated with ZnO nanofins were also investigated. The sample was optically excited by a frequency-tripled 355 nm pulsed (120 ps, 10 Hz) Nd:YAG laser in open air with ambient temperature of 300 K. A spherical lens was used to focus a pump beam of ~1 mm in diameter onto the sample’s surface. Emission was collected in the direction perpendicular to the surface of the sample. The sample was mounted on an electrical ceramic heater of size 1×1 cm² and the substrate temperature was allowed to
vary between 300 and 700 K. The Oriel MS257 monochromator was used to measure the lasing spectra of the samples.

Figure 4(a) plots the emission spectra and light-light curve of the sample with substrate temperature equal to 700 K. It is observed that when the excitation power exceeds a threshold of \( \sim 4.2 \) MW/cm\(^2\), sharp peaks at round 400 nm with linewidth less than 0.4 nm were emerged from the emission spectra. In addition, the intensities of the sharp peaks are much higher than the intensity of background noise level. It is believed that the sharp peaks are the lasing modes obtained from the formation of closed-loop paths of light inside the hierarchical nanostructures. In addition, only ZnO nanofins can produce sufficient optical gain to sustain random lasing action at high temperatures. The formation of closed-loop cavity modes is due to the strong scattering of light from both ZnO nanofins and SnO\(_2\) nanowires. On the other hand, it is noted that the number of sharp peaks increases with the pump intensities. In addition, it can be shown that (i) the emission spectra are different at different observation angles and (ii) \( A_{\text{th}}^{2/3} \) versus \( P_{\text{th}} \) exhibits a linear relationship, where \( A_{\text{th}} \) is the threshold excitation area and \( P_{\text{th}} \) is the threshold pump intensity. Hence, all of the essential characteristics of random lasing action have been observed, it is verified that the corresponding lasing mechanism of the sample with substrate temperature equal to 700 K is due to random lasing action.

It is observed from Fig. 4(a) that the wavelength of the lasing peaks is independent on the pump intensity. This implies that the sample can maintain high optical gain even at high substrate temperature and the origin of the optical gain may be due to excitonic recombination in ZnO nanofins. The radiative recombination mechanism of the sample can be studied by plotting the emission spectra versus substrate temperature under a constant optical excitation of \( \sim 0.45 \) MW/cm\(^2\) [see Fig. 4(b)]. At substrate temperature equal to 300 K, the hierarchical nanostructures supported lasing emission at \( \sim 383 \) nm, which is close to the expected energy level of exciton-exciton scattering radiative recombination in ZnO.\(^1\)\(^-\)\(^3\) With the increase in substrate temperature from 300 to 700 K, the shrinkage of the bandgap redshifts the lasing peaks. There is only one broad peak (see the red dashed curves) in each lasing spectrum and the broad peak remains dominant at even high pump intensities. Furthermore, the emission spectra versus pump intensities at different substrate temperature will have similar characteristics to that given in Fig. 4(a) so they are not repeated. Therefore, it is verified that over the entire range of substrate temperature, only one radiative recombination mechanism is dominated and it is believed due to the exciton-exciton scattering radiative recombination. On the other hand, it is observed that the linewidth of the lasing peaks maintained to be less than 0.4 nm for the entire range of substrate temperature; this implies that coherent random lasing action is the lasing mechanism of the nanostructures.

In order to verify that the large heat transfer rate of SnO\(_2\) backbone nanowires coated with ZnO nanofins to the surrounding is mainly contributed to the high-temperature lasing performance of the sample, the above experiment was repeated for the ambient temperature increased to 350 K and in vacuum (\( \sim 10^{-3} \) torr). Figure 5(a) compares the threshold pump intensity versus substrate temperature of the sample in open space with ambient temperature equal to 300 and 350 K as well as in vacuum. Maximum allowed substrate temperature (characteristic temperature) is found to be about 700 K.
heat transfer rate. Hierarchical nanostructures in open air are related to its high density that the high-temperature lasing characteristics of the wires. It is noted that the corresponding lasing wavelength of 300 and 350 K as well as in vacuum.

For the case of vacuum, the random lasing action is significantly suppressed when the substrate temperature increases to 450 K. This is because convection is not allowed so that lasing characteristics of ZnO nanofins are limited by its optical properties at high-temperature. However, for the nanostructures operating in open air with ambient temperature of 300 K, lasing emission can be sustained at or above 700 K. This implies that the high heat transfer rate of ZnO nanofins coating in open air cools down the nanostructures even at high substrate temperature. Furthermore, if the ambient temperature increases, the amount of heat transfers to the surrounding will be reduced so that the corresponding high-temperature lasing characteristics are deteriorated. Figure 5(b) compares the emission wavelength versus substrate temperature of the ZnO nanofins on SnO2 backbone nanowires. It is noted that the corresponding lasing wavelength are redshifted in the same trend. Hence, this is another evidence that the high-temperature lasing characteristics of the hierarchical nanostructures in open air are related to its high heat transfer rate.

IV. THEORETICAL STUDIES ON THE HEAT TRANSFER OF THE SnO2 BACKBONE NANOWIRES COATED WITH ZnO NANOFINs

Figure 6 shows the schematic of a hierarchical nanostructure to be analyzed. The variation in temperature, $T(x)$, along the length, $x$, of the nanostructure from its base at $x=0$ can be approximated by a classic heat transfer model

$$T(x) = T_s + (T_b - T_s)\exp(-\mu x),$$

where $\mu = \sqrt{h/pA_c}$, $k$ is the thermal conductivity, $h$ is the heat transfer coefficient, $A_c$ is the cross sectional area, and $T_b$ and $T_s$ are the base and surrounding temperatures, respectively, of the nanowires. Although energy transport in nanostructures can differ from that in the macrostructures, the size of the nanostructure is larger than that of the phonons wavelength (i.e., $>20$ nm) so that the phonons can be modeled as incoherent particles for the calculation of energy transport. Hence, the influence of substrate and ambient temperature on the temperature distribution, $T(x)$, along the nanostructure can be estimated by Eq. (1) provided that the corresponding values of $k$ and $h$ can be found.

It is noted for Eq. (1) that the heat distribution along the nanostructure is dependent on the ratios $p/A_c$ and $h/k$. If the SnO2 backbone nanowires have a shape of a long square rod with side of $d$, then $p/A_c = 4/d$ where $d \sim 0.08$ $\mu$m is the average value of the SnO2 backbone nanowires. Due to the influence of classical size effects, the value of $k$ for the SnO2 backbone nanowires will be reduced from its bulk magnitude to about 10 W m$^{-1}$ K$^{-1}$ at 300 K. The value of $k$ can be further decreased with the increase in temperature so that the value of $h$ at 700 K can drop to 8 W m$^{-1}$ K$^{-1}$. On the other hand, there is no report on the direct measurement on the value of $h$ for either SnO2 or ZnO materials. However, it was estimated that the value of $h$ for carbon nanotubes with diameter of 40 nm under free convection can be as large as 1000 W m$^{-2}$ K$^{-1}$. As the size of carbon nanotubes is comparable with that of SnO2 nanowires, it may be reasonable to guess that the $h$ value of SnO2 nanowires to be in order of 1000 W m$^{-2}$ K$^{-1}$. Furthermore, the ZnO nanofins are equivalent to heat spreaders on the SnO2 nanowires. Experiment has shown that the use of nanostructured heat spreaders can improve heat transfer coefficient of flat surface by more than 1.8 times. Therefore, it is believed that the value of $h$ for the SnO2 backbone nanowires coated with ZnO nanofins on its four faces can be as larger than 7000 W m$^{-2}$ K$^{-1}$. Figure 7 plots that the heat distribution over a SnO2 backbone nanowire coated with ZnO nanofins for different values of $k$ and $h$. The values of $T_b$ and $T_s$ are set to 700 and 300 K, respectively, in the calculation. It is observed that for $h$ equal to 7000 W m$^{-2}$ K$^{-1}$, two-thirds of the nanowire has temperature less than 450 K. This may be the reason why the nanostructures can sustain UV lasing even at substrate temperature of 700 K as half of the nanowires can still provide optical gain.

As indicated in Eq. (1), heat distribution along the SnO2 backbone nanowires can be affected by the ambient temperature, $T_s$. It is also indicated in Fig. 7 (see the dashed-dotted
line) that increase in $T_s$ to 350 K can increase the temperature of the nanowire by almost 65 K. This can be used to explain the reason why the increase in $T_s$ to 350 K can reduce the optical gain and characteristic temperature of ZnO nanofins as shown in Fig. 5. For the ZnO nanofins on SnO$_2$ backbone nanowires in vacuum, this is equivalent to have $h=0$ so that $T(x)=T_b$ can be obtained from Eq. (1). This implies that the temperature distribution of ZnO nanofins is equal to the substrate temperature so that the high-temperature characteristics of ZnO nanofins are mainly determined by its material properties.

V. CONCLUSION

Randomly assembled SnO$_2$ backbone nanowires coated with ZnO nanofins provide optical gain to amplify spontaneous emission at UV wavelength. Optical feedback can also be obtained from the hierarchical nanostructures. As a result, coherent random lasing action is obtained via the formation of closed-loop cavity modes inside the randomly assembled hierarchical nanostructures. Furthermore, the presence of ZnO nanofins significantly increases the heat transfer from the SnO$_2$ backbone nanowires to the surrounding so that the temperature of some portion of the nanostructures can be well below the substrate temperature. Hence, ZnO nanofins can provide optical gain to sustain lasing even at substrate temperature higher than 700 K and the corresponding characteristic temperature is found to be about 390 K.

In order to verify that the mechanism of heat transfer is the main course of high-temperature lasing emission, the lasering characteristics of the nanostructures at different ambient temperature and pressure are investigated. It is noted that the maximum allowed substrate temperature and characteristic temperature of the nanostructure decrease with the increase in ambient temperature. In addition, the maximum allowed substrate temperature and characteristic temperature reach their minimum values for the nanostructures operating at vacuum. This is because the heat transfer reduces with the increase in ambient temperature and convection ceases at vacuum. Our theoretical studies have predicted that the high heat transfer coefficient of ZnO nanofins significantly enhance the equivalent heat transfer coefficient of the ZnO nanofins coated SnO$_2$ backbone nanowires so that large portion of the nanostructures can still maintain at temperature lower than 450 K even the corresponding substrate temperature is at 700 K. It is also estimated that the heat transfer coefficient for the nanostructures should be around 7000 W m$^{-2}$ K$^{-1}$ to achieve the observed lasing characteristics at high substrate temperature.

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