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COMMUNICATION

# Electrically pumped random lasers fabricated from ZnO nanowire arrays

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**Vertically aligned ZnO nanowires have been prepared, and structural characterization shows that the nanowires have relatively high crystalline quality. The dominant free exciton emission and the appearance of B-type exciton emissions at low temperatures reveal the high optical quality of the nanowires. Au–MgO–ZnO nanowire structures have been constructed, and random lasing has been observed from the structure under the injection of continuous current.**

## Introduction

Random lasers are lasing phenomena that occur in random media, in which resonant cavities are formed by the scattering among the grain boundaries of the random media.[1] Compared with regular lasers, random lasers have some unique features such as broad angular distribution, low fabrication cost, simple processing procedure, *etc*.[2] Meanwhile, the scattering-based feedback mechanism of random lasers offers an advantage in the preparation of lasers in the short wavelength region where highly reflective mirrors are still not available. The above features make random lasers a promising candidate in a variety of applications including displaying, document encoding, biological imaging, *etc*.[1–3] Because of its versatile potential applications, random lasing has received much attention in recent years, and many reports on optically pumped random lasers have been demonstrated.[3–6] Recently, electrically pumped random lasers have also been reported by several groups,[7–11] which address a step towards the applications of random lasers.

Zinc oxide (ZnO) is a wide band gap semiconductor, the most noteworthy property of which lies in its large exciton binding energy (60 meV). This large exciton binding energy ensures low threshold lasers may be realized in ZnO in relatively simple structures.[12,13] Actually, ZnO has been one of the most active materials for the fabrication of random lasers. Another interesting character of ZnO lies in the fact that rich nanostructures can be created from this material using relatively easy approaches,[14–16] and the large surface area of these nanostructures is favorable for strong scattering, which is essential for the operation of random lasers. Also the relatively high crystalline quality of the nanostructures favors random lasing. Therefore, if ZnO nanostructures can be employed as the active layer, higher performance random lasing may be expected. However, although some reports demonstrated optically pumped random lasing in ZnO nanowires.[6,17] reports on electrically pumped random lasing in ZnO nanowiress are still rare.[8,9]

In this paper, well-aligned ZnO nanowires have been prepared, and the nanowire arrays show high crystalline and optical quality. Au–MgO–ZnO nanowire structures have been constructed, and electrically pumped random lasing has been observed from the structures. It is believed that both the large surface and high crystalline and optical quality of the ZnO nanowires facilitate the random lasing.

## Experimental

The ZnO nanowire arrays were grown on sapphire substrates using a metal–organic chemical vapor deposition technique. Prior to the growth, the sapphire substrates were pretreated at 750 °C under $10^{-5}$ Pa for 30 min to remove any absorbed contaminants. The precursors used were diethylzinc and oxygen, and high-purity (7 N) nitrogen was used as a carrier to lead the precursors into the growth chamber. The substrate temperature was fixed at 700 °C, and the pressure in the growth chamber was kept at 680 Pa during the growth process. In this way, ZnO nanowire arrays are obtained without using any catalysts or buffer layers. Then, a MgO layer was deposited onto the ZnO nanowires using a radio-frequency magnetron sputtering technique. Finally, a gold anode contact and an indium cathode contact, respectively, were deposited onto the MgO–ZnO nanowire arrays by vacuum evaporation. The morphology of the ZnO nanowires was characterized in a Hitachi S4800 field-emission scanning electron microscope (SEM). A Bruker D8 X-ray diffractometer (XRD) was used to evaluate the crystalline properties of the ZnO nanowires. Temperature-dependent photoluminescence (PL) measurement of the nanowires was characterized using an SPEX 1404 spectrometer, and the 325 nm line of a He–Cd laser was employed as the excitation source. The optically pumped lasing of the nanowires was studied by employing the 266 nm line of the fourth harmonic of a YAG:Nd pulse laser. Electroluminescence (EL) measurements were carried out using a Hitachi F4500 spectrometer with a continuous current power source. Note that all the measurements were performed at room temperature.

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## Results and discussion

The surface morphology of the as-grown ZnO nanowires is shown in Fig. 1a. From the 40° tilted SEM image of the samples, one can see that rod-like nanowires have been fabricated on the substrate, and the area density of the nanowires is about $5.0 \times 10^{10}$ cm$^{-2}$. The cross-sectional image of the nanowires is shown in Fig. 1b. Well-aligned nanowires grown vertically on the substrate are visible from the image, and the size of the nanowires tapers from around 25 nm at the bottom to less than 15 nm at the top. The length of the nanowires is about 700 nm. Note that underneath the nanowires, there is an 80 nm ZnO grain layer, which is the initial precursor that deposited onto the substrate. The XRD pattern of the ZnO nanowire arrays is illustrated in Fig. 1c. Only a peak at 34.4° is visible from the pattern besides the diffraction from the sapphire substrate, which can be indexed to the diffraction from the (0001) facet of ZnO. The X-ray rocking curve of the nanowires is displayed in the inset of Fig. 1c, from which a Gaussian peak with a full width at half maximum (FWHM) of around 0.85° can be observed. The Phi-scan spectrum of the nanowires is shown in Fig. 1d, and six peaks can be defined from the spectrum, indicating the six-fold symmetry of the nanowires, which is consistent with the X-ray powder diffraction result. The structural characterizations shown above indicate that the ZnO nanowires have relatively high crystalline quality.

To assess the optical properties of the nanowires, the temperature-dependent PL spectra of the ZnO nanowires were investigated, and the result of which is shown in Fig. 2. The 12 K PL spectrum shown in Fig. 2a shows six peaks at around 3.380 eV, 3.371 eV, 3.361 eV, 3.312 eV, 3.243 eV, and 3.173 eV. Among these peaks, the one at 3.371 eV dominates the spectrum, which according to its position can be attributed to the type A free exciton ($FX_A$) emission of ZnO.[18] We note that although free exciton emission has been frequently observed in the low-temperature PL spectra of ZnO films and nanostructures, it is usually weak, and the emission from excitons localized by impurities, especially by donors, usually dominates the PL spectrum of ZnO.[19–21] Based on the reported energy separation of the A and B excitons (in the range of 9–15 meV),[21,22] the emission at around 3.380 eV can be attributed to the type B exciton ($FX_B$) emission in ZnO. The peaks at 3.361 eV and 3.312 eV have been frequently observed in the PL of ZnO, and they can be attributed to the emission from the neutral donor-bound excitons ($D^0X$) and the transition between the free electrons in the conduction band to the acceptor levels ($eA^0$) of ZnO, respectively.[20] As for the peaks at 3.243 eV and 3.173 eV, since their energy differences with $eA^0$ are 69 meV and 139 meV, respectively, which is almost identical to the phonon energy of ZnO (72 meV),[21] they can be attributed to the first and second phonon replicas of $eA^0$. From the temperature-dependent PL spectra shown in Fig. 2b, one can find that the intensity of $FX_B$ decreases, and finally merges into $FX_A$. The dominant free exciton and the appearance of $FX_B$ at low temperatures reveals the high optical quality of the ZnO nanowires, which lays a solid ground for the production of random lasing in these nanowires.

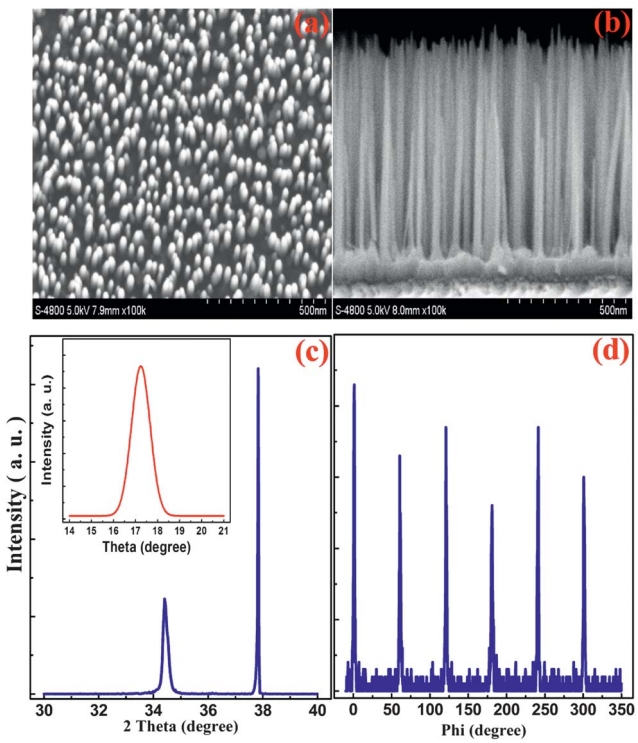


**Fig. 1** (a) The 40° tilted SEM image and (b) a cross-sectional image of the nanowire arrays (c) The XRD powder pattern and (d) the X-ray phi-scan spectrum of the ZnO nanowire arrays. The inset of (c) shows the X-ray rocking curve of the nanowire arrays.

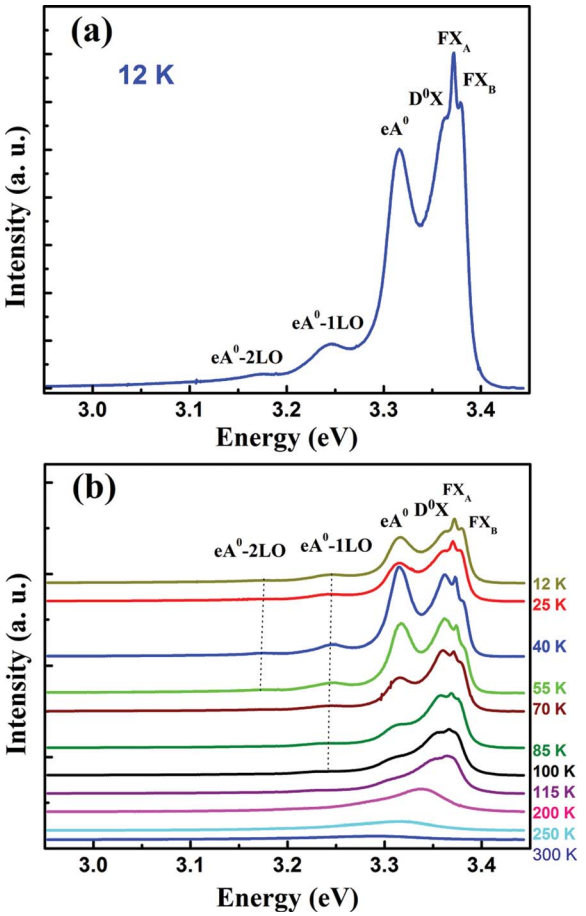


**Fig. 2** (a) 12 K PL spectrum of the ZnO nanowire arrays; (b) temperature-dependent PL spectra of the ZnO nanowire arrays.

To explore the possibility of using the ZnO nanowires in random lasers, the 266 nm line of the fourth harmonic of a YAG:Nd laser has been used to excite the nanowire arrays, the spectra of which are shown in Fig. 3. When the excitation intensity is 6 kW, the spectrum of the nanowires shows a broad spontaneous emission with its FWHM of around 25 nm, while when the excitation intensity increases to 10 kW, a sharp peak appears on the low-energy side of the spectrum, whose FWHM is less than 1 nm, indicating that lasing has been obtained from the nanowire arrays. The optically pumped lasing result reveals that the ZnO nanowire arrays can be used to study electrically pumped random lasing.

To achieve electrically pumped random lasing from the ZnO nanowire arrays, Au–MgO–ZnO structures employing the nanowire arrays as an active layer have been fabricated, and the schematic illustration of the structure is shown in the inset of Fig. 4. Note that the spacing between the two electrodes is around 2.5 mm. The current–voltage (*I–V*) curve of the structure is shown in Fig. 4. Although the leakage current is large, an obvious nonlinear behavior can be observed from the structure, and the turn-on voltage is about 3.6 V.

The EL spectrum of the structure under the injection of continuous current is shown in Fig. 5. When the injection current is 3.8 mA, a broad emission at around 392 nm with a FWHM of about 16 nm is visible, which can be attributed to the near-band-edge emission of ZnO. When the injection current is increased to 7.6 mA, some spikes superpose the broad emission, and the FWHM of the spikes is around 1.0 nm. When the injection current is further increased to 9.4 mA, the intensity of the spikes increases greatly, and they become more dominant. The reduction in width and the increase in emission intensity suggest that lasing has been achieved with the Au–MgO–ZnO structure. Since no Fabry–Perot cavity has been designed in this structure, the lasing is believed to come from a random laser. It is worth noting that the spikes in the intensity appear when the injection current is about 7.6 mA, which is smaller than previously reported values for ZnO nanowire-based electrically pumped random lasers (about 20 mA for ref. 8 and tens of mA for ref. 9). It is believed that the reduced threshold might arise from the high optical and crystalline quality of the nanowires in addition to the relatively large surface area of the nanowires that serves as a platform for strong scattering which is indispensible for a random laser.

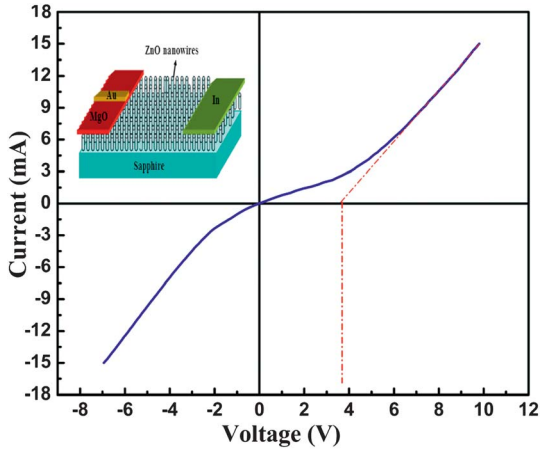


**Fig. 4** *I–V* characteristics of the Au–MgO–ZnO nanowire structure. The inset shows a schematic illustration of the structure.

The mechanism for the random laser achieved in the Au–MgO–ZnO structures has been elucidated in our previous publication.[10] Briefly, emission will occur in a certain nanowire due to the recombination of holes generated *via* impact ionization process and electrons accumulated at the ZnO–MgO interface. When the photons are emitted, they will be scattered strongly by the relatively large surface of the ZnO nanowires because the refraction index of ZnO is about 2.45, while that of MgO is about 1.7. Thanks to this strong scattering, some photons may be scattered back to the nanowire which they were emitted from, forming a closed loop. If the optical gain in the loops is larger than the loss, random lasing will occur in the closed loops.[1,2,23] We note here that the emission spectrum below or even above the threshold is noisy, which has been frequently observed in either optically pumped or electrically pumped random lasers.[5,8–10,23–26] The noise in the spectrum can be understood well in terms of the above mechanism for the random lasers: in some closed loops, the optical gain surpasses the loss, and lasing occurs, and the lasing mode in different loops varies greatly, leading to multi-mode lasing. Meanwhile, in many other loops, the gain may still be smaller than the loss so that weak spontaneous emission occurs. That is, the spectrum

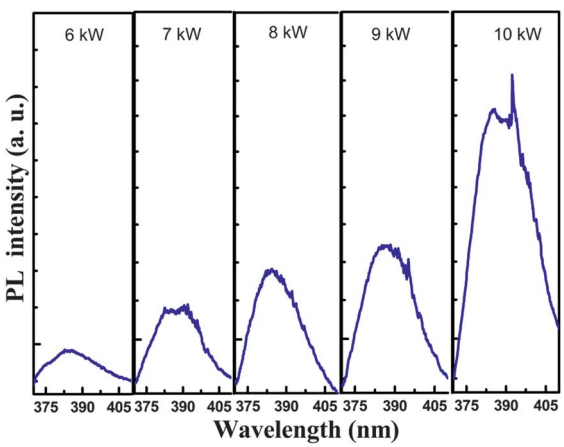


**Fig. 3** Room temperature photoluminescence spectra of the nanowires under various excitation intensities.

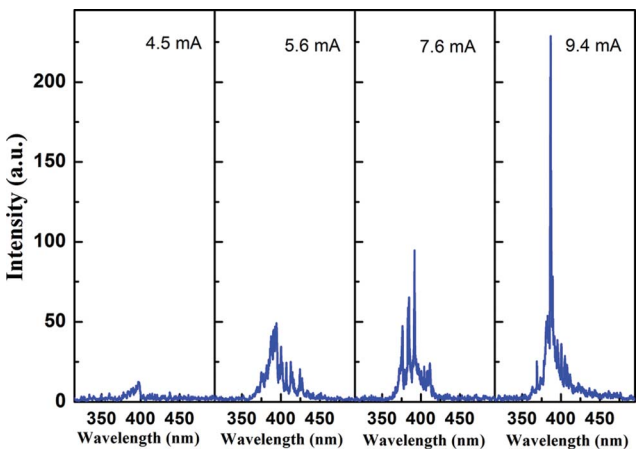


**Fig. 5** EL spectra of the Au–MgO–ZnO nanowire structure under different injection current.

recorded is a combination of the multi-mode lasing and spontaneous emissions, and thus it is reasonable that the spectra are noisy.

## Conclusion

Well-aligned ZnO nanowires have been prepared on a sapphire substrate and X-ray diffraction data reveals that the nanowires have relatively high crystalline quality. The dominant free exciton emission and the appearance of type B exciton emissions at low temperatures demonstrate the high optical quality of the nanowires. By employing the nanowires as an active layer, Au–MgO–ZnO structures have been constructed, and random lasing has been observed from the structure under the injection of continuous current. It is believed that both the large surface and the high crystalline and optical quality of the nanowires facilitate the random lasing.

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