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Electrically driven ultraviolet lasing behavior from phosphorus-doped p-ZnO nanonail array/n-Si heterojunction

Jun-Yan Zhang,^{a)} Qi-Feng Zhang, Tian-Song Deng, and Jin-Lei Wu^{a)}

Department of Electronics, Key Laboratory for the Physics and Chemistry of Nanodevices, Peking University, Beijing 100871, People's Republic of China

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Electrically driven ultraviolet lasing behavior from p-ZnO:P nanonail array/n-Si heterojunction was demonstrated. Phosphorus-doped ZnO nanonail arrays were grown by chemical vapor deposition method. The constructed heterojunction with indium tin oxide films as the contacted electrodes demonstrated clear rectifying behavior, and the turn-on voltage was about 2.5 V. The p-n junction lowered the excitation threshold effectively and the electrically driven ultraviolet lasing behavior exhibited high monochromaticity: when the applied forward current reached 24 mA, distinct ultraviolet laser emission peaks were obtained at room temperature, and the full width at half maxims were 0.7, 0.9, and 0.5 nm, respectively. The three sharp peaks represented different lasing modes. © 2009 American Institute of Physics. [doi:10.1063/1.3268438]

In virtue of relatively large exciton binding energy (60 meV) and direct wide band gap (3.36 eV) at room temperature, ZnO has been regarded as one of the most promising material candidates for ultraviolet light emitting diodes^{1–3} and laser devices.^{4–6} Recent optically pumped lasing action of ZnO nanomaterials has been achieved from ZnO film,⁷ particle,⁸ nanowire (nanorod, nanoneedle, nanoribbon, and nanonail),^{9–13} etc.¹⁴ Nevertheless, due to the deficiencies that the excitation sources were lasers and the power thresholds were high, the application field of these optically pumped ZnO lasers was restricted. To be employed more widely in technologies ranging from telecommunication, information storage to integrate circuit miniaturization,¹⁵ researches of electrically driven ZnO lasers with low excitation threshold are necessary to be promoted. Nevertheless, electrically driven lasing actions based on ZnO nanomaterials have few been reported,^{16–19} and these researches were restricted in random lasers of ZnO particles and films. Research of Huang *et al.*¹¹ confirmed that ZnO one-dimensional nanomaterials were ideal miniaturized laser light sources. In our experiments, p-n junctions based on ZnO one-dimensional nanonails were fabricated to lower the excitation threshold. Room-temperature electrically driven ultraviolet lasing behavior of p-ZnO:P nanonail array/n-Si heterojunction was demonstrated and exhibited high monochromaticity: under a low applied forward current 24 mA, distinct ultraviolet electroluminescence (EL) laser emission peaks, which centered at 386.8, 390.4, 394.0 nm, were obtained at room temperature, and the corresponding full width at half maximum (FWHM) were 0.7, 0.9, and 0.5 nm, respectively. The three sharp peaks represented different lasing modes.

Among various possible dopants, phosphorus has recently been reported as an efficient dopant to make p-type ZnO, and ZnO:P exhibited high carrier concentration, reasonable mobility, and low resistivity.^{20,21} We developed an effective and reproducible route to prepare phosphorus-

doped p-type ZnO nanonail array by chemical vapor deposition (CVD) method.²²

Field emission scanning electron microscopy (FE-SEM) (Tecnai XL 30 SFEG), which was showed as Fig. 1(a), clearly revealed the morphology of the ZnO nanonail array grown on the Si substrate. The diameters of the nanonail bodies ranged from 80 to 130 nm. The phase identification of the ZnO nanonail array was carried out by x-ray diffraction (XRD) using monochromatic Cu K α radiation ($\lambda=1.54$ Å) scanning between 10° and 80° (2 θ) at room temperature. The XRD pattern in Fig. 1(b) showed a strong and sharp peak

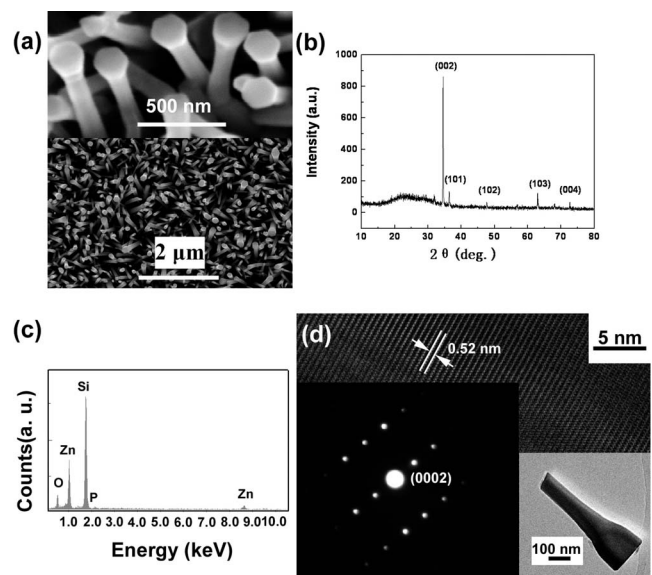


FIG. 1. (a) The SEM image of ZnO:P nanonail array grown on low resistivity n-Si substrate. The scale bars were 2 μm and 500 nm, respectively. (b) The XRD θ -2 θ profile of the ZnO:P nanonail array grown on the low resistivity n-Si substrate. The XRD pattern showed a strong and sharp peak from the (002) plane, which confirmed the high quality of single-crystal ZnO nanonails with the growth axis along the c -direction. (c) The EDX spectrum of the ZnO:P nanonail array grown on the low resistivity n-Si substrate. The existence of phosphorus dopants was confirmed. (d) The HR-TEM image taken from the single ZnO:P nanonail body. The inset was the electron diffraction pattern, which indicated that the ZnO nanonail was a wurtzite type structure grown along the c -axis direction.

^{a)} Authors to whom correspondence should be addressed. Electronic addresses: jacintazjy@pku.edu.cn and jlwu@pku.edu.cn. FAX: 86-10-62761333.

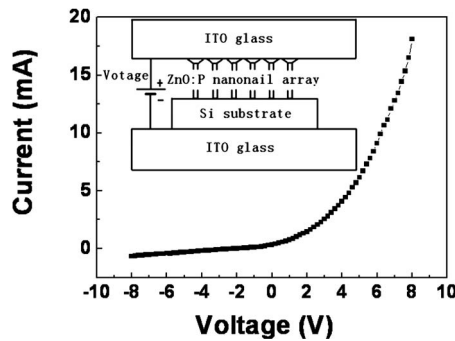


FIG. 2. Current-voltage curve of the p-ZnO:P nanonail array/n-Si heterojunction. The turn-on voltage was about 2.5 V. The inset showed the schematic diagram of the device structure of the p-ZnO:P nanonail array/n-Si.

from the (002) plane, which further confirmed the high quality of single-crystal ZnO nanonails with the growth axis along the *c*-direction.^{23,24} Furthermore, as shown in Fig. 1(c), the existence of phosphorus dopants were confirmed by an energy-dispersive x-ray spectroscopy (EDX) which attached to the FE-SEM.²⁵ By analyzing the spectrum with the software of the equipment, the content of phosphorus in the sample was quantified as P:Zn $\approx$ 1.5% (at. %). As shown in Fig. 1(d), the high-resolution transmission electron microscopy (HRTEM) image taken from the body of the nanonail showed perfect lattice structure, which further confirmed that the ZnO nanonail had good crystal quality. The small inset selected area diffraction pattern indicated that the nanonail was a wurtzite type structure grown along the *c*-axis direction.

With the voltage applied on the two sides of the sample, we could obtain the ultraviolet EL spectra. The device structure was simply illustrated as the inset of Fig. 2. The dimension of the sample (viz., Si substrate) was nearly 1×1 cm². Transparent conductive Indium Tin Oxide (ITO) films were closely pressed to the sample as the top and bottom contact electrodes. Meanwhile, the ITO glass and the sample were clamped together by two clips. The two clips were symmetrically distributed in order to avoid uneven pressure distribution. The top electrode, which connected with the ZnO:P nanonail array, was applied on a forward-bias voltage. Measured by a source meter (Keithley 6487), the corresponding current-voltage (I-V) curve of the samples was shown in Fig.

2. Clear rectifying behavior of the structure was observed. The turn-on voltage was about 2.5 V under forward-bias voltage and the reverse breakdown voltage was lower than -8 V. Therefore, the formation of p-ZnO/n-Si heterogeneous p-n junctions was confirmed by the I-V characteristics of the structure.

The EL measurement of the ZnO:P nanonail array/n-Si structure was performed at room temperature by a fluorescence meter (F4500 Hitachi), and the results were shown in Fig. 3(a). The EL spectra were obtained under a forward-voltage applied on the ZnO:P nanonail array. Under low excitation current 13 mA, a weak broad spontaneous ultraviolet emission with a FWHM of 10.5 nm began to appear. Following the increase in the current input, the intensity of the ultraviolet EL also increased correspondingly. When the current reached a certain value of 24 mA, lasing behavior appeared on the ultraviolet EL spectra. The three peaks centered at 386.8, 390.4, and 394.0 nm, respectively. It was remarkable that the FWHMs of the three peaks were 0.7, 0.9, and 0.5 nm, respectively (the minimum resolving power of the fluorescence meter was 0.2 nm), and the space of the peaks was 3.6 nm. The corresponding full spectrum in Fig. 3(b) exhibited following two independent bands: one strong near-band-edge emission centered at 390 nm was accompanied by a weak deep-level emission band around 510 nm. The weak greenish emission might be ascribed to the defects introduced by phosphorus doping and the residual oxygen vacancies or zinc interstitials. Above the threshold current input, the EL intensity increased rapidly with the increase in the current, as shown in the inset of Fig. 3(b).

No matter optically pumped lasers or electrically driven lasers, if the mechanism was that the electrons were excited directly from E_v to E_c of ZnO, the pump threshold was need to be high enough to overcome the energy gap ($E_g = 3.36$ eV). Whereas taking p-ZnO/n-Si junction into consideration, the excitation threshold would be lowered effectively. When the applied forward current on the p-ZnO was higher enough, the electrons were afforded to inject from n^+ -Si to p-ZnO, and the holes transferred in a reverse pathway meanwhile.^{26,27} Due to the existence of higher ΔE_c , the holes were available in abundance around the barrier of ZnO side. Then the combination probability was increased effectively. The spatial confinement of one-dimensional ZnO

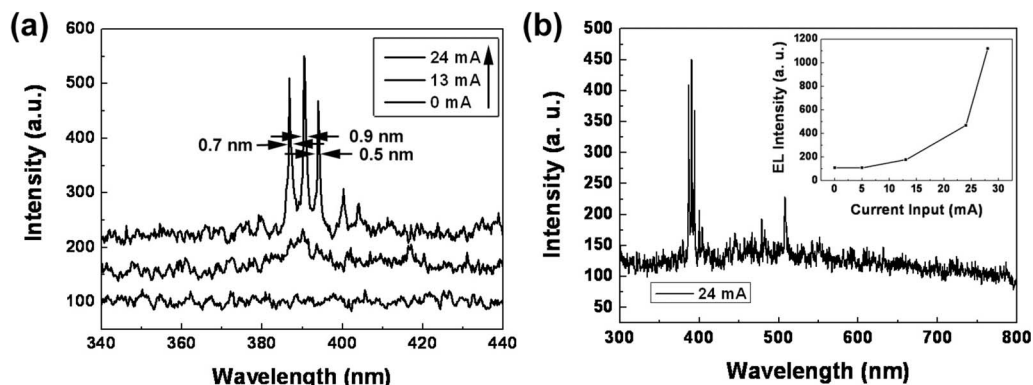


FIG. 3. (a) Ultraviolet EL spectra obtained from the p-ZnO:P nanonail array/n-Si structure with injection current of 0, 13, and 24 mA. The spectra were offset by 50 intensity units for clarity. When the current reached 24 mA, lasing behavior appeared on the spectra. The three peaks centered at 386.8, 390.4, and 394.0 nm represented different lasing modes. The FWHMs of the three peaks were 0.7, 0.9, and 0.5 nm, respectively (the minimum resolving power of the fluorescence meter was 0.2 nm), and the space of the peaks was 3.6 nm. (b) The whole EL spectrum of the p-ZnO:P nanonail array/n-Si structure when the corresponding applied current was 24 mA. The inset showed the EL intensity vs the corresponding applied forward-current.

also increased the binding energy and the life time of exciton, which both led to higher radiative recombination efficiency and lower current input threshold.

The narrow linewidth and the rapid increase in emission intensity indicated that stimulated emission took place.¹¹ The three sharp peaks represent different lasing modes at wavelength ranging from 386 to 394 nm. The electrically driven ultraviolet lasing behavior of p-ZnO:P nanonail array/n-Si heterojunction might be explained by the morphology characteristics of the nanonails. Well faceted nanonails were served as natural resonance cavities.^{10–12} When the ITO glass and the sample were clamped together by two symmetrically distributed clips, the top ITO film contacted the nanonails with an even pressure. In virtue of the pressure applied on the nailheads, those nanonails stood perpendicularly to the top and bottom electrodes, and formed several perfect Fabry–Perot type resonator cavities.¹¹ When the current input reached the threshold, the nanonailhead facet and the epitaxial interface between the Si and ZnO served as good laser cavity mirrors. The longitudinal modes spacing $\Delta\lambda$ can be determined by the equation $\Delta\lambda = (1/L)[(\lambda^2/2) \times (n - \lambda dn/d\lambda)^{-1}]$, where L is the cavity length, n is the refractive index of ZnO (2.45), λ is the resonant wavelength (~ 390 nm), and $dn/d\lambda \approx -0.015 \text{ nm}^{-1}$.^{28,29} The observed mode spacing 3.6 nm was calculated corresponding to the cavity length $\sim 2.5 \text{ }\mu\text{m}$.

In summary, we developed an effective and reproducible route to prepare phosphorus-doped p-type ZnO nanonail array by CVD method. Desirable rectifying behavior was observed from the current-voltage curve of the as-fabricated structure with transparent conductive ITO films as the top and bottom electrodes. The p-n junction lowered the excitation threshold effectively and the electrically driven ultraviolet lasing behavior exhibited high monochromaticity. It is really a feasible route to fabricate efficient monochromatic ultraviolet electrically driven laser devices based on phosphorus doped ZnO one-dimensional nanomaterials. These ultraviolet electrically driven laser devices would be employed more widely in technologies ranging from telecommunication, information storage, integrate circuit miniaturization to medical diagnostics and therapeutics.

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