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# Influence of annealing time on random lasing from ZnO nanorods

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## ABSTRACT

Highly stabile single mode and multi-mode random lasing emissions were observed from ZnO nanorods array prepared on glass substrates using chemical deposition technique. By varying the post-growth-annealing time, nanorod diameters between 54 and 78 nm with population densities between 75 and 95 nanorods/μm$^2$ were obtained. Depending on the population density and diameter of the nanorods, single, double and triple random lasing emissions were observed with lowest threshold of 209 mJ/cm$^2$. Furthermore, the lasing threshold showed an obvious dependency on the nanorods density. The lasing emission maintained its wavelength with increasing pump power, indicating high stability of the lasing mode(s).

## Introduction

Ultraviolet (UV) lasing from nanoscale structures and devices, specifically random lasers, have the added advantage of lasing without a conventional cavity made of mirrors. The "cavity" of a random laser is a result of light scattering in a random media [1]. In coherent random lasers, multiple modes of lasing appears above the broad spontaneous emission peak [2–6]. Various method have been proposed to control the number of modes or wavelength of such lasers, such as by introducing point defects using polymer particles [7], controlling absorption [8], and by changing the Mie resonances [9]. However, the control was towards the number of modes at a specific power and not in maintaining the same modes at different pump powers.

When the pump power is varied, random lasers typically show a shift in the wavelength and/or a change in the number of lasing modes [10–12]. Maintaining the same mode(s) in terms of number and wavelength with increasing power is of high interest for ultra-sensitive sensing that can be achieved by a random laser [13–15]. This has been just observed in liquid-based random lasers with dyes whereby polymer was incorporated with Rhodamine 6G as the gain medium [16]. However, dyes such as Rhodamine degrade with time. Hence, solid-based random lasers without dyes as the gain medium is favored for a stable and long lasting lasing emission. Consistent double-modes random lasing emission has been observed in vertical ZnO nanowire matt with increasing pump power [17]. However, mode competition and a shift in the mode(s) wavelength were observed. Thus, determining the amount of randomness to control the random lasing emission remains challenging.

Our present work provides a demonstration of a stable random lasing emission from ZnO nanorods array achieved by controlling the growth conditions of the samples, in particular the post-growth annealing time. The ZnO nanorods were prepared by chemical bath deposition (CBD) on pre-treated glass substrates. The pre-treatment process on glass substrates has been proven to be an effective approach to enhance the uniformity of the ZnO nanorods compared to the standard CBD process [18]. To reduce point-related defects, annealing was introduced in ambient air after the deposition. A previous report on random lasing from ZnO nanorods grown on pre-treated glass structures has showed that annealing is vital to obtain random lasing [19]. In our work, we investigated the effects of nanorod size and distribution on random lasing when the annealing time is varied. Lasing was observed in all studied samples, and the wavelength of the lasing mode(s) uncommonly maintained with increasing pump power. This indicates the stability of the mode(s) even with the presence of mode competition.

## Experimental methods

In our CBD technique, all chemicals were used without further purification, and the aqueous solution was prepared using deionized water. Glass substrates were pre-coated with a 150-nm-thick ZnO thin film using radio frequency (RF) magnetron sputtering. The CBD solution was prepared by mixing 0.05 M of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) with 0.05 M hexamethylenetetramine (HMT). The pre-coated substrates were vertically placed inside a beaker containing the solution. The solution was then heated in a binder oven for 3 h at a fixed temperature

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of 96 °C. The samples were post-growth annealed at 600 °C under ambient condition for 30, 60, 90, 120, 150 and 180 min respectively.

To investigate the morphology of the nanorods formed, field emission scanning electron microscope (FESEM) was utilized. Image J software was used to determine the average diameter and the population density of the nanorods. Random lasing measurements were performed using a micro- photoluminescence (μ-PL) system with an Nd:YAG pulsed laser source operating at 266 nm at a 20-kHz repetition rate with a 550 ps pulse width. The excitation focus was set to 8 μm in diameter. Continuous wave PL (cw-PL) measurements were performed using a 325-nm He:Cd laser source.

## Results and discussions

Fig. 1(a)–(f) shows FESEM images obtained for the studied samples annealed for 30, 60, 90, 120, 150 and 180 min, respectively. Well distributed nanorods with hexagonal heads are observed. The average nanorod diameter ranges between 53.6 nm and 78.2 nm while the nanorod population density ranges between 75 nanorods/$\mu m^2$ and 95 nanorods/$\mu m^2$. Some of the nanorods slightly incline from the c-axis; a similar behaviour has been reported in ZnO nanorods prepared by other simple methods like sol–gel [20]. A summary of the morphological properties for the studied samples is provided in Table 1. When the anneling time is increased, an increase in the mean diameter of the ZnO nanorods is observed, as shown in Fig. 2(a). A similar behaviour has been observed when ZnO nanorods were annealed under oxygen environment [21].

Fig. 2(b) shows the cw-PL spectra of the samples. All samples showed strong band edge emission at 378 nm with no emission in the visible spectral region, indicating minimal point defects in these samples. Quenching of deep level emissions due to defects have been reported in ZnO nanostructures annealed in air [22,23]. When the annealing time was increased, we observed an enhancment in the PL signal of the samples. However, the PL emission intensity decreases when the annealing time is longer than 90 min. Bidier et al. reported that annealing of ZnO nanorods at temperatures higher than 500 °C results in poor optical quality due to degradation of the crystalline quality [22]. It is likely that annealing of our samples for a time period longer than 90 min has created the same effect and hence reduced the band edge emission from these samples. A comparison of the crystallinity was done on samples annealed at 90, 120 and 150 min using X-ray diffraction (XRD) measurements (PANalytical X'Pert PRO MRD PW3040). Fig. 2(c) shows a zoom-in of the peak of the XRD patterns near 34.4° which is indexed to hexagonal wurtzite ZnO corresponding to crystal plane (0 0 2) [24]. A decrease in the peak intensity by a factor of 0.5 is obviously observed when the annealing time is increased from 120 min to 150 min. Furthermore, we obtained the average crystallite size, D, using Scherrer equation [25]:

$$D = \frac{k\lambda}{\beta cos\theta}$$

where $k$ is a constant with a value of 0.9, $\lambda$ is the radiation source wavelength (0.154 nm), $\beta$ is the full width at half maximum intensity (FWHM) and $\theta$ is the diffraction angle. The average crystallite size obtained for the samples annealed for 90, 120 and 150 min are 53.13 nm, 52.72 nm, and 47.43 nm, respectively. This decrease in the average crystallite size of the samples indicates degradation in the crystalline quality with increasing annealing time beyond 90 min.

Fig. 3 shows the random lasing emission from the ZnO nanorods under different pump powers. Upon the lasing threshold, the FWHM of the emission drastically shrinks from 15 nm to less than 0.6 nm. The threshold values and other lasing characteristics of the samples are summarized in Table 1. Interestingly, the lasing emission maintains its wavelength (no noticeable shift) with increasing pump power even though additional mode(s) appear(s) at some higher pump powers, e.g., Fig. 3(b) of the samples annealed for 60 min. Typically, when the pump power is varied, a shift in the laser wavelength is expected [26]. Furthermore, with increased pump power, the number of modes of random laser emission increases, associated with mode competition [27–32]. However, in some of our samples, e.g., ZnO nanorods annealed for 30 min, the single mode emission maintained with no addi-



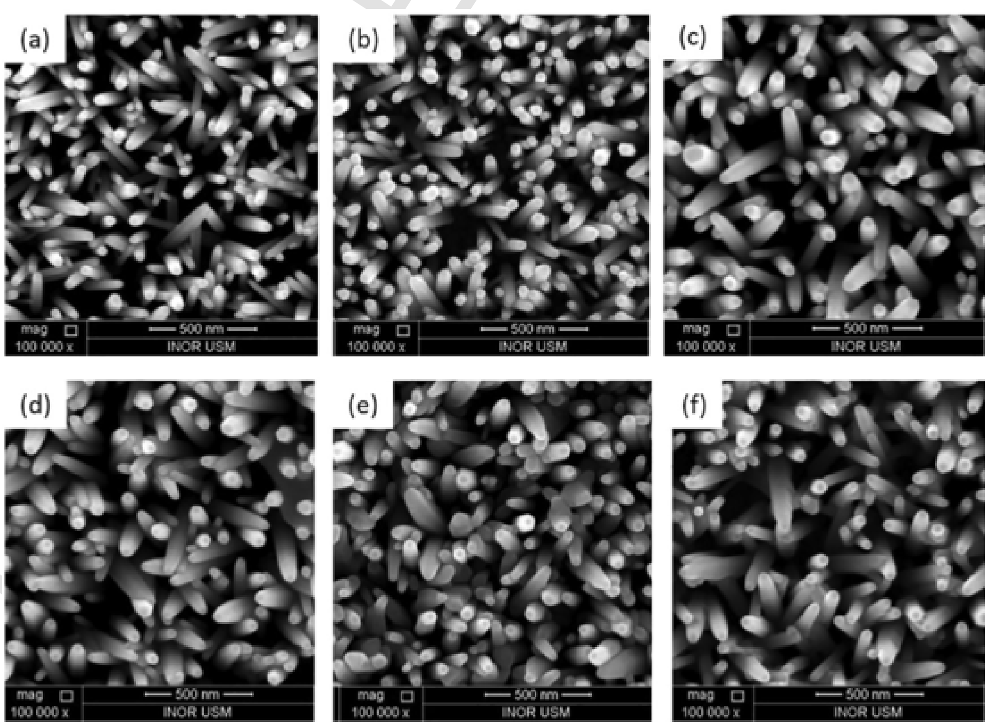


**Fig. 1.** (a)–(f) FESEM images of ZnO nanorods annealed for 30, 60, 90, 120, 150 and 180 min respectively. The nanorods have hexagonal tips with diameters ranging between 53.6 nm and 78.2 nm.

**Table 1**
Morphological and lasing properties of the studied samples.

| Annealing time (min) | 30 | 60 | 90 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|
| Average nanorod diameter (nm) | 53.6 | 60.7 | 67.2 | 74.3 | 75.4 | 78.2 |
| Threshold energy density (mJ/cm $^2$) | 209 | 209 | 259 | 259 | 209 | 209 |
| Population density (nanorods/µm $^2$) | 87 | 84 | 77 | 75 | 95 | 85 |
| Number of lasing modes | 1 | 2 | 1 | 1 | 3 | 2 |
| Estimated number of nanorods under excitation | 4736 | 4225 | 3873 | 3772 | 4779 | 4275 |

tional lasing modes with increasing pump power. To the best of our knowledge, no such observations have been reported for random lasing emission from ZnO nanostructures.

Fig. 4(a) shows the emission intensity of the first lasing mode as a function of the pump energy for the studied samples. Except for the sample with 120 min annealing time, increasing the annealing time does not reduce the lasing threshold. The lasing threshold as a function of the nanorod diameter is shown in Fig. 4(b). The threshold value first increases when the nanorod diameter increases from ~61 nm to ~67 nm, and then it decreases when the nanorod diameter increases above ~74 nm. This behavior contradicts with a previous work on random lasing from ZnO prepared by laser-induced hydrothermal synthesis in which the increase of the average particle diameter resulted in a reduced lasing threshold [33]. However, when the lasing threshold is plotted against the nanorod density, as shown in Fig. 4(c), we observed a tendency whereby increasing the nanorod density above 84 nanorods/µm$^2$ results in a reduced threshold. This tendency is in line with random lasing observed in other strongly scattered systems [1,34]. Our results suggest that the nanorod density plays a more important role for reducing lasing threshold and may be a key element to control random lasers based on nanorods.

## Conclusion

Random lasing has been observed from annealed ZnO nanorod array prepared on pre-treated glass substrates by chemical bath deposition synthesis. The lowest lasing threshold was observed at 209 mJ/cm$^2$ when the nanorod population density was below 84 nanorods/µm$^2$. For all samples, the lasing wavelength(s) did not shift with increasing pump power, indicating mode stability. It would be interesting for future investigations to find out the minimum number of nanorods required to achieve lasing and to further reduce the threshold for lower turn-on power.

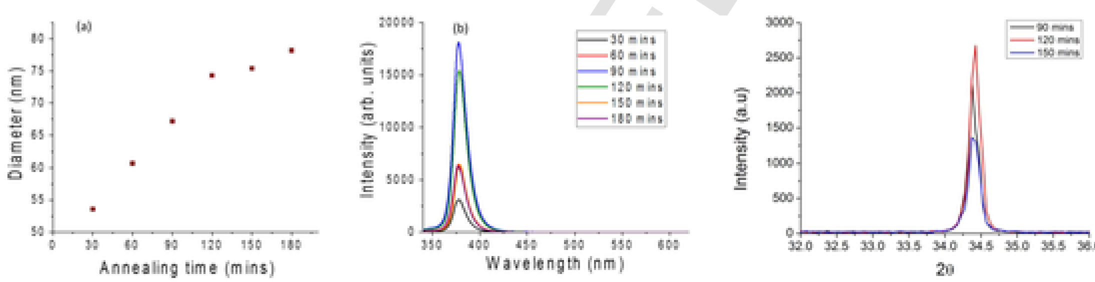


**Fig. 2.** (a) Annealing-time dependence of the mean diameter of the ZnO nanorods. (b) Emission spectra of all samples measured by CW laser source operating at 325 nm. (c) XRD diffractogram centered at 34.4 degrees of samples annealed for 90, 120 and 150 min.

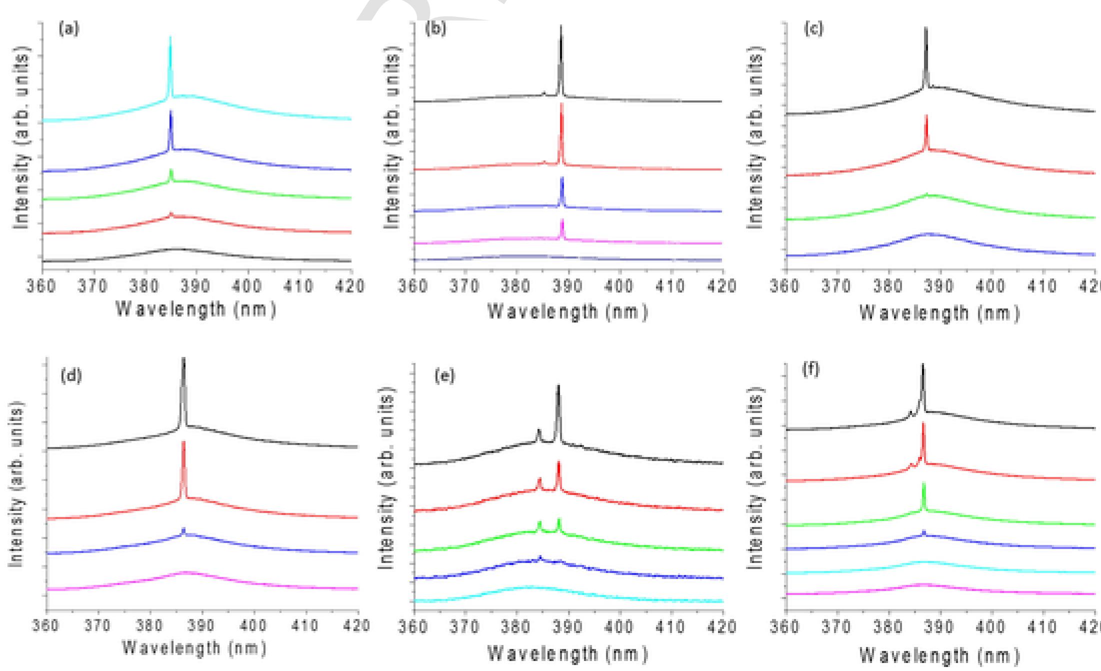


**Fig. 3.** (a)–(f) Random lasing emissions under different pump power for ZnO nanorods annealed for 30, 60, 90, 120, 150 and 180 min respectively.

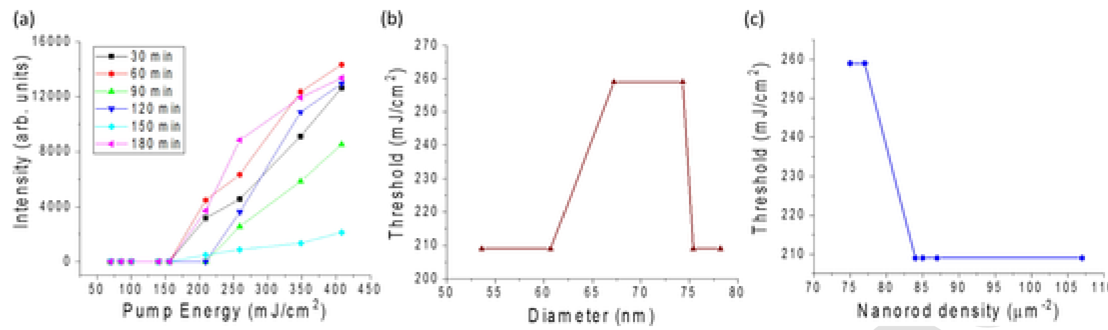


**Fig. 4.** (a) Emission intensity against pump power; (b) and (c) show the lasing threshold as a function of the nanorod diameter and density, respectively.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Author contribution

WM designed the experiment, did the optical measurements and drafted the manuscript. MKS did the lasing measurements and edited the manuscript. WM, MMH, MKS and MRH analysed the results. MNN prepared the sample and did the characterization measurements. All authors prepared the final manuscript.

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