ZnO nanorod array random lasers fabricated by a laser-induced hydrothermal synthesis

This content has been downloaded from IOPscience. Please scroll down to see the full text.

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 133.50.96.35
This content was downloaded on 26/10/2016 at 01:21

Please note that terms and conditions apply.
ZnO nanorod array random lasers fabricated by a laser-induced hydrothermal synthesis

Hideki Fujiwara, Takemasa Suzuki, Ryo Niyuki and Keiji Sasaki
Research Institute for Electronic Science, Hokkaido University, N20W10, Kitaku, Sapporo, 001-0020, Japan
E-mail: fuji@es.hokudai.ac.jp

Keywords: random laser, zinc oxide, nanorod array, hydrothermal synthesis

Abstract
We demonstrate random lasing in ZnO nanorod array (NRA) structures fabricated by a laser-induced hydrothermal growth, which would make it possible to control structural parameters, such as diameter, length, density and so on, by adjusting the laser irradiation time and intensity. To realize low-threshold ZnO NRA random lasers, we attempt to optimize the structure by changing the laser irradiation time (growth time). From the results, we confirmed that the fabricated ZnO NRAs after CO$_2$ laser annealing could induce UV random lasing and their thresholds strongly depend on the growth time. Thus, we succeed to realize ZnO NRA random lasers and suggest the possibility to control the random lasing properties by adjusting the irradiated laser conditions.

1. Introduction

Random lasers, which are induced by the interference effect of multiply scattered light and the existence of gain materials [1–5], have recently attracted attention as unique light sources based on their low spatial coherence property due to the randomness [6]. However, due to the randomness, there are several issues for their applications, such as the difficulties in the control of localized mode properties, efficient light input–output, electrode formation, and electrical pumping. For the modal control, we have proposed a method by use of resonant scatterers [7, 8] and experimentally demonstrated unique resonance-controlled random lasers realizing quasi-single mode and low-threshold random lasing [9–11]. Considering their potential applications such as light emitting and photovoltaic devices, it is necessary to achieve efficient input–output and electrical pumping. For this purpose, we paid attention to nanorod array (NRA) structures, in which comparing with the conventional random structures composed of agglomerated nanoparticles, in-plane light scattering by nanorods can realize photon localization, but in vertical direction where is an open system, it would be possible to make the efficient light input–output and electrode formation. Therefore, because the electrical conductivity of semiconductor NRAs can be better than agglomerated nanoparticles and NRAs can also be utilized as structures for supporting catalysts or dyes, it has been applied to not only electrically pumped random lasers [12–14], but also the fields of fluidic devices [15, 16], the light extracting/harvesting structures [17–19], sensors [20], and so on.

Recently, novel methods for selective hydrothermal growth of semiconductor NRAs have been proposed, in which joule-heating using a resistive nano-heater [21, 22] inkjet-printing of nanoparticle seeds [23, 24], or laser-assisted local-heating [15, 25–27] are utilized for selective thermo-chemical reactions. Comparing with conventional bulk heating method, these novel methods make it possible to fast, low-cost, and selective growth of NRAs, which are important advantages for realizing controlled assembly of nanorods onto the electrodes of nanorod/wire-based devices. Among these methods, we have paid attention to a laser-induced hydrothermal growth (LIHG) [15, 25–27], which is the method of promoting chemical synthesis of semiconductor NRAs by local heating of a laser that focused on a substrate. The fast heating/cooling process by the laser irradiation enables us to complete chemical reactions of NRAs around a limited laser-irradiated local area in a few minutes. Therefore, it would make possible to control the structural properties (diameter, length, density) of NRAs by adjusting the irradiated laser conditions, such as intensity, time, and solution concentration.
In this study, we experimentally succeeded to induce ZnO NRA random lasers fabricated by the LIHG and demonstrated that by changing the laser irradiation time (growth time), their lasing thresholds from ZnO NRAs having different mean diameters changed, which means that the resonant scattering of nanorods would improve the lasing properties of ZnO NRAs. In addition, it suggest the possibility that when we optimize the ZnO nanorod diameters by adjusting the fabrication conditions, the resonance-controlled random lasers can easily be realized even in NRA structures, like our previous studies using agglomerated mono-dispersive spherical ZnO nanoparticles [9–11].

2. Experiment

According to the previous studies [15, 25–27], we fabricated ZnO NRA structures. For the preparation of a precursor solution, 0.1 ml of hexamethylenetetramine aqueous solution (25 mM) was mixed with 0.1 ml of zinc nitrate hexahydrate aqueous solution (25 mM). The mixed solution was dropped on a glass substrate and covered by a cover glass with a 50 nm gold thin film. Then, as shown in figure 1, a 405-nm CW laser beam was focused vertically onto the gold thin film from the backside of the gold coating (2.0 kW cm$^{-2}$, 5–15 min) and ZnO NRA was grown in the area of the laser focusing spot (diameter ~ 50 μm) on the gold film. To investigate the influence of the structural parameters on random lasing properties, we fixed the irradiation laser intensity (~2 kW cm$^{-2}$) and changed the irradiation time from 5 to 15 min. After finishing the growth of ZnO NRA, the sample was rinsed by pure water and dried.

Figure 2 shows the SEM images of fabricated ZnO NRAs with different growth times and the summary of the average nanorod size against the growth time. When the growth time becomes longer (from 5 to 15 min), the mean diameter of nanorods increases from ~110 to ~210 nm. In addition, according to the increase in the nanorod diameter, the number density of nanorods decreases from 23.4 to 9.8 μm$^{-2}$. However, we note that, from the rough estimation of surface-filling factors from the mean diameters and number densities, even when the nanorod size becomes larger and the number density becomes smaller with the increase in the growth time, the surface-filling factor remains almost constant (~30%). From the SEM images of ZnO NRAs with different growth times, we confirmed that the nanorod lengths did not so much changed (about 1 μm), but the mean diameters of ZnO nanorods changed by changing the growth time, similar to the results in [15]. Thus, the LIHG could roughly control the scatterer size by the control of the laser irradiation time (growth time), which results were almost similar to the previous studies [26, 27].

The sample was set on a microscope stage and pulses of the excitation UV laser (355 nm, 300 ps, 1 kHz) were irradiated on the sample with the spot size of ~70 μm through an objective lens (N.A. = 0.9, 100x, Air).

![Figure 1. (a) Schematic of a laser-induced hydrothermal growth. (b) Microscope and (c) SEM images of fabricated ZnO NRA.](image-url)
Emission from the sample was collected by the same objective and was introduced into the spectrophotometer equipped with a high sensitive CCD camera to measure emission spectra. To observe the emission image, emission from the sample was detected by a color CCD. In order to examine random lasing, we repeatedly measure the emission spectra by changing the excitation intensity.

When we measured emission spectra from as-grown samples (figure 3(a)), we mainly observed broad green–red emission, neither UV emission intrinsic to ZnO nor UV laser emission could not be observed from as-grown ZnO NRAs. To improve the emission property of ZnO NRAs, the samples was annealed by the irradiation of a CW CO\textsubscript{2} laser (intensity $\sim$ 2 kW cm$^{-2}$, spot size $\sim$ 300 $\mu$m) for 60 s, by reference to [28], in which UV emission from a ZnO substrate was improved by scanning a CW CO\textsubscript{2} laser. When the emission spectra from the same samples after the laser annealing were measured again, we found that UV emission was much enhanced, but the broad green–red emission did not change and remained low emission intensity (figure 3(b)). Furthermore, we confirmed that no noticeable change in ZnO NRAs was observed by comparing the sample SEM images before

Figure 2. SEM images of fabricated ZnO NRAs with different growth times ((a) 5, (b) 7, (c) 10, (d) 13, and (e) 15 min). White bars indicate the scale of 1 $\mu$m. (f) Growth time dependence of mean diameters of ZnO nanorods. Irradiation laser intensity was fixed at $\sim$ 2 kW cm$^{-2}$ for each sample.
and after the laser annealing. Thus, after the fabrication of ZnO NRAs with different growth times, all samples were annealed by the CW CO₂ laser.

3. Result and discussion

Figure 4(a) shows typical emission spectra from a ZnO NRA with different excitation intensities (10, 18, 29 MW cm⁻²), which was fabricated with the growth time of 10 min. The inset shows the lasing emission image at the excitation intensity of 29 MW cm⁻². By increasing the excitation laser intensity, we observed that discrete sharp...
peaks appeared and laser oscillation could be induced in the ZnO NRA. From the plot of the emission intensity against the excitation intensity (figure 4(b)), the peak intensity steeply increased at the threshold intensity of 18 MW cm$^{-2}$. By repeating measurements for different NRAs, we observed similar results, in which lasing were initiated at the thresholds about 20 MW cm$^{-2}$ and the lasing wavelengths around 385 nm. Thus, we succeeded to induce UV lasing in ZnO NRAs.

From the simple estimation of mode spacing of Fabry–Perot cavity [29, 30], it was estimated to be about 20 nm, assuming that the nanorod length and refractive index were 1.5 μm and 2.3 μm. However, from the emission spectra, the peak spacing was much smaller (several nm or less) than the estimated value. In addition, according to [31, 32], we evaluated the equivalent cavity diameter to be about 25 μm from the power Fourier transformation of the random lasing spectra, which was much longer than the nanorod lengths. Thus, these results suggested the possibility that the observed laser oscillations were not induced in individual nanorods forming Fabry–Perot cavity, but by the multiple light scattering of ZnO NRAs (random lasers).

To examine the influence of the growth time on random lasing, the emission spectra from ZnO NRAs with different growth times (5, 7, 13, 15 min) were also measured (figures 5(a)–(d)). From the samples with the growth times from 7 to 15 min, we could observe laser oscillations, in which discrete sharp peaks appeared when the excitation intensity exceeded each threshold depending on the growth time. However, from the samples with the growth time of 5 min, we could not observe laser oscillation, even when the excitation intensity increased close to the damage threshold (∼100 MW cm$^{-2}$). To clarify the influence of the growth time on the random lasing property, we plotted the thresholds against the growth times (figure 5(e)). In the figure, we found that the lasing thresholds strongly depended on the growth time, in which the growth times of 7 and 10 min show the lowest thresholds (∼20 MW cm$^{-2}$) and, increasing the growth time, the thresholds became higher. However, we could not find laser oscillation from the samples with the growth time of 5 min, although the mean diameter of nanorods was about 110 nm that was slightly smaller than that with the growth time of 7 min. It has been

**Figure 5.** Emission spectra from ZnO NRAs with different growth times ((a) 5, (b) 7, (c) 13, (d) 15 min). The numbers in each figure indicate the excitation intensity. (e) Growth time dependence of lasing thresholds.
reported that random lasing thresholds are strongly dependent on the mean diameter of scattering nanoparticles [33, 34], in which when the particle mean size decreases from enough larger size, threshold gradually decreases and shows a minimum at a certain size and suddenly increases in the threshold with further decrease in the nanoparticle size. These behaviors have been explained by the particle mean size dependence of the transport mean free path, resulting in the change in the optical confinement and threshold [33, 34]. Like these previous studies, we considered that similar dependence of lasing thresholds on the nanorod mean diameter would be observed in our experiments. Therefore, in the case of larger nanorods (7–15 min), the thresholds changed and exhibited a minimum at the growth time of 7 and 10 min with changing the mean diameter. However, at the growth time of 5 min or less, we considered that because the mean diameter further decreased, the threshold would increase according to the mean diameter dependent mean free path and exceed the damage threshold of the NRA structure (∼100 MW cm⁻²), resulting that the laser oscillation was not observed.

4. Conclusion

In summary, we fabricated ZnO NRAs by use of the LIHG and succeeded to demonstrate UV laser oscillation in ZnO NRAs. From the results, lasing thresholds were strongly dependent on the growth time (laser irradiation time) and the samples with the growth times of 7 and 10 min exhibited the lowest thresholds of ∼20 MW cm⁻², while we could not observe any lasing action from the samples with the growth time of <5 min. Because the nanorod size could be controlled by the laser irradiation time (growth time), it would be possible to realize not only lowering the threshold, but also the control of lasing modes by use of the resonance properties of individual nanorods, like our previous proposed method using agglomerated size-monodispersed spherical ZnO nanoparticles [9–11]. In addition, we also found that the optimal CO₂ laser annealing was indispensable for inducing the laser oscillation in ZnO NRAs, which would improve the ZnO crystalline quality, resulting in UV emission efficiency. As long as we use a substrate that can absorb a laser and a material that can be synthesized by a hydrothermal/solvothermal synthesis, there is a possibility that this method can also be applicable to the fabrication of various semiconductor NRAs on any substrates. Therefore, because the fabrication of resonance-controlled NRA structures using the LIHG method would open the way to provide benefits to improve light confinement and harvesting as well as easy, low-cost, and selective fabrication, we believe that our findings would have the potential for technological applications related to optoelectronic and optofluidic devices, such as light emitting devices, sensors, photovoltaic devices, photocatalysis, and so on.

Acknowledgments

This work was supported by JSPS KAKENHI (Grant Numbers 15J01516, 16K13647, 26246028, 26600037, 16H06506), the Murata Science Foundation, the Amada Foundation, and the Cooperative Research Program of ‘Network Joint Research Center for Materials and Devices’. SEM images of ZnO NRAs were accomplished using a field emission scanning electron microscope system (JEOL, JSM-6700FT) at the Open Facility, Hokkaido University Sousei Hall. We thank T Shintaku for the measurement of SEM images.

Author Contributions

HF developed the concept for ZnO NRA random lasers. TS, RN, and HF carried out the lasing experiments. HF, TS, and KS discussed the results and wrote the manuscript.

References