Random laser behavior in Gold-doped Zinc Oxide nanorods structures

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Abstract. The random laser was investigated in gold-doped Zinc Oxide nanorods (Au-doped ZnO NRs) under a range of pumping power 0.25 - 4.66 mW. The Au-doped ZnO NRs prepared by chemical bath deposition (CBD) on the ZnO seed layer, were pre-coated on glass substrate using radio frequency magnetron sputtering (RF-sputtering ). The morphological of Au-doped ZnO NRs shows a hexagonal and strong vertically alignment against the substrate. The Energy dispersive spectroscopy (EDX) spectrum and elemental mapping results confirmed that Au atoms (at.%) are doped and spread over the ZnO NRs. More interestingly, the random laser of Au-doped ZnO shows a redshift of ~38 nm. This study showed the ability of using doping as a tuning parameter in the random laser, also provided an emphasis on Au-doped ZnO NRs as suitable options for controllable random laser devices.

Keywords: Doped ZnO nanorod; tunable emission; photonic devices; nanotechnology

1. Introduction

In recent decades, the random lasers has potential in many industrial and medical applications [1,2], due to their simple (mirrorless) structure [2,3]. This contrasts with conventional lasers, where the medium is placed in a custom optical cavity with a mirror. Random lasing phenomena are induced by multiple photons scattering in a disordered medium [4]. Threshold power, lasing tunability and directionality of guided wave plays an important role in determining a random laser characterization. On the other hand, a randomness of multi-scattering hinders the random laser from being easily controlled. A considerable amount of research on tunable random lasers has been conducted to move random lasers from theory to practical application [5–10]. Nonetheless, most reported research showed that the intensity of a random laser decreases as the temperature or applied voltage increased, which is far from practical use. in addition, most tuning parameters are external controls, like temperature, voltage, or electromagnetic wave, etc., not considered as suitable controls in terms of the embedded optoelectronic devices (like- photodetectors). However, despite these difficulties, the tuning random laser using doping technique is more reliable in terms of low-cost and applicability.

Random laser has been investigated in different nanostructure materials, such as, ZnO [11], GaAs [12], ZnSe [13], as well as organic molecules [14,15] have been used as scattering medium for random
lasing. On the other hand, the simplicity and low-cost fabrication techniques of the nanostructured materials, such as ZnO profile, bringing a random laser as an attractive candidate for employment in a various range of light-emitting devices [1].

The UV lasing induced by ZnO nanostructures has stimulated a great deal of interest due to its wide range applications for UV devices. As well as large bandgap (3.37 eV) and having high excitonic binding energy (60 meV) [16–18], the ZnO considered is an attractive lasing material, and the hexagonal ZnO nanorods (NRs) with high crystallinity and the ability to doped with group-IB elements, could be fabricated in simple methods, such as chemical bath deposition [19–22]. In this paper, the random laser investigated by Au-doped ZnO nanorods were fabricated by low-cost method (CBD), under a sequence of pumping power to study the threshold and tunability of the random laser emissions.

2. Experimental procedure
Au-doped ZnO NRs were synthesized via CBD. A thin film (100 nm) of ZnO seed layer was coated on glass slide (25mm×10mm×1.2 mm) by RF-magnetron sputtering. Then, the samples were heated in the furnace at 350°C for 1 hour under air ambient. Next, an aqueous solution of 1:1 (0.08M) zinc nitrate [Zn(NO$_3$)$_2$.6H$_2$O] and Hexamethylenetetramine [HMT; C$_6$H$_12$N$_4$] was stirred for half an hour. At the same time, another aqueous solution of 0.008 M of gold chloride [HAuCl$_4$.4H$_2$O] were stirred separately for 30 minutes. Then, both solutions were mixed, and stirred for a further 15 minutes and poured into semi autoclave glass bottles. The sample was positioned 45° faced down against bottle wall, And the caps were secured tightly. Afterwards, the glass bottles were left in an oven already preheated at 80°C for 4 hours. Finally, the samples were collected from the glass vials, rinsed with distilled water multiple times, and then slowly dried with high-purity nitrogen.

The morphological and compositional variations of the samples were determined using field emission scanning electron microscope (FESEM; Nova NanoSEM 450, FEI, Japan) coupled with energy dispersive X-ray (EDX). The random laser measurements were carried out using a micro-PL system equipped with a Nd:YAG pulsed laser source operating at 355 nm, 1 KHz repetition rate, and pulse width of 350 ps. The sample holder was mounted on a three-axis translational stage to concentrate the laser light on the sample, which was viewed through a camera positioned at an angle from the sample holder. The laser emission was captured by optical cable that was linked to a spectrograph with a liquid-N2 CCD array detector. All tests were carried out at room temperature, and the beam spot size set at about 100 µm in diameter.

3. Results and discussion
FESEM top view and cross section as-grown Au-doped ZnO NRs are presented in figure 1(a-b). As observed, the average nanorods diameter of doped sample is around 380 nm while the average length is about 1.85 µm. The surface morphology of the Au-doped ZnO NRs has a hexagonal shape and is vertically aligned against the surface of the substrate. However, the Au-doping has no discernible effect on the morphology of ZnO nanorods. Nonetheless, compositional analysis of the sample using EDX (figure 1(d)) confirms the presence of elemental gold (< 0.2 %atomic) in ZnO NRs. This low atomic percentage is due to the relatively low concentration of gold chloride in the precursor solution as compared to zinc nitrate during the synthesis. Figure 1(c) obtain corresponding Zn, O and Au EDX mapping images. These EDX mapping images reveal that Au atoms were distributed uniformly inside ZnO NRs.
Figure 1: (a-b) top view and cross section of Au-doped ZnO NRs, (c) Elemental mapping images of Au-doped ZnO nanorods sample, and (d) EDX results showing the atomic percentage of elements in the sample.

Figure 2 shows the lasing emission with different pumped powers applied in the Au-doped ZnO NRs samples. The minimum lasing threshold value was 1.13 mW. Also, we founded the intensity of lasing peaks was increased upward against decreasing FWHM with increasing pump power (figure 2b). Interestingly, when the doped sample is pumped above 4 mW, the lasing peak shifted to ~38 nm, towards the visible wavelength range. The incorporation of the foreign atoms into a semiconductor structure acts to broaden the valance band, which in turn leads to narrow or contraction of the bandgap states [23]. As a Group-IB element, the occupied d orbital energies of Au are close to the oxygen p level, and both the O p and Au d orbits exhibit t2 symmetry in the tetrahedral environment. [19]. When the Au atom is doped in Zn, the strong p-d coupling between Au and O occurs, raising the O 2p level up and reducing the direct fundamental bandgap. Therefore, the narrowing bandgap in the Au-doped ZnO structure leads to the shifting of lasing peaks towards the higher wavelengths. But in our study, the shifting occurs only at high pumping powers. Ryo Niyuki et al, reported for the first time, a red-shift of lasing peak founded in ZnO nanoparticles when the excitation intensity increased above 10 MW/cm² [24]. This lasing peak transition was explained due to the involvement of exciton recombination. However, with high enough excitation power, and with existing Au atoms doped in ZnO structure, which might be causing more exciton recombination, especially at the O 2p level that affected by Au d orbit, and the transition to lasing photon with population inversion will occur at the lowered energy levels, thus the lasing peaks transitions to the higher wavelength regions.
Figure 2: (a and c) Optical pumping power dependence lasing measurement from Au-doped ZnO NRs, and (b) FWHM and the highest intensity lasing mode that appeared at different pump powers

4. Conclusion
Au-doped ZnO NRs were synthesized via (CBD) at 80°C growth temperature. The hexagonal Au-doped ZnO NRs deposited on glass substrates were vertically well aligned. The compositional analysis of the sample using EDX elemental gold (< 0.2 %atomic) in ZnO NRs and the EDX mapping images reveals that Au atoms were distributed uniformly inside ZnO NRs. The minimum random lasing threshold value is 1.13 mW, and we noticed that the intensity of lasing peaks was increased upward versus decreasing of FWM with increasing the pumping power. Moreover, changing the power pumping, shifted wavelength, giving tunability about ~38 nm. This study showing that Au-doped ZnO NRs is the promising candidate for controlling the random lasing device.

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