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Synthesis, morphology and random laser action of ZnO nanostructures

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Abstract

Three-dimensional (3-D) ZnO random-wall nanostructures and one-dimensional (1-D) ZnO nanorods were prepared on silicon substrates by a simple solid–vapour phase thermal sublimation technique. Optical pumped random lasing has been observed in the ZnO random-wall arrays with a threshold intensity of 0.38 MW/cm^2 in the emission wavelength from 380 to 395 nm. The optical gain was attributed to the closed-loop scattering and light amplification of the ZnO random-wall. The experimental result suggests that the morphology of nanostructure is the key factor to effect random lasing.

Keywords: S.3. Evaporation and sublimation; M.1. Zinc oxide; M.2. Nanostructure; M.3. Semiconducting surfaces; Random lasing

1. Introduction

Znic oxide (ZnO) with a wide band gap (~3.37 eV) and a large exciton binding energy (~60 meV), is one of the most promising candidates for the development of ultra-violet (UV) optoelectronic at room temperature [1]. Compare to its main competitor, GaN, ZnO has several significant advantages, such as larger exciton binding energy, high-energy radiation stability, and amenability to wet chemical etching. Ever since the discovery of UV lasing emissions from ZnO nanowires [2], much attention has been paid to the stimulated emission from ZnO nanostructures. Amplified spontaneous emission (ASE) and lasing have been achieved from ZnO thin films fabricated by filtered cathodic vacuum arc (FCVA) technique [3,4], laser molecular beam epitaxy (MBE) [5], metalorganic chemical vapour deposition [6], pulsed laser deposition (PLD) [7], and ZnO nanoneedles [8]. The requirements of complicated vacuum equipment, expensive substrate may limit the use of ZnO for UV optoelectronics. Therefore, it is necessary to develop an alternative technique to achieve low-cost, high quality ZnO thin film or nanostructure for UV random laser. In this work, we describe the use of a solid–vapour phase thermal sublimation technique in tube furnace to fabricate low-cost and mass-production of ZnO 3-D random-wall structure on $ZnO/SiO_2/Si$ substrate without any catalyst and additive. The effects of some parameters on laser action, such as: crystal quality, morphology and masking pattern, were investigated systematically. Random laser action with coherent feedback has been firstly observed under 355 nm optical excitation with threshold pumping intensity 0.38 MW/cm^2 in ZnO 3-D random-wall

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nanostructure. To the best of our knowledge, this is the first report on 3-D ZnO nano-wall random lasing.

2. Experiment

ZnO nanostructures were synthesized on silicon substrate by a simple method of thermal evaporation of ZnO powder mixed with graphite in a horizontal quartz tube furnace. The key steps in the synthesis process include (i) the formation of a 400-nm-thick SiO_2 on Si by thermal oxidation; (ii) the deposition of a 300-nm-thick ZnO thin film by helicon magnetron sputtering; (iii) the growth of ZnO nanostructures in the tube furnace through thermal evaporation. There are two roles for employing SiO_2 layer: (a) to get high quality of ZnO film by reducing the mismatch between ZnO and Si; (b) the thick SiO_2 layers ensures the confinement of the light in a waveguide structure for the laser action measurement.

Zinc oxide powders (high purity chemicals, 99.9%) and graphite powders (high purity chemicals, 99.9%) were mixed together and spread in the middle of a horizontal quartz tube, while the substrate was placed in the bottom of the tube in order to adjust the vapour transport direction. Then the tube was inserted into the horizontal furnace. The parameters, such as: total pressure, gases, heating time, heating temperature, molar ratio of raw materials, are optimized. The optimal experimental conditions are summarized in Table 1 on the synthesis of samples for random lasing measurement. "Patterning" denotes ZnO thin film was masked by using Cu mesh in the sputtering process. ZnO powders of 500 mg mixed with graphite of 20 mg were used as raw materials. The temperature of furnace was 1000 °C and the oxygen flow was 150 ml/min, respectively. Graphite powders and its reaction resultants with oxygen, carbon oxide (CO), acted as reduction agents during the formation of ZnO products. ZnO powders were reduced into Zn or its sub-oxide (ZnO_x, $x < 1$) with low melting point in vapor phase, which acted as nuclei of ZnO nanorods [9].

The morphology of nanostructure was observed by scanning electron microscopy (SEM). The crystal quality was evaluated by X-ray diffraction (XRD) and photoluminescence (PL). The random laser action of ZnO nanostructure was studied under optical excitation by a frequency-tripled Nd:YAG laser (355 nm) at pulsed operation (6 ns pulse width, 10 Hz). Optical pump was achieved by using a cylindrical lens to focus a pumping strip of 5 mm length and 60 μm width onto sample. A polarization was set before the detector in order to analyze the polarization properties of lasing light.

Table 1
The fabrication conditions of the samples for laser action measurement

Sample no.	Substrate temperature (°C)	Heating time (min)	Patterning
a	630	30	×
b	730	30	○
c	730	30	×

3. Results and discussion

3.1. SEM images

Fig. 1 shows the SEM images of samples *a*, *b* and *c*, respectively. Except sample *c*, samples *a* and *b* display vertically well aligned nanorods with averaged diameters in ~100–200 nm, and the lengths range from 500 to 1700 nm. Although the substrate temperature is a little different, the main difference between samples *a* and *b* is the patterned growth for sample *b*. Selective nanorod growth has been readily achieved by patterning the ZnO thin film during sputtering process before vapor deposition as shown in Fig. 1b. The SEM image in Fig. 1d for sample *c* shows quite different in morphology due to the rough surface of the ZnO thin film on Si/SiO_2 substrate. Any isolated nanorod is not observed in sample *c*, and the nanorods are coalesced to form the honeycomb wall with 80–100 nm in thickness, about 1700 nm in depth. The cavities with 20–200 nm in diameters are holed throughout the layer. We call this structure as 3-D random-wall structure. Hexagon-end planes of the nanorods can be clearly identified in the SEM images in Fig. 1a and c, providing strong

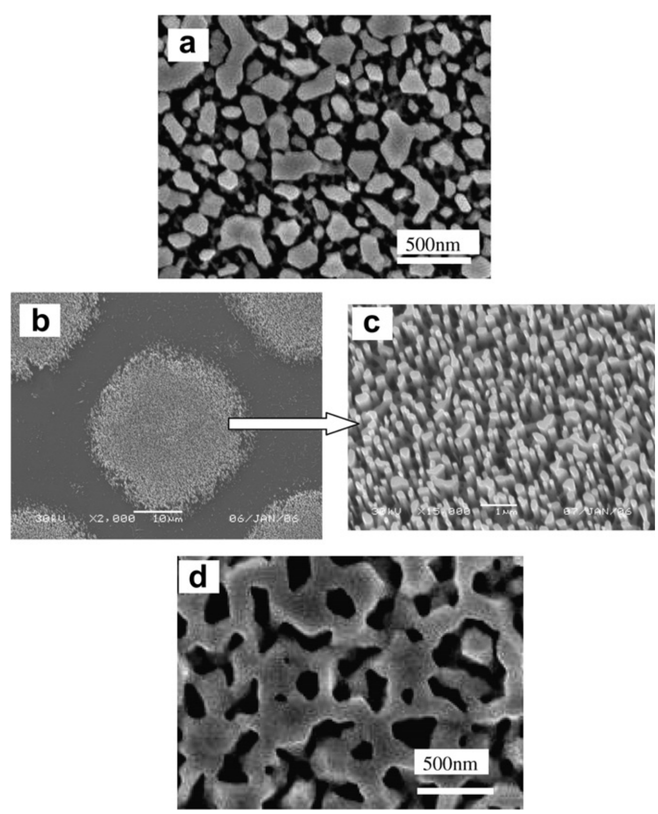

Fig. 1. SEM images of ZnO nanostructures synthesized in the conditions listed in Table 1. (a) Image of nanorods, (b) low-magnified image of nanorods with mesh patterning, (c) high magnified image of (b), and (d) image of nano-wall, respectively.

evidence that these nanorods grow along the [0001] direction. Because of the good epitaxial interface between ZnO nanorods and ZnO thin film substrate, nearly all of the nanorods grown vertically from the substrate. The growth direction along the [0001] direction is further confirmed by XRD results.

3.2. Laser action

Room temperature optical characteristics of ZnO nanostructures were studied under optical excitation. Fig. 2 exhibits the emission spectra of samples *a*, *b* and *c* under pumping power of 0.8, 0.38 and 0.8 MW/cm^2, respectively. For samples *a* and *b*, the spectra consist of a single broad spontaneous emission peak (amplified spontaneous emission, ASE) with a full width at half maximum of ~20 nm although under high pumping power as shown in Fig. 2a and b. On the other hand, the spectrum of sample *c* in Fig. 2c shows narrow emission peak under pumping power of 0.38 MW/cm^2. Fig. 3 gives the evolution of emission spectra of the ZnO 3-D random-wall as a function of pumping power. Below the threshold, ASE was observed. When the pump power reached a threshold as high as 0.38 MW/cm^2, a dramatic emission oscillation in a line width as narrow as 0.4 nm emerged from the single-broad emission spectra. As the pumping power increased, multiple laser modes with strong coherent feedback at the wavelengths between 375 and 395 nm were detected. This phenomenon of emission spectra was attributed to random lasing with coherent feedback.

There are two theories on the mechanism of random lasing so far: (1) the closed-loop paths formed through multiple scattering by media (i.e. ZnO powders) serve as lasing cavities [10]. (2) Well-faceted end planes of nanowires (i.e. hexgonal end planes of ZnO) and substrate with high refractive index (i.e. sapphire) were reported as conventional Fabry–Perot (FP) laser cavities [2]. There is still discussion among the experts of this field on the credibility and/or reliability of two mechanisms. Both two cases have not happened in the lasing results of ZnO nanorods for samples *a* and *b*. One reason may attribute to the dissatisfaction of diameter and density of the grown nanorods for the conditions to form closed-loop paths, and the other one may account to low refractive index of the substrate which can not form FP laser cavities with well-faceted end planes of nanorods.

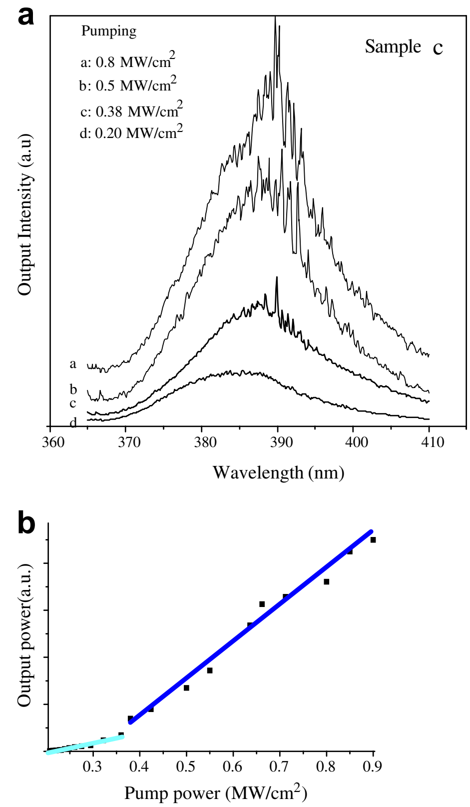

Fig. 3. (a) Evolution of emission spectra of ZnO nano-walls under different pump intensities, and (b) light–light curves of ZnO nano-walls.

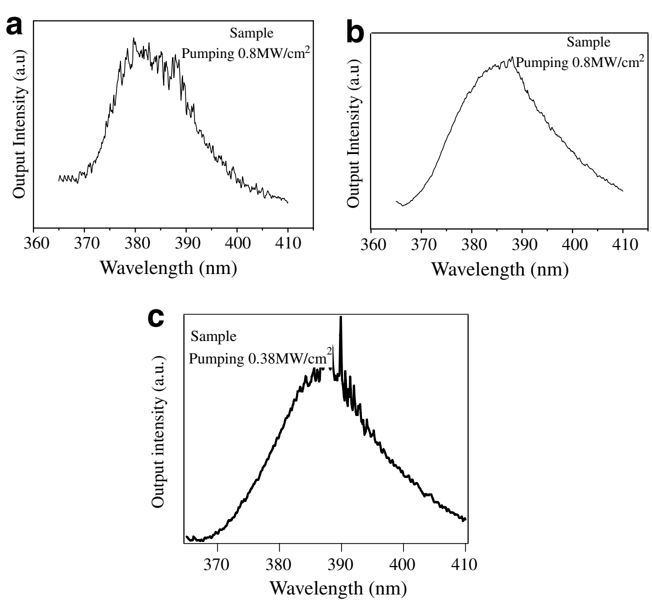

Fig. 2. Emission spectra of (a) ZnO nanorods, (b) patterned nanorods, and (c) nano-walls under pumping power of 0.8, 0.8 and 0.38 MW/cm^2, respectively.

Random laser action was observed only for sample *c*. No laser action can be found for the other well-aligned nanorods even they show strong near band edge emission in photoluminescence spectra due to their high crystal qualities. It is worthwhile to note that we have observed the reproducibility by other samples with similar 3-D morphology. The lasing result indicates the morphology of ZnO is the key parameter for controlling random lasing action. Compared the lasing result of sample *a* with that of *c*, the lasing cavities of sample *c* are considered to realize through multiple scattering by the walls of the fabricated 3-D nanostructures, not between the well-faceted end-planes of the wall structure and substrate. In an active random medium, light is scattered and undergoes a random walk before leaving the medium. When scattering gets stronger, after multiple scattering light may return to the scattering center from which it was scattered before, forming a closed-loop path for light. When the amplification along the loop reaches the loss, lasing oscillation occurs in the loop which serves as a cavity [11]. In our case, the lateral facets of the irregular ZnO nano-wall or scatters can provide a strong optical scattering that forms closed-loop paths of light (laser cavities). The band gap of ZnO determined the wavelength of the random laser. When the high quality ZnO nano-wall was excited by Nd:YAG laser (355 nm), strong near band edge emission can observe at about 380 nm.

The threshold pump intensity of ZnO 3-D nanostructure (0.38 MW/cm^2) was comparable to that of ZnO nano-needles (0.35 MW/cm^2) [8] and ZnO thin films annealed at 900 °C (0.32 MW/cm^2) [3]. The relatively lower pump threshold of ZnO 3-D random-wall structure compared to ZnO nanorods arrays embedded in ZnO epilayers (0.8 MW/cm^2) was due to the high crystal quality of the grown nano-wall. From both our experimental results and reported Ref. [11], the crystal quality of the sample which determines the band edge emission, and scattering length, gain length, and sample size are considered to be responsible for the threshold of the random lasing. Our result was also significant due to the ZnO 3-D random-wall structure could be synthesized by a simple method of thermal evaporation of ZnO powder mixed with graphite in a horizontal quartz tube furnace.

As this random-wall structure shows no aligned groove, there is no significant difference between the feedback intensity of polarization on transverse electric (TE) and transverse magnetic (TM).

4. Conclusions

As conclusions, 3-D random-wall nanostructure and well-aligned ZnO nanorods were densely grown on ZnO thin film using Si substrate without any catalyst and additive by a simple method of thermal evaporation. The experimental result suggests that the morphology is the key parameter for controlling random lasing. Closed-loop scattering and coherent amplification of lights are realized by 3-D random-wall nanostructure with a threshold of 0.38 MW/cm^2. This lower pump threshold is attributed to the relatively stronger optical scattering among ZnO thin film and ZnO interface of the designated 3-D structure. It is note that the 3-D random-wall structure can be easily achieved by a solid–vapour phase thermal sublimation technique on Si substrate. Therefore, our method to fabricate mirrorless UV lasers on silicon substrate is unique and this will make the mass production of low-cost UV lasing sources and their integration with silicon-based electronics feasible.

References

[1] S.F. Yu, Clement Yuen, S.P. Lau, Y.G. Wang, H.W. Lee, B.K. Tay, Appl. Phys. Lett. 83 (21) (2003) 4288.
[2] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science 292 (2001) 1897.
[3] S.F. Yu, Clement Yuen, S.P. Lau, H.W. Lee, Appl. Phys. Lett. 84 (17) (2004) 3244.
[4] Clement Yuen, S.F. Yu, S.P. Lau, George C.K. Chen, J. Cryst. Growth 287 (2006) 204.
[5] Z.K. Tang, G.K.L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Appl. Phys. Lett. 72 (1998) 3270.
[6] X. Wu, A. Yamilov, X. Liu, S. Li, V.P. Dravid, R.P.H. Chang, H. Cao, Appl. Phys. Lett. 85 (2004) 3657.
[7] H. Cao, Y.G. Zhao, H.C. Ong, S.T. Ho, J.Y. Dai, J.Y. Wu, R.P.H. Chang, Appl. Phys. Lett. 73 (1998) 3656.
[8] S.P. Lau, H.Y. Yang, S.F. Yu, H.L. Li, M. Tanemura, T. Okita, H. Hatano, H.H. Hng, Appl. Phys. Lett. 87 (2005) 013104.
[9] B.J. Chen, X.W. Sun, C.X. Xu, B.K. Tay, Physica E 21 (2004) 103.
[10] H. Cao, Y.G. Zhao, S.T. Ho, E.W. Seelig, Q.H. Wang, R.P.H. Chang, Phys. Rev. Lett. 82 (1999) 2278.
[11] H. Cao, J.Y. Xu, L. Yong, A.L. Burin, E.W. Seeling, L. Xiang, R.P.H. Chang, IEEE J. Sel. Top. Quant. Electron. 9 (1) (2003) 111.