Sol–Gel ZnO–SiO_2 Composite Waveguide Ultraviolet Lasers

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***Abstract*—Random laser action with coherent feedback is realized in ZnO–SiO_2 composite films, which consists of ZnO clusters embedded in SiO_2 dielectric matrix prepared by sol–gel technique. The films are deposited on silicon substrate with a SiO_2 buffer layer to form a waveguide structure. Ultraviolet lasing at room temperature is observed from the composite films with ZnO : SiO_2 molar ratio varying between 1 : 5 and 1 : 30. The corresponding lasing wavelength and linewidth under 355-nm optical excitation are found to be ~388 nm and less than 0.6 nm, respectively. Our experiment has shown that the proper control of light confinement inside the random cavities leads to coherent random lasing.**

***Index Terms*—Random lasing, sol–gel waveguide, zinc oxide.**

RANDOM LASER action has been observed in semiconductor particles dispersed in inert inorganic matrices [1]–[4]. Active random media used for these random lasers can be the composition of active particles (i.e., ZnO) and passive hosts (i.e., polymers–dielectric matrices). Experiments have shown that ZnO–SiO_2 (with ZnO : SiO_2 molar ratio of 20 : 80 and Zn : Si molar ratio of 1 : 10) composite films demonstrated high ultraviolet photoluminescence [1], [2]. Incoherent random lasing is also observed from ZnO-epoxy (with 30% of ZnO) composite films under high optical excitation [3], [4]. However, the realization of coherent random lasing in such random cavities requires high concentration of ZnO particles [5]. This is because low concentration of ZnO particles does not provide sufficient optical gain and three-dimensional light confinement (i.e., by scattering) to sustain closed loop paths of light. In this letter, a ZnO–SiO_2 composite waveguide laser is designed and fabricated by using sol–gel technique. It is shown that if the optical confinement of ZnO–SiO_2 composite films is properly controlled, coherent random lasing can be achieved even at low concentration of ZnO particles.

The proposed ZnO–SiO_2 composite waveguide laser is shown in Fig. 1. A SiO_2 buffer layer (of refractive index ~1.45) is inserted between the composite film (of effective refractive index varying between 1.5 and 1.9, depending on the concentration of ZnO powder) and Si substrate so that transverse optical confinement can be achieved in the composite film with minimal absorption loss. Hence, light can only be scattered in a direction parallel to the surface of the composite films (i.e., two-dimensional light confinement).

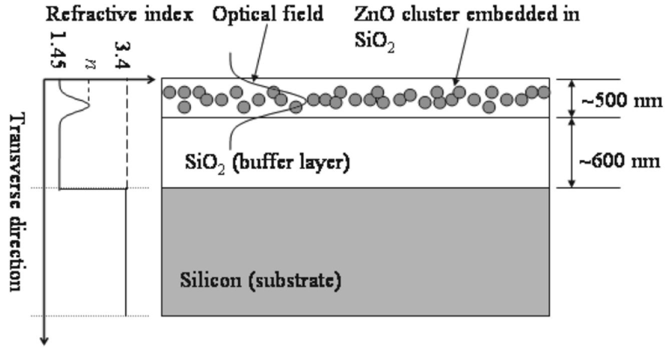

Fig. 1. Schematic of a ZnO–SiO_2 composite waveguide laser. The peak effective refractive index n is varied between 1.5 and 1.9, depending on the molar ratio of ZnO : SiO_2.

In the sol–gel fabrication of the ZnO–SiO_2 composite film, tetraethylorthosilicate (TEOS) was mixed with two-propanol before the addition of water and nitric acid. TEOS acts as the precursor for silica and two-propanol as the solvent. Nitric acid and water are meant for hydrolysis process. The molar ratio of TEOS : two-propanol : water was fixed at 1 : 10 : 4 while that of ZnO : SiO_2 was varied from 1 : 5 to 1 : 30. The resulting sol was then stirred at room temperature for 4 h before the addition of ZnO powder (ZnO Puratronic, Alfa Aesar, of average diameter 120 nm). After aging the mixture for another 20 h, the ZnO embedded SiO_2 thin film of ~500 nm thick was deposited by spin coating at 3500 rpm for 30 s on the Si (100) substrates with SiO_2 buffer layer of ~600 nm. After deposition, the ZnO–SiO_2 composite films were annealed in furnace at 950 °C in open air for 5 min. It is noted that ZnO clusters are formed on the SiO_2 surface with a parallel-stripe pattern, as evident in Fig. 2 and the stripe spacing increases with the molar ratio.

The optical characteristics of ZnO–SiO_2 composite waveguide lasers at room temperature were studied under optical excitation by a frequency-tripled Nd : YAG laser (355 nm) at pulsed operation (6 ns, 10 Hz). Optical pump was achieved using a cylindrical lens to focus a pumping stripe of length ~0.5 cm and width ~400 μm at an angle, θ, to the parallel-stripe pattern of ZnO clusters to realize random laser action with coherent feedback. Fig. 2(c) and (d) shows the possible mechanism of two-dimensional light confinement inside the ZnO–SiO_2 composite waveguides under optical excitation. The ZnO clusters act as scatterers with gain to scatter the light to form a closed loop path along the pump stripe. The light emitted from the edge of the samples was then collected by an objective lens coupled to a monochromator. It is noted that for small θ, light is almost propagating parallel to the stripe patterns of the ZnO clusters so that long travel-distance of

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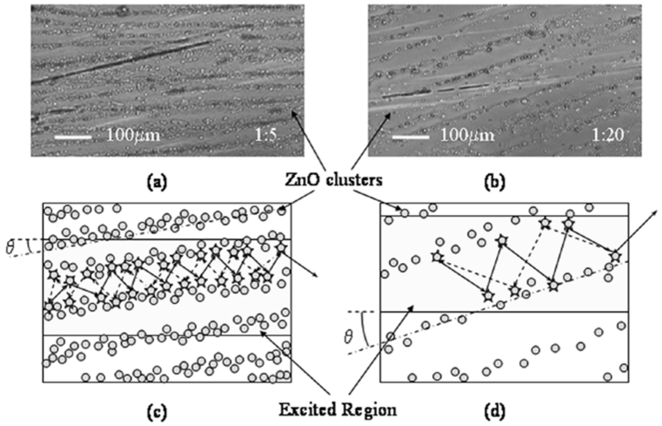

Fig. 2. Macroscopic pictures of the surface of the ZnO–SiO$_2$ composite films with molar ratio of (a) 1 : 5 and (b) 1 : 20 taken at ×5 magnifications. Schematic of the formation of one possible closed loop path of light inside the ZnO–SiO$_2$ composite films with molar ratio (c) 1 : 5 and (d) 1 : 20 under optical excitation. θ is the angle between the parallel-stripe pattern of the ZnO clusters and the pump stripe.

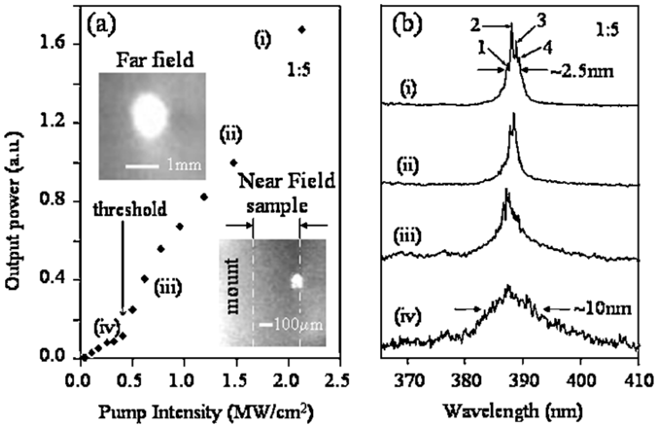

Fig. 3. (a) Light–light curve and (b) emission spectra of the sample with molar ratio 1 : 5 versus pumped excitation intensities. The inserts of (a) are the near and far field profiles for the TE mode at excitation intensity of ∼1 MW/cm^2.

light is required before being amplified and scattered to other clusters. Hence, the amplification is insufficient to overcome the loss of the random cavities and lasing is difficult to sustain. For large θ, although more scattering and amplification will occur, light will also have a high chance of escaping to the unpumped region rather than emitting from the edge and weak output intensities are detected instead. It is found that $\theta \sim 10^\circ$ is an optimum value to achieve maximum output intensity and this value of θ will be used in the following measurement for all the samples.

Fig. 3 shows the light–light curve and emission spectra of the sample with molar ratio 1 : 5 (ZnO : SiO$_2$). At pump intensities below threshold, a single-broad spontaneous emission spectrum with a full-width at half-maximum (FWHM) of ∼10 nm is observed. Increase in pump intensity above threshold results in sharp peaks (lasing modes) emerging from the emission spectra, indicating the formation of closed loop paths of light. However, further increase in pump intensity does not excite more sharp peaks. Instead, narrowing of emission spectra occurs and the FWHM of the emission spectrum reduces to ∼2.5 nm at an excitation intensity of ∼2.2 MW/cm^2. The narrowing of emission spectrum, which limits the number of excited sharp peaks, is due to intense amplification of light arisen from the high density of active scatterers (i.e., narrow stripe spacing of ZnO clusters). As shown in Fig. 3, four sharp peaks, having spectral separation and linewidth of ∼0.7 and ∼0.6 nm, respectively, are distinct from the emission spectrum at high pump intensities. The wider linewidth as compared to [5] could be attributed to the weaker disorder due to the stripe patterns that leads to overlapping modes [6]. The corresponding near and far fields are inserted in Fig. 3(a) at the excitation intensity of ∼1 MW/cm^2. It is noted that the light emission from the edge is transverse electric (TE) dominant due to the strong transverse and lateral confinement of light (i.e., bright single-spot emission). Similar behaviors of the emission spectra and field profiles have also been observed for samples with molar ratio 1 : 10 and 1 : 15.

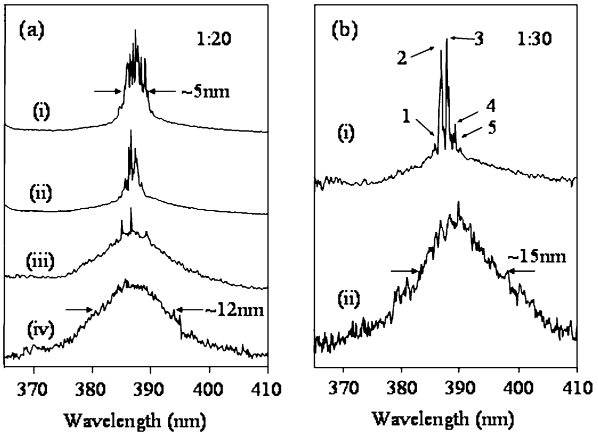

Fig. 4. Emission spectra of samples with molar ratio (a) 1 : 20 with pump intensities (i) 2.2 MW/cm^2, (ii) 1.48 MW/cm^2, (iii) 0.62 MW/cm^2, and (iv) 0.26 MW/cm^2, and (b) 1 : 30 with pump intensities (i) 2.2 MW/cm^2 and (ii) 1.48 MW/cm^2. The corresponding excitation conditions are the same as Fig. 3.

Fig. 4(a) shows the emission spectra of the sample with molar ratio 1 : 20. At low pump intensities, a single-broad emission spectrum with an FWHM of ∼12 nm is observed. When the excitation intensity exceeds a threshold, sharp peaks at around 387 nm with linewidth less than ∼0.6 nm emerged from the emission spectrum. Further increase in pump intensity increases the number of sharp peaks and the FWHM of the entire spectrum is reduced to ∼5 nm. The wider spectrum width (compared to Fig. 3) is attributed to the wider parallel-stripe spacing of ZnO clusters as the corresponding density of active scatterers is reduced. Sharp peaks are still observed from the emission spectra of sample with even higher molar ratio (1 : 30) under high pump intensities [see Fig. 4(b)]. This implies that closed loop paths of light can still be formed inside the sample with low concentration of ZnO clusters, but at the expense of high threshold pump. The polarization and field profiles observed from these samples are similar to that given in Fig. 3 and are not repeated here.

The variations of threshold pump and number of peaks (at pump intensity of ∼2.2 MW/cm^2) versus molar ratio are plotted in Fig. 5. As molar ratio increases, the reduction in optical gain and the increase in scattering loss lead to an increase in the

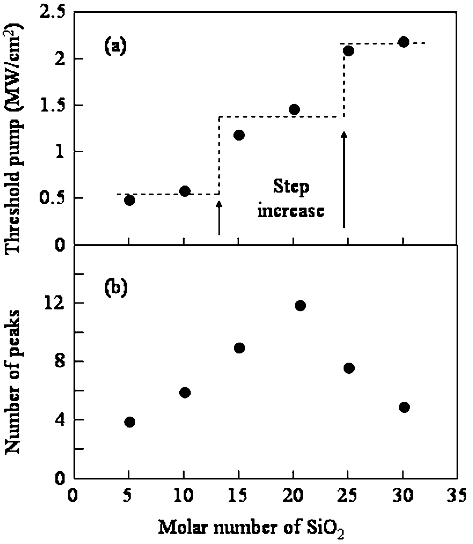

Fig. 5. Plots of (a) threshold pump intensity and (b) number of sharp peaks (lasing modes) versus molar ratio of the ZnO–SiO$_2$ composite waveguide lasers.

threshold pump. However, they do not hold a linear relationship. Fig. 5 shows that the threshold pump exhibits a step change with the variation of molar ratio. From molar ratio 1 : 5 to 1 : 10 (1 : 25 to 1 : 30), the change in scattering loss and optical gain is small. Thus, the threshold does not increase by a lot. However, a step increase in threshold (by >40%) is observed when the molar ratio is increased from 1 : 10 to 1 : 15 and from 1 : 20 to 1 : 25. This implies that the optical gain is reduced more rapidly than the increase of scattering loss. Furthermore, it is shown that the number of sharp peaks is maximized at molar ratio 1 : 20 but minimized at both lower and higher molar ratios. At higher molar ratio (i.e., 1 : 30), the wider spacing (i.e., longer scattering mean-free path, hence, higher scattering loss) between the parallel-stripes of ZnO clusters and the low concentration of ZnO clusters (i.e., lesser optical gain) imply a lower possibility of sustaining closed loop paths and thus lesser modes are observed. At low molar ratio 1 : 5, the narrowing of emission spectra and gain competition may explain for the decrease in the number of lasing peaks. At molar ratio of 1 : 20, the gain length and scattering mean-free path satisfy the random lasing conditions [5] so that the number of lasing peaks is maximized. From the above experiment, it is noted that incoherent random lasing is not observed in all the samples. In order to verify that coherent random lasing is due to the proposed configuration of composite waveguide, a layer of ZnO powder mixed with water was sprayed on quartz substrate to form a film with concentration of ZnO powder similar to that given in Fig. 4(a). It can be shown that only incoherent random lasing is supported in the ZnO powder film (after dried) under optical excitation and our claim is justified.

In summary, room-temperature random laser action with coherent feedback is realized in ZnO–SiO$_2$ composite waveguide lasers prepared by the sol–gel technique. The proposed waveguide lasers provide two-dimensional confinement of light inside the ZnO–SiO$_2$ composite films. In addition, the formation of different spacing of parallel-stripe pattern of ZnO clusters, which can be controlled by selecting the desired concentration of ZnO clusters, further enhanced the possibility of realizing closed loop paths of light along the surface of the composite films. Hence, coherent random lasing can be found in our waveguide lasers even at low concentration of ZnO clusters. More importantly, we have demonstrated that lasing characteristics of random cavity lasers can be controlled and this will contribute to the future development of random lasers for practical applications.

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