Nanoparticle lasers

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Flexible Ultraviolet Random Lasers Based on Nanoparticles**

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Organic semiconductor lasers have received considerable interest due to their ease of fabrication and mechanical flexibility.[1] Organic semiconductors play a particularly important role for such devices since they offer the prospect for laser sources of virtually any shape, which would not be possible with conventional inorganic semiconductor materials. However, electrically pumped organic lasers have not yet been demonstrated since they suffer from degradation problems similar to those observed for their organic light-emitting diode counterparts.[2] Here we explore a novel strategy for inorganic flexible lasers by using the random laser principle. Random lasers do not require a regular cavity but instead depend on a scattering material, such as a fine powder.[3,4] In a random laser, light waves are trapped by multiple light scattering, which takes over the role of the cavity in a regular laser. Zinc oxide (ZnO) is a wide-bandgap (3.37 eV) semiconductor, for which ultraviolet lasing action has been reported in thin films and nanostructures.[5–7] In 1998, Cao et al. demonstrated an efficient random laser at room temperature from ZnO nanoparticles.[8] The discovery of random lasing has stimulated many experimental and theoretical studies. However, no practical random laser has been fabricated as it is very difficult to process powders or solutions into devices. Yu et al. demonstrated ZnO thin-film random lasers on silicon substrates using a simple thermal annealing technique.[9] Laser cavities, due to closed-loop optical scattering from the lateral facets of the irregular ZnO grains, were generated through post-growth annealing of ZnO films. This approach has opened up a new way to construct random lasers on silicon. However, the high annealing temperature, usually more than 400 °C, makes it impossible to realize lasers on temperature-

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sensitive substrates such as plastics. Clearly, a breakthrough in the fabrication of inorganic lasers on plastic substrates is urgently needed for flexible optoelectronic devices. In this Communication, we report the design, fabrication, and characterization of UV random lasers on plastic substrates by utilizing ZnO thin films and nanoparticles. The realization of random laser action in nanoparticle-embedded ZnO thin films on flexible substrates may lead to the development of a new class of electrically pumped laser diodes. In fact, electrically pumped random lasing from δ-alumina nanoparticles doped with Ce^{3+} and Pr^{3+} ions has been demonstrated.[10]

To create a random laser, light scattering must be combined with light amplification. For our random laser, nanoparticles are the scattering centers and high-quality ZnO thin films deposited at low temperature act as the optical gain medium. The high-crystal-quality ZnO films were successfully deposited at room temperature by the filtered cathodic vacuum arc (FCVA) technique.[11] ZnO or In_2O_3 nanoparticles, with a mean diameter of 100 nm, can be used as scattering centers. ZnO nanoparticles were chosen because UV random lasers based on ZnO powder have been demonstrated and ZnO powder may also serve as a gain medium. Thus, In_2O_3 nanoparticles were also used in order to verify the role of the particles in the random laser mechanism.

The room-temperature photoluminescence (PL) spectra of the ZnO and In_2O_3 nanoparticles coated on a Si substrate were measured (Figure 1 a). For the ZnO nanoparticles, the observed sharp peak at around 390 nm and weak peak at 520 nm represent the band-to-band and defect emissions, respectively. No band-to-band emission is observed for the In_2O_3 particles, which may be due to the poor crystal quality of the particles. However, a broad emission at around 640 nm is detected, which may be attributed to the defects or oxygen deficiencies from In_2O_3.[12] Figure 1 b shows the design of the UV laser on a plastic substrate where nanoparticles are embedded into the ZnO thin films. Figure 1 c shows a cross-sectional SEM image for such a device bent inwardly with a radius of curvature of 3 cm, which typifies the flexibility of the device. Polycarbonate with a refractive index of 1.59 was used as a transparent and flexible substrate. The low refractive index of the plastic substrate as compared to the ZnO film (≈ 2.1) allows transverse optical confinement of light in the ZnO thin film to be achieved with minimal absorption loss. A 200-nm-thick layer of ZnO was first deposited on the substrate to provide better adhesion of the nanoparticles. The nanoparticles were then deposited on the ZnO thin film by a spray method and another 200-nm-thick ZnO thin film was further deposited. This layer not only confines the nanoparticles and forms a robust film, but also serves as an optical gain medium. The surface morphology of the ZnO nanoparticles embedded in the ZnO film is shown in Figure 1 d. The nanoparticles tend to form large clusters on the film after the spray process.

Figure 2 a shows the evolution of the emission spectra from the ZnO nanoparticles embedded in the ZnO films with a pump intensity ranging from 0.6 to 2.5 $MW\,cm^{-2}$ at a spot size of 3.0×10^{-3} cm^2. When the pump intensity reaches a threshold, a significant narrowing occurs. As shown in the inset of Figure 2 a, when the incident pump power exceeds 0.8 $MW\,cm^{-2}$, the linewidth quickly reduces to 5 nm, and the peak emission intensity increases rapidly with the pump intensity. Optical scattering by the ZnO nanoparticles increases the path length of the emitted light in the film. Under optical pumping, the ZnO film has a broad gain spectrum. The gain length is at its shortest at the peak of the gain spectrum. As the pump intensity increases, the gain length decreases. When the gain length becomes equal to the average path length of light in the gain medium, amplified spontaneous emission (ASE) occurs. Thus, the intensity at the wavelength of gain maximum builds up quickly, which leads to an apparent narrowing of the emission spectrum. Since there is a clear threshold for the ASE, light amplification is considered to be lasing with incoherent feedback.[13] It should be noted

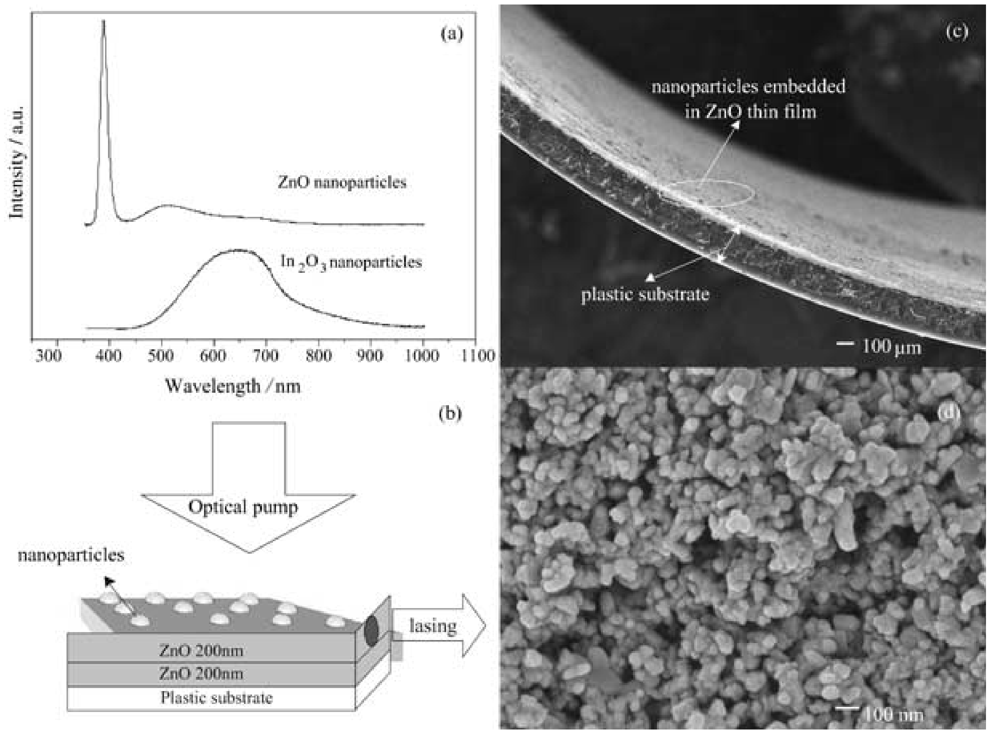

Figure 1. a) Photoluminescence spectra at room temperature for ZnO and In_2O_3 nanoparticles on Si substrates. b) Schematic diagram of nanoparticles embedded in the ZnO films. c) Cross-sectional SEM image of the device bent inwardly with a radius of curvature of 3 cm. d) Surface morphology of the device.

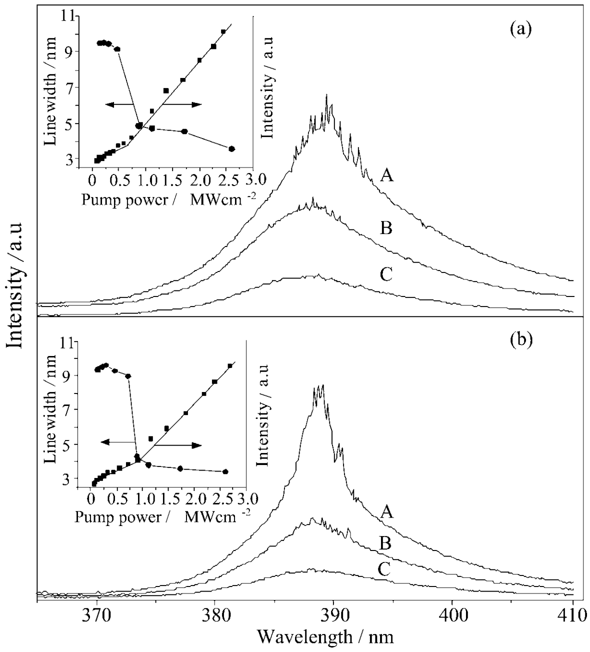

Figure 2. Evolution of emission spectra with a pump intensity ranging from 0.6 to 2.5 MW cm^{-2}: a) ZnO nanoparticles and b) In_2O_3 nanoparticles embedded in ZnO thin films on a plastic substrate. Insets: the linewidth and output intensity versus the input power intensity. Curves A, B, and C represent pump intensities of 2.5, 1.6, and 0.6 MW/cm^2, respectively.

that no lasing was observed from nanoparticles on plastic and Si substrates with a 420-nm-thick SiO_2 layer. Random lasing with coherent feedback in ZnO nanoparticles can only occur with a certain density and size of particles.[13] Furthermore, it was also found that no lasing emission could be observed from the ZnO thin films alone, even when the pumping power exceeded 2.5 MW cm^{-2}.

In order to investigate the role of the nanoparticles in the laser action process, In_2O_3 nanoparticles were also used to fabricate the device structure as shown in Figure 1 b. In_2O_3 nanoparticles were chosen because the bandgap (3.55 eV) and refractive index (1.95–2.15) of In_2O_3 are close to that of ZnO (3.37 eV and 2.1, respectively).[9,12,14] Due to the broad PL band (Figure 1 a), In_2O_3 nanoparticles cannot be a gain medium at 390 nm in the device. Figure 2 b shows the evolution of emission spectra from In_2O_3 nanoparticles embedded in the ZnO films as a function of pump intensity. When the pump intensity reaches the threshold, the linewidth of the emission peak at around 390 nm becomes narrower. There is no significant difference between the threshold pump intensity (0.8 MW cm^{-2}), emission peak position ($\approx$390 nm), and intensity for the two types of nanoparticle samples. It seems that the role of ZnO nanoparticles is mainly to act as scattering centers as no change in lasing threshold and intensity are observed for the two types of nanoparticles (Figure 2 a and 2b). Hence, this confirms that the nanoparticles act as scattering centers and the ZnO film serves as an optical gain medium in this design.

Furthermore, the effect of various pump areas (0.5×10^{-3} to 3.0×10^{-3} cm^2) on the lasing spectrum was also investigated under a constant pump intensity of 2.5 MW cm^{-2}. It was observed that before the critical area (1.0×10^{-3} cm^2) is reached, no narrowing of the linewidth was obtained. However, when the excitation area exceeds the threshold, linewidth narrowing is observed. The linewidth decreases as the excitation area increases. This behavior is in good agreement with the random laser theory.[13] In addition, Figure 3 a shows the plot of $A_{th}^{2/3}$ (A_{th} = threshold excitation area) versus P_{th}^{-1} (P_{th} = threshold pump intensity) for ZnO nanoparticles embedded in the ZnO films. A linear relationship between $A_{th}^{2/3}$ and P_{th}^{-1} is obtained and this conforms to the formula devised by Yu et al. to describe the linear relationship A_{th} and P_{th}, which is given by $A_{th}^{2/3} \approx KP_{th}^{-1}$, where K is a constant.[9] This again proves that random laser action exists in our samples.

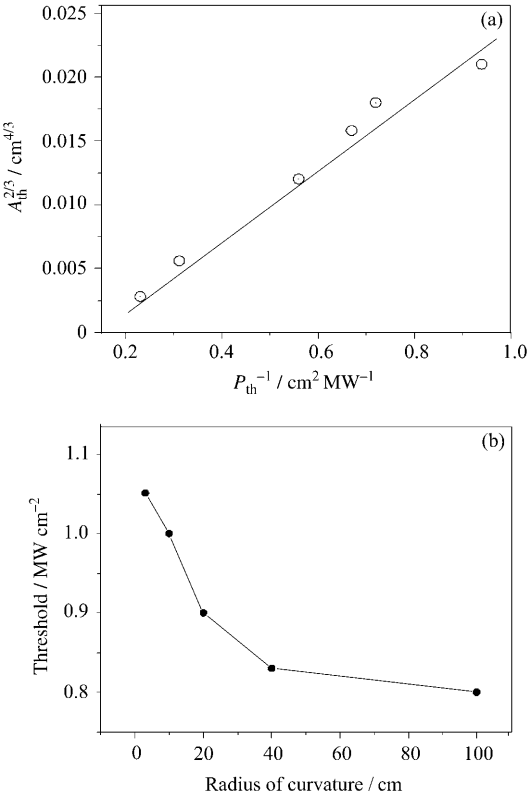

Figure 3. a) Plot of $A_{th}^{2/3}$ versus P_{th}^{-1} for ZnO nanoparticles embedded in ZnO thin films under different excitation areas. The pump power was 2.5 MW cm^{-2}. b) Lasing threshold versus the radius of curvature for the device when bent inwardly. The pump intensity and excitation area are 2.6 MW cm^{-2} and 3×10^{-3} cm^2, respectively.

The flexibility of the laser device was also tested by bending the device during optical pumping. There is no significant difference in the lasing spectra when the device is bent inwardly or outwardly. However, the lasing threshold is increased from 0.8 to 1.1 MW cm^{-2} as the radius of curvature of the device (bent inwardly) decreases from 100 to 3 cm, as shown in Figure 3 b. The increase in the pump threshold is due to the increase in bending loss with the radius of curvature.[15]

Although the random laser action from the nanoparticle-embedded ZnO film is incoherent, we believe that by optimizing the density and thickness of the nanoparticle layer, coherent random laser action can be obtained. It should be noted that the lasing emission intensity could also be enhanced further if a ZnO film deposited at a higher temperature ($\approx 200\,^{\circ}\mathrm{C}$) could be used. However, this will require the use of a high-performance plastic substrate. This approach provides an alternative way to realize inorganic semiconductor flexible lasers in the ultraviolet region, which should have significant implications for the future development of flexible lasers.

In summary, we have demonstrated a flexible UV random laser by utilizing nanoparticles embedded in a high-quality ZnO film deposited at 100 °C on a plastic substrate. Upon optical pumping at 355 nm, a drastic spectral narrowing occurs at around 390 nm when the pump-pulse power reaches $0.8\,\mathrm{MW\,cm^{-2}}$. The lasing threshold characteristics are in good agreement with the theory of random lasers. It has been verified that the nanoparticles act as scattering centers, while the ZnO film provides an optical gain medium.

Experimental Section

A 200 nm ZnO film was deposited by the FCVA technique at 100 °C with an oxygen partial pressure of 2×10^{-4} Torr. The apparatus for the FCVA setup has been described elsewhere.[11] Nanoparticles of ZnO or In_2O_3 with an average diameter of 100 nm were first dispersed in distilled water in the proportion of 1:20. A dispersant (Sokalan CP10, BASF) was then added to the solution. This mixture was stirred vigorously in an ultrasonic bath. The nanoparticles were then sprayed onto the ZnO film using a spray gun. After drying the sample, another ZnO layer of 200 nm thickness was deposited onto it. The photoluminescence spectrum was acquired at room temperature with the 325 nm line of a He-Cd laser as an excitation source. The surface morphologies of the samples were studied using field-emission scanning electron microscopy (JEOL JSM-6340F) operated at 5 kV. Optical characteristics of the devices at room temperature were studied under optical excitation by a 355 nm frequency-tripled Nd:YAG pulse laser (10 Hz, 6 ns pulse width). A convergent lens with a focal length of 10 cm was used to focus the light onto the sample. By adjusting the distance between the sample and the lens, the pump spot sizes were changed accordingly.

Keywords:
indium oxide • lasers • nanoparticles • photoluminescence • zinc oxide

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