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Microscopy Study of Morphological and Optical Changes in ZnO Nanostructures Induced by Pulsed Optical Excitation

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The photoluminescence intensity and morphology of zinc oxide (ZnO) nanowires have shown inherent instability under high light intensities [1, 2]. We present scanning electron microscope (SEM) results that indicate accumulation of morphological changes under strong light exposure. In ZnO nanostructures, one typically finds a strong enhancement of the luminescence intensity up to some optimum annealing time, followed by a decrease as illumination continues [1, 2]. Here we show that a similar metastable behavior applies to the threshold and intensity of random lasing in ZnO nanoparticle films. In combination with a detailed analysis of the lasing behavior we conclude that local melting affects the electronic and optical properties of the material and can give rise to large lasing threshold and efficiency changes. Improvement as well as deterioration of the optical performance can be observed.

Random lasers are optical devices that utilize random scattering in micrometer volumes to establish optical feedback and coherent laser emission. Since the optical feedback is not optimized, high pump intensities provided in short pulses are usually needed to achieve lasing. ZnO nanoparticle assemblies were among the first solid state random lasers to show promise for applications where small lasers sources for blue and ultraviolet light are needed [3]. Here we show that in simple ZnO random lasers the lasing threshold undergoes significant changes under typical pumping conditions. Among the various possible mechanisms we identify light induced melting and movement of individual nanoparticle scatterers during pumping.

Our lasing samples were pumped and annealed with nanosecond UV laser pulses. Before imaging, we initially burn a reference spot into the sample with a high intensity laser pulse. The sample is then translated horizontally a specified distance and a reference area is imaged in SEM. Between annealing steps, the sample was again imaged in SEM to monitor morphology changes and the lasing properties of the sample were measured.

When pumped with low intensity UV light, ZnO nanoparticles on Si substrate show strong excitonic photoluminescence with FWHM of ~15 nm. Steady improvement of the photoluminescence over time can also be observed, similar to previous reports [1, 2]. At high pump intensity we see a clear narrowing of the linewidth to ~3 nm. We also observed the characteristic fluctuations in the peak emission wavelength and intensity from shot-to-shot due to nanosecond pumping [3]. We show that adding scattering magnesium oxide (MgO) nanoparticles without gain to a ZnO nanoparticle random laser also decreases the threshold for lasing. The sample containing 30% MgO by weight had the lowest threshold and highest probability for lasing when compared to the other samples. Replacing MgO with an equal volume fraction of titanium dioxide (TiO_2) had the opposite effect: the threshold was greatly increased.

Pumping with single shots at high pump energies (141 mJ/cm^2) did not show any visible changes in the film morphology. After 550 mJ of energy is supplied to the sample by laser annealing, however, accumulated damage to the nanostructure can be seen in SEM. The morphology changes due to melting that are visible in our nanoparticle samples are similar to the changes observed in ZnO nanowires that were laser annealed at exposures of ~160 mJ/cm^2 (equivalent total energy of 624 mJ) with the same laser we used for pumping and annealing [1, 2]. Another area of the sample was annealed with 60 mJ/cm^2 pumping energy with a total annealing energy of 1700 mJ. Similar melting could also be seen due to high annealing energies at moderate intensity.

We have presented experimental results for threshold changes in a ZnO nanoparticle random laser on Si substrate. Adding 30% MgO (by weight) to ZnO showed the optimal decrease in the lasing threshold and corresponding increase in lasing probability and intensity. The threshold was also shown to change due to annealing by the pump laser. By extrapolating the rate of emission intensity change down to zero, our ZnO random lasers will have a stable morphology and average intensity when pumped with nanosecond pulse energies below ~20 mJ/cm^2. Our data indicate that significant morphology changes can only be observed after accumulated exposure to the pump laser. These results motivate research for further methods for reducing the lasing threshold in ZnO random lasers.

References:

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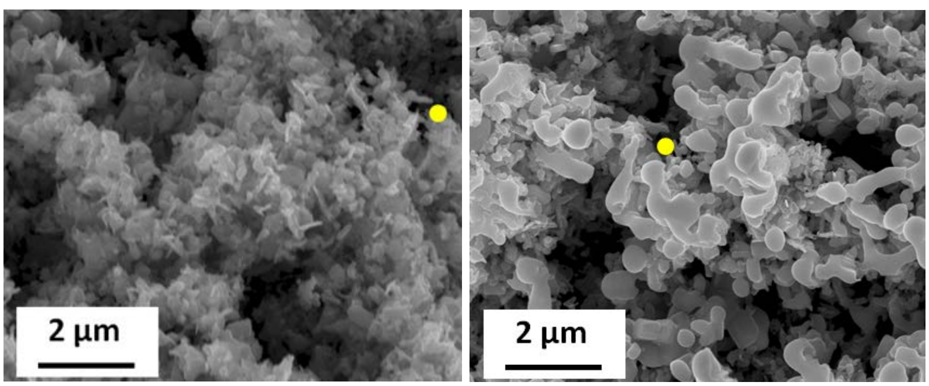

Figure 1. SEM micrographs before (left) and after laser annealing (right) with visible melting after annealing with energy density of 141 mJ/cm^2 (total energy = 550 mJ). Yellow dots mark the same location in each image.

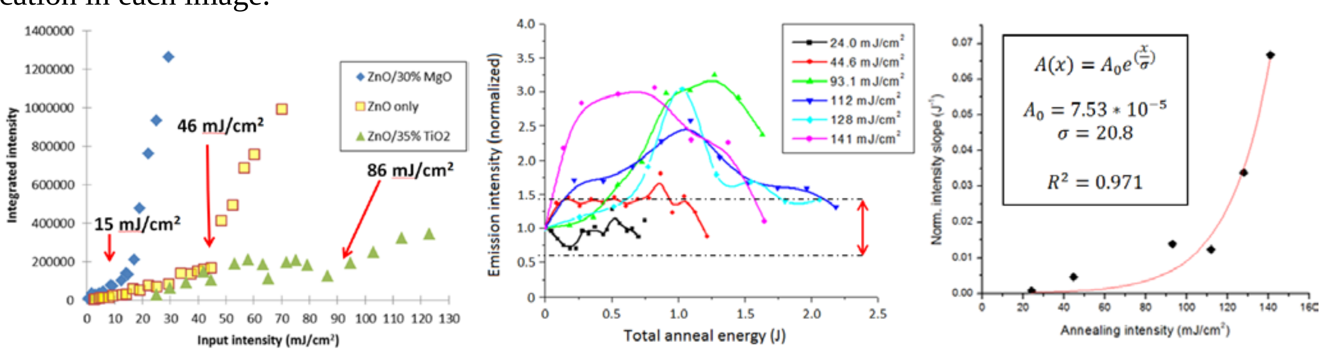

Figure 2. (Left) Amplification thresholds for random lasing in ZnO (yellow), ZnO/30% MgO (blue), and ZnO/35% TiO_2 (green). (Center) Emission intensity improvement due to various laser annealing intensities. The pumping energy density for each data point is 60 mJ/cm^2. Dashed lines mark the standard deviation in the intensity fluctuations of single-shot spectra. (Right) Initial slopes for each curve in the center figure versus the corresponding annealing intensity.