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Surface plasmon enhanced electrically pumped random lasers

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Electrically pumped random lasing has been realized in Au/MgO/ZnO structures. By incorporating Ag nanoparticles, whose extinction spectrum overlaps well with the emission spectrum of the structures, the threshold of the random lasing can be decreased from 63 mA to 21 mA. The decrease in the threshold has been attributed to the resonant coupling between the carriers in the active layer of the structures and the surface plasmon of the Ag nanoparticles.

Introduction

Surface plasmons are collective charge oscillations of free electrons that occur at the interface between a metal and a dielectric.[1–3] When the excited surface plasmons are resonant with the incident light, localized electromagnetic fields near the metal will be enhanced by several orders of magnitude. Recently, surface plasmons have been actively employed to enhance the emission efficiency of light-emitting materials and devices, and a significant improvement of photoluminescence (PL) intensity has been observed from fluorescent molecules, dye-doped polymers, Si quantum dots, CdSe quantum dots, InGaN quantum wells, and ZnO films due to the resonant excitation of surface plasmons.[2–8]

Random lasing is a lasing phenomenon that is usually observed in random media such as nanoparticles, dyes, and colloids.[9–11] Compared with the conventional lasers with defined optical cavities, random excitation of lasing modes and divergence of lasing beam are the unique characteristics of random lasers. Optically pumped random lasers have been achieved in some material systems including dye solutions with scattering particles,[11] polymer dispersed liquid crystals,[12] liquid crystal films,[13] and semiconductor nanostructures.[14–16] Recently, electrically pumped random lasers have also been fabricated in ZnO films and nanostructures.[17–20] However, the relatively high threshold, which arises from the high scattering loss at the grain boundaries of the random media, is almost unavoidable in random lasers. Some groups have demonstrated that the threshold of the electrically pumped ZnO random laser can be decreased by using a double heterostructure or enhancing multiple light-scattering in ZnO films.[21–23] Surface plasmons have also been employed to reduce the threshold of random lasings.[24–29] However, all these surface plasmon enhanced random lasers were realized under optical pumping, while no report on surface plasmon enhanced electrically pumped random lasers can be found to date.

In this communication, we show that by using the surface plasmons of Ag nanoparticles, the threshold of electrically pumped random lasers can be decreased significantly, and the decrease can be attributed to the strong coupling between the carriers in the random laser structures and the surface plasmons of the Ag nanoparticles.

Experimental section

In order to fabricate the surface plasmon enhanced electrically pumped random lasers, colloidal Ag nanoparticles were prepared by reducing silver nitrate with sodium borohydride in the presence of sodium citrate as a stabilizer.[30] ZnO layers are employed as the active layers of the random laser, and they are grown on *a*-plane sapphire substrates in a VG V80H plasma-assisted molecular-beam epitaxy system. Prior to growth, the sapphire substrate was pretreated at 800 °C for 30 min to remove any possibly adsorbed contaminants and produce a clean surface. High-purity (6 N) elemental zinc was used as the precursor for the growth, and the oxygen source used was radical oxygen produced in a plasma cell operating at 300 W. The pressure in the growth chamber during the growth was fixed at

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2×10^{-3} Pa. Firstly, a 600 nm ZnO layer and a 10 nm MgO layer were deposited onto the sapphire substrate in sequence at 750 °C. The ZnO layer shows *n*-type conduction with an electron concentration of 1.4×10^{19} cm^{-3} and a Hall mobility of 43 cm^2 V^{-1} s^{-1}. Then the prepared colloidal Ag nanoparticles in aqueous solution were dropped onto the surface of the sample and spin-coated at 2000 rpm for 10 s. The coated sample was dried in a furnace for 10 min at 150 °C in order to remove the water solvent. This procedure was repeated three times. Subsequently, a 50 nm MgO layer was deposited onto the Ag nanoparticles by a radio-frequency magnetron sputtering technique. Finally, gold and indium layers were deposited onto the MgO and ZnO layers by vacuum evaporation acting as contacts. For comparison, an Au/MgO/ZnO structure without Ag nanoparticles was also prepared under the same conditions.

The morphology of the ZnO layer was characterized by a Hitachi S4800 scanning electron microscope (SEM). The crystal structure of the layer was studied using a Bruker D8 X-ray diffractometer. The morphology of the Ag nanoparticles was characterized in a JEOL JEM-2100 transmission electron microscope (TEM) operating at 200 kV. The optical absorption spectra of the Ag nanoparticles were recorded in a Shimadzu UV-3101PC spectrometer. The PL spectrum of the ZnO layer was recorded using a JY-630 micro-Raman spectrometer with the 325 nm line of a He–Cd laser as the excitation source. The optically pumped stimulated emission of the ZnO layer with and without Ag nanoparticles was excited by the fourth harmonic 266 nm line of a Nd:YAG laser at pulsed operation (~6 ns, 10 Hz). The diameter of the laser spot was around 4 mm. The stimulated emission spectra were collected from the normal direction of the sample through an objective lens, and the scanning step size was 0.1 nm. Electroluminescence (EL) measurements of these devices were carried out in a Hitachi F4500 spectrometer, and a continuous-current power source was used to excite the structure. The scanning speed was 1200 nm min^{-1} and the scanning step size was 0.2 nm.

Results and discussion

The typical morphology of the ZnO layer, which will be used as the active layer of the optically and electrically pumped random lasers, is shown in Fig. 1a. The ZnO layer consists of grains (with an average diameter of about 200 nm) and voids. The X-ray diffraction (XRD) pattern of the layer is shown in the inset of Fig. 1b. Besides the diffraction from the substrate, only one peak at 34.44° can be observed from the pattern, which can be indexed to the diffraction from the (0002) facet of wurtzite ZnO. The XRD data reveal that the ZnO layer is hexagonal-wurtzite structured with a *c*-axis preferred orientation. Fig. 1b illustrates the room-temperature PL spectrum of the ZnO layer excited by the 325 nm line of a He–Cd laser. The spectrum shows a dominant sharp near-band-edge (NBE) emission

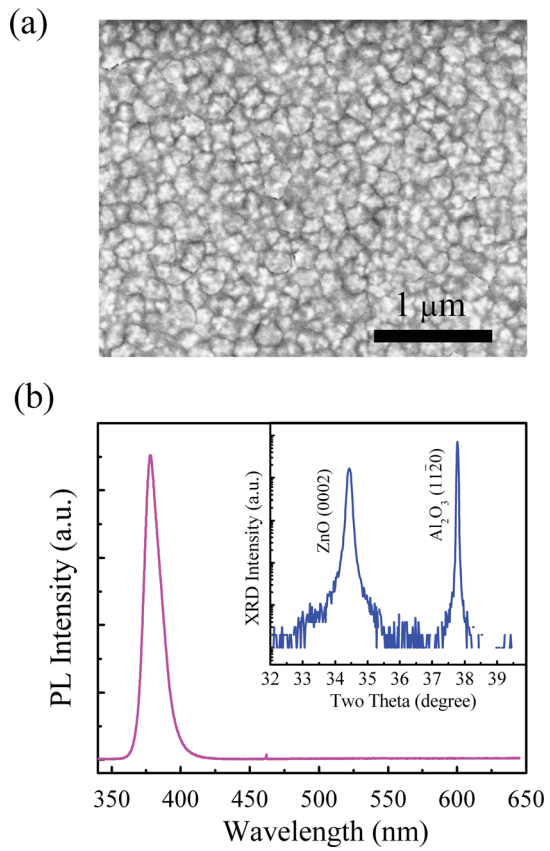

Fig. 1 (a) SEM topography of the ZnO layer; (b) room-temperature PL spectrum of the ZnO layer, and the inset shows the XRD pattern of the layer.

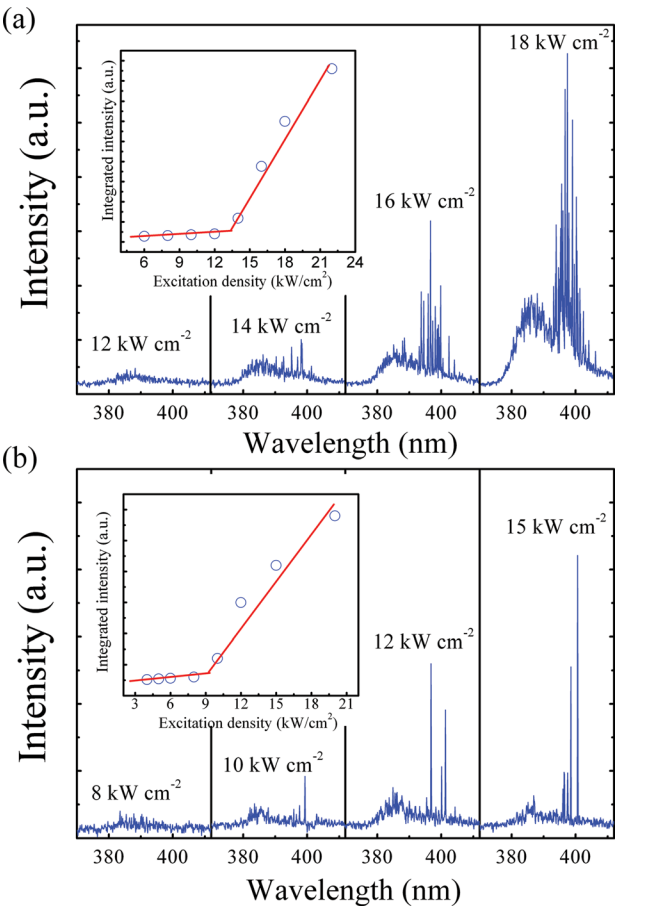

Fig. 2 Optically pumped lasing spectra of the ZnO layer without (a) and with Ag nanoparticles (b) at different excitation densities under 266 nm laser pulsed excitation, and the insets show the dependence of the integrated emission intensity on the excitation density.

at around 377 nm, and the full width at half maximum (FWHM) of the emission is about 12 nm, while the deep-level emission that is frequently observed in ZnO is almost undetectable.

Fig. 2 shows the optically pumped random lasing characteristic of the ZnO layer without and with Ag nanoparticles. From Fig. 2a, one can find that at low excitation intensity, the spectrum shows a broad spontaneous emission peak at around 383 nm and the FWHM of the emission is about 16.5 nm. As the excitation intensity is increased to 14 kW cm^{-2}, some narrow peaks with a FWHM of around 0.2 nm emerge. When the excitation intensity increases further, more such sharp peaks are visible. The inset of Fig. 2a shows the integrated emission intensity as a function of the excitation intensity, and a threshold of about 13.5 kW cm^{-2} can be derived for the ZnO layer without the decoration of Ag nanoparticles. Based on the above facts, one can conclude that the ZnO layer can serve as an arena for the study of random lasing. When Ag nanoparticles were spin-coated onto the ZnO layer and optically pumped spectra were collected under the same measurement conditions, it can be found that the Ag nanoparticle decorated ZnO layer exhibits a similar optically pumped random lasing characteristic as the bald ZnO layer, as shown in Fig. 2b. Nevertheless, the threshold of the lasing from the ZnO layer decreased to about 9.1 kW cm^{-2} with Ag nanoparticle decoration. The above facts indicate that the optically pumped random lasing threshold of the ZnO layer can be reduced by the Ag nanoparticles.

To realize electrically pumped random lasers, an Au/MgO/ZnO structure has been constructed, and the schematic diagram of the structure is shown in the inset of Fig. 3b. The thickness of Au, MgO, and ZnO layers are 20 nm, 60 nm, and 600 nm, respectively. Note that the Au contact is patterned into a single interdigital configuration to increase the surface distribution of the injection current. Fig. 3a depicts the room-temperature EL spectra collected from the top face of the Au/MgO/ZnO structure. As shown in the figure, a broad spontaneous emission centered at around 387 nm is visible when the injection current is 50 mA, which can be attributed to the NBE emission of ZnO. When the injection current is increased to 73 mA, sharp peaks with a FWHM of less than 1 nm appear superimposed on the broad spontaneous emission. Furthermore, the number and intensity of the sharp peaks increase with the injection current. The dependence of the integrated intensity of the emission on the injection current is plotted in Fig. 3b, from which a threshold current of about 63 mA can be derived. The random excitation of sharp peaks over the spectrum above threshold verifies that random lasing action appears in the structure. The origin of the random lasing has been elucidated in our previous report and is not repeated here.[20]

A relatively high threshold is one of the troublesome issues of a random laser; if an approach can be adopted to decrease the threshold of a random laser, the importance of such an approach will be self-evident. Here we employ the surface plasmon of Ag

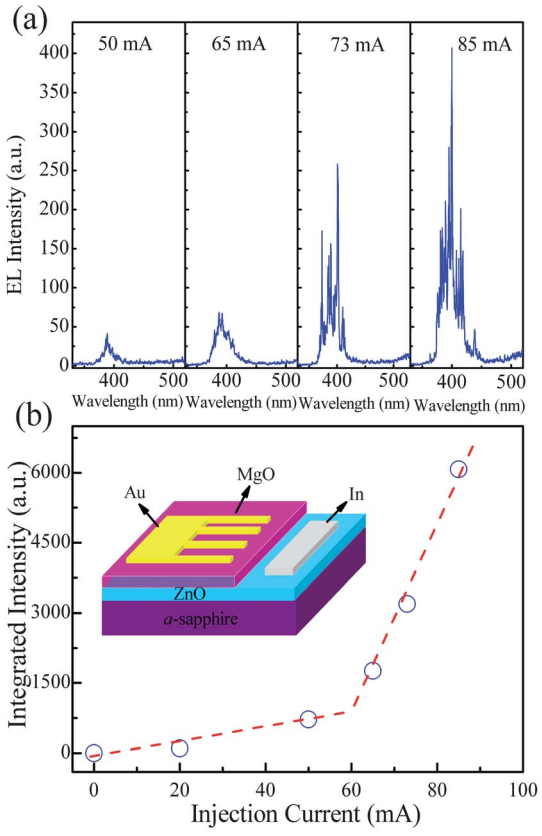

Fig. 3 (a) EL spectra of the Au/MgO/ZnO structure under different injection currents; (b) the dependence of the emission intensity of the structure on the injection current, and the inset of (b) shows the schematic illustration of the Au/MgO/ZnO structure.

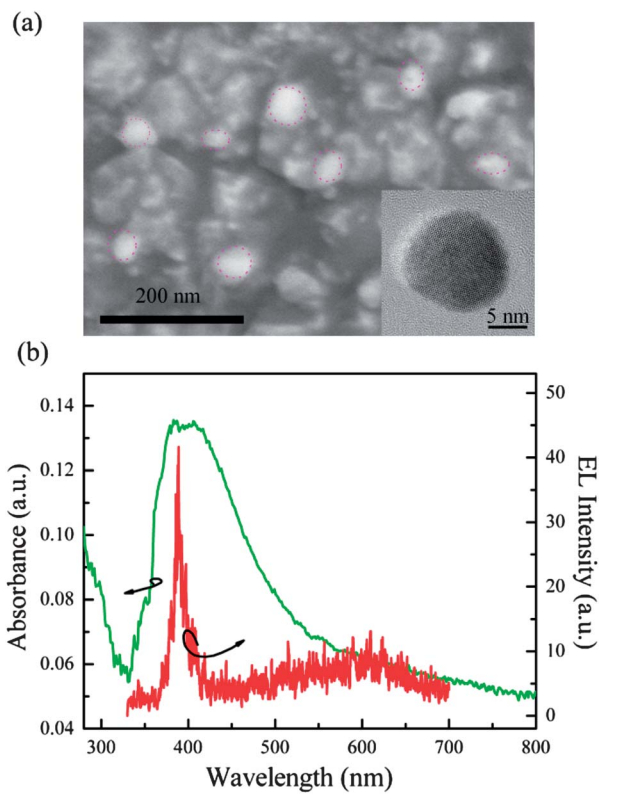

Fig. 4 (a) SEM image of Ag nanoparticles deposited on a MgO/ZnO/sapphire structure, and the inset shows a typical TEM image of an individual Ag nanoparticle; (b) extinction spectrum of the Ag nanoparticles coated onto the ZnO layer, and a typical EL spectrum of the Au/MgO/ZnO structure is also displayed for comparison.

nanoparticles to realize this purpose. Fig. 4a shows the SEM image of Ag nanoparticles randomly deposited onto the MgO/ZnO/sapphire structure, and the inset of Fig. 4a illustrates a typical TEM image of an individual Ag nanoparticle. One can see that the average size of the Ag nanoparticles is around 10 nm. The extinction spectrum of the Ag nanoparticles is plotted in Fig. 4b, from which an absorption band centered at around 400 nm can be observed. A typical emission spectrum of the Au/MgO/ZnO structure is also shown in the figure. It is noted that the extinction spectrum of the Ag nanoparticles overlaps well with the EL spectrum of the Au/MgO/ZnO structure, which promises that the emission of the Au/MgO/ZnO structure may be enhanced resonantly by the surface plasmons of the Ag nanoparticles.

The inset of Fig. 5b shows the schematic diagram of the Au/MgO/ZnO structure decorated with Ag nanoparticles, in which the Ag nanoparticles were sandwiched by two MgO dielectric layers to reduce the ohmic loss of Ag nanoparticles.[31–34] The EL spectra of the Ag nanoparticle decorated Au/MgO/ZnO structure under different injection currents are shown in Fig. 5a. Sharp peaks can also be observed superposed onto the broad spontaneous emission of the structure at an increased injection current. The dependence of the integrated emission intensity on the injection current is shown in Fig. 5b, and the threshold for the lasing is about 21 mA, which is much lower than that of the Au/MgO/ZnO structure without Ag nanoparticles (63 mA). The above results reveal that the threshold of the random lasing can be reduced by incorporating Ag nanoparticles.

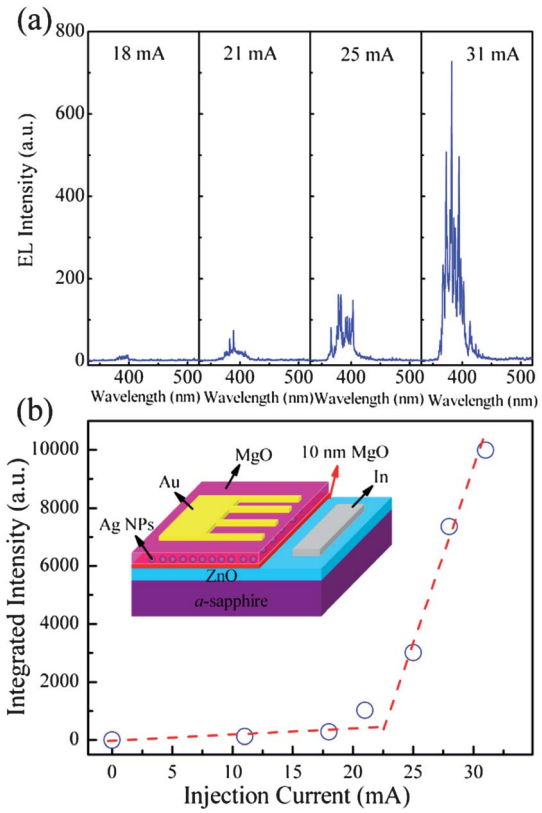

Fig. 5 (a) EL spectra of the Au/MgO/ZnO structure with the decoration of Ag nanoparticles under different injection currents; (b) the dependence of the integrated emission intensity of the structure on the injection current. The inset of (b) shows the schematic diagram of the Ag nanoparticle decorated Au/MgO/ZnO structure.

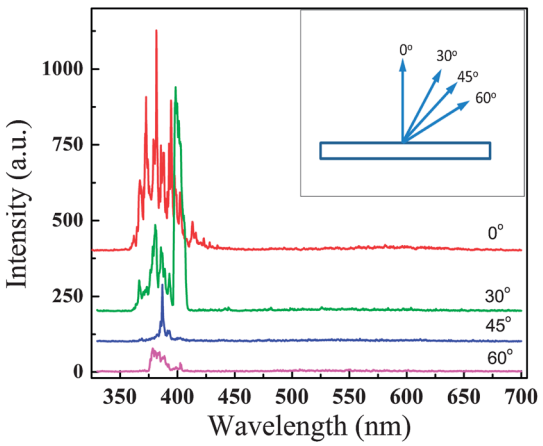

Fig. 6 Electrically pumped random lasing spectra of the Ag nanoparticle decorated Au/MgO/ZnO structure observed at an angle of 0°, 30°, 45° and 60° in the plane normal to the structure, and the inset shows the schematic recording configuration.

The lasing spectra of the Ag nanoparticle decorated Au/MgO/ZnO structure observed at different angles of 0°, 30°, 45° and 60° in the plane normal to the sample are shown in Fig. 6. One can see that sharp peak symbolized lasing action has been observed in all the four recording configurations but the spectrum varies greatly, which is a typical characteristic of random lasing.[14,20]

The enhancement of emission intensity from the Au/MgO/ZnO structure with Ag nanoparticles can be explained as follows: the energy of the carriers in the ZnO layer injected from the external circuit can transfer to the surface plasmon modes of the Ag nanoparticles, and the generated surface plasmon modes can then be extracted as light. The emission efficiency of the Au/MgO/ZnO structure with Ag nanoparticles can then be increased because the surface plasmon coupling rate is much faster than the lifetime of the electron–hole pairs.[5,6,35] Therefore, the emission intensity of the Au/MgO/ZnO structure with Ag nanoparticles will be much higher than that without Ag nanoparticles due to the presence of coupling between the excited carriers and surface plasmons of the Ag nanoparticles, as evidenced from Fig. 7. In this figure, the emission

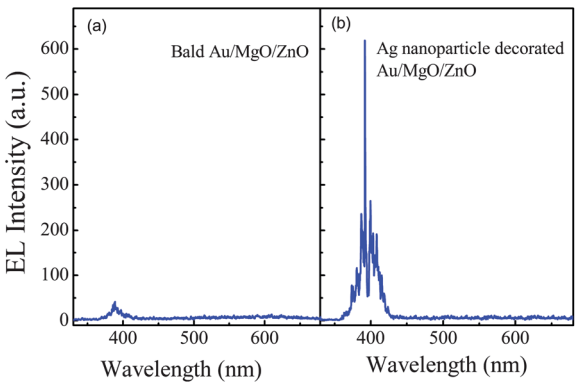

Fig. 7 EL spectra of the Au/MgO/ZnO structure without (a) and with the Ag nanoparticle decoration under the same injection current.

intensity of the Ag nanoparticle decorated Au/MgO/ZnO structure is significantly larger than that of the bald one under the same injection current. In this case, fewer injection carriers are required to excite lasing modes so that the corresponding threshold current can be reduced.

Conclusions

In summary, electrically pumped ZnO based random lasers have been realized in Au/MgO/ZnO structures, and Ag nanoparticles have been embedded into the structures. It is found that the threshold of the random lasing can be decreased greatly by the Ag nanoparticles, and the mechanism for this decrease can be attributed to the resonant coupling between the surface plasmon of the Ag nanoparticles and the carriers in the structures. Hence, we have verified that the use of surface plasmons can improve the performance of the electrically pumped random lasers and this may be of significance for the development of novel lasing optoelectronic devices using surface plasmons.

Acknowledgements

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