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COMMUNICATION

Low-threshold electrically pumped ultraviolet laser diode

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Electrically pumped ultraviolet lasing has been realized in a Au/MgO/MgZnO/*n*-ZnO structure. The lasing is located at around 330 nm. Notably the threshold of the lasing is about 30.0 mA, over one order of magnitude smaller than the corresponding values reported before.

The ultraviolet (UV) spectral region can be divided into four bands in terms of their effect on bio-organic and chemical substance: UV-C (shorter than 290 nm), UV-B (290–340 nm), and UV-A (340–400 nm). Laser diodes operating in UV region have attracted much attention in recent years because they are essential in a variety of applications, such as data storage, medical diagnosis and therapy, water or air sterilization, *etc.*[1,2] Although quite a few reports have demonstrated laser diodes operating in the UV-A band,[3] the developing of shorter wavelength electrically pumped laser diodes has encountered huge challenges. Up to now, only one report on laser diodes operating in the UV-B band can be found to the best of our knowledge, which was realized in AlGaN, and the lasing peak is located at 336 nm.[4] It is noteworthy that the threshold of the UV-B laser diode is about 440 mA. It is accepted that relatively high threshold current will cause a severe heating problem that is one of the largest troublesome issues in laser diodes. Therefore, it will be of significance if a low-threshold short-wavelength laser diode can be realized.

Zinc oxide (ZnO) and related materials are another promising candidate for short-wavelength laser diodes for its direct wide bandgap. Especially, ZnO and its alloys with magnesium have much larger exciton binding energy (60 meV for ZnO), which is favorable for realizing low-threshold lasers because lasing action may be realized through an exciton-exciton scattering process, the threshold of which is over two orders of magnitude smaller than that of lasing realized *via* electron-hole plasma process that is frequently employed for semiconductor with small exciton binding energy.[5–7] A trace for the feasibility that low-threshold lasers can be realized in ZnO based materials lies in the fact that many optically pumped lasers have been reported in ZnO films, nanostructures, quantum wells, or even powders.[8–10] Nevertheless, the shortest electrically pumped lasing wavelength ever reported in ZnO-based materials is about 380 nm,[11–13] while for laser diodes operating in the UV-B band or shorter, no report can be found to the best of our knowledge.

In this communication, electrically pumped UV lasers have been demonstrated in MgZnO nanocolumns. The lasing peak is located at around 330 nm, which is one of the shortest wavelengths ever reported for an electrically pumped laser diode to the best of our knowledge. Notably, the threshold for the lasing is only about 30.0 mA, over one order of magnitude smaller than the threshold value ever reported in the only UV-B laser diode (440 mA).

To realize the UV laser diode, a Au/MgO/MgZnO/*n*-ZnO structure has been constructed. The ZnO film was grown on microscope glass using an atomic layer deposition technique, and the detailed growth process can be found elsewhere.[14] A MgZnO layer was then grown onto the ZnO film in a plasma-assisted molecular beam epitaxy technique. The precursors used for the MgZnO layer growth were elemental zinc (6 N in purity), elemental magnesium (6 N in purity) and O_2 gas (5 N in purity). The O_2 gas was activated in an Oxford Applied Research plasma cell (Model HD25) with radio frequency operating at 13.56 MHz. The substrate temperature was fixed at 550 °C, and the chamber pressure at 3×10^{-6} mbar during the growth process. Then a MgO layer was deposited onto the MgZnO layer in a radio-frequency magnetron sputtering technique. Finally, Au and In were deposited onto the MgO and ZnO layer employing as electrodes by vacuum evaporation.

The morphology of the MgZnO layer was characterized in a Hitachi S4800 field-emission scanning electron microscope (SEM), and the Mg content in the MgZnO layer was determined to be 0.25 by energy-dispersive X-ray spectroscopy. The electrical properties of the ZnO films are characterized in a Lakeshore 7707 Hall measurement system. The optical properties of the layers was measured in a Jobin-Yvon Triax 550 spectrometer by employing the fourth-harmonic (266 nm) of a Nd:YAG pulse laser as the excitation source. A Bruker-D8 Discover X-ray diffractometer (XRD) with Cu-Kα radiation (1.54 Å) was used to evaluate the crystalline properties of the layers.

Fig. 1a shows the cross-sectional image of the MgZnO layer grown on ZnO film. The image reveals that dense ZnO film has been obtained on the glass substrate. Note that the electron concentration and mobility in the *n*-ZnO film are about 2.3×10^{19} cm^{-3} and 23 cm^2 V^{-1} s^{-1}, respectively. Closely packed vertical MgZnO nanocolumns are formed on the ZnO film. The size of the nanocolumns ranges from 50 to 100 nm. It has been demonstrated that for ZnO based

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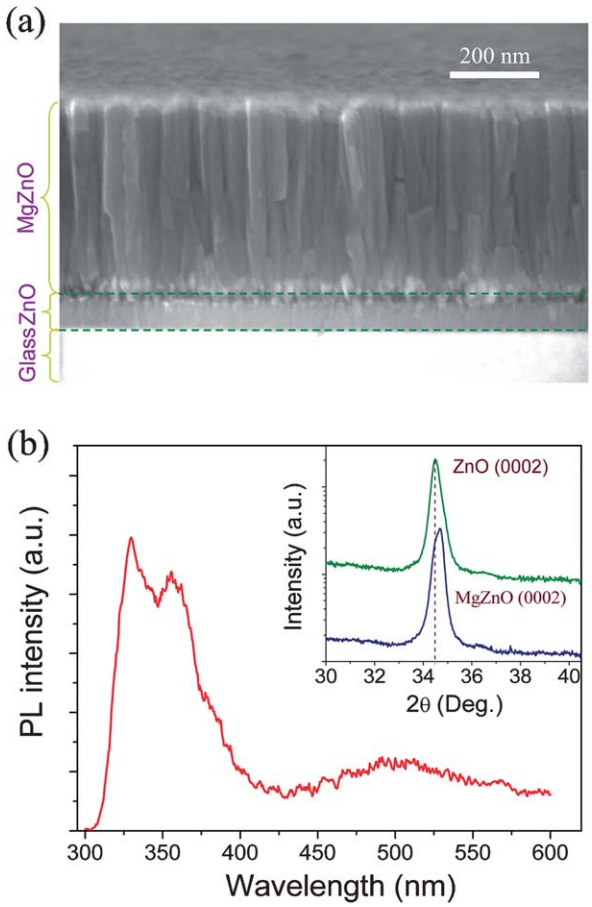

Fig. 1 (a) Cross-sectional SEM image of the $Mg_{0.25}Zn_{0.75}O$ nanocolumns grown on ZnO film. (b) Room temperature PL spectrum of the $Mg_{0.25}Zn_{0.75}O$/ZnO structure, and the inset shows the XRD pattern of the $Mg_{0.25}Zn_{0.75}O$ nanocolumns grown on ZnO film.

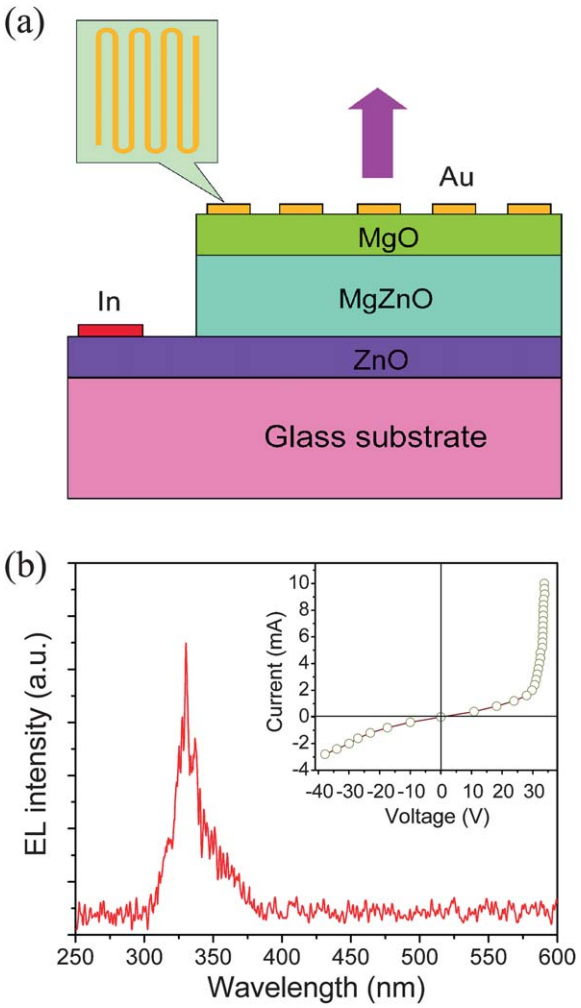

Fig. 2 (a) Schematic illustration of the Au/MgO/MgZnO/*n*-ZnO structure. (b) EL spectra of the Au/MgO/MgZnO/*n*-ZnO structure under the injection of continuous current, and the inset shows the *I*–*V* curve of the structure.

materials, the optical gain of small-sized nanostructures can be over one order of magnitude larger than that of bulk materials,[8,15] which is greatly advantageous for realizing lasers. The room temperature photoluminescence (PL) spectrum of the $Mg_{0.25}Zn_{0.75}O$/ZnO structure is illustrated in Fig. 1b. The spectrum shows a dominant emission at 329 nm (3.76 eV), which is in reasonable agreement with the band gap of $Mg_{0.25}Zn_{0.75}O$ ($E_g = 3.83$ eV).[16] Therefore, this emission can be attributed to the near band edge emission of the $Mg_{0.25}Zn_{0.75}O$ nanocolumns. Also an emission band at around 356 nm can be observed, which may come from the scattered light from the Nd:YAG laser. Additionally, a broad weak emission at around 500 nm appears in the spectrum, which is the typical deep-level related emission in ZnO-based materials. A typical XRD pattern of the MgZnO nanocolumns grown on the ZnO film is shown in the inset of Fig. 1b. There appear two peaks at 34.48° and 34.70°, which can be indexed to the diffraction from (0002) facet of wurtzite ZnO and $Mg_{0.25}Zn_{0.75}O$ layer, respectively. The XRD data reveal that the ZnO and MgZnO are both hexagonal wurtzite structured with *c*-axis preferred orientation.

A schematic illustration of the Au/MgO/MgZnO/*n*-ZnO structure is shown in Fig. 2a. The thickness of the MgO, MgZnO, and ZnO layer is 60 nm, 400 nm and 100 nm, respectively. The Au contact was patterned into an S-shape using photolithography and wet-etching technique to broaden the current distribution. The inset of Fig. 2b shows the current–voltage (*I*–*V*) curve of the Au/MgO/MgZnO/*n*-ZnO structure. An obvious rectification characteristic with a turn on voltage of about 30.0 V can be observed from the *I*–*V* curve. Note that the relatively large turn-on voltage may be resulted from the large resistivity of the MgO and MgZnO layer. A characteristic electroluminescence (EL) spectrum of the Au/MgO/MgZnO/*n*-ZnO structure under the driven of continuous current is illustrated in Fig. 2b. As shown in the figure, only one emission peak centred at around 330 nm can be observed in the spectrum. This peak is very close to PL emission of the MgZnO layer shown in Fig. 1b, thus it may come from the near band edge emission of the MgZnO nanocolumns.

To explore the mechanism of the EL emission, the band diagram of the Au/MgO/MgZnO/*n*-ZnO structure is illustrated in Fig. 3. The conduction band offset (ΔE_C) between ZnO and $Mg_{0.25}Zn_{0.75}O$ is about 0.26 eV,[17] and a triangle shaped potential barrier will form at the $Mg_{0.25}Zn_{0.75}O$/ZnO interface. Because the conduction band of $Mg_{0.25}Zn_{0.75}O$ will bend significantly under forward bias, thus the effective width of the triangle barrier will be reduced significantly. Under such circumstance, some electrons in the ZnO layer can tunnel through the triangle barrier and inject into the MgZnO layer. On the other hand, the conduction band offset between $Mg_{0.25}Zn_{0.75}O$ and

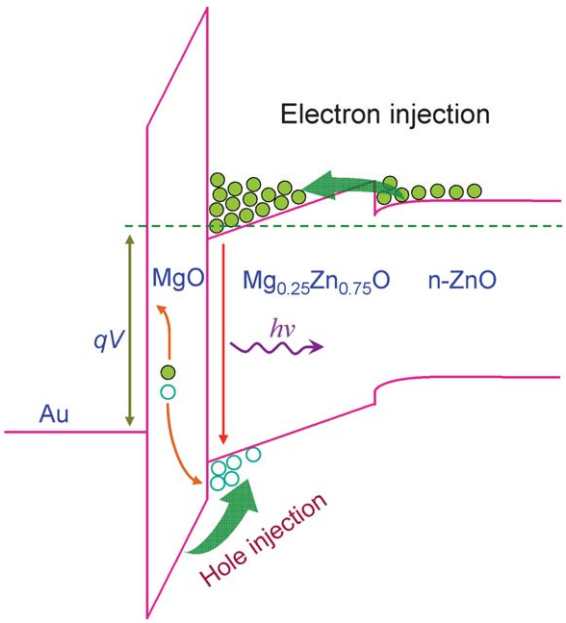

Fig. 3 Schematic diagram showing the band alignment of the Au/MgO/MgZnO/*n*-ZnO structure under forward bias. The presence of MgO layer will confine electrons into the MgZnO, while holes generated in MgO *via* an impact ionization process can be injected into the MgZnO layer.

MgO is as large as 2.8 eV, which forms a large barrier that prevents electrons in the MgZnO layer from drifting into the Au electrode. As a result, electrons will be confined in the MgZnO layer. Considering that most of the voltage will be applied onto the MgO layer due to its dielectric nature, the electric field in the MgO layer can be in the order of 10^6 V cm^{-1}. Under such a high electric field, some carriers in the MgO will gain much energy, and impact with the lattice of MgO, thus additional electron-hole pairs will be generated by an impact ionization process.[18,19] In the presence of the bias, the generated holes will be injected into the MgZnO layer, and may recombine radiatively with the electrons confined in the MgZnO layer. As a result, EL emission from the MgZnO layer will be observed.

Since the MgZnO layer is shaped in closely packed nanocolumns, and the refraction index of $Mg_{0.25}Zn_{0.75}O$ ($n \approx 2.3$) is much larger than that of air ($n = 1.0$),[11] the light emitted in the MgZnO nanocolumns may undergo a strong scattering process in the presence of many grain boundaries.[20,21] On some occasions, the emitted light can return to a scattering path from which it was scattered before. Consequently, close-loop resonant cavities are formed.[22] By increasing the injection current to a certain value when the optical gain exceeds the optical loss in the close-loops, lasing action may be realized. Experimentally, lasing emission has been observed in the Au/MgO/$Mg_{0.25}Zn_{0.75}O$/*n*-ZnO structure at increased injection current, as stated below.

The lasing characteristics of the Au/MgO/$Mg_{0.25}Zn_{0.75}O$/*n*-ZnO structure under the injection of continuous current are shown in Fig. 4. When the injection current is 21 mA, a broad spontaneous emission at around 330 nm can be observed, and the full width at half maximum (FWHM) of the emission is about 17 nm. As the current is increased to 28 mA, some sharp peaks can be observed superposing on the broad emission band, and the FWHM of the sharp peaks can be as small as 2.0 nm. When the injection current is further increased to 40 mA, the FWHW of the sharp peaks can be less than 0.5 nm. More of these sharp peaks appear when further increasing the injection current to 45 mA, and the sharp peaks can span from 323 nm to 341 nm. The appearance of sharp peaks at increased injection current indicates that lasing may be realized. This is one of the shortest wavelengths ever reported in a semiconductor laser diode to the best of our knowledge. The inset of Fig. 4 shows the dependence of the integrated intensity of the emission at around 330 nm on the injection current, from which a threshold current of about 30.0 mA can be derived. Note that the threshold current is over one order of magnitude smaller than the corresponding value of the laser diodes with comparable wavelength ever reported before (390 mA for 342 nm lasing,[3] and 440 mA for 336 nm lasing[4]). Because no elaborate resonant cavity is established in our experiment, and the lasing spectrum observed in the same record configuration varies under different injection currents, which is very similar to the phenomenon observed in random lasers,[23,24] it is thus believed that the lasing action observed in our case comes from a random laser. In the randomly formed close-loop cavities, the optical gain in more such cavities can surpass the loss at larger injection current. As a result, more lasing peaks were observed under the driven of higher current, as shown in Fig. 4.

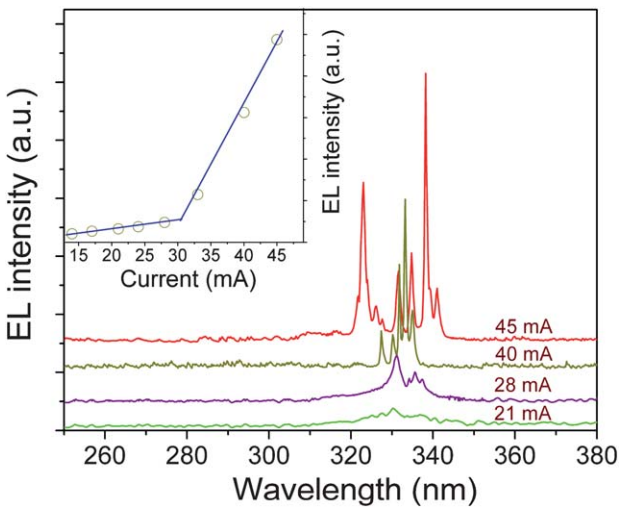

Fig. 4 Lasing spectra of the Au/MgO/MgZnO/*n*-ZnO structure under different injection current. The inset shows the integrated intensity of the emission at around 330 nm as a function of the injection current.

In summary, an electrically pumped UV laser has been realized in MgZnO nanocolumns in a Au/MgO/$Mg_{0.25}Zn_{0.75}O$/*n*-ZnO structure. The lasing peak is located at around 330 nm, this is one of the shortest wavelengths ever reported in a semiconductor laser diode. The threshold current of the lasing is only 30.0 mA, over one order of magnitude smaller than the previously reported value in UV laser diodes with similar operation wavelength. The results reported in this communication provide a simple route to a UV laser diode with low threshold, thus may address a significant step towards the future applications of this kind of lasers.

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