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Plasma induced deep ultraviolet emissions from MgZnO films

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ABSTRACT

Cubic rocksalt structured $Mg_{0.54}Zn_{0.46}O$ films have been prepared, and the films show a wide bandgap of 5.47 eV. Obvious emission at around 276 nm has been detected when the films are placed in the ambient of plasma, and the output power of the plasma induced deep ultraviolet emission can reach around 56 μW, which is the highest value ever reported for ZnO-based DUV light-emitters. The deep ultraviolet emission is believed to come from the $Mg_{0.54}Zn_{0.46}O$ films excited by the kinetic radicals of the plasma.

1. Introduction

Light sources that can work in deep ultraviolet (DUV) region (with wavelength shorter than 300 nm) have versatile potential applications including but not limited to sterilization, food or water purification, clinical diagnostics, etc. [1,2]. Thus much attention has been paid to develop high performance DUV light sources in recent years. Nevertheless, mercury, deuterium, excimer and xenon based lamps are still prevail in DUV light sources. It is accepted that these lamps have disadvantages in terms of lifetime, stability and portability. DUV light-emitting devices (LEDs) fabricated from GaN-based wide bandgap semiconductors have witnessed great progress in the past decades, and quite a few such reports have been demonstrated [3,4]. Generally speaking, to realize efficient semiconductor LEDs, a *p-n* junction should be constructed. For DUV LEDs, the bandgap of the active layer should be larger than 4.13 eV (corresponds to around 300 nm). Although there have been some reports on DUV emission from wide bandgap semiconductors [5–9], intentional doping, especially *p*-type doping, of such wide bandgap semiconductors is still a huge challenge because of the relatively large activation energy of acceptors. For example, the activation energy of Mg acceptors in GaN is around 170 meV, while that in AlN reaches around 500 meV [10–12]. Such a large activation energy makes the efficient *p*-type doping of wide bandgap semiconductors problematic, thus the realization of high performance wide bandgap semiconductor *p-n* junction based DUV LEDs almost impossible. Under such circumstance, a route to DUV emission by avoiding the problematic *p*-type doping of wide bandgap semiconductors is greatly desired. Electron beam pumped DUV light-emitters have been proposed recently, and some interesting results have been obtained from BN, AlGaN, etc. [1,5,7,13]. It has been mentioned that plasma can be employed as an excitation source for luminescence [14], and visible emissions have been obtained from polymers under the excitation of helium plasma [15,16]. Plasma has also been employed to excite the minerals and artificially activated luminophors, and UV–visible emissions have been acquired [14]. Nevertheless, none report on plasma induced DUV emissions from wide bandgap semiconductors can be found up to date.

In this paper, DUV emissions have been realized from rock-salt structured MgZnO films induced by plasma ambient. Here MgZnO has been employed as the active layer of the device because of the relatively strong resistance of ZnO-based materials to particle irradiation [17–19]. Additionally, the bandgap of ZnO-based materials can be extended from 3.37 eV to 7.7 eV when alloyed with MgO, which covers the DUV spectrum region, implying that ZnO-based materials may find applications in short-wavelength LEDs [20–23]. Under the excitation of a plasma ambient, an emission peaked at around 276 nm has been realized from the MgZnO films, and the output power of the DUV emission can reach 56 μW, which is the highest value ever reported for ZnO-based DUV light-emitters.

2. Experimental detail

The MgZnO films employed as the active layer of the DUV emissions were grown on sapphire substrate by metal-organic chemical vapor deposition (MOCVD) technique. Oxygen (O_2), diethylzinc (DEZn), and dimethyl dicyclopentadienyl magnesium

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($MeCp_2Mg$) were employed as the precursors for the growth, and nitrogen (5N) was used as the carrier gas. It has been reported that phase-separation will occur in MgZnO films when the Mg content is in the range of 0.4–0.6 [24,25]. By employing a relatively low growth temperature and oxygen-rich strategy, single-phased rocksalt MgZnO films have been prepared, and the detailed growth conditions of the MgZnO films can be found elsewhere [26,27]. Briefly, the growth was carried out at a substrate temperature of 450 °C and a chamber pressure of around 150 Torr, and the mole ratio of the DEZn and $MeCp_2Mg$ to O_2 that were introduced to the growth chamber during the growth process was around 300. The structural properties of the films were evaluated by an x-ray diffractometer (XRD) with CuKα line (0.154 nm) as the radiation source. The composition of the MgZnO films was determined using energy-dispersive x-ray spectroscopy (EDS), and the absorption and transmission spectra were recorded in a Shimadzu UV-3101PC scanning spectrophotometer. The photoluminescence (PL) spectrum of the films was recorded at Beam line 4B8 in Beijing Synchrotron Radiation Facilities under a dedicated synchrotron mode (2.5 GeV, 150–60 mA).

3. Result and discussion

The Mg content in the MgZnO films determined by EDS is 0.54. The typical absorption and PL spectra of the $Mg_{0.54}Zn_{0.46}O$ films are shown in Fig. 1a. One can see that the film shows a strong absorption in the UV region with a sharp absorption edge at around 226 nm. From the absorption spectrum, a bandgap of around 5.47 eV can be derived by employing the $\alpha^2 \propto (h\nu - Eg)$ expression, where α is the absorption coefficient and $h\nu$ is the photon energy. The PL spectrum displays an emission peak at around 276 nm, which corresponds to an energy of 4.49 eV. Note that the emission energy is significantly smaller than the bandgap of the $Mg_{0.54}Zn_{0.46}O$ film determined from the absorption spectrum (5.47 eV). We think the absence of the near band-edge emission may indicate that the crystalline quality of the $Mg_{0.54}Zn_{0.46}O$ films needs further improving. The structural characterizations of the $Mg_{0.54}Zn_{0.46}O$ films were assessed by XRD, as shown in Fig. 1b. An obvious peak located at 36.73° can be observed in the pattern, which can be attributed to the diffraction of the (1 1 1) facet of $Mg_{0.54}Zn_{0.46}O$ [28]. The above results reveal that the $Mg_{0.54}Zn_{0.46}O$ films are crystallized in cubic rocksalt structure.

To realize plasma induced DUV emission, a setup has been built, and the schematic illustration of the setup is shown in Fig. 2. In this setup, a rotary pump was used to produce a vacuum ambient in a quartz tube. A commercial available handheld plasma jet was placed near the quartz tube to provide a high-frequency electric field. An Ocean Optics USB2000 UV–vis spectrometer was employed to record the emission signals.

Fig. 3a shows the typical emission spectrum of the plasma, one can see several sharp peaks in the region from 3.0 eV to 4.0 eV from the spectrum, which are the typical second ($C^3\Pi_u \rightarrow B^3\Pi_g$) positive emission band of N_2 excited by the high-frequency electric field in the plasma jet [29,30]. The emission spectrum of the setup when the $Mg_{0.54}Zn_{0.46}O$ film is placed in the ambient of the plasma is shown in Fig. 3b. A broad peak located at around 276 nm is visible in the spectrum besides the sharp peaks, which is in agreement with the PL spectra of the $Mg_{0.54}Zn_{0.46}O$ film shown in Fig. 1b (276 nm). Therefore, the broad emission should come from the $Mg_{0.54}Zn_{0.46}O$ film. We note that the emission at around 276 nm can not be excited by the sharp peaks in the range from

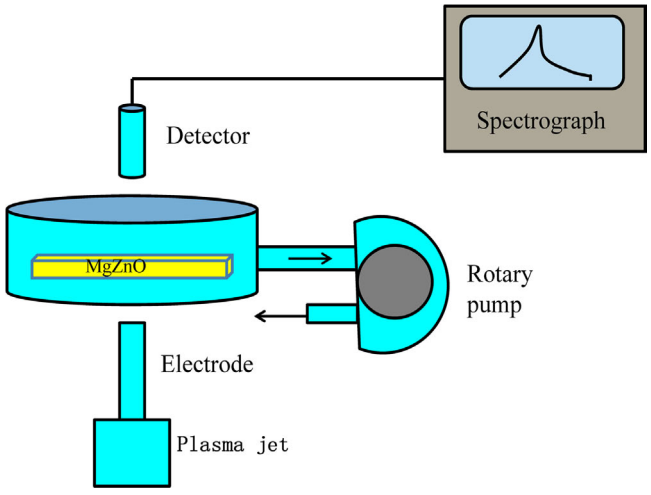

Fig. 2. Schematic illustration of the plasma induced luminescence setup.

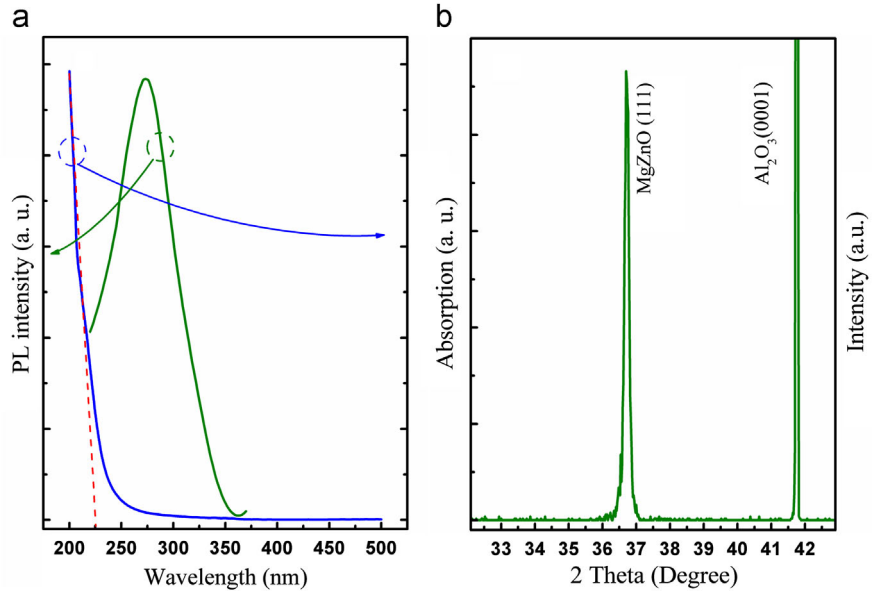

Fig. 1. PL and absorption spectrum (a) and XRD pattern (b) of the $Mg_{0.54}Zn_{0.46}O$ films.

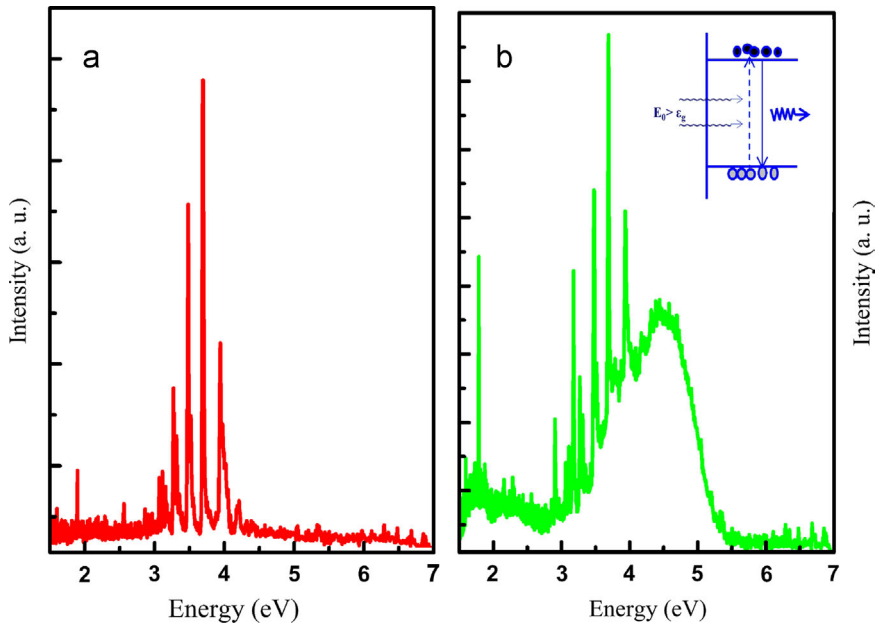

Fig. 3. Emission spectra of the plasma (a) and plasma excited $Mg_{0.54}Zn_{0.46}O$ films (b), and the inset shows the schematic mechanism of the plasma induced emissions.

3.0 eV to 4.0 eV since its energy is larger than that of the latter. It is thought that the DUV emission from the $Mg_{0.54}Zn_{0.46}O$ films is excited by the ionized radicals including electrons, cations, and anions, etc. in the plasma ambient. When the plasma jet is switched on, the high-frequency electric field generated in the jet will crack the nitrogen and oxygen molecules into ionized radicals. The radicals will be accelerated greatly by the electric field, and their energy may be much larger than the bandgap of the $Mg_{0.54}Zn_{0.46}O$ films. Thus, when they impact with the films, electrons in the valence band of the films will be excited to the conduction band. Then the excited electrons will recombine with the holes, and in this way emission from the $Mg_{0.54}Zn_{0.46}O$ films will be obtained. The above emission mechanism has been schematically illustrated in the inset of Fig. 3b. Note that none report on plasma induced DUV emission from wide bandgap semiconductors can be found before.

The output power of the plasma induced DUV emission from the $Mg_{0.54}Zn_{0.46}O$ film has been measured by an optical power meter (NOVA METER ASSY RoHS). Note that the emission power of the second positive emission band of N_2 (namely the sharp peaks) has been excluded when measuring the emission power of the DUV emission. It is found that the pressure in the quartz tube has a great influence on the output power of the DUV emission, as illustrated in Fig. 4. Note that the output power shown in this figure is recorded by fixing all the other parameters constant but the pressure in the quartz tube. From the plot, one can see that the emission intensity increases firstly and then decreases with the decrease of the pressure in the quartz tube, and a maximum output power of 56 μW has been obtained when the pressure in the tube is around 1000 Pa. We note that only one report demonstrated the output power for ZnO-based DUV emissions in literature, and it is in the order of nanowatt [22], and the results reported in this paper is over four orders of magnitude higher than the results reported before.

To understand the dependence of the output power on the pressure clearly, the emission spectra of the plasma under different pressure has been measured, as shown in Fig. 5. Note that the emission intensity of the second positive emission spectrum may reveal the power intensity of the radicals to some extent. One can see that the emission intensity increases firstly then decreases

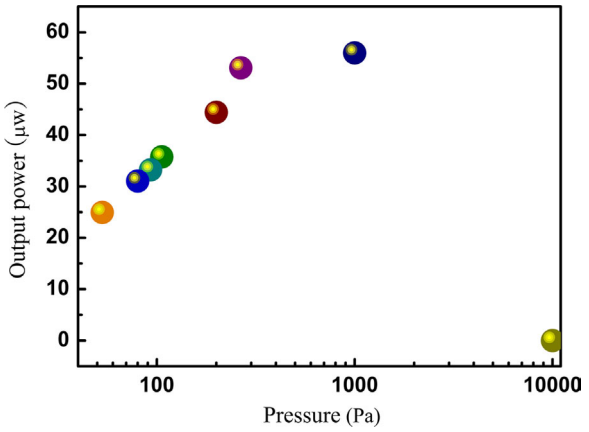

Fig. 4. The dependence of the output power of the plasma induced DUV emission on the vacuum pressure in the quartz tube.

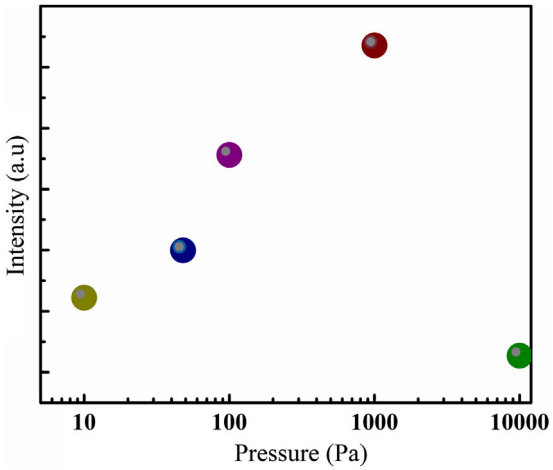

Fig. 5. The dependence of the plasma intensity on the vacuum pressure in the quartz tube.

with the pressure in the tube, and it reaches maximum when the pressure is around 1000 Pa. The above phenomenon can be understood as follows: at low pressure, the number of the molecules that can be cracked into ionized radicals is less, thus the emission intensity of the plasma is weak. With the increase of the pressure, more radicals can be produced by the high frequency electric field, thus the emission intensity of the plasma increases with the pressure in the tube. While when the pressure is high, there are so many molecules in the plasma ambient that the movement of the accelerated radicals will be obstructed, thus the emission intensity of the plasma decreases gradually. One can see that the dependence of the output power of the $Mg_{0.54}Zn_{0.46}O$ film on the vacuum pressure (shown in Fig. 4) is very similar with that of the plasma, thus the intensity variation of the plasma induced DUV emission from $Mg_{0.54}Zn_{0.46}O$ film on the vacuum pressure should mainly come from the change of the excitation intensity.

4. Conclusions

In conclusion, DUV emissions have been obtained by employing $Mg_{0.54}Zn_{0.46}O$ film as an active layer under the excitation of energetic radicals induced by a plasma jet. An obvious DUV emission at around 276 nm has been obtained from the device. Note that no report on plasma induced DUV emission from wide bandgap semiconductors can be found before. The output power can reach around 56 μW, which is the highest value ever reported for ZnO-based DUV emissions. Considering that the realization of efficient wide bandgap *p-n* junction structured DUV LEDs is still a challenging issue, the results reported in this paper may provide a promising alternative route to DUV emissions.

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