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Ultraviolet emission from a multi-layer graphene/MgZnO/ZnO light-emitting diode

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We report on ultraviolet emission from a multi-layer graphene (MLG)/MgZnO/ZnO light-emitting diodes (LED). The p-type MLG and MgZnO in the MLG/MgZnO/ZnO LED are used as transparent hole injection and electron blocking layers, respectively. The current-voltage characteristics of the MLG/MgZnO/ZnO LED show that current transport is dominated by tunneling processes in the MgZnO barrier layer under forward bias conditions. The holes injected from p-type MLG recombine efficiently with the electrons accumulated in ZnO, and the MLG/MgZnO/ZnO LED shows strong ultraviolet emission from the band edge of ZnO and weak red-orange emission from the deep levels of ZnO. © 2014 AIP Publishing LLC.

ZnO has a wide band gap (3.3 eV) and large exciton binding energy (60 meV), so it has been widely investigated for optoelectronic applications.1 However, ZnO-based p-n homojunction light-emitting diodes (LEDs) have been reported by only a few groups because it is difficult to obtain high-quality p-type ZnO. Recently, considerable research effort has been devoted to ZnO-based heterojunctions and Schottky diodes using a variety of p-type and highly conductive layers such as p-GaN, poly(3,4-ethylenedioxythiophene):poly(styrenesulphonic acid), p+-Si, and metal.2–5 Graphene, which has unique physical properties such as high optical transmittance in the ultraviolet (UV) wavelength range, high carrier mobility, and mechanical flexibility, is also considered a promising material for optoelectronic devices operating in the UV wavelength region and nanogenerators.6–9 Diode characteristics were observed in a graphene/ZnO-based heterostructure because a Schottky barrier can be formed at the interface between ZnO and graphene because of the difference of their work functions.8,9 However, graphene/ZnO Schottky diodes are not suitable for application in light-emitting devices because carriers are poorly confined at the interface between graphene and ZnO. As an alternative approach, a metal/insulator/semiconductor (MIS) structure with a potential barrier between graphene and ZnO was proposed to develop LEDs containing graphene/ZnO-based heterostructures because it can efficiently confine carriers at the insulator/semiconductor interface.10 ZnO-based MIS-type LEDs containing semi-metallic p+-Si instead of the metal layer in the MIS structure also showed good performance because of enhanced hole injection into the ZnO active layer.4,11 In this paper, we report the electrical and optical properties of a multi-layer graphene (MLG)/MgZnO/ZnO MIS-type LED. We found that a p-type semi-metallic MLG layer can be used as a transparent hole injection layer in the MLG/MgZnO/ZnO MIS structure because of its high transparency in the UV wavelength range. Efficient hole injection occurs from p-type MLG into the ZnO active region.

A MgZnO film with a thickness of 20 nm was grown on an undoped ZnO substrate with a donor concentration of $4 \times 10^{17} \text{cm}^{-3}$ by radio-frequency (rf) magnetron sputtering using a ZnO target mixed with 20 wt. % MgO. The rf power density of the plasma source was 12.8 W/cm², and the flow rate of Ar and O₂ gases was 20 sccm. A MLG film was synthesized on a Ni/SiO₂/Si substrate by a Ni catalytic growth process with flow rates of 10 sccm of CH₄ gas, 20 sccm of H₂, and 480 sccm of an Ar gas mixture at 1000 °C for 5 min. To obtain the MLG layer, the Ni film was etched in aqueous iron chloride solution and then the MLG films were transferred onto the high-quality MgZnO/ZnO structure. The MLG layer synthesized by chemical vapor deposition (CVD) showed p-type conductivity with a hole concentration of $1.16 \times 10^{12} \text{cm}^{-2}$ and mobility of $1480 \text{cm}^{2}/\text{V} \cdot \text{s}$, similar to previously reported values.8,13 Ti/Au (20/100 nm) metal electrode were deposited on the MLG layer and backside of the ZnO substrate, respectively. Figure 1(b) shows Raman spectra of MgZnO/ZnO and MLG/MgZnO/ZnO. In the Raman spectrum of MgZnO/ZnO, two major peaks at 435 and 1158 cm⁻¹ are consistent with the high-frequency E₂ mode (E₂-high) and E₁-second order longitudinal optical (E₁-2LO) mode, respectively.14 The MLG/MgZnO/ZnO Raman spectrum indicates that the MLG layer has been transferred onto the MgZnO/ZnO structure. MLG/MgZnO/ZnO LEDs were fabricated on the high-quality MgZnO/ZnO substrate. The Raman spectra of MLG/MgZnO/ZnO show a strong peak at 1350 cm⁻¹, which corresponds to the first-order Raman shift of graphene.15,16 Figure 1(c) shows the transmittance of ZnO, MgZnO, and MLG/MgZnO. To measure the transmittance of MLG and MLG/MgZnO, the

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MLG layers were transferred onto glass substrates with and without an MgZnO layer, respectively. MgZnO and MLG are both highly transparent at a wavelength of 383 nm, which corresponds to a band-edge UV emission of ZnO. As shown in the inset of Fig. 1(c), the optical band gap of MgZnO is 5.85 eV, which corresponds to a Mg composition of 56%. This indicates that MgZnO is transparent to the UV emission from the ZnO band edge and it can also be used as an electron blocking layer to confine electrons in the active ZnO layer. As shown in Fig. 1(c), the UV light emitted from the ZnO active layer can be transmitted effectively through MLG and MgZnO because the measured transmittance of MLG/MgZnO is 75% at 383 nm, which is much higher than that of p-type ZnO (16.7%). The MLG layer can reduce the self-absorption of UV light in the p-n homojunction, while the UV light is readily absorbed by the p-ZnO layer.

Figure 2(a) shows the current-voltage (I-V) characteristics of an MLG/MgZnO/ZnO diode and MLG/ZnO/ZnO LED. The I-V curve obtained for the MLG/MgZnO/ZnO LED shows well-defined diode characteristics compared with those of the MLG/ZnO diode without the MgZnO barrier. The MLG/ZnO diode shows typical Schottky diode characteristics with a low forward turn-on voltage of 1.2 V, which is similar to that of a reported graphene/ZnO-based Schottky diode. The I-V characteristics of the MLG/MgZnO/ZnO LED show better rectification because of the insertion of the MgZnO layer with a higher barrier height than that of ZnO/MLG. In addition, the I-V characteristics of MLG/MgZnO/ZnO LED show better rectification because of the insertion of the MgZnO layer with a higher barrier height than that of ZnO/MLG. In addition, the I-V characteristics of MLG/MgZnO/ZnO LED and MLG/ZnO diode are similar to those of a semi-metallic p-type InGaN/GaN diode. The series resistance (R_s) under forward currents from 10 to 40 mA in the high-voltage region (V > E_g/q, where E_g is energy band gap) can be determined from the slope of dV/d(lnI)-I plot. The estimated R_s of the MLG/ZnO diode and MLG/MgZnO/ZnO LED are 9.3 and 20.9 Ω, respectively. The increase in R_s is associated with the high energy barrier of the MgZnO layer, which has a band gap of 5.85 eV.

We investigated the current transport process through the MgZnO layer under forward bias to better understand the...
electrical properties of the MLG/MgZnO/ZnO LED by further examination of its I-V characteristics. A log-log plot of the I-V curve obtained for the MLG/MgZnO/ZnO LED is presented in Fig. 2(b). This plot shows that the current transport mechanisms in the three regions are different depending on the applied voltage. The current in region (I) (below 1.0 V) shows a linear dependence on voltage, indicating that current transport is dominated by direct tunneling of carriers through the MgZnO barrier at low voltages.\(^1\) The I-V curve in region (II) (1.0–4.0 V) was fitted well by the relation \(I \sim \exp(cV)\) (where \(c\) is a constant). This indicates that the carrier transport in region (II) is dominated by carrier tunneling and recombination via defect states.\(^5,22\) The I-V curve of the MLG/MgZnO/ZnO LED above 4 V changes abruptly in region (III), as shown in Fig. 2(a). When the applied voltage exceeds 4 V, the barrier gradually transforms into a triangular shape because of the high electric field, and Fowler-Nordheim (FN) tunneling is expected.\(^20\) The FN tunneling current follows Eq. (1):\(^21\)

\[
I \propto V^2 \exp\left(-\frac{4t\sqrt{2m^*\phi_0}}{3hqV}\right),
\]

where \(t\), \(h\), \(\phi\), and \(m^*\) are the barrier width, Planck constant, barrier height, and effective mass of carriers, respectively. The inset of Fig. 2(b) showing the plot of \(
\ln(I/V^2)
\)
as a function \(I/V\) reveals a linear dependence at high bias voltage above 4 V, confirming FN tunneling of carriers through MgZnO in region (III). These results show that electrons and holes are transported under forward bias through the MgZnO barrier layer in the MLG/MgZnO/ZnO LED by tunneling processes.

Figure 3(a) shows electroluminescence (EL) spectra of the MLG/MgZnO/ZnO LED. The room temperature EL emission is dominated by the sharp near-band-edge emission (NBE) at 383 nm and a broad deep-level emission (DLE) from 650 to 850 nm. It has been reported that the red-orange emission is related to the transition from defect levels such as oxygen interstitial and oxygen vacancies in ZnO.\(^23,24\) The EL intensities of both NBE and DLE increase with injection current from 10 to 90 mA. Figure 3(a) also shows that the EL intensity of the NBE increases rapidly with injection current compared with that of DLE. Figure 3(b) illustrates the relative EL intensities of NBE and DLE with increasing injection current. As shown in Fig. 3(b), the DLE intensity increased with injection current, whereas the intensity of NBE increased rapidly when the injection current reached 40 mA and was saturated at currents above 60 mA. The differences in these changes of NBE and DLE intensities are closely related to the radiative recombination of carriers, which depends strongly on the current transport in the MLG/MgZnO/ZnO LED.

![EL spectra of the MLG/MgZnO/ZnO LED at injection currents from 10 to 90 mA. (b) Relative EL intensity for NBE and DLE versus injection current.](image)

Energy band diagrams of the MLG/MgZnO/ZnO LED under different bias voltages are depicted in Fig. 4. In Fig. 4(a), the electron affinity of ZnO (\(\phi_{ZnO}\)) and work function of MLG (\(\Phi_{MLG}\)) are taken as 4.3 and 4.5 eV, respectively.\(^9\) The band gap offsets of MgZnO/ZnO at the conduction and valence bands are \(\Delta_E = 1.5\) eV and \(\Delta_E_v = 1\) eV, respectively.\(^25\) Under low bias, the Fermi level of MLG moves to lower energy (Fig. 4(b)), and becomes closer to the deep defect level of ZnO. The holes in p-type MLG can tunnel through the MgZnO barrier into the defect level and recombine with the accumulated electrons at the MgZnO/ZnO interface. As shown in Fig. 3(b), the DLE is gradually increased by radiative recombination under low current injection conditions, which corresponds to region (II) in Fig. 2(b). However, the NBE increased rapidly at injection currents exceeding 40 mA, corresponding to an applied voltage of 3.37 V, which is close to the band gap energy of ZnO at room temperature.\(^4\) When the Fermi level of MLG reaches the valence band of ZnO, the NBE over the current range from 40 to 60 mA increases rapidly, as indicated in Figs. 3(b) and 4(c), because holes can be injected from p-type MLG into the valence band of ZnO by resonant tunneling through the thin MgZnO layer. However, the EL intensity of NBE is saturated at high injection current (\(>60\) mA), which corresponds to an applied voltage of 4 V. When the applied voltage exceeds 4 V, the accumulated electrons at the MgZnO/ZnO interface can undergo FN tunneling process, as explained in region (III) of Fig. 2(b). As a result, the EL intensity of the NBE is saturated above 60 mA, because the electron concentration at the interface of MgZnO/ZnO decreases via FN-tunneling. This indicates that the MLG/MgZnO/ZnO LED has a maximum NBE efficiency at an operating voltage that is close to the band gap energy of ZnO.
In conclusion, we demonstrate that p-type MLG can be used as a transparent hole injection layer in a ZnO-based MIS-type UV LED. The I-V characteristics of the MLG/MgZnO/ZnO LED show that the carriers are injected by three different tunneling processes through the MgZnO layer under forward bias conditions. The MLG/MgZnO/ZnO LED shows strong UV emission and weak, broad red-orange EL emission as a result of NBE and DLE, respectively. The intensity of the NBE reveals that the holes injected from the p-type MLG layer by tunneling through the MgZnO barrier layer are efficiently recombined with the electrons in the ZnO active layer. These results show that CVD-grown p-type MLG can be used effectively as a transparent hole injection layer in UV EL devices.

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FIG. 4. (a) Energy band diagrams of MLG/MgZnO/ZnO LED under (a) zero bias, (b) low bias, and (c) high bias.