ZnO-Based Fairly Pure Ultraviolet Light-Emitting Diodes With a Low Operation Voltage

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***Abstract*—A ZnO-based metal–insulator (HfO_2)–semiconductor diode was synthesized on a commercially available n^+-GaN/sapphire substrate using a radio-frequency magnetron sputtering system. Electroluminescence measurements revealed that the diode exhibited fairly pure ultraviolet (UV) emission peaking at ~370 nm with a line width of less than 8 nm. By choosing a proper thickness of the insulator HfO_2 layer, the threshold voltage of the emission could be reduced to 2 V, demonstrating that this ZnO-based fairly pure UV light-emitting diode can be driven by two ordinary dry batteries. The reason for low threshold voltage is proposed in terms of the n^+-GaN/sapphire substrate and the high-k insulator HfO_2 layer.**

***Index Terms*—Electroluminescence (EL), HfO_2, light-emitting diode (LED), metal–insulator–semiconductor (MIS), ultraviolet (UV), ZnO.**

I. Introduction

Over the years, ZnO is considered as a promising material replacing the III-nitride semiconductors to be used for blue/ultraviolet (UV) light-emitting diodes (LEDs). This is because of its advantages over the III-nitride semiconductors, such as large exciton binding energy (60 meV), availability of high-quality bulk substrates, ease of wet etching, etc. [1], [2]. A variety of device structures, such as homojunction [3], [4], heterojunction [5], [6], and metal–insulator–semiconductor (MIS) structure [7], [8], are used to realize electroluminescence (EL) from ZnO. Among all of these structures, the MIS structures could increase the carrier density in the radiative recombination region by confining the carriers in the semiconductor–insulator interface on certain conditions, thus resulting in an enhancement of the light emission [7].

As we know, the ordinary commercial LED can be driven by two dry batteries (3 V), but most of the reported ZnO-based LEDs required higher operation voltage. For example, the ZnO-based homojunction fabricated by Tsukazaki *et al.* [3] emits violet light when applied with a forward bias over 10 V.

Manuscript received June 11, 2009; revised July 24, 2009. First published September 11, 2009; current version published September 29, 2009. This work was supported by the Special Fund of Ministry of Education for Doctor's Conferment Post (20070486015), the National High Technology Research and Development Program of China (2009AA03Z219) and the Natural Science Foundation of Jiangsu Province (BK2009143). The review of this letter was arranged by Editor P. K.-L. Yu.

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Digital Object Identifier 10.1109/LED.2009.2028904

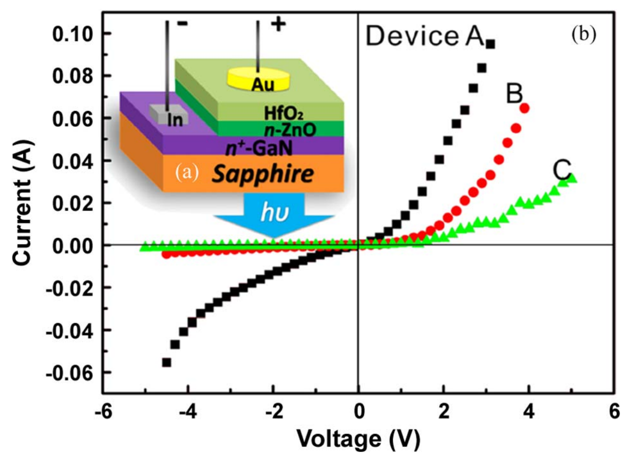

Fig. 1. (a) Schematic diagram of the $Au/HfO_2/n$-ZnO MIS structure on an n^+-GaN/sapphire substrate. (b) Current–voltage characteristics of the ZnO-based MIS LED devices of A, B, and C.

The hybrid (n-ZnO NWs/p-GaN film) blue LED fabricated by Zhang *et al.* [5] also needs a high forward bias over 10 V. Even the ZnO-based metal–insulator (SiO_x)–semiconductor structure on a silicon substrate fabricated by Chen *et al.* [7] emits pure UV light when it is under a forward bias over 8 V. ZnO-based LEDs, particularly the pure UV LEDs, which can be driven by two dry batteries (3 V), are seldom reported. In this letter, we report the fabrication of ZnO-based MIS LEDs with a low operation voltage. The MIS diode was synthesized on a commercially available n^+-GaN/sapphire substrate using a radio-frequency (RF) magnetron sputtering system. By choosing a proper thickness of the insulator HfO_2 layer, fairly pure UV EL emission with a line width of less than 8 nm was observed from the ZnO-based MIS diode when it applied with a forward bias of less than 3 V.

II. Experimental Section

Fig. 1(a) shows the schematic diagram of the ZnO-based MIS LED and the emission recording geometry. Undoped ZnO layer with a thickness of 100 nm was deposited on a commercially available n^+-GaN/sapphire substrate by RF magnetron sputtering from a ZnO target at 300 °C. Then, the insulator HfO_2 layers with different thicknesses of 10 nm (device A), 50 nm (device B), and 100 nm (device C) were deposited by RF sputtering on the as-deposited ZnO films for comparison. During HfO_2 deposition, a 99.99% pure HfO_2 ceramic pellet was used as the sputtering target while keeping the flow rate

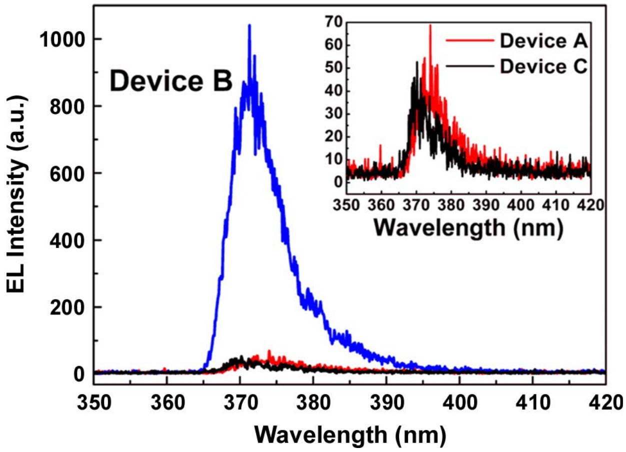

Fig. 2. EL spectra of the ZnO-based MIS LED devices of A, B, and C when applied with a forward bias of 3 V. The inset shows the same EL spectra of devices A and C in a smaller range.

ratio of oxygen and argon, substrate temperature, sputtering power, and chamber pressure at 1 : 3, 100 °C, 130 W, and 1.0 Pa, respectively. Monolayer Au and In electrodes were employed as the contacts for the i-HfO_2 and n^+-GaN layers, respectively. The Hall measurements revealed that the ZnO layer presented an n-type conduction with an electron concentration around $\sim 10^{15}$ cm^{-3}, which is extremely lower than that of the n^+-GaN layer ($\sim 10^{18}$ cm^{-3}). The morphology was observed by Sirion field emission scanning electron microscopy (SEM, Philips XL30). The crystal structures of the films were characterized by X-ray diffraction (XRD, Burker Axs, D8 Advance). Current–voltage (I–V) characteristics of the devices were measured by a Keithley 4200 electrometer. The EL measurements were carried out in an iHR320 Imaging Spectrometer with the scanning step size of 0.1 nm. All of these measurements were carried out at room temperature in ambient atmosphere.

III. Results and Discussion

The SEM and XRD of the as-deposited ZnO film revealed that the ZnO layer is composed of closely packed quasi-hexagon-shaped columns with an average size of 20 nm and shows the c-axis oriented growth on crystalline matched GaN substrate (see details in the supplemental material) “details not shown, due to space limitations.” The current–voltage (I–V) characteristics of the ZnO-based MIS LED of devices A, B, and C are shown in Fig. 1(b). As shown, the I–V curves of devices B and C demonstrate a diodelike rectifying behavior, while the I–V curve of device A has a larger leakage current than that of devices B and C. It can be seen that under the same forward voltage, the current decreases as the thickness of the HfO_2 layer increases. The EL spectra of devices A, B, and C are shown in Fig. 2. Under the same forward bias of 3 V, UV emissions peaking around 372 nm, with a full-width at half-maximum (FWHM) of less than 10 nm, are detected in all of the devices. It can also be seen that the EL intensity of device B is extremely larger than those of devices A and C under the same forward bias. It should also be noted that no EL was detected from the device without the insulator HfO_2 layer between the Au electrode and the ZnO film. In the case

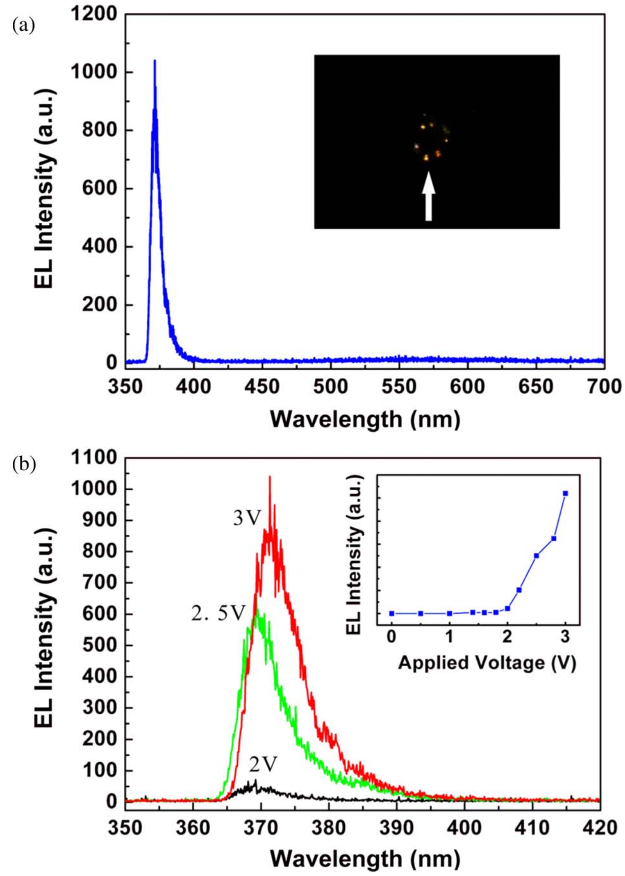

Fig. 3. (a) RT EL spectrum of the ZnO-based MIS LED with ∼50-nm-thick HfO_2 layer applied with a forward bias of 3 V. The inset shows the lighting image of the ZnO-based MIS LED device. (b) RT EL spectra of the ZnO-based MIS LED device under various forward bias voltages of 2, 2.5, and 3 V. The inset shows the plot of EL intensity versus forward bias fixing the emission wavelength at 371 nm.

of device A, due to the very thin insulator HfO_2 layer, most of the electrons in the conduction band of ZnO tunnel through the narrow energy barrier, so there are only a few electrons accumulating in the interface between the ZnO and HfO_2 layers [7]. In the case of the device B, the HfO_2 layer is thick enough to prevent more electrons in ZnO from tunneling through the HfO_2 layer than the device A. Thus, a substantial confinement of electrons in the conduction band of ZnO beneath the HfO_2 barrier is necessary for generating UV EL from ZnO [7]. As the thickness of the insulator HfO_2 layer increases to 100 nm (device C), however, although the HfO_2 layer is thick enough to confine substantial electrons in the semiconductor–insulator interface, the capacitance of the HfO_2 film decreases at the same time. Therefore, under the same forward bias, the carrier density confined in the semiconductor–insulator interface of the device with ∼100-nm-thick HfO_2 layer is smaller than that of the device with ∼50-nm-thick HfO_2 layer. On the other hand, the origin of the holes injected into ZnO in the MIS device is the key to understanding the mechanism of UV EL, which has been discussed in the previous report made by Chen *et al.* [7]. Although the insulator layer they used was SiO_x, we think that the explanation is apt in this case as well.

To further investigate the EL properties of the ZnO-based MIS diode with suitable thickness of HfO_2 layer, more EL measurements of this sample were taken, which is shown in Fig. 3. The RT EL spectrum of the MIS LED applied with a forward bias of 3 V in both the UV and visible regions (350–700 nm) is shown in Fig. 3(a). It can be clearly demonstrated that there is a dominant sharp peak around 372 nm with an FWHM of 7.8 nm, and it also can be seen that the emission intensity in the visible region is relatively extremely weak compared with that in the UV region. The inset is a lighting image of the Au/i-HfO_2/n-ZnO LED device under a forward bias of 3 V recorded using a commercial digital camera. Fig. 3(b) shows the EL spectra of the Au/i-HfO_2/n-ZnO LED device under various forward bias voltages. It can be seen that the emission peak was significantly enhanced when the forward bias increased from 2 to 3 V. It should be noted that the emission peak redshifts from 369 to 372 nm as the forward bias increases from 2.5 to 3 V, which is due to temperature-induced bandgap variations [9]. The inset shows the plot of EL intensity versus forward bias by fixing the emission wavelength at 371 nm. As can be seen, the UV EL intensity increases significantly with the forward bias over 2 V. In order to confirm that the UV emission is originated from the ZnO layer and not from the n^+-GaN layer, the PL spectrum of the as-deposited ZnO layer (on an n^+-GaN/sapphire substrate) and the EL emission of the Au/HfO_2/n-ZnO MIS LED (on an ITAZO/i-GaN/sapphire substrate) are shown in the supplemental material "details not shown, due to space limitations."

The low threshold voltage of the MIS device is due to the following three factors: 1) The GaN layer used in this structure is considered as the ideal substrate to grow ZnO layer because of their similarity in crystalline structure and closely matched lattice constant [10]; 2) the n^+-GaN substrate injects sufficient electrons to the ZnO layer when the device applied with a forward bias, so the amount of electrons accumulated in the semiconductor–insulator interface is greatly enhanced when they are drawn by the forward bias; and 3) the insulator HfO_2 layer is considered as a very promising candidate to replace SiO_2 in metal–oxide–semiconductor field-effect transistors [11] because it is a high-k dielectric material compared with SiO_2, which suggests that, under the same circumstance (equal thickness, forward bias, etc.), the MIS structure with HfO_2 as the insulator layer could confine more electrons in the semiconductor–insulator interface than that with SiO_2 as the insulator layer. Therefore, the threshold voltage of this ZnO-based MIS LED is brought down.

IV. Conclusion

In summary, we have fabricated ZnO-based MIS LED devices on n^+-GaN/sapphire substrates using an RF magnetron sputtering system. Fairly pure UV EL emission with a line width of less than 8 nm was observed from the ZnO-based MIS diodes. The MIS LED device with a proper thickness of the insulator HfO_2 layer has a low threshold voltage of 2 V. The reason for low threshold voltage may lie in the n^+-GaN/sapphire substrate and the high-k insulator HfO_2 layer. Even though further research work is needed to be done to improve the quality of the UV-LED, we think this study demonstrates the possibility of fabricating ZnO-based UV LED devices which can be driven by two ordinary dry batteries.

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