Single-Crystalline ZnO/Graphene Quantum Dots Phosphors-Converted White Light-Emitting Diodes

Mirgender Kumar, *Member, IEEE*, Anuj Kumar, Sunny, *Member, IEEE*, Kwang-Su Seong, and Si-Hyun Park, *Member, IEEE*

***Abstract*— In this letter, phosphor-converted white light-emitting diodes (LEDs) were analyzed based on the single-crystalline (SC) ZnO film/graphene quantum dots (GQDs) as phosphors with ultraviolet (UV) excitation. Color rendering index (CRI) and correlated color temperature (CCT) are found to be improved with injection current. The luminous efficiency of 245 lm/W at 260 mA has been achieved with 98 CRI and 5064 K CCT. The results show that the UV excited SC ZnO coated with GQDs white LEDs are more optically compatible for solid-state lighting, compared to the conventional blue chip-excited yellow phosphors LEDs.**

***Index Terms*— Phosphor-converted white LEDs, ZnO film, graphene quantum dots, cool white light.**

I. Introduction

PHOSPHORS-CONVERTED white light-emitting diode (pc-WLED) technology is continuously improving with respect to device architecture and material quality for achieving high luminous efficiency, high brightness, and longer operational life. Present technology relies mostly on the use of highly luminescent phosphors pumped with blue LEDs. The level of blue band increases faster than the other visible bands with pumping current which restrict the device to achieve a rich color rendering index (Ra) for white luminescence [1]. In addition, this high level of blue light in LEDs than conventional light source might be a potential risk of chronic exposure for human eyes [2]. However, conventional pc-LED performance has also been limited by phosphors embedded in epoxies and resins, which degrades under the operation of high irradiation intensities and high temperature, thus reducing the efficiency and color rendering with time [3]. Moreover, the rare earth free phosphors are also in demand for environmental prospective [4], [5]. To resolve this issue, single-crystalline phosphors (SCPs) have become an inevitable demand for the next generation white solid state lighting, which is an alternative to conventional ceramic powder phosphors (CPPs) and avoids the use of resins [6]. Superior thermal conductivity of SCPs delivers higher stable internal quantum efficiency even with the rise in temperature of phosphors film. Recent SCPs research has been focused around the conventional YAG based phosphor such as Ce:YAG, Gd co-doped Ce:YAG because of nontoxic nature and wide availability, though these suffers from the poor color rendering indices [7], [8].

Recently, our earlier study established the white-light emission from single-crystalline (SC) ZnO thin films by tuning the process of post thermal treatment based on the creation of different stable mid gap states [9]. Therefore, SC ZnO thin films have been recognized as a potential contender for single crystalline phosphors for solid-state white-lighting applications. Furthermore, maintaining the luminous efficacy and stable Ra are also a vital part for actual product and can be achieved by using high intensity excitation source along with high absorbent phosphors. The luminous efficiency can also be enhanced by using a hybrid composite with lower work function material as compared to actual phosphors, which helps through photo induced charge transfer process and leads to increase in the carrier concentration. In recent years, the graphene quantum dots (GQDs) and their composites have been studied for LED applications as actual phosphors and charge transfer process [4], [10]. It is worth noticing that GQDs also offer good optical absorption in the UV band and provides photon recycling to 'phosphors converted' based a device which in turn enhances the emission efficiency.

Hence, this work emphasizes to analyze the pc-WLED by using single crystalline ZnO thin film as phosphors along with the astonishing characteristics of GQDs as photon recycler to boost the device performance. This has been achieved by coating the solution processed GQDs over ZnO lift-off film. The effect of coated GQDs concertation on luminescence of ZnO films are discussed along with the influence on electroluminescence (EL) spectra of pc-WLEDs. UV LED chip has been used as an excitation source for SCs phosphors film.

II. Experimental Details

A c-axis orientated single-crystalline ZnO film has derived by sol-gel spin-coating method on sapphire substrate with an ITO interfacial layer. ITO works as sacrificial layer for the next step of lift-off process. The two step post heat treatment proposed in our earlier work has been used to achieve white luminescence from SC ZnO film [9]. Subsequently, laser lift-off process has been utilized to separate ZnO film from ITO/Sapphire substrate and transferred onto the glass

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M. Kumar, K.-S. Seong, and S.-H. Park are with the Department of Electronics Engineering, Yeungnam University, Gyeongsan 38541, South Korea (e-mail: sihyun_park@ynu.ac.kr).

A. Kumar is with the School of Chemical Engineering, Yeungnam University, Gyeongsan 38541, South Korea.

Sunny is with the Department of Electronics and Communication Engineering, Indian Institute of Information Technology, Allahabad 211015, India.

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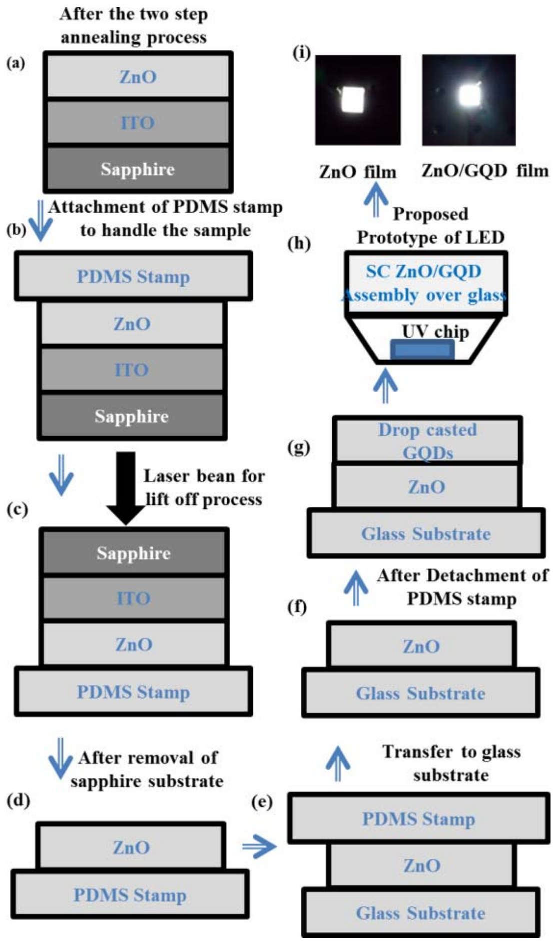

Fig. 1. Schematic representation of lift-off process and pc-LED structure.

substrate. ITO has been selected as sacrificial layer because of two order larger thermal diffusivity as compared to ZnO for achieving the sharp temperature-depth gradient at the ITO/sapphire interface. Hence, heat tends to accumulate near the ITO/ZnO interface which in turn helps in protecting the ZnO films from heat fluence. Lift-off process was performed by XeCl excimer laser at 4.02 eV (308 nm), which is well above the absorption edge of ITO and explained in Fig. 1 by block diagrams. There is no crystallographic change observed in ZnO film, which is examined by x-ray diffraction (Supplementary Fig. S1b).

Graphene quantum dots (GQDs) were synthesized through the dehydration of glucose by microwave-assisted hydrothermal method [11]. Aqueous ammonia was also used during the reaction for nitrogen doping. The morphology of the GQDs is examined by using the TEM, which exhibits the average lateral size around 10 nm (Supplementary Fig. S2a). The UV-Vis measurement is also performed for synthesized GQDs to find out the bandgap by corresponding Tau's plot analysis (Supplementary Fig. S2b). The ITO (10% Sn) and ZnO films are derived by sol-gel spin coating method. The GQDs was coated after the two steps annealing process on the ZnO film surface by dispensing drops in methanol solvent by a pipette and followed by heating on hot plate. This unique annealing process makes the ZnO film porous and provides a perfect environment to GQDs for making bond

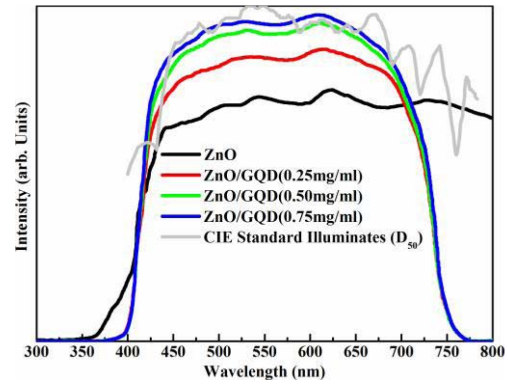

Fig. 2. PL spectra of the GQD-doped ZnO with different GQD concentrations.

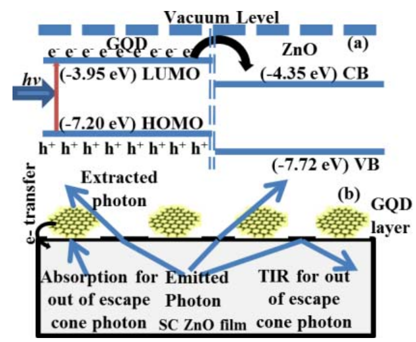

Fig. 3. (a) Band diagram to explain charge transfer process; (b) Mechanism to explain photon recycling process.

to surface vacancies and defects (Supplementary Fig. S1a). Different concentrations of GQDs were tested by drop-casting process, keeping the volume of the solution same. Coating of GQDs on ZnO film facilitate for enhancing the absorbance in UV region especially (Supplementary Fig. S2c). The UV LED chip with 365 nm peak wavelength is used as an excitation source (Supplementary Fig. S4).

III. Results and Discussion

The effect of GQDs doping on the ZnO film has been examined by Photoluminescence (PL) measurement as shown in Fig. 2, with different concentrations. The enhancement in the visible region luminescence is observed along with the suppression in UV region, which confirms the improved absorption of UV by charge transfer mechanism from GQDs. Further, Fig. 3(a) shows the mechanism of charge transfer from the lowest unoccupied molecular orbital LUMO to ZnO conduction band, which is also confirmed by the calculation of band parameters of GQDs through the cyclic voltammeter measurement (Supplementary Fig. S2d). This charge transfer process may increase the charge density in ZnO film, which is supposed to be the main cause of enhanced visible emission. This phenomenon has found to be strengthened with increasing concentration of GQDs. However, further increase in GQD concentration results in the luminescence saturation because of saturation in the UV absorption. GQDs might also be facilitating the out of emission cone photon through the recycling process, transferring the generated charge carriers to ZnO film as shown in Fig. 3(b), as reported by Lin *et al.* [10]

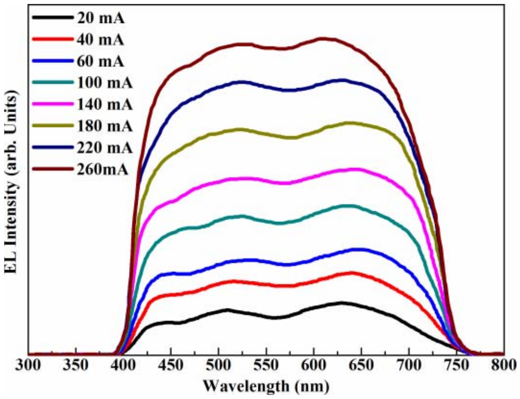

Fig. 4. EL spectra of ZnO/GQD pc-LED.

for performance improvement of UV LED. Therefore, both the physical processes of photo induced charge transfer from GQDs to ZnO and photon recycling process contribute for performance enhancement. The reduced refractive index at ZnO/GQD interface (because of low index of refraction of graphene) helps in improving extraction efficiency by lowering the total internal reflection (TIR) and hence boosting the luminescence. Moreover, the luminescence in the longer wavelength region (>750 nm) also found to be suppressed after the GQDs coating because of passivation of surface states pertaining to oxygen vacancies [9].

Fig. 4 shows the EL spectra of the device under injection currents from 20 mA to 260 mA, representing the consistent increase in the intensity of all visible bands with the increase in current. Obviously, the GQDs doped device has much faster rate of increment in EL intensity because of high absorption edge of GQDs in UV region along with photon recycling process as discussed (Supplementary Fig. S5).

There is no major shift in EL spectrum observed with the increase in injection current. The correlated color temperature (CCT) and color rendering index (Ra) corresponding to these spectra are also examined (Supplementary Fig. S3). The CCT found shifted from 4300K to 5000K and Ra from 91 to 98 with the increase in injection current from 20 mA to 260 mA. With enough high Ra value and no substantial change with current, device is good for the different lighting applications such as indoor and outdoor lighting from natural to cool white.

The luminous efficacy of radiation (LER) is one of the benchmark for the white light LEDs to show the how effectively emissive power is concentrated into spectral function of human eye (V(λ)). The LER of the GQDs based device is found to be 245 lm/W, which is much higher than the device without GQDs (~192 lm/W). LER improvement might be attributed to the squeezed spectral power density into the wavelength range of V(λ) (as shown in PL measurement, Fig. 2) after GQD doping along with the higher absorption capability of excitation source.

IV. Conclusion

This study demonstrates single crystalline ZnO/GQDs coated phosphors converted LEDs for cool white light with high brightness luminescent application by embedding a UV LED chip, without using traditional tricolor rare earth phosphors. The application of GQDs also enabled this device design to achieve a good LER value of 245 lm/W and might be helpful in increasing the reliability by reducing the total internal reflection at semiconductor/air interface which is supposed to lower down the thermal effect. The proposed WLEDs with high luminous efficiency are suitable for various high quality lighting applications from natural white to cool white by tuning the injection current.

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