# Investigation of the Inverted ZnCuInS/ZnS Based Quantum-Dot Light-Emitting Diode Fabricated by Sputtered ZnO Film Layers

**Mohammad Mostafizur Rahman Biswas**[1], **and Hiroyuki Okada**[2]

okada@eng.u-toyama.ac.jp
[1, 2] University of Toyama, Graduate School of Science and Engineering
930-8555, Toyama shi, Toyama, Japan

Keywords: Cadmium-free quantum dot light emitting diodes (QLED), sputtered Zinc Oxide, quantum yield (QY), inverted structure.


## ABSTRACT

*The performance of the fabricated QLED (Quantum dot Light Emitting Diode) was measured, using the sputtered ZnO film. The thickness of the ZnO film was varied to control the electron mobility. Consequently, the maximum current efficiency of 3.96 cd/A, and EQE 2.13% was achieved for the commercially available ZnCuInS/ZnS based QLEDs at yellow emission.*


## 1 INTRODUCTION

Quantum dot light-emitting diode (QLED) is one of the emerging research fields due to the rapid growth of display industries [1]. The key consideration of the QLED is quantum dots, as it has some remarkable attributes, for example, tunable spectrum, high stability, and narrow emission with full-width half maximum [2]. However, Cadmium (cd) substances will cause serious environmental and human health problems [3]. Therefore, at present, researchers are trying to improve the use of cd free quantum dots. The key performances are quietly dependent on not only the structure of the QD but also the device structure, ETL (Electron Transport), and HTL (Hole Transport) to balance the carrier mobility. However, the inverted structure is suitable for QLEDs due to its direct exciton recombination between QDs and ETL with a long operational lifetime [4]. Additionally, for the fast recombination of the excitons, the inverted structure is mainly focused on the oxide layer, generally, used as electron transport layer (ETL). ZnO is suitable as ETL for its high electron mobility, low recombination loss, wide bandgap, and high exciton binding energy at room temperature (RT) [5].

In this paper, we have fabricated QLED, using commercially available I-III-VI type QD (quantum dot), ZnCuInS/ZnS with the PLQY 33.65% and particle size 4-5 nm, whereas the ZnO film is used as ETL on the ITO substrate at room temperature (~20℃) fabricated by using the R. F. (Radio Frequency) sputtering technique. The effect of the ZnO film thickness (20, 50, and 80 nm) on the QLED was measured by checking the performance of the device.

## 2 EXPERIMENT

At first, the patterned ITO substrate was thoroughly cleaned using organic cleaning solvents and UV ozone chamber. Then, the pure ZnO (99.99%) was sputtered on the ITO substrate using R. F magnetron sputtering technique. Before sputtering, the chamber was evacuated at the base pressure below $2\times10^{-6}$ torr, and the working gas is Argon (Ar) only. The thickness of the ZnO was controlled by varying the sputtering time, while the other parameters were constant. The material resistivity and carrier mobility was measured using the Hall measurement technique. The mobility of the ZnO was measured 7.5, 14.9 and 9.22 $cm^2$/Vs, where the resistivity of the material $2.25\times10^{-3}$, $6.9\times10^{-3}$ and $9.07\times10^{-3}$ Ωcm was found for 20, 50 and 80 nm.

Polyethylenimine-ethoxylated, PEIE (4 wt. %) solution was prepared with ethanol, and it was coated on ZnO film using the rinse method. Then, it was baked for 1h at 55℃. After that, the QD solution (4mg/mL) was coated at 3000 rpm for 60s, then baked at 100℃ for 10 min. Then, the substrates were shifted from glove box to vacuum chamber, where the other layers were deposited using the thermal evaporation technique. The device structure is ITO (100 nm)/ ZnO (20, 50, 80 nm)/ PEIE (1nm)/ ZnCuInS/ZnS (QD, 10 nm)/ 4-4 bis, 9H-Carbazole by-phenyl-9-yl biphenyl (CBP, 60 nm)/ Molybdenum oxide ($MoO_3$, 10 nm)/ Al (70 nm). The QD (ZnCuInS/ZnS) was purchased from PlasmaChem Ltd, PEIE from Sigma-Aldrich, CBP and $MoO_3$ from Lum. Tech. Ltd., and ZnO sputtering disc from Furu-uchi Chemical Co. Ltd.

## 3 RESULTS

Figure 1 (a) shows, the *J-V* (current density-voltage) and *L-V* (luminance-voltage) characteristics of the QLED. The *J-V* characteristics exhibited the voltage ($V$) and the current density ($J$) pattern on the variation of the thickness of the ZnO layer. The turn on voltage ($V_T$) was gradually increased according to the increment of ZnO thickness layer, the minimum turn on voltage is 2.4 V for the thickness of 20 nm (ZnO layer) based device, whereas it was maximum at 5.6 for 80 nm. The turn on voltage for the 50 nm based QLED device is 4 V. Additionally, the highest operating voltage is 8.8 V, 10.2 V, and 11.2 V for the 20, 50 and 80 nm, which indicates the stability during the operating time.

At the *L-V* (luminance-voltage) characteristics section, the starting luminance is considered at 1 cd/$m^2$, which followed the maximum luminance is 533 cd/$m^2$, 1,775 cd/$m^2$ and 565 cd/$m^2$ according to the increment of the thickness 20, 50 and 80 nm respectively. From the above data, it can concluded that the initial luminance pattern for the device (20 nm) is high, however for the maximum luminance (1,775 cd/m$^2$) is observed for the device belongs to the thickness of 50 nm of ZnO layer.

The current efficiency, *CE* (*cd/A*) and external quantum efficiency, *EQE* (%) is shown in figure 1(b). The device with 20 nm, 50 nm and 80 nm of ZnO layer is showing steady and uniform behavior. The maximum current efficiency, CE and EQE was observed 0.8, 3.96 and 2.52 cd/A and 0.19, 2.13 and 1.63% respectively.

Considering the normalized EL spectrum, Figure 1(c), it was observed that the intensity peak is shifted according to the increment of the ZnO layer thickness. In detail, the obtained wavelength for the intensity peak is 574, 578, and 582 nm for the increment of the ZnO layer accordingly. Therefore, it can conclude that the luminance peak is shifted a little with the increment of layer thickness. Moreover, it is also observed that for the device with the 20 nm has a small spike between the 400 to 500 nm. This is happened due to unbalanced carrier recombination, which creates the illumination of ZnO. This phenomenon was not observed for the 50 and 80 nm based device.

Smooth surface, compact grain-boundary and suitable mobility is the prime pre-requisite for the excellent performance of the QLED. Considering this, we have used as deposited pure ZnO with the flow of Ar gas only during sputtering. Therefore, significant carrier mobility and material resistivity was observed from the Hall measurement. During the operational time of the devices, the variation of the thickness has a visible impact on the luminance (*L*) and current density (*J*). Therefore, the 50 nm based device has the highest CE and EQE due to comparative high luminance (*L*) with the optimum current density (*J*), followed by proper carrier recombination.

## 4 CONCLUSIONS

To sum up, the lowest thickness of ZnO can be used with the mentioned device structure is 20 nm and the highest one is 80 nm. However, the QLED with the thickness of 50 nm of ZnO layer showed comparatively better luminance and efficiency (1,775 cd/m$^2$, 3.96 cd/A and 2.13%). However, by optimizing the other parameters during the sputtering, and increasing the PLQY (%), further improvement can be possible.

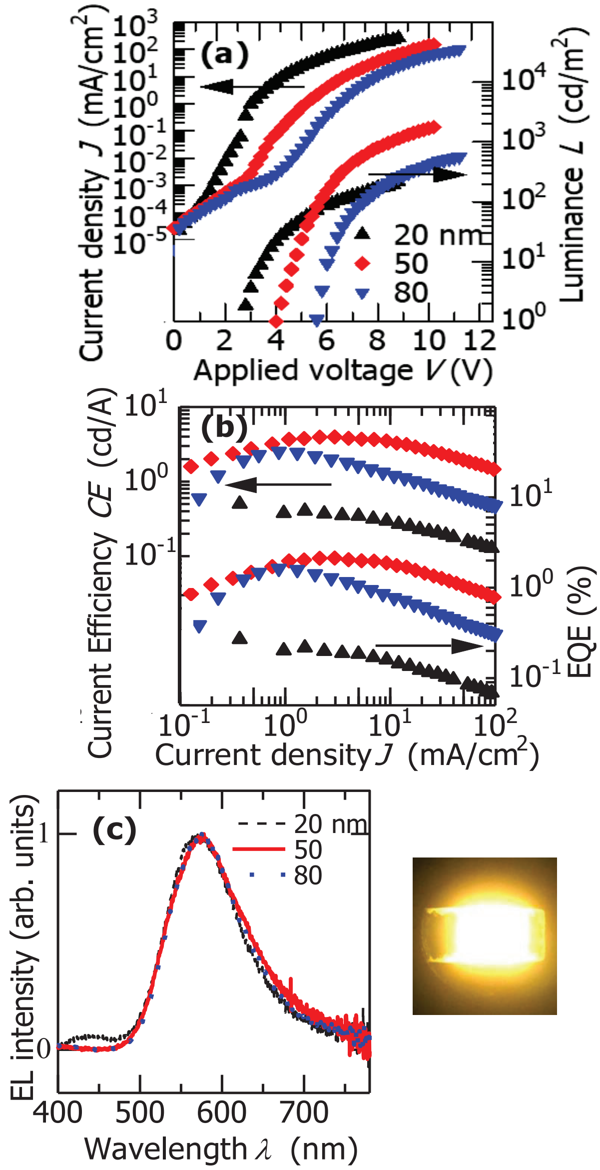


Figure 1: Characteristics curve of (a) *J-V,* (b) *L-V* (c) EL spectrum of fabricated QLED at different ZnO thickness layer.


## REFERENCES

[1] J. W. Jo, Y. Kim, J. Choi, F. de Arquer, G. Walters, B. Sun, O. Ouellette, J. Kim, A. Proppe, R. Quintero-ermudez, J. Fan, J. Xu, C. Tan, O. Voznyy, and E. Sargent, “Enhanced Open-Circuit Voltage in Colloidal Quantum Dot Photovoltaics via Reactivity-Controlled Solution-Phase Ligand Exchange,” Adv. Mat. Vol. 29, No. 43, pp. 1703627 (2017).

[2] M. Kovalenko, L. Manna, A. Cabot, Z. Hens, D. Talapin, C. Kagan, V. Klimov, A. Rogach, P. Reiss, D. Milliron, P. Guyot-Sionnnest, G. Konstantatos, W. Parak, T. Hyeon, B. Korgel, C. Murray, and W. Heiss, “Prospects of Nanoscience with Nanocrystals,” ACS Nano, Vol. 9, No. 2, pp.1012-1057, (2015).

[3] J. Grim, L. Manna and I. Moreels, "A sustainable future for photonic colloidal nanocrystals", Chem. Soc. Rev., Vol. 44, No. 16, pp. 5897-5914, (2015).

[4] R. Wang, Xi-Y. Dong, H. Xu, Ru-Bo Pei, M. Ma, S. Zang , H. Hou and T. C. W. Mak,” A super water-stable europium–organic framework: guests inducing low-humidity proton conduction and sensing of metal ions” Chem. Com. V. 50, pp. 9153-9156, (2014).

[5] M. Hossain, T. Takahashi and S. Biswas, "Nanorods and nanolipsticks structured ZnO photoelectrode for dye-sensitized solar cells", Elec. Comm., Vol. 11, No. 9, pp. 1756-1759, 2009.