

Enhanced Performance of All-Inorganic QLED using Double Heat Treatment of NiO HTL

Sun-Kyo Kim, Yong-Seog Kim

yskim@hongik.ac.kr

Hongik University, Seoul, Korea

Keywords: QLED, NiO, HTL, Heat Treatment, Current Efficiency

ABSTRACT

A double heat treatment scheme, crystallization heat treatment at elevated temperatures followed by vacuum annealing treatment at lower temperatures, was introduced to form a crystalline NiO single phase as well as surface phases with reduced defect concentration. With the modification of processing conditions, the luminance of QLED with the NiO HTL was improved from 30 cd/m² to 11,500 cd/m² and the current efficiency from 0.25 cd/A to 23 cd/A, respectively.

1 INTRODUCTION

Many studies have conducted to use metal oxide semiconductors as the HTL of QLED. The metal oxides are expected to have better stabilities against oxygen and humidity of the environments. Besides, the metal oxide HTLs have been projected to have higher charge carrier mobility compared to that of the organic counterparts. This should enhance the charge balance in the QD EML, which would eventually lead to higher efficiency and longer lifetime of the QLED devices.

For the semiconducting metal oxide HTLs, nickel oxide (NiO)¹, molybdenum oxide (MoO₃)², tungsten oxide (WO₃)³, copper oxide (CuO)⁴, and vanadium oxide (V₂O₅)⁵ have been considered. Among the oxides, NiO has been investigated most since it is an intrinsic p-type wide bandgap semiconductor with a high ionization potential. This ensures a deep energy level of the valence band and facilitates hole injection to QD EML, eventually helping the charge balance in the QD EML.

In an attempt to prepare the QLEDs via all solution process, the solution coating process using crystalline NiO nanoparticles has been attempted.^{10, 13} Powder-like precipitates were prepared via colloidal processing of NiO precursor.^{13c} The precipitates were annealed at temperatures ranging from 200 to 280 °C. After the heat treatment, the NiO nanoparticles were redispersed in a solvent and the suspension was used to form the NiO HTL. The maximum luminance and current efficiency of the all-inorganic QLEDs using the NiO nanoparticles annealed at 200 °C were 17,818 cd/m² and 7.11 cd/A, respectively. These results are significant improvements over the all-inorganic QLED using the NiO thin film formed via the RF sputtering process¹² but are still relatively poor compared with those of the conventional hybrid QLEDs.¹⁻³

Despite such tremendous progress that has been made for the device performance of QLEDs with NiO HTLs of sol-gel-derived NiO HTLs over the past few years, there are many unanswered questions regarding the major factors

affecting their efficiencies. The sol-gel-processed NiO film in the as-prepared state is an amorphous phase and therefore needs to be heat-treated for its crystallization. Also, such as-prepared NiO film contains various functionalities such as hydroxyl and carboxyl, requiring heat treatments to remove them via thermal decomposition reactions. The concentration of point defects such as nickel, oxygen vacancies, and Ni³⁺ is very sensitive to temperature and oxygen partial pressure of the heat treatments. Therefore, it is believed that the heat treatment condition of the NiO film would be very critical in the formation of HTL that may affect the performance of the QLED devices.

This work reports an attempt made to improve the current efficiency of the QLEDs with the sol-gel-processed NiO HTL by modifying their heat treatment conditions. Especially, the heat treatment for its crystallization was decoupled from the treatment for the surface defect reduction. For the former, the heat treatments were conducted at the atmospheric condition and the later was performed under vacuum condition. The vacuum heat treatment condition was selected to reduce the polar functionalities as well as atomic defects on the NiO surface responsible for the exciton quenching. Also, an organic interlayer between HTL and QD EML was inserted to investigate the effect of exciton quenching as well as planarization on the current efficiency of the device. The maximum current efficiency of 30 cd/A with a maximum luminance of 11,500 cd/m² was obtained with the QLEDs prepared in this study.

2 EXPERIMENT

The all-inorganic QLED device with the NiO HTL consisted of layers of ITO film (100 nm) on a glass substrate, NiO (20 nm), QD EML (40 nm), ZnO (30 nm), and Al film (130 nm) as illustrated in Fig. 1(a). Glass substrate with the patterned ITO electrode was washed with acetone, ethanol, and DI water in sequence before the NiO HTL coating. The cleaned substrate was dried in an oven at 90 °C and then subjected to O₂ plasma treatment for 5 min at a power of 50 W.

NiO sol-gel solution for the HTL film was prepared by adding monoethanolamine to 0.4 M nickel acetate tetrahydrate in ethanol. The solution was homogenized with a magnetic bar at 300 rpm for 24 h at ambient temperatures. Then, the solution was spin-coated on the ITO electrode patterned glass substrate and annealed in an oven at temperatures ranging from 230 to 500 °C for 20 to 60 min under atmospheric condition. After the heat

treatment, the NiO film was annealed at temperatures ranging from 150 to 350 °C for 1 h in a vacuum oven which was evacuated to 10^{-3} torr using a mechanical vacuum pump. This vacuum heat treatment was to reduce the surface defects such as polar functionality of the NiOOH phase and nickel vacancies in the film. The processing steps of the NiO film preparation is schematically shown in Fig. 1(b).

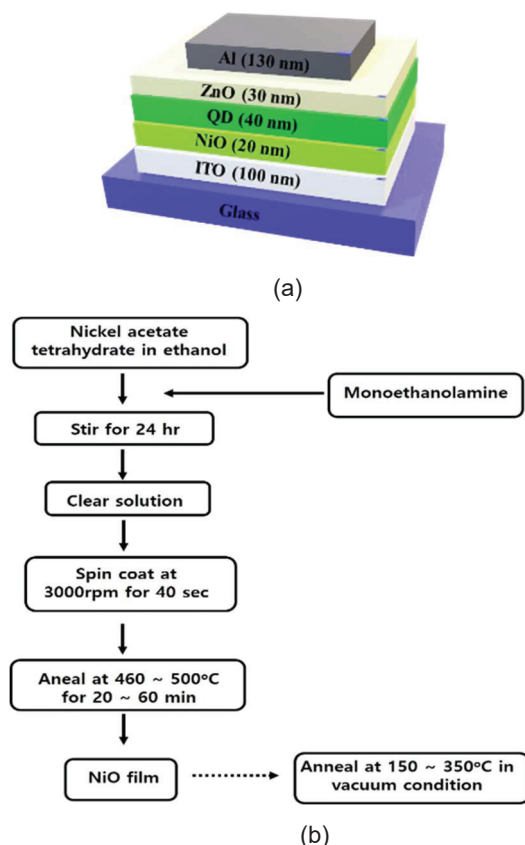


Fig. 1. (a) device structure of all-inorganic QLED and (b) schematic flow chart for synthesis and heat treatments of NiO film.

3 RESULTS

To investigate the actual crystallization behavior of the NiO film formed via the sol-gel process, the films were heat-treated at various temperatures and the phases formed were analyzed using the XRD.

As shown in Fig. 2, the films heat-treated at 230 and 330 °C consisted of an amorphous phase with a trace of Ni_2O_3 phase. As the temperature was increased to 400 °C, the crystalline NiO phase appeared along with the Ni_2O_3 phase. The peaks from (111), (200) and (220) planes of crystalline NiO phase were observed with additional peaks from Ni_2O_3 phase at 33°, 45°, and 52°. At this temperature, the crystalline phases were formed, but the metastable Ni_2O_3 phase remained in the film. This indicates that the previously reported NiO films treated at temperatures lower than 400 °C should consist of an amorphous phase as well as NiO and Ni_2O_3 ones. Therefore, the NiO sol-gel film heat-treated at temperatures lower than 400 °C may not be qualified as the crystalline single phase NiO HTL

thin film. As the heat-treating temperature was increased further to 450 °C, the peaks only from the crystalline NiO phase appeared. The peaks of Ni_2O_3 phase disappeared completely at this temperature and the film heat treated at this temperature may be qualified as a single-phase crystalline NiO HTL thin film. Further temperature increase to 500 °C did not generate new peaks but increased peak intensity as well as decreased peak width, suggesting the grain growth of the crystallized NiO phase in the film.

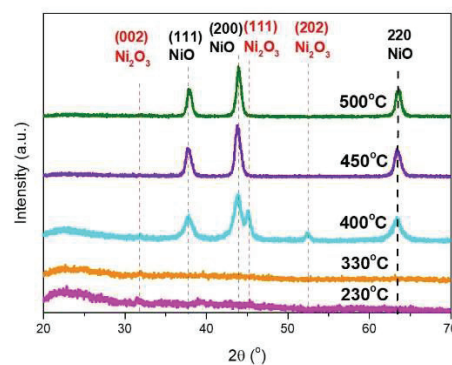


Fig. 2. XRD patterns of the NiO films heat-treated at different temperatures

To further examine the phases formed by the heat treatment, NiO films heat-treated at 400 and 500 °C were analyzed using the XPS. As shown in Figure 3, the peaks of 854.1, 855.9, and 861.4 eV in the Ni $2p_{3/2}$ bonding analysis represent NiO, Ni_2O_3 and NiOOH phase bonding, respectively, and the peaks of 529.6 and 531.3 eV in the O $1s$ signals represent NiO and Ni_2O_3 phase bonding, respectively. The NiO film heat-treated at 400 °C has the NiO phase along with a significant amount of Ni_2O_3 and NiOOH phase. The NiOOH phase which was not detected by the XRD analysis was identified to exist in the film. XPS is typically used for the surface chemistry analysis of inorganic materials as its signal is generated mainly from the shallow surface, typically less than 10 nm thick. The fraction of such phases in the NiO HTL needs to be reduced further to improve the performance of the QLED. As the heat-treating temperature was increased from 400 to 500 °C, the intensity of NiO peak in Ni $2p_{3/2}$ and O $1s$ was increased, but the intensity of Ni_2O_3 peak decreased significantly. This is in agreement with the XRD in the general trend, but it appears that there are Ni_2O_3 and NiOOH phase remains after the heat treatment at 500 °C.

Effects of vacuum annealing treatment on phases formed in NiO film

The effects of the vacuum heat treatments on the phase and roughness of NiO films were also examined using the XRD and the AFM. As shown in Fig. 4, a new peak was not detected after the vacuum heat treatment, indicating that the Ni_2O_3 phase observed after the crystallization heat treatment at 400 °C must be the unconverted metastable phase of the crystallization process of the sol-gel product. The grain size of the NiO

film calculated by the Scherrer equation showed a slight increase from 15 to 16 nm with the post-treatment. The surface roughness of NiO film essentially remained unchanged at 1.86 nm (not shown here). These observations seem to validate the necessity of decoupling the vacuum heat treatment from the crystallization heat treatment of NiO sol-gel film.

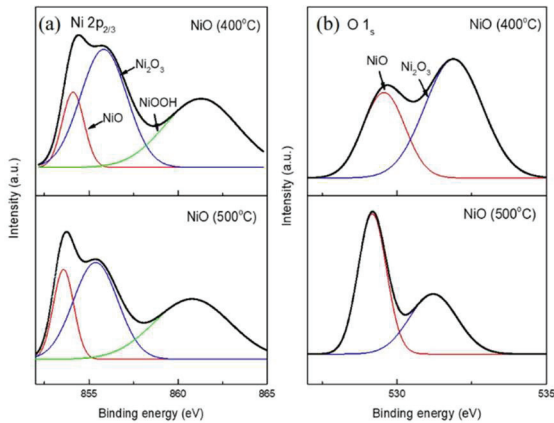


Fig. 3. XPS spectra of NiO film with different annealing temperatures (a) Ni 2p_{3/2} (b) O 1s.

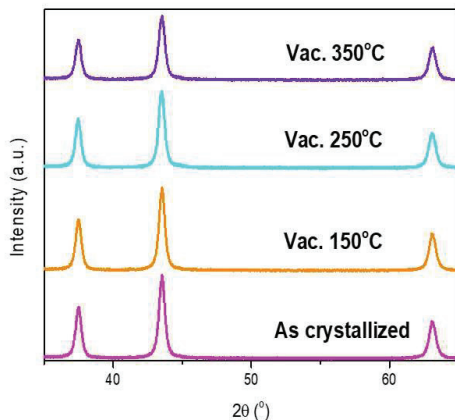


Fig. 4. XRD patterns of NiO film after vacuum heat treatment.

The luminance of the devices increased with the vacuum annealing temperature. The maximum luminance of the device with NiO HTL just underwent crystallization heat treatment was 33 cd/m² as in Fig. 5(a). As the vacuum annealing temperature was increased to 150, 250, and 350 °C, the maximum luminance was also increased to 250, 1474, and 2165 cd/m², respectively. The vacuum heat treatment of NiO thin film has resulted in an increase of luminance by a factor of 70. The current efficiency of the QLED devices measured is shown in Fig. 5(c). In the case of the device using the NiO HTL with the crystallization heat treatment only, the current efficiency was very poor. (0.2 cd/A) This value is in the range of the results reported by previous studies.⁶ As the vacuum annealing temperature was changed from 150 to 250 and 350 °C, the

maximum current efficiency was 0.83, 4.44, and 7.76 cd/A, respectively. The maximum current efficiency obtained with 350°C vacuum heat treatment of NiO HTL thin film was one of the best outcomes among the all-inorganic QLED devices using the sol-gel processing route.⁷⁻⁹

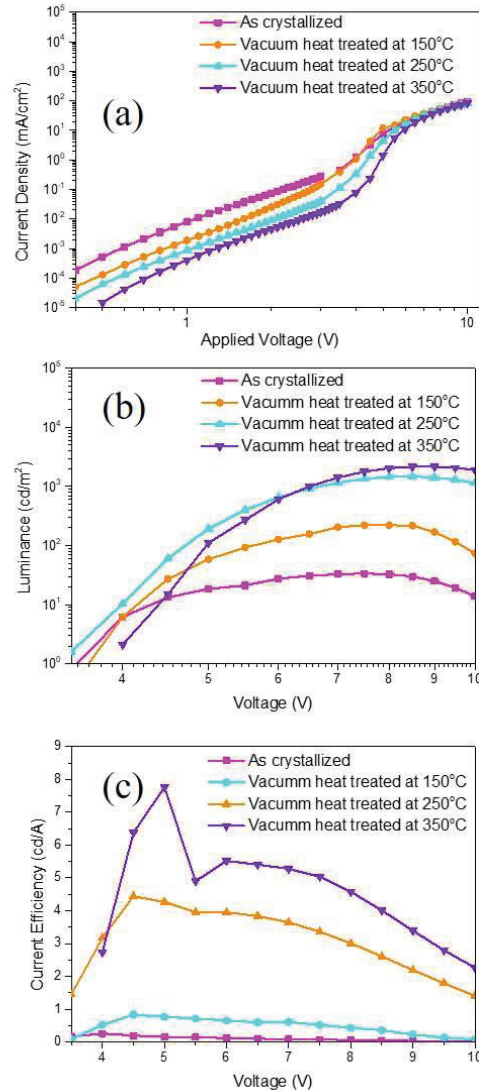


Fig. 5. Effects of vacuum heat treatment temperature on (a) J-V curve, (b) Luminance – voltage, (c) current efficiency – voltage relationships of QLED devices with NiO HTL.

4 CONCLUSIONS

Parameters affecting the performance of all-inorganic QLED devices using NiO HTL thin film via a sol-gel process route were explored. The heat treatment of the NiO HTL thin film showed that the film is in an amorphous state with a trace amount of crystalline Ni₂O₃ phase when the treatment temperature is lower than 330 °C. XRD pattern analysis of the film heated over 450 °C indicated that the film has transformed completely to the crystalline NiO single phase. Further analysis of the film

with XPS showed that the film surface is rich with bondings of Ni₂O₃ and NiOOH phases, which could be the sites for exciton quenchings. To reduce the polar functionality of the NiOOH phase, vacuum annealing treatment was introduced to the NiO HTL thin film which underwent crystallization heat treatments. The decoupling of crystallization and vacuum annealing treatment of NiO HTL thin film was effective in improving the performance of the QLEDs.

REFERENCES

- [1] Liu, S.; Liu, R.; Chen, Y.; Ho, S.; Kim, J. H.; So, F., Nickel oxide hole injection/transport layers for efficient solution-processed organic light-emitting diodes. *Chemistry of Materials* **2014**, *26* (15), 4528-4534.
- [2] Murase, S.; Yang, Y., Solution processed MoO₃ interfacial layer for organic photovoltaics prepared by a facile synthesis method. *Advanced materials* **2012**, *24* (18), 2459-2462.
- [3] Wood, V.; Panzer, M.; Halpert, J.; Caruge, J.-M.; Bawendi, M.; Bulovic, V., Selection of metal oxide charge transport layers for colloidal quantum dot LEDs. *ACS nano* **2009**, *3* (11), 3581-3586.
- [4] Ding, T.; Yang, X.; Bai, L.; Zhao, Y.; Fong, K. E.; Wang, N.; Demir, H. V.; Sun, X. W., Colloidal quantum-dot LEDs with a solution-processed copper oxide (CuO) hole injection layer. *Organic Electronics* **2015**, *26*, 245-250.
- [5] Meyer, J.; Zilberberg, K.; Riedl, T.; Kahn, A., Electronic structure of Vanadium pentoxide: An efficient hole injector for organic electronic materials. *Journal of Applied Physics* **2011**, *110* (3), 033710.
- [6] Caruge, J.-M.; Halpert, J. E.; Bulović, V.; Bawendi, M. G., NiO as an inorganic hole-transporting layer in quantum-dot light-emitting devices. *Nano letters* **2006**, *6* (12), 2991-2994.
- [7] Ji, W.; Shen, H.; Zhang, H.; Kang, Z.; Zhang, H., Over 800% Efficiency Enhancement of Solution-Processed All-Inorganic Quantum-Dot Light Emitting Diodes with an Ultrathin Alumina Passivating Layer. *arXiv preprint arXiv:1803.02497* **2018**.
- [8] Chen, F.; Guan, Z.; Tang, A., Nanostructure and device architecture engineering for high-performance quantum-dot light-emitting diodes. *Journal of Materials Chemistry C* **2018**, *6* (41), 10958-10981.
- [9] Wang, T.; Zhu, B.; Wang, S.; Yuan, Q.; Zhang, H.; Kang, Z.; Wang, R.; Zhang, H.; Ji, W., Influence of Shell Thickness on the Performance of NiO-Based All-Inorganic Quantum Dot Light-Emitting Diodes. *ACS applied materials & interface*