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

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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), molybdenum oxide (MoO₃), tungsten oxide (WO₃), copper oxide (CuO), and vanadium oxide (V₂O₅) 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.

In an attempt to prepare the QLEDs via all solution process, the solution coating process using crystalline NiO nanoparticles has been attempted. Powder-like precipitates were prepared via colloidal processing of NiO precursor. The precipitates were annealed at temperatures ranging from 230 to 500 °C for 20 to 60 min under atmospheric condition. After 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 heat 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 crystallized by a double heat treatment scheme. 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. The maximum luminance of 11,500 cd/m² and the current efficiency from 0.25 cd/A to 23 cd/A, respectively.
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).

![Diagram of NiO film preparation](image)

**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 Ni₂O₃ phase. As the temperature was increased to 400 °C, the crystalline NiO phase appeared along with the Ni₂O₃ phase. The peaks from (111), (200) and (220) planes of crystalline NiO phase were observed with additional peaks from Ni₂O₃ phase at 33°, 45°, and 52°. At this temperature, the crystalline phases were formed, but the metastable Ni₂O₃ 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 Ni₂O₃ 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 Ni₂O₃ 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.

![XRD patterns of NiO films heat-treated at different temperatures](image)

**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 Ni₂O₃ 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 2p3/2 (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.7,8

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 NiO2 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

816 IDW ’20