Effect of Substrate Temperature of n-type Charge-Generation Layer on the Electrical Properties of Charge-Generation Unit

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Abstract

In this study, we investigated the impact of substrate temperature (T_{sub}) on the electrical properties of the n-type charge generation layer (nCGL) composed of bathophenanthroline (Bphen) and Ytterbium (Yb) deposited under different T_{sub} conditions (-4, 20, and 40 °C). The charge generation unit fabricated at -4 °C exhibited superior electrical properties compared to those fabricated at 20 °C and 40 °C. To investigate the cause of this improvement, we analyzed the electron mobility and molecular orientation characteristics of nCGL. The results showed that a more well-ordered horizontally oriented layer was formed at lower T_{sub}, leading to an increase in electron mobility. However, there was no significant difference in molecular orientation between the film composed only of Bphen and Bphen with Yb. The ultraviolet photoelectron spectroscopy analysis revealed that the lowest unoccupied molecular orbital energy level decreased when the Bphen was doped with Yb, indicating that an interaction occurred between the two materials. Nevertheless, this had little impact on molecular orientation. Therefore, if a host material more favorable for molecular orientation is used, the electrical properties are expected to improve more effectively.

Author Keywords

n-type charge generation layer, substrate temperature, mobility, molecular orientation

1. Introduction

The performance of tandem organic light-emitting diode (*OLED*) devices is significantly influenced by the properties of their common layers, particularly the charge generation layer (*CGL*), which plays a critical role in enhancing charge injection and transport. Among the various factors that determine the performance of the *CGL*, the substrate temperature (T_{sub}) during deposition has been recognized as a key parameter affecting the molecular orientation, and electrical properties of the layer.[1–2] Proper control of T_{sub} can lead to improved charge transport characteristics and enhanced device efficiency, making it a vital focus of research in the development of next-generation *OLED* devices.

In multilayer *OLED* structures, the charge generation unit (*CGU*) serves as a critical component, facilitating efficient carrier injection and transport between adjacent layers. The n-type charge generation layer (*nCGL*), composed of electron-transporting materials doped with metals, plays a pivotal role in the efficient generation and movement of electrons. 4,7-Diphenyl-1,10-phenanthroline (*Bphen* with T_g of 62 °C, where T_g is the glass transition temperature) as an *nCGL* host material and ytterbium (*Yb*) as a dopant are widely utilized in *nCGL* due to its favorable electron transport properties. Therefore, investigating the relationship between T_{sub} and nCGL is important, and precise control of the T_{sub} can lead to a significant improvement in device performance.

Previous studies have indicated that the orientation of molecules within thin films can be controlled by adjusting T_{sub} during physical vapor deposition (*PVD*) process.[3–4] At lower T_{sub}, molecules tend to adopt a more horizontally ordered orientation, which is correlated with improved charge mobility and better electrical performance. This behavior is attributed to the reduced kinetic energy of the deposited molecules at lower temperatures, promoting a denser and more ordered packing structure.[5] Such horizontal molecular alignment is advantageous for electron transport in the *CGL*, as it facilitates efficient charge transfer pathways.

In this study, we investigate the impact of T_{sub} on the electrical properties of an *nCGL* composed of *Bphen* doped with 10 *wt.% Yb*. The *nCGL* films were deposited at T_{sub} conditions of -4, 20, and 40 °C, and their effects on molecular orientation, electron mobility, and bandgap energy difference were systematically examined. Our findings confirm that controlling T_{sub} during deposition influences several properties, with lower T_{sub} leading to increased electron mobility and a more well-ordered, horizontally oriented molecular structure that enhances the electrical performance of the CGU. This study provides new insights into the role of T_{sub} in the deposition process and suggests an optimal approach for improving the electrical properties of charge generation layers in tandem OLED devices.

2. Experiment

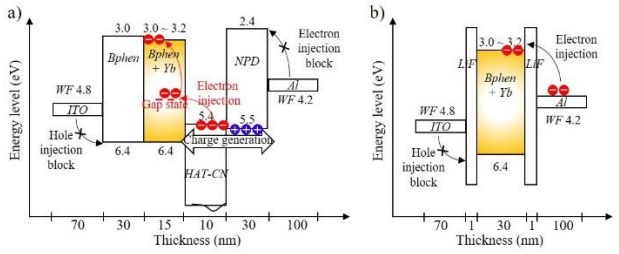

Figure 1. a) Charge generation mechanism and schematic diagram of the charge generation unit. b) schematic diagram of electron-only devices. The substrate temperature was controlled at -4, 20, and 40 °*C* only during the deposition of the *nCGL*, which was composed of *Bphen* with 10 *wt.% Yb*. The *WF* means the work function.

To investigate the effect of differences in T_{sub} during deposition on *CGU* performance, three *CGU* devices at -4, 20, and 40 °*C* T_{sub} was fabricated. The T_{sub} conditions were controlled only during *nCGL* deposition, while all other layers were deposited at room temperature. The *CGU*s were composed of indium tin oxide (*ITO*)

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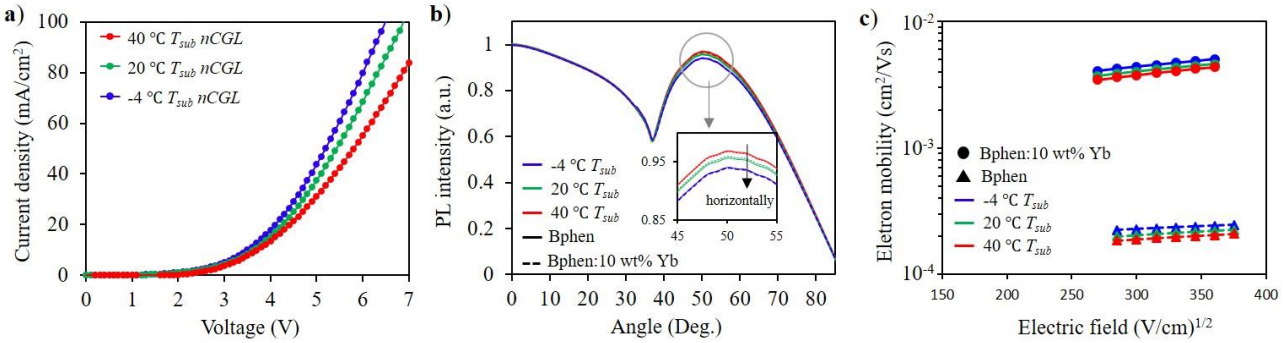

Figure 2. a) Current density-voltage characteristics of charge generation unit under different conditions of *nCGL*: -4, 20, 40 ℃ T_{sub}. The blue line represents -4 ℃ T_{sub}, the green line represents 20 ℃ T_{sub}, and the red line represents 40 ℃ T_{sub} condition. b) The molecular orientation characteristics of Bphen and Bphen doped with 10 wt% Yb under the conditions of *nCGL*: -4, 20, 40 ℃ T_{sub}. The orientation factor 0, 33, and 100 % represent horizontal, random, and vertical molecular orientation, respectively. The blue, green, and red lines indicate the T_{sub} conditions of -4, 20, and 40 ℃, respectively, while the solid line represents Bphen and the dashed line represents the Bphen doped with 10 wt% Yb. c) The electron mobility characteristics of Bphen and Bphen doped with 10 wt% Yb under the conditions of *nCGL*: -4, 20, 40 ℃ T_{sub}. The blue, green, and red lines indicate the T_{sub} conditions of -4, 20, and 40 ℃, respectively, while the triangle symbol represents Bphen and the circle symbol represents the Bphen doped with 10 wt% Yb.

70 *nm*/*Bphen* 30 *nm*/*Bphen* with 10 *wt.% Yb* 15 *nm*/dipyrazino[2,3-f,2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (*HAT-CN*) 10 *nm*/N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (*NPD*) 30 *nm*/aluminum (*Al*) 100 *nm* as shown in Figure 1a. The reason for the Yb (ρ 6.96 g/cm^2, Δd 1.5 × 10^{-9} cm, molecule weight 173.04 g/mol) concentration being 10% in nCGL is that it allows a 1:1 matching condition between Bphen (ρ 1.26 g/cm^2, Δd 13.5 × 10^{-9} cm, molecule weight 330 g/mol) molecules and Yb ($n=\rho \cdot A \cdot \Delta d/M$, where n is the number of moles, ρ is the density, A is the deposition area, Δd is the deposition thickness, and *M* is the molecule weight). All layers for the device fabrication were deposited by vacuum evaporation under a pressure of ~ 5 × 10^{-7} *Torr* with rotating. The deposition rate for all layers was maintained at 1 *Å/s*. To cool or heat the T_{sub}, the chamber was modified, and the minimum real T_{sub} is -4 *℃*. For the case of *CGU*, At the interface between *HAT-CN as a pCGL* and *NPD* as a hole transfer layer, under an applied electric field, charge generation occurs through the interaction between the lowest unoccupied molecular orbital (LUMO) of *HAT-CN* and the highest occupied molecular orbital (HOMO) of *NPD*, as shown in Figure 1a. The generated holes are transported through the *NPD* layer, while the electrons are transferred from the *LUMO* of *HAT-CN* into the gap states of the *nCGL* introduced by the *Yb* dopant. These electrons subsequently move into the *Bphen* layer as an electron transfer layer, which facilitates their efficient transport towards the cathode. This charge generation mechanism of *CGU* enables effective charge balance and current flow between the stacks of the tandem *OLED* device, allowing for stable and efficient operation of the tandem *OLED* device.

Additionally, to analyze the key factors influencing the electrical performance of *CGU*s under different T_{sub} conditions, we fabricated thin films, which was only deposited with *nCGL*. First, to analyze the molecular orientation under different T_{sub} conditions, we fabricated samples consisting of a Bphen layer and a Bphen layer doped with 10 wt.% Yb varing T_{sub} conditions and analyzed the difference in their molecular orientation using the angular and polarization dependent photoluminescence (*ADPL*) method.[6] Second, we fabricated electron-only devices (*EODs*) to investigate the electron mobility characteristics of the *nCGL* in relation to the T_{sub}, as show in Figure 1b. The *EODs* were fabricated with the structure *ITO* 70 *nm*/*LiF* 1 *nm*/*nCGL* 30 *nm*/*LiF* 1 *nm*/*Al* 100 *nm*. The *ITO* with *LiF* layer on the anode side optimizes energy level alignment and blocks unwanted hole transport. On the cathode side, *LiF* reduces the work function of aluminum (~3.8 *eV*), enabling efficient electron injection. This design ensures that under an applied electric field, electrons are injected from the cathode, transported through the *nCGL*, and collected at the anode, while holes are effectively blocked. By analyzing current density and voltage characteristics, the electron mobility and transport properties of the *nCGL* can be measured, particularly in relation to T_{sub} conditions. the difference in ionization potential energy between Bphen and Bphen doped with 10 wt.% Yb was compared using the ultraviolet photoelectron spectroscopy (UPS) measurements.

3. Result

To investigate the effects of *nCGL* on CGU devices under different substrate temperature (T_{sub}) conditions, CGU devices were fabricated, and the current density vs. voltage (*J-V*) characteristics were measured, as shown in Figure 2a. At a current density of 10 mA/cm², the turn-on voltage was 3.5 V at T_{sub} -4 °C, 3.6 V at T_{sub} 20 °C, and 3.7 V at T_{sub} 40 °C, showing a slight decrease in turn-on voltage as the T_{sub} decreased. Additionally, it was observed that the slope of the *J-V* curve became steeper with increasing voltage at lower T_{sub}.

To investigate the reason of the increase in electrical performance, the molecular orientation and electron mobility characteristics were measured of *nCGL* under different T_{sub} as shown in Figure 2b and c. The molecular orientation of Bphen and Bphen doped with 10 wt% Yb was measured using the *ADPL* method. The orientation factor (Θ) of both films was 30 *%* at T_{sub} -4 *°C*, 32 *%* at T_{sub} 20 *°C*, and 33 *%* at T_{sub} 40 *°C*, indicating equal molecular orientation characteristics between both films and minimal changes in molecular orientation characteristics with different T_{sub}. Here, 0 *%* corresponds to horizontal orientation, 33 *%* to random orientation, and 100 *%* to vertical orientation. For the undoped Bphen film, the Θ error margin was within ±0.5. However, due to the potential influence of nCGL metal dopants on absorption and reflection characteristics, the error margin of Bphen doped with 10 wt% Yb increased to approximately ±1. Although molecular orientation characteristics showed no

significant variation under different T_{sub} conditions, a slight decrease in the orientation factor at lower T_{sub} suggests a minor improvement in molecular packing.

Previous studies have shown that lowering the T_{sub} enhances molecular packing through stronger intermolecular interactions, thereby improving electron mobility.[7] This enhancement is particularly notable in rod-shaped organic molecules with strong anisotropic properties. However, the host material of *nCGL* used in this study is nearly round-shaped, making it less favorable for significant changes in molecular orientation. The Figure 2c represent the electron mobility characteristics of EOD devices composed of Bphen and Bphen doped with 10 wt% Yb. The electron mobility of Bphen was measured as 2.20×10^{-4} at -4 ℃, 2.01×10^{-4} at 20 ℃, and 1.86×10^{-4} cm²/Vs at 40 ℃ T_{sub}. When doped with 10 wt% Yb, the electron mobility was measured as 3.91×10^{-3} at -4 °C, 3.64×10^{-3} at 20 °C, and 3.22×10^{-3} cm²/Vs at 40 °C T_{sub}. These results demonstrate that electron mobility improves as the T_{sub} decreases, likely due to the slight improvement in molecular packing, which enhances intermolecular interactions.

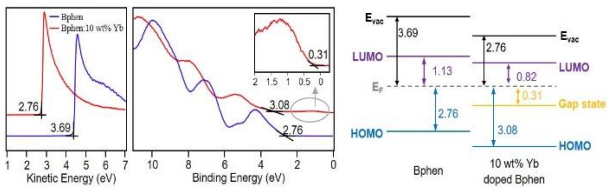

Figure 3. a) Ultraviolet photoelectron spectroscopy (UPS) spectra of Bphen and Bphen doped 10 wt% Yb films on ITO galss substrate with different T_{sub} conditions at the kinetic energy and low binding energy region near the fermi level. b) Schematic showing the energy levels of Bphen and Bphen doped 10 wt% Yb.

Figure 3a shows UPS spectra, including the kinetic energy and binding energy regions of Bphen and Bphen doped with 10 wt% Yb. When 10 wt% Yb was doped into Bphen, the work function in the kinetic energy region shifted from 3.69 to 2.76 eV, and the HOMO level relative to the Fermi level became deeper, shifting from 2.76 to 3.08 eV. Additionally, a gap state of 0.31 eV was formed, indicating that Yb atoms elevate the fermi level of Bphen closer to the LUMO level. Consequently, when Yb atoms are doped into Bphen, we could expect that the LUMO level is formed 0.31 eV lower than that of pristine Bphen as shown in Figure 3b, indicating that the chemical or charge transfer interaction happened between doped Yb and Bphen. As observed in CGU experimental results, when Yb interacts with Bphen on a one-to-one molecular basis, the electronic structure of Bphen, especially HOMO and LUMO, changes, resulting in the creation of new gap states. However, since the molecular orientation difference under different T_{sub} conditions in Yb-doped Bphen thin films is the same as that in pristine Bphen films, it can be inferred that the three-dimensional structure of Bphen, which exhibits a strong isotropic tendency, does not significantly change upon bonding with Yb. Therefore, it did not contribute to a dramatic change in electron mobility and J-V curve characteristics depending on the substrate temperature. These results also suggest that if materials with strong anisotropic properties, which are advantageous for molecular orientation, are used and T_{sub} is optimized, electron mobility could be further enhanced, leading to significant improvements in the electrical performance of the devices.

4. Conclusion

This study demonstrates the significant impact of T_{sub} during *nCGL* deposition on the performance of *CGU* devices, particularly highlighting its effects on molecular orientation, electron mobility, and electrical properties. Although the nearly spherical molecular shape of *Bphen* limited significant changes in molecular orientation, lower T_{sub} condition at -4 ℃ improved horizontal molecular orientation. The improved molecular orientation at lower T_{sub} promoted more efficient charge transport pathways, leading to enhanced electron mobility and a slight reduction in turn-on voltage compared to higher T_{sub} conditions. These findings point out the importance of optimizing T_{sub} to enhance the electrical performance of *nCGL* and suggest the potential for further improvements by using host materials with more anisotropic properties. This study offers an opportunity to advance the design of highly efficient and stable tandem *OLED* devices through precise control of T_{sub} during deposition.

5. Acknowledgements

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6. References

1. Wang S., Zhu Z., Shi C., Li S., Liu Y., Zhang D., Wang Q., Zhao L., Wang W., Dong X., "Enhanced performance of solution-processed OLEDs by altering the molecular transition dipole moment orientation of emission layers" *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **2022**, *271*, 120933.
2. Esaki Y., Tanaka M., Matsushima T., Adachi C., "Active Control of Spontaneous Orientation Polarization of Tris (8-hydroxyquinolinato) aluminum (Alq3) Films and Its Effect on Performance of Organic Light-Emitting Diodes" *Adv. Electron. Mater.* **2021**, *7*, 2100486.
3. Lee C. H., Kim S. H., Yi Y., Lee J. H., Lee G. D., "P-196: Control of the Molecular Orientation in EML Using Substrate Temperature for Improving the Electro-Optical Characteristics and Lifetime" *SID Symposium Digest of Technical Papers* **2024**, *55*, 2134–2137.
4. Lee, C. H., Kim, S. H., Lee, H., Seol, T. H., Lee, J. H., Yi, Y., Lee, G. D., "In Situ Substrate Temperature Control for High-Performance Blue-Emitting OLEDs with Extended Operational Lifetime" ACS Appl. Mater. Interfaces **2025**, *17*, 15755–15763
5. Arai H., Yoshida N., Sasabe H., Sagae Y., Hoshi K., Yokoyama D., Kido J., "Fundamental guidelines for the active control of the molecular orientation of heteroleptic iridium complexes enabled by carbazole-based host materials" *J. Mater. Chem. C* **2024**, *12*, 2772.
6. Schmidt T. D., Lampe T., Djurovich P. I., Thompson M. E., Brütting W., "Emitter orientation as a key parameter in organic light-emitting diodes" *Phys. Rev. Appl.* **2017**, *8*, 037001.
7. Esaki Y., Komino T.,Matsushima T., Adachi C., "Enhancedelectrical properties and air stability of amorphous organicthin films by engineering film density" J. Phys. Chem. Lett. 2017, 8, 5891–5897.