

Interface formation between tris-(8-hydroxyquinoline) aluminum and room temperature stable electrider: C12A7:e⁻

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Abstract

Interface formation between $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7:e⁻) and Alq_3 was investigated using in-situ ultra-violet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). The work function and vacuum level shift of C12A7:e⁻ were change by different surface treatment from 2.6eV to 4.2eV. Also vacuum level shift (Δ) at the interface were from +0.3eV to -0.3eV.

1. Introduction

The electrider of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7:e⁻) is a interesting material because of its very low work function ($\Phi=2.4\text{eV}$) and chemical stability (up to 300°C) in the air.[1] Due to its unique properties, C12A7:e⁻ has possibility of various application such as tip for the electron gun or electron emitter of field emission display (FED).[2] On the other hand, Alq_3 (tris 8-hydroxyquinoline aluminum) is the most widely used electron transporting material for organic light-emitting diode (OLED). [3-4] However, because of small electron affinity of Alq_3 , a low work function cathode is required to reduce the electron injection barrier. Numerous studies have been performed to lower the electron injection barrier at the cathode interface of OLED. Most of these studies are able to be categorized in two groups. One is to insert ultra thin (below 0.5nm) insulating layer of metal fluoride between cathode and organic film. However, to uniformly deposit the thin film of metal fluoride in sub-nanometer scale is very difficult process. The other is to use low work function metals such as Ca, Mg, Yb for the cathode or to dope alkali metals such as Li and Cs into the organic layer by

co-depositing with organic material. In the case of using low work function metals, these chemically active elements can change the properties of Alq_3 and there is potent possibility to diffuse in to organic layer. [5]

In this point of view, C12A7:e⁻ has advantages of low work function and chemical stability at the same time. In this work, we wanted to check out the possibility of C12A7:e⁻ as a cathode for OLED by investigating the energy level alignment at the interface with Alq_3 .

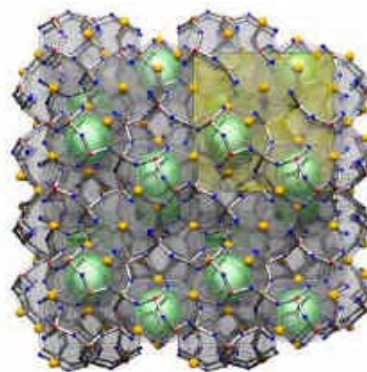


Figure 1. Schematic structure of C12A7:e⁻. A square and a large sphere denote unit-cell and electron in the cage.

2. Experiment

Polycrystalline C12A7:e⁻ thin films were fabricated on the MgO(100) substrate by PLD process. Detailed fabrication condition can be found elsewhere. [6] We explored appropriate

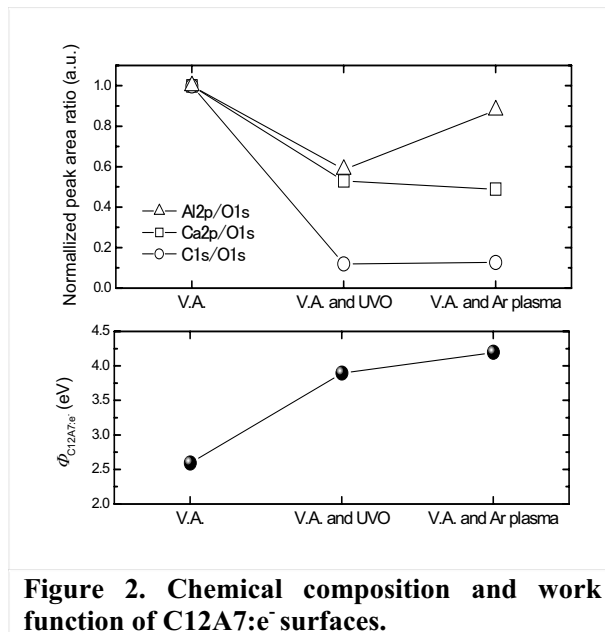
surface treatment processes such as vacuum annealing, UV-ozone cleaning and Ar plasma treatment. The conditions of each process are shown in Table 1. In this experiment, samples were prepared in 3 kinds of process schemes (1) vacuum annealed (2) vacuum annealed and UV-ozone treated (3) vacuum annealed and Ar plasma treated. After surface treatment processes, samples were loaded to preparation chamber to measure the chemical composition and work function by XPS (Mg K α , 1253.6eV) and UPS (He I, 21.2eV). Energy level alignment at the interface was observed by repeating UPS measurement and Alq₃ deposition in stepwise manner. Alq₃ overlayer was deposited by thermal evaporation in the preparation chamber (2×10^{-6} Pa) and deposition rate (0.02 - 0.05 nm/s) was monitored with pre-calibrated quartz micro balance. After finishing a deposition step, samples were transferred to analysis chamber (3×10^{-8} Pa) in the vacuum. The highest occupied molecular orbital (HOMO) level of Alq₃ and work function of C12A7:e⁻ were measured until they were saturated as a function of Alq₃ thickness (0 - 5nm).

Table 1. Process conditions of surface treatments

Surface treatment	Process condition
Vacuum annealing	600 °C, 5×10^{-5} Pa, 10min
UV-ozone cleaning	100 °C, O ₂ 10sccm, 5min
Ar plasma	50W, 6×10^{-1} Pa, 1min

3. Results and discussion

Fig. 2 shows the chemical composition and work function of the samples after surface treatment process. Those are measured by XPS and UPS respectively. Work functions of samples were determined by the distance from secondary electron emission when the sample bias of -5V was applied during the UPS measurements. The element ratio was compared with the peak area ratio of Al2p, Ca2p, C1s and O1s peaks.



For the simplicity of comparison, data were normalized to vacuum annealed sample. When compared with vacuum annealed sample, UV-ozone and Ar plasma treatment drastically decreased C1s/O1s ratio. This may suggest those treatments can effectively remove residual carbon contaminant on the surface. UV-ozone treatment decreased Ca2p/O1s ratio and Al2p/O1s ratio together. This is considered to be related with the formation of oxygen rich surface by the ozone during the process. On the other hand, Ar plasma treatment decreased Ca2p/O1s ratio by far than Al2p/O1s ratio.

It can be deduced that Ca deficient surface was formed by the selective sputtering during the Ar plasma treatment. The work function of each samples are shown at the lower side of Fig. 2. Work function of vacuum annealed, UV-ozone treated and Ar plasma treated samples were measured to be 2.6eV, 3.9eV and 4.2eV respectively. This result shows that the vacuum-annealed C12A7:e⁻ had the lowest work function while the work function was significantly increased by the other treatments. The work function increase of UV-ozone treatment and Ar plasma treatment can be explained by the formation of oxygen-rich layer and non-stoichiometry of Ca/Al ratio. To solve this side effect of surface treatment, it is required to develop “damage-free” surface treatment which

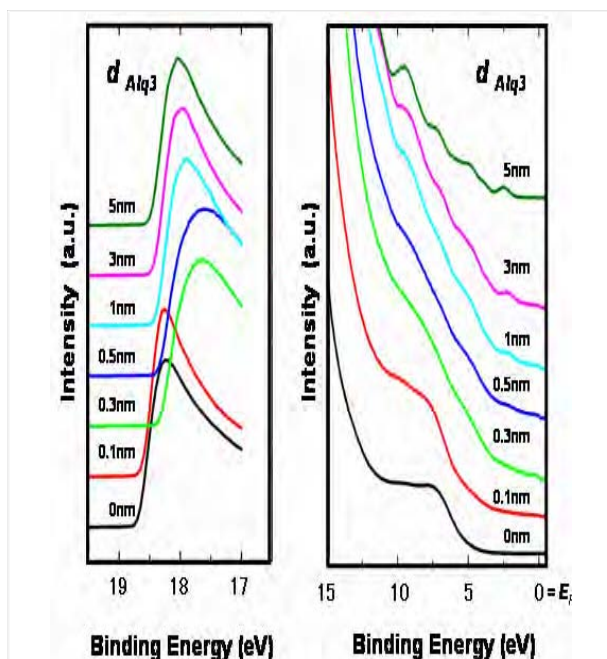


Figure 3. UPS spectra at the interface of vacuum annealed C12A7:e⁻/Alq₃. Left side is cut-off region and right side is valance band region.

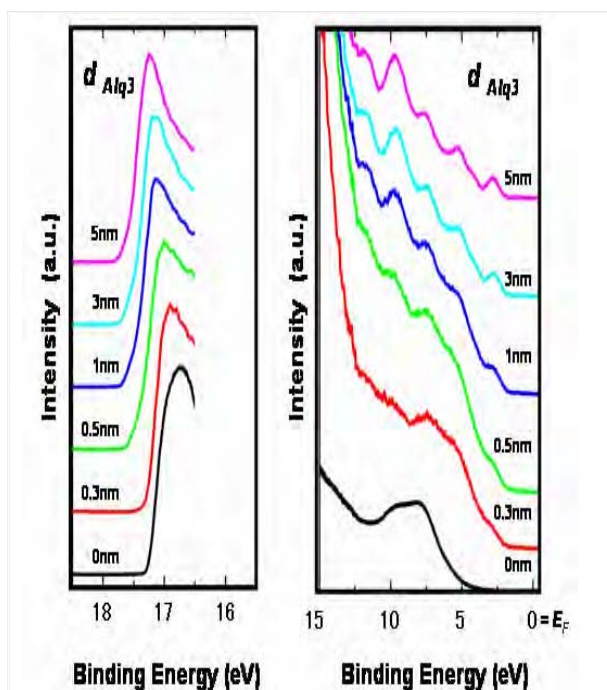


Figure 4. UPS spectra at the interface of UV-ozone treated C12A7:e⁻/Alq₃. Left side is cut-off region and right side is valance band region.

can make the surface of C12A7:e⁻ clean with maintaining low work function.

Fig. 3 is the UPS spectra of vacuum annealed C12A7:e⁻ / Alq₃ interface measured with the function of Alq₃ overlayer thickness. When $d=0\text{nm}$, the spectrum shows that of C12A7:e⁻ bare surface and the work function of vacuum annealed C12A7:e⁻ surface was obtained from the position of secondary electron cut-off. In Fig. 3, vacuum level shifted to lower binding energy by 0.3eV when the thickness of Alq₃ over layer was 0.3nm. And there was no further change after $d=0.3\text{nm}$. Right side of Fig. 3 shows the valance band spectra of vacuum annealed C12A7:e⁻ / Alq₃ interface. The valance band maximum (VBM) of the C12A7:e⁻ is at 5.5eV and The HOMO of the Alq₃ is 2.5eV below the E_F .

UPS spectra at the interface of UV-ozone treated C12A7:e⁻/Alq₃ is in Fig. 4. Vacuum level shifted to higher binding energy by 0.2eV when the thickness of Alq₃ over layer was 0.3nm. As can be seen in valance band spectra of Fig. 3 and Fig. 4, there was no sign of interfacial gap state at the C12A7:e⁻/Alq₃ interface, that is reported by Yokoyama et al in the case of Al/Alq₃ interface. [7] This may suggest that there is no chemical reaction between C12A7:e⁻ and Alq₃.

Fig. 5 shows the energy diagrams of vacuum annealed C12A7:e⁻/Alq₃ and UV-ozone treated C12A7:e⁻/Alq₃ interface based on the UPS spectra of Fig. 3 and Fig. 4. The value of the lowest unoccupied molecular orbital (LUMO) and LUMO* was calculated using optical band gap ($E_{\text{opt}}=2.9\text{eV}$) and transfer gap ($E_t=4.6\text{eV}$) of Alq₃. [8]. From this diagrams, actual electron injection barrier can be calculated by the distance from E_F of C12A7:e⁻ to LUMO* of Alq₃. The injection barrier heights of these correspond to 2.2eV and 1.9eV respectively. This comparison made us know the small work function of electrode material does not mean small injection barrier directly. Ishii et al. [9] have reported dependence of vacuum level shift (Δ) on the work function of electrode (Φ_m). According to their study, in most cases Δ occurs to negative direction like as UV-ozone treated C12A7:e⁻/Alq₃ interface and it brings lowering of vacuum level. However, in the case of vacuum annealed C12A7:e⁻/Alq₃ interface, vacuum level was shifted in positive direction. Consequently, this made the distance from E_F of C12A7:e⁻ to LUMO* of Alq₃ became further.

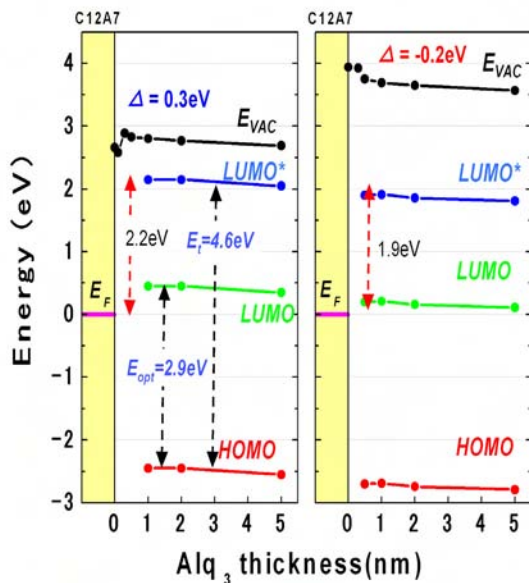


Figure 5. Band diagram of C12A7:e⁻/Alq₃ interfaces. Left side is for vacuum annealed C12A7:e⁻/Alq₃ and right side is for UV-ozone treated C12A7:e⁻/Alq₃.

4. Summary

Until now, low work function of cathode material was believed to be a key to the efficient electron injection in OLED.[10] However, by the result of this study, we came to know that only adopting a low work function cathode material is not sufficient to form a low injection barrier interface.

If the work function of electrode is much smaller than that of organic material, vacuum level shifts up and as a result, electron injection barrier becomes larger. To make low electron injection barrier at the cathode and Alq₃ interface, the energy shift (Δ) at the interface should be counted as well.

5. References

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