Chemical structure of the bilayer Ag/Li$_2$O cathode interface in organic light-emitting diodes

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Abstract

The chemical structure of the interface between Ag with Li$_2$O and tri (8-hydroxyquinoline) aluminum (Alq) was investigated by using in-situ characterization of x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). Li$_2$O on Ag had lower barrier height than LiF on Ag. XPS and UPS results show the interaction between Li$_2$O and Alq leads to gap state formation in HOMO of Alq.

1. Introduction

Since efficient electroluminescence (EL) from bilayer organic light emitting diode (OLED) was reported [1], OLEDs have the high potential to achieve high-contrast, full-color, and low driving voltage in flat panel displays. Achieving improved device performance requires optimization of charge injection transport at interfaces. For the cathode/organic interface, enhanced electron injection is desired in order to balance charge carriers in the active layer. Currently, the most widely used cathode is the bilayer Al/LiF, and the effect of LiF in improving device efficiency is well documented. Dramatic improvement of Al performance as a cathode was achieved by the use of a thin interlayer at Al/organic interface. Ag is known to be an excellent electrode due to high reflectivity and low electrical resistivity [2]. However, the Ag electrode has poor electron-injection property due to its high work function (~4.3 eV). Previous studies have reported the formation of anode characteristics for top emission OLED [2-5]. In the case of cathode application of Ag, semitransparent LiF/Al/Ag is commonly used for top emission OLED [2, 6, 7]. Recent investigations have been intensively focused on the working mechanism of the improvement on device performance by the insertion of the interlayer materials [8-12]. However, the working mechanism that enhances the OLED performance by insertion of inter layer is not completely understood.

In this letter, we report an effective bottom cathode structure for enhancing the electron injection in OLEDs using Ag/Li$_2$O bilayer cathode. Such a cathode structure does not involve handling reactive metals during fabrication and permits use of highly refractive material. We show the results of our investigation on the electronic structure of an interface between a very low coverage Li$_2$O and Alq layer using an evaporation technique and *in-situ* photoemission spectroscopy characterization. The chemical and electronic structure changes with the deposited Li$_2$O on Ag and Alq were examined using x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). *I-V* characteristics of OLED covering with Ag/Li$_2$O bilayer cathode show high performance and were well consistent with photoemission results.

2. Results

The OLED structures were fabricated with a configuration of Ag/interlayer/Alq/NPD/ITO. Interlayer was varying with Li$_2$O and LiF layer deposited on Alq, and then followed by metal deposition. The active area of OLEDs was 2×2 mm^2. The current-voltage (*I-V*) characteristics were measured using Keithley 236 source measurement unit. The XPS and UPS experiments were carried out in an ultra high vacuum chamber which was connected to a preparation chamber where all deposition processes took place *in situ*. Spectra were recorded on PHI 5400 system using a He I (21.2 eV) radiation source for UPS and a Mg K_α (1253.6 eV) radiation for XPS. The base pressure of the
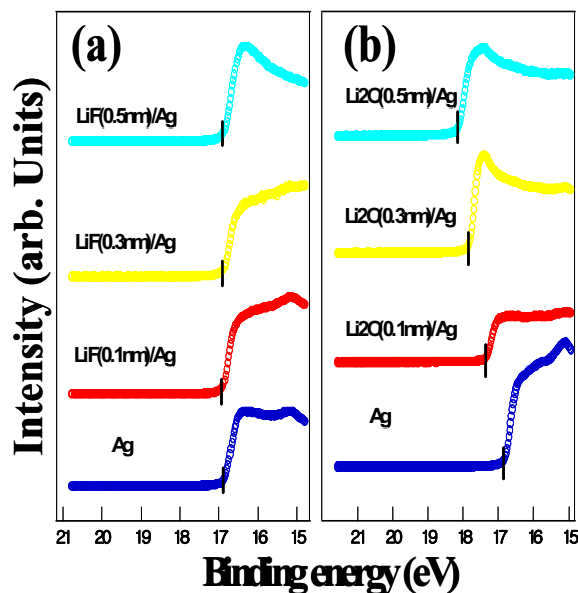
Figure 1. Work function shift as a function of (a) LiF and (b) Li_2O coverage deposited on Ag substrate.

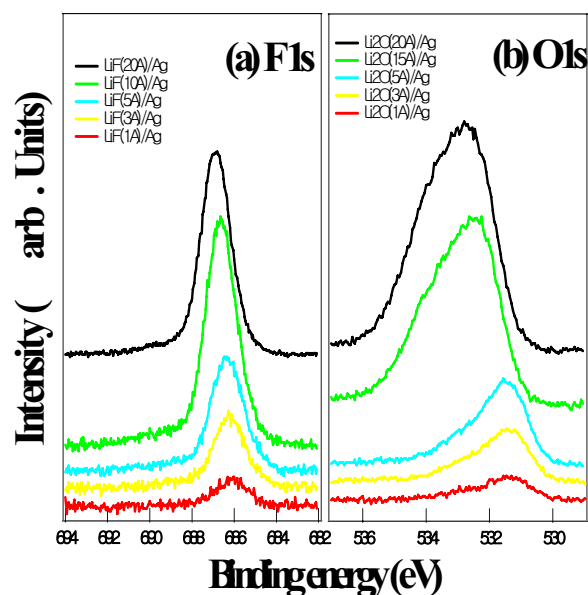Figure 2. (a) F 1*s* and (b) O 1*s* core level spectra using 1253.6 eV of incident photon energy as a function of LiF (a) or Li_2O (b) coverage deposited on Ag substrate.

preparation chamber and the analysis chamber were 5 $\times$ 10^{-8} and 1×10^{-10} Torr, respectively. UPS spectra were recorded with a bias -20 V on the sample for the observation of the low energy cutoff. The deposition rate was monitored by crystal quartz microbalance.

Secondary cut-off edge was measured for work function shift shown in figure 1. The sample bias of -20 V and the incidence photon energy of 21.2 eV (He I) were used for the measurement of secondary cut-off. The Ag substrate was a reference sample before LiF or Li_2O evaporation. It is noticeable that Li_2O on Ag has lower work function than LiF on Ag. As seen in figure 1, the deposition of LiF on the Ag substrate causes no significant work function shift, but the coverage of Li_2O on Ag leads to a distinct work function shift from metal atoms.

The evolution of the F 1*s* and O 1*s* core level peak shift for Ag/LiF and Ag/Li_2O are shown in figure 2. The O 1*s* peak shift on the higher binding energy side cause drastic change of work function with coverage of Li_2O on Ag in figure 1. However, the reaction between F and Ag was very weak result in small change of work function shift as shown in figure 1. Common feature of these reports is the shift to higher binding energy of core-level peak of O 1*s*. In addition, a broadening of O 1*s* peak was observed. These results suggest a dissociation of Li_2O at Ag/Li_2O interface.

Figure 3 shows core-level spectra of O 1*s* and F 1*s* measured as a function of LiF or Li_2O coverage on Alq/Ag. Ag was used for conducting material removing charging effects during photoemission characterization. These XPS studies represent the reaction of interlayer (LiF or Li_2O) with Alq excepting the contribution of cathode metal. In the case of LiF on Alq/Ag, the appearance of weak O 1*s* peak causes small change of peak shift and forms F 1s shoulder peak to higher binding energy showing F 1s peak shift. However, O 1*s* peak of Li_2O on Alq/Ag displays a drastic shift of the occupied molecular orbitals of Alq to higher binding energy, which may lead to a reduction of the barrier height for electron injection at the interface.

The evolution of the N 1*s* core level peak for LiF/Alq and Li_2O/Alq is shown in figure 4. The appearance of N 1*s* shoulder peak on the lower binding energy side. However, LiF on Alq/Ag cause no clear evolution of N 1*s* peak shoulder to lower binding energy side. In Al/NaF/Alq or Al/LiF/Alq case, Lee *et al*. suggested the Al deposition forms strong gap state as a result of significant charge transfer [13], which results
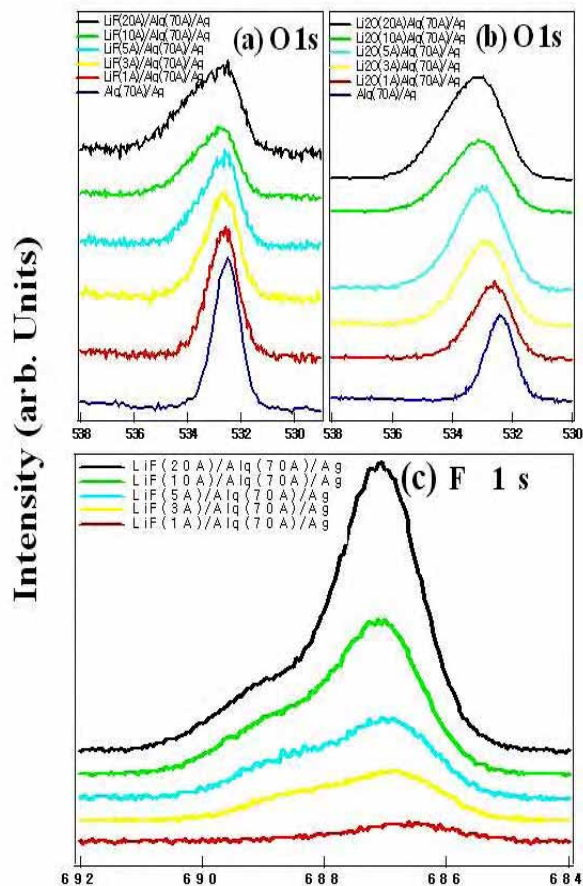
Figure 3. XPS core level spectra of O 1*s* peak with (a) LiF and (b) Li₂O deposition on Alq/Ag. (c) F 1*s* spectra for LiF on Alq/Ag.

were somewhat different from our photoemission results because of the exception of cathode metals. Therefore, these results clearly show what the main reason for the improved OLED performances is. In LiF/Alg/Ag system, molecular orbital shift may be caused by the attachment of F to π-electrons on the conjugated ligand as mentioned by Grozea *et al.* [12]. N 1*s* shoulder peak of Alq shows strong interaction with O in Li₂O, and forms HOMO gap state in Alq confirmed by valence band UPS spectra in figure 5. Figure 5 shows the evolution of valence band spectra while two different types of interlayer (LiF and Li₂O) on Alq/Ag. The binding
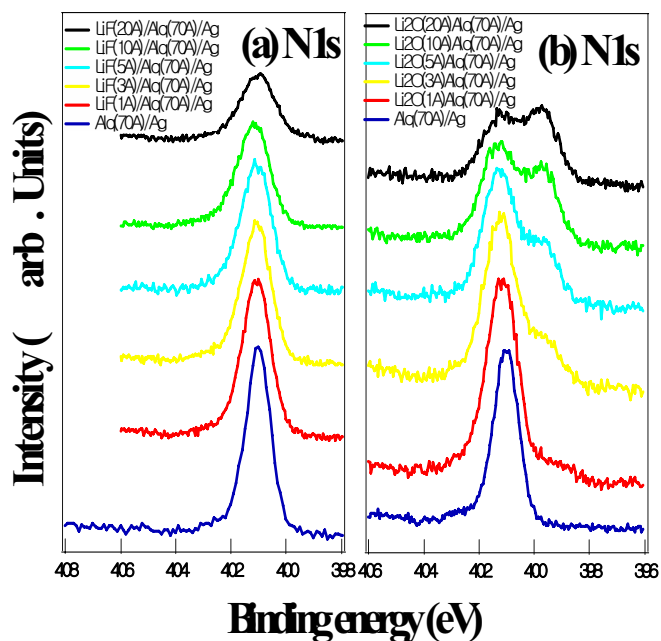

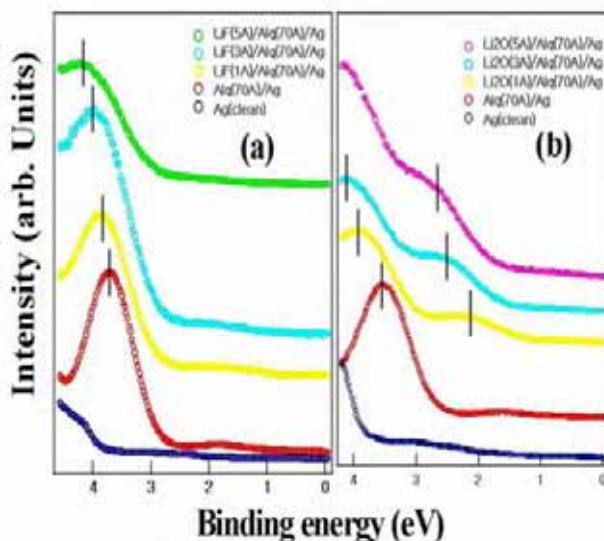Figure 4. XPS core level spectra of N 1*s* peak with (a) LiF and (b) Li₂O deposition on Alq/Ag.

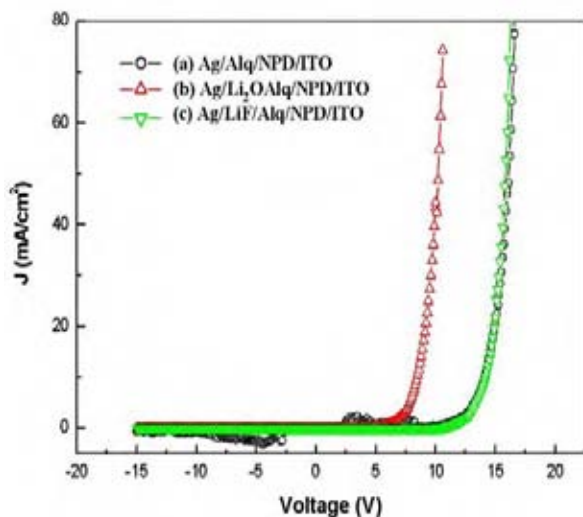Figure 5. The evolution of valence band UPS spectra with increasing LiF and Li₂O coverage on Alq/Ag.

Figure 6. *I-V* characteristics of various cathode structures: using (a) Ag-only, (b) Ag/Li$_2$O (0.5 nm), and (c) Ag/LiF (0.5 nm).

energy in figure 5 is relative to the Fermi level, E_F. The onset of the peak at the lowest binding energy is referred to the HOMO level. The vertical bars indicate the HOMO position and the formation of gap states. For LiF deposition on Alq/Ag, there is no formation of gap state from Alq. However, Li$_2$O deposition on Alq/Ag leads to gap state formation of Alq.

Figure 6 represents the *I-V* characteristics of three devices with different interlayer, Ag-only, Ag/Li$_2$O (0.5 nm), Ag/LiF(0.5 nm). It is clear that the performance of Ag/Li$_2$O device was greatly improved over Ag-only and Ag/LiF devices in terms of turn-on-voltage. As mentioned above, XPS and UPS results were referred to the barrier height lowering for electron injection at interface. And the HOMO level shift is correlated with OLED performance. Ag/Li$_2$O on Alq/Ag plays an important role in reduction of barrier height, which also shows lower turn-on-voltage.

3. Conclusion
In summary, the bilayer Ag/Li$_2$O cathode in Alq-based OLED plays an important role in device performance. Our spectroscopic results from both sides of interface show strong reaction. The Li$_2$O deposition causes gap state formation and a shoulder in N 1s core level peak. Device performance results indicate that the valence band shift is correlated with the enhancement of the OLED performances.

4. References
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