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Experimental study of Ag/LiF/PFO interface for Top Emission PLEDs by synchrotron

radiation photoemission spectroscopy

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1. Introduction

To achieve active matrix organic light-emitting displays, to integrate organic light-emitting diodes (OLEDs) with silicon-based electronics is necessary. Hence, the development of top-emitting OLEDs is essential. A transparent cathode is required for top-emitting OLEDs. In previous reports, ITO is used most frequently to be the transparent cathode [1-2], due to high transmittance and low resistivity. However, to realize an efficient OLED, effective carrier injection from the electrodes to organic materials is significant. ITO with higher work function and resistivity is unfavorable for electron injection. Therefore, an insulating layer, LiF [3], which has been employed between cathode metals and organic materials for the improvement of electron injection efficiency and a noble metal, Ag [4], which has the highest electrical conductivity and low absorption in the visible light region are introduced to form bilayer fabrication, Ag/LiF, between ITO and organic materials for enhancing electron injection and reducing the bombard damage. The devices with Ag/LiF cathode show that the current density will have a lot of enhancement. In order to have a clear understanding of the reaction between Ag and LiF on organic layer, therefore, synchrotron radiation photoemission, which can provide sensitive surface electronic structure, because researchers can tune the photon energy to result in the excited electrons with a short inelastic mean free path, will be used for the investigation of interface behavior, since it is responsive to level shift as well as to the charge imbalance of the organic atoms.

2. Experiment

PFO was spin coating on the Au/Silicon substrate. The deposition of materials was carried out in the ultrahigh vacuum photoemission chamber with a base pressure of 2*10⁻¹⁰Torr. Ag and LiF were deposited by the OMICRON EFM3 electron-beam evaporators. The experiments of photoemission, the photoelectrons which is excited by photons, are measured by a 125-mm hemispherical analyzer. The photons were provided by a low-energy spherical grating monochromator (LSGM) with energy range from 20 to 160eV. They have advantages such as High Intensity, Continuous Spectrum and Excellent Collimation which are better than single source instruments such as XPS and UPS.

3. Result and discussion

Fig. 1 shows the current density-voltage (J-V) plot of devices with ITO and ITO/LiF(1.5nm) cathodes. The device with inserting LiF buffer layer demonstrates higher

injection of charge carriers and lower turn-on voltage than the device without one. It can be attributed to the formation of dipoles at both sides of insulator layer, and a considerable voltage can be dropped across the LiF layer through the dipole as a forward bias is applied on devices. Consequently, it can bring about the reduction of energy barrier height for electrons injection from metal to organic layer [3]. Fig. 2(a) shows the valence-band (VB) spectra as a function of increasing deposition of LiF on PFO. The onset of HOMO was determined by deducing two solid lines from the background and straight onset in the spectra. The Fermi-level (FL) position was fixed at 0 eV of the binding energy (BE). The energy difference between HOMO of pristine PFO and FL is 2.5 eV. With the incremental LiF coverage, the energy difference between HOMO and FL was getting larger up to 0.5eV (deposition of LiF 700 sec). It means that the LUMO shifted close to FL and resulted in the barrier lowering. It can be explained by dissociation of LiF and liberates Li to dope into PFO to cause band bending at the near region interface of PFO. The photoemission spectra of Li 1s core level with deposition of incremental LiF coverage on PFO was shown in Fig. 3(a). With increasing deposited time of LiF, the core level signals of Li 1s are also increasing. It shows no chemical reaction with none of shoulders to take place during LiF deposited on PFO. However, shifts of HOMO were shown in Fig. 2(a). It means that some chemical reaction occurred during LiF deposited on PFO. Therefore, to derive detailed information, each spectrum was treated with an analytic fit and exhibited the results as solid curves, and the experimental data were drawn as dotted curves in Fig. 3(b)-(e). The Li 1s core levels are composed of two mail components, one is the Li⁺ in LiF (green one), and the other is Li⁺ which is produced by the dissociation of LiF (red one). Fig. 3(b) shows the experimental data which is fitted to combined with two main components of green and green ones. It exhibited that the area ratio of the Li⁺ which is produced by the dissociation of LiF (red one) and the Li⁺ in LiF (green one) was 0.1546 to 0.8454. With incremental deposited time of LiF to 60, 145 and 400 sec, the areas of red one and green one were reducing and enhancing, respectively, as shown in Fig. 3(c) and (d). It can be demonstrated that LiF dissociates slightly at the interface of LiF and PFO, as a result of PFO with thicker LiF layer shows diminishing area of red one. This effect can result in releasing Li to dope into PFO and brings about band bending of PFO at LiF/PFO interface. It can be suggested that the effective barrier reduction of device with inserting

LiF may not only dipole effect but also chemical reaction. Moreover, the band diagrams of ITO/PFO and ITO/LiF/PFO were shown in Fig. 2(b) -(i) and -(ii). Fig. 2(b) -(ii) exhibits that the electron injection barrier lowering is composed of dipole effect and chemical reaction from the bending of LiF layer and the near region interface of PFO, respectively, after inserting LiF layer.

A J-V plot of ITO/Ag/LiF cathodes with various Ag thicknesses 1, 3, 5, 10, 20nm shows in Fig. 1. From J-V curves of Figs. 1(a) and (b), it reveals that the insertion of thin Ag (1, 3, 5nm) between ITO and LiF facilitates electron injection than a cathode with ITO/LiF. Thereafter, the current density is gradually reduced with enhancing Ag coverage up to 20nm. Further on, Fig. 4(a) depicts the VB spectra as a function of increasing of Ag thickness on LiF/PFO. It shows that HOMO with no shift at thin Ag coverage, after that it shifts continuously toward low BE to be close to FL with thick Ag deposition. Moreover, a small feature arises at about 0.25 eV of BE after 103 min of Ag deposition shown in Fig. 4(b). The shifts of HOMO toward FL indicate the appearance of negatively charged layer at Ag and LiF/PFO interface which charge transfer from Ag to F LiF/PFO. Besides, Li 1s and F 2s peaks of LiF, as shown in Fig. 4(c) and (d), exhibit to shift to low BE. It indicates that LiF obtain electrons coming from Ag. This negatively charged layer will enhance the electron injection barrier with increasing Ag thickness, leading to the lowering of device performance. Furthermore, it can be explained by the band diagrams shown in Figs. 5(a)-(c). Although the barrier at the interface of Ag/LiF is lowering with incremental Ag coverage, the barrier at the interface of LiF/PFO is increasing. The barrier lowering at Ag/LiF interface has the maximum value of 0.3 eV (ITO 4.6 - Ag 4.3eV), however, the enhancement of barrier at LiF/PFO interface is higher than 0.3 eV. Consequently, the device with inserting thicker Ag will increase the effective barrier for electron injection.

Fig. 6 reveals the I-V data in $\ln(I/E^2)$ vs 1/E to see the [±] change of barrier height with different cathode fabrications, such as ITO, ITO/LiF, ITO/Ag/LiF. Since anode structure comprise ITO and PEDOT:PSS in all devices, it can be conjectured that the great part enhancement of current density with changing cathode fabrication is contributed by electron injection. The slope of linear part of FN curves at high electric field can reveal that the effective barrier height by Fowler-Nordheim tunneling formula, $I \propto E^2 e^{-\kappa/E}$, where E is electric field strength and к, 着 $\kappa = 8\pi (2m^*)^{1/2} \varphi^{3/2} / 3qh$, is a parameter that depends on the barrier sharp. Therefore, it reveals that inserting LiF layer between ITO and PFO can enhance probability of electron injection by the appearance of linear part curve. Thereafter, the devices with thin Ag (1, 3, 5nm) show that the slopes were decreasing. It indicated the lowering of barrier height with inserting thin Ag layer up to 5nm. However, the devices with thicker Ag layer, such as 10 and 20nm, display the enhancement of barrier height. These results agree with the photoemission data with Ag on

LiF/PFO.

4. Conclusion

LiF deposited onto PFO layer cause LiF dissociation resulted in lowering electron injection barrier. Thin Ag layer added onto LiF will not bring about injection barrier increasing but reducing resistivity and ion bombard damage. However, Thicker Ag layer will offer electron to LiF/PFO led to HOMO toward to low BE and increase electron injection barrier.

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Fig. 6. FN plot with ITO, ITO/LiF, ITO/Ag(1, 3, 5, 10, 20nm)/LiF as cathode.