

(一) 期中報告之中文摘要

本研究計畫為新進人員研究計畫，執行期間為兩年，在第一年，我們用最短的時間提前完成了超高真空表面分析系統的建構，並且在此超高真空系統裏裝置了一組X光電子能譜偵測儀 (X-ray photoemission spectroscopy, XPS) 和一組Auger 電子能譜偵測儀 (Auger electron spectroscopy, AES)。我們使用X光電子能譜偵測儀來研究有機發光半導體與氮化鎵光電半導體在表面與介面的化學反應與電子能階結構，並藉由Auger電子能譜偵測儀來判定有機材料與氮化鎵材料的表面原子組成成份。藉由這些電子能譜偵測儀，我們開始著手研究有機光電半導體和氮化鎵光電半導體的表面分析和介面的性質。在有機發光半導體材料方面，我們成功的測量出數種新的藍光發光二極體材料的電子能階結構，這些結果，可以用于改善有機發光二極體的操作電壓和發光效率。在氮化鎵光電半導體材料部分，我們使用氧化銦錫與鎳、金合金來當作金屬與氮化鎵半導體的介面，可以改善氮化鎵發光二極體之透光率。

在過去一年，根據本研究計畫的執行成果，我們已在國際著名的期刊雜誌 Applied Physics Letter 發表了一篇研究論文，並且受邀在國際顯示器技術研討會 (International Display Manufacturing Conference 2005) 發表研究成果。

預計在第二年，我們將在此超高真空表面分析系統之中裝置二組新的電子能譜偵測儀：紫外光電子能譜偵測儀 (Ultraviolet Photoemission Spectroscopy, UPS) 以及反轉式電子能譜偵測儀 (Inverse Photoemission Spectroscopy)。完成之後，此系統將是國內唯一一套同時具有正向和反轉式光電子能譜偵測儀的表面分析系統。我們將利用此正向和反轉式光電子能譜偵測儀同時來研究電子和電洞在有機光電半導體和氮化鎵光電半導體之間的傳輸過程，經由對電子與電洞能量結構的了解，我們可以

將這些研究成果直接應用於光電元件的發光效率改善。

(二) 論文發表

1. J.H. Lee, C.I. Wu, S.W. Liu, C.A. Huang, and Y. Chang, “Mixed Host Organic Light Emitting Devices with Low Driving Voltage and Long Lifetime”, Appl. Phys. Lett., **86**, 103506,(2005)
2. (Invited Paper) C.I. Wu, “Energy Structures at the Interfaces of Organic Semiconductors”, International Display Manufacturing Conference, Taipei, Taiwan, 2005

(三) 研究成果

I. Introduction

Conducting organic materials have attracted a lot of attention due to their applications in optical-electronic devices, such as organic light emitting diodes (OLEDs) [1-3]. The efficiency of the OLEDs strongly depends on how the carriers inject from the metal electrodes and transport in the organic materials. The band structures of organic materials are therefore exceedingly important in making these devices. The knowledge of the energy level location is the key to understanding the underlying physics of the OLED devices. However, unlike for other inorganic semiconductor materials for light emitting devices, there are only a little data on OLED materials with electronic structure measurements until recent years. Typical OLEDs consist of anodes, hole transport layers (HTL), electron emitting layers (EML), electron transport layers (ETL), and cathodes. From the device

operation point of view, an important issue concerning the organic LED materials is the charge transportation between the metal-organic interfaces and organic-organic interfaces. Chemical reactions at the interfaces could have a strong effect on the energy barrier between metals and organic materials. The formation mechanisms of energy barriers at metal-semiconductor interfaces play a key role in determining carrier injection across the interfaces into or from the organic layers. In this paper, we will present the study of electronic structures of several oligofluorene thin films (T2, T3, E3, and E4) and their interface with metal layers.

II. Experiments and Results

Measurements of electron affinity, ionization energy and work function are extremely important to realize the band alignment at these interfaces. They all involve correct measurements of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and Fermi level of ETL, HTL, EML, and metals. The experiments are carried out via photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) in an ultra-high vacuum system. Organic thin films were deposited *in-situ* in UHV environments. Metallic atoms were evaporated from an electron-beam heated sources and the deposition of metal were verified by the X-ray photoemission spectroscopy. The energy spectra of photoelectrons were collected with a hemispherical analyzer with overall resolution better than 0.05 eV. Organic thin films were thermally evaporated and deposited *in-situ* on gold substrates. The Fermi level of the system is measured on the gold surface before the organic thin film deposition. LiF was evaporated from an OMICRON EFM3 electron-beam evaporators and the deposition of

LiF was verified by lithium 1s and fluorine 2s core level spectra measured with 100 eV photons.

III. Discussions

The organic opto-electronic materials studied in this work are ter(9,9-diarylfluorene)s. The homologous oligofluorenes, labeled with T2, T3, E3, and E4, were synthesized at the Department of Chemistry of National Taiwan University [4,5]. The chemical structures of E-series and T-series materials are shown in Figure 1(a) and 1(b), respectively. These fluorine-based molecules have been demonstrated as efficient blue emitters with promising electrochemical and thermal stability [6]. The electron mobilities of these amorphous organic molecules are about 10^{-3} cm²/V sec, which are unusually high for disordered organic thin films. The electron transport mechanisms in organic thin films are through hopping processes. It is suspected that the high electron mobility might be due to the large solid-state electron affinity (EA) to form stable anions in organic solids and to reduce trapping [7,8]. However, there was no reported EA data on fluorine-based materials to confirm this hypothesis. The EA of the materials can be either measured with IPES or combination of PES and optical absorption data. The photoemission spectra of these oligofluorene thin films are shown in Figure 2, along with Alq3 and m-MTDATA. The electron energy spectra, representing the density of states of the occupied molecular orbitals close to the Fermi level, at 20-37 eV are similar for all four oligofluorene thin films. It indicates that the highest occupied molecular orbitals are evolved from the core benzene

rings. The length of the chain and the size of the molecules do not affect the electronic density of states around the top of the valence band significantly.

From the onset of the photoemission spectra, we can also find the energy position of vacuum level. The ionization energy (IP), which is defined as the energy difference between HOMO and vacuum level, of these oligofluorene thin films are between 6 to 7 eV. The optical band gaps of these oligofluorenes are 3.3 eV, as measured from the optical absorption spectra. The EA of these films are therefore about 3 to 4 eV. The relative large EA also is consistent with the aforementioned assumption regarding the high electron mobility in these organic thin films.

We also studied the chemistry of the metal-organic interfaces on these materials. As we know, chemistry at the metal-organic interfaces not only has direct bearing on the stability of these OLED devices, but also affects how the carriers transport across the metal-organic interfaces and inject into HTL and ETL from anodes and cathodes, respectively. We found the deposition of LiF on several organic materials leads to drastically different effects on the Fermi level of the organic materials. LiF would not react with Alq3 and change the Fermi level unless the subsequent aluminum deposition, which is similar to the data reported before [9,10]. However, the deposition of LiF immediately changes the Fermi level position of all the oligofluorene material. Figure 3 and 4 show the UPS spectra of oligofluorene T3 and E4 with increment deposition of LiF, from 15 seconds up to more than 15 minutes of deposition time. As shown in the spectra, the Fermi level moves about 0.6 eV on T3 thin film. We found similar Fermi level shift for all four oligofluorene thin films we investigated. The changes of Fermi levels imply that the organic materials

were n-type doped at the interfaces with the LiF deposition. The n-doping species could result from the lithium ions dissociated from LiF immediately after deposition. The presence of lithium ions was verified by soft X-ray photoemission spectroscopy (XPS) with the chemical shift of core-level electron binding energy of Li atoms due to different bonding configurations. Fluorine is also detected on the sample with XPS. This result indicates that the lithium and fluorine dissociation occurs in or at the surface of organic materials. The dissociation of LiF is not due to the thermal evaporation.

IV. Acknowledgements

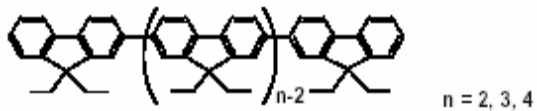
This work is supported by National Science Councils (NSC93-2120-M-002-013). The author also thanks Professor Chung-Chih Wu and Professor Ken-Tsung Wang for providing the organic materials and Doctor Tun-Wen Pi and Chen-Pei Ouyang for their support with photoemission experiments at NSRRC.

References

- [1] L. S. Hung, C. W. Tang, and M. G. Mason, [*Appl. Phys. Lett.* **70**, 152 \(1997\)](#).
- [2] C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987)
- [3] C. W. Tang, S. A. VanSlyke, C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989)
- [4] C.-C. Wu, T.-L. Liu, W.-Y. Hung, Y.-T. Lin, K.-T. Wong, R.-T. Chen, Y.-M. Chen, and Y.-Y. Chien, [*J. Am. Chem. Soc.* **125**, 3710 \(2003\)](#).

- [5] K.-T. Wong, Y.-Y. Chien, R.-T. Chen, C.-F. Wang, Y.-T. Lin, H.-H. Chiang, P.-Y. Hsieh, C.-C. Wu, C. H. Chou, Y. O. Su, G.-H. Lee, and S.-M. Peng, [J. Am. Chem. Soc.](#) **124**, 11576(2002).
- [6] C.C. Wu, Y.T. Lin, K.T. Wong, R.T. Chen, and Y.Y. Chien, *Adv. Mater.*, **16**, 61, (2004)
- [7] P. Strohhriegl, *Adv. Mater.* **14**, 1439 (2002)
- [8] Y. Shirota, *J. Mater. Chem.* **10**, 1 (2000)
- [9] Q.T. Le, L. Yan, Y Gao, M.G. Mason, D.J. Giesen, and C.W. Tang, *J. Appl. Phys.* **87**, 375 (2000)
- [10] D. Grozea, A. Turak, X.D. Feng, Z.H. Lu, D. Johnson, and R. Wood, *Appl. Phys. Lett.* **81**, 3173, (2002)

E-Series



T-Series



Figure 1: The chemical structures of E- and T- series of oligofluorenes

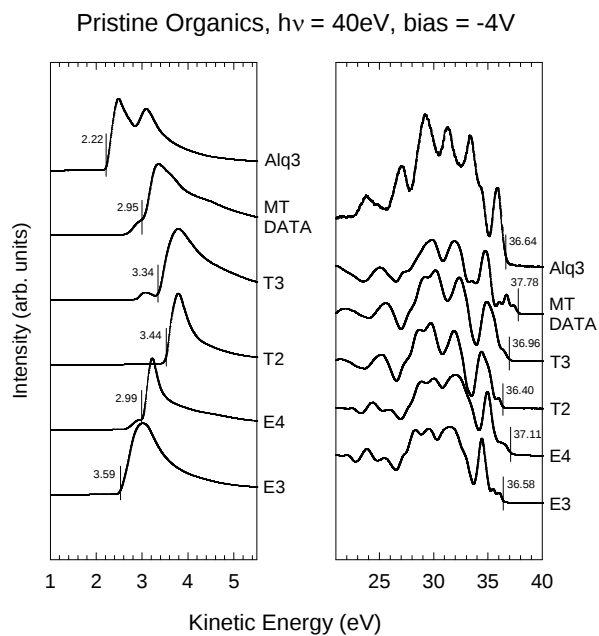


Figure 2: The onset and valence band spectra of Photoemission Spectra on several organic thin films.

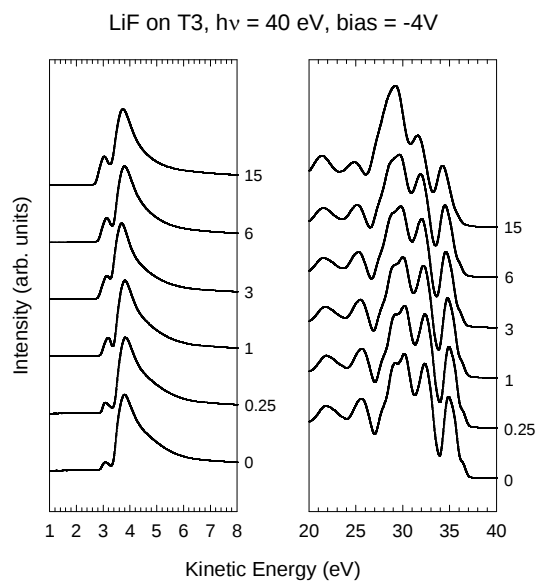


Figure 3: Photoemission Spectra of oligofluorene, T3, with LiF deposition.

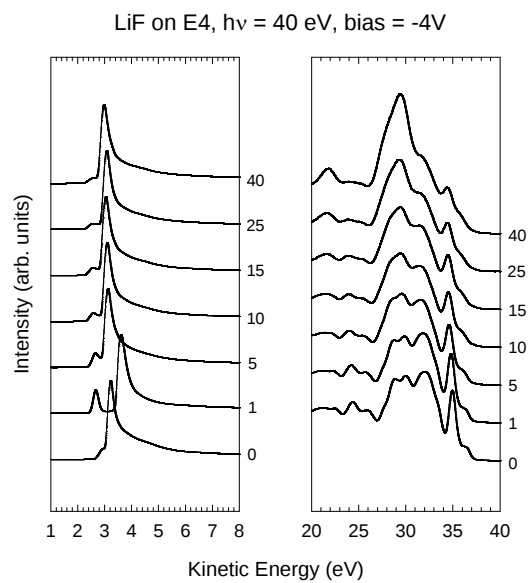


Figure 4: Photoemission Spectra of oligofluorene, E4, with LiF deposition.

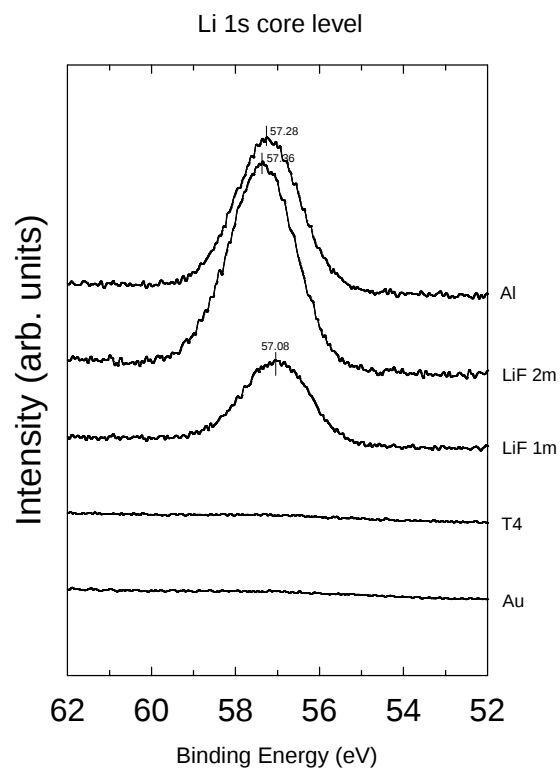


Figure 5: X- ray Photoemission Spectra of oligofluorene, T4, with LiF deposition.