

Surface Characterization of Organic Electroluminescent Thin Film Materials

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(Received January 29 1999; accepted February 11 1999)

Thermally evaporated tris(8-hydroxy-quinoline) aluminum (Alq_3) and N,N'-diphenyl-N,N'-bis(3-methyl phenyl)-1,1'-bi-phenyl-4,4'-diamine (TPD) organic electroluminescent thin films have been characterized by XPS and SIMS. For a better understanding of the molecular thin films, $\pi \rightarrow \pi^*$ shake-up peaks of the C 1s photoelectron line have been measured and compared with the optical energy gap of the organic molecules. The strongest shake-up peak of Alq_3 and TPD, however, coincides well with the strongest electronic absorption band of quinoline and benzene, respectively. This was also observed from the calculations of molecular orbitals with AM1 semi-empirical method. It means that the $\pi \rightarrow \pi^*$ shake-up peak of the C 1s photoelectron line reflects more the local $\pi \rightarrow \pi^*$ transition than HOMO \rightarrow LUMO excitation of the whole molecule. Using static mode SIMS, some characteristics of the molecular thin film of Alq_3 were compared with that of polymeric thin film of PPV. Strong ion yield reduction above 60 amu was observed. It means that there is less cascade effect at molecular organic thin film than polymeric thin film. Change of ion formation was also observed which can be explained with the relative abundance of C and H in matrix.

1. Introduction

In recent years, there has been considerable interest in developing organic electroluminescent (EL) devices [1,2] using both polymeric [3-5] and molecular thin films with multilayer structures [6-11]. A simple configuration of EL cell is a sandwich structure of electron and hole transport layer between metallic cathode and transparent anode on a glass substrate. The typical organic molecule for the electron transport layer is tris(8-hydroxy-quinoline) aluminum (Alq_3) [6] and for the hole transport layer is N,N'-diphenyl-N,N'-bis(3-methyl phenyl)-1,1'-bi-phenyl-4,4'-diamine (TPD). The molecular structures of the organic molecules are shown in Fig. 1.

An important factor for the performance of such organic EL devices is the interfacial characteristic of each molecular thin film. Thus it is necessary to understand first the physical and chemical properties of the surface of each organic thin film. In this work surface characterization of Alq_3 and TPD has been performed with common surface analytical techniques such as x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). In addition to the commonly used mode of analysis, $\pi \rightarrow \pi^*$ shake-up peaks of the C 1s photoelectron line have been measured and compared with the

optical energy gap of the organic molecules. Some characteristics of the observed spectra of the molecular thin films have been given and compared with that of polymeric thin film such as poly (p-phenylene vinylene) (PPV).

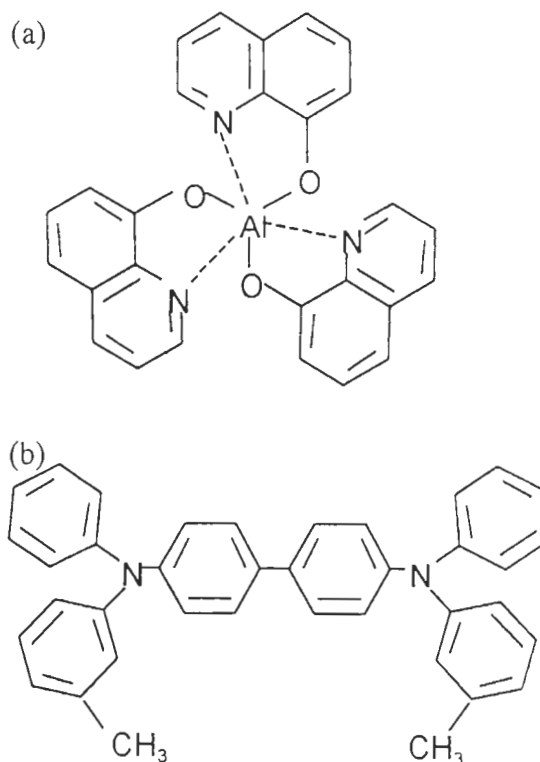


Figure 1. Molecular structures of (a) Alq_3 and (b) TPD.

2. Experimental

The organic electroluminescent molecular thin films, Alq₃ and TPD, were deposited on a silicon wafer by thermal evaporation. The thickness of each thin film was about 100 nm and the deposition rate was about 3 nm/min. The organic materials were purified powders and the base pressure of the evaporation chamber was about 2.5×10⁻⁶ Torr.

The XPS analyses were performed by PHI-5400 system with a monochromatized Al Kα X-ray source (E=1486.6 eV) at 12 kV and 350 W. Monochromator is essential for the study of organic materials because of the possible damage when standard source is used. The measured spectra were obtained at the pass energy of 35.75 eV. The resolution was 0.7 eV FWHM for Ag 3d_{5/2}. The binding energy was calibrated at 84.0 eV for Au 4f_{7/2} and shifted to the reference of the hydrocarbon C 1s main peak at 285.0 eV. The base pressure in the analysis chamber was about 5×10⁻¹⁰ Torr. To reduce the charging effect at the sample surface, a neutralizer was used during the measurements.

The SIMS analyses were performed by PHI-6300 system using 5 keV Cs⁺ primary ion beam. The primary ion beam was directed at an angle of 60° with respect to the sample surface normal and rastered over 1.5×1.5 mm². The base pressure in the analysis chamber was about 1.5×10⁻⁹ Torr. To compensate the charging effect at the sample surface, a neutralizer was also used during the measurements.

3. Results and Discussion

Figure 2 shows the XPS survey spectra of Alq₃ and TPD. One can see the C1s, O1s, N1s and the two weak Al photoelectron lines of Al2s and Al2p. No other elements, which can be originated from impurities, can be found. In Table 1 the theoretical and measured atomic concentrations of C, O, N, and Al of Alq₃ are given in percentage. The theoretical values are calculated from the number of atoms of C, O, N, and Al in Alq₃ that can be obtained from the molecular structure of Fig. 1. They are 27,

Table 1. Atomic concentrations (%) of Alq₃.

	C	O	N	Al
Theory	79.4	8.8	8.8	3.0
Experiment	78.6	10.4	8.5	2.5

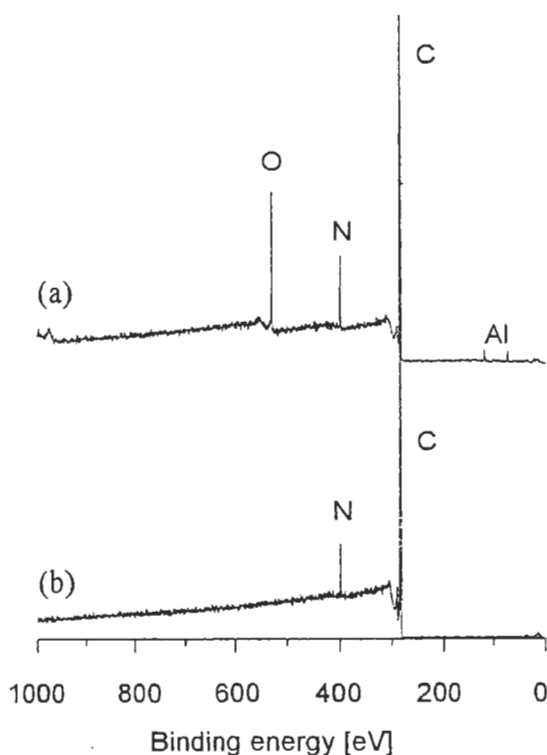


Figure 2. XPS survey spectra of (a) Alq₃ and (b) TPD.

3, 3, and 1, respectively. The theoretical values are in good agreement with the measured values except for the oxygen concentration, which is a little higher than the ideal one. It may come from the exposure of the sample to the atmosphere during the transportation from the evaporation chamber to the analysis chamber. In case of TPD, however, the oxygen concentration is under the detection limit. Table 2 shows the theoretical and measured atomic concentrations of C and N. They are also in good agreement.

Table 2. Atomic concentrations (%) of TPD.

	C	N
Theory	95.0	5.0
Experiment	94.2	5.8

Figure 3 shows the C1s main photoelectron lines with their energy loss peaks, especially the π→π* shake-up peaks, which are presented in dotted lines with 10 times magnification. The π→π* shake-up peak of Alq₃ lies 5.5 eV above the C1s main peak and that of TPD lies 6.7 eV above the main peak.

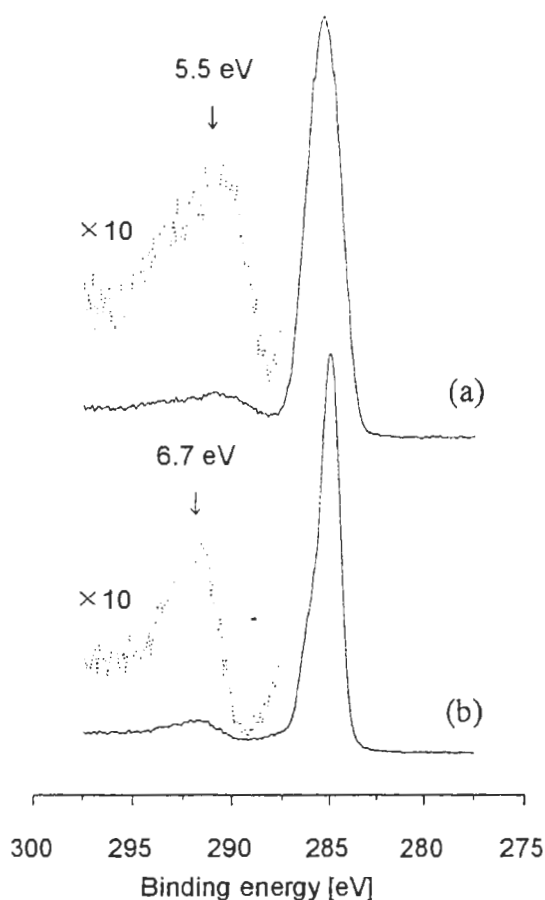


Figure 3. C1s main peak with the magnified $\pi \rightarrow \pi^*$ shake-up peak (dotted line) of (a) Alq₃ and (b) TPD.

The optical energy gap, namely the energy difference between LUMO and HOMO, of Alq₃ and TPD is 2.7 eV and 3.1 eV, respectively [10,11]. These values are roughly the half of the amount of the $\pi \rightarrow \pi^*$ energy loss of the C1s photoelectrons. The electronic absorption band of quinoline and benzene, however, coincides well with the measured $\pi \rightarrow \pi^*$ shake-up peak. The strongest absorption wavelength of quinoline is 227 nm (5.5 eV) and benzene is 184 nm (6.7 eV). From the molecular structure, we know that Alq₃ has 3 quinoline molecules and TPD has 6 benzene molecules.

In order to understand the coincidence, we calculated the molecular orbitals of Alq₃, TPD, quinoline, and benzene molecules with AM1 semi-empirical method [12] on a Silicon Graphics O2 workstation. The used software was MOPAC of Cerius2 of Molecular Simulations Inc. We found that the energy levels of the dense molecular orbital region of Alq₃ are in good agreement with the energy

levels of quinoline. This kind of good agreement was also found in case of TPD and benzene. It means that the maximum of the shake-up peak reflects more the local $\pi \rightarrow \pi^*$ transition than HOMO \rightarrow LUMO excitation of the whole molecule.

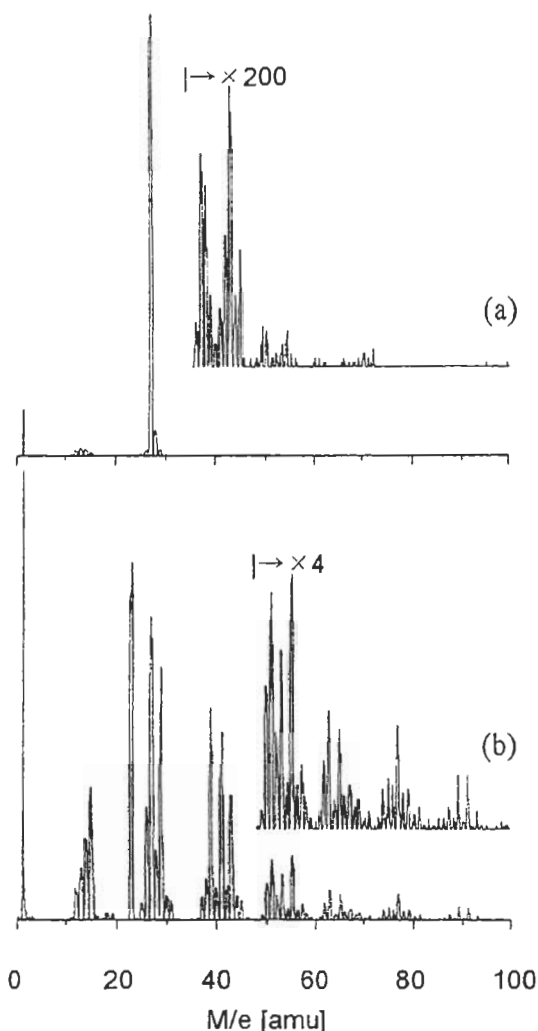


Figure 4. Positive SIMS survey spectra of (a) Alq₃ and (b) PPV with magnification.

Figure 4 shows the positive SIMS survey spectra of Alq₃ and PPV. PPV is a conducting polymer, which is also used for organic electroluminescent devices. We would like to compare the difference between the molecular thin film and polymeric thin film. In case of Alq₃, the intensity of Al is relatively higher than the other fragments of the molecule. Another point is that the ion yield above 60 amu is strongly reduced. Especially the C₆H₅ fragment at 77 amu, which comes from the benzene component, is difficult to observe.

This is not the case in PPV. Such a strong ion yield reduction in Alq₃ means that there is less cascade effect at the molecular thin film than polymeric thin film like PPV. The SIMS spectrum of PPV shows typical hydrocarbon fragments such as C₂H₃ (27 amu) and C₃H₃ (39 amu) with normal intensity distribution. In case of Alq₃, however, the intensity of C₃H₃ is strongly reduced against C₃H₂ and C₃H. This can be explained with the relative abundance of C and H in matrix. Such a change of ion formation can be used for monitoring hydrocarbon contamination at the Alq₃ surface.

4. Summary

Thermally evaporated Alq₃ and TPD organic electroluminescent thin films have been characterized by XPS and SIMS.

The maximum of the shake-up peak of Alq₃ and TPD coincides well with the strongest electronic absorption band of quinoline and benzene, respectively. This was also observed from the calculations of molecular orbitals with AM1 semi-empirical method. It means that the $\pi \rightarrow \pi^*$ shake-up peak of the C 1s photoelectron line reflects more the local $\pi \rightarrow \pi^*$ transition than HOMO \rightarrow LUMO excitation of the whole molecule. But further investigation is needed in order to understand the fine structure of the $\pi \rightarrow \pi^*$ shake-up peaks.

Using static mode SIMS, some characteristics of the molecular thin film of Alq₃ were compared with that of polymeric thin film of PPV. Strong ion yield reduction above 60 amu was observed. It means that there is less cascade effect at molecular organic thin film than polymeric thin film. Change of ion formation was also observed which can be explained with the relative abundance of C and H in matrix.

References

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Discussion

Referee 1: Prof. N. Suzuki (Utsunimiya Univ.)
 1) Abstract; Referee thinks that the abbreviated words 'Alq₃ and TPD' can not be understood by readers. Please consider to insert the full names of those as 'tris(8-hydroxy-quinoline) aluminum (Alq₃)' and 'N,N'-diphenyl-N,N'-bis(3-methyl phenyl)-1,1'-bi-phenyl-4,4'-diamine (TPD)'.

Answer: I have inserted the full name of the molecules in the abstract as you mentioned.
 2) Page 1, left column, 18th to 19th lines; 'the interface' can not be considered to be a 'factor'. Another appropriate wording is appreciated like 'the interfacial structure' or 'the interfacial characteristic'.

Answer: I have corrected 'the interface' to 'the interfacial characteristic'.

3) Captions of Table 1 and 2; '(%)' should be moved after the word 'concentration' like 'Table 1 Atomic concentrations (%) of Alq₃'.

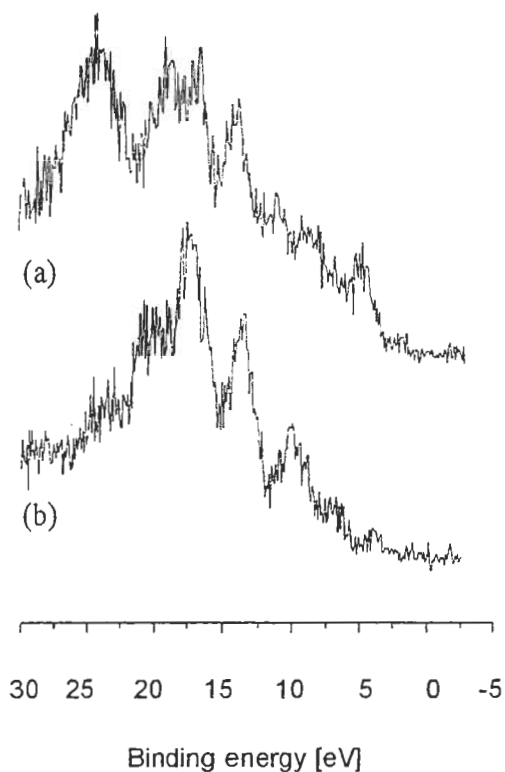
Answer: I have corrected the position of '(%)' as you mentioned.

Referee 2: Dr. Y. Shichi

1) If you have measured the valence band spectra, please show me Fermi edge. Do you compare Fermi level between Alq₃ and TPD.

Answer: Yes, we have also measured the valence band of (a) Alq₃ and (b) TPD which

are shown below. But it is very difficult to identify clearly the Fermi edge from the measured spectra because of the noise level.



2) Please let know what kind of sensitive factor for quantitative analysis in tables 1 and 2.

Answer: We used the sensitivity factors of the book "Handbook of x-ray photoelectron spectroscopy", PHI, 1990. The authors are J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben.

3) Do you notice any difference of high mass spectra above 100 amu between Alq₃ and TPD, especially the C₉H₅N fragment at 127 amu, which comes from the quinoline component.

Answer: In the region between 120 amu and 140 amu, we could only observe the Cs ion peak at 133 amu. I think, in order to measure the 127 amu, one must use a TOF-SIMS instrument.

4) Do you notice any difference of negative ion spectra between Alq₃ and TPD, especially the C₉H₅NO fragment at 143 amu, which comes from the quinoline component.

Answer: We could not observe the peak at 143 amu with our system.