

The electronic band structure analysis of OLED device by means of in situ LEIPS and UPS combined with GCIB

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Low-energy inverse photoelectron spectroscopy (LEIPS) and ultraviolet photoelectron spectroscopy (UPS) incorporated into the multitechnique XPS system were used to probe the ionization potential and the electron affinity of organic materials, respectively. By utilizing gas cluster ion beam (GCIB), in situ analyses and depth profiling of LEIPS and UPS were also demonstrated. The band structures of the 10-nm-thick buckminsterfullerene (C₆₀) thin film on Au (100 nm)/indium tin oxide (100 nm)/glass substrate were successfully evaluated in depth direction.

KEYWORDS

electronic band structure, GCIB depth profile, LEIPS-UPS, OLED device

1 | INTRODUCTION

In the development of organic optoelectronic devices (e.g., organic LEDs [OLEDs] and organic photovoltaics), identification of accurate energy levels of both lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) from each individual organic layer is of vital importance for optimizing the device architectures. It has been generally accepted that the HOMO can be determined by ultraviolet photoelectron spectroscopy (UPS). On the other hand, a nondestructive and reliable method in measuring the LUMO of organic samples has been missing. Conventional inverse photoelectron spectroscopy (IPES),^{1,2} which is used in determining the electron affinity, often damages the target sample because of its high electron energy (5 eV or above), leading to inaccurate results especially for the organic materials.

In order to evaluate an accurate energy level of LUMO, we employed low-energy IPES (LEIPS).³⁻⁵ LEIPS realizes extremely low chemical degradation on the organic materials, which has been difficult by conventional IPES, by using electrons of 5 eV or less as an excitation source. LEIPS is an ideal method to evaluate the unoccupied conduction band of organic materials. Figure 1 shows the energy-level diagram of semiconductors and the principle of UPS and LEIPS. UPS provides information about the occupied valence band by observing the photoelectrons (e⁻), which were excited by ultraviolet light (hν). From UPS results, the energy level of HOMO and ionization

potential (IP) can be determined. In contrast, LEIPS reverses the role of light and electrons as it measures the near-ultraviolet light (hν) emitted from a sample by irradiating low-energy electrons (e⁻). LEIPS provides information about the unoccupied conduction band with low chemical degradation so that accurate energy level of LUMO and electron affinity (EA) can be determined. By combining UPS and LEIPS, it is possible to know the electronic band structure of organic materials. Furthermore, when we consider multilayer film analysis, weakness of the conventional method (UPS/IPES/deposition source)⁶⁻⁷ is that although many device physicists focus on bending of the energy levels across material interfaces, the study of interfacial status using UPS/IPES requires moving the target sample to and from the deposition chamber and the analyzing chamber, which are time-consuming and unreliable.

In this work, UPS and LEIPS incorporated into the multitechnique XPS system were used to evaluate the electronic band structure of the OLED materials. By utilizing gas cluster ion beam (GCIB)⁸⁻¹⁰ sputtering, in situ depth profiling for interface of multilayer film was realized.

2 | EXPERIMENTAL

The sample is 10-nm-thick buckminsterfullerene (C₆₀) thin film on Au (100 nm)/indium tin oxide (100 nm)/glass substrate. LEIPS, UPS, and

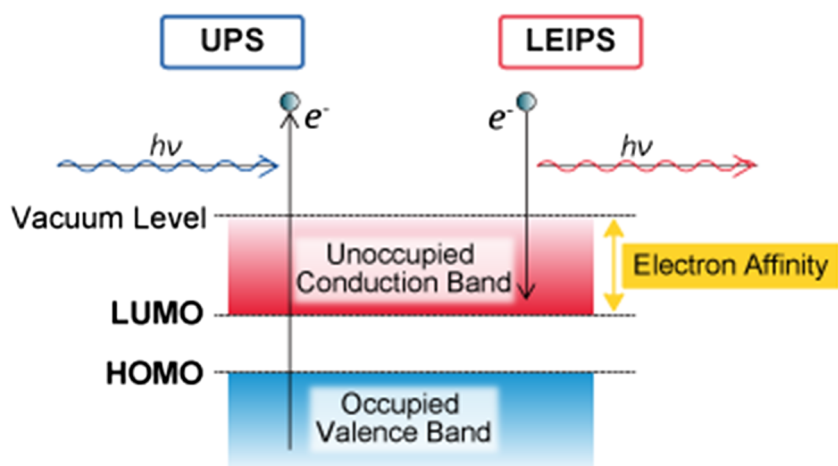


FIGURE 1 UPS and LEIPS energy diagram of a semiconductor. HOMO, highest occupied molecular orbital; LEIPS, low-energy inverse photoelectron spectroscopy; LUMO, lowest unoccupied molecular orbital

GCIB incorporated into the PHI5000 VersaProbe III multitechnique XPS (ULVAC-PHI, Japan) were employed in this study. Figure 2 shows the schematic diagram of LEIPS configuration. LEIPS consists of low-

energy electron gun, optical lens, band-pass filter, and photomultiplier. Then, the low-energy electron beam is set to a fixed energy, and the bias voltage applied to the sample is swept so that the incident

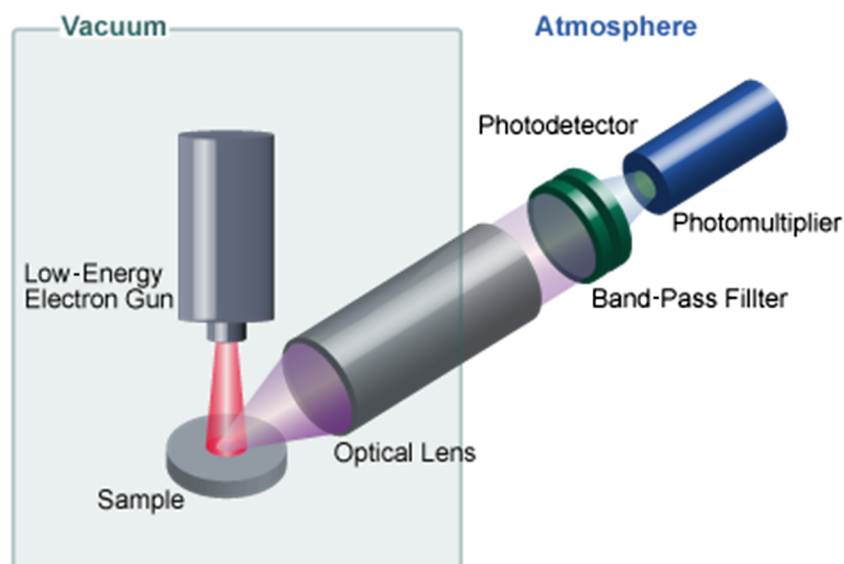


FIGURE 2 Low-energy inverse photoelectron spectroscopy system consists of low-energy electron gun, optical lens, band-pass filter, and photomultiplier. Band-pass filter is located at atmosphere side, easy exchangeable

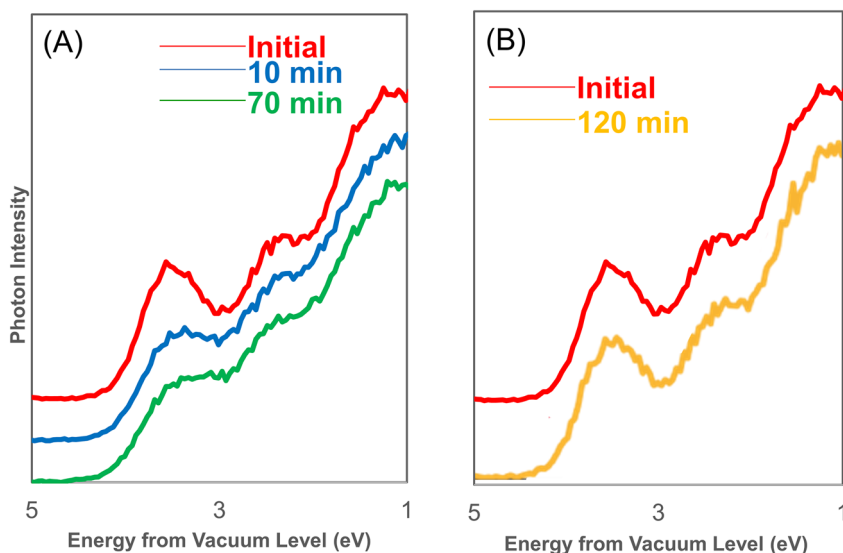


FIGURE 3 Comparison of C_{60} thin film using (A) conventional inverse photoelectron spectroscopy (IPES) and (B) low-energy IPES. "Conventional IPES (left) showed changes in spectral shape." Low-energy IPES (right) showed almost no spectral changes

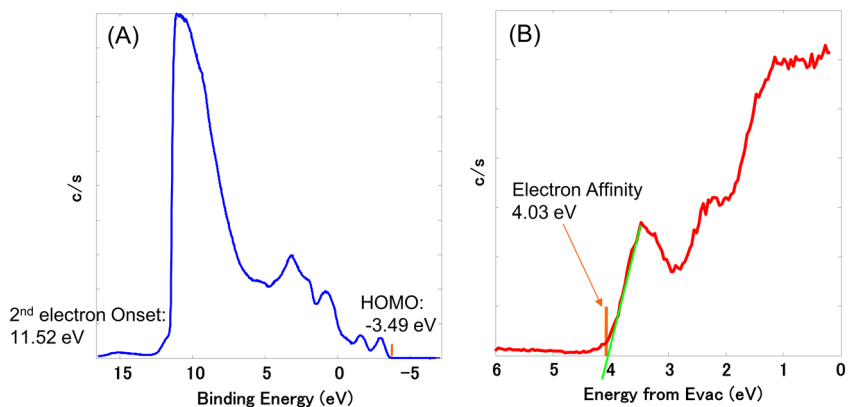
electron energy varies from 0 to 5 eV. The near-ultraviolet light emitted from the sample is selected by a band-pass filter (4.79 eV) and detected with a photomultiplier. The band-pass filter is located in atmospheric section so that the filter of various energies (3.70, 4.35, 4.43, 4.79, and 4.88 eV are available) can be easily exchanged. In the present study, a 4.79 eV band-pass filter was selected to cover the range of the electron affinity from the top surface of the C₆₀ thin film (~4.0 eV) to the interface between the C₆₀ thin film and Au layer (~4.5 eV). In the spectral acquisition, the absorption current spectrum in the sample is plotted simultaneously with the LEIPS spectrum. In the absorption current spectrum, the inflection point corresponds to the potential where the current begins to flow into the sample. In LEIPS spectrum, that potential corresponds to the level 4.79 eV below the vacuum level. As a result, the vacuum level of the sample in the LEIPS spectrum was determined. Al K α (1,486.6 eV) for XPS and He I (21.2 eV) for UPS were used as excitation sources on the photoelectrons from the surface. And the photoelectrons were collected through the energy analyzer. A 2.5-kV GCIB (Ar₈₅₀⁺) with 5 × 5-mm raster size was used to take depth profiles of XPS, UPS, and LEIPS.

3 | RESULTS AND DISCUSSION

3.1 | Advantage of LEIPS

Differences between LEIPS and conventional IPES are the incident electron energy and collected wavelength of the light. LEIPS employs the lower energy incident electron and detection of the near ultraviolet through the band-pass filter in contrast to the conventional IPES where the vacuum ultraviolet is detected. So the less chemical degradation for the organic materials and also better energy resolution are expected for LEIPS. Figure 3 shows the results of repeated measurements on the C₆₀ thin film to make comparison of the accumulated damage by the electron irradiation with conventional IPES and LEIPS. The spectral line shape taken (with 10-min irradiation of 10-eV electrons), assuming the conventional IPES, completely changed (Figure 3A). On the other hand, LEIPS (5 eV or less) spectra showed almost no change in the line shape after long time acquisition (Figure 3B). This result indicated that the LEIPS has less chemical damage on organic materials.

FIGURE 4 Surface spectra of C₆₀ thin film using (A) UPS (with -5-V bias) and (B) low-energy inverse photoelectron spectroscopy. HOMO, highest occupied molecular orbital



3.2 | Determination of ionization potential and electron affinity

Figure 4 shows the UPS (with -5-V bias) and LEIPS spectra of C₆₀ thin film. The ionization potential was calculated from the spectrum obtained by UPS (Figure 4A). The secondary electron onset value (E_0), the valence band maximum value (E_{VBM}), and the energy of He I ($h\nu$) were used to calculate the IP by applying the following formula.

$$\text{Ionization Potential} = h\nu - (E_0 - E_{VBM}) \quad (1)$$

As a result, ionization potential of 6.19 eV was obtained. The electron affinity was calculated from the cutoff position on the LEIPS spectrum with reference to the vacuum level (Figure 4B). As a result, electron affinity of 4.03 eV was obtained. Moreover, by combining UPS and LEIPS spectra, the band gap of 2.16 eV of this material was obtained, corresponding to the energy difference between HOMO and LUMO (Figure 5).

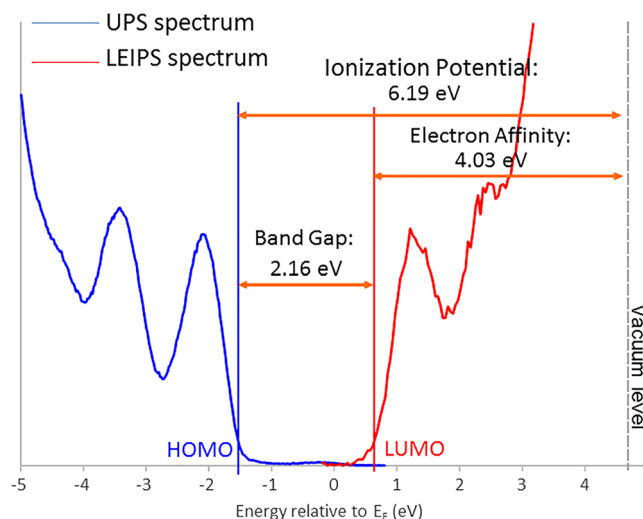


FIGURE 5 UPS and LEIPS spectra of C₆₀ thin film plotted as a function of the energy relative to E_F (eV). HOMO, highest occupied molecular orbital; LEIPS, low-energy inverse photoelectron spectroscopy; LUMO, lowest unoccupied molecular orbital

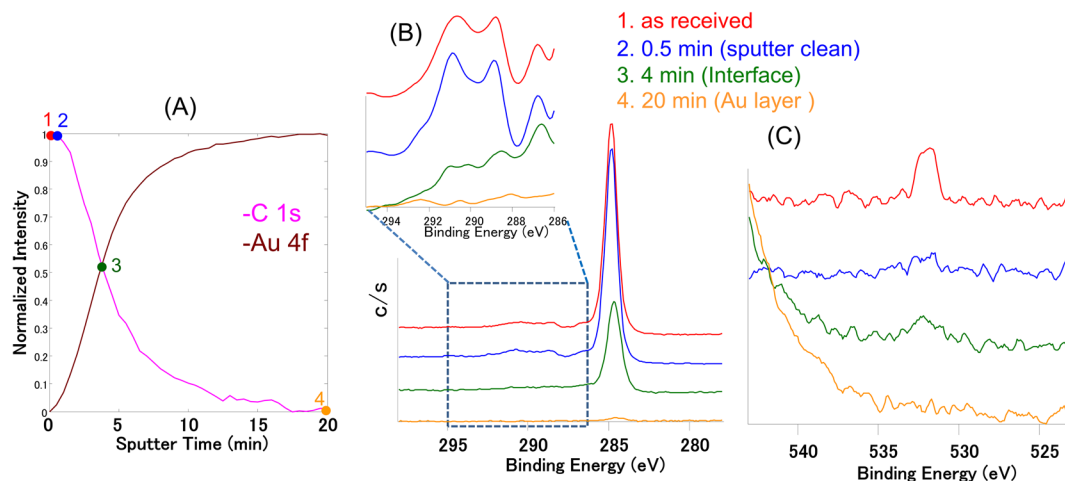


FIGURE 6 XPS depth profile of C_{60} thin film: (A) depth profile of C 1s and Au 4f and changes in (B) C 1s spectra and (C) O 1s spectra

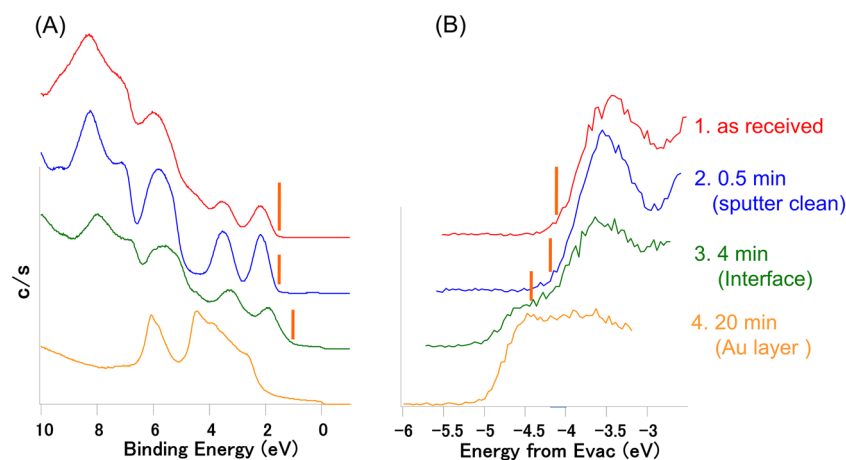


FIGURE 7 UPS and low-energy inverse photoelectron spectroscopy depth profile of C_{60} thin film: changes in (A) UPS spectra and (B) low-energy inverse photoelectron spectroscopy spectra

3.3 | In situ LEIPS and UPS depth profiling using GCIB

Before taking the LEIPS and UPS depth profile, XPS depth profile using GCIB was performed. Figure 6 shows the XPS depth profiles of C 1s and Au 4f. C 1s spectra of each depth were extracted from depth profile result. In order to see the chemical state of C 1s, the spectrum, at the top surface (No. 1), after 0.5-min sputtering (No. 2), after 4-min sputtering (No. 3), and after 20-min sputtering (No. 4), was extracted from the profile (Figure 6A). Figure 6B shows the C 1s spectra, and Figure 6C shows the O 1s spectra. Focusing on the spectrum after 0.5-min sputter cleaning, oxygen was removed, and satellite peak of C 1s derived from C_{60} was observed more clearly than as received. The result suggests that ideal spectrum of C_{60} was obtained by GCIB cleaning. Likewise, the spectrum of each depth was measured by UPS and LEIPS, and the energy level of HOMO and LUMO at each depth was determined (Figure 7). Change in the depth profile from the organic layer to inorganic layer for both UPS and LEIPS was observed. Spectral line shape of UPS and LEIPS after sputter cleaning reveals more clear features than as received the same as XPS. In addition,

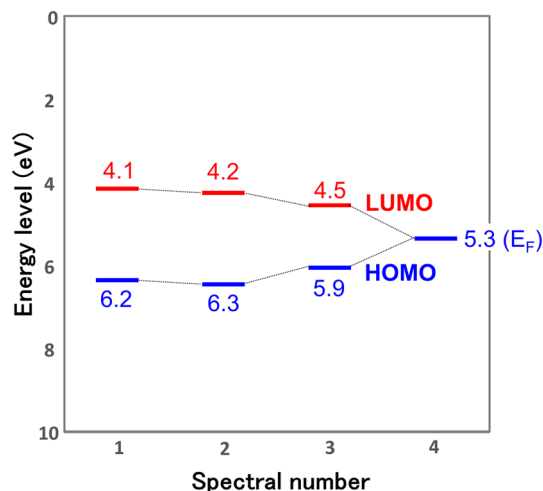


FIGURE 8 Energy level of HOMO and LUMO was plotted with reference to the vacuum level. Spectrum number indicates each depth—1: as received, 2: 0.5 min (sputter clean), 3: 4 min (interface), and 4: 20 min (Au layer). HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital

electronic structure information of C₆₀/gold interface and gold layer was obtained from the spectra of 4-min sputtering and 20-min sputtering, respectively. Figure 8 shows the energy level of HOMO and LUMO of each depth with reference to the vacuum level. The energy level of LUMO was determined by LEIPS, and the energy level of HOMO and Fermi level were determined by UPS. Changes of LUMO and HOMO in the depth profile could be confirmed. It was certified that the band structure in the depth direction of the organic/inorganic structure can be evaluated.

4 | CONCLUSION

In this work, the HOMO and the LUMO of C₆₀ thin film on Au (100 nm)/indium tin oxide (100 nm)/glass substrate were successfully evaluated in depth direction. LEIPS incorporated into the multitechnique XPS realizes reliable evaluation of the unoccupied state of the OLED materials, which has been difficult by conventional method. The depth profiling is thought to be more important to investigate the interface of the multilayer thin films. In the future works, it is important to evaluate the electronic band structure at the interface of organic/organic multilayers more precisely, assuming the actual organic electronic devices.

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