# Maximum probing depth of low-energy photoelectrons in an amorphous organic semiconductor film

Yusuke Ozawa [a], Yasuo Nakayama [a,*], Shin'ichi Machida [a], Hiroumi Kinjo [a], Hisao Ishii [a,b]

[a] Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan
[b] Center for Frontier Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

## ABSTRACT

The attenuation length (AL) of low energy photoelectrons inside a thin film of a π-conjugated organic semiconductor material, 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole), was investigated using ultraviolet photoelectron spectroscopy (UPS) and photoelectron yield spectroscopy (PYS) to discuss their probing depth in amorphous organic thin films. The present UPS results indicated that the AL is 2–3 nm in the electron energy range of 6.3–8.3 eV with respect to the Fermi level, while the PYS measurements which collected the excited electrons in a range of 4.5–6 eV exhibited a longer AL of 3.6 nm. Despite this still short AL in comparison to a typical thickness range of electronic devices that are a few tens of nm-thick, the photoemission signal penetrating through further thicker (18 nm) organic film was successfully detected by PYS. This fact suggests that the electronic structures of "buried interfaces" inside practical organic devices are accessible using this rather simple measurement technique.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Interfaces are crucial places where essential processes that dominate the output performance of organic electronic devices occur. Because charge carrier injection into organic semiconducting materials is generally essential for the functioning of organic devices [1], the elucidation of interfacial electronic structures within devices is one of the key issues for understanding and improving device performance. The electronic structures of a wide range of organic materials and their interfaces with conductive substrates have been investigated using photoelectron spectroscopy [2]. The surface sensitivity of this method is, however, problematic if one wishes to probe the *interfaces*. The probing depth of conventional ultraviolet photoelectron spectroscopy (UPS) is approximately 1 nm caused by short attenuation lengths (ALs) of photoelectrons with kinetic energies of 10–50 eV. This surface sensitivity forces researchers to investigate model interfaces consisting of a very thin organic layer deposited on electrodes. Such model systems do not represent the *exact* interfaces found in organic devices due to probable energy shift by screening effects of "photo-holes" [3–5] and/or band bending-like behavior within the organic films [6–8], and thus the investigation of the 'buried' interfaces in a deposited thick organic layer, such as those found in real devices, is highly desired.

As a barometer of the probing depth of the electron spectroscopy techniques, the so-called "universal curve (UC)" is commonly adopted, which exhibits an empirically derived relationship between the kinetic energy ($E_k$) and the inelastic mean free path (IMPF) of electrons in various inorganic and organic solids [9]. Note that the Fermi level is taken as the energy standard of $E_k$ throughout this article. Because it was predicted that the IMPF grows proportionally to $E_k^{-2}$ when $E_k$ is "very low" [9], photons with an energy lower than several eV are expected as promising probes for the investigation of buried interfaces by photoemission [10,11]. In this context, photoelectron yield spectroscopy (PYS), which measures the total photoelectron yield as a function of the incident photon energy (typically 4–9 eV) [11,12], is potentially a suitable technique for surveying the interface electronic structures underneath the few tens of nanometers-thick organic films of actual devices. Other advantages of using PYS are its durability against sample charging [12] and the reduction of "radiation damage" by restricting photoelectron excess energies below 5 eV with respect to the vacuum level [13,14]. These two drawbacks, sample charging and radiation damaging, are inevitable problems with UPS analysis of major organic materials.

The "universality" of the IMFP in the medium- and high-energy regions has been established for both inorganic and organic materials [15–18]. In the low $E_k$ range, however, the cross section of the photoelectron energy loss processes has to be influenced by miscellaneous material-dependent properties e.g. the energy gap width and phonon energy [19], it remains controversial whether

or not the photoelectron AL actually extends along the *universal* trend in the low $E_k$ range [19–21]. In this study, we therefore investigated the AL of low $E_k$ photoelectrons in amorphous films of a typical organic semiconductor material, 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) using both UPS and PYS for the sake of proposing a direct indication of the accessible probing depth within actual organic devices by photoemission-related techniques. As a result, it was demonstrated that PYS can be practically applied for the characterization of buried interfaces.

## 2. Experimental details

UPS measurements were conducted using two types of energy tunable excitation light sources: synchrotron orbit radiation and a deuterium arc discharge lamp. For the former experiments, photoelectron energy distribution curves were obtained with a concentric hemispherical analyzer (CHA) (ARUPS-10, VG) equipped at the vacuum ultraviolet beam line (BL-8B UVSOR-II), Institute for Molecular Science (IMS), Japan. The excitation energy used in these experiments ranged 20–50 eV. The experimental conditions were identical to those reported previously [2]. The latter UPS experiments were carried out in a home-build system equipped with a retarding field electron analyzer (RFA), where a sample was placed at the center of a hollow hemispherical anode and photoelectrons with a certain $E_k$ were selected by sweeping the retarding electric potential with a small modulation (100 mV, 4.18 Hz) to differentiate the photocurrent using a lock-in amplifier (Stanford Research Systems, model SR830 DSP) after amplification with an ammeter (Keithley, model 6485). The incident photon energy ($h\nu$) was varied from 6.3 eV to 8.3 eV. The photon incident direction was the surface normal, and the measurements were conducted under high vacuum ($1.0 \times 10^{-4}$ Pa) conditions.

PYS measurements were carried out with the same RFA–UPS system [22]. A positive electrostatic potential (+9 V) was applied to the anode to collect all of the emitted photoelectrons. The incident photon energy was swept from 4.0 eV up to 9.3 eV, and the total photocurrent and photon flux were measured using a precise ammeter (Keithley, model 6430) and photomultiplier (Hamamatsu Photonics, R6836), respectively, at each photon energy. The photoelectron yield $Y$ was obtained by dividing the photocurrent by the photon flux.

TPBi was adopted for testing the probing depth inside amorphous organic materials because it is known to generally form pinhole-free flat overlayers when deposited at room temperature [23]. TPBi was evaporated onto Au-coated Si substrates in a step-by-step manner, and photoemission measurements were subsequently conducted throughout in vacuum. The evaporation rate was maintained in the range 0.01–0.03 nm/s, which was monitored with a quartz oscillator and calibrated afterwards using a step profilometer. The pressure during the sample fabrication was $4 \times 10^{-3}$ Pa for the CHA–UPS experiments and was maintained below $5 \times 10^{-4}$ Pa for the RFA–UPS and PYS analyses. The film morphology was confirmed to be flat and uniform, as shown in Fig. 1, where no pinhole except several hollows no deeper than 5 nm was found in randomly selected fifteen 100 $\mu m^2$ areas over the film surface, by means of atomic force microscopy (AFM) (SII, SPA-400) in air.

## 3. Results and discussion

Fig. 2(a) shows the CHA–UPS spectra of a pristine Au substrate and a thick (6.7 nm) overlayer taken at $h\nu = 30$ eV. The threshold edge due to the highest occupied molecular orbital (HOMO) of TPBi was located at a binding energy (BE) of 2.4 eV, which corresponds
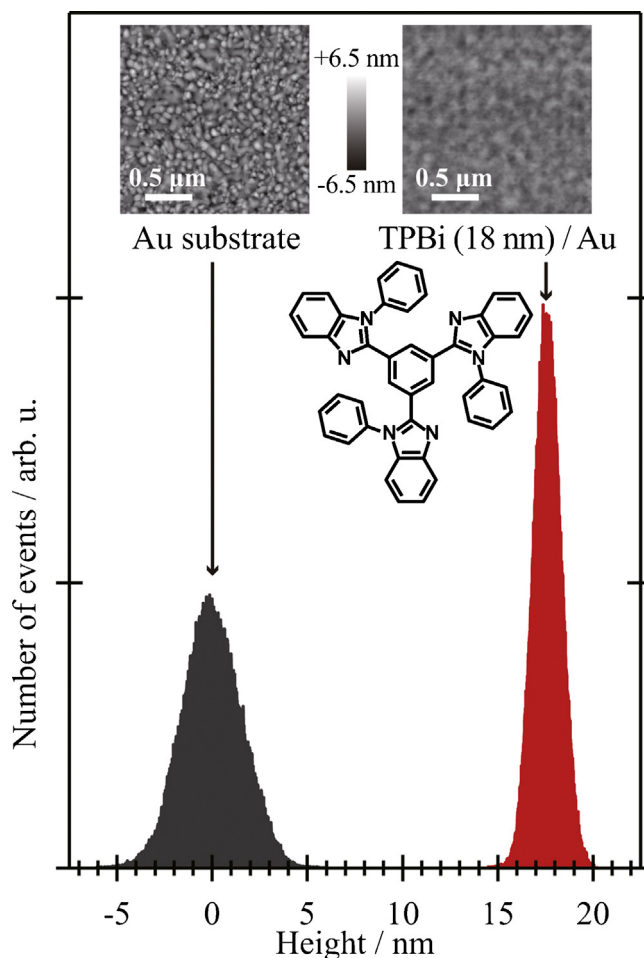


**Fig. 1.** Typical AFM images of the Au substrate (upper left) and 18 nm-thick TPBi overlayer (upper right) represented together with the height histograms of the respective images. Both AFM images are equally scaled. The molecular structure of TPBi is also shown as the middle inset.

to the hole injection barrier from Au to TPBi. Because the energy gap for TPBi has been reported to be at least 3.5 eV [24], the lowest unoccupied molecular orbital must be located more than 1 eV above the Fermi level. Therefore, the photoelectron signals at the Fermi level (BE = 0 eV) were attributed to the Au substrate exclusively.

As shown in Fig. 2(b), the photoelectron intensity of the Fermi edge decayed with increasing overlayer thickness. A photoelectron excited inside a solid loses its energy due to several scattering events with certain probabilities on its way toward the surface. The relative population of the photoelectrons that preserve the primary excitation energy after passing though the solid of a thickness $x$ can be expressed as:

$$\frac{N}{N_0} = \exp\left(-\frac{x}{\lambda}\right), \tag{1}$$

where $\lambda$ is the AL of the primary electrons which is related to the scattering probability. In the present case, $N$ corresponds to the Fermi edge intensity in the spectrum for the TPBi overlayer with a thickness $x$, while $N_0$ is given by the spectrum of the pristine Au substrate ($x = 0$). Fig. 2(c) shows the relative intensity ($N/N_0$) of the Fermi edge derived from the present CHA–UPS spectra plotted in a semi-logarithmic scale as a function of the TPBi thickness for various excitation energies. These plots show good linearity, suggesting uniform growth of the overlayer. The ALs were determined using the gradients of these plots to be 1.0–1.5 nm for excitation energies of 20–50 eV. In the present UPS works, we only consider