

Correlation between photoelectric and optical absorption spectra of thermally evaporated pentacene films

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We have measured the spectral photoresponse of Al/pentacene Schottky junction photodiodes and optical absorption spectra of pentacene films thermally evaporated on glass. The photoelectric response exhibited the genuine highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) transition at 1.97 eV and interband absorption peaks at 2.3 and 2.5 eV. These peaks are also identified in the optical absorption spectra, but they are dominated by additional strong exciton peaks at 1.82 and 2.1 eV. By comparing these complementary measurements, we determine the HOMO–LUMO gap energy of 1.97 eV and the fundamental exciton binding energy of 0.15 eV for thin solid pentacene. © 2004 American Institute of Physics. [DOI: 10.1063/1.1668328]

Over the last two decades, organic thin-film devices, such as organic light-emitting diodes, organic thin-film transistors, photodetectors, and solar cells, have made steady progress in device performance with ever increasing range of applications.^{1–4} Among various organic materials, polycyclic aromatic hydrocarbon pentacene is one of the most promising organic semiconductors mainly due to its high hole mobility. Many researchers have extensively studied the material to develop high-performance pentacene-based OTFTs, focusing on improving their electrical properties.^{5–7} However, not much effort has been made on pentacene-based photonics research although pentacene may have substantial photosensitivities.^{8,9} In early studies on solid pentacene prepared by vacuum evaporation, photoconductivity measurements with a thick pentacene layer sandwiched between Al and a semitransparent Au electrode were made to investigate the photogeneration of charged carriers.⁸ But such studies on the photoelectric properties with an Al/thick pentacene/transparent Au sandwich were inherently limited as the information on the basic optical properties of pentacene, such as its optical band gap, was not readily available. In our previous work, we reported on the band gap of thermally evaporated pentacene films identified by ellipsometry and absorption spectroscopy.^{9,10}

In the present work, we report on the photoelectric properties of a specifically designed pentacene-based Schottky photodiode, which reveals the genuine highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap of pentacene films without complications arising from exciton effects, which dominate the direct absorption spectra.

For photoelectric property measurements, our pentacene Schottky diode structure was prepared as shown in its schematic cross section and photographic plan views in Fig. 1. Prior to deposition, glass (Corning 7059—root-mean-square roughness of 8.7 Å) substrates were ultrasonically cleaned with boiling acetone, ethanol, and deionized water, in that

order. A 100 nm thick Al thin film was deposited by thermal evaporation on the cleaned glass using our first shadow mask to obtain a patterned Al bottom electrode. Then, a 200 nm thick pentacene layer was evaporated on the Al-patterned glass through the second shadow mask to form an Al/pentacene Schottky junction, and simultaneously on the cleaned glass situated in the same vacuum chamber for direct absorption measurements. The base pressure in the vacuum chamber was 5×10^{-7} Torr and the film thickness of pentacene was 200 nm, as measured by ellipsometry. The pentacene powder was of high purity (99.8%, Aldrich Chem. Co.) and the deposition rate was fixed to ~ 1 Å/s. Subsequently, 200 nm thick Au was patterned on the pentacene layer by thermal evaporation at room temperature (RT), using our final shadow mask.

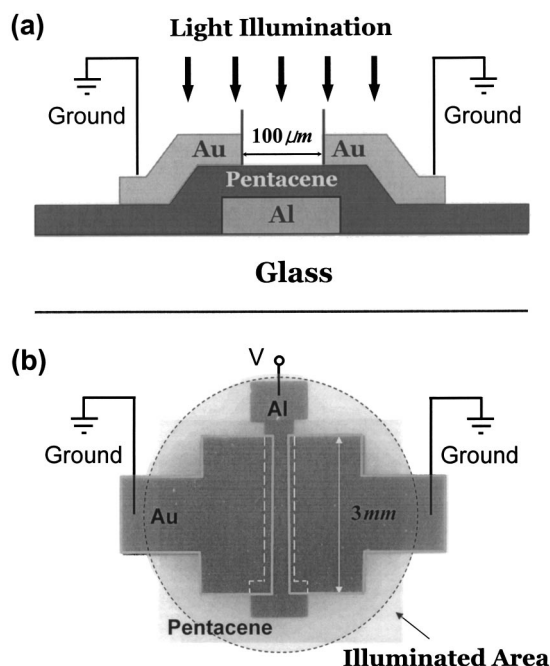


FIG. 1. Our Al/pentacene photodiode structure. (a) Schematic cross-sectional view and (b) photographic plan view.

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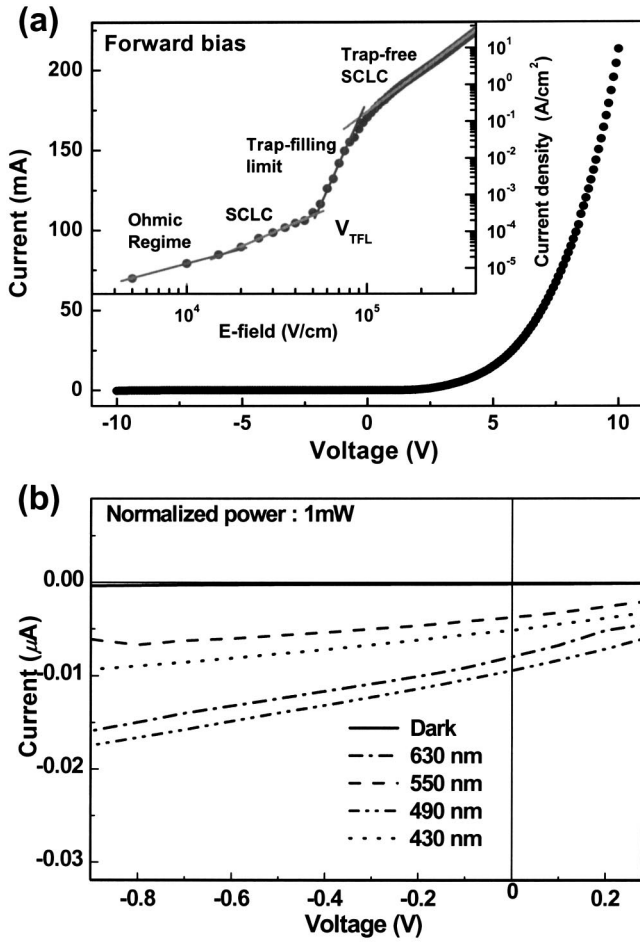


FIG. 2. (a) I - V characteristics of Al/pentacene photodiode. The inset shows current vs electric-field plot at a forward bias regime. (b) I - V characteristics in the dark and under various monochromatic illuminations. For the photo- I - V measurements, an identical illumination power of 1 mW was used.

Direct absorption measurements on pentacene thin films deposited on the cleaned glass substrates were performed with a Varian Cary 5G Spectrophotometer. Current-voltage (I - V) measurements on our Schottky diodes with and without illumination were performed with Oriel Optical System, which employed a 500 W Hg (Xe)-arc lamp and a monochromator covering the range of 325–670 nm. The illuminated region (dotted circle) was wide enough to cover the entire area of our device as indicated by the dashed circle shown in Fig. 1. All I - V measurements were carried out with a Keithley 236 source measurement unit at RT.

Figure 2(a) shows the I - V characteristics obtained from our Al/pentacene Schottky diode in the dark. The device exhibits strong rectifying behavior. Under forward bias, our organic Schottky diode reveals four distinct regimes as shown in the inset: Ohmic, space-charge limited (SCL), trap filling limit (TFL), and trap-free SCL regimes.¹¹ With the SCL current method, the trap density can be estimated according to the following formula for the onset voltage, V_{TFL} in the TFL,¹¹

$$V_{\text{TFL}} = \frac{2qd^2N_t}{3\epsilon_s},$$

where q is the electronic charge, N_t is the trap density, $d=200$ nm is the film thickness, and $\epsilon_s \sim 4\epsilon_0$ is the permit-

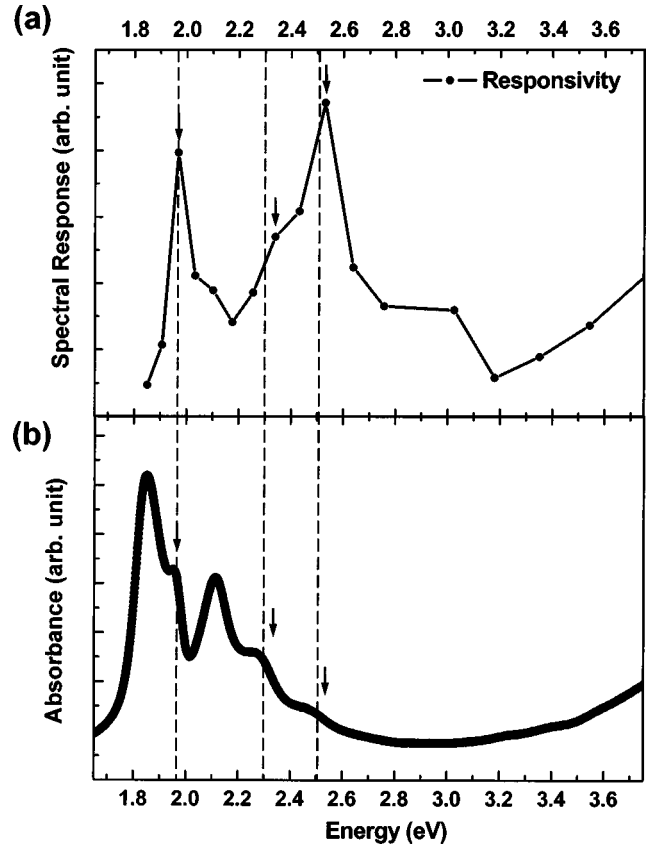


FIG. 3. (a) Spectral response of Al/pentacene photodiode. Arrows indicate the inferred UMO levels at 1.97, 2.3, and 2.5 eV. (b) The direct absorption spectra taken from the pentacene film deposited on clean glass.

tivity of pentacene (determined by ellipsometry).¹⁰ The calculated trap density, N_t was thus determined (with $V_{\text{TFL}}/d = 5 \times 10^4$ V/cm) to be about $8.3 \times 10^{15} \text{ cm}^{-3}$, which is comparable to the values reported by other researchers.^{12,13}

Figure 2(b) displays the dark- and photo- I - V curves obtained from the Schottky diode under monochromatic illumination at various wavelengths with identical normalized optical power of 1 mW. Although the photocurrent level of our diode did not appear high probably due to its limited photocarrier-collection efficiency, the photocurrent signals obtained under various monochromatic illuminations were distinct enough because our Schottky diode showed quite low current leakage in the dark. The photocurrent was found to increase linearly with reverse bias voltage, and the photo-voltaic or photoelectric effects were the most prominent for the wavelengths of $\lambda=630$ nm (photon energy 1.97 eV) and $\lambda=490$ nm (~ 2.5 eV). The linear photocurrent-voltage relationship is quite understandable because the drift velocity of photogenerated electrons and holes in the depleted region within pentacene is itself linearly proportional to the electric field loaded between Al and Au.

Figure 3(a) presents the responsivity of our Schottky diode, based on the photocurrent measurements [of Fig. 2(b)] at various photon energies under fixed bias of 0 V under the identical illumination of 1 mW. Two distinct peaks at 1.97 and 2.5 eV along with a shoulder feature at 2.3 eV are revealed as indicated by the three arrows. We believe that the optical transition represented by the first sharp peak corresponds to the fundamental gap of 1.97 eV between the HOMO and LUMO levels in thin pentacene film. The shoul-

der at 2.3 eV and the strong peak at 2.5 eV should represent optical transitions to higher-lying unoccupied molecular orbital (UMO) levels. Thus, the spectral photoresponse measurements provide a reliable means to determine the UMO structure without complications due to exciton effects.

The three weak features near 1.97, 2.3, and 2.5 eV appear again in Fig. 3(b) in the absorption spectra (indicated by the three arrows) as a result of aforementioned optical transitions. However, these features are dominated by intense absorption peaks at 1.82 and 2.1 eV due to the formation of Frenkel excitons. The RT exciton represented by the 1.82 eV peak has a binding energy of 0.15 eV, which is fairly larger than typical values found in inorganic semiconductors.¹⁴ The previous assignment of 1.82 eV for the HOMO–LUMO gap¹⁰ did not take into account the exciton effect and should actually be reinterpreted to represent an excitonic absorption threshold. (However, the exciton binding energy, 0.15 eV is still an upper limit value because excitons in usual conjugated polymers need some additional energy over a genuine exciton binding energy to become free electrons and holes.)¹⁵ The second exciton peak at 2.1 eV lies at about 0.2 eV below the second lowest UMO. Obviously, both exciton features of 1.82 and 2.1 eV are absent in the spectral response of Fig. 3(a). Higher-order exciton peaks were not observed possibly due to spectral broadening or weak intensity.

The fundamental band gap, unoccupied energy levels, and exciton binding energy are not so easily obtainable in the case of inorganic solids. The band gap is often indirect and is broadened by various mechanisms, and exciton features are difficult to detect at RT. Interband transitions are often unclear to yield reliable information on unoccupied energy levels. These features often mix with one another to make the task even harder. In contrast, molecular organic semiconductors are much more amenable in that interband transitions and excitonic absorption features are *selectively* detected by combining the spectral photoresponse measurements and optical absorption spectroscopy. Highly narrow energy levels typically found in molecular solids add further advantages for the detection of higher-lying unoccupied states. Reliable values for the HOMO–LUMO gap and the Frenkel exciton binding energy, which are critically important for electronic and photonic device applications, can be obtained, as we have demonstrated here for the case of pentacene.

In summary, we have fabricated Al/pentacene Schottky photodiodes that exhibit typical strong rectifying behavior

and have measured their spectral photoresponses for the spectral range of 325–650 nm under zero bias. The most intense response was obtained between 630 nm (1.97 eV) and 490 nm (2.5 eV). By combining the responsivity and direct absorption spectra, we were able to assign 1.97 eV for the fundamental HOMO–LUMO gap energy and 0.15 eV for the fundamental Frenkel exciton binding energy. Additional features associated with UMOs and excitons were also observed. It is concluded that our complementary set of measurements adopted in this work should be an effective means to study the basic physical properties of organic semiconductors and probe their potential applications in electronics and photonics.

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- ¹C. W. Tang and S. A. Van Slyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- ²A. Tsumura, H. Koezuka, and T. Ando, *Appl. Phys. Lett.* **49**, 1210 (1986).
- ³D. J. Gundlach, Y. Y. Lin, T. N. Jackson, S. F. Nelson, and D. G. Schlom, *IEEE Electron Device Lett.* **18**, 87 (1997).
- ⁴C. W. Tang, *Appl. Phys. Lett.* **48**, 183 (1986).
- ⁵D. J. Gundlach, C. C. Kuo, S. F. Nelson, and T. N. Jackson, *57th Annual Device Research Conference Digest* (1999), p. 164.
- ⁶C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, and J. M. Shaw, *Science* **283**, 822 (1999).
- ⁷J. Lee, K. Kim, J. H. Kim, S. Im, and D. Y. Jung, *Appl. Phys. Lett.* **82**, 4169 (2003).
- ⁸E. A. Silinsh and V. Čápek, *Organic Molecular Crystals: Interaction, Localization, and Transport Phenomena* (AIP, New York, 1994), pp. 379–404.
- ⁹S. S. Kim, Y. S. Choi, K. Kim, J. H. Kim, and S. Im, *Appl. Phys. Lett.* **82**, 639 (2003).
- ¹⁰S. P. Park, S. S. Kim, J. H. Kim, C. N. Whang, and S. Im, *Appl. Phys. Lett.* **80**, 2872 (2002).
- ¹¹M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed. (Oxford University Press, New York, 1999), pp. 379–397.
- ¹²Y. S. Lee, J. H. Park, and J. S. Choi, *Opt. Mater. (Amsterdam, Neth.)* **21**, 433 (2003).
- ¹³Y. S. Yang, S. H. Kim, J.-I. Lee, H. Y. Chu, L.-M. Do, H. Lee, J. Oh, T. Zyung, M. K. Ryu, and M. S. Jang, *Appl. Phys. Lett.* **80**, 1595 (2002).
- ¹⁴R. Farchioni and G. Grosso, *Organic Electronic Materials: Conjugated Polymers and Low Molecular Weight Organic Solids* (Springer, Berlin, 2001), pp. 241–282, 391–441.
- ¹⁵V. I. Arkhipov, E. V. Emelianova, S. Barth, and H. Bässler, *Phys. Rev. B* **61**, 8207 (2000).