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Temperature dependence of optical properties of pentacene thin films probed by spectroscopic ellipsometry

Chih-Chiang Shen [a], Wei-Yang Chou [b], Hsiang-Lin Liu [a,*]

[a] Department of Physics, National Taiwan Normal University, Taipei 11677, Taiwan
[b] Department of Photonics, National Cheng Kung University, Tainan 70101, Taiwan

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ABSTRACT

The pentacene thin films with thickness of around 80 nm were grown on glass substrates by the thermal evaporation technique. Their optical properties were determined in the spectral region of 0.73–9.0 eV and at temperatures between 200 and 450 K by spectroscopic ellipsometry. The parameters of the dispersive structures were derived by numerical fitting of the experimental data to the stacked layer model. The room-temperature optical absorption spectrum shows a direct band gap of about 1.90 eV. With increasing temperature, the overall blueshift in the optical band gap reflects on the modification of the electron–phonon interactions. Moreover, the Davydov splitting of the pentacene thin films is decreasing from 0.13 eV at 200 K to 0.08 eV at 450 K. We interpret these results in terms of molecular reorientations that cause changes in mutual molecular overlap within the unit cell.

1. Introduction

In recent years, organic molecular materials have received enormous attention due to their potential for development of optoelectronic devices, such as light-emitting diodes [1,2], field-effect transistors [3,4], and photovoltaic cells [5,6]. One highly studied organic molecular material is pentacene. It is a polycyclic aromatic hydrocarbon molecule consisting of five benzene rings. The organic field-effect transistors based on ultrapure pentacene single crystals have shown a field-effect mobility up to 15–40 $cm^2 V^{-1} s^{-1}$ and a high on-off current ratio of 10^6 [7]. Moreover, the optical response of pentacene thin films in the visible and ultraviolet frequency region is very promising for use in organic phototransistors [8,9].

Up to now, the diverse optical properties of pentacene thin films at room temperature have been reported by different groups [10–13]. In earlier studies, Kim et al. [10] presented the results of infrared and optical transmittance measurements of 100 nm thick pentacene films grown on Si, Al_2O_3, and glass substrates by thermal evaporation. The observed main absorption peak at about 1.85 eV is assigned to the fundamental transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in solid pentacene. This HOMO–LUMO gap does not show much variation with the deposition temperature or the choice of substrates. Park et al. [11,12] examined the room temperature refractive index and extinction coefficient spectra of the pentacene thin films deposited on n-Si substrates using spectroscopic ellipsometry. The extinction coefficient of the thin films deposited at room temperature and 60 °C exhibit strong peak at about 1.82 eV and additional weak features at higher energy. Lee et al. [13] investigated both spectral photoresponse and direct optical absorption spectra of the pentacene thin films thermally evaporated on glass substrates. They reinterpreted the absorption peak at about 1.82 eV as the exciton feature. The temperature dependence of optical properties of the pentacene thin films, however, has remained relatively unexplored [14–16]. Moreover, to investigate the temperature dependence of optical constants and bang gap of the pentacene thin films is crucial to understand the electronic and optical properties of devices based on such thin-film structures [17,18]. In this paper, we study the temperature-dependent optical spectra of the pentacene thin films. A variable-angle spectroscopic ellipsometry measurements combined with a data processing method was employed to determine essential optical properties such as refractive index, extinction coefficient, and band gap of materials. Our goal is to understand the intrinsic mechanisms of the optical features of these materials and their temperature evolution, which are critically important for optoelectronic device applications.

2. Experiment

The pentacene thin films were grown on glass substrates using physical vapor deposition technique [19]. These thin films with a

* Corresponding author.
E-mail address: hliu@ntnu.edu.tw (H.-L. Liu).

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thickness of 80 nm were deposited at a rate 0.1 nm/s and the pentacene was thermally sublimated in a vacuum at a pressure of 10^{-5} Torr. The pentacene molecule belongs to a $D_{2\,h}$ point group symmetry in the thin-film phase and crystallizes with two molecules per primitive cell with having triclinic $(P-1)$ space group symmetry [20].

Ellipsometric spectra have been measured under multiple angles of incidence between 60° and 75° over a wide photon energy range using two spectroscopic ellipsometers. A Woollam M-2000U rotating compensator multichannel spectroscopic ellipsometer was used in a spectral range from 0.73 to 6.42 eV, while the higher photon energy region was covered using a Woollam VUV-VASE Gen-II spectroscopic ellipsometer. For temperature dependence measurements, the ellipsometer was equipped with a LINKAM heating/cooling vacuum stage system. Due to the 70° angle of the two stage windows, only a single angle of incidence is possible. The raw ellipsometry data Ψ and Δ are related to the complex Fresnel reflection coefficients for light polarized parallel (R_p) and perpendicular (R_s) to the plane of incidence:

$$e^{i\Delta}\tan\Psi=\frac{R_p}{R_s}. \quad (1)$$

To determine the complex dielectric response of the pentacene thin films, the experimental data were processed using the stacked layer model consisting of glass substrate/thin film/surface roughness/air ambient structure. Then the error function σ was minimized in the entire spectral range:

$$\sigma^2=\frac{1}{m}\sum_{i=1}^{m}[(\Delta_{exp}-\Delta_{calc})^2+(\Psi_{exp}-\Psi_{calc})^2], \quad (2)$$

where Δ_{calc}, Ψ_{calc} and Δ_{exp}, Ψ_{exp} are, respectively, the calculated and experimental ellipsometric data and m is the number of points in the spectrum.

3. Results and discussion

Fig. 1 displays the room-temperature experimental and best-fit calculated data of the pentacene thin films. The parameters of the stacked layer model used to fit the raw ellipsometry data are listed in Table 1. The independently measured experimental data with two different ellipsometers at 60° and 70° incident angles and the modeled curves are in good agreement. We notice that pentacene grown on glass substrate is a polycrystalline film whose optical properties vary spatially due to crystal-to-crystal orientation. In our samples, a mixed local response of three dielectric functions (i.e., *a*-, *b*-, and *c*-axis components of the dielectric tensor) can be justified because the grain size is much smaller than the wavelength of the light in the range of our interest. Thus, we treat the pentacene thin films using a complex pseudo-dielectric function. The real $\langle n\rangle$ and the imaginary part $\langle k\rangle$ of the pseudo-refractive index derived from the ellipsometric parameters of Ψ and Δ are shown in Fig. 2. The dispersive response in the refractive index exhibits several anomalous dispersion features below 3 eV and approaches a constant value of 1.6 at higher energy. Optical transitions can be identified in the spectrum of resonance features that appear in the extinction coefficient, with detailed analysis shown below.

Fig. 3 shows the room-temperature absorption spectrum of the pentacene thin films. As we can see the absorption increases rapidly, reaches a maximum value about 1.86 eV, then a small shoulder at about 1.97 eV, and additional two peaks near 2.13 and 2.90 eV. The inset shows the energy-dependent first derivative, and from this, a broad feature near 1.97 eV could be more clearly resolved. The first two absorption bands at about 1.86 and 1.97 eV are assigned to the Davydov-splitted exciton states [21]. This Davydov doublet, which arises from the exchange electron–hole interaction, is linked to all molecular solids made

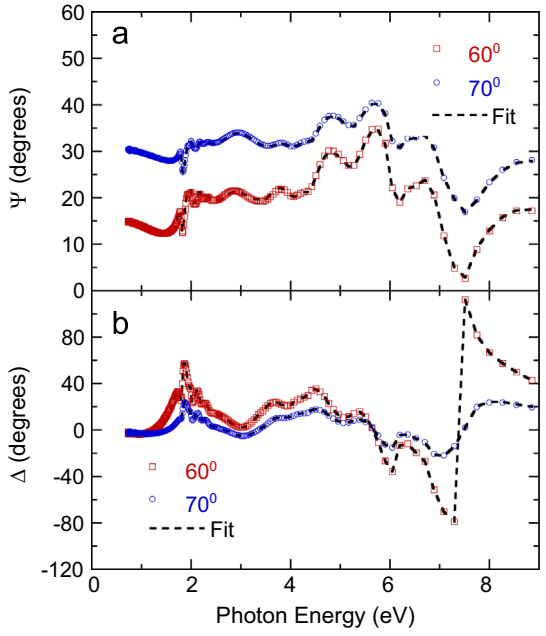

Fig. 1. (Color online) Room temperature experimental (symbols) at 60° and 70° incident angles and fitted (dashed lines) values of ellipsometric parameters of (a) Ψ and (b) Δ of the pentacene thin films.

Table 1
Parameters of stacked layer model fit for the pentacene thin films. All units are in nm.

	Pentacene
Glass substrate	1 (mm)
Film	82.7
Roughness	3.26

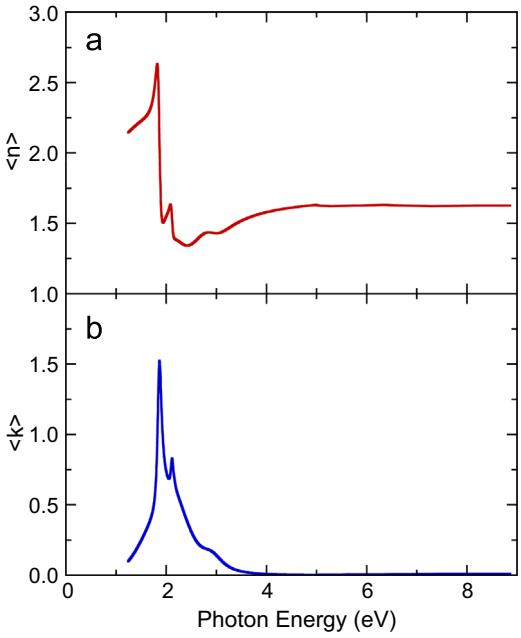

Fig. 2. (Color online) Room temperature (a) real and (b) imaginary parts of the pseudo-refractive index of the pentacene thin films.