



Structural and optical properties of 6,13-pentacenequinone film

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Abstract

We report on the structural and optical properties of 6,13-pentacenequinone film deposited on *n*-Si by thermal evaporation at room temperature. According to X-ray diffraction, films were found to have good crystallinity and also to have two crystalline phases mixed. Photoluminescence (PL) spectra exhibited double peaks at 1.97 and 2.09 eV while the corresponding (double) peaks related to highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) transition were observed from direct absorption spectra at 2.94 and 3.11 eV. The PL intensity was very strong under a UV illumination. It also seems that such a large Stokes shift as ~ 1 eV exist in this organic crystal system. Au/organic/*n*-Si structures using 6,13-pentacenequinone films on *n*-Si showed rectifying behavior but with a relatively high level of leakage current due to many traps in the organic film.

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1. Introduction

Organic thin film devices, such as organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs), organic photo-detectors, and solar cells, have been extensively studied over the last decade, and

the performance of these devices has made consistent progresses [1–6]. It is mainly because the organic films have clear advantages over inorganics in several aspects: large areal coverage, mechanical flexibility, low temperature process, and low-cost processing [7,8]. All those aspects are potentially important for modern flat panel display industries.

The 6,13-pentacenequinone is one of the linear para-acenequinones, which are organic compound formed by substituting two hydrogen atoms with two

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oxygen atoms in polycyclic aromatic hydrocarbon. Para-quinones and their derivatives play an important role in the area of industrial dyes, pigment, and photochromic molecules [9,10]. While the spectroscopy and the crystal structure of 6,13-pentacenequinone in solution phase or bulk phase have been studied [11–13], the properties of thin film phase have not been reported yet.

In the present study, we initially report on the structural and optical properties of the organic thin films deposited by thermal evaporation at room temperature, examining the possibility of 6,13-pentacenequinone films toward new organic semi-conducting devices.

2. Experimental

Our 6,13-pentacenequinone films were deposited in (1 0 0)-oriented *n*-Si substrates (1–5 Ω cm). Prior to deposition, the wafers were ultrasonically cleaned with boiling acetone, methyl alcohol, and de-ionized water, in that order. The samples were then dipped into buffered oxide etchant (HF: H₂O, 1:7) to remove native oxide. The organic films were deposited using a thermal evaporation crucible in a vacuum chamber with a base pressure of 1×10^{-6} Torr at a substrate temperature of 20 °C [room temperature (RT)]. The 6,13-pentacenequinone powder was of high purity (99%, Aldrich Chem. Co.) and the organic films were evaporated on *n*-Si to investigate their optical and structural properties with a fixed deposition rate of ~ 1 Å/s at crucible temperature of 140 °C. The film thickness of 6,13-pentacenequinone was ~ 100 nm as monitored by a quartz crystal oscillator and confirmed by ellipsometry. Subsequently, the 200-nm thick Au dots with a diameter of 300 μ m were patterned on the 6,13-pentacenequinone film by thermal evaporation at RT, using a shadow mask to make an organic/*n*-Si diode structure. The large-area ohmic back contact on *n*-Si was achieved by applying In onto the back side of *n*-Si.

X-ray diffraction (XRD) measurements were performed with monochromatic Cu K α ($\lambda = 1.54$ Å) radiation to investigate the crystallinity of the deposited organic films. Photoluminescence (PL) measurements were carried out at RT using a light source (Oriel Optical System) with the wavelength

and power of 313 nm and 2.1 mW, respectively, which employed a 500 W Hg (Xe)-Arc lamp and a monochromator covering the range of 310–670 nm. Direct absorption measurements were performed on the 200-nm thick organic film, which had been deposited on clean Al₂O₃ (sapphire) substrates under the same evaporation condition. The current–voltage (*I*–*V*) measurements of organic diodes were performed with a semiconductor parameter analyzer (Agilent 4155C) in the dark at RT.

3. Results and discussion

Fig. 1 displays the XRD spectra (logarithmic scale) obtained from the 6,13-pentacenequinone films evaporated on *n*-Si at RT. Films were found to have good crystalline quality as judged by their diffraction intensity and the full widths at half maximum of diffraction peaks. The 6,13-pentacenequinone bulk crystal phase obtained from solution is known to have a monoclinic structure ($\beta = 93.25^\circ$) packed along the long axis of the rod-like molecule (a schematic shape of the molecule is shown in the inset of Fig. 1) [11]. The diffraction pattern of our pentacenequinone film deposited on *n*-Si substrate basically shows preferred orientations, compared to those of other organic crystalline films such as pentacene or tetracene [14,15]. Actually present organic film appeared to have some orientations, e.g. the second peak located at

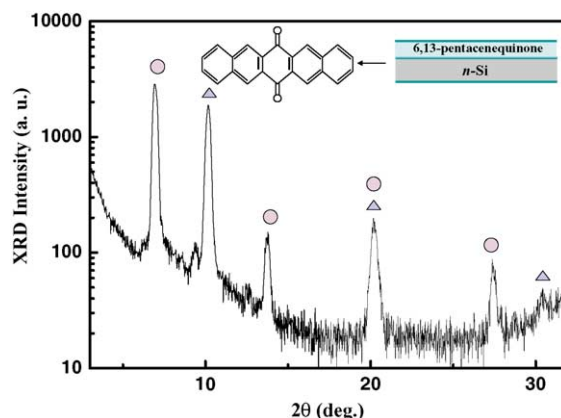


Fig. 1. XRD spectra taken from the 6,13-pentacenequinone film deposited at RT. The inset is the molecular structure of the 6,13-pentacenequinone.

$2\theta = 10^\circ$ represents the diffraction from (0 0 2) planes (plane spacing, $d = 8.7 \text{ \AA}$) according to the JCPDS card data [11]. When Bragg law, $n\lambda = 2d \sin\theta$ is considered in the order of n ($=1, 2, 3, \dots$), the diffraction peaks are identified to be $2\theta = 10.1, 20.4$, and 30.8° , respectively, as indicated by triangle symbols, although the last peak at 30.8° appears very weak in intensity. However, the first peak located at 6.95° was unknown one in respect of the JCPDS information of the bulk phase crystalline 6,13-pentacenequinone. We do not clearly know the identity of this diffraction plane but only presume that this phase probably generates due to the thin film formation, which is usually influenced by substrate-induced strain [14]. It is interesting to note that the new meta-stable plane (estimated $d' = 12.7 \text{ \AA}$) also follow the diffraction rule for a preferred orientation, i.e. when $n = 1, 2, 3$ and 4 , 2θ s are clearly identified to be $6.95, 13.8, 20.7$ and 27.7° , respectively, as indicated by circular symbols. Based on above results, our organic thin film certainly consists of the two mixed crystalline phases with the two different preferred orientations.

Fig. 2 exhibits the normalized direct absorption spectra of the 200-nm thick 6,13-pentacenequinone film deposited on Al_2O_3 (sapphire) substrate at RT and the normalized photoluminescence spectra of the organic films evaporated on n -Si at RT. The main absorption events of the organic film related to the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) transition were

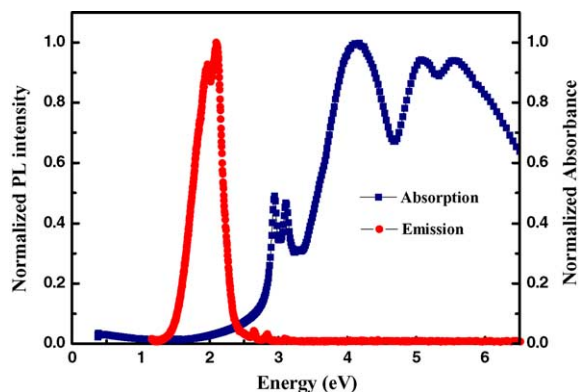


Fig. 2. Normalized absorption and PL spectra of the 6,13-pentacenequinone films deposited on Al_2O_3 (sapphire) and n -Si at RT, respectively.

observed at 2.94 and 3.11 eV. Those absorption peaks are corresponding to those from 6,13-pentacenequinone monomer (a molecular rod), which was previously reported through the spectroscopy in a solution state and also through a quantum chemical calculation [12]. Likewise the HOMO/LUMO gap in our thin films was found to be almost the same as that in one molecule [12]. It is interesting because the absorption spectra of some other films such as pentacene and tetracene thin films are different from those of corresponding monomers. Once the pentacene and tetracene monomers form crystalline phase films, their absorption peaks or HOMO/LUMO gaps appear shifted to lower energies [16,17]. Why our thin pentacenequinone film acts as a molecule is probably because of weak intermolecular interactions between the 6,13-pentacenequinone monomers forming crystalline aggregates.

Photoluminescence (PL) spectra also exhibited two luminescence peaks at 1.97 and 2.09 eV (yellow light), which are corresponding to the double peaks found in the absorption spectra although it seems that this organic thin film system has such a large Stokes shift as $\sim 1 \text{ eV}$ (In the case of typical amorphous Alq_3 films, the Stokes shift was reported to be about $\sim 0.9 \text{ eV}$ [18]). The observed yellow luminescence was so intense under a UV-light ($\lambda = 313 \text{ nm}$, 2.1 mW) that it was compared to the PL from conventional Alq_3 films. As we measured the PL intensities from the Alq_3 and our pentacenequinone film under an identical UV incidence, the yellow luminescence appeared about few times weaker than the green luminescence from the Alq_3 film in intensity. The strong light-emitting results are rare to see in organic crystal systems because becoming crystalline usually quenches any light-emitting tendency in organic materials systems [19]. In this point, our thin crystalline film is unique. Besides, the 6,13-pentacenequinone film can be a relatively stable material for a UV-light detector or UV-detecting card because usual amorphous light-emitting materials are very unstable and easy to be dissociated under normal UV-light.

Fig. 3 present the I - V curves obtained from our 6,13-pentacenequinone/ n -Si diode in the dark. The inset of Fig. 3 also shows the schematic cross-sectional view of our diode. The diode showed rectifying behavior although relatively high leakage current (compared with the reference $\text{Au}/n\text{-Si}$

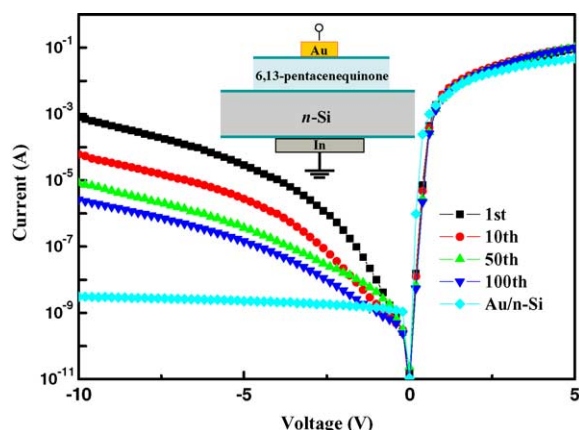


Fig. 3. I - V characteristics of the 6,13-pentacenequinone/ n -Si diodes (an Au/ n -Si Schottky diode was also tested as a control sample). The inset shows the schematic cross-sectional view of our diode.

Schottky diode) was observed under reverse bias conditions. The leakage current gradually decreased as voltage sweep (from -10 to 5 V) was repeated up to 100 times on the same device. This means that the organic film has many leakage sources (traps) probably within grains or from the boundaries between the thin film phase and bulk phase (as aforementioned in Fig. 1). The charges trapped in point defects or phase boundaries are swept under the repeated voltage stress.

4. Conclusion

In summary, we have deposited 6,13-pentacenequinone films on n -Si by thermal evaporation at RT and investigated their structural and optical properties. According to X-ray diffraction, films were found to have two different crystalline phases mixed and also one of the phases is unknown and metastable. Photoluminescence (PL) spectra exhibited double peaks at 1.97 and 2.09 eV while the corresponding double peaks related to highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) transition were observed from direct absorption spectra at 2.94 and 3.11 eV. Because the PL intensity of our organic crystal film was so strong under a UV illumination, it can be a relatively stable material for a UV-light detecting card. Au/organic/ n -

Si structures using 6,13-pentacenequinone films on n -Si showed rectifying behavior but with a relatively high level of leakage current due to many traps in the organic film.

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