Structural and optical properties of 6,13-pentacenequinone thin films

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We report on the structural and optical properties of 6,13-pentacenequinone thin films deposited on n-Si substrates by thermal evaporation at room temperature. X-ray diffraction data indicate excellent crystallinity but the films have two crystalline phases mixed. Photoluminescence (PL) spectra exhibited double peaks at 1.97 and 2.09 eV while the corresponding (double) peaks, associated with the highest occupied molecular orbital–lowest unoccupied molecular orbital transition, were also observed from direct absorption spectra at 2.94 and 3.11 eV. The yellow PL band was quite intense under UV illumination; the intensity was comparable to that from Tris-(8-hydroxyquinoline) aluminum (Alq$_3$) thin films. A large Stokes shift of $\sim$1 eV found in our 6,13-pentacenequinone thin films suggests potential applications to UV-detectors and UV-detecting cards. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1832759]

Organic thin-film devices, such as organic light-emitting diodes, organic thin-film transistors, organic photodetectors, and organic solar cells, have been extensively studied over the last few decades, and the performance of these devices has made consistent progress.[1–6] It is mainly because organic films have clear advantages over inorganic counterparts in several aspects: large area coverage, mechanical flexibility, low temperature process, and low-cost processing.[7,8] All of these aspects are quite important for the modern flat-panel display industries.

6,13-pentacenequinone is a member of the linear para acenequinones, which are organic compounds formed by replacing two hydrogen atoms by two oxygen atoms in polycyclic aromatic hydrocarbons. Para quinones and their derivatives play an important role in industrial dyes, pigment material, and photochromic molecules.[9,10] While the optical spectra and crystal structure of bulk phase 6,13-pentacenequinone have been studied,[11–13] the properties of the thin film phase have not been reported so far.

In the present study, we report on the structural and optical properties of 6,13-pentacenequinone thin films deposited on n-Si substrates by thermal evaporation at room temperature, presenting potential applications of 6,13-pentacenequinone thin films to organic semiconductor devices.

Our 6,13-pentacenequinone thin films were deposited on (100)-oriented n-Si substrates (1–5Ω cm) 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 films were evaporated on n-Si at a fixed deposition rate of $\sim$1 Å/s at a crucible temperature of 140 °C. The film thickness was $\sim$100 nm as monitored by a quartz crystal oscillator and confirmed by ellipsometry. X-ray diffraction (XRD) measurements were performed with monochromatic Cu $K\alpha$ ($\lambda = 1.54$ Å) radiation to investigate the crystallinity of the deposited films. Atomic force microscopy (AFM) was employed to observe the surface morphology. Photoluminescence (PL) measurements were carried out at RT using a light source (Oriel Optical System) with the wavelength and optical power set to 313 nm and 2.1 mW, respectively. The light source consists of 500 W Hg(Xe)-Arc lamp and a monochromator covering the range of 310–670 nm. Direct absorption measurements were performed on 200-nm-thick films deposited on Al$_2$O$_3$ (sapphire) substrates under the same evaporation condition in order to measure transmission over a broad spectral range.

Figure 1 displays the XRD spectra (logarithmic scale) obtained from the 6,13-pentacenequinone films evaporated on n-Si at RT. High crystalline quality was confirmed by the intensity and full widths at half maximum of the diffraction peaks. The 6,13-pentacenequinone bulk crystal phase obtained from solution is known to have a monoclinic structure ($\beta = 93.25°$) packed along the long axis of the rodlike mol-
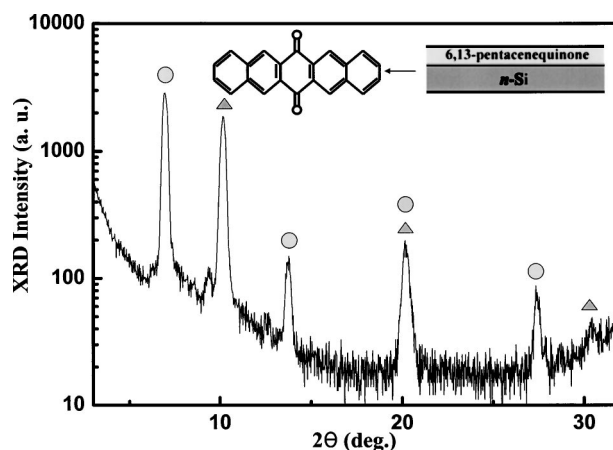

FIG. 1. XRD spectra taken from the 6,13-pentacenequinone film deposited at RT. The inset is the molecular structure of the 6,13-pentacenequinone.

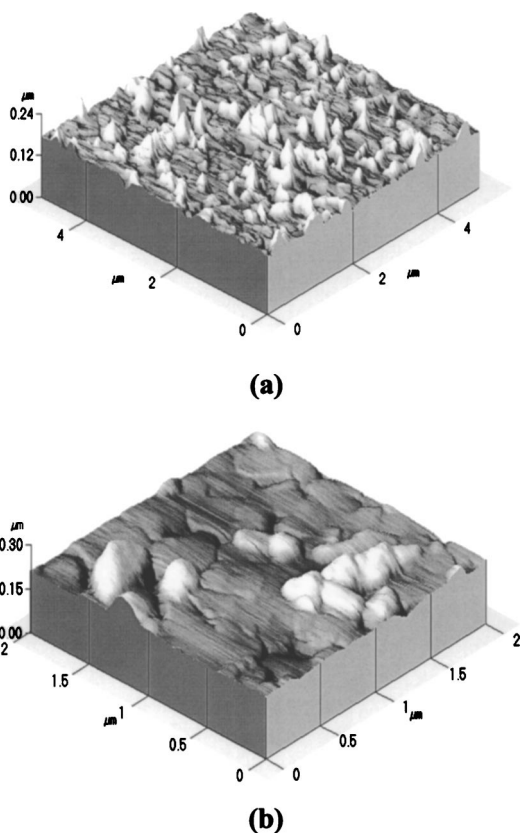[a)]Author to whom correspondence should be addressed; electronic mail: semicon@yonsei.ae.kr

(a)

(b)

FIG. 2. AFM micrographs of the 6,13-pentacenequinone film, (a) 5 μm $\times$5 μm (R_{rms}=10.7 nm) and (b) 2 μm$\times$2 μm (R_{rms}=16 nm).

FIG. 3. Normalized absorption and PL spectra of the 6,13-pentacenequinone films deposited on Al_2O_3 (sapphire) and *n*-Si at RT, respectively.

ecule (the molecular structure is schematically shown in the inset of Fig. 1).[11] The diffraction pattern of our pentacenequinone films deposited on *n*-Si substrates basically shows preferred orientations, similar to those of other organic crystalline films such as pentacene or tetracene.[14,15] Actually our organic films appeared to have some preferred orientations, e.g., the second peak located at $2\theta=10°$ represents the diffraction from (002) planes (plane spacing d=8.7 Å) according to the Joint Committee on Powder Diffraction Standards (JCPDS) card data.[11] When Bragg law, $n\lambda=2d\sin\theta$ is considered in the order of n ($=1,2,3,\ldots$), the diffraction peaks are identified to be 2θ=10.1°, 20.4°, and 30.8°, respectively, as indicated by the triangle symbols, although the last peak at 30.8° appears very weak in intensity. However, information on the first peak located at 2θ=6.95° was unavailable from the JCPDS card data on the bulk phase crystalline 6,13-pentacenequinone. We cannot clearly identify the relevant diffraction plane but only presume that this phase probably originates due to the substrate-induced strain, which usually occurs during film deposition.[14,16] It is interesting to note that the new meta-stable plane (estimated d'=12.7 Å) also follows the diffraction rule for a preferred orientation, i.e., for n=1,2,3,4, 2θ's are clearly identified to be 6.95°, 13.8°, 20.7°, and 27.7°, respectively, as indicated by the circle symbols. Based on the above-noted results, our organic thin films certainly consist of two mixed crystalline phases with two different preferred orientations.

Figures 2(a) and 2(b) display the AFM micrographs of 5 μm $\times$ 5 μm and 2 μm $\times$ 2 μm area, respectively, exhibiting the surface of our organic films. The rms surface roughness was as large as 10 nm but according to the figures mountainous area and flat area are actually well-
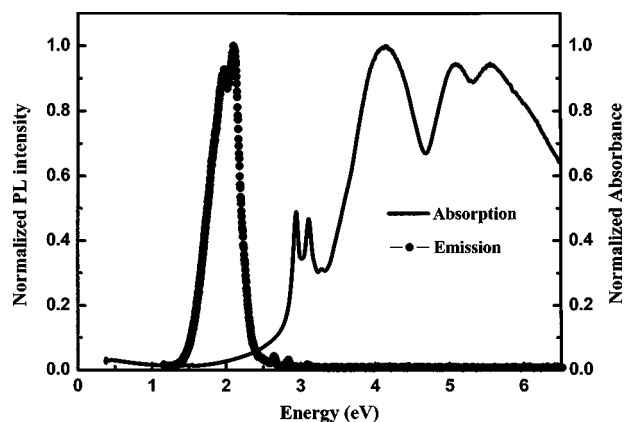
distinguished from each other. In particular, the more detailed surface image of 2 μm $\times$ 2 μm size shows grain-like morphologies along with some grain-boundary-like contours. It is thus inferred that these two areas represent the bulk phase (flat) and the meta-stable phase (mountainous) as shown in the XRD results.

Figure 3 exhibits the normalized direct absorption spectra of a 200-nm-thick 6,13-pentacenequinone film deposited on an Al_2O_3 (sapphire) substrate at RT and the normalized PL spectra of the films evaporated on *n*-Si at RT. The main absorption features associated with the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) transition were observed at 2.94 and 3.11 eV. These absorption peaks correspond to those from the 6,13-pentacenequinone monomer (a molecular rod), which was previously reported through spectroscopic studies 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 the molecule.[12] It is interesting because the absorption spectra of other related organic films such as pentacene and tetracene thin films are different from those of the corresponding monomers. Once the pentacene and tetracene monomers form crystalline phase films, their absorption peaks or the HOMO-LUMO transition appear to be shifted to lower energies.[17,18] The reason our thin pentacenequinone films act like individual molecules is probably because of weak intermolecular interaction between the 6,13-pentacenequinone monomers when forming crystalline aggregates.

PL spectra also exhibited two luminescence peaks at 1.97 and 2.09 eV (yellow light), which clearly correspond to the double peaks found in the absorption spectra. Surprisingly our organic thin-film system has such a large Stokes shift as ~1 eV. (In the case of typical amorphous Tris-(8-hydroxyquinoline) aluminum (Alq_3) films, the Stokes shift was reported to be about ~0.9 eV.[19]) We thus observed the yellow luminescence only under an UV radiation with an energy higher than 2.94 eV. The observed yellow luminescence was so intense under an UV radiation (λ=313 nm, 2.1 mW) that it was comparable to that from conventional Alq_3 films. As we measured the PL intensities from Alq_3 and our pentacenequinone films under an identical UV incidence-condition, the yellow luminescence intensity appeared about a few times weaker than the green luminescence from Alq_3 film (see Fig. 4). Nevertheless, the intensity of the yellow
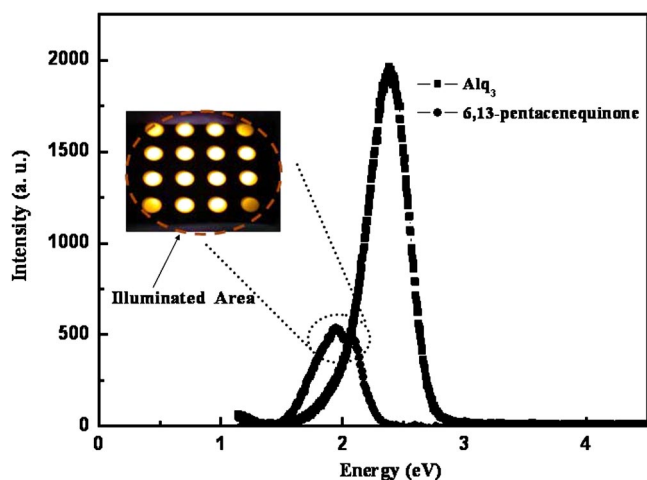
FIG. 4. PL spectra obtained from 100-nm-thick 6,13-pentacenequinone and identically thick Alq₃ films under the same UV incidence.

luminescence was still unexpectedly strong as shown in the inset photograph of Fig. 4. The strong light emission is rare in organic crystal systems because crystal formation usually quenches any light-emitting tendency in organic materials systems.[20] 6,13-pentacenequinone films can be a comparatively stable material for an UV-light detector or UV-detecting card because usual amorphous light-emitting materials are very unstable and susceptible to dissociation under a normal UV radiation.

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 the XRD data, the films were found to have two different crystalline phases mixed, one of the phases being unknown and metastable. PL spectra exhibited double peaks at 1.97 and 2.09 eV while the corresponding double peaks related to HOMO-LUMO transition were observed in the direct absorption spectra at 2.94 and 3.11 eV. Because the PL intensity of our organic crystal film was unexpectedly quite strong under an UV illumination, it can be an excellent candidate material for

a stable UV-light detector or a detecting card.

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