Substrate induced molecular conformations in rubrene thin films: A thickness dependent study

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ABSTRACT

A systematic study about substrate induced molecular conformation in rubrene thin films by varying film thickness from sub-monolayer to multilayer, which currently attracts substantial attention with regard to its application in organic electronics, is performed. The clean polycrystalline Au and Ag were used as noble-metals, whereas, H passivated and SiO_2 terminated Si (100) were used as dielectric substrates. Angle dependent near edge x-ray absorption fine structure spectroscopy (NEXAFS) was employed to understand the molecular conformation and orientation whereas atomic force microscopy (AFM) was used to investigate the surface morphologies of the film. X-ray absorption spectrum (XAS) of rubrene molecules with twisted conformation was calculated using density functional theory (DFT). Percentage of twisted rubrene molecules are gradually reducing with increasing film thickness. But the change of degree of molecular conformationa is found to depend on substrate surface properties. Deposited molecules retain the twisted geometry of the free rubrene molecule at sub-monolayer coverage on four studied substrates. At 200 Å thick rubrene film, molecules are in lying configuration on the Ag substrate and randomly oriented on other three substrates. The Ag surface comprised of comparatively wider, flatter terrains separated by large height differences help to achieve rubrene film with larger closely packed grains. The results have important implications for the understanding of the substrate induced molecular conformations in rubrene thin films with its thickness and are beneficial for the improvement of the device performance.

1. Introduction

Recently, organic electronic technologies are emerging as prospective future options for their high application potential in electronic devices. In contrast to inorganic semiconductors, whose physical principles of growth have been solidly established and successfully exploited to control the fabrication of desired morphologies and structures, the present-day knowledge on the growth of ordered organic films is still limited [1,2]. Rubrene ($C_{42}H_{28}$) has been recently identified as a promising material due to its high charge-carrier mobility. Organic field effect transistors (OFET) based on rubrene single crystal currently hold the record of hole mobilities ($\sim 40\ cm^2/V.s$) among all organic semiconductors [3]. This remarkably high carrier mobility is ascribed to efficient cofacial π-π stacking in the single crystal [4,5]. Unfortunately, rubrene thin film transistors (TFTs) prepared by conventional organic molecular beam deposition techniques did not exhibit superior carrier mobilities, ranging from 10^{-6} to $10^{-2}\ cm^2/V.s$,

because of difficulty in achieving highly-quality crystalline rubrene active layer [6–8]. It is important to understand the growth process in detail to realize better-quality rubrene thin films. Rubrene is a non-planar and flexible molecule comprising of a tetracene backbone core with two pairs of phenyl substituents symmetrically attached on either side of the backbone. The intra-molecular steric hindrance between the phenyl side groups results in a significant strain within the molecule which is minimized in two stable configurations, one with a twisted (Fig. 1(a)) and the other with a flat tetracene backbone (Fig. 1(b)) [9–11]. The twisting of the tetracene backbone is responsible for a complicated three dimensional structure of rubrene molecule which hampers the crystal formation. Moreover, our theoretical calculation showed that rubrene molecule with twisted backbone has lower total energy of about 285 meV compared to that with flat backbone [12]. Earlier it was observed that the substrate supply the required energy for flattening the backbone which helps to achieve ultimately good rubrene crystalline thin film. Moreover it was found that the surrounding
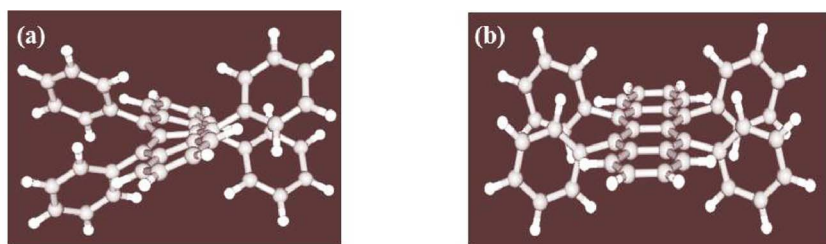

Fig. 1. Rubrene molecule's (a) twisted conformation in gas phase and (b) flat conformation in condensed phase.

molecules also play a decisive influence to get a planar molecular conformation [9,13]. Hence a study of the substrate induced molecular conformation in rubrene thin films by varying film thickness from sub-monolayer to multilayer is important to derive a more deeper understanding and get better device performance in thin film phase. In this context, it may be mentioned here angle dependent near edge x-ray absorption fine structure spectroscopy (NEXAFS) is a very powerful tool for determining molecular conformation and orientation in organic films, even at submonolayer thicknesses [14,15].

Under this circumstance, in this report, we have carried out a study on the molecular conformation in rubrene thin films by varying film thickness from sub-monolayer to multilayer on polycrystalline Au, polycrystalline Ag, SiO_2 terminated Si (100) and H passivated Si (100) substrates. We employed angle dependent near edge x-ray absorption fine structure spectroscopy (NEXAFS) to get information about molecular conformation plus orientation and atomic force microscopy (AFM) was utilized to investigate about surface morphologies of the samples. X-ray absorption spectra (XAS) spectra of rubrene molecules with flat and twisted conformations were calculated using density functional theory (DFT). We have shown that percentage of twisted rubrene molecules are gradually reducing with film thickness. On the other hand the change of degree of molecular conformation is found to depend on substrate surface properties. We have also revealed that the deposited molecules retain the twisted geometry of the free rubrene molecule at sub-monolayer coverage on four studied substrates. Furthermore, we have observed that rubrene molecules are in lying configuration on the Ag substrate and randomly oriented on other three substrates at 200 Å thick films. In addition, we have exhibited that the Ag surface comprised of wide, flatter terrains separated by large height differences help to achieve rubrene film with larger closely packed grains. Our results have substantial inferences for the understanding of the substrate induced molecular conformations in rubrene thin films with thickness and are beneficial for the rubrene based device performance.

2. Methodology

2.1. Experimental details

The NEXAFS experiments were carried at Beam-line (BL24A) of the storage ring of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The organic vapor deposition chamber was directly attached to the analysis chamber at the BL24A station allowing the samples to be studied without breaking the vacuum. We have used clean polycrystalline (poly) Au and Ag as noble-metal substrates. The gold coated Si substrate was purchased from Sigma Aldrich and the Ag coated (~75 nm) substrate was prepared by depositing Ag thin films on H terminated Si (100) using DC magnetron sputtering (PLS 500, Pfeiffer). H terminated Si (100), designated as Si-H, was prepared by etching the native oxide of Si (100) with 10% hydrofluoric acid for about 3 min. The SiO_2 coated (~100 nm) Si (100), designated as Si-O, was prepared by thermal oxidation of Si (100) and was cleaned by

sonication in chloroform and methanol for 10 min each. The substrates were loaded into the UHV chamber immediately after preparation. To obtain clean metal substrates Ar^+ sputtering was used until the C 1 s and O 2p XPS signals were vanished and consistent values of the work functions were obtained. Rubrene films were grown in a stepwise manner by thermal evaporation of rubrene powder (Acros Organics, 99%) from a resistively heated quartz crucible of a home-made organic material effusion cell. The nominal thickness of the rubrene films were calibrated by monitoring the evaporation rate with a quartz crystal microbalance (Inficon XTC controller). The evaporation rate for all the films was kept within 0.04-0.06 Å/s. For a systematic comparison, rubrene thin films with the same thickness but on different substrates (Au, Ag, Si-O and Si-H) were prepared together in the same chamber. After each deposition the samples were characterized by in-situ NEXAFS spectroscopy. To overcome the difficulty of performing a reliable C− K edge NEXAFS measurement for ultra-thin adsorbate films, the incident photon flux monitoring was done by measuring ion current of the ion chamber situated between the beam-line and the sample chamber, instead of traditional gold mesh method. The ion chamber is filled with Ar up to a working pressure of 10^{-3} torr and terminated with 0.1 μm thick Ti foils at both ends [16]. The NEXAFS spectra were measured in the partial electron yield (PEY) detection mode using a homemade electron detector based on a micro-channel plate and a retarding field of −150 V to optimize the signal to noise ratio. The polarization dependent NEXAFS spectra were obtained by varying the X-ray incident direction between normal incidence (90°) and glancing incidence (20°). The base pressure of deposition and analysis chambers were 1.0×10^{-8} torr and 1.0×10^{-10} torr respectively. The use of ion chamber for monitoring the incident photon flux also simplifies the NEXAFS data normalization schemes. The step of so-called mesh current normalization is not required here. Rest of the raw data background correction and normalization were carried out according to the established procedure [17].

Surface morphologies of the films were studied by using tapping mode AFM (Innova, Veeco) in air. The images were analyzed by using WSxM software [18]. Scans of different area over several regions of the films were taken to check the consistency of the morphology of the samples.

All the depositions and characterizations were performed at room temperature.

2.2. Computational methods

The equilibrium geometry and XAS spectra of the free molecule were calculated by DFT with the computer code STOBE-deMon [19,20]. A gradient corrected RPBE exchange/correlation functional was applied [21,22]. To calculate the equilibrium geometry and the X-ray absorption spectra, we used all-electron triple-ζ valence plus polarization (TZVP) atomic Gaussian basis sets for carbon centers, while the hydrogen basis sets were chosen to be of the double-ζ (DZVP) type [23]. The starting geometries for the optimization procedure were obtained using Avogrado (http://avogadro.cc/). To calculate X-ray absorption