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Impedance spectroscopy on copper phthalocyanine diodes with surface-induced molecular orientation

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ABSTRACT

Molecular orientation and packing motif governs charge-transport property of organic semiconductor films, especially for planar small molecules. We analyze the surface-induced orientation of copper phthalocyannine (CuPc) molecules deposited on graphene or poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) covered indium-tin-oxide (PEDOT:PSS/ITO). The CuPc films deposited on graphene are templated with preferential face-on stacking, whereas the molecules on PEDOT:PSS/ITO crystallize with edge-on ordering. Static current–voltage measurement and small-signal impedance spectroscopy are combined to elucidate the structural impact on the electrical response when those films are part of a rectifying diode. The graphene-templated diode shows enhanced out-of-plane hole conduction as compared to the diode with a PEDOT:PSS/ITO contact. Equivalent circuits describing charge injection and transport properties are proposed.

1. Introduction

Organic electronics is under continuous progress with synergistic development of novel materials, process techniques, and theoretical understanding of fundamental aspects [1]. Many viable organic optoelectronic applications require 'transparent electrodes' as an essential part, the studies of which have been active in the broader context of conventional and emerging device concepts [2]. For applications such as flat-panel displays, touch screens, and solar cells, indium-tin-oxide (ITO) has been the material of choice due to the superior and well-balanced optical/electrical characteristics. However, there are critical drawbacks of ITO in long-term perspectives, notably the scarcity of indium and the mechanical instability of ITO films [3,4]. Currently, various materials and/or compositions are being investigated as an alternative, to overcome the challenges related to the predominant use of ITO, and also to enable new functionalities based on combined optical transparency and electrical conductivity [5].

Graphene is considered to be one of the most promising materials for next generation transparent electrodes. Since the first report in 2004 [6], tremendous research effort has been put into this special two-dimensional carbon network. Consequently, many material characteristics have been revealed, and large-area production methods for industrial applications have been demonstrated [7–10]. The ability to efficiently conduct electrons within an only atomically thin structure is the key attribute of graphene, which is expected to meet the strict requirements concerning the general trade-off between optical and electrical properties of transparent conductors. More recently, an

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interesting property of graphene as 'molecular templates' has gained growing attention. In 2012, Singha Roy and co-workers reported on the observation that evaporating copper phthalocyannine (CuPc) on graphene led to lying-down molecules (so-called 'face-on' stacking), as templated by the underlying flat carbon mesh [11]. In contrast, the molecules deposited on bare glass or metal surfaces were standing up (so-called 'edge-on' stacking). By putting forward the 'epitaxial-growth' concept, Xiao and co-workers showed similar structural analysis in 2013, while suggesting first-principle calculation data that accounted for the substrate–molecule interactions [12]. In view of charge transport and π–π stacking directions, the face-on orientation is advantageous for (vertical) diode-type devices represented by organic light-emitting diodes (OLEDs) and organic photovoltaic cells (OPVs). This clearly indicates that exploring the templating property is an efficient approach to fully realize the potential of graphene as transparent electrodes.

In this study, we present a systematic correlation between surface-induced film structure and electrical response of CuPc diodes. Rectifying organic diodes were fabricated and compared on two model substrates; poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) covered indium-tin-oxide (PEDOT:PSS/ITO) and single-layer graphene. Higher current density at bulk-limited forward bias regime of the graphene sample was clear evidence for enhanced out-of-plane conductivity, associated with close molecular packing along the charge-transport direction. We performed impedance spectroscopy on these diodes to further identify interface and bulk charge transport processes. The proposed characteristic equivalent circuit models well described the experimental spectra, the parameters of which are interpreted in relation to the structural features.

2. Experimental

2.1. Sample preparation

For graphene devices, large-area monolayer graphene films were grown by chemical vapor deposition (CVD) and transferred to the Si or glass substrates using well-established procedures [13,14]. For PEDOT:PSS/ITO devices, prepatterned ITO substrates were solvent cleaned and exposed to UV-ozone for 10 min. PEDOT:PSS (HC Starck) was spin-coated at 5000 rpm for 45 s and baked at 140 °C for 20 min in air. Both graphene/glass and PEDOT:PSS/ITO substrates were then transferred into a nitrogen glove box-coupled vacuum deposition system where CuPc thin films were thermally evaporated simultaneously in a single deposition run with the thickness of 80 nm as measured by a calibrated quartz crystal microbalance. The organic diodes were completed by evaporating 80 nm of Al top contact through a shadow mask. The active device area (A) defined by the geometrical overlap between the anode and cathode was 0.16 cm^2 for the PEDOT:PSS/ITO anode sample and 3.5×10^{-3} cm^2 for the graphene anode sample. For grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments, the graphene/Si substrates with ~20 nm-thick CuPc films were employed to minimize the background scattering.

2.2. Structural characterization

GIWAXS measurements were performed at the undulator-based X9 endstation at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Two-dimensional scattering images were collected using an area detector, positioned 217 mm away from the center of the sample stage. The incident X-ray beam (λ = 0.10332 nm) was collimated using slits and focused onto the sample position using Kirkpatrick–Biaz mirrors providing the beam size of 100 μm horizontal width with 50 μm vertical width. The sample stage was located inside a vacuum chamber (pressure ≈ 40 Pa), where both the incident angle and sample translation are computer-controlled. Measurements were performed at the incident angle of 0.1°. Data conversion to q-space was accomplished by calibration, using silver behenate powder. Scanning electron microscopy (SEM) characterization was performed with a Hitachi S-4800 model at 5 kV.

2.3. Electrical characterization

Current–voltage (J–V) characteristics of the diodes were recorded using a Keithley 4200 semiconductor characterization system. Impedance data were obtained using an Agilent 4294A precision impedance analyzer. The available small-signal frequency f range was 40 Hz to 110 MHz and a fixed small-signal oscillation amplitude of 500 meV was used. A commercial software EC-Lab (V10.34) from Bio-Logic was used for impedance data fitting and parameter extraction. J–V and impedance measurements were conducted under dark at ambient atmosphere.

3. Results and discussion

3.1. Surface-induced film structure

Structural information on the CuPc films deposited on each substrate is collected in Fig. 1. SEM images Fig. 1a and b show that the morphologies of the CuPc films fabricated under the same condition are significantly different due to the substrate surface property; the film on PEDOT:PSS is relatively smooth and homogeneous, whereas the graphene/Si substrate leads to more polycrytal-like texture of CuPc with rougher top surface. 2-D GIWAXS patterns in Fig. 1c and d exhibit strikingly different crystalline structures in those two films. Well-defined peaks in both images assure high degree of molecular ordering, with their positions corresponding to a characteristic set of the scattering planes. The peak analyses show that the CuPc film on PEDOT:PSS/ITO mainly consists of edge-on crystallites, whereas the molecules on graphene/Si are templated with face-on stacking. By combining SEM and GIWAXS analysis, the illustrations in Fig. 1e and f can be deduced. We infer that the tendency of CuPc to aggregate laterally to form grains on graphene leaves rooms between the domains, thus resulting in a larger surface roughness compared to the PEDOT:PSS/ITO case [11,12].