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Application of phosphonic acid self-assembled monolayer in organic field-effect transistors

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ABSTRACT

This study explores a strategy of using phosphonic acid derivative as self-assembled monolayer (SAMs) on Si/SiO_2 surface and using 6,13-pentacenequinone (PQ) as the template layer to induce the crystallization of 6,13-diphenylpentacene (DPP) in vacuum deposited thin film transistors, which showed the field-effect mobility as high as 8.3×10^{-3} cm^2/V s. It is found that n-Octadecylphosphonic acid (ODPA) SAMs plays a unique role in modulating the morphology of PQ to form flat layer, which is helpful for crystallization of DPP. This indicated that ODPA bilayer-step surface play important roles in controlling the growth of both PQ and DPP by vacuum thermal deposition.

1. Introduction

Organic thin-film transistors (OTFTs) offer various electronic applications and offer great potential for application in chemical and biological sensing for environmental monitoring, industry manufacturing [1–4]. However, since most organic semiconductor thin films are polycrystalline, it is difficult to deconvolute the effects of molecular structure, dielectric properties gain boundaries traps by ambient species etc. from the measured OTFT mobility on/off ratio and threshold voltage. In order to design electronic devices with good electrical properties, SAMs fabricated on Si/SiO_2 gate dielectrics was introduced in the process of making devices. SAMs provide a converient, flexible, and simple system with which to tailor the interfacial properties of dielectric layer and semiconductor layers [5,6]. SAMs is an excellent surface modification method, and tuning of the interface can be achieved through changing the rigidity, length, and terminal functional group of the molecule, which in turn affects the uniformity, packing, conformation, polarity, and charge density of the surface [7]. In addition, by tuning the surface terminal group of the SAM, it is possible to modify the interface between the organic semiconductor and dielectric by exploiting compatible organic/organic interactions resulting in improved device performances [8,9]. Phosphonic acids as SAMs material are more desirable for self-assembly on metal oxides and silicon dioxide surface. Also, phosphonic acid monolayer shows greater hydrolytic stability than siloxane monolayers [10]. Liakos et al. compared phosphonic acid monolayers to a variety of binding chemistries and found that phosphonic acid readily formed well-packed monolayers compared to the amine, trimethoxysilane, trichlorosilane, and epoxy-binding groups. They also noted an inability to form trichlorosilane monolayers due to self-polymerization [11–14].

Organic template layer can be used to induce semiconductor layer form orderly film by weak epitaxy growth [15]. This technique was used to fabricate high quality organic semiconductor thin films with highly oriented and large domains, in which the molecules are epitaxial on the substrate, by increasing the substrate temperature and introducing a monodomain film of a rod-like molecule on an amorphous substrate. The organic electronic devices with such films serving as active layers exhibited very high charge carrier mobility [16,17].

In this study, we selected ODPA as SAMs and PQ as template layer to induce DPP crystallization and form orderly thin film, firstly PQ itself is very easy to form crystal thin film, and then it is an insulating molecule. After studying the morphology of DPP on ODPA modified SiO_2 with PQ as template layer, we found DPP shows good crystal thin film by epitaxy growth. The resulting device had the field-effect mobility of 8.3×10^{-3} cm^2/V s. If without the PQ as template layer, DPP just shows amorphous film without field-effect mobility. It is found that ODPA SAMs plays a unique role in modulating the morphology of PQ to form flat and orderly layer, which is helpful for crystallization of DPP.

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2. Experimental

2.1. Synthesis of 6,13-diphenyl-6,13-pentacenediol

To a stirred suspension of 6,13-pentacenedione (462 mg, 1.5 mmol) in 40 ml of anhydrous THF was added 1.5 mL of a solution of phenyl magnesium bromide (3.0 M in diethyl ether, 4.5 mmol, 3.0 eq.) via a syringe under a nitrogen atmosphere at room temperature. After the suspension was dissolved, the resulting dark green solution was refluxed with stirring under a nitrogen atmosphere for 30 min, cooled to room temperature and then poured into 40 mL of saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was further extracted with 2×20 mL of diethyl ether. The organic layers were combined, dried with anhydrous $MgSO_4$, concentrated under reduced pressure. Chromatography on silica gel (65% CH_2Cl_2 in hexanes) yielded 6,13-diphenyl-6,13-pentacenediol (403 mg, 58%) as light yellow powder. 1H NMR ($CDCl_3$) δ (ppm): 2.98 (s, 2H), 6.74–6.90 (m, 10H), 7.50 (dd, 4H), 7.90 (dd, 4H), 8.37 (s, 4H). HRMS (FAB+): cald. for $C_{34}H_{24}O_2$: 464.1776, found: 464.1777.

2.2. Synthesis of 6,13-diphenyl-pentacene (DPP)

To a solution of 6,13-diphenyl-6,13-pentacenediol (376 mg, 0.81 mmol) in 20 mL of THF was added 4 mL of a saturated solution of tin (II) chloride in concentrated HCl with stirring. The resulting dark purple mixture was stirred at room temperature for 10 min and diluted with 30 ml of water. The resulting solid was filtered, washed with 1 mol/L HCl, water, methanol and hexanes subsequently and dried in the air. 6,13-Diphenyl-pentacene was yielded as purple powder (272 mg, 80%). 1H NMR (CD_2Cl_2) δ (ppm): 7.23 (dd, 4H), 7.63–7.78(m, 14H), 8.34 (s, 4H). HRMS (EI+): cald. for $C_{34}H_{22}$: 430.1722, found: 430.1716. DPP was purified by sublimation in N_2 protection before making device.

2.3. SiO_2 surface modification with ODPA

An oxidized silicon wafer (Si is highly n-doped with resistivity smaller than 0.005 G cm and the thermally grown SiO_2 is 300 nm thick) was used as substrates for organic thin film transistors. The following surface treatments of the SiO_2 were performed on the dielectric surface before vacuum sublimation of the semiconductor film: a 10 min sonication in acetone, followed by a 70:30 H_2SO_4/H_2O_2 (piranha) etch for 1 h at 100 °C, then a 1:1:5 $NH_3{\cdot}H_2O/H_2O_2$/deionized H_2O wash for 20 min at 70 °C, and the silicon wafer was held vertically using a small clamp in a solution of ODPA (1 mM in THF) in a 50 mL beaker. The solvent was allowed to evaporate slowly over 3 h, until the level of the solution fell below the silicon wafer. Under these conditions, the concentration of the ODPA in the remaining solution increased by about 30%, but was still below its CMC of ca. 100 mM [18]. The treated Si sample was then removed from its holder and was heated at 140 °C in a simple glass tube for 2 days to bond the SAMs to the SiO_2/Si as octadecylphosphonate. ODPA/SiO_2/Si substrate was sonicated in THF for 10 min. The dielectric surface was characterized using contact angle measurements, which were <5° after cleaning and >93° after ODPA layer formation.

2.4. Transistor fabrication

The thin films composed of PQ and DPP (sublimation and purification in N_2 protection) were vacuum-deposited by an Edwards Auto 306 vacuum coater with the Turbo-molecular pump at a pressure of 1.0×10^{-6} Torr or lower, with a deposition rate of ca. 0.2 Å/s to the desired thickness. The temperature of substrate was 70 °C for PQ and 80 °C for DPP. During vacuum deposition the distance between source and substrate was 18 cm. Different substrate temperatures for deposition were achieved using a radiant heater and measured with a thermocouple. Top-contact drain and source gold electrodes were vacuum-deposited through a shadow mask onto the films of DPP in the same vacuum chamber, and the resulting semiconducting channels were 50 μm(L) × 1 mm(W), 100 μm(L) × 1 mm(W), 50 μm(L) × 2 mm(W) and 100 μm(L) × 2 mm(W). In these transistors highly n-doped silicon functioned as gate electrode and SiO_2 of 300 nm thick (untreated or treated with ODPA) functioned as dielectrics.

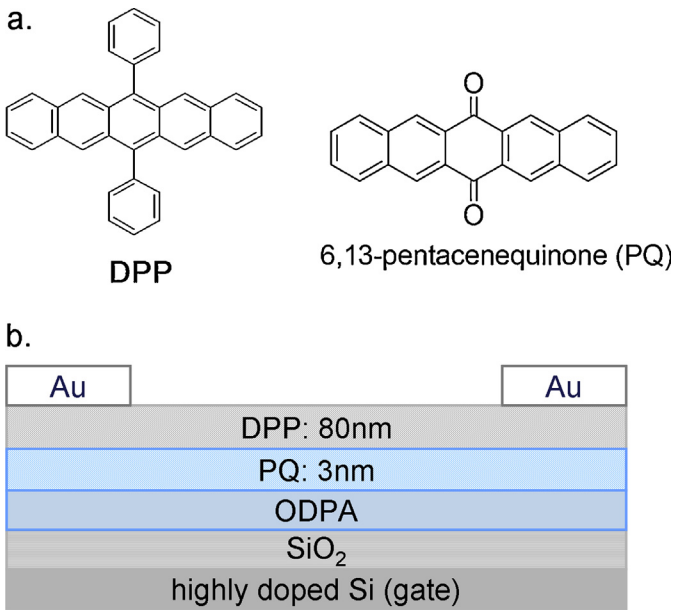

Fig. 1. (a) Chemical structures of the relevant molecules, (b) schematic device structure of the thin film transistors.

2.5. Characterization and apparatus

The current–voltage measurement for thin-film transistors was carried out on a probe station using a HP 4145B semiconductor parameter analyzer. During the measurement, the samples were kept at room temperature in the ambient atmosphere. The topographic images were obtained using a Nanoscope IIIa Multimode Microscope from Digital Instruments. All AFM images were collected using tapping mode and in air under ambient conditions. The topographic images were collected from multiple samples, and for each sample, different regions were scanned to ensure the reproducibility. Polarized optical images of the devices were obtained from Nikon 50IPOL microscope.

3. Results and discussion

Thin film transistors of DPP with a template layer of PQ were fabricated by thermal evaporation under vacuum. A layer of PQ with an average thickness of 3 nm as measured by a crystal balance was first deposited on a highly doped silicon wafer with a 300 nm thick layer of SiO_2, which was treated with a self-assembled monolayer of organic molecules. Two molecules, octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$, OTS) and ODPA were used in this study to form a self-assembled monolayer on the SiO_2 surface by following the reported procedures. On the PQ layer was then deposited 80 nm of DPP without breaking the vacuum at different