Synthetic Metals 210 (2015) 336–341

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Air-stable and high-performance organic field-effect transistors based on ordered, large-domain phthalocyanine copper thin film

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ARTICLE INFO

Article history:
Received 6 September 2015
Received in revised form 22 October 2015
Accepted 27 October 2015
Available online 12 November 2015

Keywords:
Organic field-effect transistors
Copper phthalocyanine
Kelvin probe force microscopy
Domain boundary
Air-stability

ABSTRACT

The development of air-stable and high-performance organic field-effect transistors (FETs) is highly important for practical applications. In present research we studied how the domain size and boundary influence the electrical properties and the stability of CuPc thin films fabricated by the weak epitaxial growth (WEG) method. The electrical properties of fresh CuPc devices have a strong dependence on the domain size, which has been demonstrated based on the analysis of film morphology, electrical properties, and kelvin probe force microscopy (KPFM) measurements. The field-effect mobility of fresh CuPc devices increased with the domain sizes, and the mobility as high as of 0.18 cm^2/Vs was obtained for a large crystalline domain size of about 60 μm^2. Furthermore, the CuPc/*p*-6P FETs with large domains of ordered crystallites show excellent stability after being exposed to ambient conditions for 20 days. In contrast, it was found that the device with randomly aligned crystallites stored in atmosphere with the same temperature and humidity for 20 days exhibited large changes in the electric characteristics including positive-shifted threshold voltage, much lower I_{on}/I_{off} and mobility. X-ray photoelectron spectroscopy (XPS) results proved that the oxygen content in ordered, large-domain CuPc thin film is much less than that in randomly aligned CuPc thin film with small-size crystallites as stored in the same conditions. It results from the diffusion of more oxygen and water into the randomly aligned CuPc thin film with small-size crystallites, which has more boundaries and higher degree of misorientation than the one with ordered, large-domain crystallites. The investigation reveals the importance of domain boundaries in the device stability, and provides a guide for rational optimization of film morphology for air-stable, high-performance organic FETs.

1. Introduction

Organic field-effect transistors (OFETs) based on polycrystalline small molecules have attracted considerable interest from the scientific community owing to its applications in low-cost, flexible, large-area electronics such as organic active matrix displays, sensors and radio-frequency identification card [1–6]. In recent years, tremendous progress has been achieved in both the design of organic semiconductors and the fabrication techniques to optimize the performance of OFET devices. There are several organic small molecule materials exhibiting excellent field-effect mobility, which can rival to that of hydrogenated amorphous silicon [7,8]. However, the stability of OFETs should be considered for practical applications besides the charge mobility [9,10]. The family of phthalocyanines represents one of the most promising candidates for organic electronics. Particularly, phthalocyanine copper (CuPc) was widely studied as one of good small molecular semiconductors because of their large π-conjugated system, excellent film growth and unique electronic characteristics [11]. A large number of studies have been devoted to improve the carrier mobility by optimizing the thin film morphology and engineering the interface of devices [12–15]. Nevertheless, because of the inherent anisotropy of organic small molecules and the van der Waals nature of the intermolecular interactions, it is difficult to obtain large-size domains of ordered crystallites and continuous

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http://dx.doi.org/10.1016/j.synthmet.2015.10.023
0379-6779/

CuPc thin film, and the deposited films are usually polycrystalline with high-density grain boundaries (GBs). Because of the abrupt collapse of the π-π stack and large disorder in films, the present of the GBs is the main transport barriers for charge carriers, which result in inferior device performances. Furthermore, some studies have also showed that the high-density GBs are responsible for the instability of the OFETs. Mariucci et al. have demonstrated that higher density of GBs contributes to a higher sensitivity to air ambient [16]. Chosh et al. have also found that OFETs with larger grain size could lead to higher stability [17]. Weak epitaxial growth (WEG) is a very effective technique to fabricate highly ordered organic semiconductor thin films with large crystalline domains (>10 μm^2) for high-performance OFETs [18,19]. The highly oriented and continuous CuPc thin film with standing-up molecular orientation on *para*-sexiphenyl (*p*-6P) layer fabricated by the WEG technique leads to a significant improvement in the carrier transportation in OFET devices. However, it seldom studies the air stability of OFET fabricated by WEG.

In present research we studied how the domain size and boundary influence the electrical properties and the stability of CuPc thin films fabricated by the WEG method. The mobility of CuPc OFETs fabricated by WEG was strongly domain-size dependent. A hole field-effect mobility as high as 0.18 cm^2/Vs was obtained in CuPc devices with a large crystalline domain size of about 60 μm^2, which can be comparable to CuPc single crystals [20,21]. In addition, the CuPc/*p*-6P FETs with large domains of ordered crystallites show high stability as exposed to air ambient for 20 days. But the devices with randomly aligned crystallites stored in atmosphere with the same temperature and humidity for 20 days exhibited the large changes of electric characteristics including positive-shifted threshold voltage, much lower I_{on}/I_{off} and mobility. Stored under the same conditions, the oxygen content of the CuPc sample with large domains of ordered crystallites is much less measured by XPS. It is because that more oxygen and water can diffuse into CuPc thin film with randomly aligned crystallites, which has more number of boundaries and higher misorientation degree than the film with large domains of ordered crystallites. The study provides a guide for rational optimization of film morphology for high performance and air stable OFETs.

2. Experimental

The oriented CuPc-based FETs were fabricated on a heavily doped n-type silicon wafer serving as the gate electrode and substrate. About 200 nm-thick SiO_2 layer with a capacitance of C_i = 17 nF/cm^2 was deposited on the Si wafer as gate insulator. The SiO_2/Si substrate (Si-Mat, silicon materials) was ultrasonically cleaned in acetone, alcohol and distilled water for 15 min respectively, then dried by N_2 flow and treated by ozone for 15 min. The CuPc and *p*-6P materials were purchased from Sigma-Aldrich and Jilin OLED Material Tech Company, respectively. CuPc was purified twice before the use and *p*-6P was used as received. All organic thin films were deposited at 10^{-4}–10^{-5} Pa at a rate of about 1 nm/min recorded by a quartz crystal oscillator and the substrate temperatures were held at 180°C. The *p*-6P layer with different thicknesses was deposited on SiO_2 layer. After that, CuPc with 30 nm was epitaxially grown on the surface of *p*-6P thin-film. Subsequently, the source and drain electrodes were prepared by evaporating gold through a carbon fiber shadow mask on the top of the CuPc film. The schematic procedure for fabricating micro-gap Au electrodes is shown in Fig. 1a. The width and length of the channels were 200 μm and 12 μm, respectively. These devices were stored in constant temperature and humidity (30 °C, ~25%).

Kelvin probe force microscropt (KPFM) measurements were performed in situ for operating devices with an Agilent Technologies 5500 AFM/SPM System (USA) operated in air at ambient temperature. The morphology and surface potential line profiles are recorded by tapping-mode simultaneously. The potential sensing tip was the PPP-EFM-50 probe purchased from NanoWorld AG. Electrical properties of the devices were measured by a Keithley 4200 semiconductor parameter analyzer in air and at room temperature. The spectroscopies of films were measured by X-ray photoelectron spectroscopy (XPS) system (Specs, Germany) with monochromatic SPECS XR-MF Microwave X-ray source (Al Kα = 1486.7 eV) in a UHV system. The ultrahigh vacuum (UHV) system includes a SPECS PHOIBOS 150 hemispherical energy analyzer and the based pressure is superior to 2×10^{-10} mbar. For XPS, the resolution of the spectrometer was chosen to be 0.65 eV with the pass energy setting of 40 eV.

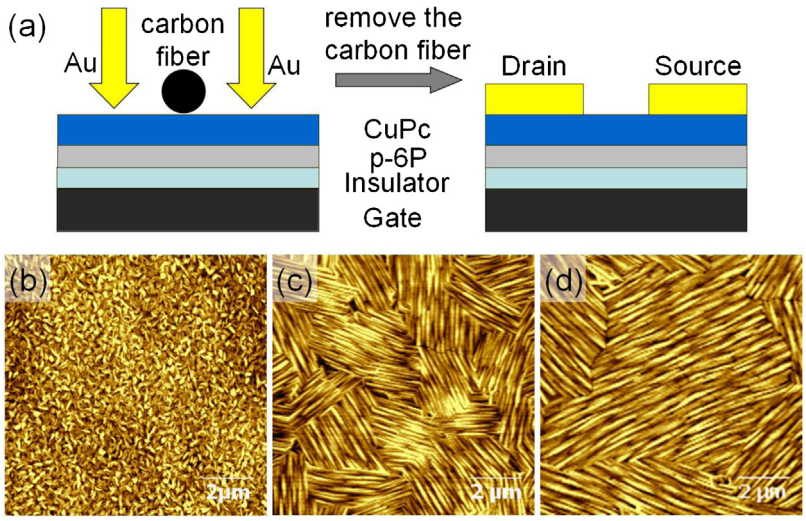

Fig. 1. (a) Device configuration in this study and the schematic procedure for fabricating micro-gap Au electrodes, the length of gap is about 12 μm. Morphology of the CuPc/*p*-6P film imaged by AFM with different size of domains, (b) randomly aligned crystallites (0 μm^2), (c) small domains of ordered crystallites (5 μm^2), (d) large domains of ordered crystallites (60 μm^2). The value of the size 0 μm^2 is from CuPc thin film grown on bare SiO_2 substrate with complete disorder. The scan area is 10 μm × 10 μm.