Solid-State Electronics 54 (2010) 1650–1656

Contents lists available at ScienceDirect

Solid-State Electronics

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

The surface energy-dictated initial growth of a pentacene film on a polymeric adhesion layer for field-effect transistors

Jaehoon Park [a], Jin-Hyuk Bae [b], Won-Ho Kim [b], Sin-Doo Lee [b], Jin Seog Gwag [c], Dong Wook Kim [a], Jeong Cheol Noh [a], Jong Sun Choi [a,*]

[a] Department of Electrical, Information and Control Engineering, Hongik University, Seoul 121-791, Republic of Korea
[b] School of Electrical Engineering, No. 32, Seoul National University, Seoul 151-600, Republic of Korea
[c] Department of Physics, Yeungnam University, Gyeongsangbuk-do 712-749, Republic of Korea

ARTICLE INFO

Article history:
Received 14 April 2010
Received in revised form 4 August 2010
Accepted 8 August 2010
Available online 30 August 2010

The review of this paper was arranged by Y. Kuk

Keywords:
Field-effect transistor (FET)
Organic semiconductors
Growth
Surface energy

ABSTRACT

We describe how the surface energy of a polymeric adhesion layer affects the initial growth of a pentacene film for field-effect transistors (FETs). Three types of adhesion layers having different surface energies and morphologies were produced with varying the composition ratio of two different polyimides. For the pentacene film of 0.4 nm thick, the monolayer coverage of pentacene grains increases from 26.3% to 64.9% with increasing the surface energy of the underlying adhesion layer from 12.9 to 25.8 mJ/m^2. The surface energy of the adhesion layer is found to play a more dominant role on the initial growth of a pentacene film than the surface roughness. The field-effect mobility in the pentacene FET depends strongly on the monolayer growth of pentacene grains.

1. Introduction

Organic field-effect transistors (OFETs) have emerged as a class of essential components for flexible electronic devices because organic materials have inherent potential for large-area processes at low temperatures and the mechanical flexibility [1]. For example, building an array of the OFETs on a flexible substrate is a prerequisite for bendable displays, chemical sensors, and disposable chips [2–4]. Among several transistor parameters, the field-effect mobility is the primary one because it governs the dynamic properties such as the driving frequency and the response time for various types of applications. Previously, it was reported that the field-effect mobility in the OFET strongly depends on the layer-by-layer growth and the resultant crystallinity of an organic semiconductor film [5–8]. Therefore, it is very important to control the initial growth of an organic semiconductor layer on a variety of substrates for practical applications.

In general, the processing optimization, such as the substrate temperature and the deposition rate, is widely used to improve the crystalline quality of the film. It is also believed that the growth of organic semiconductors including pentacene into films depends strongly on the surface properties of a underlying gate insulator, such as the surface energy and the morphological roughness, in bottom-gate OFETs from the viewpoints of the nucleation rate and the dimensional growth. A number of physically and chemically modified surfaces were used to enhance both the alignment and the crystallinity of the pentacene molecules in films on gate insulators [9–12]. In certain cases, either an extra self-assembled monolayer [13–16] or a smoothing layer [17,18] between the insulator and the pentacene film was introduced to alter the surface energy and/or the surface morphology. Nevertheless, a physical picture of the monolayer coverage during the pentacene film growth has not been fully described in terms of the surface properties of gate insulators so far.

In this work, we present a systematic study on the monolayer coverage in pentacene films on three types of adhesion layers. Two different polyimide (PI) materials, one of which is generally used for the vertical alignment and the other for the horizontal alignment of liquid crystal (LC) molecules, were adopted to prepare different types of adhesion layers. The surface properties of the adhesion layer can be varied with the composition ratio of two PIs. Our experimental results for the contact angles and the atomic force microscopic (AFM) images revealed that the monolayer coverage of pentacene grains increases linearly with increasing the surface energy of the adhesion layer. It is found that the enhancement in the field-effect mobility of the pentacene FET is directly related to the monolayer coverage of pentacene grains in the early growing stage.

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* Corresponding author. Tel.: +82 2 320 1488; fax: +82 2 320 1193.
E-mail address: jschoi@wow.hongik.ac.kr (J.S. Choi).

0038-1101/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.sse.2010.08.004

2. Experiment

Two different PI materials were dissolved in *n*-methyl-2-pyrrolidone (NMP) solvent with the concentration of 0.8 wt.% to form solutions for polymeric adhesion layers. One of the PIs is AL-00010 (Japan Synthetic Rubber Co.) and the other is SE-7492 (Nissan Chemical Industries). AL-00010 is a widely used material for vertical alignment of LCs [19], which has hydrophobic alkyl side chains, while SE-7492 is generally used for horizontal alignment of LCs because of its hydrophile property determined by the main chain backbone [20]. The chemical structures of AL-00010 and SE-7492 are shown in Fig. 1. Five different PI solutions were prepared; the composition ratio of SE-7492 to AL-00010 was varied as 0%, 20%, 50%, 80%, and 100%. For the fabrication of the FET, a 50-nm-thick Al gate electrode was thermally deposited onto a glass substrate through a shadow mask. Poly(4-vinylphenol) (PVP, Aldrich) with a cross-linking agent was spin-coated on the top of the gate electrode and baked at 200 °C for 1 h in a dry oven, producing a cross-linked PVP (cPVP) film with the thickness of 300–310 nm [21]. Each adhesion layer was formed on the cPVP gate insulator via simple spin-coating from each solution and baked at 180 °C for 1 h 30 min in a dry oven, followed by precuring at 90 °C for 5 min. The thicknesses of the adhesion layers were measured as about 10 nm by using an ellisometer. Note that the cPVP film is chemically resistant to NMP solvent. Pentacene was purchased from Tokyo Chemical Co., Ltd. and was used without further purification. A 30-nm-thick pentacene layer was thermally deposited at a rate of 0.1 nm/s onto the adhesion layer through a shadow mask, under a chamber pressure of about 1.6×10^{-6} Torr. During the pentacene deposition, the substrate was kept at room temperature to prevent any temperature declination among different substrates. Bottom-gate/top-contact OFETs were constructed using 50-nm-thick Au source and drain electrodes, where the channel length (L) and width (W) were 100 and 500 μm, respectively. Each deposition process for OFETs having different adhesion layers was simultaneously performed in the same batch to avoid undesired variations in the fabrication conditions. And the samples were fabricated several times to analyze the effects of the surface properties of an adhesion layer on the growth of a pentacene layer and the resulting performance of the pentacene FET.

The surface energy of each adhesion layer was evaluated from the contact angle measured using a contact angle meter GSA10 (KRUSS Co., Ltd.). The surface morphologies of the adhesion layers and the pentacene films on each adhesion layer were examined by AFM (XE150, PSIA Inc.). The dielectric properties of the gate insulators and the electrical characteristics of the pentacene FETs were measured with an impedance analyzer (HP 4192A, Agilent Technologies) and a semiconductor analyzer (EL 421C, Elecs Co.), respectively.

3. Results and discussion

We first analyze the surface properties of the adhesion layers formed on the cPVP gate insulator. From the distilled-water contact angle on each adhesion layer, the surface energy of the adhesion layer (γ_P) was evaluated by the following equation,

$$\gamma_P = \frac{\gamma_W}{4}(1 + \cos\theta_0)^2$$

where γ_W is the water surface free energy (73.0 mJ/m^2) and θ_0 is the measured contact angle at equilibrium [22]. Fig. 2a shows the variation in the surface energy of the adhesion layer according to the composition ratio of SE-7492 to AL-00010 in PI solutions. The surface energy is found to increase monotonically with increasing the composition ratio of SE-7492 in the adhesion layer, where the standard deviation was less than 3% from the samples manufactured three times. This surface energy variation is thought to originate from the hydrophilic nature of SE-7492 with respect to AL-00010 because a hydrophilic solid surface generally makes a low contact angle with a distilled water drop. From the insets of

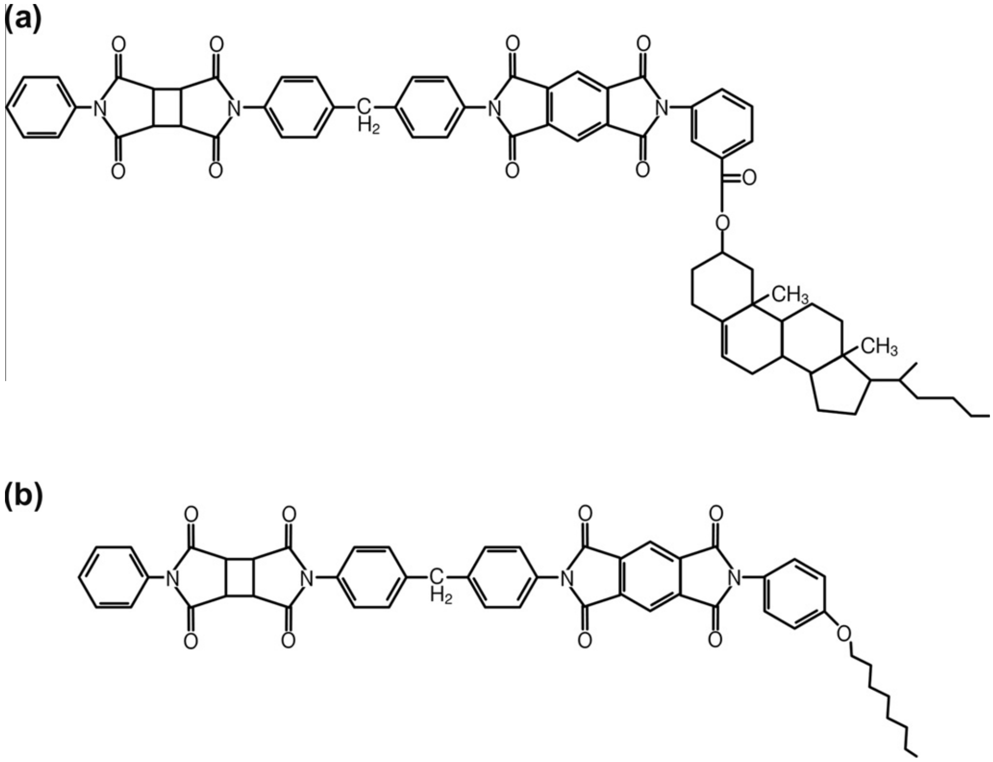

Fig. 1. The chemical structures of (a) AL-00010 and (b) SE-7492.