Thin-film field-effect transistors of copper phthalocyanine on a rubbed polyethersulfone

Hyun Gi Kim [a,c], Jung Soo Jang [a,c], Sung-Taek Hur [b,c], Suk-Won Choi [b,c,*], Sung Soo Kim [a,c], Hiroyuki Tada [d], Hideo Takezoe [d], Ken Ishikawa [d]

[a] Department of Chemical Engineering, Kyung Hee University, Yongin, Gyeonggi-do 446-701, Republic of Korea
[b] Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Yongin, Gyeonggi-do 446-701, Republic of Korea
[c] Regional Innovation Center-Components and Materials for Information Display, Kyung Hee University, Yongin, Gyeonggi-do 446-701, Republic of Korea
[d] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152-8552, Japan

ARTICLE INFO

ABSTRACT

We fabricated copper phthalocyanine (CuPc) thin-film field-effect transistors (FETs) on a rubbed flexible polyethersulfone (PES) substrate. Rubbing the PES film induced a unidirectional orientation of CuPc crystallites, which were oriented perpendicular to the rubbing direction. Favorable conditions for fabricating a CuPc FET were determined after fabricating CuPc FETs of two different types and evaluating their output performance. Well-aligned CuPc crystallites along the direction connecting source and drain electrodes can play an important role in improving the output performance of the fabricated FETs.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Organic field-effect transistors (OFETs), which were fabricated using organic semiconductor (active) materials, were first developed in the middle of the 1980's [1]; subsequently, OFETs have been intensively researched in both academia and industry. Thus far, several organic semiconductor materials have been proposed and reported as promising active materials for OFETs [2]. Among them, copper phthalocyanine (CuPc), which is grown in columnar structures by π–π stacking, is considered as a good organic active material because of its thermal stability, non-toxicity, and good field-effect properties [3].

Well-aligned active layers are also desirable for improving the electric performance of organic semiconductor devices; this is because the charge transport in organic materials occurs via the hopping mechanism, which effectively depends on the degree of the orbital overlap between molecules [4]. Therefore, several alignment treatments for active layers such as mechanical drawing [5], nanoimprinting [6], and rubbing treatment [7] have been reported. The rubbing treatment, in particular, is a well-known technique that is used to obtain the unidirectionally anisotropic orientation of CuPc deposited films [8].

While the performance of organic semiconductor devices is not comparable with that of inorganic semiconductor devices, organic semiconductor devices offer a considerable number of advantages; i.e., they are flexible, can be manufactured economically, and are compatible with plastic substrates [9]. These advantages have motivated many researchers to intensively study OFETs fabricated on flexible plastic substrates.

In this study, we fabricated CuPc FETs on a rubbed flexible polyethersulfone (PES) substrate. Rubbing the PES layers induced a unidirectional orientation of the CuPc layers, which were oriented perpendicular to the rubbing direction. Well-aligned CuPc crystallites along the direction connecting source and drain electrodes could play an important role in improving the output performance of the fabricated FETs.

2. Experimental procedures

Fig. 1 shows the schematic of the procedures used to fabricate CuPc FETs. First, a flexible PES substrate (Glastic, i-components Co. Ltd.) with a thickness of 200 μm was cut into pieces and ultrasonically cleaned with isopropyl alcohol (IPA) for 10 min. Then, the pieces were sufficiently dried at 100 °C in an oven. Gold was vacuum deposited on one side of pieces through a shadow mask to form source and drain electrodes. The mask defined the channel length (L) and channel width (W), which were 25 mm and 1 mm, respectively. A typical test

* Corresponding author. Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Yongin, Gyeonggi-do 446-701, Republic of Korea.
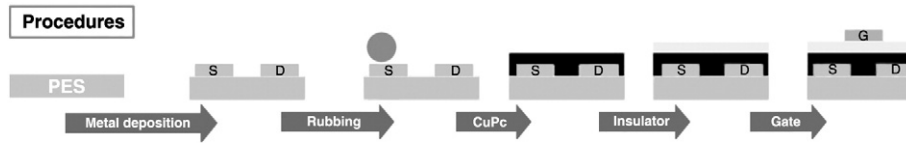E-mail address: schoi@khu.ac.kr (S.-W. Choi).

Fig. 1. Schematic of the procedures to fabricate CuPc FETs on rubbed PES.

piece (15 mm×15 mm) had 10 source–drain pairs on its surface. Next, the substrate with source and drain electrodes was rubbed with a cotton velvet cloth (Agehara velvet, #8007-090). Rubbing treatment of the substrates was performed using a commercial rubbing machine (EHC, RM-50) for liquid crystal alignment. In order to obtain a highly aligned CuPc, an extremely high rubbing pressure was needed compared to that for liquid crystal alignment. Purchased CuPc (Aldrich, 97%) was purified three times by carrier-gas sublimation and vacuum deposited onto the rubbed PES substrate using a bell-jar evaporator (background pressure, ~3×10⁻⁵ Pa). A CuPc film was deposited on the heated plastic substrate (100 °C). Film thickness was monitored by a crystal thickness monitor (Leybold Inficon, XTM/2) and calibrated ex situ by a stylus surface profiler (Sloan Technology, Dektak3ST). The deposition rate and final thickness of the CuPc film were controlled manually at around 0.6 Å/s and 50 nm, respectively. CYTOP (Asahi Glass Co. Ltd.) was spin-coated with a thickness of

400 nm as a gate dielectric layer, and finally, aluminum was deposited as the gate electrode.

The orthogonal directions of the induced orientation to the rubbing directions were characterized by absorption anisotropy from polarized ultraviolet (UV) absorption spectroscopy and an atomic force microscopy (AFM) image. Favorable conditions for fabricating a CuPc FET were determined after fabricating CuPc FETs of two different types and evaluating their output performance. The FET characteristics were examined in air at room temperature using tungsten probes and an Agilent 4156 C semiconductor parameter analyzer.

3. Results and discussion

Figs. 2(a) and (b) show the surface morphologies on untreated and rubbing-treated PES films, respectively, obtained by using AFM. On the untreated surface, no preferred direction was observed;
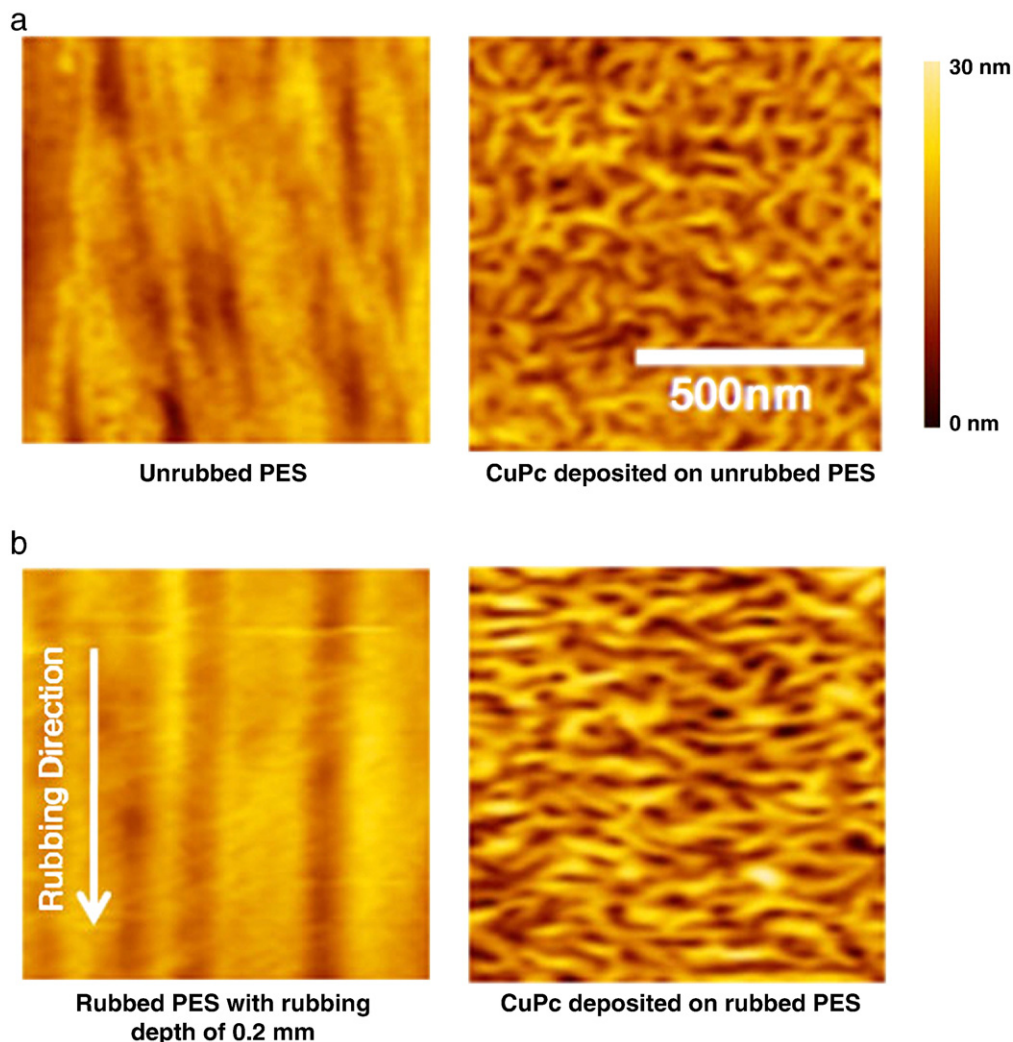

Fig. 2. AFM images of surface morphologies on (a) untreated and (b) rubbing-treated PES films.

consequently, in the case of CuPc deposited on the unrubbed PES substrate, the CuPc nanocrystallites were grown randomly. By contrast, fine, nano-groove-like structures were induced on the rubbing-treated PES surfaces according to the rubbing direction. In the case of CuPc deposited on the rubbed PES substrate, the CuPc films exhibited a very regular morphology consisting of uniaxially oriented nanocrystallites.

Fig. 3 shows the optical absorption of a CuPc film measured for parallel (∥) and perpendicular (⊥) orientation of the incident polarized light with respect to the rubbing direction of the PES film and the corresponding surface topography of the CuPc thin film deposited on the PES substrate. In the case of CuPc deposited on the unrubbed PES substrate, absorption anisotropy was not observed because the CuPc nanocrystallites were grown randomly, as shown in Fig. 3(a). On the other hand, in the case of CuPc deposited on the rubbed PES substrate, distinct absorption anisotropy was observed between the parallel and perpendicular directions because of a highly uniaxial orientation for CuPc on the rubbed PES substrates, as shown in Fig. 3(b). Namely, although clear absorption anisotropy was not observed on rubbed bare PES, distinct absorption anisotropy was induced between the parallel and perpendicular directions after the CuPc deposition on the rubbed PES substrates.

The absorption peak for light polarized along the direction parallel to the rubbing direction (x-direction) was higher than that perpendicular to the rubbing direction (y-direction). From these observations, surprisingly, it can be considered that the π-stacking direction of CuPc (long axis of nanocrystals) lies perpendicular to the rubbing direction, i.e., parallel to the crystalline lamellae of the rubbed PES substrate. Similar phenomena have been also observed that the π-stacking direction (long axis of nanocrystals) of zinc phthalocyanine (ZnPc) lies perpendicular to the rubbing direction in the case of ZnPc on the rubbed polycarbonate (PC) film [10]. However, these phenomena were discrepant from the previous Ofuji's reports [8]; the nanocrystallites of CuPc could be unidirectionally aligned parallel to the rubbing direction in the case of the rubbed silicon wafers. Thus, the orientation mechanism of CuPc on rubbed PES substrates can be different from the mechanism on the rubbed silicon wafers; unidirectionally stretched crystalline lamellae of the rubbed PES surface can play an important role in aligning nanocrystallites of CuPc in our case. The details on the effect of stretched crystalline lamellae of plastic substrates will be reported soon.

In general, the rubbing strength can be expressed in terms of the rubbing depth; the deeper the rubbing depth, the higher is the rubbing strength [11]. Figs. 3(b) and (c) show the polarized absorption spectra of CuPc films on PES with rubbing depths of 0.1 mm and 0.2 mm, respectively. Here, we defined the degree of anisotropy (dichroic ratio) as $A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the optical densities of the maximum absorption wavelength for polarizations parallel (x-direction) and perpendicular (y-direction) to the rubbing direction of the PES substrate, respectively. The higher the value of $A_{\parallel}/A_{\perp}$, the higher the anisotropy induced in the CuPc layer. The evaluated values of $A_{\parallel}/A_{\perp}$ for the PES substrate with rubbing depths of 0.1 mm and 0.2 mm were 2.047 and 2.334, respectively. Thus, the increase of the dichroic ratio measured at a maximum absorption wavelength with increasing rubbing strength results in a corresponding increase of the uniaxial orientation of CuPc.

We fabricated CuPc FETs with three different orientation structures between the source and the drain electrodes. (Type I, Type II and Type III), as shown in Fig. 4(a). Type I and II were fabricated with the CuPc films on rubbed PES, whose values of $A_{\parallel}/A_{\perp}$ were about 2.334, respectively. However, these two CuPc FETs show two orthogonal rubbing directions between the source and the drain electrodes. The π-stacking direction of CuPc (long axis of nanocrystals) was perpendicular to the rubbing direction, as described in the previous AFM result. Hence, the π-stacking directions of the CuPc crystallites were parallel (Type I) or perpendicular (Type II) to the direction from the source electrode to the drain electrode depending on the rubbing directions. By contrast, Type III was fabricated with the CuPc film on unrubbed PES, whose value of $A_{\parallel}/A_{\perp}$ was ca. 1.
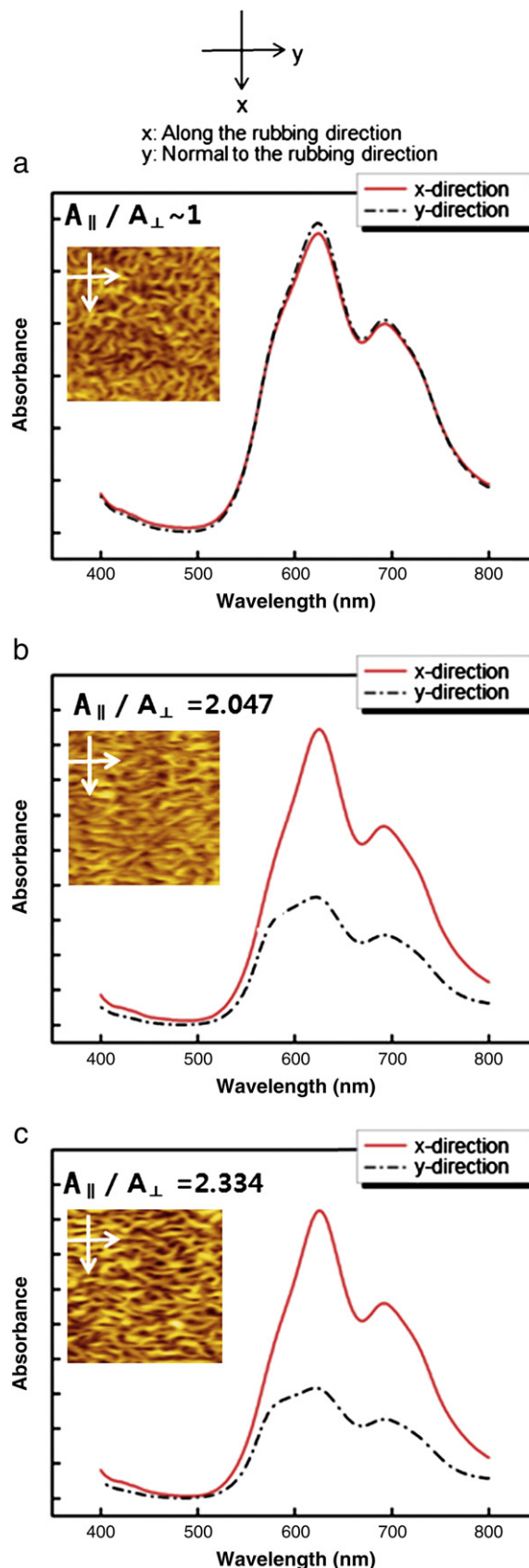

Fig. 3. (Color online) Optical absorption of a CuPc film for parallel (∥) and perpendicular (⊥) orientation of the incident polarized light with respect to the rubbing direction of the PES film and the corresponding surface topography of CuPc deposited on (a) the unrubbed PES substrate, (b) the rubbed PES substrate with rubbing depth of 0.1 mm, and (c) the rubbed PES substrate with rubbing depth of 0.2 mm.
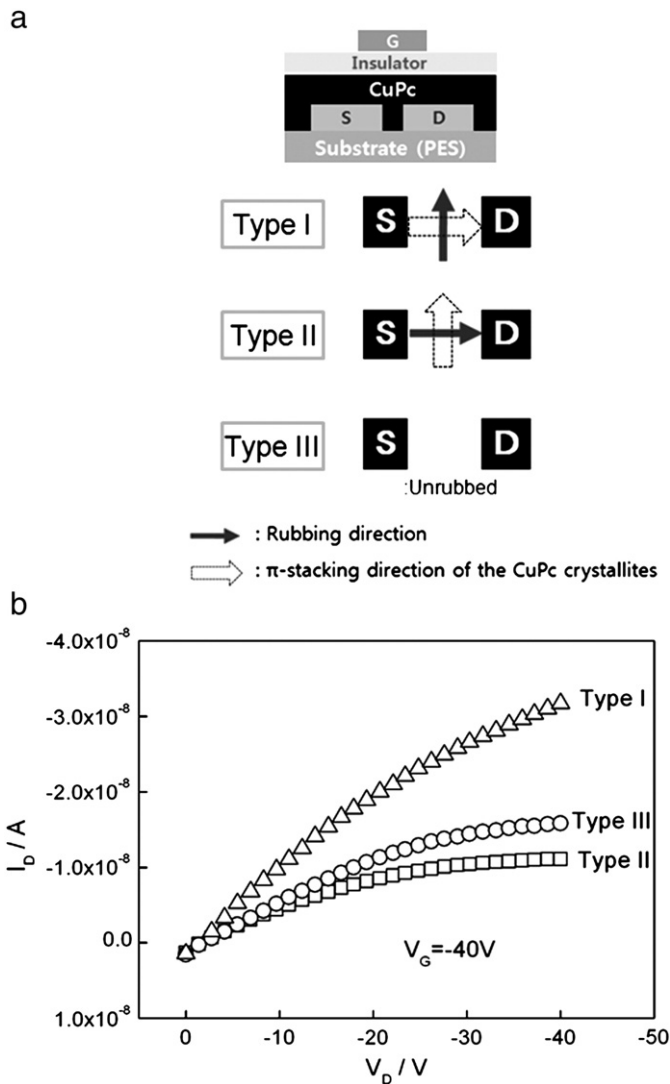
a

b

Fig. 4(b) shows the output characteristics of Type I-, Type II- and Type III-CuPc FETs. Type I device showed the best output characteristics among the three devices, as shown in Fig. 4(b). On the other hand, Type II device exhibited the worst output characteristic among the three devices. From comparing Type I with Type II, it was concluded that the π-stacking

direction of the CuPc crystallites grown along the direction from the source electrode to the drain electrode exhibits a good performance due to the favorable transport of charge carriers. In addition, from comparing Type I with Type III, FETs with a higher value of $A_{\parallel}/A_{\perp}$ showed better electric performance. Thus, well-aligned CuPc crystallites along the direction from the source electrode to the drain electrode can play an important role in improving the electric performance of the fabricated FETs.

4. Conclusion

In summary, we fabricated thin-film FETs with aligned CuPc on flexible plastic substrates. Rubbing the PES film induced a unidirectional orientation of the CuPc crystallites, which were oriented perpendicular to the rubbing direction on the PES film. Favorable conditions for fabricating a CuPc FET were determined after fabricating CuPc FETs of two different types and evaluating their output performance. It was found that well-aligned CuPc crystallites along the direction from the source electrode to the drain electrode exhibited good output characteristics.

Acknowledgements

References

[1] K. Kudo, M. Yamashina, T. Moriizumi, Jpn. J. Appl. Phys. 23 (1984) 130.
[2] M. Mas-Torrent, P. Hadley, S.T. Bromley, X. Ribas, J. Tarres, M. Mas, E. Molins, V. Jaume, C. Rovira, J. Am. Chem. Soc. 126 (2004) 8546.
[3] R. Zeis, T. Siegrist, C. Kloc, Appl. Phys. Lett. 86 (2005) 022103.
[4] S. Liu, W.M. Wang, A.L. Briseno, S.C.B. Mannsfeld, Z. Bao, Adv. Mater. 21 (2009) 1217.
[5] C. Wittmann, P. Smith, Nature 352 (1991) 414.
[6] Z.J. Zheng, K.H. Yim, M.S.M. Saifullah, M.E. Welland, R.H. Friend, J.S. Kim, W.T.S. Huck, Nano Lett. 7 (2007) 987.
[7] M.L. Swiggers, G. Xia, J.D. Slinker, A.A. Gorodetsky, G.G. Malliaras, R.L. Headrick, B.T. Weslowski, R.N. Shashidhar, C.S. Dulcey, Appl. Phys. Lett. 79 (2001) 1300.
[8] a) M. Ofuji, K. Ishikawa, H. Takezoe, K. Inaba, K. Omote, Appl. Phys. Lett. 86 (2005) 062114;
b) T. Manaka, K. Taguchi, K. Ishikawa, H. Takezoe, Jpn. J. Appl. Phys. 39 (2000) 4910;
c) M. Ofuji, K. Inaba, K. Omote, H. Hoshi, Y. Takanishi, K. Ishikawa, H. Takezoe, Jpn. J. Appl. Phys. 41 (2002) 5467;
d) M. Ofuji, K. Inaba, K. Omote, H. Hoshi, Y. Takanishi, K. Ishikawa, H. Takezoe, Jpn. J. Appl. Phys. 42 (2003) 7520.
[9] J.H. Lee, S.H. Kim, G.H. Kim, S.C. Lim, H. Lee, J. Jang, T. Zyung, Synth. Met. 139 (2003) 445.
[10] M. Brickmann, S. Pratontep, C. Chaumont, J.-C. Wittmann, Macromolecules 40 (2007) 9420.
[11] N.A.J.M. van Aerle, M. Barmentlo, R.W.J. Hollering, J. Appl. Phys. 74 (1993) 3111.