High-quality crystalline rubrene thin film on electron-irradiated PS

Hyeok Moo Lee, Yong Nam Kim, Jae Joon Kim and Sung Oh Cho
Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-Dong Yuseong-Gu, Daejeon, Republic of Korea
Corresponding author: socho@kaist.ac.kr

1. Introduction

From much of recent works, it was found that charge carrier transport in organic thin film transistors (OTFTs) is strongly affected by the first several semiconductor monolayers next to the semiconductor insulator interface [1]. Among the interfacial factors, insulator surface roughness, surface energy, surface polarity and dielectric constant of dielectrics are considered as important parameters to affect performance of the OTFT. Thus, recently, a lot of efforts to optimize the conditions of surface of dielectrics using various treatment techniques have been performed. Among these techniques, surface modification using polymeric materials is very simple and qualities of polymer surface are hardly affected by preparation conditions. However, surface chain segmental motions near the glass transition temperature disrupts the growth of large-grain morphologies leading low carrier mobility [2]. Thus, there is limitation in temperature to fabricate the organic semiconductor active layer.

Here we present a strategy to fabricate high-quality crystalline rubrene thin film using combination of abrupt heating technique and electron irradiation of common homopolymer dielectrics of polystyrene (PS). Electron irradiation induces crosslinking of hydrocarbon chains of PS that restricts chain segmental motion even at the high temperature of 170 ℃. Through this method, high quality crystalline rubrene film can be remarkably rapidly produced on PS/SiO_2 bilayer dielectrics in just 1 min.

2. Methods and Results

2.1 Experimental Methods

PS films were prepared by spin-coating PS (M_W = 2,500–200,000 g/mol) dissolved in chlorobenzene on SiO_2 dielectric surfaces underlying heavily doped n-type silicon substrates. Rubrene powder (sublimed grade) was purchased from Sigma-Aldrich Inc. Amorphous rubrene thin films were deposited on 100 nm thick PS/SiO_2 dielectric surfaces that were kept at room temperature through thermal evaporation in a vacuum chamber with a base pressure below 10^{-5}. After the deposition, the as-deposited rubrene thin films were abruptly heated by placing the samples onto a preheated hot plate and taken out of the plates after the abrupt heating process.

2.2 Crosslinking of electron-irradiated PS

Figure 1 shows the crosslinking ratio of PS as function of electron irradiation fluence. PS is one the crosslinking type materials by the electron irradiation, thus the degree of crosslinking of PS increased with electron irradiation. On the other hand, it is well known that the glass transition temperature of polystyrene can be elevated with increase the degree of crosslinking [3]. Therefore, it can be expected that the glass transition temperature of PS should be increased with electron irradiation that leading reduce the segmental dynamics of the polymer chains even at the high temperature.

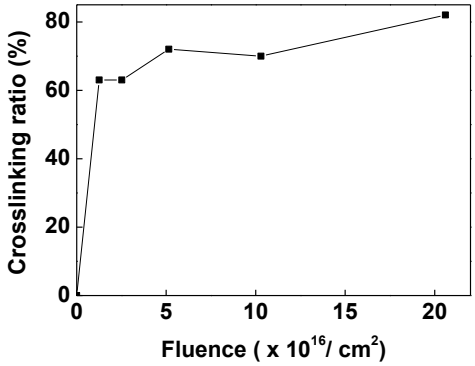

Fig. 1. Crosslinking ratio of polystyrene as function of electron irradiation dose

2.2 Rubrene crystalline film on electron-irradiated PS

The polarized optical microscopy (POM) image of rubrene thin films fabricated on the PS and electron-irradiated PS modified substrate by abrupt heating shows that electron irradiation is crucial to produce the high-quality crystalline film (Fig. 2). When non-irradiated was PS used, although amorphous rubrene film abruptly heated at optimized temperature of 170 ℃, only a small amount of dendritic-like structures appeared. The glass transition temperature of PS is about 95 ℃, thus this undesired structures might be caused by chain segmental motion of PS at the high temperature. The chain dynamics of the polystyrene surface disrupt crystallization and molecular ordering at the initial layer. Interestingly, however, we found the formation of platelet crystallites inside the amorphous rubrene film when the electron-irradiated PS modified substrate was used. In addition, the rubrene crystallites

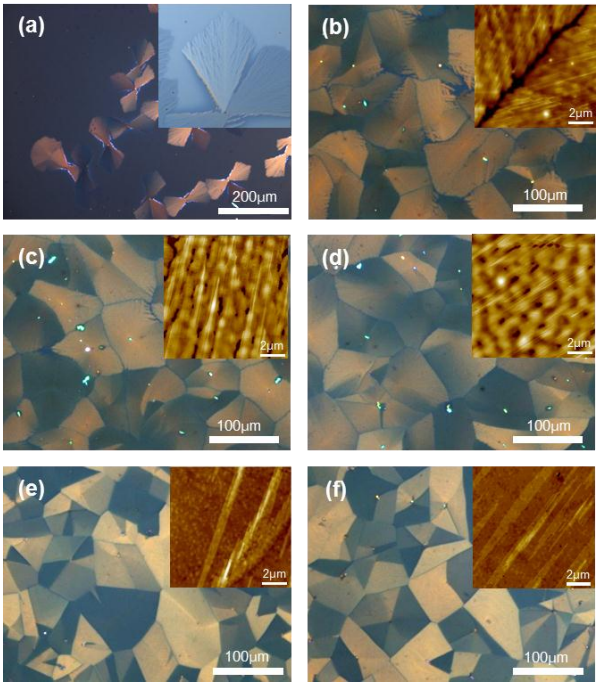

Fig. 2 POM images of the crystalline rubrene thin films fabricated by the abrupt heating process on (a) pristine PS and electron-irradiated PS modified SiO_2 with fluence of (b) 1 x 10^{16} cm^{-2}, (c) 2 x 10^{16} cm^{-2}, (d) 4 x 10^{16} cm^{-2}, (e) 2 x 10^{17} cm^{-2} and (f) 4 x 10^{17} cm^{-2}. The inset of (a) is the magnified optical image of dendritic-like structures and the inset of (b)-(f) is the corresponding AFM image

gradually changed from dendritic-like structures to continuous platelet structures with the increase of electron irradiation dose. Finally, the morphology features of the crystalline film measured by POM and AFM shows that high-quality rubrene crystalline film were produced, when the electron irradiation dose was large than 2x10^{17} cm^{-2}. These results indicate that crosslinks in PS induced by electron irradiation restricts chain segmental mobility, and thus high-quality crystalline film can be formed at even high temperature. In addition, crosslinking ratio of PS should be larger than 80 % to fabricated high-quality crystalline film.

2.2 Crystallinity of the rubrene crystalline film on electron-irradiated PS surface

2D GIXD patterns of rubrene crystalline film fabricated on irradiated-PS modified dielectrics shows many strong and sharp reflection spots along the q_z at a given q_{xy} (Fig. 3b). This result indicates that the rubrene crystalline film consisted with orthorhombic crystallites which are highly ordered in both vertical and lateral directions [4]. The 2D GIXD pattern further reveals that the c-axes of all the crystals in the film are uniaxially aligned perpendicular to the substrate surface, while *ab* planes of all the crystals in the film are perfectly oriented parallel to the substrate surface, which is desirable to obtain high charge carrier mobilities [5].

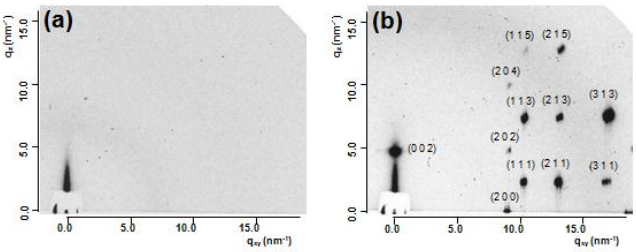

Fig. 3. Two dimensional GIXD patterns of (a) as-deposited rubrene film and (b) the crystalline rubrene thin films produced by abrupt heating at 170 ℃ for 30 sec on electron-irradiated PS modified SiO_2 (electron fluence: 2x10^{17} cm^{-2}).

3. Conclusions

We have presented a straightforward approach to fabricate high-quality crystalline rubrene thin film on electron-irradiated PS/SiO_2 dielectric surfaces. Electron irradiation induces the crosslinking of PS that restricts chain segmental motion. Thus, even at the high temperature, crystalline rubrene semiconductor thin films comprising large, interconnected single-crystalline grains can be controllably fabricated. We believe that our approach is very promising for practical applications of rubrene semiconductors to OTFTs

REFERENCES

[1] X. Sun, C.-A Di, and Y. Liu, Engineering of the dielectric-semiconductor interface in organic field-effect transistors, J. Mater. Chem. 20, p.2599, 2010.
[2] C. Kim, A. Facchetti, T. J. Marks. Polymer gate dielectric surface viscoelasticity modulates pentacene transistor performance. Science, 318, p.76, 2007.
[3] J. H. Glans, and D. T. Truner, Glass transition elevation of polystyrene by crosslinks, Polymer, 22, p.1540, 1981.
[4] J. A. Lim, et al., Self-organization of ink-jet-printed triisopropylsilylethynyl pentacene via evaporation-induced flows in a drying droplet. Adv. Funct. Mater. 18, p.229, 2008.
[5] G. Nan, X. Yang, L. Wang, Z. Shuai, Y. Zhao, Nuclear tunneling effects of charge transport in rubrene, tetracene, and pentacene. Phys. Rev. B 79, 115203, 2009.