

## Fabrication of Rubrene Thin Film Transistor on Polystyrene Irradiated by Electron Beam

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### 1. Introduction

Among many organic semiconducting materials, rubrene (5, 6, 11, 12-tetraphenyl-naphthalene) is one of the most ideal candidates. Sublimed grade rubrene is already commercially available and highly soluble in common solvents such as toluene or acetone, without using chloride-based harmful solvents or functionalizing of additional side chain groups to increase solubility [1]. Additionally, rubrene shows outstanding charge carrier mobility and enhanced stability in the form of an orthorhombic phased single-crystal [2]. However, for the real application, rubrene thin film transistors with high charge mobility and large area are desirable and for this, various dielectric materials are needed to be tested.

Here, we present an unprecedented method to fabricate high-crystalline rubrene TFTs by combining of the abrupt heating technique and the polystyrene buffer layer irradiated by electron beam. For this PS buffer layer, we irradiated electron beam of optimized fluences.

By electron beam irradiation, the hydrocarbon chains of PS were cross-linked without any initiators or agents, and chain segmental motions of PS were appeared at the irradiated area. Subsequently, abrupt heating of samples changed the crystalline phase of rubrene from as-deposited amorphous to orthorhombic phase only at irradiated samples without giving any damage to semiconductor.

### 2. Methods and Results

#### 2.1 Preparation of rubrene thin film transistors

PS layers were prepared by spin-coating of PS (Sigma Aldrich, Mw= 200000 g mol<sup>-1</sup>) dissolved in chlorobenzene on a SiO<sub>2</sub> (100 nm) gate dielectric underlying heavily doped n-type silicon substrate. After spin-coating, 30 keV electron beam is irradiated by a thermionic electron gun under a vacuum (a pressure less than 10<sup>-5</sup> torr) to induce the crosslinking of the coated PS. After electron beam irradiation, the samples were cleaned in isopropyl alcohol and dried under nitrogen follow. Amorphous rubrene film (20 nm) was then deposited by a thermal evaporation of rubrene powders (sublimed grade, Sigma-aldrich, Inc.) and subsequently the as-deposited rubrene thin films were abruptly heated by placing the samples onto a pre-heated hot plate in dark room. The abrupt heating process was carried out in ambient air at 170 °C for 90 sec.

#### 2.2 Characterization of crystal

POM images were captured using an Olympus BX51 microscope and the topographies were examined with an AFM (XE-70, Park Systems). The cross-linking ratio of irradiated PS is measured using gel permeation chromatography (Waters, Alliance 2690) in Korea Research Institute of Chemical Technology (KRICT).

#### 2.3 Measurements of OFET characteristics

The OFET characteristics were evaluated using a probe station (Semiconductor Characterization System 4200 SCS/F and Summit 11862B, Keithley and Cascade) under ambient conditions. The channel length and width is 50, 1000 μm each and the carrier motilities were extracted in the saturation regime using the equation based on parallel-plate model,  $I_D = \mu C_i (W/2L)(V_G - V_T)^2$ , where  $I_D$  is the drain current,  $C_i$  is the capacitance per unit area of the gate dielectric layer, and  $V_G$  is the gate bias voltage. The dielectric constant of electron irradiated PS is measured as 3.38 at the fluence of  $2 \times 10^{17}$  cm<sup>-2</sup> by the fabricated metal-dielectric-metal structures and calculated from the capacitor equation,  $C_i = k\epsilon_0 A/d$ , where  $k$  is dielectric constant,  $\epsilon_0$  is  $8.85 \times 10^{-12}$  F/m  $A$  is the size area and  $d$  is the thickness of dielectric.

#### 2.4 Fabrication Procedures

The fabrication procedure of patterned rubrene thin films is illustrated in Figure 1. First, PS layers were spin-coated on a 100 nm SiO<sub>2</sub> / Si substrate and subsequently, electron beam was irradiated. The samples with PS layers were then moved into the vacuum chamber and rubrene was thermally evaporated as amorphous phase. After rubrene deposition, as-deposited rubrene was thermally crystallized by placing samples on a hot plate in ambient condition. By this thermal crystallization induced by abrupt heating, rubrene was crystallized and rubrene thin films were fabricated.

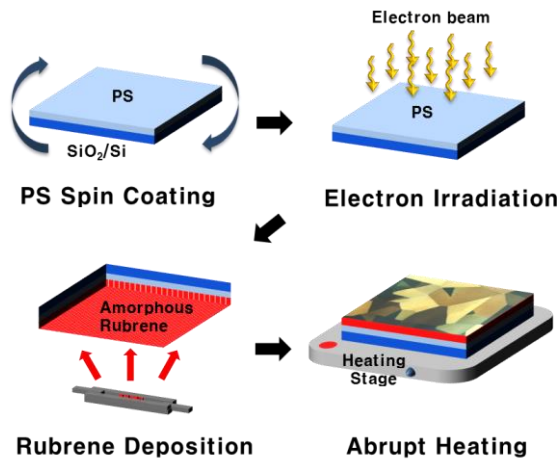


Fig. 1. A schematic illustration of the fabrication of rubrene thin films.

### 2.5 The Effect of Electron Irradiation Fluence to the Crystallization of Rubrene

To investigate the effects of electron beam irradiation to the crystallization of rubrene, we fabricated non-irradiated or differently irradiated PS layer without patterning. Figure 2a-d show the polarized optical microscopy (POM) images and corresponding atomic force microscopy (AFM) images of abruptly heated rubrene films on the PS/SiO<sub>2</sub> dielectrics irradiated at various electron fluences. The POM images of the crystalline rubrene films fabricated on the non-irradiated or irradiated PS layer indicate that the electron beam irradiation is crucial to produce the high-quality crystalline rubrene film. As Figure 2a, the abruptly heated rubrene films on the non-irradiated PS show non-crystallized amorphous rubrene films, even though it was heated at an optimum crystallization temperature of orthorhombic; 170 °C. This inadequate crystallization was caused by chain segmental motions of PS at a high temperature because PS has a low glass transition temperature of about 95 °C. During abrupt heating the temperature of PS is increased much higher than the glass transition temperature of PS, so vigorous chain movements of PS disrupt molecular ordering of the deposited semiconductors. However, we found that the quality of the crystalline rubrene films had dramatically improved when the PS buffer layers were irradiated with electron beams, which induced the crosslinking of the PS chains. Unlike amorphous rubrene film of Figure 2a, the POM and AFM images of Figure 2a-d show that the morphologies of rubrene thin films were gradually changed from amorphous phase to many adjacent plate pieces with increasing electron fluences.

Finally, when the electron fluence was as high as  $2 \times 10^{17} \text{ cm}^{-2}$ , the morphology features of the crystalline films measured by POM and AFM were very similar with those of high quality crystalline rubrene films growth on the bare SiO<sub>2</sub> surface [3]. The continuous crystalline rubrene films composed of domains of large

size and well faceted were created over the whole PS/SiO<sub>2</sub> surfaces. No color variation was observed within a single domain under POM investigation, suggesting that the domains were composed of a single crystalline grain. The average grain size was about 80 μm and the grains were interconnected with one another, as shown in the POM image of Figure 2d.

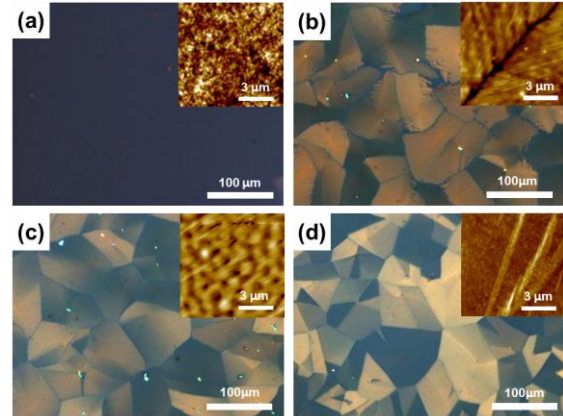


Fig. 2. POM images of crystalline rubrene thin films fabricated by an abrupt heating on the irradiated PS with different fluences; (a) pristine PS, (b)  $1 \times 10^{16} \text{ cm}^{-2}$ , (c)  $5 \times 10^{16} \text{ cm}^{-2}$ , and (d)  $2 \times 10^{17} \text{ cm}^{-2}$ . The insets are AFM images of the magnified image.

To analyze the cause and effect of crystalline morphology change as electron beam irradiation fluences, we measured the crosslinking ratio and the carrier mobility each. As shown in Figure 3a, crosslinking ratio of PS was increased as increasing electron beam irradiation fluence and reached about 80 % at  $2 \times 10^{17} \text{ cm}^{-2}$ . Because these increased crosslinking ratios imply that less polymeric chain movements or increased thermal stability [4], the crystalline structure of rubrene crystal on irradiated PS can be changed as Figure 2a-d. Also, Figure 3b displays the carrier mobility obtained from a typical rubrene TFTs fabricated with irradiated PS of various electron fluences. The amorphous rubrene on the pristine PS, shown in Figure 2a, exhibited very low charge carrier mobility (of the order of  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). However, as the electron fluence increased, rubrene crystallites changed from amorphous to continuous platelet structures and the carrier mobilities of the rubrene TFTs were increased. When the rubrene films completely composed of the high-quality platelet structures at an electron fluence of  $2 \times 10^{17} \text{ cm}^{-2}$ , the fabricated devices exhibited the highest performance with the saturated value of charge carrier mobility,  $0.90 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  under ambient conditions. Furthermore, it can be guessed that the saturation of charge carrier mobility shown at the fluence of  $4 \times 10^{17} \text{ cm}^{-2}$  was due to the saturation of crosslinking ratio with electron beam irradiation fluence higher than  $2 \times 10^{17} \text{ cm}^{-2}$ .

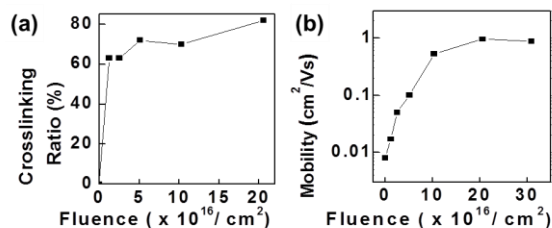


Fig. 3. (a) Crosslinking ratio and (b) charge carrier mobility as a function of the electron irradiation fluences of PS.

### 3. Conclusions

In summary, we have presented an unconventional approach to fabricate crystalline rubrene active layers and high quality rubrene thin film transistors. By using electron beam irradiation of PS and subsequent crystallization induced by abrupt heating, orthorhombic phase rubrene with high crystalline quality was fabricated successfully. By adjusting the fluence of electron irradiation, we could find optimized conditions for the rubrene thin film. We believe that this unprecedented technique using crosslinking of dielectric layer can be applied to not only PS but also many polymeric materials which can be cross-linked by electron beam. Furthermore, we could expect that by patterning of electron beam, in other words selective irradiation of electron beam, patterned rubrene with high resolution can be realized by adopting direct electron beam lithography techniques.

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