Supporting Information

Effect of Electron-Beam Irradiation on Organic Semiconductor and Its Application for Transistor-Based Dosimeters

Jae Joon Kim,[†] Jun Mok Ha,[†] Hyeok Moo Lee,[‡] Hamid Saeed Raza,[§] Ji Won Park,[†] and Sung Oh Cho*[,†]

[†]Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

[‡]Department of Informative Electronic Materials, LG Chemistry Research Park, Daejeon 305-738, Republic of Korea

[§]Safety Analysis Center (SAC), Pakistan Nuclear Regulatory Authority 42-C, 24th Commercial Street, Phase-II Ext., DHA, Karachi 75500, Pakistan.

[*] E-mail: socho@kaist.ac.kr.

1. Fabrication and electron beam irradiation of rubrene thin film transistors

A p-type organic semiconducting material, rubrene (sublimed grade, Sigma-Aldrich, Inc.), was evaporated and abruptly heated to make polycrystalline thin films. The rubrene powder was thermally evaporated in a vacuum chamber (pressure of less than 10^{-5} torr) onto carefully cleaned substrates of heavily doped n-type silicon with a 100 nm thermally grown silicone oxide (SiO_2) layer. After the deposition, the thermal crystallization of the rubrene molecules was carried out by placing the samples onto the 170 °C pre-heated hot plate in ambient conditions in a dark room. The heating process lasted for 180 s, and the whole substrate became covered with crystallites of orthorhombic rubrene. The samples were irradiated with a 30 keV electron beam generated with an assembled thermionic electron gun under a pressure of less than 10^{-5} torr. The lowest current density of 0.5 μA cm^{-2} and the cooling of the sample stage through the circulation of 0 °C coolant were used to minimize thermal damage during electron beam irradiation.

2. Measurement of electron fluence and dose

For the measurement of X-ray and gamma ray, dose is widely used after the calibration procedure. However, for other radiations in the forms of particles such as electron, proton, alpha, and neutron, fluence as well as dose is widely used due to easy and precise measurement. To evaluate irradiated electron dose of devices, first we measured fluence of accelerating electrons by the following equation: Φ = Number of electron / A = I·t / e·A, where Φ is the fluence, A is the irradiated area, I is the current of irradiated electron, e is the charge of an electron, and t is total irradiated time. Because most of electrons are accelerated to the sample and the amount of

charges are monitored by the current flow through the sample holder, we could know exact value of the fluence of electron beam. The measured fluence can be easily transformed to the dose by the following equation: $D = \Phi \cdot S / \rho$, where D is the dose, S is the stopping power, and ρ is the density of the material.

In addition, when electron beam is irradiated to a transistor, the doses or absorbed energies of accelerated electrons can be different as each layer of transistor; semiconductor, dielectric, and substrate. So the dose of the whole device must be defined as the sum of the dose of each layer with different stopping powers and densities. To determine stopping power of accelerated electron on each layer of transistor, we used Monte Carlo N-Particle (MCNP) transport code with the same experimental system of our sample. The calculated fluences and doses were shown at Table S1.

Type of Source	Layer	Dose per electron	Dose (Rad) at 10^{14} cm^{-2}	Dose (Rad) at 10^{15} cm^{-2}	Dose (Rad) at 10^{16} cm^{-2}	Dose (Rad) at 10^{17} cm^{-2}
Electron	Rubrene	2.20×10^{-10}	2.20×10^{4}	2.20×10^{5}	2.20×10^{6}	2.20×10^{7}
	SiO_2	1.11×10^{-10}	1.11×10^{4}	1.11×10^{5}	1.11×10^{6}	1.11×10^{7}
	Si	6.23×10^{-12}	6.23×10^{2}	6.23×10^{3}	6.23×10^{4}	6.23×10^{5}
Photon	Rubrene	1.21×10^{-13}	1.21×10	1.21×10^{2}	1.21×10^{3}	1.21×10^{4}
	SiO_2	6.44×10^{-14}	6.44	6.44×10	6.44×10^{2}	6.44×10^{3}
	Si	4.03×10^{-14}	4.03	4.03×10	4.03×10^{2}	4.03×10^{3}

Table S1. Calculated doses as the irradiation source type, layer, and fluences.

3. The effect of photon generated from the electron irradiation

When electron beam is irradiated to the material, not only electrons but the energetic photons can appear from acceleration and from the energy relaxation of excited electrons. So to investigate any differences of the material due to the electron beam, the absorbed dose of photons must be considered together. Therefore, we compared the absorbed dose of each layers of the accelerated electrons to the dose of photons in Table S1. It can be clearly shown that doses of photon irradiation are negligible and most of the changes of the semiconducting properties are originated from the electron irradiation.

4. The influence of source and drain electrodes

To prevent any influence by adding the gold source and drain electrodes during the irradiation, we irradiated the samples prior to the deposition of electrodes and thermally evaporated electrodes just prior to the electronic measurements. However, for the real application, the transistor dosimeters with source and drain are more preferred because of it enables in-situ measurement during irradiation. For this reason, the investigation about the effects of gold (or other metal) electrode addition is highly demanded and we calculated the simulation with and without gold layer on the top-surface of the rubrene layer and the results are shown on Table S2. By adding 20 nm of gold, very small amount of electrons are absorbed on gold layer compare to the rubrene and dielectric layer with the ratios of 1:20:10 approximately. Additionally, the dose of rubrene and silicon dioxide were slightly increased than the sample without gold layer. These slight increases of the electron doses can be explained by the stopping effect of gold layer. After

the electrons penetrates or interact with gold layer, the energies of electrons are decreased so the chance of absorption into the underlaid layers can be enhanced. Though the amount of dose increase was not high, we think that the additional consideration about areas of metal electrodes can make our dosimetry more accurate.

Structure	Layer	Dose per electron	Dose (Rad) at 10^{14} cm^{-2}	Dose (Rad) at 10^{15} cm^{-2}	Dose (Rad) at 10^{16} cm^{-2}	Dose (Rad) at 10^{17} cm^{-2}
Without Au Electrodes	Rubrene	2.20×10^{-10}	2.20×10^{4}	2.20×10^{5}	2.20×10^{6}	2.20×10^{7}
	SiO_2	1.11×10^{-10}	1.11×10^{4}	1.11×10^{5}	1.11×10^{6}	1.11×10^{7}
	Si	6.23×10^{-12}	6.23×10^{2}	6.23×10^{3}	6.23×10^{4}	6.23×10^{5}
With Au Electrodes on Top	Au	1.52×10^{-11}	1.52×10^{3}	1.52×10^{4}	1.52×10^{5}	1.52×10^{6}
	Rubrene	2.98×10^{-10}	2.98×10^{4}	2.98×10^{5}	2.98×10^{6}	2.98×10^{7}
	SiO_2	1.37×10^{-10}	1.37×10^{4}	1.37×10^{5}	1.37×10^{6}	1.37×10^{7}
	Si	5.93×10^{-12}	5.93×10^{2}	5.93×10^{3}	5.93×10^{4}	5.93×10^{5}

Table S2. The electron doses of the rubrene thin-film transistor with and without gold as different layers and fluences.

5. The effect of heating induced by the electron beam irradiation

Likewise other radiation and etching processes, the accelerated particles can increase the temperature of sample especially when it contains insulating materials like dielectric layer of organic transistor. This heating effect can be more severe at higher doses and at the organic

materials which are known to thermally less stable. Therefore, we placed sample on the metal plates with circulating cooling system of 0 ^{o}C and maintained the current density of the irradiated electrons as low as possible. In addition, we monitored the surface temperature of sample during the irradiation through the thermocouple connected to the surface of the sample. Even in case of the highest dose of 10^{7} rad, the temperature of the sample surface was lower than 30 ^{o}C. Considering together the high thermal-crystallization temperature of orthorhombic rubrene, 170 ^{o}C, the thermal effect is minor to change the performances of organic transistors.

6. Measurements of optical and electronical properties of organic semiconductors

The photoluminescence spectroscopy (LabRAM HR UV/Vis/NIR PL, Horiba Jobin Yvon) were measured at room temperature with a Xenon lamp of the 325 nm line as the excitation source. The UPS (Sigma Probe, Thermo VG Scientific) was measured in an ultrahigh vacuum (a pressure of less than 10^{-10} torr) with a radiation source of He I (21.2 eV) from a Helium discharge lamp. For the UPS measurement, 10 nm of Au was thermally evaporated onto the SiO_2/Si substrates prior to the rubrene deposition. To characterize the electrical properties, rubrene thin-film transistors were fabricated by depositing Au electrodes on the surface of rubrene thin films with a metal mask. Through this process, 20 nm thicknesses of gold electrodes with 1000 μm channel width, and 50 μm channel length were successfully added. The characteristics of the fabricated TFTs were evaluated using a probe station (Semiconductor Characterization System 4200 SCS/F and Summit 11862B, Keithley and Cascade) in ambient conditions. The mobilities and threshold voltages of the TFTs were obtained by measuring the

electronic characteristics of at least 10 different samples and using the equation: $I_D = (\mu WC_i / 2L)(V_G–V_T)^2$. I_D is the drain current, μ is the mobility, W is the width of the channel, C_i is the capacitance of unit area, L is the length of the channel, V_G is the gate voltage, and V_T is the threshold voltage.

7. The structure changes of rubrene thin films

The structural changes between pristine and irradiated rubrene thin films were observed with polarized optical microscope (POM) (Figure R1) and X-ray Diffraction (XRD) (Figure R2). With POM, the shape of overall crystals is maintained and brightness decrease was observed only at the highest dose of 10^7 rad. Since amorphous rubrene appears dark under POM, we could speculate that the rubrene became less ordered under high dose of irradiation. Additionally, XRD allowed for a more quantitative analysis of this interpretation. The irradiated crystals all showed only one phase of orthorhombic rubrene, the same as the pristine sample.

However, the positions of the (002) peak is slightly changed to lower angle at the highest dose of 10^7 rad and this corresponds to the increase of the molecular packing distance of orthorhombic rubrene. In addition, the peaks are started to be broaden at a dose of 10^6 and even more at 10^7 rad. This increase of FWHM (full width at half maximum) from XRD can be interpreted as the radiation-induced diversification of rubrene molecular system as we observed in other characterization methods of PL and UPS. Therefore, the structure changes of rubrene could be found at highly irradiated samples and from the decrease of peak position and increase of FWHM, the transformation of the molecular packing to less ordered structure can be guessed.

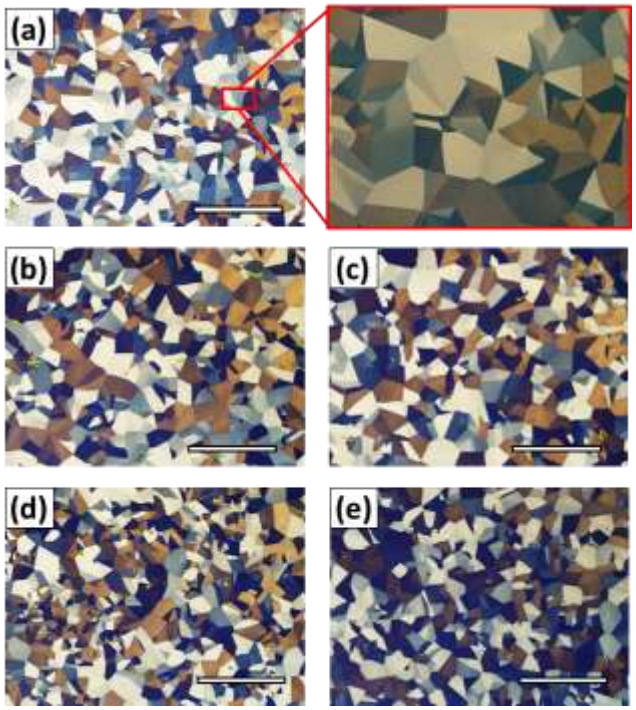

Figure S1. POM images of (a) pristine with the magnified view and (b-e) irradiated rubrene thin film. On the magnified image, well-faceted orthorhombic rubrene crystals are appeared. The dose of each is (b) 10^4, (c) 10^5, (d) 10^6, (e) 10^7 rad. Scale bar is 1 mm.

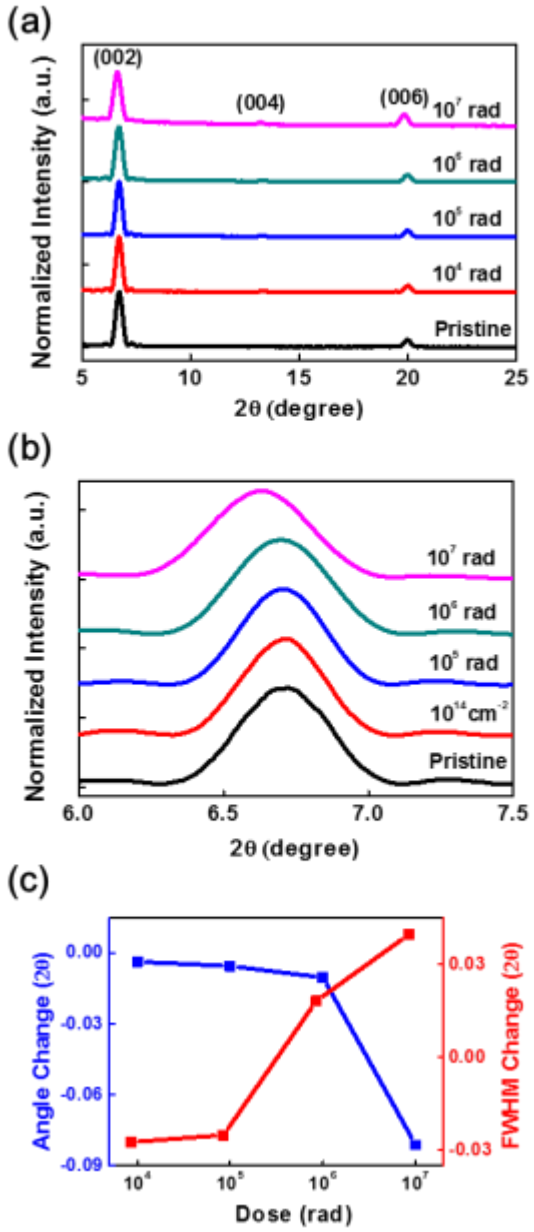

Figure S2. Crystalline properties of pristine and irradiated rubrene thin films. (a) XRD spectra measured on broad range. Only the peaks correspond to the orthorhombic phase rubrene are appeared. (b) Magnified view of (002) peak. (c) Angle and FWHM change of 2θ as a function of dose.