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Citation: *Appl. Phys. Lett.* **95**, 073303 (2009); doi: 10.1063/1.3211125

View online: <http://dx.doi.org/10.1063/1.3211125>

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Control of the molecular orientation of a 2,2'-bithiophene-9,9-dioctylfluorene copolymer by laser annealing and subsequent enhancement of the field effect transistor characteristics

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(Received 26 June 2009; accepted 31 July 2009; published online 20 August 2009)

We controlled the orientation of a 2,2'-bithiophene-9,9-dioctylfluorene (F8T2) copolymer spin-coated film on a polycarbonate substrate using a laser-annealing technique and demonstrated an enhancement of the field-effect transistor characteristics. We used a semiconductor laser, having a lasing wavelength of $\lambda=405$ nm, with a small spot size of 400 nm. Using polarizing optical microscopy and x-ray diffraction analysis, we confirmed enhancement of the orientation of the molecular chains of F8T2, along the laser scanning direction. Following laser annealing, the field-effect hole mobility resulted in a value of $\mu=1.6\times 10^{-3}$ cm²/V s, which is about three times higher than that of the unannealed sample. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3211125]

Conjugated polymers have unique semiconducting and photophysical properties and have therefore attracted significant interest for their application as active materials in organic optoelectronic devices including organic field-effect transistors (OFETs),^{1,2} organic light-emitting diodes (OLEDs),³ and organic solar cells (OSCs).⁴ To enhance these device characteristics, control of the molecular orientation is one of the fundamentally most important issues⁵ and many attempts have been made to achieve highly ordered-structures using, for example, rubbing^{6,7} and friction transfer deposition techniques.^{8,9} Although these mechanical treatments resulted in a significant enhancement in the device characteristics, more sophisticated methods are required to realize higher molecular orientation, focusing on noncontact, large area uniformity, and rapid mass production with high controllability. In addition, we are interested in orientation techniques applicable to low temperature processes since plastic substrates, which require process temperatures of typically less than 200 °C, are indispensable for plastic based flexible devices.

A laser-annealing method, traditionally used in the conversion of an amorphous Si film to a polycrystalline film,¹⁰ is one of the potential methods that could be used. However, there are very few reports in the literature related to the laser annealing of organic materials. Nakayama *et al.*¹¹ demonstrated the recrystallization and growth of a large crystal of a copper phthalocyanine (CuPc) derivative with the preferred orientation, by laser annealing. Furthermore, Gaffo *et al.*¹² demonstrated molecular rearrangement of Langmuir-Blodgett (LB) films by laser annealing, although this simply resulted in the destruction of the *J* aggregates. Hitherto, no successful attempts have been reported on controlling molecular alignment to obtain enhanced electrical characteristics such as producing high carrier mobilities in OFETs.

In this letter, we apply the laser-annealing technique, using a very small irradiation area, to organic semiconducting polymer layers formed on polycarbonate plastic substrates.

We demonstrate here that highly focused laser annealing is a promising technique for inducing molecular orientation at low temperatures. We selected a 2,2'-bithiophene-9,9-dioctylfluorene copolymer (F8T2) as an active layer (Fig. 1) since F8T2 is a liquid crystalline main-chain polymer that can relax without the occurrence of surface cracks during heat impingement. Furthermore, due to the presence of the fluorene and bithiophene moieties, it provides excellent electrical characteristics in the polymer films. These characteristics include the presence of rigid conjugated segments, which provide high charge transport ability, two long octyl alkyl chains providing good solubility in various kinds of solvents, and thermotropic liquid crystalline characteristics allowing tight packing via a self-assembling nature. However, in order for the main-chain orientation of F8T2 to occur by the rubbing technique, a temperature range of 275–285 °C (Ref. 6) is required while a temperature of 230 °C (Ref. 13) is needed for it to occur by the friction transfer deposition technique. This is due to the high intrinsic liquid crystal transition temperature $T_L=274.2$ °C. Subsequently, these high temperature treatments exceed the thermal resistance of the

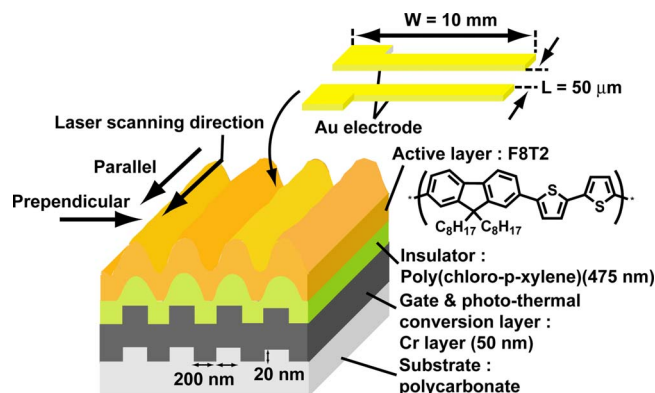


FIG. 1. (Color online) Schematic view of the structure of the device used for laser annealing and the molecular structure used in this experiment. Source/drain electrodes configuration and substrate shape having lines and spaces are shown. Laser scanning direction and x-ray diffraction are indicated as arrows.

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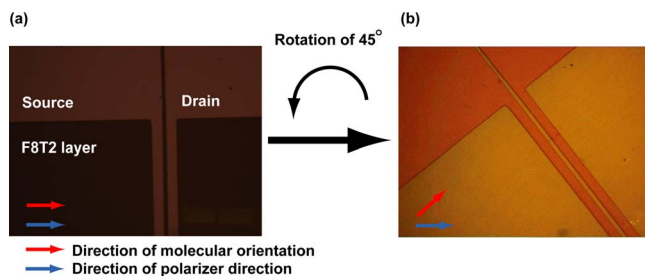


FIG. 2. (Color online) Polarization micrograph under cross-nicol condition: angle between laser scanning direction and polarizer, (a) 0° and (b) 45° .

conventional plastic substrates, leading to serious obstacles for practical device applications.

Figure 1 shows the cell configuration for laser annealing. In this study, in order to clarify the effect of molecular orientation from the standpoint of electrical characteristics, we incorporated the FET architecture as shown in Fig. 1. A 50-nm-thick Cr layer was deposited in vacuum onto a polycarbonate substrate having spiral grooves with a line and space (L/S) of 200 nm and a depth of 20 nm. The Cr layer has two roles: a photothermal converting layer during laser annealing and a gate electrode for the FET operation. Next, a 475-nm-thick poly(chloro-*p*-xylylene) dielectric layer¹⁴ was deposited onto it and a 30-nm-thick F8T2 was spin coated on as an active layer.

Laser annealing was conducted with a DVD-TESTER (LM330A, Shibasoku) under atmospheric conditions. The emission wavelength was set at $\lambda = 405$ nm, which is mostly absorbed by the Cr layer and is virtually unabsorbed by the F8T2 layer. Here, the output power and scanning speed were 3.5 mW and 4.5 m/s, respectively, and the exposure time was about 2.2 ms/cm. Finally, 100-nm-thick Au electrodes were deposited as source/drain electrodes through a shadow mask, by vacuum deposition. The channel length (L) and width (W) were 50 μm and 10 mm, respectively. FET measurements were performed in vacuum ($< 5 \times 10^{-3}$ Pa) using a semiconductor parameter analyzer (B1500A, Agilent). We scanned the gate bias between $V_{\text{gs}} = 10$ and -20 V. The optical anisotropy was confirmed by using a polarizing optical microscope (POM), under cross-nicol and open-nicol conditions and by rotating the substrates. Molecular orientation was investigated by both in-plane and out-of-plane XRD methods at the Japan synchrotron radiation research (BL46XU, SPring-8) with an x-ray wavelength of 0.1 nm. Here, the out-of-plane XRD was measured using a conventional θ - 2θ method and the in-plane XRD was measured at a fixed incident angle and at a take off angle of 0.12° .

Figure 2 shows POM images of the FET device after the treatment of laser annealing under the crossed-nicol condition. We observed a dark image when the direction of the laser annealing was parallel to the polarizer (a), which then became a bright image when the laser scanning direction was set at 45° under the crossed-nicol condition (b). This birefringence behavior clearly indicates the uniaxial orientation of F8T2, following the laser annealing.

Figures 3(a) and 3(b) show the out-of-plane and in-plane XRD patterns. Each pattern was measured perpendicular to and parallel to the laser scanning direction (Fig. 1). For comparison, a spin-coated F8T2 with no laser annealing was also measured. The peak at $q = 3.67 \text{ nm}^{-1}$ can be attributed to a layered distance (d_{100}) of 1.7 nm [Fig. 3(a)], corresponding

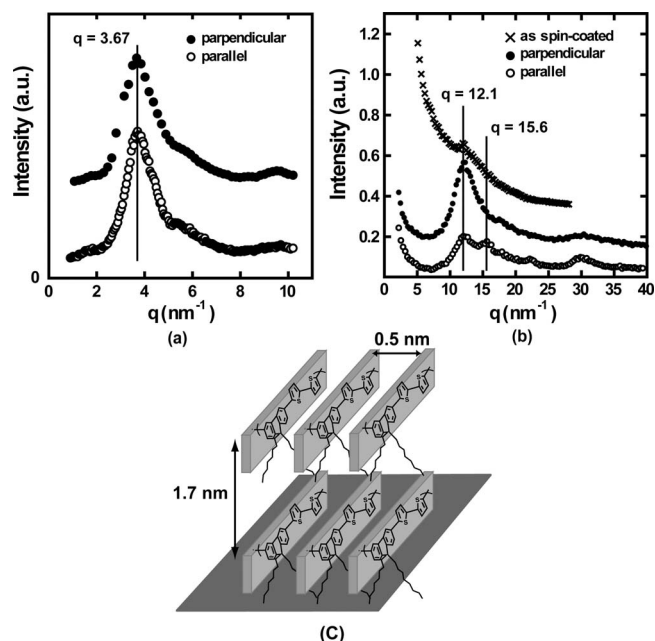


FIG. 3. (a) Out-of-plane XRD and (b) In-plane XRD: (●) perpendicular direction against laser scanning direction and (○) parallel direction against laser scanning direction. In addition, XRD from unannealed film is also shown as comparison (×). (c) Schematic view of orientated F8T2 after laser annealing.

to the distance between the F8T2 chains which have layered packing, perpendicular to their longitudinal axes.^{15,16} This lamellar structure appears due to the F8T2 chains' separation by the rather bulky octyl side chains stretching normal to the aromatic planes. Furthermore, in Fig. 3(b), the peak at $q = 12.1 \text{ nm}^{-1}$ can be attributed to a lateral distance of 0.5 nm between the polymer chains within the layers.¹⁷ Here, the diffraction intensities in the perpendicular case are significantly stronger than both those of the parallel direction and of the laser unannealed sample. In addition, the appearance of another peak at $q = 15.6 \text{ nm}^{-1}$ in the parallel case suggests the occurrence of another in-plane molecular alignment along the laser scanning direction. These results clearly suggest enhancement of packing of the polymer chains, after the laser annealing.

The FET characteristics before/after laser annealing are shown in Fig. 4. The FET characteristics after laser annealing exhibited a higher carrier mobility of $\mu = 1.6$

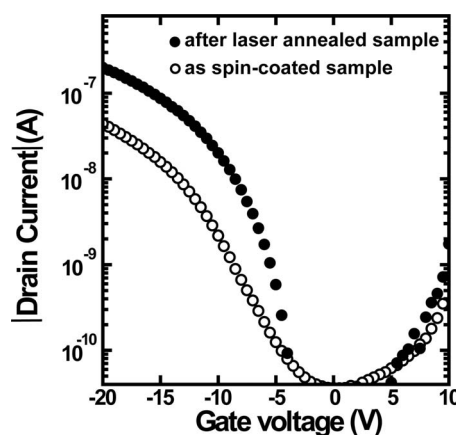


FIG. 4. Transfer characteristics of FET characteristics with $V_{\text{gs}} = 10$ to -20 V: (●) after laser-annealed sample and (○) unannealed sample.

$\times 10^{-3} \text{ cm}^2/\text{V s}$ along the scanning direction, compared with the mobility of the preannealed sample which was $\mu = 0.5 \times 10^{-3} \text{ cm}^2/\text{V s}$. This clearly indicates an improvement in the carrier mobility, which can be attributed to the main-chain alignment occurring in the laser scanning direction. We then attempted to measure the mobilities in the direction perpendicular to the laser scanning direction, but we were unsuccessful as the FET characteristics were unstable and even with no laser annealing, we still failed to measure them. This could be due to the presence of grooves, which may prohibit the stable FET operation. AFM observation indicates the presence of partial discontinuous and very thin thickness area of the F8T2 films between the grooves. We also note that the enhancement of the mobility obtained here is still at a lower value compared with previously reported values using the rubbing technique ($\mu = 4.4 \times 10^{-3} \text{ cm}^2/\text{V s}$) and the friction transfer ($\mu = 3.5 \times 10^{-2} \text{ cm}^2/\text{V s}$) deposition methods.^{13,17} One of the possible reasons for this could be the influence of the presence of oxygen and water, as it was difficult to completely remove them during the laser annealing, which occurred under atmospheric conditions. We expect the mobility will be greatly improved by modification of the procedure by working in an inert atmosphere.

Finally, we will discuss the orientation mechanism, which occurred using laser annealing. We presume that the orientation of F8T2 was caused by a thermal gradient over a very narrow region and at a high scanning speed. The laser scanning process involves extremely rapid cycles of heating and cooling at a speed of 4.5 m/s, providing a short sojourn time of 89 ns for each radiation spot. Here, we note that the rotation of the sample disk at 4.5 m/s induces a rather intense airstream on the surface, resulting in a rapid cooling decay time of nanoseconds. Therefore, such a fast heating and cooling process would induce a driving force for molecular orientation to occur parallel to the scan direction. Since we observed no appreciable damage in the polycarbonate substrate, it is probable that the F8T2 film was heated up to between 120 and 180 °C. Here, a finite element method (FEM) (Marc2007.1, MSC Software Co. Ltd.) was used to simulate temperature distribution with surface temperature in the multilayers. From the results of the FEM, we estimated that the F8T2 film was heated up to about 140 °C which is significantly lower in temperature compared with the T_L of the F8T2 film. In fact, the FEM indicates that the Cr layer must be heated up to between 500 and 600 °C to obtain T_L in the F8T2 film. However, these conditions would lead to complete damage of the polycarbonate substrate and we have not observed such degradation in our devices. The possible mechanism is that the phase transition temperatures of the 30-nm-thick films would be pronouncedly lower compared with those of the bulk state. This has been reported for other polymers and is due to the excess free volume induced by the preferential surface segregation of chain end groups on the polymer surface area.¹⁸ We propose that a similar situation

occurs here in the thin films due to the nonequilibrium film formation process of the spin-coating method.

In conclusion, we have demonstrated we can control the orientation of F8T2 on a polycarbonate substrate with spiral grooves of $L/S = 200 \text{ nm}$ by laser annealing under both rapid heating and cooling cycles. Using this method, the mobility was enhanced by a factor of 3 compared with that of the unannealed sample. Additionally we observed parallel molecular orientation conformation in the scan direction of the polymer main chain. In our future experiments, we will aim to optimize laser scanning parameters such as scan speed and density of energy in order to achieve further increases in mobility using laser annealing.

This work was supported partly by a Grant-in-Aid for the global COE program, "Science for Future Molecular Systems" and a Grant-in-Aid for scientific research, Grant No. 20245046, from the Ministry of Education, Culture, Sports, and Technology of Japan. The authors thank Mr. Hiroshi Miura for his helpful support in carrying out the laser annealing. Finally, we acknowledge the Japan Synchrotron Radiation Research Institute for the x-ray diffraction measurements (Grant No. 2008B1947).

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