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Author(s)	Nagamatsu, Shuichi; Takashima, Wataru; Kaneto, Keiichi; Yoshida, Yuji; Tanigaki, Nobutaka; Yase, Kiyoshi
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Polymer field-effect transistors by a drawing method

Shuichi Nagamatsu,^{a)} Wataru Takashima, and Keiichi Kaneto

Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu 808-0196, Japan

Yuji Yoshida, Nobutaka Tanigaki, and Kiyoshi Yase

Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan

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We demonstrated the polymer field-effect transistors (FETs) utilizing regioregular poly(3-alkylthiophene)s (P3AT) films prepared by a drawing method. The P3AT film exhibited large optical dichroic ratio, which originated in the polymer backbones aligned to the drawing direction. In-plane anisotropy and enhancement of FET characteristics have been observed that are caused by molecular alignment. In the case of poly(3-dodecylthiophene), the hole mobility along the drawing direction was enhanced by a factor of 25 compared with that of spin-coated film. © 2004 American Institute of Physics. [DOI: 10.1063/1.1751222]

Conjugated polymers are promising organic materials, due to excellent electrical and optical properties, reasonable chemical stability, and easy processability. The thin film devices, such as light-emitting diodes (LEDs),¹ photovoltaic cells,² and field-effect transistors (FETs),^{3,4} which used the conjugated polymer for active semiconducting layer, are usually built by solution processing. The solution processing has the advantage of much easier device manufacture and low-cost, low-temperature processes. Recent research efforts focus on the adaptation of solution processing such as ink jet printing.⁵ However, solution processing has limitations with respect to solubility, surface wetting, and chemical incompatibility between the solvents and conjugated polymers.

Here we suggest the conjugated polymer thin film preparation solving the problems of solution processing. The friction-transfer technique using poly(tetrafluoroethylene) (PTFE) was proposed by Wittmann and Smith in 1991.⁶ They demonstrated the deposition of a PTFE film on clean metal or glass surfaces by squeezing and drawing a PTFE block on those suitable substrates. The friction-transfer technique is useful for direct film preparation for solid-state materials. Therefore, the friction-transfer technique has a possibility of preparing the polymer films without using solvents regardless of the solubility. Moreover, since the thin film of PTFE is formed only in the confined area which drew a PTFE block by friction-transfer technique, it is possible to easily pattern a polymer film by a drawing method. In addition, from the results of transmission electron microscopy (TEM)⁶ and x-ray diffraction (XRD) analysis,⁷ it was confirmed that the friction-transferred PTFE film was having highly oriented polymer backbones along the drawing direction. The friction-transfer technique can form polymer aligned film without any underlying alignment layer. Siringhaus *et al.* reported that the liquid-crystalline conjugated polymer was aligned regularly on rubbed polyimide film, and that aligned polymer film was applied to high-performance

FET devices.⁸ Thus, arranging the polymer backbones is essential for fabricating organic optoelectronic devices. The friction-transfer technique offers attractive advantages for polymer film preparations. We have applied the friction-transfer technique to the film preparations for both insoluble and soluble conjugated polymers. Some successful results have been obtained in various conjugated polymers, such as polysilane, poly(*p*-phenylene), poly(*p*-phenylenevinylene), poly(3-alkylthiophene), and their derivatives.^{9–12}

In this letter, we demonstrate the FET device utilizing regioregular poly(3-dodecylthiophene) (P3DDT) thin films prepared by friction-transfer technique. Regioregular poly(3-alkylthiophene)s (P3AT) are the most promising conjugated polymers because of their high charge carrier mobility in the range of 10^{-4} – 10^{-1} cm²/V s.⁴ The friction-transferred P3AT (hexyl-, octyl-, decyl-, and dodecyl-) film exhibited high anisotropic optical property, and polymer molecule arrangement was already investigated.¹² P3DDT-FET produced by a drawing method was found to consist of an aligned polymer film. It shows a typical *p*-channel device operating and enhanced FET characteristics.

The P3DDT with more than 98% head-to-tail coupling (Aldrich Chem. Co.) was used as purchased. The P3DDT powder was compressed into a pellet, with an applied load of 1250 kgf/cm² under dynamic vacuum. The thin film of P3DDT was prepared by friction-transfer technique. The friction-transfer process was carried out by squeezing and drawing a P3DDT pellet on the substrate heated at 370 K under inert N₂ atmosphere. The applied load for squeezing was 30 kgf/cm², and the drawing speed was 1 m/min (see Fig. 1). The films thus prepared had an area of 1.5 cm² (pellet width of 1.0 cm × drawing length of 1.5 cm) and a thickness of around 50 nm. For the fabrication of the FET devices with top-contact-type configuration, we used heavily doped *n*⁺-Si wafers with the surface of a 300-nm-thick SiO₂ (*C_i* = 10 nF/cm²) as the substrate. The oxidized silicon wafers provide a convenient substrate, gate electrode, and gate dielectric for fabricating organic FET test structures. Prior to the deposition of the polymer, the surface of the

^{a)}Author to whom correspondence should be addressed; electronic mail: s.nagamatsu@aist.go.jp

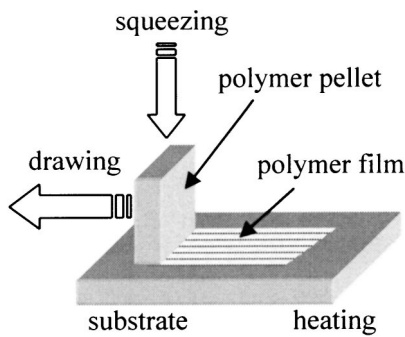


FIG. 1. Schematic picture of the friction-transfer process.

SiO₂ was treated with 1,1,1,3,3,3-hexamethyldisilazane. The conjugated polymer thin film was deposited on SiO₂ surface by friction-transfer technique. To complete the devices, gold source-drain electrodes were evaporated on top of polymer films through a shadow mask, defining with channel length $L=20\ \mu\text{m}$ and channel width $W=5\ \text{mm}$. The FET characteristic measurements were performed under vacuum ($<10^{-6}$ Torr) at 300 K.

The degree of polymer backbone alignment is quantified by polarized optical absorption spectra with Glam-Tomson polarized prism. The friction-transferred P3DDT film showed a considerable difference in amplitude and spectra shape of absorption for the light polarized parallel to the drawing direction compared to light polarized orthogonal direction (Fig. 2). A dichroic ratio for two polarization direction was more than 10, which is higher than published values for P3AT.¹³ This result indicated that the polymer backbones in the friction-transferred film were well aligned along the drawing direction. We have reported the details of polymer molecules arrangement in friction-transferred P3AT films by XRD analysis.¹² Therefore, if this friction-transferred conjugated polymer film is utilized as an active semiconducting layer of FET, having an enhanced FET characteristic from polymer backbone alignment is expected.

Figure 3 shows the drain current–drain voltage (I_D – V_D) characteristics of the friction-transferred P3DDT-FET devices on the same film with the current flows in the channel parallel (a) and orthogonal (b) to the drawing direction, respectively. The I_D value increased with increasing the negative gate voltage (V_G). The I_D – V_D characteristics showed normally off p -channel transistor action with on–off current

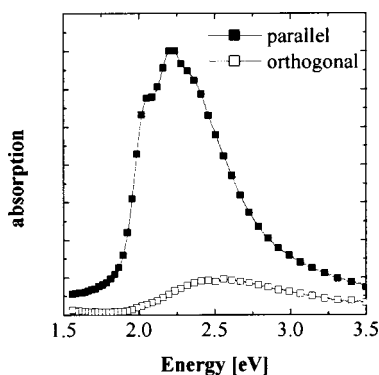


FIG. 2. Polarized optical absorption spectra of a friction-transferred P3DDT film on quartz substrate. The incident light is polarized parallel (closed squares) and orthogonal (open squares) to the drawing direction.

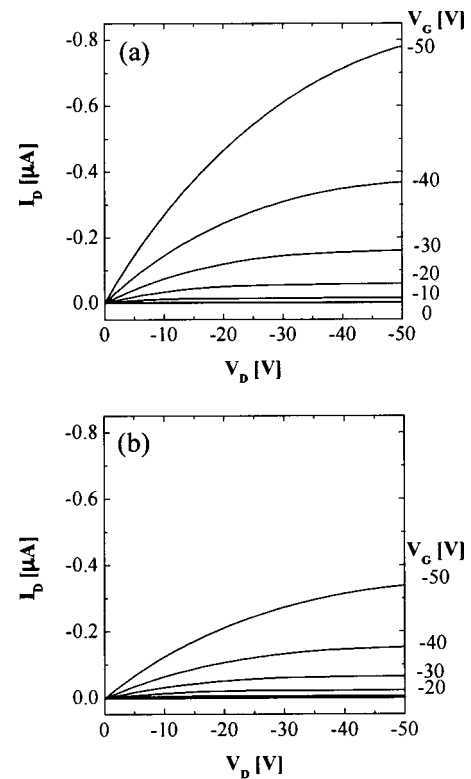


FIG. 3. I_D – V_D characteristics of the friction-transferred P3DDT-FET with current flow parallel (a) and orthogonal (b) to the drawing direction.

ratios exceeding 10^3 . The parallel current flow shows saturation current that is larger than the orthogonal current flow, indicating higher field-effect mobility in parallel to the drawing direction (i.e., polymer backbone direction). The field-effect mobility was calculated from saturation current regions with the classical equation

$$I_D^{\text{sat}} = \frac{WC_i}{2L} \mu (V_G - V_{\text{th}})^2, \quad (1)$$

where I_D^{sat} is the observed drain current at saturation region, W and L are the conduction channel width and length, respectively, C_i is the dielectric capacitance of the insulating SiO₂ layer per unit area, μ is the field-effect mobility, V_G is the gate voltage and V_{th} is the threshold voltage. From the square root of I_D^{sat} vs V_G plot, the field-effect mobility values calculated using Eq. (1) with the device characteristics shown in Figs. 3(a) and 3(b) are $7.4 \times 10^{-4}\ \text{cm}^2/\text{V s}$ for polymer backbone direction and $0.9 \times 10^{-4}\ \text{cm}^2/\text{V s}$ for orthogonal direction, respectively. The in-plane anisotropy of mobility, with a value was 8, was obtained in this film, and that originated in polymer backbone alignment. As a comparison, we also fabricated P3DDT-FET by spin-coating method from a chloroform solution with same top-contact-type device configuration. The spin-coated P3DDT-FET device has a mobility of $0.3 \times 10^{-4}\ \text{cm}^2/\text{V s}$ in our experiments. The hole mobility for polymer backbone direction in friction-transferred film showed enhanced value as expected, compared with that in spin-coated film. Values of the mobility enhancement are 25 and 3 for polymer backbones direction and orthogonally, respectively.

Although the mobility enhancement in polymer backbones direction was as expected, that in the orthogonal di-

rection, which was along in the alkyl side chain, was unexpected. It is known that polymer molecules in solution-processed regioregular P3AT films form self-organized microcrystalline domains and amorphous fractions, and these domains have random orientation. On the other hand, in friction-transferred regioregular P3AT films, since polymer molecules were aligned forcibly at a drawing process, these domains have uniaxial orientation. In addition, from the results of XRD analysis¹² and TEM, the friction-transferred P3AT films have highly crystallized structure. We consider that these remarkable enhancements in friction-transferred film occurred from high crystallinity and uniaxial orientation of microcrystalline domains.

In the case of regioregular poly(3-hexylthiophene) which is generally used in polymer FET, the mobility enhancement occurs in a drawing direction as was anticipated. Therefore, we consider that enhancement is expectable in polymer FET based on all the conjugated polymers which can apply this drawing method.

In conclusion, we demonstrated fabricating the P3AT-FET by a drawing method. The friction-transfer technique provides an excellent method to prepare well-aligned, highly crystallized conjugated polymer thin films without using solvents and without using underlying alignment layers. The P3AT-FET by a drawing method showed enhanced and in-plane anisotropic FET characteristics, which originated in the

polymer molecules arrangement. We are certain that this drawing method is really effective not only to fabricate organic optoelectronic devices but also to prepare polymer film for evaluation of fundamental physical properties of polymers.

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