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Description	

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Enhanced charge-carrier injection caused by molecular orientation

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Current densities of hole-only devices based on alpha-sexithiophene (α-6T) and N-N'-diphenyl-N-N'-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD) increase 42 times at 1 V by rubbing α-6T with a Nylon cloth. Results of absorption spectroscopy with normal and oblique light incidence reveal that the rubbing induces a change from standing to lying orientations of α-6T in a film surface region. The increased current densities are attributed to enhanced α-6T-to-α-NPD hole injection due to the lying orientation. © *2011 American Institute of Physics*.
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Organic films and crystals based on face-to-face stacked orientation of molecules relative to each other exhibit favorable charge transport due to overlap of π orbitals.[1–3] Control of molecular orientation in a multilayer structure is expected to improve the charge injection at heterojunction interfaces as well as to increase the charge mobility, enhancing performance of organic devices. Era *et al.*[4] used homoepitaxial growth of p-sexiphenyl (6P) on a rubbed surface to obtain polarized electroluminescence from an oriented 6P film. Yanagi *et al.*[5] constructed organic light-emitting diodes (OLEDs) by depositing 6P and additional layers on a KCl (001) surface and transferring the multilayer structure to an indium tin oxide (ITO) substrate. A lying orientation of 6P, deposited at a lower temperature, resulted in a lower drive voltage than a standing orientation. However, it is still underdeveloped to control orientation of organic small molecules in solid-state films whereas there are many techniques used to align long-chain polymers along a certain direction.[6] In this study, we use a rubbing technique to induce a change from standing to lying orientations of alpha-sexithiophene (α-6T) in a film surface region. The lying orientation enhances hole injection from α-6T to N-N'-diphenyl-N-N'-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD), resulting in increased current densities of hole-only devices by 42 times at 1 V. An enhanced injection of this sort has never been reported in small molecule-based devices. Although vacuum-deposited organic films naturally form an amorphous or polycrystalline structure with random molecular orientation, we stress that such positive control of molecular orientation using the simple rubbing offers a possibility of manufacturing sophisticated organic electronic devices with a high power conversion efficiency.

The hole-only devices are composed of a glass substrate coated with a 150 nm ITO anode layer, a rubbed α-6T layer, a 100 nm α-NPD layer, a 10 nm MoO_3 layer, and a 100 nm Al cathode layer [Fig. 1(a)]. High-purity source materials of α-NPD (Nippon Steel Chemical), MoO_3 (Mitsuwa Chemical), and Al (Nilaco) were used as received and a source material of α-6T (Aldrich) was purified twice using vacuum sublimation. The substrates were cleaned using ultrasonication and ultraviolet (UV)-ozone treatment. After vacuum deposition of a 15 nm α-6T layer on the ITO, this layer was rubbed 0, 1, 5, 7, 10, or 15 times with a nylon cloth inside a nitrogen-filled glove box. Then, the other layers were vacuum-deposited on the rubbed surface to complete the devices. The base pressure inside the evaporator was $\approx 2.0 \times 10^{-5}$ Pa and the deposition rates were set at 0.1 nm/s (α-6T and α-NPD), 0.05 nm/s (MoO_3), and 0.5 nm/s (Al) using a calibrated quartz crystal microbalance. The device without α-6T was also fabricated for comparison. The devices were encapsulated using a glass cap and an UV curing epoxy resin. All fabrication processes were conducted without exposing the samples to air. The current density-voltage ($J-V$) curves of the devices were measured using a computer-controlled sourcemeter (2400, Keithley) at room temperature. We define "positive" bias for positively biased ITO and "negative" bias for negatively biased ITO. No electroluminescence is observed under the measurements, meaning hole currents dominate. The exposure of the devices to nitrogen during the rubbing did not affect the $J-V$ curves (see Fig. S1, Ref. 7).

We prepared 8–12 devices on different substrates using separate fabrication processes. The representative $J-V$ curves of the devices are shown in Fig. 1(b). The obtained

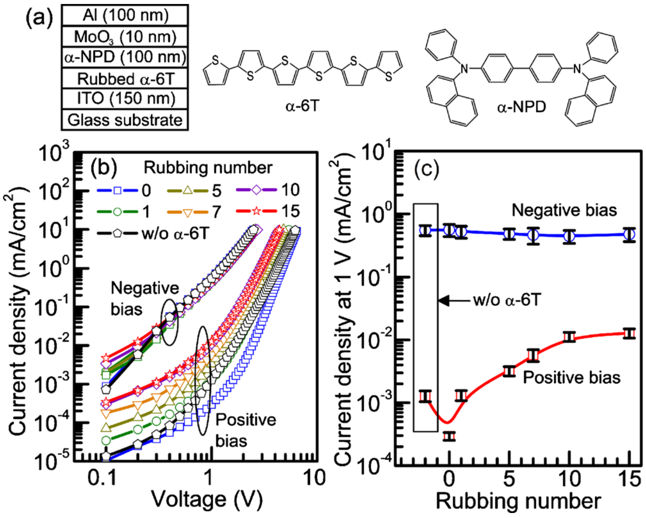

FIG. 1. (Color online) (a) Schematic structure of devices and molecular structures of α-6T and α-NPD, (b) $J-V$ curves of positive and negative biased devices, and (c) plots of current densities of positive and negative biased devices at 1 V versus rubbing numbers.

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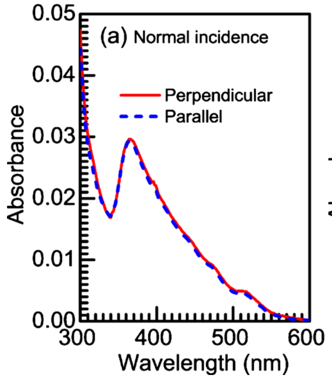

FIG. 2. (Color online) Polarized absorption spectra of as-deposited α-6T film measured with (a) normal and (b) oblique light incidence.

current densities at 1 V are averaged and plotted versus the rubbing numbers in Fig. 1(c). The small margin of error for the currents indicates good reproducibility. The 1 V current densities of the negative biased devices are independent of the rubbing numbers. Under the positive bias, the current densities of the unrubbed α-6T device are lower than those of the device without α--6T probably due to an increased hole-injection barrier at the α-6T/α-NPD interface (the energy-level diagram is presented later), but the current densities at 1 V increase 42 times as the rubbing numbers are increased from 0 to 15 times. We speculate that the increased current densities arise from a change in molecular orientation. To verify this hypothesis, the molecular orientations of α-6T and α-NPD are evaluated using UV-visible absorption spectroscopy (V670, JASCO).

The polarized absorption spectra of the as-deposited α-6T film on a fused silica substrate are measured with light incidence normal and oblique (45°) to the substrate [Figs. 2(a) and 2(b)]. For the oblique incidence, the direction of the light propagation is in the plane defined by the rubbing direction and the normal to the substrate. The absorption in this wavelength range originates from $\pi-\pi^*$ transition of α-6T having an electronic transition moment along the long molecular axis.[8] We assume that the strong absorption peak at ≈360 nm and the weak absorption peaks ranging from 400 to 600 nm arise from aggregated and unaggregated molecules, respectively (see Sec. 2, Ref. 7).

There is no absorption dichroism under the normal incidence [Fig. 2(a)], meaning that both aggregated and unaggregated molecules are random in the film plane. With the oblique incidence, the p-polarized spectrum is much larger in absorbance than the s-polarized spectrum in the shorter-wavelength region and the longer-wavelength absorption is unpolarized [Fig. 2(b)]. Thus, it is inferred that unaggregated molecules are also random in the thickness direction, but the standing orientation of aggregated molecules is dominant for the as-deposited film (see Fig. S2, Ref. 7). It has been reported that vacuum-deposited α-6T molecules are standing on a hydrophilic substrate,[8] which agrees with the result obtained here.

The unpolarized absorption spectra of the as-deposited and rubbed α-6T films measured with the normal and oblique incidence are shown in Figs. 3(a) and 3(b), respectively. The shorter-wavelength peaks decrease and the longer-wavelength peaks relatively increase in absorbance by the rubbing. No shorter-wavelength peak is observed in the films rubbed 10 and 15 times. This observation indicates that the rubbing induces decomposition of aggregated molecules into unaggregated molecules and/or removal of large aggregates with the cloth.

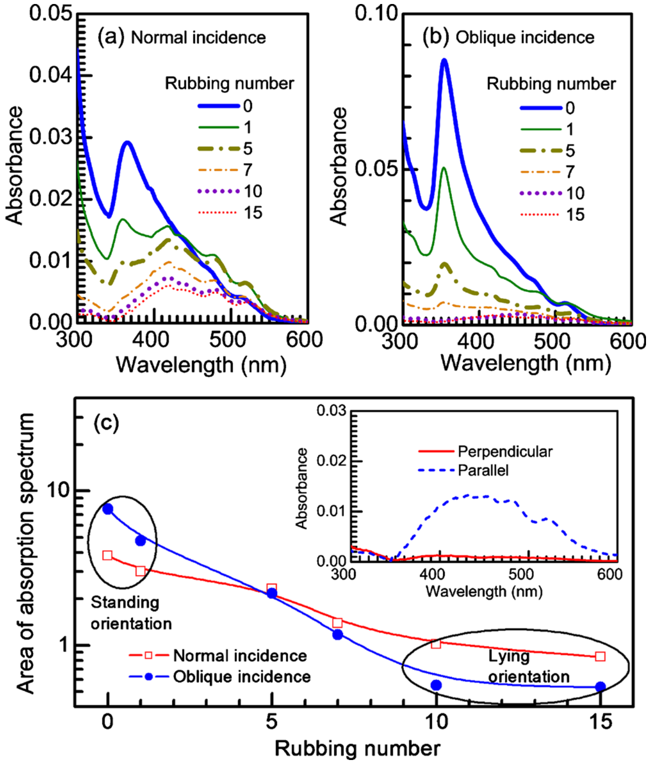

FIG. 3. (Color online) Unpolarized absorption spectra of as-deposited and rubbed α-6T films measured with (a) normal and (b) oblique light incidence and (c) plots of spectral areas obtained with normal and oblique incidence vs rubbing numbers. Inset shows polarized absorption spectra of 15 times rubbed α-6T film measured with normal incidence.

The areas of the unpolarized absorption spectra in the wavelength range from 300 to 600 nm are plotted versus the rubbing numbers in Fig. 3(c). The oblique-incidence measurement increases the areas by $\sqrt{2}$ compared with the normal-incidence measurement because of an increase in path length of light. However, for the as-deposited film, the area obtained with the oblique incidence is about two times larger than that obtained with the normal incidence, indicating again the standing orientation of α-6T because standing molecules can absorb the oblique-incidence light more strongly than the normal-incidence light.

The areas gradually decrease with increasing the rubbing numbers due to a decrease in film thickness. When the films are rubbed 10 and 15 times, the areas obtained with the oblique incidence become smaller than those obtained with the normal incidence. Moreover, a large absorption dichroic ratio of 13 is observed from the 15 times rubbed film under the normal incidence [the inset of Fig. 3(c)]. These observations suggest that the standing orientation is changed into the lying orientation along the rubbing direction. Results of x-ray diffraction measurement using a $2\theta/\theta$ technique (M18XHF, MAC Science) reveal that the as-deposited and rubbed films exhibit no clear diffraction peak (see Figs. S3–5, Ref. 7), indicating rather little crystallization.

The surface morphologies of the as-deposited and rubbed α-6T films are measured using atomic force microscopy (AFM) (VN-8000, KEYENCE). The 7 times rubbed

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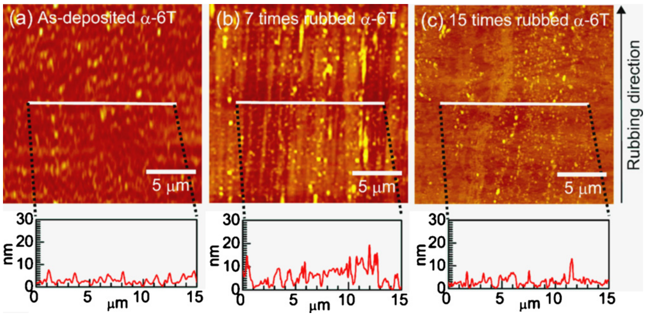

FIG. 4. (Color online) AFM images and their cross section profiles of (a) as-deposited, (b) 7 times rubbed, and (c) 15 times rubbed α-6T films.

surface has an uneven striped texture along the rubbing direction [Fig. 4(b)] while the smooth surface is observed from the as-deposited film [Fig. 4(a)], meaning that the films are not rubbed uniformly using the cloth. The whole surface seems to be planed in the 15 times rubbed film [Fig. 4(c)]. Thus, we assume that the lying orientation occurs under the partially rubbed surface region and the lying orientation region gradually spreads through the films as the rubbing numbers are increased (see Fig. S6, Ref. 7).

Polarized absorption spectra of a 10 nm α-NPD film on the 15 times rubbed α-6T surface were measured with the normal and oblique incidence (see Fig. S7, Ref. 7). No absorption dichroism is observed from the α-NPD film, indicating that α-NPD molecules are completely random on the rubbed surface.

The energy-level diagram of the unrubbed device estimated from photoelectron onset energies of each layer using an AC-2 photoelectron yield spectrometer (Riken Keiki) is shown in Fig. 5(a). The hole-transport level of α-6T is slightly above the Fermi level of ITO, meaning barrier-free ITO-to-α-6T hole injection under the positive bias. On the other hand, since there is a large difference of 0.45 eV in hole-transport level between α-6T and α-NPD, the $J-V$ curves of the positive biased devices are presumably limited by the α-6T-to-α-NPD hole injection. Efficient charge generation occurs at the MoO_3/α-NPD interface,[9] indicating barrier-free MoO_3-to-α-NPD hole injection under the negative bias as well [Fig. 1(c)]. The rubbing-independent and higher current densities of the negative biased devices suggest that an energy barrier at the α-6T/α-NPD interface is absent under the negative bias and that a built-in voltage defined by a difference between Fermi levels of an anode and a cathode is not changed significantly by the rubbing.

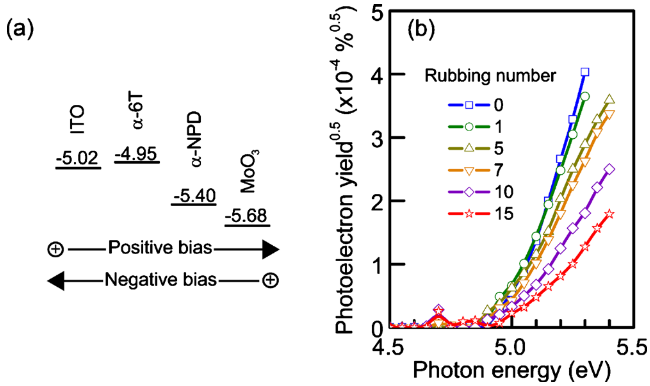

FIG. 5. (Color online) (a) Energy-level diagram of unrubbed device and (b) photoelectron yield spectra (electrons per incident photons) of as-deposited and rubbed α-6T films.

It has been reported that the hole mobility of α-6T is measured to be $10^{-4}-10^{-2}$ cm^2/V s using a thin-film transistor structure,[10] which is presumably higher than that of α-NPD ($10^{-4}-10^{-3}$ cm^2/V s) measured using a time-of-flight technique.[11] Because of the higher mobility of α-6T and the rubbing-independent $J-V$ curves of the negative biased devices, it is not necessary to consider whether the hole mobility of the rubbed α-6T layer affects the $J-V$ curves of the positive biased devices. In the as-deposited layer, the standing orientation of α-6T is dominant, meaning less efficient α-6T-to-α-NPD hole injection due to poor overlap of π orbitals between standing α-6T and random α-NPD. Since the lying orientation of α-6T caused by the rubbing improves the overlap of π orbitals, we conclude that the increased current densities originate from the improved α-6T-to-α-NPD hole injection.

It has been reported that the change from standing to lying orientations of α-6T increases ionization energies by 0.4 eV.[12] To verify this report, the photoelectron yield spectra of the as-deposited and rubbed α-6T films are measured using AC-2 [Fig. 5(b)]. The spectral slopes gradually decrease, at least in part due to a reduction in film thickness by the rubbing. The ionization energies estimated from the photoelectron onset energies are independent of the rubbing numbers, perhaps because some regions containing standing α-6T molecules are still present in the rubbed films. Although the orientation-dependent ionization energies are not observed here, the increased current densities could be induced by the reduced hole-injection barrier as well as the improved overlap of π orbitals. Recently, we have found that the rubbing of α-6T results in reduced drive voltages and improved operational stability of OLEDs, which will be published elsewhere.

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