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Two-dimensional orientation control of organic semiconducting amorphous films by mechanical brushing

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We demonstrate that horizontally oriented organic semiconducting molecules in amorphous films can be oriented uniaxially by mechanical brushing. The absorption of polarized light in the direction parallel to the brushing direction was higher than the absorption in the perpendicular direction. Thus, simultaneous uniaxial and in-plane molecular orientation in amorphous films was realized by brushing. In addition, we demonstrate a polarized electroluminescence from the films treated by mechanical brushing. © *2011 American Institute of Physics*. [doi:10.1063/1.3608315]

Recent developments of organic semiconductor devices have been remarkable, with applications including flat-panel displays and lighting. This has in part been because of their advantages over well-established inorganic semiconductor devices based on silicon and compound semiconductors. For example, unique high-performance optical and electrical properties and the possibility of low-temperature and low-cost fabrication are being demonstrated by taking advantage of unlimited molecular designs. Although much effort has been devoted to the development of organic light emitting diodes (OLEDs),[1] organic field effect transistors (OFETs),[2] and organic solar cells (OSCs),[3] further improvement of the performance of the devices is anticipated to accelerate their practical applications.

As a means for enhancing organic device performance, attention has been focused on control of molecular orientation in amorphous films, because the orientation significantly affects light out-coupling efficiency in OLEDs, charge injection and transport ability, and the amplified spontaneous emission (ASE) threshold.[4–7] Liquid crystalline molecules can be aligned in a particular direction by using a thin polymer orientation layer rubbed unidirectionally. In the same vein, uniaxially oriented sexiphenyl films prepared through epitaxial growth by vacuum deposition on rubbed substrates have been reported.[8] In the present study, we demonstrated simultaneous uniaxial and in-plane molecular orientation by mechanical brushing[9,10] of horizontally oriented semiconducting amorphous films and propose a mechanism for the effects caused by brushing. Furthermore, we fabricated OLEDs using simultaneous uniaxial and in-plane orientated molecules and observed polarized electroluminescence (EL) parallel to the brushing direction.

Organic films for optical measurements were fabricated by thermal evaporation under high vacuum (ca. 7×10^{-4} Pa) onto clean quartz and silicon substrates. Anisotropic refractive indices and extinction coefficients were measured using a fast spectroscopic ellipsometer (J. A. Woollam, M-2000U). Brushing was done manually by wiping a surface with a Nylon cloth in one direction at 6–7 N/cm^2. The processed films were observed with a polarizing microscope equipped with a hot stage (Olympus, DP72). Polarized absorption and fluorescence spectra of the films were recorded with a spectrometer (PerkinElmer, Lambda 950-PKA) and a multi-channel spectrometer (Hamamatsu, PMA-11) with a visible sheet polarizer (Sigma Koki, SPF). In addition, the temperature at the surface of a film during brushing was measured *in situ* using an infrared camera (NEC/Avio, TVS-500EX). The camera allowed capture of 60 frames per second. OLEDs were fabricated by conventional thermal evaporation under high vacuum (ca. 7×10^{-4} Pa) onto clean indium tin oxide (ITO) coated glass substrates. Current density−voltage−luminance (*J-V-L*) characteristics were obtained using a semiconductor parameter analyzer (Agilent, E5273A) with an optical power meter (Newport, 1930C). Polarized EL spectra of OLEDs were obtained using a multi-channel spectrometer (Hamamatsu, PMA-11) with visible sheet polarizer under short-pulse excitation.

We investigated the optical anisotropy of 4,4′-bis[(N-carbazole)styryl]biphenyl (BSB-Cz) and 4′-bis[(N-carbazole)styryl]bipyridyl (BSBpy-Cz) amorphous films. In a previous study of ours, the optical anisotropy of a BSB-Cz film was confirmed.[5] Very similar anisotropic refractive indices and extinction coefficients were observed for the BSBpy-Cz film (see Supplementary Information[11]). From the results of the anisotropic extinction coefficient measurements, we quantified the molecular orientation in amorphous films using the orientation parameter S given by

$$S = \frac{3}{2}\langle \cos^2\theta \rangle - \frac{1}{2} = \frac{k_e - k_o}{k_e + 2k_o}, \tag{1}$$

where $\langle \ldots \rangle$ indicates the ensemble average, θ is the angle between the long molecular axis and the direction perpendicular to the substrate surface, and k_o and k_e are ordinary and extraordinary extinction coefficients, respectively, at the peak wavelength. $S = -0.5$ if the molecules are wholly parallel to the surface; $S = 0$ if they are randomly oriented; and $S = 1$ if they are wholly perpendicular to the surface. The

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orientation parameters of BSB-Cz and BSBpy-Cz films were $S = -0.33$ and -0.35, respectively, indicating that the molecules in the amorphous films were horizontally oriented with the average values $\langle\theta\rangle = 70.3°$ and 71.4°, respectively.

The absorptions of polarized light in BSB-Cz and BSBpy-Cz films (100 nm) in the direction parallel to the brushing direction were higher than in the perpendicular direction, respectively (see Supplementary Information[11]). Optical anisotropy of the films was confirmed by polarized fluorescence spectra and polarizing microscopy using crossed nicols (see Supplementary Information[11]). Since BSB-Cz and BSBpy-Cz molecules have transition dipole moments in the same direction as the molecular long axis,[7] these results indicate that the molecular long axes of BSB-Cz and BSBpy-Cz molecules were uniaxially aligned by brushing.

We evaluated the degree of molecular orientation in the in-plane direction using the order parameter S_A defined by the equation

$$S_A = \frac{R-1}{R+1}, \tag{2}$$

$$R = \frac{A_{//}}{A_{\perp}}, \tag{3}$$

where $A_{//}$ and $A_{\perp}$ are absorption of polarized light at the peak wavelength in the directions parallel and perpendicular, respectively, to the brushing direction. Figure 1 shows the thickness dependence of the order parameter in BSB-Cz film after one brushing. Below 25 nm thickness, S_A is independent of the thickness and has a value that is comparable to that of nematic liquid crystals. Above 30 nm thickness, S_A decreased with an increase of the thickness. These results suggest that molecules located within a depth of about 25 nm can be aligned by one brushing. The inset of Fig. 1 shows the change of the order parameter in a 100 nm thick BSB-Cz film with the number of brushings. S_A increased with repetitive brushing, indicating that repetitive brushing increases the depth within which molecules can be aligned.

To investigate the surface morphology induced by brushing, the glass transition temperature on the surface of a BSB-Cz film was compared with the surface temperature during brushing. The glass transition temperature was measured using a hot stage polarizing microscope with crossed nicols.

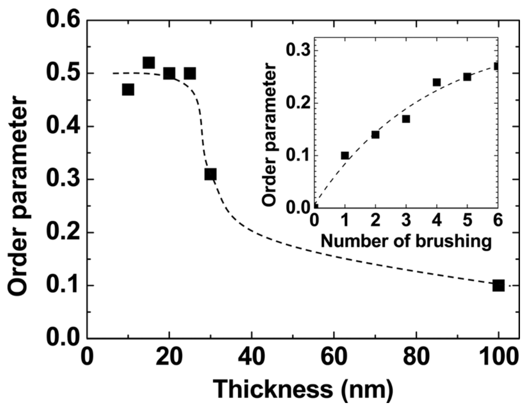

FIG. 1. Thickness dependence of the order parameter (S_A) in BSB-Cz film after one brushing. Inset: Change of order parameter in 100 nm thick BSB-Cz film with the number of brushings.

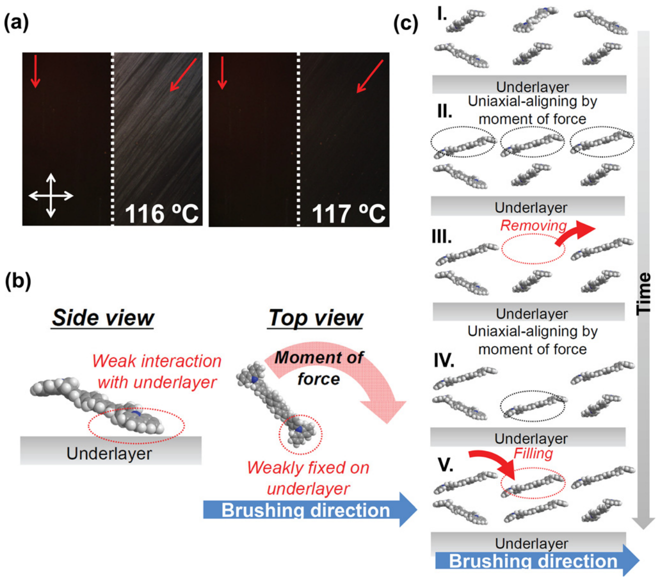

FIG. 2. (Color online) (a) Images observed at 116 and 117 °C with a polarizing microscope with crossed nicols, for 25 nm thick BSB-Cz film after one brushing. The white arrows indicate the crossed nicols, and the red arrows the brushing direction. (b) Mechanism by which molecules located in the topmost surface are aligned by brushing. (c) Mechanism of uniaxial-molecular orientation in the nearby surface.

In uniaxially oriented organic semiconductor films, the brightness of transmitted light alternates between light and dark at a 90° angle with respect to each other with a rotating polarizing stage and polarizing microscope with crossed nicols. This effect is due to anisotropic refractive indices in the in-plane direction. Figure 2(a) shows the images observed at 116 and 117 °C under a polarizing microscope with crossed nicols for a 25 nm thick BSB-Cz film after one brushing. No change between light and dark was observed at 117 °C; thus, this temperature corresponds to the glass transition temperature of the surface of the BSB-Cz film. The glass transition temperature on the surface was lower than that of the bulk, which was estimated as 126 °C by differential scanning calorimetry. The surface temperature during brushing was estimated as ~40 °C using an infrared camera. Consequently, the surface morphology during brushing would have remained as the solid state without melting.

Here, we discuss the mechanism of the uniaxial molecular orientation caused by brushing. We divide the surface of films into the topmost and nearby surfaces. Figure 2(b) shows a possible mechanism of molecular alignment at the topmost surface due to brushing. The molecules located in the topmost surface are lying with the molecular long axis direction parallel to the underlying molecules (top view). This is due to the weak interaction, i.e., van der Waals force, with the underlying layer. From the side view, the molecules are oriented with average angle ~70°, indicating that one of the end carbazole units sits on the underlying layer. Therefore, the force applied by brushing would change the molecular angle (II in Fig. 2(c)). The in-plane angular momentum is largest for the molecules located in a position vertical to the brushing direction, while no change would occur to the molecules with angular momentum parallel to the rubbing direction. Consequently, the direction of the molecular long axes of horizontally oriented molecules located in the topmost surface would be uniaxially aligned by brushing. Figure 2(c) shows the subsequent mechanism of uniaxial molecular orientation in the nearby surface. Brushing would impart not only in-plane angular momentum but also kinetic momentum, i.e., local heating, to molecules located in the topmost surface. The kinetic momentum would cause surface migration and relocation of aligned molecules in the topmost surface (III in Fig. 2(c)). As a result, molecules from the second layer appear in the topmost surface (IV in Fig. 2(c)) and are also uniaxially oriented by brushing. While brushing hollows the topmost surface by removing aligned molecules, another molecule fills in the dent by simultaneous surface migration of other molecules. The repeated hollowing and filling would thus cause uniaxial orientation of molecules in the topmost and nearby surfaces.

Finally, we investigated application of these films, with brushing, to polarized OLEDs, consisting of ITO/4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α-NPD) (30 nm)/BSB-Cz with brushing (50 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (20 nm)/tris(8-hydroxyquinoline) (Alq_3) (20 nm)/MgAg/Ag. The EL through a polarizer showed higher intensity in the direction parallel to the brushing direction and was weakened in the perpendicular direction (see Supplementary Information[11]), suggesting that brushing provides an effective tool to realize polarized OLEDs consisting of amorphous films.

We demonstrated that the direction of the molecular long axes of linear shaped molecules in amorphous films was uniaxially aligned by brushing. We found that BSB-Cz and BSBpy-Cz molecules can be aligned by just one brushing and that the aligned depth was located within about 25 nm. Based on brushing while maintaining the solid state, we proposed a mechanism of the simultaneous uniaxial and in-plane molecular orientation caused by brushing. Furthermore, we realized polarized OLEDs consisting of an amorphous film with brushing. Application of mechanical brushing to molecules with horizontal orientation provides a simple method for controlling two-dimensional molecular orientation.

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[11] See supplementary material at http://dx.doi.org/10.1063/1.3608315 for optical anisotropy.