

Reorganization of the molecular orientation at the organic/substrate interface in spirofluorene thin films

Takeshi Komino^a, Hiroko Nomura^a, Masayuki Yahiro^a, Chihaya Adachi^{a,b,*}

^a Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motoooka, Nishi, Fukuoka 819-0395, Japan

^b International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motoooka, Nishi, Fukuoka 819-0395, Japan

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ABSTRACT

The thermal annealing treatment of an organic non-crystalline film of spirofluorene causes the randomization of the molecular orientation through molecular migration. However, the magnitude of the randomization depends on the depth in the film. The comparison of variable-angle spectroscopic ellipsometry, thermally stimulated current, and field-effect transistor characteristics measurements revealed that the molecular orientation in the bulk was randomized by annealing but was still partially maintained at the organic/substrate interface. This difference in condensed states between the interface and the bulk originates from a difference in glass transition temperature.

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1. Introduction

Organic non-crystalline films fabricated by vacuum deposition have homogeneous photonic and electronic properties over a large area, and thus are frequently used in optoelectronic devices. However, their properties are often inferior to those of crystalline films having well-ordered and well-orientated structures. To improve the properties of non-crystalline films, control of the condensed state is a promising strategy. Herein, the condensed state is defined by the molecular orientation and density. Numerous efforts have been made to clarify the condensed state and functional relationships governing device performance, especially in terms of the effect of the molecular orientation on the photonic and electronic properties. To date, these studies have demonstrated that a preferred orientation contributes to an improvement in device performances including the carrier mobility [1], the light out-coupling efficiency of an organic light emitting diode [2–6], and the amplified spontaneous emission threshold [7–9]. While the studies focused on the properties of the entire film, the interfaces are important since the condensed state at the interface plays a key role in governing the electronic processes of carrier injection and extraction in vertical-type devices and carrier transport in lateral-type devices. In fact, short- and long-range ordered dipole orientation was reported to induce an interfacial dipole layer and giant surface potential [10,11].

Temperature plays a crucial role in the control of the condensed state. We have previously reported that heating a substrate during

deposition and thermal annealing can control the molecular orientation from the preferential orientation parallel to the substrate to a random orientation [1,9,12–16]. The glass transition temperature, T_g , is particularly important since glass transition involves molecular migration, leading to reorganization of molecular configurations. However, the condensed state might not always be homogeneously controllable. In fact, it is well known that T_g varies within thin polymer films [17–33]. While the distribution of T_g in neat films of small molecules has been scarcely reported, we recently found that a non-crystalline film of spirofluorene derivatives has a T_g distribution that varies in the direction normal to the substrate [34]. This T_g distribution led us to consider that the condensed states at the interface might differ from those in the bulk during thermal treatment. A possible strategy for investigating the reorganization of the condensed state at the interface is to use a field-effect transistor (FET) since only the first one or two monolayers [35–37] (or at most the first few monolayers [38]) contribute to carrier transport in the channel. In particular, the charges located at the interface have the highest mobility, which reinforces their contribution to the conductivity [39]. Kim et al. used the dependence of the field-effect carrier mobility for pentacene on temperature to investigate T_g of polystyrene (PS) gate dielectric at the surface [40,41]. In this study, we investigated the transition of the condensed state at the interface considering FET characteristics and thermally stimulated current (TSC) measurements and that in the bulk (the average for the entire film) considering variable-angle spectroscopic ellipsometry (VASE) measurements in the case of the a spirofluorene derivative 4,4'-(9,9'-spiro[fluorene]-2,7-diyl)bis(*N,N*-diphenylaniline) (SFBDPA, Figure 1a), which forms non-crystalline film because of the bulky and twisted structure of the spirofluorene unit [9]. As a result, anomalous reorganization of the molecular configuration was found at the interface

* Corresponding author at: Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motoooka, Nishi, Fukuoka 819-0395, Japan. Fax: +81 92 802 6920.

E-mail address: adachi@cstf.kyushu-u.ac.jp (C. Adachi).

when we annealed the film above T_g ; the condensed state was still partially maintained at the organic/substrate interface.

2. Experimental details

The condensed state in a bulk (an average for the entire film) was probed considering optical anisotropy through VASE (Figure 1b). The substrates of heavily doped n-type silicon wafers with 300-nm-thick SiO_2 were cleaned by immersion in piranha solution, sonication in pure water, boiling in 2-propanol, and ultraviolet-ozone treatment. SFBDDPA thin films with thickness of 50 nm were then fabricated on the substrates by thermal evaporation under a vacuum of less than $<1 \times 10^{-3}$ Pa at an evaporation rate of 0.1 nm/s. $T_{\text{deposition}}$ was varied from room temperature to 385 K, and some of the films fabricated at room temperature were treated by thermal annealing for 10 min at T_{anneal} ranging from 323 to 463 K. The substrate temperature in vacuum was monitored by a thermometer (E5CN, Omron) with a type K thermocouple junction attached to a substrate holder plate, which is made of copper. VASE measurements were performed at incident angles of 45–75° with steps of 5° in the spectral range of 245–1000 nm under atmospheric conditions. The anisotropic extinction coefficient k and refractive index n of the films were obtained by analyzing the ellipsometric angles with a uniaxial anisotropy model using Tauc–Lorentz-type and GAUSSIAN-type oscillators. The mean square error values obtained were 20–30 in all films examined.

In addition to the ellipsometry measurements, the condensed states at an organic/substrate interface were investigated by making FET and TSC measurements (Figure 1c) [45]. A bottom gate/bottom contact structure was fabricated using the same type of silicon wafer as used in the VASE measurements. A 50-nm-thick Au layer with a 3-nm-thick Cr underlayer was deposited on pre-cleaned Si/ SiO_2 substrates by thermal evaporation and patterned by photolithography to produce source and drain electrodes with a wide/length ratio of 7.6 cm/25 μm . SFBDDPA thin films with thickness of 50 nm were then fabricated on the substrates. The FET and TSC measurements were performed for both SFBDDPA films fabricated on the heated substrates and the thermally annealed films in the same manner as in the VASE measurements. The output and transfer characteristics of all devices were measured using a pair of picoammeter/voltage source units under a vacuum condition of less than 1×10^{-3} Pa. For the transfer characteristics, the field-effect mobilities were extracted in the saturation regime ($V_d = -100$ V) using the relation; $\mu = (2I_d L) / [WC_i (V_g - V_{th})^2]$, where V_d is the drain voltage, I_d is the drain current, C_i is the capacitance per unit area of the SiO_2 gate dielectric (11.5 nF/cm²), V_g is the gate voltage, and V_{th} is the threshold voltage. For the TSC measurements, the devices were cooled to 90 K with helium coolant and were biased with a gate voltage of $V_g = -100$ V for 1 min to fill hole trap states at the SiO_2 /SFBDDPA interface. The TSC signal was then collected using a femtoammeter by gradually heating the devices to 383 K at a heating rate of 10 K/min. During heating, a drain voltage of $V_d = 1$ V was applied to collect the TSC signal.

To evaluate the hole mobilities in the bulk as the reference of the FET measurements, single carrier devices were fabricated with device structures of glass/ITO (100 nm)/ MoO_3 (0.8 nm)/SFBDDPA (200 nm)/ MoO_3 (10 nm)/Al (80 nm). A layer of SFBDDPA was fabricated at $T_{\text{deposition}}$ of 300–385 K, while the other organic layers were deposited at room temperature. Some of the SFBDDPA films fabricated at 300 K were thermally annealed for 10 min at T_{anneal} ranging from 420 to 460 K prior to deposit a 10-nm-thick MoO_3 layer and an Al cathode. Current density (J) vs voltage (V) characteristics of the hole only devices were measured by an electrometer under dark conditions, varying the applied voltage from 0 to 10 V in 0.1 V increments.

3. Results and discussion

3.1. Effect of deposition temperature

Figure 2a and b show the n and k spectra of the films fabricated at deposition temperature $T_{\text{deposition}} = 299$ and 383 K, respectively (Figure 1b). Herein, subscripted o (ordinary) and e (extraordinary) indicate directions parallel and perpendicular to the substrate. The film fabricated at $T_{\text{deposition}} = 299$ K exhibited large optical anisotropy, while the film fabricated at $T_{\text{deposition}} = 383$ K was isotropic, meaning that the two films differ in their molecular orientation. The orientation order parameter (S) is calculated by

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle = \frac{k_e - k_o}{k_e + 2k_o} \quad (1)$$

where θ is the angle between the normal of the substrate and the transition dipole (inset of Figure 2c). The S values at the peak wavelength (374 nm) of k spectra were estimated to be -0.40 at $T_{\text{deposition}} = 299$ K and 0.01 at $T_{\text{deposition}} = 383$ K, indicating that the molecules tended to be oriented parallel to the substrate at $T_{\text{deposition}} = 299$ K and randomly oriented at $T_{\text{deposition}} = 383$ K. Figure 2c shows the dependence of the S values on $T_{\text{deposition}}$. The $S - T_{\text{deposition}}$ curve reveals that the randomization of the molecular orientation, which is structural disorder, occurred at a temperature much lower than T_g (432 K⁹). This trend of the molecular orientation is similar to that in films fabricated on a bare silicon substrate [9], and we recently found that this orientational randomization at $T_{\text{deposition}} < T_g$ comes from the relative low T_g at the film surface compared with that in the bulk [34].

Figure 3a–d shows the output and transfer characteristics of the devices fabricated at $T_{\text{deposition}} = 299$ and 385 K (Figure 1c). The

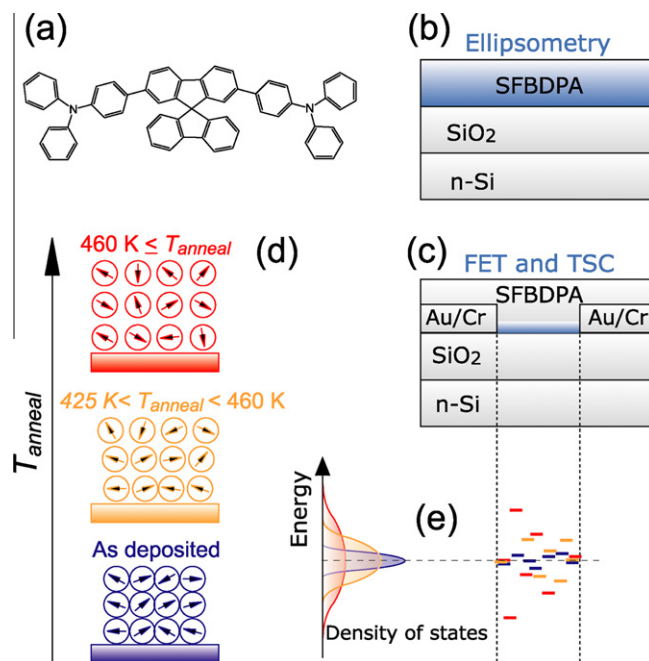


Figure 1. (a) Molecular structure of SBDPA. Structures of the samples in (b) VASE and (c) FET and TSC measurements. Colored regions represent the objects for each measurement. (d) Change in the condensed state accompanied with thermal expansion and orientational randomization during annealing. Arrows represent a transition dipole parallel to the long axis of the molecule. The change in condensed state preferentially occurs from the surface at $425 \text{ K} < T_{\text{anneal}} < 460 \text{ K}$. (e) Energy distribution of localized hopping sites the density of states. The distribution of the density of states becomes broader as T_{anneal} increases, thus producing a deep trap. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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