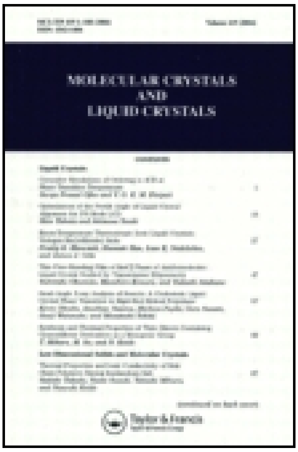

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Interface Phenomena of Self-Assembled Monolayer with Various Alkyl Chain as a Hole-Injection Layer for Organic Light-Emitting Diodes

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Interface Phenomena of Self-Assembled Monolayer with Various Alkyl Chain as a Hole-Injection Layer for Organic Light-Emitting Diodes

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We investigate the effect of the interface phenomena of a self-assembled monolayer (SAM) molecules on hole injection. A SAM represents an easy and accurate approach to the modification of surface properties. The dipole moment of a fluorinated SAM (FSAM) improves hole injection from Indium Tin Oxide (ITO). We prepare several kinds of FSAM with different number of fluorine atoms FnSAM. As the number of fluorine atom increases, the dipole moment also increases. Increasing the chain length increases the van der Waals interaction between alkyl chains. We examine the interface characteristics of SAM molecules on the hole injection.

Keywords Self-assembled monolayer; Dipole moment; Organic light-emitting diodes

1. Introduction

Organic light emitting diodes (OLEDs) have received considerable interest due to their potential application in future flat panel display (FPD) technology. FPD has been commercially available for more than 20 years. Inexpensive, light and low powered flat panel displays with vibrant and clear image have become increasing sought after not only for mobile devices but also for large televisions. OLED has been placed under the spotlight as a next generation display technology. Since OLED allows a wider viewing angle with flexible displays like plastic, it should become an important technology to replace existing display in future. OLED performance, operating voltage and efficiency is, critically affected by carrier injections. Used as carrier injection layers, a self-assembled monolayer (SAM) can easily control the surface electronic state of the substrate. A SAM layer can be formed by submerging the substrate in a solution made with an active surfactant [1]. The active surfactant molecules combined with the substrate surface molecules to form a single layer of molecules. The active surfactant consists of three elements. That is a bond part, a mid section, and an end functional group. The bond part can combined with the substrate surface molecules. The mid section is usually a long chain structure, e.g. an alkyl group, which can interacts with neighboring chains via Van der Waals forces to form a single

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molecule layer. The end functional group eventually becomes the surface molecular structures of the newly formed layer [2]. Many researchers have already reported the application of SAM to OLEDs, because a SAM can be fabricated comparably easily. In addition, it is an effective and powerful form of material modification for organic electronic devices [3–6]. SAM markedly alters the surface properties of substrates, including the electrical characteristics. For example, organosilane SAMs have been used to control the characteristics of organic field-effect transistors through the modification of the interface between an organic semiconductor layer and a gate oxide film [7]. Recently, SAM formed from dipolar organic molecules have been used to modify the effective work function of electrodes to reduce the charge-injection barriers and minimize the onset voltage [8–10]. It is well-known that a close relationship between the surface potential of SAM and dipole moments of the molecules consisting of the SAMs is of primary importance for such an application [11–13]. The authors have studied the influence of the fabrication process and film structure on the performance of organic electronic devices [14–17]. The authors have already reported the excellent properties of a fluorinated SAM (FSAM, (heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane). The modification of FSAM on an indium-tin-oxide (ITO) anode enhances hole-injection from ITO and prolongs the lifetime of OLEDs [18]. The device performance of OLEDs with inhomogeneous FSAM molecules exhibited intermediate behavior, which suggests that the anode interface condition plays an important role in the conduction and degradation mechanisms of OLEDs. In addition, the authors found the novel fabrication of organic nanodots on roughness ITO using FSAM, Molecular Aggregation During Self-Assembled monolayer Treatment method (MADSAT) [19]. In this paper, the authors investigated the effect on hole injection using four kinds of FSAM with different fluorinated alkyl chains.

2. Experimental Method

FnSAM (n: C_nH_{2n+1}-, the number of F atoms = 2n-3) was used as a hole-injection material (Gelest co.). N,N′-di(1-naphthyl)-N,N′-diphenyl-1,1′-diphenyl-1,4′-diamine) (α-NPD) and tris(8-hydroxyquinolinato)aluminum (Alq3) were used as hole-transport and emission materials (Nippon Steel Chemical Co.), respectively. A special ITO substrate for OLEDs was purchased from Geomatic Co., Ltd. The ITO substrates were cleaned by UV-ozone treatment (5 min; Nippon Laser and Electronics Lab.) after washing in pure water, acetone, and 2-propanol with ultrasonication. FSAM was fabricated by a gas-phase method. FSAM-modified ITO substrates were rinsed by ultrasonic washing in 2-propanol to remove excess FSAM molecules that were not adsorbed by the ITO surface. The contact angle of pure water was measured using an automatic contact angle meter (CA-VP, Kyowa Interface Science Co.). Organic thin films were prepared by vacuum deposition at a rate of ca. 0.2 nm/s under a pressure of 4×10^{-4} Pa at room temperature. The work functions of FSAM-modified ITO were measured by photoemission yield spectroscopy in air (AC-2, Riken Keiki Co.). Luminance-current-voltage characteristics were measured using a high current source measurement unit (Keithley 238) and a luminance meter (Topcon BM-8). Electrical measurements were carried out under vacuum conditions of ca. 0.1 Pa. The calculation of dipole moment used semi-empirical molecular orbital calculation software (SCIGRESS MO. Fujitsu Co.)[20].

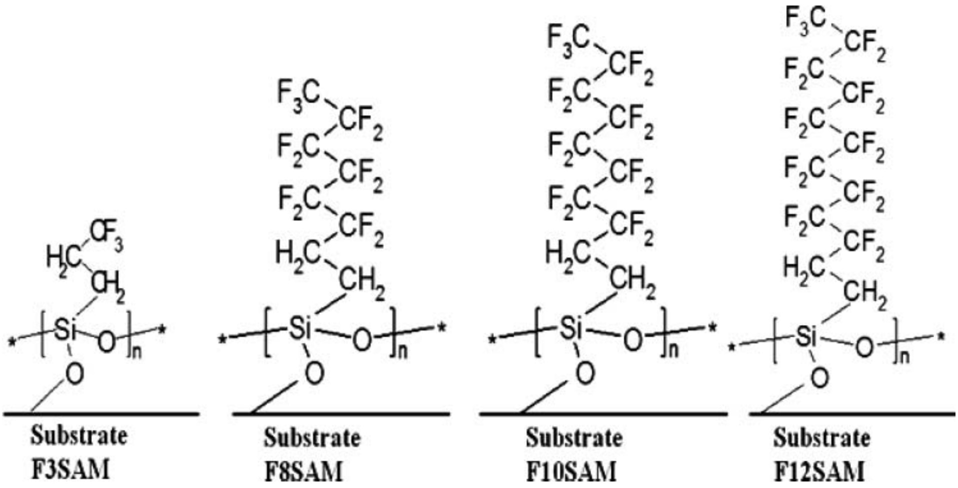

Figure 1. Chemical structures of FnSAM molecules.

3. Results and Consideration

3.1. Interface characteristics of Self-Assembled Monolayer as a hole injection layer

The device's structure consisted of an ITO/Hole injection layer(HIL)/ α−NPD(50 nm)/Alq3(50 nm)/LiF(0.6 nm)/Al(150 nm). Figure 1 shows the structures of compounds used to modify the substrate.

We fabricated OLED of four kinds with different fluorine atom number, FnSAM. The interface dipole occurs between the substrate and the adsorbate. The dipoles of the absorbed molecules form an electrical double layer between the ITO and hole transport layer. And the dipoles of the absorbed molecules can produce changes in the barrier height of hole injection [21]. Figure 2 shows dipole moment – number of carbon curve characteristics. For the calculation of dipole moment, we used SCIGRESS MO. PM3 is determined by least squares of 12 atoms (H, C, N, O, F, Al, Si, P, S, Cl, Br, I). As the quantity of fluorine increases, the dipole moment also increases. The dipole moments of F3SAM, F8SAM, F10SAM and F12SAM are estimated to be 2.39, 2.70, 2.74 and 2.76 [D], respectively.

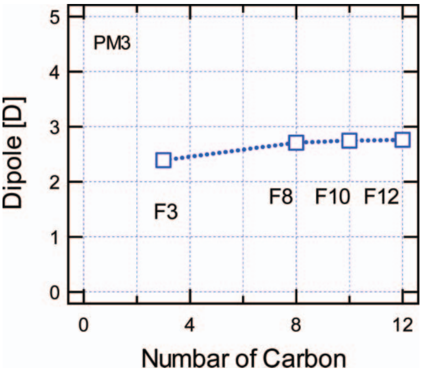

Figure 2. Dipole moment – number of carbon characteristics.

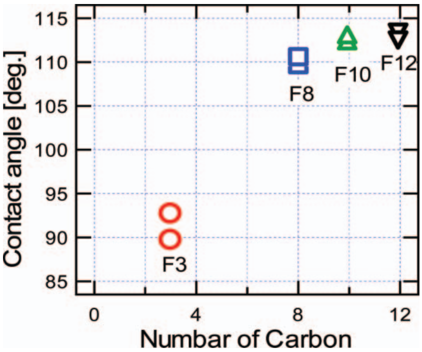

Figure 3. Contact angle – number of carboncharacteristics.

The contact angles of the FSAM-modified ITO substrates are measured. As shown in Fig. 3, the contact angle of the F12SAM-modified ITO substrate is higher than those of the others. The F12SAM has the largest. It is thought that F12SAM-modified ITO is more hydrophobic than the others. As the quantity of fluorine (carbon) decreases, FSAM molecules incompletely cover the substrate surface. The contact angles of F3SAM, F3SAM, F8SAM, F10SAM and F12SAM are estimated to be 91.0°, 110.1°, 112.5° and 112.7°, respectively. As the alkyl chain is shortened, FSAM molecules may incompletely cover the substrate because of the weak van der Waals force. Especially F3SAM molecules with shortest alkyl chain are thought to be disordered.

The change of work function is related to $n\mu_{\perp}/\varepsilon_r\varepsilon_0$, where n is the density of dipoles, $\perp$ is the dipole moment along the normal surface of the substrate, ε_0 is the permittivity of free space and ε_{r} is the dielectric constant of the SAM [22]. The orientation of dipole will affect on the change of work function. Figure 4 shows the work function – number of carbon characteristics. The work function of the FSAM-modified ITO increases from 4.9 ~ 5.0 eV to 5.40 ~ 5.46 eV. It is thought that FSAM-modified ITO substrate have a lower than the HOMO level of α–NPD (5.4 eV). FnSAM have been used to modify the effective work function of substrate to reduce the barrier height of carrier-injection. The work function is considered to depend on the difference in a interface dipole moment. The work function

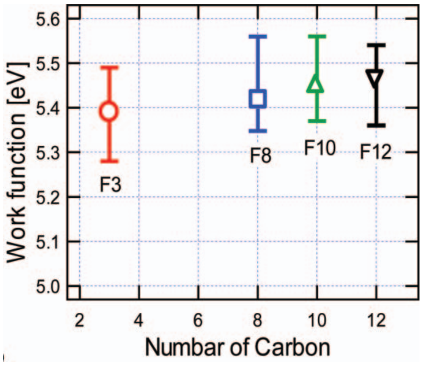

Figure 4. Work function – number of carbon characteristics.

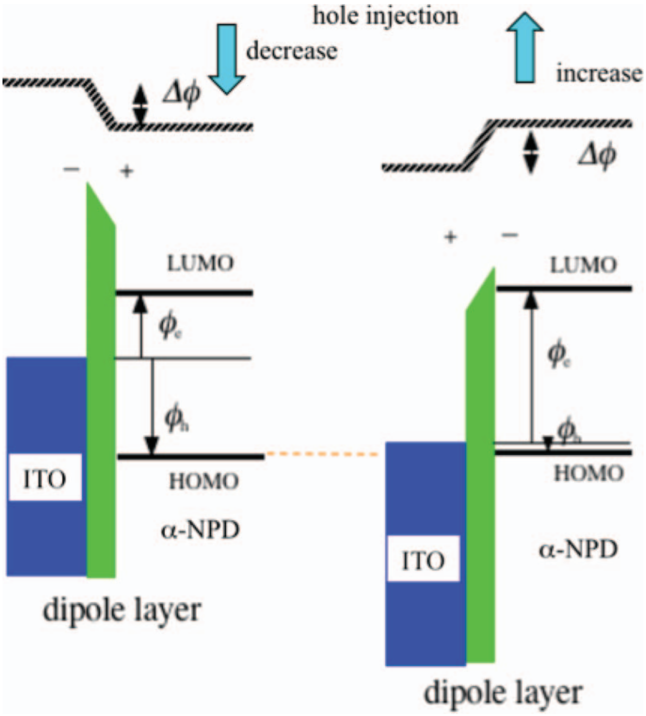

Figure 5. The diagram of energy shifts due to interface dipole layer: Left, the right-dipole direction (decrease in vacuum level(VL)); Right, the left-dipole direction (increase in VL); $\Delta\phi$, the shift of VL, ϕ_e and ϕ_h, the barrier heights of electron and hole, respectively.

of FSAM modified ITO increases from F3SAM to F12SAM. The hole injection barrier between the ITO and $\alpha-$NPD decreases, so hole injection will be enhanced.

Figure 5 shows the image of interface dipole layer effect. The value and direction of the vacuum level shift depends on the value and direction of interface dipole moment. In the left case, the barrier height of hole injection from ITO to α-NPD will increase and then the hole injection from ITO will be suppressed. On the other hand, in the right case, the barrier height will decrease and then the hole injection will be enhanced. All dipole moments of FnSAM can be regarded as the right case. It is important to understand how the different number of fluorine atoms FnSAM influences the electrical properties of OLED. Figure 6 shows the current density - voltage characteristics for ITO/FnSAM/$\alpha-$NPD(50 nm)/ Alq3(50 nm)/LiF(0.6 nm)/Al. The inset shows the extended part of threshold voltage in the low current region. It is thought that the FSAM-modified ITO substrate have a lower work function the HOMO level of $\alpha-$NPD($\sim$5.4eV) so that there is a small energy barrier and the hole injection is influenced mainly by the dipole moment. The threshold voltage in the low current region little depends on FSAM materials. In addition, the hole injection is little influenced by the alkyl chain length (an insulating part).

By increasing the dipole moment due to fluorine atom with the largest electronegativity, the work function of FSAM-modified ITO substrate is also enhanced. Because the hole injection barrier of the FSAM-modified ITO substrate is thought to decrease, the hole injection of FSAM-modified ITO substrate is enhanced, and the current density will be also enhanced. This can be ascribed to the hole-dominating nature of these devices. As a

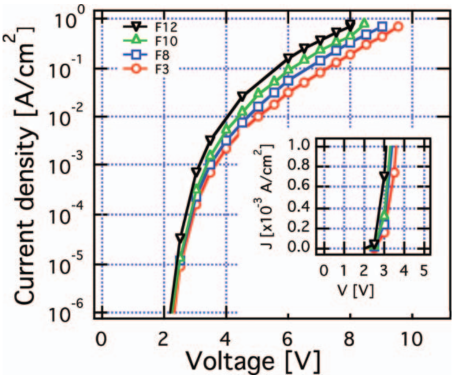

Figure 6. Current density – voltage characteristics for ITO/FnSAM/α-NPD(50 nm)/Alq3(50 nm)/LiF(0.6 nm)/Al. The inset shows the extended part of threshold voltage in the low current region.

result of the current density - voltage characteristics, the driving voltage of F12SAM is the lowest. The current density appears to be considerably influenced by the contact angle of various FSAM with their different numbers of fluorine atoms, as shown in Fig. 3.

Figure 7 shows the luminance - current density characteristics for OLEDs with Fn-SAM. The OLEDs of FnSAM have the same luminance per current density. Since the barrier heights of hole-injection for devices with FnSAM decrease, the hole-injection is enhanced. The EL efficiency of the luminance per current density does not change with different numbers of fluorine atoms. Since the LiF/Al cathode can provide a sufficient electron injection to Alq3 layer, the carrier balance between hole and electron flows in the recombination zone does not reduce. Consequently the EL efficiency per current is thought not to lower.

Figure 8 shows the necessary voltage at a constant current - FnSAM. The necessary voltage depends of the number of alkyl group of FSAM. As the number of fluorine atoms SAM increases, the driving voltage decreases. However, although the work function of FnSAM-modified ITO does not change remarkably, the driving voltage slightly depends on the number of alkyl group of FnSAM in the low current region and it strongly depends on that in the higher current region. This suggests that the effect of the dipole moment due

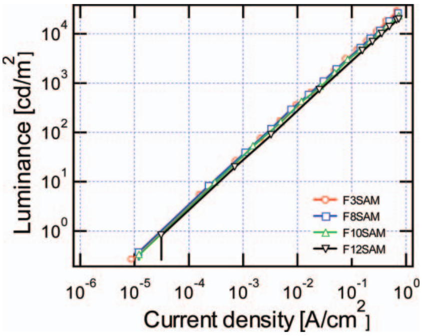

Figure 7. Luminance - Current density characteristics for ITO/FnSAM/α-NPD(50 nm)/Alq3(50 nm)/LiF(0.6 nm)/Al.

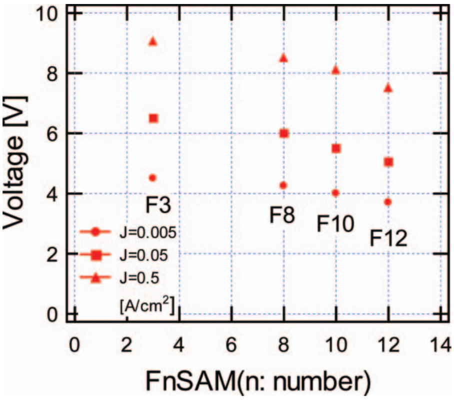

Figure 8. The necessary voltage at a constant current against FnSAM.

to strong fluorine atom influences the hole injection condition at the ITO/α-NPD interface as well as the conductivity of α-NPD region around FSAM.

4. Conclusion

In this paper, OLED surfaces were modified using FSAM as a HIL and interface characteristics were analyzed. It was proven that the dipole moment of FSAM-modified ITO substrate can be used to modulate work function. It was also shown to affect the barrier height of hole injection. As the barrier of hole injection changed, driving voltage was modulated, so it appears that the driving voltage is dependent on dipole moment. The study of interface characteristics of FSAM as a hole injection layer will become an increasingly important application technology for OLEDs.

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