

Formation mechanism of spontaneous orientation polarization in evaporated films of organic light-emitting diode materials

Yutaka Noguchi¹, Kohei Osada¹, Hisao Ishii²

¹School of Science & Technology, Meiji University, Kanagawa 214-8571, Japan.

²Center for Frontier Science, Chiba University, Chiba 263-8522, Japan.

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ABSTRACT

Spontaneous orientation polarization (SOP) affects the device performance of OLEDs. To understand and control SOP, we have studied the formation mechanism. The SOP formation likely results from a balance between an electrostatic interaction of permanent dipole moment and van der Waals interaction on the film surface during deposition.

1 INTRODUCTION

Molecular orientation has been recognized as an important factor for the device performance of organic light-emitting diodes (OLEDs), because it dominates the charge carrier transport, light-outcoupling efficiency, and so on [1,2]. The molecular orientation has been often evaluated by measuring orientation degree of transition dipole moment (TDM) intensity ($\propto \langle \cos^2 \theta \rangle$), where the head and tail of the molecule are not distinguished. However, it is not sufficient to describe the film property, if the molecule possesses a permanent dipole moment (PDM). For instance, orientation polarization is formed due to the anisotropic orientation of PDM in the film. The orientation polarization is proportional to $\langle \cos \theta_p \rangle$, where θ_p is a tilt angle of PDM with reference to the surface normal, indicating that the head and tail of the molecule is distinguished.

Interestingly, the orientation polarization is spontaneously formed in the evaporated films of some organic semiconductors. This spontaneous orientation polarization (SOP) was discovered for the first time in the evaporated film of a typical OLED material, Alq₃ [3]. The surface potential of the Alq₃ film grows linearly as a function of film thickness due to SOP, and it exceeds over 10 V without saturation. This significant phenomenon is called giant surface potential (GSP). The GSP slope of Alq₃ film is typically 50 mV/nm, and it corresponds to the polarization charge density of 1.3 mC/m² that is induced on the Alq₃ film surface. In stacked multi-layer devices such as OLED, the polarization charge appears at the hetero interfaces, and 1.3 mC/m² is more than 10% of the total amount of accumulated charge carrier density in an operating OLED [4-6].

The SOP is not a unique property of Alq₃ but has been observed in several materials, and the polarization charge influences the device properties of OLEDs, such as charge injection, accumulation, and device degradation [4-6].

Accordingly, we need to design the device structure and analyze the device characteristics taking into account the presence of polarization charge. However, the understanding of SOP is not sufficient. In this study, to understand and control SOP, we examined the surface potential characteristics of the evaporated films of various materials that are commonly used in OLEDs [7]. Moreover, the surface potential of co-evaporated films was also examined. Based on these results, we propose the formation mechanism of SOP, where an electrostatic interaction between PDMs, and van der Waals interaction on the film surface during deposition are key factors.

2 EXPERIMENT

The surface potential of the evaporated films of various OLED materials was measured as a function of film thickness (5 to ~300 nm) by a Kelvin probe method in a high vacuum. The substrate was typically an indium-tin-oxide (ITO) coated glass or evaporated gold. The samples were kept in the dark or under red light (peak wavelength: 640 nm, FWHM: 25 nm) to avoid the generation of photocarriers in the film, which would decay the surface potential [3].

3 RESULTS

Figure 1 shows the surface potential characteristics of the various materials [7]. The materials are divided into three classes with different qualitative TDM orientations, namely, random, unknown, and horizontal. A typical GSP behavior, such as linear growth over several volts without saturation, was observed regardless of the TDM orientations.

In Fig. 2, we summarized the absolute value of the GSP slope against PDM intensity of the materials that were measured in this study and ever reported [7]. It is obvious that the SOP is very common in the evaporated films of OLED materials.

4 DISCUSSION

Although the plots are widely distributed in Fig. 2, we focused on some materials, such as B3PyMPM, Znq₂, Ir(ppy)₃, and DCJTb, appearing in the bottom region. Since the slope in Fig. 2 is proportional to the orientation degree of PDM, these materials have a small orientation degree in the film. Looking at the molecules, they seem to show a strong electrostatic interaction ($\propto p^2/r^3$)

between molecules, because of their relatively large PDM intensity (p) and compact molecular size ($\sim r$). The strong electrostatic interaction between PDMs is expected to be a negative factor of the SOP formation, since the molecules are stabilized by canceling total PDM.

We performed DFT calculations to estimate the intermolecular interaction energy between two molecules, where the molecule's PDM was arranged in an anti-parallel configuration. The intermolecular interaction energies of B3PyMPM, Znq₂, Ir(ppy)₃, and DCJTB were indeed negatively much larger than those of the other molecules in Fig. 2 [7].

Moreover, we have found that the orientation degree of PDM is enhanced in a co-evaporated film of TPBi and CBP, where CBP is a nonpolar molecule. This result is also consistent in terms of the electrostatic interaction. The concentration of PDM is diluted by the nonpolar molecule, and thus the electrostatic interaction energy is reduced. As suppressing negative factor, the orientation degree of PDM is enhanced.

On the other hand, the molecular shape is considered to be a positive factor of SOP formation [8,9]. Because of the asymmetric shape of polar molecules, the molecular orientation with reference to the surface normal would be anisotropic on the film surface. Recently, a molecular simulation has revealed that a short-range van der Waals interaction between the outermost part of the molecule and the film surface dominates the molecular orientation [10]. However, if the PDM interaction is comparable to the van der Waals interaction, the orientation degree of PDM can be reduced as described above. Finally, the anisotropic molecular orientation on the film surface is fixed in the bulk covered by the subsequent deposition [11].

We have also examined the surface potential characteristics of the TPBi film deposited on a gold substrate with/without a self-assembled monolayer (SAM) of 1-dodecanethiol. The surface potential of the SAM treated sample was lower than that of the untreated sample. The result can also be explained by the proposed mechanism. By reducing surface free energy, van der Waals interaction on the film surface is suppressed and PDM interaction becomes relatively dominant, consequently SOP is suppressed.

5 CONCLUSIONS

We have investigated the formation mechanism of SOP in the evaporated films of OLED materials. The SOP formation likely results from a balance between positive and negative factors, where the positive factor is the van der Waals interaction between the molecule and film surface, and the negative factor is the PDM interaction between molecules on the film surface.

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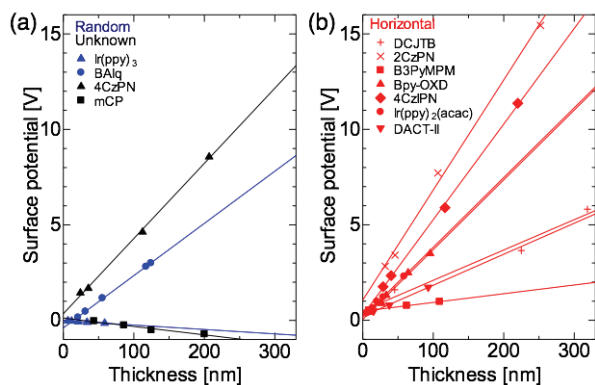


Fig. 1 Surface potentials of evaporated films as a function of film thickness. (a) "Random" and "Unknown" materials. (b) "Horizontal" materials. Reprinted with permission from Ref. [7]

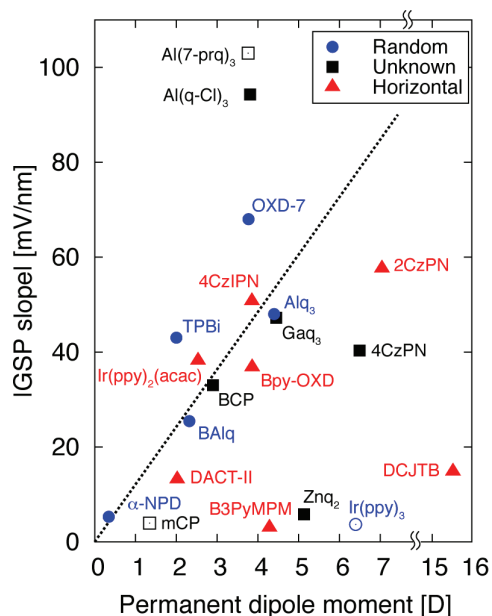


Fig. 2 Relationship between the absolute value of the GSP slope and PDM intensity for various organic materials. Reprinted with permission from Ref. [7]