

Control factors of molecular orientation in OLED films

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Amorphous organic semiconductor films used in OLEDs have the advantage of nanometer-scale surface smoothness, which is a property indispensable for constructing a multilayer device structure precisely. On the other hand, however, the higher-order structures of the films are generally more random than those of polycrystalline organic films, and this disorder often leads to inferior optical and electrical properties of the films and devices. Thus, it is important for the development of high-performance OLEDs to deliver the full potential of amorphous organic materials under the restriction of this disadvantage in higher-order structures. Although the higher-order structures of small-molecule amorphous organic films had long been regarded as completely random, it is currently well-known that molecules in vacuum-deposited amorphous organic films are loosely oriented depending on the molecular shape and intermolecular interaction [1,2]. Furthermore, we now make the most of this orientation to improve the optical and electrical characteristics of OLEDs [2]. Most of the recently-reported high-performance OLEDs include horizontally oriented molecules in the devices. However, since amorphous organic films do not have a periodic structure with a long-range order, the details of the higher-order structures and their formation mechanism have not yet been understood sufficiently.

This “order in disorder” in amorphous OLED films has recently been investigated in detail by some spectroscopic methods, and a lot of information on higher-order structures that had been overlooked was obtained. To understand the structures and mechanism, the control factors of molecular orientation and the relationship between fabrication processes and molecular orientation should be clarified. In particular, the difference between molecular orientations in vacuum- and solution-processed films is important because the device fabrication by solution processes is attracting much attention for developing low-cost and large-area processes.

In this presentation, the formation mechanism of molecular orientation in small-molecule amorphous organic semiconductor films will be discussed in detail. The important keywords to understand it are “metastable states”, “energy landscape”, “step-by-step single-molecule process”, “surface diffusion”, “variety of conformation structures (internal degree of freedom)”, and “number of states”. Because a higher-order structure of an amorphous films is kept just as a metastable state, the films have a local minimum energy in the energy landscape. In the process of vacuum deposition, films are formed by step-by-step single-molecule process. Each molecule just after deposition is horizontally oriented loosely to lower the surface energy, but it can diffuse at the surface for several seconds and change its conformation structure [3]. In this diffusion time, it can grope for a more stable state through conformational change and aggregation with other molecules, and the molecular orientation becomes more random. When the deposition rate is high, or the substrate temperature is low, the molecule cannot sufficiently diffuse at the surface before the successively deposited molecules overlay and fix it, leading to a high degree of horizontal molecular orientation [3]. Thus, in vacuum processes, the deposition rate and substrate temperature can be important control factors of molecular orientation in addition to molecular shape of materials. On the other hand, in solution processes of small-molecule OLED films, it is not easy to fabricate a film with a high degree of horizontal molecular orientation because many molecules are simultaneously condensed and solidified [3,4]. The system does not have a time to grope for a more stable state, and the higher-order structure of random orientation is fixed as a “relatively unstable” metastable state, which has a larger number of equivalent states. The details of experimental results and their interpretation will be shown in the presentation for the clear understanding of this mechanism.

【References】 [1] D. Yokoyama *et al.*, *Org. Electron.* **10**, 127 (2009). [2] D. Yokoyama, *J. Mater. Chem.* **21**, 19187 (2011). [3] M. Shibata *et al.*, *J. Mater. Chem. C* **3**, 11178 (2015). [4] Y. Sakai *et al.*, *Appl. Phys. Express* **8**, 096601 (2015).