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Material Design of Transparent Oxide Semiconductors for Organic Electronics: Why Do Zinc Silicate Thin Films Have Exceptional Properties?

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Device application of organic electronics demands materials with seemingly incompatible properties. A material with a low work function, high mobility, high visible transparency, and chemical stability for electron injection/transport of organic light-emitting diodes is required. Typical n-type organic semiconductor materials with a low work function do not satisfy the requirements for high mobility, transparency, and chemical stability. In contrast, conventional transparent oxide semiconductors do not meet the criterion of low work function. A zinc silicate thin film has a low work function (≈3.5 eV); it also satisfies the other requirements. The present paper elucidates the reasons for such exceptional properties. It is revealed that the zinc silicate thin films comprise ZnO nanocrystals, each of which is optically separated by an extremely thin amorphous ZnO–SiO_2 layer. Such a unique nanostructure gives rise to the quantum-size effect of ZnO nanocrystals, leading to low work functions and hopping conduction; this enables it to meet the criterion for a low work function and also enables relatively higher mobility (0.3–1.0 $cm^2 V^{-1} s^{-1}$) than those of the n-type organic semiconductors. Based on these findings, a material design idea is proposed to realize incompatible properties even using compositions of naturally abundant constituents.

1. Introduction

An advantage of organic-electronic devices is the ability to employ precise molecular design to obtain the desired functions and to tune processes.[1–3] The material for each layer of an organic light-emitting diode (OLED) is designed for a specific function such as carrier injection, carrier transport, or light emission to realize process compatibilities and performance excellence. Moreover, organic materials can be printed to form thin films, which deform easily to follow the curvature of a flexible substrate. Several flexible devices that utilize these features have already been proposed, such as electronic paper and flexible sensors.[4,5]

Although numerous p-type organic semiconductor materials with high mobility (μ > 0.1 $cm^2 V^{-1} s^{-1}$) and chemical stability under atmospheric conditions exist, few n-type materials exhibit characteristics that are comparable with those of p-type semiconductors,[6,7] mainly because the energy level of the lowest unoccupied molecular orbital from the vacuum level, i.e., the electron affinity, is rather low (2–3 eV).[8] As a result, injecting electrons from a cathode such as one fabricated from metallic aluminum with a work function of ≈4 eV is difficult. The situation is reversed for oxide semiconductors; that is, rather few p-type semiconductors, but many n-type semiconductors with superior characteristics exist, such as ZnO and amorphous In–Ga–Zn–O.[9–11] This preferred polarity of conduction-type between organic and inorganic semiconductors is thus complementary. Accordingly, it is straightforward to replace an n-type organic semiconductor layer with an n-type inorganic semiconductor layer to realize new functions and/or improvements in organic-device performance.

In this paper, inorganic electron-injection and -transport layers (EIL/ETLs) for OLEDs with the following requirements are focused upon: (1) low work function; (2) ohmic contact with cathode materials; (3) high mobility (μ > 0.1 $cm^2 V^{-1} s^{-1}$); (4) high visible transparency; (5) surface smoothness; and (6) chemical stability under atmosphere conditions. Most inorganic materials besides $12CaO \cdot 7Al_2O_3$ electride (C12A7:e^-) have work functions larger than 4.0 eV.[12,13] However, while C12A7:e^- is favorable for electron injection to an adjacent organic layer, it is not useful for ETL, because of its low mobility.[14] Therefore, new inorganic materials with low work functions need to be developed for inorganic EIL/ETLs. For such cases, ohmic contacts with conventional electrode materials such as aluminum or indium tin oxide are rather difficult, because the contact characteristics are of the Schottky type, due to the low work function of an inorganic EIL.

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