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Introduction

1.1 Operating Mechanism of Organic Light-Emitting Diodes: Device Physics and Molecular Chemistry Pictures

Electroluminescence (EL) is a general term describing the phenomenon in which a solid emits light upon electrical stimulation. In the broad sense, the phenomenon whereby a p–n junction in an inorganic semiconductor emits light when forward current is applied is classified as EL. However, it is specifically referred to as a light-emitting diode (LED) because it is essentially a two-terminal semiconductor device possessing rectifying properties. In contrast, the electroluminescence phenomenon obtained by applying a direct current through an organic semiconductor thin film sandwiched between two electrodes is called organic electroluminescence or, in short, organic EL. In terms of device structure, which implies a semiconductor layered between two electrodes, organic EL is analogous to inorganic semiconductor LED and hence is also referred to as organic light-emitting diode (OLED). In Japan, the term "organic EL" is widely used, but globally, the acronym OLED is more prevalent. Throughout this book, we will generally use the term OLED, and when emphasizing a specific device configuration, we will use the expression "OLED device."

From the standpoint that both are two-terminal semiconductor devices driven by a direct current, one might be tempted to assume that the operating principle of an OLED is fundamentally the same as that of an inorganic semiconductor LED. However, this analogy does more to hinder understanding than to help. Inorganic semiconductor LEDs exploit a p–n junction structure in a doped semiconductor whose electrical conductivity characteristics are precisely controlled to be p-type or n-type. OLEDs, on the other hand, use multilayer films of highly purified organic solids that are essentially undoped, exhibiting very high electrical resistance. Apart from a superficial analogy that arises because both devices use a two-electrode configuration, encompassing electron and hole injection from the electrodes, carrier transport, carrier recombination, and subsequent light emission, there is little common ground between inorganic and organic devices. Accordingly, starting from Chapter 2, we will indeed use the superficial resemblance between OLEDs and inorganic semiconductor LEDs as a conceptual entry point. However, we will then expand our discussion to include the unique structural, electronic, and optical properties of organic semiconductors, thereby developing our own detailed treatment of OLED operation.

To describe the basic operating principle, let us consider the simplest OLED device structure in which an organic semiconductor thin film is sandwiched between two electrodes. As shown in Figure 1.1, a layer (approximately 100 nm thick) of organic semiconductor is deposited on an indium tin oxide (ITO) thin film, functioning as the anode, formed on a glass substrate. A metallic thin film, acting as the cathode, is then deposited on top. This single-layer configuration is the fundamental device structure for an OLED. Light generated within the organic

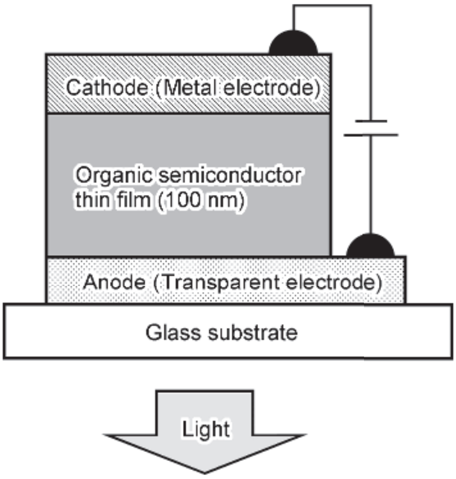


Figure 1.1 Device configuration of a single-layer OLED.

thin film is extracted as surface emission through both the transparent organic layer (which is nearly transparent to visible light) and the transparent ITO electrode. For example, suppose the organic semiconductor thin film has a molar mass of 400 g/mol and a density of 1.1 g/cm^3, forming a molecular aggregate. The number of molecules per unit volume can be estimated as $(6.02 \times 10^{23} \times 1.1)/400 \approx 1.0 \times 10^{21}$ molecules/cm^3. Hence, on a 1.0-cm^2 interface, the number of molecules in contact with the electrode is on the order of 1.0×10^{14} molecules/cm^2. Now consider a single-layer OLED under a constant applied voltage V. A steady current density J (A/cm^2) flows from the anode to the cathode. Suppose $J = 1.0$ mA/cm^2. The number of electrons or holes injected per unit area per second into the organic layer from each electrode is given by $J/e = 1.0 \times 10^{-3}/1.60 \times 10^{-19} \approx 6 \times 10^{15}$ cm^{-2}s^{-1}, where e is the elementary charge ($e = 1.60 \times 10^{-19}$ C). This indicates that each molecule at the electrode interface accepts electrons or holes around 60 times per second.

When an OLED is driven by a steady current and is in a steady state, the steps from hole and electron injection at the electrodes to light emission can be described by the following six elementary processes:

(1) Injection of holes from the anode/organic interface and electrons from the cathode/organic interface (holes are injected at a rate of J/e cm^{-2}s^{-1} from the anode and electrons at the same rate from the cathode).
(2) Drift transport of holes in the vicinity of the anode toward the cathode under the applied voltage, while drift transport of electrons in the vicinity of the cathode toward the anode.
(3) Recombination of injected and transported electrons and holes within the organic semiconductor and formation of molecular excited states (excitons). Since J/e holes and J/e electrons are injected per second per unit area, up to J/e excitons can be formed by their recombination.
(4) Exciton diffusion within the organic semiconductor.
(5) Radiative decay (light emission) of excitons within the organic semiconductor. Up to J/e photons can be emitted.
(6) Extraction of the generated light through the transparent electrode and substrate into the external (air) environment.

Figure 1.2 uses an energy-level diagram for the organic semiconductor, anode, and cathode to conceptually illustrate the processes (1)–(3). By analogy with the band diagrams typically used for conventional semiconductor devices, we can consider an electron transport level and a

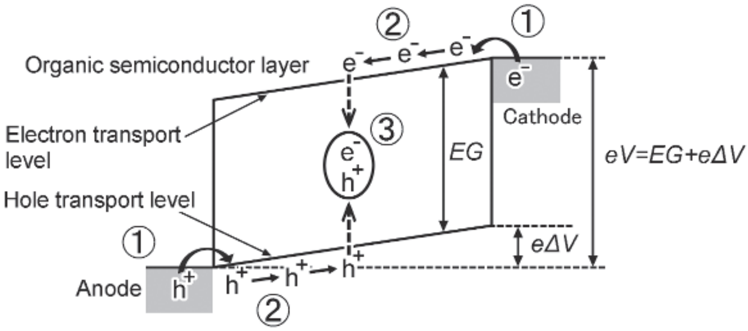


Figure 1.2 Energy-level diagram of the elementary processes from carrier injection to recombination in a single-layer OLED.

hole transport level in the organic semiconductor, separated by an energy gap *EG* (eV). For an OLED emitting visible light, *EG* will generally range from about 2.0 eV (red light) to about 3.5 eV (near-ultraviolet). Let us assume the Fermi level of an anode (its work function) is approximately aligned with the hole transport level, while the Fermi level of a cathode is aligned with the electron transport level. For example, a transparent ITO thin film may serve as the anode (which is nearly transparent to visible light) and a reflective metal thin film as the cathode. Figure 1.2 schematically shows the situation in which a voltage $V = EG\ /e + \Delta V$ is applied between the anode and cathode, enabling electron and hole injection into the organic layer. Processes (1)–(3), from carrier injection at the electrodes to exciton generation via recombination, are shown in Figure 1.2. However, processes (4) and beyond are not depicted in the figure. The first three steps involve charged carriers, whereas from process (4) onward, neutral excitons and photons are involved. Consequently, a simple energy-level diagram does not directly visualize exciton diffusion and radiative decay.

Usually, for a semiconductor band diagram, one need not explicitly depict the physical structure of the solid device in real space because the underlying assumption is a delocalized electron system throughout the solid. However, as will be discussed in detail in Chapter 2, the organic semiconductors used in OLEDs are amorphous glassy solids composed of many organic molecules, each with its own small, isolated, localized π-electron system. Therefore, describing both charge-carrier (electron/hole) dynamics and neutral-exciton dynamics solely in terms of the π-electron energy levels is insufficient. Alongside Figure 1.2, it is often helpful to consider the molecular-level depiction of the device, as illustrated in Figure 1.3. Whereas Figure 1.2 shows a device-physics perspective, Figure 1.3 offers a molecular-chemistry perspective starting from each individual molecule. In Figure 1.3, each molecule possessing a localized π-electron system is depicted as an ellipse. Approximating each molecule as a sphere of diameter 1.0 nm, a 100-nm-thick organic semiconductor film would contain only about 100 molecules in the direction from anode to cathode. Process (1), i.e., carrier injection, can be understood as an electron addition reaction (radical anion formation) at the cathode side, in which an electron is transferred from the electrode to the lowest unoccupied molecular orbital (LUMO) of the molecule and a hole injection reaction (radical cation formation) at the anode side, in which an electron is extracted from the highest occupied molecular orbital (HOMO) of the molecule to the electrode. Process (2), i.e., carrier transport, occurs by intermolecular hopping of electrons through the LUMO (sequential transfers from one LUMO to another) and holes through the HOMO (sequential backward electron transfers from one HOMO to another). Process (3), i.e., carrier recombination, can be seen as the addition of an electron from the radical anion to the LUMO of the radical cation, or the

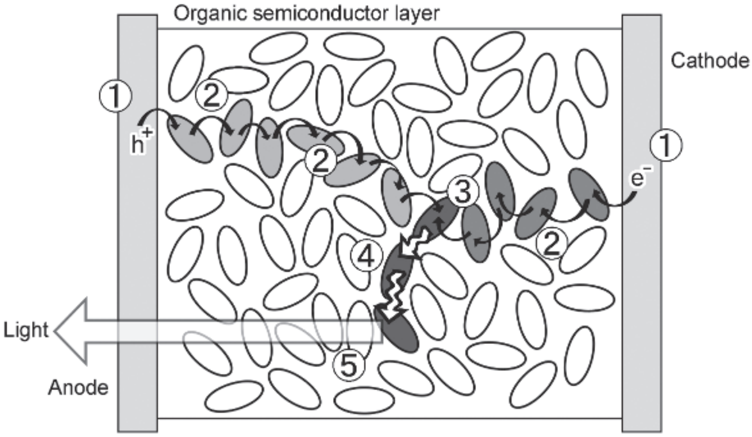


Figure 1.3 Carrier and exciton motion described by the picture of a molecule-filled organic molecular solid.

extraction of an electron from the HOMO of the radical anion by the radical cation. The resultant neutral molecular state gains the reaction energy of cation–anion recombination, becoming an excited state known as a neutral exciton. The exciton then undergoes process (4), exciton diffusion, and ultimately emits a photon, returning to the neutral ground state in process (5). Finally, regarding the correspondence between the electron/hole transport levels in Figure 1.2 and the HOMO/LUMO levels in the molecular depiction of Figure 1.3, there is considerable nuance that warrants further examination. A detailed discussion is provided in Section 5.1.

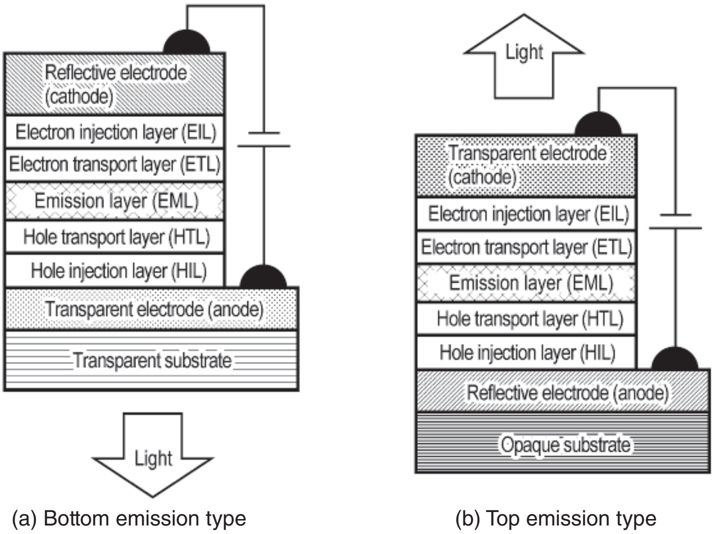
1.2 High-Performance Multilayer OLEDs

In the previous section, we described the operating mechanism of OLEDs using the most simplified classical single-layer device structure as a model. However, since the proposal of a two-layer device structure by C. W. Tang and colleagues at Eastman Kodak, the two-layer device fabricated by vacuum deposition, presented in a 1987 paper, along with several improved variations, has been widely used as a starting point for understanding the OLED operating mechanism and has greatly contributed to the progress of OLED research. Furthermore, 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), used as a hole-transport material, and tris(8-hydroxyquinoline)aluminum (Alq_3), used as an emissive electron-transport material, have been extensively investigated as the archetypal organic semiconductor materials for OLEDs, thereby making a significant contribution to fundamental OLED research [1]. Even today, these remain essential benchmarks in academic research. Nevertheless, confining the foundation of modern OLEDs to the somewhat narrow concept of the “Kodak-type” multilayer device can be inconvenient. Therefore, in this book, we will reestablish our starting point for discussing OLED operation mechanisms by choosing a “model device structure” and “model organic semiconductor materials” that reflect the device configurations and materials widely used in current mass production. We believe this approach will yield a more general, simplified, and understandable discussion when interpreting OLED operating mechanisms.

As of 2025, nearly all commercially produced OLED displays for smartphones worldwide, manufactured by Samsung and LG Display in Korea as well as by several display makers in

China, are composed of multiple stacked organic thin films formed by vacuum deposition, with extremely rare exceptions. As for OLED televisions, they are almost exclusively produced by LG Display in Korea, also using vacuum deposition. Understanding the device structure of these high-efficiency, highly reliable OLED devices that are currently mass produced is the first step toward grasping the operating mechanism of high-performance OLEDs. Of course, the most cutting-edge device architectures and the exact chemical structures of the materials used are top secret within each company and are not publicly disclosed. However, regarding the fundamental information needed to understand device operation, a body of publicly available data has been accumulated, and it is fair to say that researchers now share a common foundation of knowledge [2–4].

Figure 1.4(a) shows the most fundamental example of a multilayer device structure. Sequentially formed by vacuum deposition on a transparent ITO electrode (the anode) on a transparent substrate (often glass) are a hole injection layer (HIL), a hole transport layer (HTL), an emission layer (EML), an electron transport layer (ETL), an electron injection layer (EIL), and finally a reflective metal electrode (the cathode).[1] The method of extracting light through the glass substrate and the transparent ITO anode is called bottom emission, whereas top emission, where light is extracted through a semitransparent cathode on the side opposite the substrate (Figure 1.4(b)), is also widely used. For the purpose of understanding device operation, the distinction is not critical, so unless otherwise stated, we will assume bottom emission going forward. Typically, the HIL is made of a p-doped organic semiconductor and can have a thickness anywhere from about 30 to 100 nm. This layer is often fabricated by codeposition of a host HTL material and a small amount of an acceptor dopant, but other methods, such as a wet coating process using a polymeric HTL host with an acceptor, are also used. Both inorganic and organic molecular materials are used as acceptors. The HIL can exhibit high stability and reliability under continuous operation, forming the foundation of high-efficiency, highly reliable multilayer OLEDs. We will revisit the function of the HIL



(a) Bottom emission type (b) Top emission type

Figure 1.4 Bottom emission type (a) and top emission type (b) structures of multilayer OLEDs.

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[1] In this chapter, we have used the terms “hole injection” and “electron injection” without any detailed explanation. However, as used in the context of OLEDs, “carrier injection” simply refers to the movement of electrons or holes, driven by the applied electric field, from one thin-film layer to the next at their interface. Note that this differs from the concept of “carrier injection” commonly used in semiconductor physics.

in Chapter 5. The HTL is formed by vacuum deposition of a high-purity small molecule containing triphenylamine or carbazole-based heteroaromatic rings. Its thickness generally ranges from about 20 to 50 nm and seldom exceeds 50 nm. The HTL typically consists of a single-component film of a high-purity organic molecule. We will touch upon the distinction between the p-doped HIL and the undoped (intrinsic) HTL in Chapter 2. Carrier transport within the HTL is the main focus of Chapter 4, while issues related to carrier injection are addressed in Chapter 5.

The EML commonly consists of multiple codeposited components, with a thickness in the 20–30-nm range. The simplest and easiest-to-understand EML structure is a two-component blend film created by codepositing bipolar "host" molecules[2] and emissive "guest" molecules. In some cases, the bipolar characteristics of the host are achieved by blending electron-transport molecules with hole-transport molecules, resulting in a three-component system (two hosts plus one guest). The guest emitter may be fluorescent or phosphorescent molecules, but there are also cases that involve thermally activated delayed fluorescence (TADF) molecules, or a combination of fluorescent and phosphorescent emitters. Chapter 3 covers carrier recombination, while the details of exciton generation via carrier recombination and the subsequent light emission are discussed in Chapter 6.

Similar to the HTL, the ETL is usually a single-component film of high-purity small molecules formed by vacuum deposition, with a thickness in the range of 20–30 nm. In principle, the EIL is composed of an n-doped version of the ETL material. However, because suitable molecular electron donors with stable performance have not been identified, alkali metals such as Li or Cs are used as donors, even though their reliability remains somewhat inadequate. Therefore, it is common practice to insert an extremely thin buffer layer, less than 5 nm thick, of materials like LiF, Li_2CO_3, or 8-quinolinolato lithium (Liq) between the ETL and the metal cathode. In some cases, the EIL itself is formed by codepositing the ETL host material with the aforementioned buffer material. Bearing these practical considerations in mind, we will define the EIL somewhat abstractly. We will again discuss n-doped layers and the EIL in Chapter 2 and revisit them in Chapter 5. Although Mg–Ag alloys were initially used as cathodes, the buffer layer approach has made aluminum a viable material, widely used today as a standard cathode. Meanwhile, in top emission devices, where the cathode must be semitransparent, Mg–Ag alloys are still frequently used.

In some devices, the HTL is split into two sublayers, and the layer in direct contact with the EML is called the electron-blocking layer (EBL). Similarly, if the ETL is split into two sublayers, the layer adjacent to the EML may be called the hole-blocking layer (HBL). The role of the EBL (or HBL) is to prevent electrons (or holes) injected from the ETL (or HTL) from escaping the EML, as well as to block excitons generated in the EML from diffusing into the HTL or ETL. Such designs can increase the total number of organic layers from five to as many as seven. By inhibiting carrier or exciton leakage from the EML, the EBL and HBL improve luminous efficiency. They also prevent any escaped carriers or excitons from entering the HTL or ETL, thereby mitigating potential degradation. This effect is even more significant in improving device reliability.

The concept of the p–i–n device structure, proposed by K. Leo and others in 2002, is essentially identical to the five-layer device structure described earlier, if one views it as a sandwich of a p-doped layer, an undoped "intrinsic" semiconductor layer, and an n-doped layer [5]. In fact, in their paper, the i-layer is composed of the HTL/EML/ETL. Hence, their p–i–n device structure can be seen as a specific case of the five- or seven-layer stacked device in which the HIL functions as the p-doped layer and the EIL functions as the n-doped layer. An inorganic p–i–n junction

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[2] "Bipolar transport" means that both the hole mobility and electron mobility are relatively high, and their difference is generally within a factor of about 100. Further details will be discussed in Chapter 4.

diode features a highly doped p-type semiconductor layer and n-type semiconductor layer sandwiching an intrinsic layer, thereby operating under high-level carrier injection. In this sense, the p–i–n OLED concept proposed by K. Leo et al. is essentially the same as the well-known inorganic p–i–n junction diode. However, one should not casually conclude that OLEDs can thus be explained by the same concepts that govern conventional inorganic semiconductor diodes. The p–i–n idea merely underscores that adding p-doped and n-doped layers to facilitate carrier injection into the "i-layer" can be understood by analogy with inorganic p–i–n diodes. It does not explain the carrier behavior within the "i-layer." Indeed, the main theme of this book concerns the dynamic processes inside that i-layer, including electron and hole transport as well as the generation, migration, and annihilation of excitons.

1.3 Overview of Each Chapter

For multilayer OLEDs that use phosphorescence or TADF mechanisms in their emission layers, the external quantum efficiency[3] can reach about 40%, which is nearly the theoretical maximum. Moreover, continuous operational lifetimes of over 20,000 hours (over two years) at an initial luminance of 1000 cd/m^2 are readily achievable. The aim of this book is to offer a scientifically rigorous, fundamental explanation of the operating principles behind these high-reliability OLEDs, which operate at near-theoretical efficiency.

Part I (Chapters 1 and 2) set the stage for the discussions in Part II. After this introductory Chapter 1, Chapter 2 investigates the electronic and optical properties of amorphous glass organic semiconductors (hereafter abbreviated as ag-OS) used in OLEDs, drawing comparisons with the long-studied inorganic semiconductors. Through exploring similarities and differences, we clarify the unique characteristics of organic semiconductors used in OLEDs. In particular, we point out that conventional semiconductor physics terms, such as "junction," "carrier injection," "majority carrier," and "minority carrier," cannot be applied straightforwardly to organic semiconductors used in OLEDs, and redefinitions may be necessary.

Part II (Chapters 3–5) examine the dynamic processes involving charged carriers. Chapter 3 outlines the events from carrier injection at the electrodes to carrier recombination in the emission layer, discussing in detail why the concept of carrier balance is indispensable. Chapter 4 focuses on carrier transport in carrier transport layers and an emission layer, with particular emphasis on understanding carrier transport in thin ag-OS films. Chapter 5 reviews our current understanding of the electrode/organic and organic/organic interfaces and then delves further into the physics of carrier injection at these contact interfaces.

Part III (Chapters 6 and 7) address processes involving neutral (uncharged) excitons. Chapter 6 begins with a discussion of how neutral excitons are generated by carrier recombination. It then examines the creation of singlet and triplet excitons (an issue involving electron spin). Detailed exploration of the dynamic processes where these excitons emit light with minimal loss follows.

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[3] "External quantum efficiency" is defined as the number of photons emitted outside the device per unit area divided by the "apparent injected carrier" count per unit area (obtained by dividing the current flowing in the external circuit by the elementary charge). Alongside the current–voltage and emission spectrum characteristics, it is an important and directly measurable device parameter. On the other hand, "internal quantum efficiency" is defined as the ratio between the number of photons generated inside the device and the apparent injected carrier count. Because there is currently no direct method to quantitatively measure the number of photons generated inside the device, internal quantum efficiency is understood as a parameter used for discussing device characteristics rather than one that can be directly measured.

Central topics here include triplet–triplet annihilation (TTA) and TADF. Chapter 7 focuses on how singlet and triplet excitons, once created, move through organic semiconductor films. The processes such as intermolecular energy transfer, exciton diffusion, and annihilation of excitons are dealt with.

In Part IV (Chapters 8–11), we broaden our viewpoint to explore more advanced aspects of OLEDs. Our discussions in Parts II and III treat the organic semiconductor layers in multilayer OLEDs as amorphous-glass organic semiconductors (ag-OS), essentially random aggregates of molecules with no particular positional or orientational order, bound together by weak van der Waals forces. We assume negligible intermolecular electronic interactions, such that carriers exist locally as radical anion or cation states on individual molecules (termed “electrons” or “holes,” respectively) and move among molecules via hopping. Meanwhile, the neutral excited states (“excitons”) created by carrier recombination diffuse among molecules via self-diffusion or energy-transfer mechanisms. This simplified model, carriers and excitons localized on individual molecules, offers a solid foundation for understanding the current–voltage and luminescence characteristics of OLEDs. However, one should not too hastily conclude that because ag-OS is an amorphous glass, it lacks diversity and therefore cannot exhibit the rich electronic and optical properties seen in crystalline solids or liquid crystals. Over the past two decades or so, researchers have discovered that ag-OS, although seemingly uniform, can indeed display diverse characteristics in electronic and optical behavior. Part IV expands on these more advanced or specialized properties, presenting a forward-looking, practical discussion grounded in the unified understanding of the device physics of OLEDs established earlier.

Finally, Part V (Chapter 12) addresses device degradation mechanisms and operational lifetime, topics that lie somewhat outside the strict scope of semiconductor device physics but are indispensable for real-world applications. While it is true that reliability issues, especially performance degradation under continuous operation, might be considered more of an engineering topic rather than pure semiconductor physics, our stance is that a device lacking sufficient reliability does not merit detailed discussion of its device physics.

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