Trends in Research on Organic Light-emitting Diode

Organic light-emitting diode (OLED) is a display technology that is capable of producing high quality images and holds promise for use in next-generation displays. Japan has led the development of much of the technology in this field. In 1997, the world’s first passive matrix OLED display was put on the market by a Japanese company. Since then, many companies have entered the field, and now, many large-screen OLED displays are being shown at exhibitions. Although there are OLED displays of the 50-inch class and larger on the market, many problems remain to be solved before OLED product sales can really get off the ground. This article describes new technology for solving those problems.

1. Introduction

The term ‘OLED’ has become familiar because of its use in the displays of cell phones and TVs. These devices are thin, light, and offer high contrast and a fast response, and they hold promise for use in the next generation of large-screen displays. The first OLED TV offered by a Japanese company was an 11-inch device that appeared on the market in 2007. Since then, OLED displays have been used mainly in cell phones. In 2010 though, a 15-inch OLED TV was put on the market in Europe, and by 2013, 55-inch class and curved-screen OLED TVs were being sold in the US. The popularity of OLED TVs will probably increase gradually, as they are seen as high-end products and will continue to face strong competition from less expensive liquid crystal TVs.

One approach to expanding the market for OLED products is to develop applications that take advantage of the special features of the technology. An example would be lighting applications that use OLED as easily dimmable planar light sources. Another example is a flexible display, which is the topic of this special issue. Because the OLED display consists of stacked thin films, it can be used to realize ultrathin displays that offer great freedom in how they are used.

This technology holds promise for implementing thin and light sheet displays for viewing 8K Super Hi Vision (8K), a next-generation broadcasting system, on large-screen TVs in the home. For handheld TVs, on the other hand, the qualities of being not easily broken by dropping and excellent storability make OLED displays suitable for use anytime, anywhere. This article describes the principle of OLED, issues related to the technology, and the recent trends in research on it.

2. Principle of OLED and related issues

2.1 Principle of OLED

OLEDs are carrier injection devices. They consist of an organic thin film sandwiched between electrodes. When a direct-current voltage is applied, holes and electrons recombine in the light emitting layer, and light is emitted. For that reason, they are classified as self-luminous. The basic device structure includes a glass substrate on which a transparent electrode (ITO, etc.) is formed (Figure 1(a)). Above that layer are stacked a hole transport layer, a light emission layer, an electron transport layer, and a cathode layer. Confining the injected charge carriers to the light emitting layer for

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*1: A device that directly transfers the charge-carrying holes or electrons to the target layer.

*2: A compound in which tin is added to indium oxide.

*3: The layer that carries holes. The layer that carries electrons is called the electron transport layer.
recombination raises the emission efficiency, so there may be an electron blocking layer on the hole transport layer side of the emission layer and a hole blocking layer on the electron transport layer side. The emitted color is largely determined by the color of the emission layer. The thickness of each organic layer is from 30 to 50 nm, and the total thickness including the anode and cathode is several hundred nanometers.

Referring to the energy diagram shown in Figure 1 (b), the holes injected from the anode move to the orbitals filled by electrons in the hole transport layer and electrons injected from the cathode move to empty orbitals in the electron transport layer and arrive at the light emission layer. There, the holes and electrons recombine, and light is emitted.

OLED stands for organic light emitting diode, and they are further classified according to the material used, which is either high molecular weight\(^4\) or low molecular weight. In particular, the high molecular weight types are called polymer light emitting diodes (PLED). Low molecular weight materials of fluorescence are mainly used for manufacturing and they are formed by vacuum deposition\(^5\). Phosphorescent organic light emitting materials appeared in the late 1990s, and devices incorporating these materials that can use close to 100% of the injected charge carriers for light emission.

The difference between florescent and phosphorescent light emission is shown in Figure 2. In the material that receives the charge carriers, the recombination of the holes and electrons creates excited states\(^6\) of two energies, as shown in Figure 2(a). Molecules in such excited states are referred to as excitons. One of the excited states is a singlet exciton,\(^7\) for which fluorescent light emission easily occurs. The other excited state is a triplet exciton,\(^8\) for which energy tends to be lost as heat or molecular vibrations and does not lead to light emission. (This is called non-radiative deactivation.) Singlet and triplet excitons are generated in a proportion of 1 to 3 (25% singletons and 75% triplets.)

In phosphorescent materials, however, triplet excitons can be made to emit light. In fact, many phosphorescent materials that use organometallic compounds containing transition metals\(^9\) such as iridium, platinum, osmium, or ruthenium to generate light from triplet excitons have been reported.\(^2\) to \(^5\)

The phenomenon responsible for light emission from the triplet state is the heavy atom effect,\(^10\) in which light is rapidly emitted by heavy metals such as iridium. In phosphorescent materials, the heavy atom effect promotes inter-system crossing (ISC),\(^11\) in which singlets are converted into triplets so that 100% of the injected charge can be converted into a phosphorescent emission. However, fluorescent materials have a longer device drive lifetime, so they are more practical.

Besides the vacuum deposition method mentioned above, printing techniques are being investigated as a method of manufacturing.

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\(^4\) An organic material that has a molecular weight (the relative mass of the molecule) of 1,000 or more.

\(^5\) A technique for depositing a material on a substrate by heating the material in a vacuum to vaporize it.

\(^6\) The state that has the lowest energy of the states that an atom or molecule can take is called the ground state. States of higher energy are called excited states.

\(^7\) Molecules whose excited state electrons are singlet excitons (one type of spin state, which is a magnetic property of electrons).

\(^8\) Molecules whose excited state electrons are triplet excitons (one type of spin state, which is a magnetic property of electrons).

\(^9\) The general name for the elements in columns three through 11 of the periodic table.

\(^10\) A phenomenon in which inter-system crossing occurs more easily for elements that have higher atomic numbers. (See footnote \(^11\)).

\(^11\) A phenomenon in which the spin of electrons in excited molecules changes between singlets and triplets.

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\[ \begin{aligned} \text{Singlet exciton} & \quad 25\% \quad \text{Fluorescence} \\
\text{Triplet exciton} & \quad 75\% \quad \text{Phosphorescence} \end{aligned} \]

\[ \begin{aligned} \text{Singlet exciton} & \quad 25\% \quad \text{Fluorescence} \\
\text{Triplet exciton} & \quad \text{Non-radiative deactivation} \quad \text{Phosphorescence} \end{aligned} \]

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\[ \begin{aligned} \text{Intersystem crossing (ISC)} \quad \text{Total 100\%} \\
\text{Fluorescence} & \quad \text{Non-radiative deactivation} \\
\text{Phosphorescence} & \quad \text{Non-radiative deactivation} \end{aligned} \]

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\[ \begin{aligned} \text{Figure 2: Difference between fluorescence and phosphorescence} \end{aligned} \]
way of forming the layers of these devices. Using high-molecular-weight light emitting materials to print device layers has the advantage of high productivity. The coloring methods include printing red, green, and blue elements individually and using white OLEDs with color filters.

2.2 Comparison of OLED displays and LCDs and their issues

Figure 3 compares the features of OLED displays and liquid crystal displays. We can see from the right side of the figure that OLED displays have advantages related to image quality and freedom of form, and their performance as displays is high. Their disadvantages, however, are related to their high cost (the left side of the figure).

Regarding contrast, OLED TVs offer a contrast ratio of 100,000 to 1 or higher, which is good for movies and other video. On the other hand, the contrast ratio of LCD TVs has reached 3000 to 1, as a result of improvements such as backlight control.

As for color reproduction, there is no large difference between OLEDs and LCDs when color filters are used. But OLEDs offer high color purity for red green and blue. Furthermore, even higher color purity can be achieved by controlling the device thickness according to the color so as to use light interference. (This is called the micro-cavity effect.) The color reproduction of OLEDs is thus said to be higher than that of LCDs. Nevertheless, some high-end LCD TVs, with improved backlight color or quantum-dot\textsuperscript{12} or laser-light sources, can more or less match the performance of OLEDs on the Adobe RGB specifications\textsuperscript{13}.

The response rate is the time required to change the luminance, and for OLEDs, it is on the order of tens of microseconds, whereas it is from several milliseconds to several tens of milliseconds for LCDs. In this regard, LCDs are nonetheless capable of displaying Hi-Vision (HDTV) because its frame interval is 16.6 ms at a scanning frequency of 60 Hz. In the future, however, the number of scan lines will increase by a factor of two or four as 4K or 8K technology become popular, and the scanning frequency will also increase. In that event, OLEDs will probably be preferred for their faster response.

Looking at the panel thickness in Figure 3, the thickness of the OLED itself including the electrodes is about 0.5 μm. Accordingly, the thickness of the OLED display is governed by the thickness of the substrate and the thickness of the protective film. The thickness of the color filters is also to be considered if they are used. An 11-inch OLED TV that went on the market in 2007 was 3 mm thick, and an OLED TV that is currently being sold by a Korean company is 5 mm thick. Of course, the display could be made thinner by using a thinner glass substrate or a thin plastic film substrate, which would also make a curved TV screen possible. By comparison, LCD TVs require many parts, including a glass substrate, a backlight, a polarizing filter, and color filters, so it seems that making a very thin LCD display would be difficult. Nevertheless, commercial level LCD TV displays now have an average thickness of 10 mm, and they are getting thinner and thinner. However, the display performance of LCD TVs is sensitive to variations in the thickness of the space that is filled with the liquid

\textsuperscript{12} Metal oxide material particles scaled to a diameter of several nanometers that exhibit characteristic light absorption and light emission properties. The light wavelength varies with the particle size, so true color reproduction can be achieved by controlling the particle size.

\textsuperscript{13} A specification that represents the color reproduction range for printed materials, cameras, displays, etc. It features a wide range of reproducible colors.

![Figure 3: Comparison of organic EL displays and LCD displays](image-url)
crystal material, and this can be seen when forcefully pressing against the screen or attempting to bend one. Accordingly, OLED technology is better suited for flexible TV displays because it is resistant to deformations and impacts.

Concerning large-format screens, a Taiwanese company has fabricated a 65-inch HDTV display patterned by a vacuum deposition method using fine metal mask for each RGB color. On the other hand, a Korean company has announced a 77-inch 5K curved OLED display that uses a white OLED with color filters that the white light emitting layer is formed for all of the RGB pixels and is suitable for manufacturing large high-resolution displays since this method needs no patterning of colors.

Concerning the cost factors in Figure 3, OLED displays have the potential to consume about half the power of LCDs. Currently, however, the power consumption is twice that of LCD TVs or even higher. For example, one recent 55-inch OLED TV consumes more than 400 W.

The Energy Star initiative of the US government issued specifications (Ver. 6.0) in June 2013 requiring low power consumption (about 100 W) even for 100-inch class TVs (Figure 4). These new standards are said to be a major hurdle for OLED displays. As described in section 2.1, the reason for the high power consumption of OLEDs is that only 25% of the injected charge contributes to light emission in fluorescent materials. Another reason is that when color filters are used to produce the RGB colors in OLEDs, two thirds of the light is wasted for each color. In theory, the use of phosphorescent materials would increase light emission efficiency by a factor of four and patterning of emitters of three colors would increase light emission efficiency by a factor of three. Although the compound increase in efficiency of a factor of ten will be a challenge to reach, it would mean that even large format TVs would be energy efficient.

3. Latest OLED technology

3.1 More efficient fluorescent materials through triplet interaction and molecular orientation

As described in section 2.1, the contribution of injected charge carriers to light emission is supposed to be limited to 25% in OLED using fluorescent materials. In the last half of the 1990s, there were a number of reports on materials exceeding this theoretical limit. The materials used in these studies exploited a phenomenon in which singlet excitons are generated from multiple triplet excitons when there is a high concentration of triplets (molecules in the triplet excitation state) in Figure 5 (a). This phenomenon is called triplet-triplet annihilation (TTA) (there is also a related phenomenon called triplet-triplet fusion; TTF). Theoretically, a maximum of 40% to 62.5% of the energy can be used for light emission in that case.

The current phosphorescent materials used for green and red light are high efficiency and have a long lifetime, and they are being used in mobile devices. The blue phosphorescent materials, however, have not seen much progress in lengthening their lifetime. A present, therefore, the search is underway for ways of raising the light emission efficiency of blue fluorescent materials by using TTA technology and molecule orientation technology.

As shown in Figure 5(b), ordinary OLEDs emit light in all directions (isotropic). Therefore, some light is reflected from the substrate surface, and only about 20% of the light emitted internally is emitted to the outside. The proportion of light emitted internally can be extracted is called the light extraction efficiency and is denoted as $\eta_{\text{out}}$. Accordingly, from 8% to 12.5% of the injected electrical charge is emitted outside the substrate by the TTA described above. That value is called the external quantum efficiency (EQE). When $\eta_{\text{out}}$ is 20%, the EQE of a phosphorescent material that can emit 100% of the injected charge as light is 20%. In contrast, the EQE for ordinary fluorescent material is only about 5% at this value of $\eta_{\text{out}}$.

It is possible to improve $\eta_{\text{out}}$ by 40% or more by controlling the orientation of the light emitting molecules (Figure 5 (c)). To do so, the shapes of the light emitting molecules are made flat rather than round.

By applying the techniques described above and using blue phosphorescent material, it is possible to achieve an external quantum efficiency (EQE) of 12% and an EQE of 14% with fluorescent materials, thus approaching the value for phosphorescent materials (20%). Besides improving the internal light emission efficiency, technology for raising the extraction efficiency is also important. For lighting applications of OLED technology, various companies have achieved $\eta_{\text{out}}$ values of 50% or more by placing micro-lens arrays on the emission surface, roughening the substrate surface to diffuse the emitted light, or by using a material that has a high refraction index for the substrate.

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*14 Standard specifications for electronic products established by the U.S. Department of Energy.

*15 A regular arrangement of organic molecules.
3.2 Thermally activated delayed fluorescence (TADF) for higher efficiency

Here, we explain a new light emission mechanism for highly efficient OLEDs. Up to now, phosphorescent materials were the only materials for which nearly 100% of the injected charge could be converted into light. But phosphorescent materials use organometallic compounds that contain iridium or other precious metals. Because these compounds are expensive, there is a need for materials that offer both high efficiency and low cost. Highly efficient reverse energy movement from the triplet excitation state to the singlet excitation state has been demonstrated in inexpensive aromatic organic compounds, which had previously not been possible, by using thermally activated delayed fluorescence (TADF) materials.

**Figure 5: More efficient blue fluorescent material**

(a) Higher fluorescent emission using TTA phenomenon

(b) Usual way of extracting OLED light

(c) light extraction improved by controlling molecule orientation

**Figure 6: Higher fluorescent light emission efficiency by using thermally activated delayed fluorescence (TADF)**

(a) TADF principle

(b) Examples of TADF materials
making the energy gap \( \Delta E \) between singlets and triplets in the light emitting materials 0.1 eV \( \Delta E \) or less, even when fluorescent materials are used (Figure 6 (a)). This is a new light emission principle that can use 100% of the injected charge carriers for light emission, even in fluorescent materials. It is thus called the third generation type of organic electroluminescence after fluorescence and luminescence. Because the light emitted as a result of energy movement in this phenomenon appears after a slight delay, it is referred to as thermally activated delayed fluorescence (TADF). The material consists of organic molecules that do not contain metal and feature a structure that has a core of electron acceptor units such as cyano bases with electron donor units such as carbazole on the periphery.

### 3.3 Higher stability in air

OLEDs use electron injection materials that are damaged by oxygen and water, so sealing technology is needed to isolate these materials from the outside environment to prevent degradation. Plastic film substrates, in particular, are permeable to oxygen and water, and they need a sealing layer to prevent such intrusions. However, the formation of a layer that is sufficient to prevent degradation of the OLEDs reduces productivity, and it is difficult to fabricate a large protective layer that has no defects.

Considering these difficulties, it is desirable to develop OLEDs that are, themselves, stable in air in order to make OLED displays with a plastic film substrate. In an effort to accomplish this objective, our laboratories collaborated with manufacturers in the discovery of an electron injection material that has both high emission performance and stability in air. The light emitting performance of a device that uses the new material and has a new structure is the same as that of an ordinary OLED. When OLEDs with the ordinary structure were used with a film that had low sealing capability (a water vapor transmission rate (WVTR) of \( 10^{-4} \) g/m²/day), they deteriorated after a few days. The devices with the new structure, however, showed no degradation after three months.

The OLEDs that are stable in air have greatly improved reliability when used with plastic film substrates and thus have the potential for radically changing the OLED manufacturing process, which had previously required strict management of oxygen and moisture.

### 3.4 The latest printing technology

As described in section 2.2, printing techniques, in particular, three color differential printing, are being investigated as a method of fabricating large-screen displays.

The ink-jet printing method (Figure 7 (a)) has been investigated by a number of companies, and a 55-inch 4K curved-screen OLED TV was presented at the Consumer Electronics Show (CES) in 2014.

A 7.4-inch QHDTV display (Quarter HDTV, 149 ppi) 

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**Footnotes:**

*16 The difference in the energy levels of the electron orbitals.
*17 Electron volt: a unit of energy.
*18 A location in a material that easily accepts electrons.
*19 A location in a material where electron transfer easily occurs.
*20 Pixels per inch: The number of pixels contained in one linear inch.
was fabricated using a relief printing technique (Figure 7(b)). This technique features low facilities investment and high throughput.

The parallel plate inverted offset printing technique is a new method, and it has been used to fabricate a 7.4-inch QHDTV panel (Figure 7(c)). A feature of this printing technique is that it can be used to make high-pixel-density panels of 500 ppi. Another feature is that red and green OLED layers are first printed using the parallel plate inverted offset printing method, and then a low molecular weight blue material is vacuum deposited over the entire surface, including the red and green pixels (Figure 8). Since the lifetime of the blue materials for printing method is as yet insufficient, this method holds promise for early commercialization.

Polymer type OLED materials can be used in any of the printing methods, and low-molecular-weight materials are being developed for printing.

4. Conclusion

Organic electroluminescence is an excellent display technology that features a high response rate and high contrast. It has recently become possible to manufacture large OLED displays using glass substrates, and over 50-inch displays are currently on the market. However, the high production cost and power consumption are major problems that remain to be solved, so it will probably take more time for these displays to come into widespread use. The flexibility of the display surface has also become a necessity for the next generation of displays, a fact that some regard as an opportunity for the advantages of OLED displays to be fully appreciated.

Further development of the printing technology should be able to address problems such as high power consumption and production cost and yield a process suitable for making large screen formats. To achieve good color reproduction and a long lifetime, there is an urgent need for the development of highly efficient materials that use new light emission mechanisms.

(Takahisa Shimizu)

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*21 A printing method in which ink is first transferred from an Anilox roll (a roller that adjusts the amount of ink) to a relief plate (impressed with the desired pattern in relief) that is wrapped around a plate cylinder (a cylinder that holds the relief plate material), and the ink is then transferred from the relief plate to the substrate.

*22 A type of offset printing in which a blanket is coated with ink by a coater and then unneeded ink is removed by pressing against the printing plate. The ink that remains on the blanket is then transferred to the substrate.
References


2) Tokito, Adachi, and Murata: OLED display, Ohmsha (2005)


