Invited Paper

ELECTROLUMINESCENT MECHANISM OF ORGANIC MULTILAYER THIN FILM DEVICES

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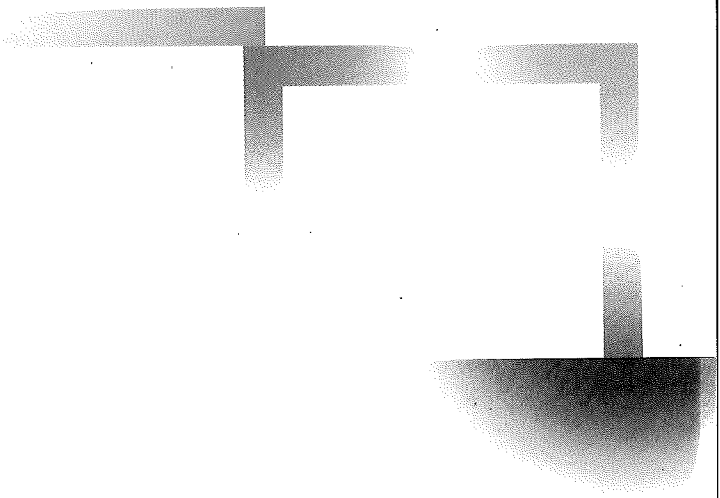

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Abstract High performance organic electroluminescent (EL) devices which are composed of organic thin multilayer films are described. The EL devices were classified into three categories and the optimization of EL cell structures was performed from the viewpoint of the electronic properties of emitter layers. The position of the emission sites in three different types of EL cells was determined by a doping method, and two important aspects in the EL mechanism for high luminance were pointed out. We concluded that high luminance was derived from the confinement of charge carriers and molecular excitons inside emitter layers. Moreover, effective confinement of charge carriers and molecular excitons within a molecular-size area was achieved in the case of double hetero structures.

1. Introduction

Several investigators have shown that bright EL emission could be observed in EL cells with a simple cell structure in which an organic layer is sandwiched between two metal injection electrodes [1]-[4]. However, both the efficiencies of luminance and the stability of cells were far from satisfactory from the technological point of view for display devices. Many researchers have attempted to improve both the efficiency of charge carrier injection and the production of molecular excitons. Tang and VanSlyke proposed to use multilayer thin films in place of a single thin film, and they succeeded in drastic improvement of EL cell performance [5]. Since Tang's report, growing interest has been shown in multilayer-type thin-film electroluminescent (EL) devices, which exhibit very high luminance and can be driven with low dc voltage [6]-[14]. One expects that the application of organic thin-film EL devices for large-area, flat-panel, and full-color displays is promising. We have reported that a variety of fluorescent dyes could be used for emitter materials, and we also proposed two novel EL cell structures having an electron transport layer [8], [10]. Using various kinds of EL cell structures, we have established a method of controlling the movement of charge carriers and molecular excitons in organic thin-films. Moreover, we could realize the confinement of charge carriers and molecular excitons within designed portions in thin film devices [10].

We believe that high EL performance of multilayer devices is attributable to the ingenious use of organic materials having electron transport ability (so-called

Key Words Electroluminescence, organic thin film, vacuum-deposition, carrier injection, molecular excitons, hetero structure, emission sites.

n-type semiconducting properties), which resulted in the construction of a multilayer structure, just as in an inorganic *p-n* junction. A few organic materials so far have been known to show *n*-type semiconducting properties [15]-[18]. The study of organic EL, however, revealed that many kinds of organic materials have the ability to transport electrons. Thus, the determination of the charge carrier transport properties of organic layers is important for the consideration of the EL mechanism. In this study, we elucidated the relation between optimal EL cell structures and charge carrier transport properties of emitter layers. To judge the carrier transport tendency of emitter layers which are incorporated in different EL cell structures, the emission sites and the width inside of emitter layers were determined by the use of the insertion of a thin fluorescent sensing layer into emitter layers [19].

2. Experimental

Four types of EL cell structures were used in this experiment.

Type SL (single layer structure)
    ITO/EML/MgAg
Type SH-A (single hetero-A structure)
    ITO/HTL/EML/MgAg
Type SH-B (single hetero-B structure)
    ITO/EML/ETL/MgAg
Type DH (double hetero structure)
    ITO/HTL/EML/ETL/MgAg

ITO : indium-tin-oxide
EML: emitter layer
HTL: hole transport layer
ETL : electron transport layer
MgAg: magnesium-silver alloy

The substrate was a piece of ITO coated glass. The thickness of the ITO layer was about 1000 Å, and the sheet resistance was about 25 Ω/□. Substrate cleanliness was found to be important in the performance of organic EL devices. Substrates were cleaned ultrasonically in detergent, acetone, and ethyl alcohol successively. Then the substrates were boiled in ethyl alcohol, carefully removed, and dried. The use of substrates with insufficient cleaning often resulted in EL cells which require a high drive voltage and show irregular and unstable emission behaviors, and in non-uniform EL emission and partial discharge.

EL cells were fabricated by conventional vacuum vapor deposition in a vacuum of 1.0×10^{-7} torr. The deposition rate for organic layers was typically 2 Å/s. Unless otherwise stated, the thickness of the organic layers was fixed at 500 Å. The upper electrode was a MgAg (10:1) alloy layer 1500 Å in thickness. This was deposited with vacuum evaporation from two metal sources which were controlled independently. The emitting area in EL cells were 0.2×0.2 cm^2.

The organic materials used in this experiment are shown in Fig. 1. We used an aromatic diamine (TAD) [20] as a hole transport layer (HTL) and an oxadiazole derivative (PBD) as an electron transport layer (ETL). For an emitter layer (EML), naphthostyrylamine derivative (NSD) [20] was used. A thiadiazole derivative [21] was used as a dopant molecule and sometimes as an EML. The dopant molecules were inserted into an EML by successive vacuum deposition. The insertion was 10 Å thick. The thiadiazole molecule forms a charge transfer complex with the NSD molecule, and the complex shows its fluorescence at around 630 nm. As the host emitter layer shows its fluorescence at around 510 nm, one can distinguish emission sites based on the observation of EL spectra; if the location of a dopant layer coincides with carrier recombination sites, EL emission from the dopant layer will be observed.

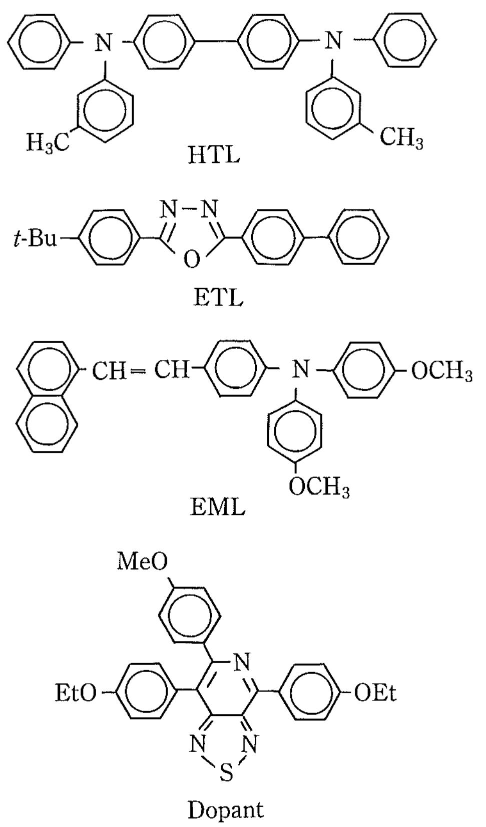

Fig. 1. Organic materials used in this study.

3. Three types of multilayer EL cell structures

In this section, three kinds of EL cell structures are briefly outlined and the determination of optimal EL cell structures using two typical emitter materials is described.

We classified EL cell structures into three categories based on the electronic properties of an EML (Fig. 2). The SH-A structure was proposed by Tang and VanSlyke [5], and the other structures were proposed by us [8], [10].

One should use one of the three cell structures through the electronic properties of an EML. In the single hetero-A (SH-A) structure cell, holes are injected from an ITO electrode into an HTL, and successively injected into an EML. Electrons are directly injected from a metal electrode into an EML and travel toward the boundary of two layers. Holes and electrons meet near the boundary

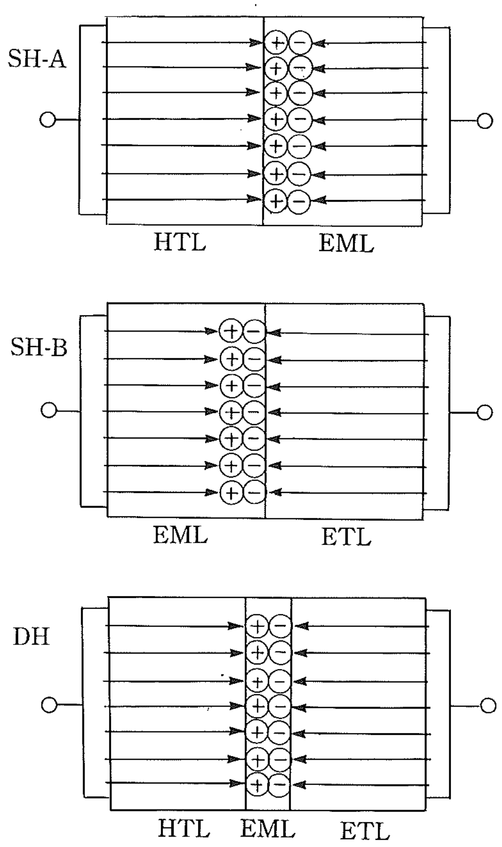

Fig. 2. Three typical cell structures in organic multilayer EL devices.

region within an EML, and carrier recombination occurs at this boundary region.

In the single hetero-B (SH-B) type cells, on the other hand, holes are directly injected into an EML which exhibits hole transporting tendency, and electrons are injected from a top MgAg electrode into an ETL and injected again into an EML. Carrier recombination and emission occur at the boundary region within an EML. The necessity of using different cell structures arises from the difference in the electronic properties of an EML; if an EML exhibits electron transporting tendency, the SH-A structure should be used, and the SH-B structure must be used when an EML has hole transporting tendency.

A double hetero (DH) structure, in which a very thin EML is sandwiched between an HTL and an ETL, is very easy to understand. Electrons and holes are injected from an HTL and an ETL into a thin EML, and recombination of holes and electrons and EL emission occur within this thin layer. The DH structure will be discussed in detail in Sec. 5.

Figures 3 and 4, which show the relations between luminance and current density in EL cells, demonstrate the significance of the three multilayer cell structures. Figure 3 compares the luminous efficiencies of the SH-A, SH-B, and SL type cells using thiadiazole derivative as an emitter [22]. The EL efficiency of the SH-A type cell was about two orders of magnitude higher than that of the SH-B type cell. This can be interpreted from the viewpoint of the electronic properties of the thiadiazole emitter; the thiadiazole emitter has electron transporting tendency. A perfectly reversed example is given in Fig. 4. When an NSD emitter was used, the situation was perfectly reversed: the SH-B type cell showed about two orders of magnitude higher efficiency than that of the SH-A type cell. These two examples clearly demonstrate the importance of proper selection of cell structures. In the next section, EL mechanism will be discussed in the relation to the detailed behavior of injected charge carriers in different EL cell structures.

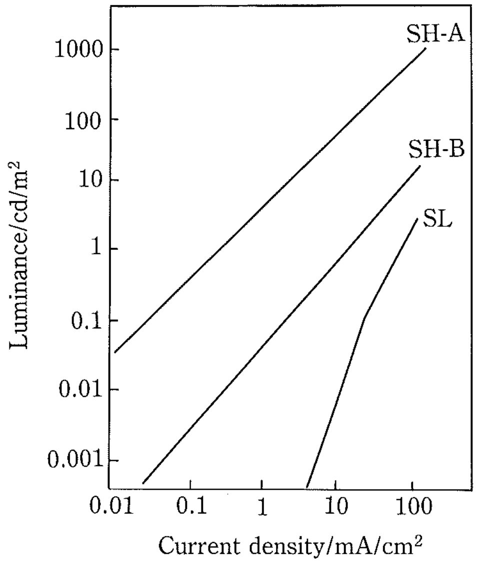

Fig. 3. Luminance-current density relations in SH-A, SH-B and SL type cells with a thiadiazole derivative as an emitter.

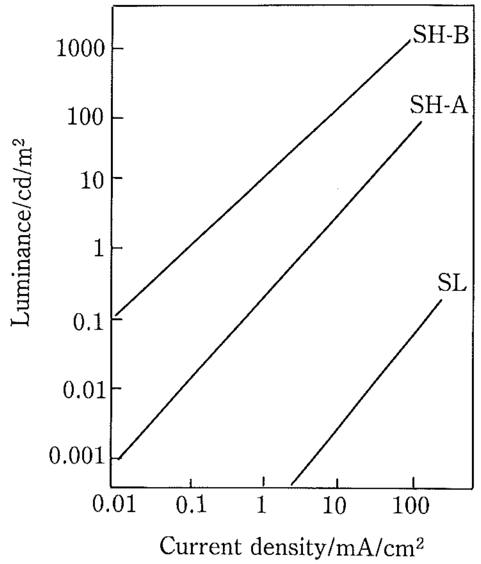

Fig. 4. Luminance-current density relations in SH-B, SH-A and SL cells with a naphthostyryl derivative as an emitter.

4. Electroluminescent mechanism in organic multilayer devices

By using the doping method, the position of the emission sites can be determined. Information on the emission sites is useful in clarifying the two important aspects of the EL mechanism for high luminance. The EL in organic films is assumed to be composed of four processes: (1) charge carrier injection from electrodes into organic layers and from carrier transport layers into an EML, (2) recombination of holes and electrons, and successive creation of molecular excitons, (3) energy migration of molecular excitons, and (4) radiative decay of molecular excitons. Thus, if dopant molecules are located around carrier recombination sites, the energy transfer of molecular excitons from host emitter molecules into dopant molecules occurs and EL from dopant molecules will be observed. On the other hand, if the locations of dopant molecules do not coincide with the carrier recombination sites, EL from host emitter molecules will be observed.

First, we describe the results on SH-B and SL structures and compare the differences. Figure 5 shows the EL emission spectra of six doped SH-B cells with an NSD emitter. In the cases of EL cells with doped A and B regions, the EL spectra are attributable to both NSD luminescence and dopant luminescence. In the cases of EL cells with doped C, D, E and F regions, on the other hand, the EL spectra are mainly due to NSD luminescence, and very little emission from the dopant molecules is observed. The EL emission sites are restricted to the EML near the interface of the EML/ETL, and the width of emission sites was found to be less than 250 Å. This result indicates that the EML (NSD) transport holes and the ETL (PBD) transport electrons selectively.

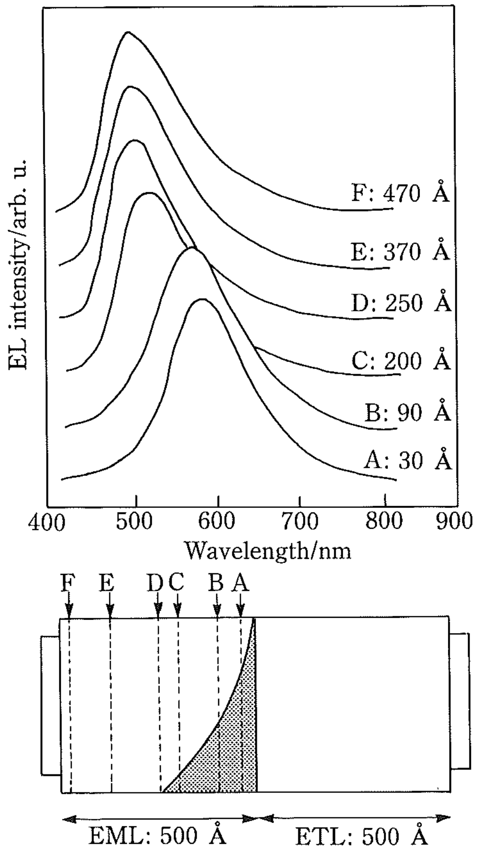

Fig. 5. EL spectra of six doped SH-B cells. The A, B, C, D, E and F indicate doped positions. The distance between a doped position and the interface of EML/ETL layers is also indicated.

Figure 6 shows the EL spectra of doped SL cells. In this case, the EL cell with a doped A region showed the strongest luminescence from dopant molecules. Further, the component of dopant luminescence decreased gradually when the doped region was caused to move toward an ITO electrode. It should be noticed that the emission was very wide in comparison with that of the SH-B structure.

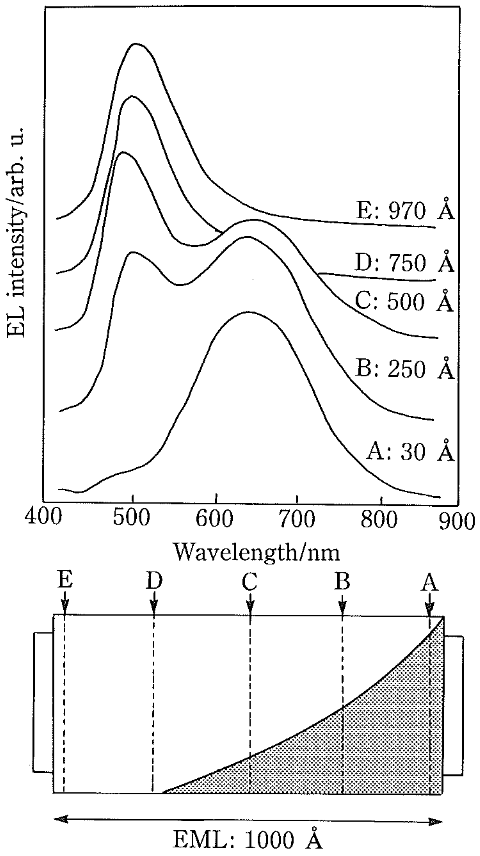

Fig. 6. EL spectra of five doped SH-B cells. The A, B, C, D and E indicate doped positions. The distance between a doped position and the interface of EML/MgAg layers is also indicated.

From the determination of emission sites of SH-B and SL structures, we can point out two important EL mechanisms for high luminance in the SH-B structure. First, the high luminance owes to the confinement of charge carriers inside an EML. The finding that the emission width of the SH-B structure was very narrow in comparison with that of the SL structure is significant from following viewpoints: The interface between the EML/ETL in the SH-B structure serves very efficient carrier recombination sites, and the ratio of electron current (J_e) and hole current (J_h) is almost unity. In the SH-B structure cells, most of the injected holes and electrons recombine at the interface and create molecular excitons, and high EL efficiency is realized. On the other hand, in the case of SL structure cells, a wide recombination width is assumed to result in low carrier recombination probability.

The second EL mechanism of high luminance is concerned with the confinement of molecular excitons. The ETL (PBD) has a larger exciton energy than that of the EML (NSD), as is assumed from their photoluminescent (PL) spectra (refer to Fig. 9). The excitons created in the EML are expected to be blocked by the ETL; if the exciton energy of the ETL is smaller than that of the EML, the energy migration of excitons into the ETL easily occurs and the number of excitons which contribute to the radiative decay is decreased [23]. It should be noticed that the inserted electron transport layer also contributes to protecting from the Förster-type energy transfer into an MgAg electrode, resulting in efficient radiative decay inside an EML. In the SL structure, on the other hand, the Förster-type energy transfer into an MgAg electrode occurs easily, because the emission sites are located near the interface of an EML/MgAg electrode [23], [24].

Finally, we show the result for SH-A cells. In this case, an unexpected result, which should be attributed to the nature of this class of organic semiconductors that work only under high bias field, was obtained. Figure 7 shows the EL spectra of doped SH-A cells. Because the EML has a hole transport tendency in SH-B and SL structures, the insertion of another HTL is expected to play a minor role, and the emission sites in the SH-A structure are expected to be located near a cathode. However, the emission sites were found to extend from the region near the interface of the HTL/EML to the central position of the EML. In this case, sufficient numbers of electrons could be injected from a cathode directly into an EML, and injected electrons moved and recombined with holes which were injected from an HTL. We have to understand that the luminous efficiency of the SH-A structure shows an intermediate value between those of SH-B and SL structures, because the location of the emission sites in the SH-A structure represents partial confinement of charge carriers and molecular excitons. This result implies that the EML shows a rather bipolar transport character, when the EML is combined with a diamine hole transport layer. This finding represents the complexity of this class of organic semiconductor materials. We should assume that organic solid films in which no donor or acceptor was added have intrinsically a certain amount of hole and electron mobility. Thus, when electrons (holes) are injected from adequate electron (hole) injection layers, the organic layer behaves as an electron (hole) conductor. Therefore, we have to take into account the charge carrier injection processes in addition to the carrier transport processes, when we design EL devices.

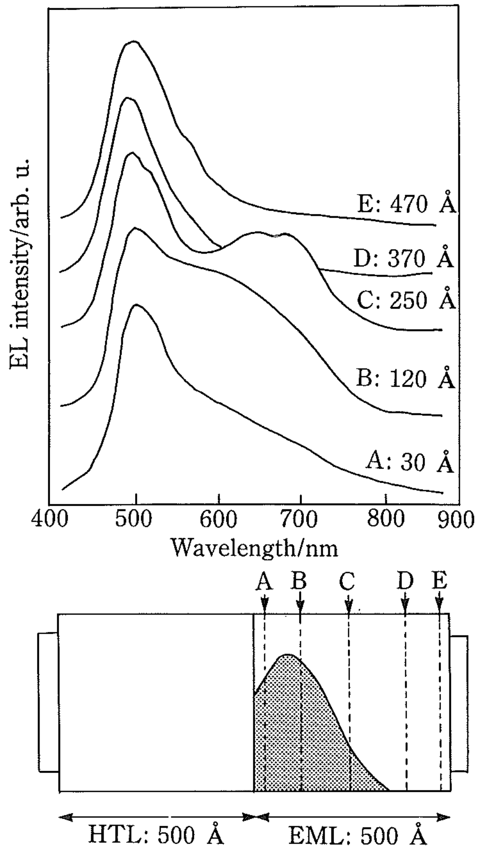

Fig. 7. EL spectra of five doped SH-A cells. The A, B, C, D and E indicate doped positions. The distance between a doped position and the interface of HTL/EML layers is also indicated.

5. Confinement of charge carriers and molecular excitons within a molecular-size area

In the previous section, we demonstrated that the SH-B structure with an NSD emitter gave the highest EL efficiency because of the confinement of charge carriers and molecular excitons. In this section, we show the achievement of their confinement within a molecular-size area with the use of the DH structure.

Figure 8 shows the relation between luminance at fixed current, 100 mA/cm^2, and EML thickness. The case of the SH-B cell was compared with that of the DH cell. With the SH-B structure, the luminance started to drop when the EML thickness was reduced to less than 250 Å. With the DH cell, in contrast, the luminance continued to be high, even when the EML thickness was reduced to less than 250 Å. We observed extremely high luminance in the case of emitter

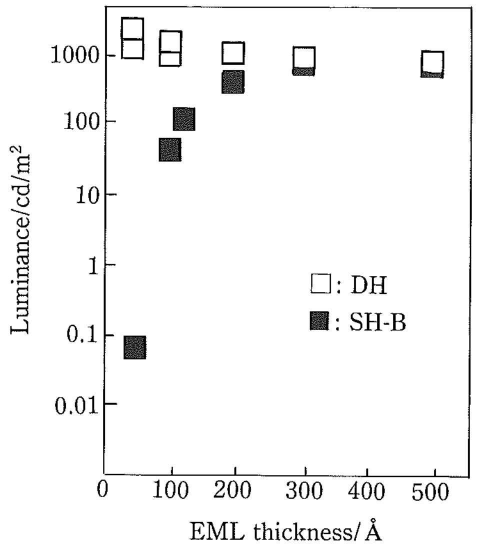

Fig. 8. Dependence of luminance at the current density of 100 mA/cm^2 upon the thickness of emitter layer in SH-B and DH type EL cells.

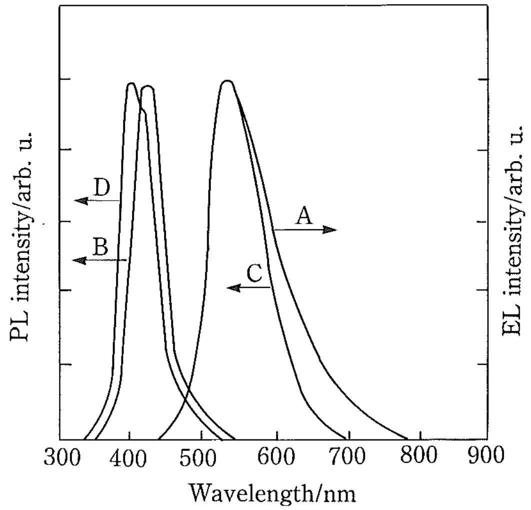

Fig. 9. EL spectrum of the DH type cell (A), photoluminescent spectra of, HTL (B), EML (C) and ETL (D).

thickness of 50 Å, which was the limit of our experimental accuracy. The confinement of holes and electrons and confinement of molecular excitons are perfect in these molecular-size devices. The attainment of the confinement of molecular excitons within a thin EML can be explained based on PL spectra of component layers. Figure 9 clearly shows that the HTL and the ETL have larger exciton energy than the EML. In the SH-B structure, on the other hand, a large portion of electrons injected from the ETL pass through the EML without an encounter with holes. Also, a significant portion of the molecular excitons produced within an EML reach the ITO electrode during a migration process and are quenched [23], [24]. The good correspondence between the width of emission sites obtained by the previous doping method and the thickness at the luminance drop supports these considerations.

We expect that the DH cells in which the EML is thinner than 50 Å will also work well. The thickness of 50 Å corresponds to a stack of several emitter dye molecules. Thus, we can say that we are really dealing with molecular-size electronic devices, at least in the direction perpendicular to the film surface. The confinement of charge carriers and molecular excitons is perfect in these molecular-size devices.

6. Conclusion

We classified EL cell structures into three categories. The selection of EL cell structures (SH-A, SH-B and DH) was found to be closely related to the charge carrier transport properties of emitters. The determination of emission sites in various EL cell structures evidently showed that high luminance was derived from the confinement of charge carriers and molecular excitons inside an EML. However, further investigation of charge carrier injection processes at organic/organic and organic/metal electrode interfaces is necessary for the elucidation of the EL mechanism.

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