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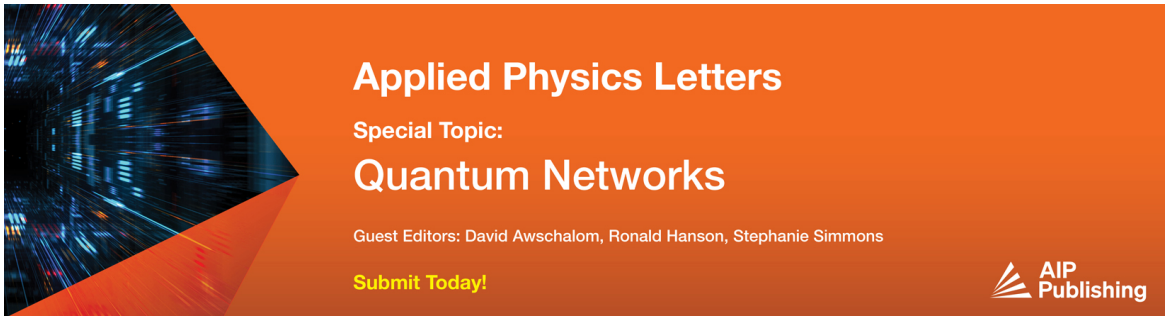

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Confinement of charge carriers and molecular excitons within 5-nm-thick emitter layer in organic electroluminescent devices with a double heterostructure

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Organic electroluminescent devices with a double-heterostructure indium-tin-oxide substrate/hole transport layer/emitter layer/electron transport layer/MgAg have been fabricated by vacuum vapor deposition. The organic carrier transport and emitter layers were composed of amorphous films. In the double-heterostructure devices, the luminance continued to lie in high level, even when the emitter thickness was 50 Å. The confinement of charge carriers and molecular excitons within a narrow emitter layer was achieved.

Recent progress in high performance organic electroluminescent (EL) devices owes to the use of multilayer cell structures which are composed of an emitter layer (EML) and carrier transport layers.[1–7] Tang and VanSlyke[1] reported that the combination of the EML which possessed electron transporting tendency with a hole transport layer (HTL) was essential for high luminance and high stability of EL cells.[1] We proposed a three-layer cell structure in which an EML was sandwiched between hole and electron transport layers based on the idea that an electron transport layer (ETL) as well as HTL should play a major role in the increase of EL efficiency, when a variety of emitter materials was employed. Due to a lack of adequate ETL materials, however, our preliminary test indicated that the introduction of ETL did not contribute to the enhancement of EL efficiency at that time.[4] In the wide search of ETL materials, we found an outstanding electron transport material, an oxadiazole derivative. Judging from its molecular structure, it was not assumed to be a perfect electron conductor, but it really worked as an excellent ETL in EL devices. Thus using this material we, for the first time, succeeded in fabricating the EL device having hole conductor as an EML.[6]

Now, we have both HTL and ETL materials and are ready to construct ideal three-layer structure cells. It is expected that the confinement of holes and electrons within a thin EML is attained in the three layer cell, which we call a double heterostructure (DH) hereafter.

In this letter, we report the fabrication of high performance DH cells and compare those cells with conventional two-layer (single heterostructure) cells. The effect of the thickness of the EML on EL efficiencies demonstrated the realization of confinement of holes and electrons within the very narrow EML. This also indicates the effective confinement of molecular excitons produced by the recombination of holes and electrons within the EML.

Two types of EL cell structures, single heterostructures (SHs) and DHs, were used in our experiment as shown in Fig. 1. The organic materials used in the experiment are also shown in the figure. We used an aromatic diamine (TAD) as the hole transport material and an oxadiazole derivative (PBD) as the electron transport material. For emitter material, triphenylamine derivative (NSD) was used. In a previous paper,[6] we showed that the SH device with NSD and PBD layers gave high EL efficiency in the case when the thickness of EML and ETL was fixed at 500 Å. In this study, the thickness of HTL and ETL was fixed at 500 Å, and the thickness of EML was varied from 500 to 50 Å.

Organic layers were deposited on a precleaned indium-tin-oxide (ITO) glass substrate and a cathode MgAg layer was deposited on ETL by codeposition in a vacuum of 10^{-7} Torr at room temperature. The thickness of the ITO layer was 1000 Å and sheet resistance was about 20 Ω/□. The deposition rate for organic layers was about 2 Å/s. The thickness of organic layers was determined from frequency shifts on a quartz oscillating thickness monitor

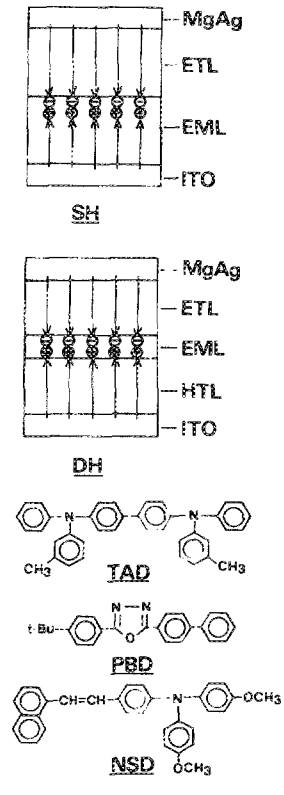

FIG. 1. Structures of the EL devices and the molecular structures of the materials used for the devices.

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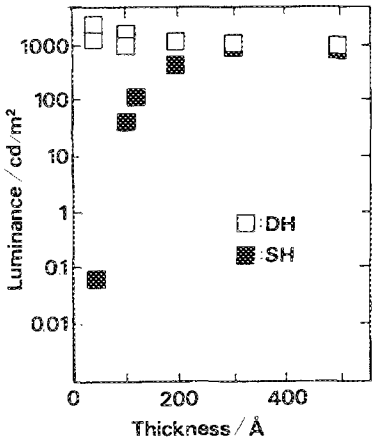

FIG. 2 Luminance at the current density of 100 mA/cm² as a function of emitter thickness in DH and SH cells; (a) ITO/TAD/NSD/PBD/MgAg, and (b) ITO/NSD/PBD/MgAg.

which was placed very close to an organic film on the substrate in the vacuum deposition chamber. The emitting area in EL cells was 0.2×0.2 cm^2. All of the deposited organic films were found to be amorphous based on the observation under a polarizing microscope.

Figure 2 shows the thickness dependence of luminance at a fixed current density of 100 mA/cm^2 for the DH and SH cells. When the emitter thickness was 500 Å, the luminance of 1000 cd/m^2 was observed in both of the SH and DH cells. The SH cell structure gave a high EL efficiency, and there was no effect of the insertion of HTL (DH). However, when the thickness of the emitter layer was reduced to less than 300 Å, a new feature appeared. The SH cell showed a drastic decrease in luminance with the decrease of the emitter thickness. In contrast, constant high luminance was retained in the wide range of the emitter thicknesses in the DH cell. The luminance continued to lie in high level, even when the emitter thickness was reduced to 50 Å. The uniform emission indicates the uniformity of the ultrathin emitter layer.

Figure 3 shows the EL spectrum of the DH cell with 50 Å emitter thickness at the current density of 10 mA/cm^2. Also, the photoluminescence (PL) spectra of NSD, TAD, and PBD layers are included. The EL spectrum corresponded exactly to the PL spectrum of the NSD film. No emission from the TAD or the PBD layer was observed. This indicates that the site of carrier recombination located only within the EML. In other words, the confinement of charge carriers within the EML is attained; electrons injected from the PBD layer into the NSD layer are blocked at the TAD/NSD boundary, and holes injected from the TAD layer into the NSD layer are blocked at the NSD/PBD boundary.

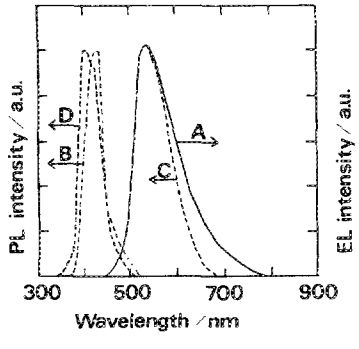

FIG. 3. EL spectrum of the DH cell and PL spectra of TAD, NSD, and PBD layers; (a) EL spectrum in a [ITO/TAD(500 Å)/NSD(50 Å)/PBD (500 Å)/MgAg] cell, (b) PL spectrum in a TAD film, (c) PL spectrum in a NSD film, and (d) PL spectrum in a PBD film.

The comparison of EL and PL spectra also gives the evidence of the confinement of molecular excitons within the EML. The carrier transport materials, TAD and PBD, which possess emission peaks at around 400 nm, are assumed to have exciton energies larger than that of the NSD layer. Thus, the excitons created within the EML have no ability to migrate into TAD or PBD layers. These considerations lead to the conclusion that the confinement of both charge carriers and molecular excitons within an EML was achieved even in the 50-Å-thick EML.

Here, we would like also to mention another advantage of the use of the DH, that is, the insertion of ETL or HTL between EML and electrodes because it serves to prevent the quenching of excitons at electrode surfaces.[8,9] According to our separate experiment, the PL intensity from the EML in a ITO/TAD(200 Å)/NSD(25 Å)/PBD(200 Å)/MgAg cell was six times larger than that in an ITO/TAD(200 Å)/NSD(25 Å)/MgAg cell. Evidently, the inserted PBD layer prevented the quenching of the molecular excitons produced by photoexcitation. This result supports the assumption that the insertion of the carrier transport layers contribute to prevent the excitons from quenching at the electrode surfaces. This effect is particularly important, when EML thickness becomes narrower than the average migration length of excitons.

Based on the above considerations, we can point out two major reasons for the lower EL efficiency in the SH cells with EML at the thickness less than 300 Å. First, a large portion of electrons injected from the PBD layer pass through the EML without the encounter with holes. Second, a significant portion of the molecular excitons produced within EML reach the ITO electrode during a migration process and are quenched.

It should be stressed that the success in the construction of the DH with extremely thin EML stimulates our EL study towards exciting possibility in organic thin-film devices. The increase of the density of charge carriers and molecular excitons within extremely thin EML can be attained by means of the DH. Even the use of a single molecular layer for EML may be possible. The increase of excited states within a very narrow region opens the prospect for the attainment of population inversion of excited states.

The second prospect is concerned with the fabrication of molecular size devices. We deal with the EML thickness of about 50 Å, which corresponds to the stack of about ten emitter molecules. Therefore, our EL devices now work at the molecular size at least along the direction of applied field. We have obtained a way to observe electronic and optical phenomena on a few molecules sandwiched between flat and smooth organic carrier injection layers. This approach, we believe, gives one of the promising entrances towards the investigation of molecular size electronic devices.

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