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Observation of spectral narrowing and emission energy shift in organic electroluminescent diode utilizing 8-hydroxyquinoline aluminum/ aromatic diamine multilayer structure

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Organic electroluminescent (EL) diode with a multilayer structure which consists of alternating layers of organic 8-hydroxyquinoline aluminum (Alq_3) and aromatic diamine has been grown by organic molecular beam deposition. The EL emission from the multilayer structure shows spectral narrowing and the emission energy has been observed to shift to higher energy compared with that in the monolayer structure. Mechanism of spectral narrowing and the emission energy shift in the diode with the multilayer structure have been discussed.

Organic electroluminescent (EL) diodes[1–8] have attracted much attention because of their potentiality in wide spectral range from blue to red and large-area display application. Tang *et al.*[1,2] developed a very efficient fluorescent material (Alq_3) and demonstrated low-voltage-driven EL diodes using Alq_3 as an emitting material. EL diodes with conducting polymers[3–8] have also been developed.

On the other hand, inorganic III-V compound semiconductor multiple quantum wells (MQWs)[9] and the laser diodes with MQW structure with III-V[10,11] and II-VI[12] compound semiconductors have demonstrated many unique optical and electrical characteristics compared with that in conventional bulk materials. Recently, So *et al.*[13,14] reported fabrication and characteristics of organic molecular crystals with a multilayer structure by using organic molecular beam deposition. More recently, we reported unique optical characteristics of organic multilayer structure.[15]

In this letter, we report characteristics of an organic electroluminescent diode with multilayer structure which consists of alternating layers of Alq_3 and TPD. The full width at half-maxima (FWHM) of the emission spectrum and the peak emission energy shift of the EL diode have been discussed. Mechanism of spectral narrowing and the emission energy shift of the EL diode with multilayer structure has been discussed.

EL diodes with multilayer structure have been fabricated by organic molecular beam deposition onto an indium-tin-oxide (ITO)-coated glass substrate. Multilayer structure has also been fabricated onto quartz substrates for optical measurement for comparison. The base chamber pressure was kept under 10^{-4} Pa during deposition. The powders of tris(8-hydroxyquinoline) aluminum (Alq_3) and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (aromatic diamine, TPD) were loaded to each separate Knudsen cell, and then cells were subsequently heated up to sublimate at a growth rate of about 0.1 nm/s which was determined by an oscillating quartz thickness monitor. Series of multilayer samples consist of alternate layers of Alq_3 and TPD, whose layer thicknesses of one period were changed from 3.6 to 45.2 nm. The layer structure of the multilayer samples was determined by x-ray diffraction (Cu-$K\alpha$ line).

The structure of the multilayer sample which consists of alternating layers of Alq_3 and TPD was determined by low angle x-ray diffraction. In Fig. 1, a typical x-ray diffraction pattern is shown for a multilayer structure which consists of 16 periods of 3.0 nm-thick Alq_3 and 11.9-nm-thick TPD layers. The strong diffraction patterns correspond to the satellite peaks of one period of the layer and the other weak periodical diffraction peaks correspond to the total layer. In the sample shown in Fig. 1, we have observed the satellite diffraction peaks in the third order. In the low angle side, leakage beam from the x-ray source is superimposed to the original diffraction pattern. We have observed no featured diffraction pattern from the deposited film which indicates crystallinity. Nevertheless we have observed the diffraction pattern in the low angle position, which corresponds to the signal of the multilayer structure. The x-ray diffraction pattern from the multilayer of Alq_3/TPD corresponds to the signal which is typical to the multilayered structure.[16] The clear satellite peak indicates that the layer structure is precisely in order. From the diffraction pattern, we can estimate the layer spacing using Bragg diffraction conditions.

EL diodes with a multilayer structure have been fab-

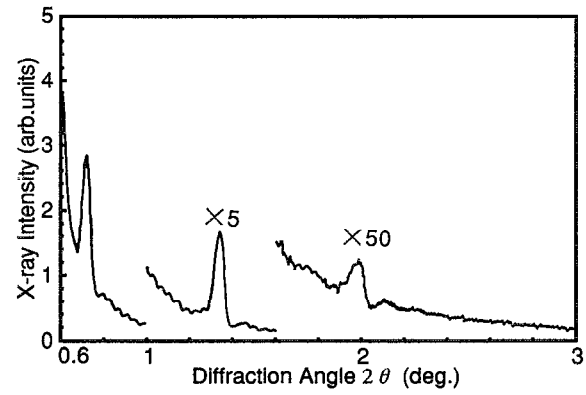

FIG. 1. X-ray diffraction pattern of Alq_3/TPD multilayer. (16 periods of 3.0-nm-thick Alq_3 and 11.9-nm-thick TPD.)

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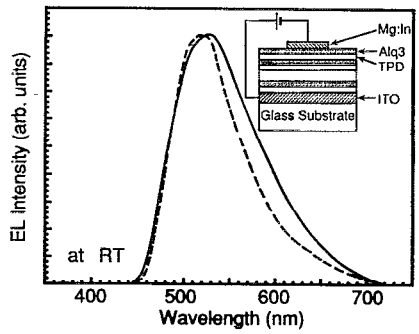

FIG. 2. EL spectrum of EL diode with Alq_3/TPD multilayer structure (dashed line) and monolayer structure (solid line) at RT. The multilayer structure consists of 15 periods of 3.9-nm-thick Alq_3 and 3.9-nm-thick TPD. The monolayer diode consists of 53.6-nm-thick Alq_3 and 53.6-nm-thick TPD. The inset shows the layer structure of the EL diode with the multilayer structure.

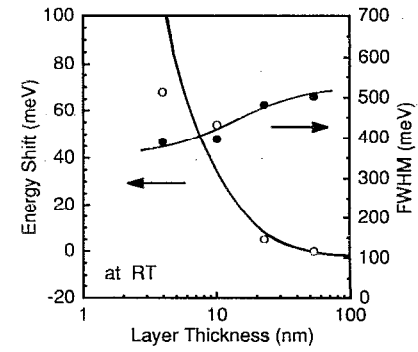

FIG. 3. Peak energy shift and FWHM of EL emission spectrum of the diode with multilayer structure measured at RT.

ricated. The EL diodes consist of the multilayer structure sandwiched by ITO-coated transparent electrode as positive bias side and the In-containing Mg (Mg:In) electrode as the negative bias side. The cross-sectional view of the EL diode with an Alq_3/TPD multilayer structure is shown in the inset of Fig. 2. The Alq_3 layer contacts to the Mg:In electrode and the TPD layer to the ITO electrode. The emission area is 2×2 mm^2. The emission spectrum is shown in Fig. 2 for the EL diode of the multilayer structure (15 periods of 3.9-nm-thick Alq_3 and 3.9-nm-thick TPD) in comparison with that of monolayer structure (one period of 53.6-nm-thick Alq_3 and 53.6-nm-thick TPD) at room temperature (RT) under the same driving condition (injection current 0.5 mA). In Fig. 2 the peak emission intensities of the diodes are normalized. The emission intensity of the diode with the multilayer structure is about 55% of that with monolayer structure. The emission peak of the EL spectrum was observed at 515 nm for the multilayer structure (dashed line) and 530 nm for the monolayer structure (solid line). The emission from the TPD layer has not been observed in the EL device. The FWHM of the emission spectrum are 87 and 113 nm for the multilayer and monolayer structure, respectively. That is, spectral narrowing has been observed for the EL diode with the multilayer structure. It should also be mentioned that the spectrum has not been changed with the injection current.

In Fig. 3, the shift of peak emission energy and the FWHM of the EL emission spectrum from the diode with multilayer structure measured at RT are shown as a function of layer thickness. Peak energy of the emission spectrum shifted to higher energy in the diode with the multilayer structure of thin layer thickness. FWHM of the emission spectrum was narrower in the diode with decreasing layer thickness. We have already reported a photoluminescence energy shift[15] in an organic multilayer structure with decreasing layer thickness. A similar energy shift in the emission spectrum has been observed in the EL diode with the multilayer structure. The spectral narrowing and the energy shift are discussed in the later section taking the energy band diagram into consideration.

Emission spectra at low temperature (77 K) are shown in Fig. 4 for the diodes with multilayer and monolayer structures which are the same samples as those shown in Fig. 2. The diode has been directly cooled with liquid nitrogen. The emission intensity is also normalized in this figure. The emission intensity of the multilayer diode is about 30% of that with monolayer structure. The emission peak wavelength of the diode with multilayer structure and the monolayer structure were 514 and 530 nm, respectively. The emission peak shifted toward a shorter wavelength by 16 nm in the diode with the multilayer structure compared with that with monolayer structure. The FWHM of the emission spectrum for the diode with the multilayer structure was 86 nm, whereas that with monolayer structure was 107 nm. That is, the narrowing of the EL spectrum for the diode with the multilayer structure has also been observed at low temperature. At low temperature (77 K), the emission intensity increased and the FWHM of the emission spectrum decreased. The emission intensity of the diode with the multilayer structure increased by about twice at 77 K compared with that at RT. On the other hand, that with the monolayer structure increased by 3 times. The increase of EL intensity is explained by the decrease of a nonradiative recombination process at lower temperature, which is normally seen in the diode with compound semiconductors or other luminescent diodes. The change in luminescent peak with temper-

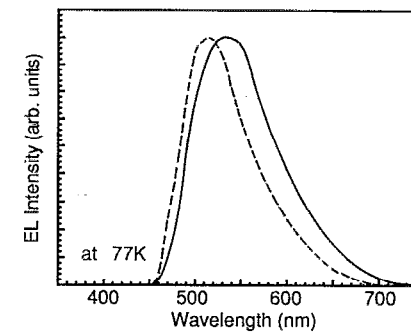

FIG. 4. EL spectrum of EL diode with multilayer structure (dashed line) and monolayer structure (solid line) at low temperature (77 K). The structure of the diode is same as that shown in Fig. 2.

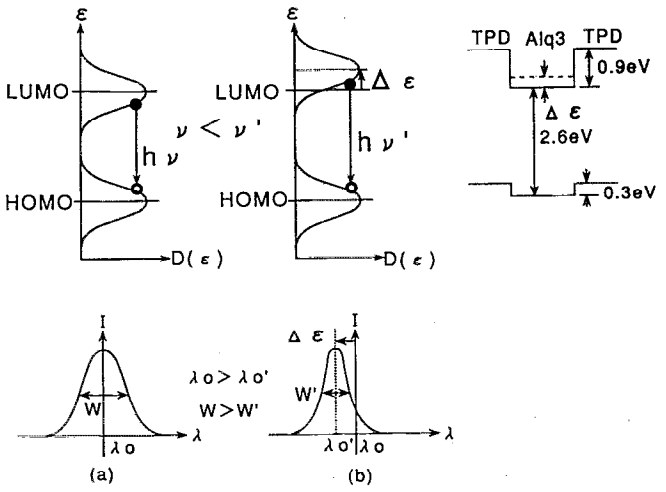

FIG. 5. Schematic description of energy band scheme and carrier population of EL diode with Alq_3/TPD monolayer structure and multilayer structure. Emission spectrum are also shown schematically. (a) Monolayer structure, (b) multilayer structure.

ature is small for both an EL diode with a multilayer structure and a monolayer structure.

The energy band scheme and the population of carriers are schematically shown in Fig. 5 together with the emission spectrum. Carrier population and the resulting emission spectrum are shown schematically in Fig. 5(a) for the EL diode with monolayer structure. The energy band diagram of the Alq_3 and TPD multilayer structure has been estimated from the optical absorption edge and the ionization potentials.[17] The energy barrier for the electrons in the Alq_3 layer is estimated to be 0.9 eV, whereas that for the holes in TPD is 0.3 eV. Quantized energy levels are indicated schematically with a dashed line in Fig. 5(b). Therefore, the energy band diagram of the multilayer structure has been found to be Type I′ superlattice as shown in Fig. 5(b). Electrons in an Alq_3 layer are sandwiched by the TPD energy barriers, and the holes in the TPD layer by the Alq_3, separately. Since the conduction in Alq_3 is reported to be *n* type,[1] electrons in Alq_3 are confined by the TPD barriers. The confined electrons in the Alq_3 layer localize at a higher energy state as indicated in Fig. 5(b). Since the density of states in the higher energy state are larger than that at the lower energy state, the recombination of carriers from the high energy state should be large and sharp. The spectral narrowing and the emission energy shift are the results of the confined carriers in the multilayer system. In the MQW laser diode with III-V compound semiconductor, similar energy shift and spectral narrowing have been reported as quantum size effect. The energy shift in the MQW laser and the spectral narrowing are reported as the result of recombination of quantized carriers from the quantized energy state. Since the quantized energy level has a steplike density of state, the recombination of carriers should have narrow emission spectrum. Since the de Broglie wavelength of confined electrons in III-V compound semiconductors is in the order of 10 nm, the quantum size effect is observed in the layer thickness less than the wavelength. However, in the case of organic multilayer structure, the quantized energy states may not clearly exist due to the lack of crystallinity or the layer fluctuations. Although the phenomena which we observed in the organic EL diode are the same as those of quantum size effect in compound semiconductors, we cannot conclude that they arise from the same quantum size effect as discussed in compound semiconductors at this stage of experiment. The energy shift and the spectral narrowing in the EL diode with organic multilayer structure are the result of recombination of injected carriers with high energy which localize at higher energy state.

In conclusion, the present experimental results are summarized as follows.

(1) EL diode with organic multilayer structure of Alq_3 and TPD has been successfully fabricated using organic molecular beam deposition. Narrowing of the emission spectrum has been observed for the diode with multilayer structure both at RT and low temperature (77 K).

(2) The peak emission energy shifts to higher energy in the diode with thin multilayer structure both at RT and low temperature (77 K). The spectral narrowing and emission peak energy shift are the results of the confinement of carriers with the organic multilayer system.

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