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Fabrication and characteristics of 8-hydroxyquinoline aluminum/aromatic diamine organic multiple quantum well and its use for electroluminescent diode

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Multiple quantum well structure consisting of alternating layers of organic 8-hydroxyquinoline aluminum (Alq_3) and aromatic diamine (TPD) has been grown by organic molecular beam deposition. The multiple quantum well structure was determined by x-ray diffraction, optical absorption, and photoluminescence. Photoluminescence peak of Alq_3 shifts to higher energy with decreasing layer thickness, suggesting a quantum size effect. An electroluminescent diode has also been fabricated by using Alq_3/TPD multiple quantum well structure.

Organic electroluminescent diode[1–7] has attracted much interest because of its potentiality in material and device process. Tang *et al.*[1] developed a very efficient fluorescent material (Alq_3) and demonstrated low-voltage driven electroluminescent (EL) diodes using Alq_3 as an emitting material. EL diodes with conducting polymers[3–7] have also been developed and reported.

On the other hand, inorganic semiconductor superlattices[8] and multiple quantum wells (MQWs) have substantially developed, and laser diodes with MQW structure[9,10] of III-V compound semiconductors have been developed. The MQWs and the laser diodes have demonstrated many unique optical and electrical characteristics compared with conventional bulk materials.

Recently, So *et al.*[11,12] reported fabrication and characteristics of crystalline organic MQWs by organic molecular beam deposition. Organic EL diode with a MQW structure will be expected to have narrow spectral emission, the improvement of emission efficiency, and even tunable emission spectrum, in the future.

In this letter, we report fabrication and characteristics of the multilayer structure of 8-hydroxyquinoline aluminum [tris(8-hydroxyquinoline) aluminum, Alq_3] and aromatic diamine {*N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine, TPD}. The characteristics of the MQW structure are determined by x-ray diffraction, optical absorption, and photoluminescence. The electroluminescent diodes with the organic MQW structure have been fabricated and the emission characteristics are discussed. Quantum size effect of the MQWs has also been discussed.

Organic multilayer structure was grown onto two kinds of substrates. The quartz substrate was used for optical measurement and the indium-tin oxide (ITO)-coated glass substrate for the EL diode, which was fabricated by organic molecular beam deposition. The base chamber pressure was under 10^{-6} Torr. The powders of Alq_3 and TPD were loaded to each separate Knudsen cell. The cells were subsequently heated up to sublimate at a growth rate of about 0.1 mm/s which was determined by an oscillating quartz thicknesses monitor. A series of multilayer samples consists of an alternate layer of Alq_3 and TPD, whose layer thicknesses were changed from 1.9 to 27.1 nm. The layer structure of the MQW samples was determined by the x-ray diffraction (Cu $K\alpha$ line). Optical absorption and photoluminescence were measured at room temperature using conventional methods.

The structure of a multilayer sample which consists of alternating layers of Alq_3 and TPD with the same thickness was determined by x-ray diffraction. Alq_3 and TPD layers deposited on substrates are reported microcrystalline (about 50 nm crystal size)[13] and noncrystalline, respectively. We have also observed no featured diffraction pattern from the deposited film in the diffraction angle 2θ from 2° to 60°. 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 was reported for multilayered thin-film semiconductors, such as GaAs/AlAs thin-film multilayers.[14] We only observed the x-ray diffraction signal from the multilayer thin films, but not from the single layer film. This fact shows that the diffraction from the multilayer structure with the organic solid can also be obtained. In Fig. 1, a typical x-ray diffraction pattern is shown for a multilayer with the total thickness of 136 nm (15 periods of each 4.6 nm Alq_3 and TPD layers). The diffraction pattern which is indicated by an arrow corresponds to the satellite peak of the monolayer period and the other peri-

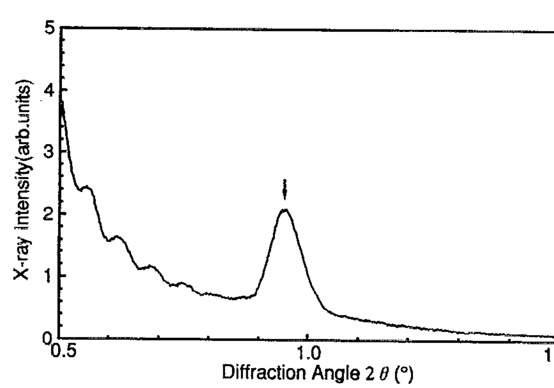

FIG. 1. X-ray diffraction pattern of Alq_3/TPD multilayer.

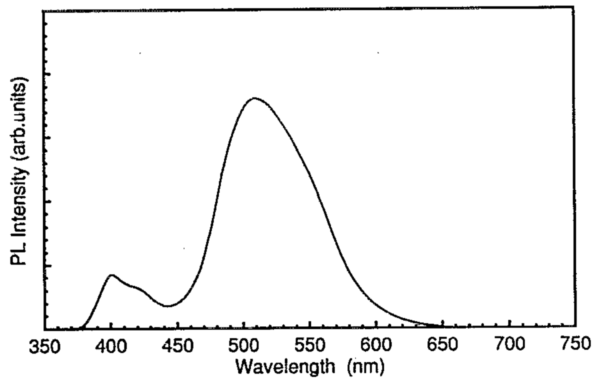

FIG. 2. Photoluminescence spectrum of Alq_3/TPD multilayer. The MQW structure consists of Alq_3 and TPD with each 10.9 nm layer thickness.

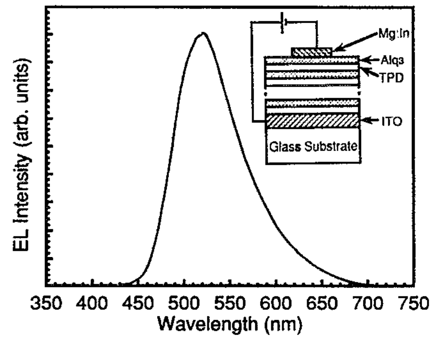

FIG. 4. Electroluminescence spectrum of the diode with Alq_3/TPD multilayer. Inset shows cross sectional view of EL diode with Alq_3/TPD multilayer structure.

odical diffraction peaks correspond to the total layer. In the low angle side, the leakage beam from a direct x-ray source are superimposed to the original diffraction pattern.

Photoluminescence measurement has been done for the samples with a multilayer structure. The multilayer samples exhibit strong fluorescence from the Alq_3 layer (at around 510 nm) and rather weak emission from the TPD layer (at around 400 nm) as shown in Fig. 2. The emission peak, which is originated from the Alq_3 layer, shifts to higher energy according to the decrease in layer thickness of the Alq_3. The energy gaps of Alq_3 and TPD were obtained from optical absorption edge, and are estimated as 2.6 and 3.2 eV, respectively. The ionization potential of the Alq_3 and TPD have been determined by photoelectron emission spectroscopy and was reported as -5.7 and -5.4 eV, respectively. Therefore, the energy band of the MQW has been found to be the type I′ superlattice as shown in the inset of Fig. 3. Electrons in an Alq_3 layer are sandwiched by the TPD energy barriers, and the holes in TPD layer by the Alq_3, separately. The energy barrier for the electrons in the Alq_3 layer is estimated as 0.9 eV, whereas the barrier for the holes in TPD is 0.3 eV. Quantized energy levels are indicated schematically in the dashed line in the figure. Since the conduction type of Alq_3 is reported to be n-type,[1] electrons in Alq_3 are localized by the TPD barrier. This is consistent with the fact that the peak emission from Alq_3 shifts to higher energy according to the decrease in layer thickness. The holes in the TPD layer should also be localized but the energy shift has not been confirmed due to the weak and broad emission band.

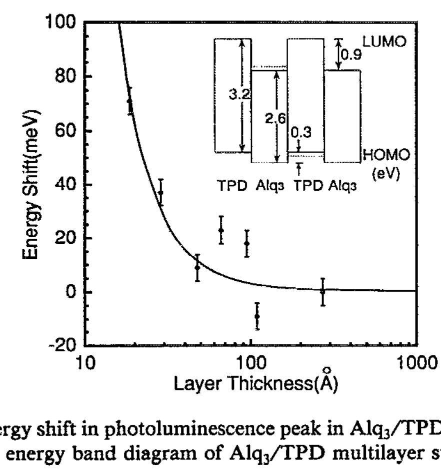

FIG. 3. Energy shift in photoluminescence peak in Alq_3/TPD multilayer. Inset shows energy band diagram of Alq_3/TPD multilayer structure.

The energy shift is evaluated using the Kronig–Penny model for the localized electrons. In the calculation, we used infinite barrier height and the effective electron mass m_e^* as a parameter. As shown in Fig. 3, the calculated value of $m_e^* = 1.5m_0$ fits best to the experimental data. The deviation of experimental data from the calculation may be due to fluctuation of the layer thickness of the actual MQWs or other irregularity of the actual structure. However, it should be pointed out that we used the simplest model for the calculation. More accurate calculations are needed to estimate the effective mass and to predict the energy level shift exactly.

Electroluminescent (EL) diodes have also been fabricated using the multilayer structure. The EL diode consists of the multilayer structure sandwiched by indium-tin oxide (ITO) coated transparent electrode as positive bias side and the In-containing Mg (Mg:In) electrode as negative bias side. The cross-sectional view of the EL diode with the Alq_3/TPD multilayer structure is shown in the inset of Fig. 4. The Alq_3 layer contacts to the Mg:In electrode and the TPD layer to the ITO electrode. The electrode area is 2 mm square. The emission spectrum is shown in Fig. 4 for the EL diode of the same MQW structure with that for the PL measurement. The emission peak of the EL spectrum has appeared at around 520 nm, whereas that of the PL spectrum at 510 nm. This discrepancy may be explained by the difference in carrier injection as discussed in the later paragraph and by the heating of the junction during carrier injection. The emission from the TPD layer has not been observed or been very weak in the EL device. This is due to the difference in carrier injection, since carriers are excited in both layers in case of photoexcitation, whereas in the case of EL diode carriers are injected and confined mainly in the Alq_3 layer due to the high energy barrier of the MQW structure.

In Fig. 5, current dependence of EL emission intensity characteristics are shown as the function of various layer thicknesses of the MQW structure. At the same injection

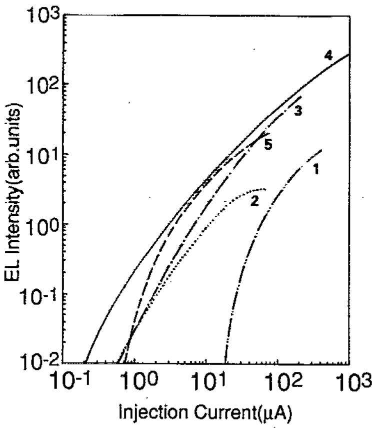

FIG. 5. Dependence of electroluminescence intensity on injection current in the diode with Alq_3/TPD multilayer structure of various layer thicknesses. Alq_3/TPD multilayer thicknesses in nm. 1: 1.9/1.9, 2: 4.6/4.6, 3: 9.5/9.5, 4: 10.9/10.9, 5: 27.1/27.1.

current, EL intensity is the strongest at Alq_3 layer thickness around 9.5–27 nm. This is consistent, since the exciton diffusion length of the Alq_3 are reported to 20 nm.[13] The quantum efficiency of the EL diode with MQW structure shows the highest with the diode of 10.9 nm thick Alq_3. This result shows that confinement of electrons in the Alq_3 layer of 10–20 nm in thickness is most efficient for the recombination of carriers for electroluminescence.

In conclusion, the experimental results are summarized as follows.

(1) Organic multiple quantum well structure of Alq_3 and TPD has been successfully fabricated using organic molecular beam deposition. The layer structure has been confirmed by low angle x-ray diffraction. (2) The quantum size effect has been observed in the emission from Alq_3. The peak emission energy shifts to higher energy with decreasing layer thickness. (3) The EL diode has been fabricated using the multilayer structure, and the diode with a MQW structure of around 10–20 nm Alq_3 layer exhibited the most efficient emission characteristics.

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