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Fabrication and optical characteristics of an organic multi-layer structure utilizing 8-hydroxyquinoline aluminium/aromatic diamine and its application for an electroluminescent diode

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Abstract. A thin film multi-layer structure consisting of alternating layers of organic 8-hydroxyquinoline aluminium (Alq_3) and aromatic diamine (TPD) has been grown by organic molecular beam deposition. The structure of the multi-layer has been confirmed by x-ray diffraction. Optical characteristics have been studied using optical absorption and photoluminescence. The photoluminescence peak of Alq_3 shifts to a higher energy with decreasing layer thickness, suggesting a quantum size effect. An electroluminescent diode has also been fabricated using the Alq_3/TPD multi-layer structure, and the emission characteristics have also been discussed.

1. Introduction

Organic electroluminescent diodes [1–7] for the visible region have attracted much interest because of their potentiality in material and device processes. Tang and VanSlyke [1] developed a very efficient fluorescent material, namely tris(8-hydroxyquinoline) aluminium (Alq_3), and demonstrated low-voltage-driven organic electroluminescent diodes using Alq_3 as the emitting layer. Electroluminescent diodes with conducting polymers [3] have also been developed and reported for the visible and blue spectral ranges.

On the other hand, inorganic semiconductor superlattices (SLs) and multiple quantum wells (MQWs) using groups III–V [8] and IV [9] have been substantially developed. Laser diodes with a MQW structure [10, 11] of III–V compound semiconductors have been fabricated. The MQWs and the MQW laser diodes have demonstrated many unique optical and electrical quantum characteristics compared with conventional bulk materials.

Recently, So and co-workers [12, 13] reported the fabrication and characteristics of crystalline organic MQWs using organic molecular beam deposition.

In this paper, we report the fabrication and optical characteristics of the multi-layer structure of Alq_3 and the aromatic diamine N,N′-diphenyl-N,N′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD). The characteristics of the multi-layer structure are determined using x-ray diffraction, optical absorption and photoluminescence (PL). Electroluminescent diodes with an organic multi-layer structure have been fabricated, and the emission characteristics have been discussed. The quantum size effect of the multi-layer structure has also been discussed.

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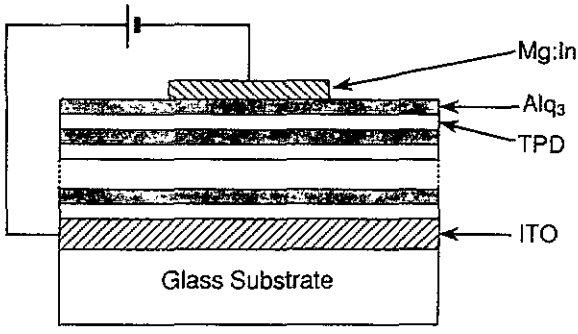
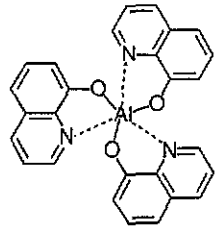
2. Experimental details

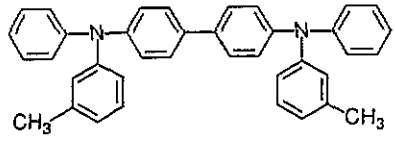
An organic multi-layer structure was grown by organic molecular beam deposition onto two kinds of substrate. A quartz substrate was used for optical measurement, and an indium tin oxide (ITO)-coated glass substrate for the electroluminescent diode. The base chamber pressure was kept below 10^{-6} Torr during deposition. Before the Knudsen cells were used, they were heated sufficiently to evacuate impurity gases. The powders of Alq_3 and TPD were loaded into each separate cell. The cells were subsequently heated to sublimate at a growth rate of about 0.1 nm s^{-1} which was determined with an oscillating quartz thickness monitor. The series of multi-layer samples consist of alternate layers of Alq_3 and TPD, the layer thicknesses of which were changed from 1.9 to 27.1 nm. The layer structure of the multi-layer samples was determined by x-ray diffraction (Cu Kα line). A schematic description of the layer structure of the electroluminescent diode together with the multi-layer and the molecular structure of the source materials are shown in figure 1. As shown in figure 1(*a*), the electroluminescent diode consists of a multi-layer structure sandwiched by the ITO-coated transparent electrode as the positive-bias side and the In-containing Mg (Mg:In) electrode as the negative-bias side. The Alq_3 layer contacts the Mg:In electrode, and the TPD layer the ITO electrode. The electrode area is 2 mm square. The molecular structures of Alq_3 and TPD are shown in figures 1(*b*) and 1(*c*), respectively. The optical absorption and PL were measured at room temperature using conventional methods.



(a)



(b) Alq_3



(c) TPD

Figure 1. Schematic description of the structure of an electroluminescent diode with an Alq_3/TPD multi-layer and their molecular structures: (*a*) electroluminescent diode structure; (*b*) Alq_3; (*c*) TPD.

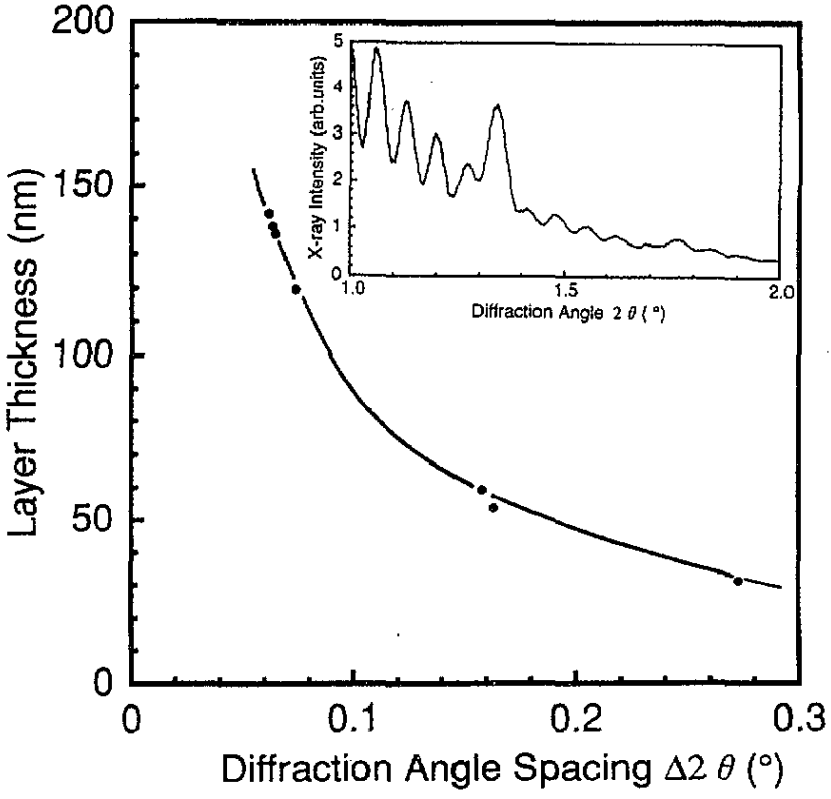


Figure 2. Relation between the diffraction angle spacing and layer thickness. The inset shows a typical x-ray diffraction pattern of an Alq_3/TPD multi-layer.

3. Results and discussion

3.1. Optical characteristics of the Alq_3/TPD multi-layer structure

The structure of the multi-layer wafer which consists of alternating layers of Alq_3 and TPD with the same thickness was determined by x-ray diffraction. We observed no diffraction pattern from the deposited film for diffraction angles from 2 to 60°, since the Alq_3 and TPD layers deposited on substrates are reported to be microcrystalline (about 50 nm crystal size) [14] and non-crystalline, respectively. Nevertheless we have observed a diffraction pattern in a small-angle position, which corresponds to the signal of the multi-layer structure. The x-ray diffraction pattern from the multi-layer of Alq_3/TPD corresponds to the signal which was reported for multi-layered thin film semiconductors, such as GaAs/AlAs SLs [15]. We observed an x-ray diffraction signal only from the multi-layer thin films and not from the single-layer film. This shows that diffraction from a multi-layer structure with organic films can also be obtained. A typical x-ray diffraction pattern is shown in the inset of figure 2 for a multi-layer structure with a total thickness of 126 nm (six periods of Alq_3 and TPD layers). The diffraction pattern shows periodic diffraction peaks which correspond to the total layer. The relatively strong emission at $2\theta = 1.32°$ and 1.78° corresponds to one period of Alq_3/TPD layers. The diffraction spacing is six times that of the periodic diffraction peak. On the small-angle side, a leakage beam from the direct x-ray source is superimposed on

the original diffraction pattern. In figure 2 the relation to the layer thickness and diffraction angle spacing is summarized for various layer thicknesses.

The PL measurement has been carried out for samples with a multi-layer structure at room temperature. The multi-layer samples exhibit strong fluorescence from the Alq_3 layer (at around 510–520 nm) and rather weak emission from the TPD layer (at around 400 nm) as shown in figure 3. Although the emission spectrum is broad, we found that the emission peak which originated from the Alq_3 layer shifts to a higher energy on decrease in the Alq_3 layer thickness. In figure 4, the energy shift of the emission peak is shown as a function of the Alq_3 layer thickness. This energy shift is interpreted as a quantum size effect arising from the layered structure of Alq_3 sandwiched by TPD as discussed in a later paragraph.

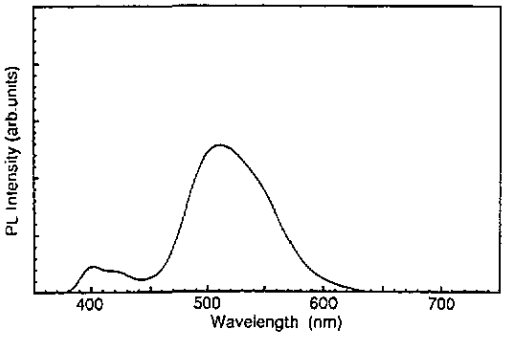


Figure 3. PL spectrum of an Alq_3/TPD multi-layer. The MQW structure consists of Alq_3 and TPD each with a 9.5 nm layer thickness.

The energy gaps of Alq_3 and TPD are obtained from the optical absorption edges and are estimated to be 2.6 eV and 3.2 eV, respectively. The ionization potential energies for Alq_3 and TPD have been determined by photo-electron emission spectroscopy and were reported to be −5.7 eV and −5.4 eV [16], respectively. Therefore, the energy band of the multi-layer structure has been found to be a type I′ SL as shown in figure 5. The electrons in the Alq_3 layer are sandwiched by the TPD energy barriers, and the holes in the TPD layer by the Alq_3, separately. The energy barrier for the electrons in the Alq_3 layer is estimated to be 0.9 eV, whereas the barrier for the holes in the TPD is 0.3 eV. Quantized energy levels are indicated schematically as broken lines in the figure. Since the conduction type of Alq_3 is reported to be n type [14], electrons in the Alq_3 are localized by the TPD barrier. This is consistent with the fact that the peak emission from Alq_3 shifts to a higher energy with decrease in the layer thickness. The holes in the TPD layer should also be localized but the energy shift has not been confirmed owing to the weak broad emission band.

The energy shift is evaluated using the Kronig–Penny model for the localized electrons. In the calculation, we used an infinite barrier height and the effective electron mass m_e^* as a parameter. The calculated value is shown for $m_e^* = 1.0m_0$, $1.5m_0$ and $2.0m_0$ as a parameter. As shown in figure 4, the curve for $m_e^* = 1.5m_0$ fits the experimental data best. The deviation in the experimental data from the calculation may be due to fluctuation in the layer thickness of the actual multi-layer 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.

3.2. Electroluminescent diode with the Alq_3/TPD multi-layer structure

EL diodes with the multi-layer structure have also been fabricated. The structure of the diode has already been shown in figure 1(*a*). The electroluminescence (EL) emission spectrum

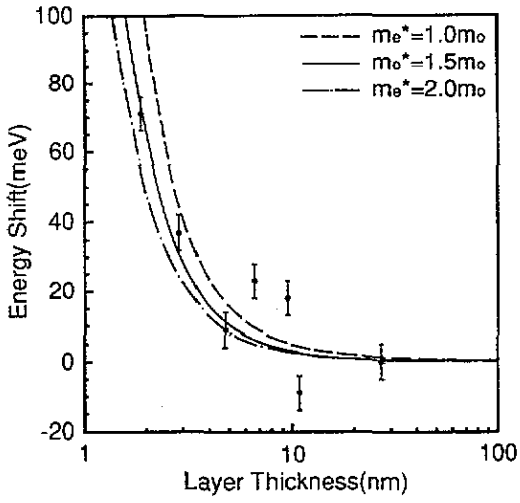


Figure 4. Energy shift of the PL peak for an Alq_3/TPD multi-layer.

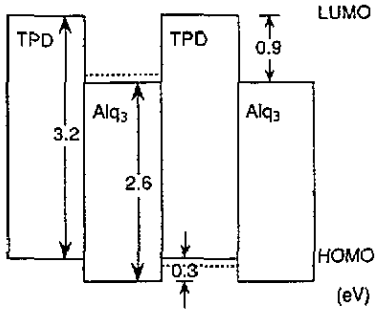


Figure 5. Schematic description of the energy band diagram of an Alq_3/TPD multi-layer structure.

is shown in figure 6 for the multi-layer structure diode with an Alq_3 layer of 4 nm. The spectra are shown measured at room temperature (RT) and 77 K at the same injection current (500 μA). The EL intensity at 77 K is about four times that at RT. However, the emission spectrum is the same. Abe *et al* [17] have discussed the EL emission intensity for the diode which consists of a 50 nm Alq_3 layer and a 50 nm TPD layer. A similar result has been reported for the temperature dependence of the EL intensity [16]. They report that the temperature dependence of the EL intensity at a constant current density (1 mA cm^{-2}) shows that the intensity at $-150\,°C$ is about four times that at 25 °C. From the result shown in figure 6, the emission spectrum does not change with the Alq_3 layer thickness, which is also consistent with the result of Adachi *et al* [2]. The emission peak of the EL spectrum appeared at around 520 nm at RT, whereas that of the PL spectrum is at 510–520 nm at RT. This discrepancy may be explained by the difference in carrier injection and by heating of the junction during carrier injection.

The emission from the TPD layer has not been observed or is very weak in the electroluminescent device. This is due to the difference in carrier injection, since carriers are excited in both layers in the case of photoexcitation whereas, in the case of the

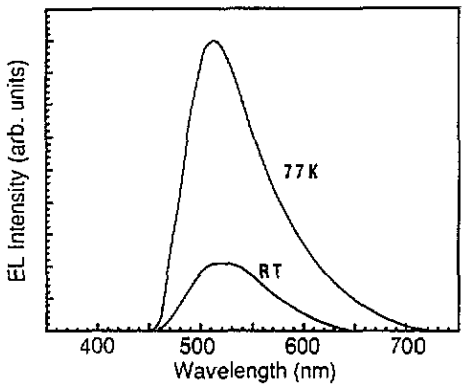


Figure 6. EL spectrum of the diode with an Alq_3/TPD multi-layer measured at RT and 77 K.

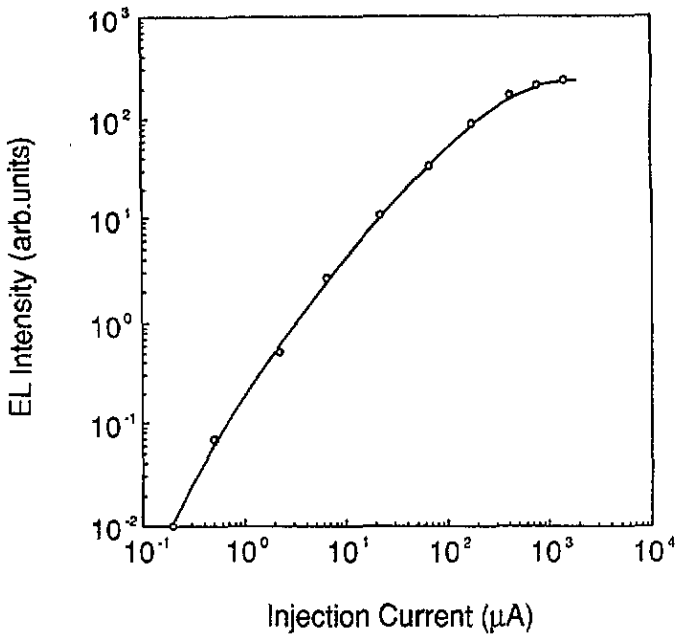


Figure 7. Dependence of the EL intensity on the injection current in the diode with an Alq_3/TPD multi-layer structure.

electroluminescent diode, carriers are injected and confined mainly in the Alq_3 layer owing to the high-energy barrier of the MQW structure. Injected electrons are mainly confined in the Alq_3 layer, and holes in the TPD layers, as shown in figure 5. The confinement is much stronger for electrons than for holes.

In figure 7 the dependence of the EL emission intensity on the injection current is shown for the diode with a multi-layer structure measured at RT. The emission intensity increases with increasing injection current, saturating at a high injection current. This result is consistent with the result that the emission intensity decreases with increasing temperature, and that the junction is heated by a high injection current.

In figure 8, the EL intensity is shown for the electroluminescent diodes with a multi-

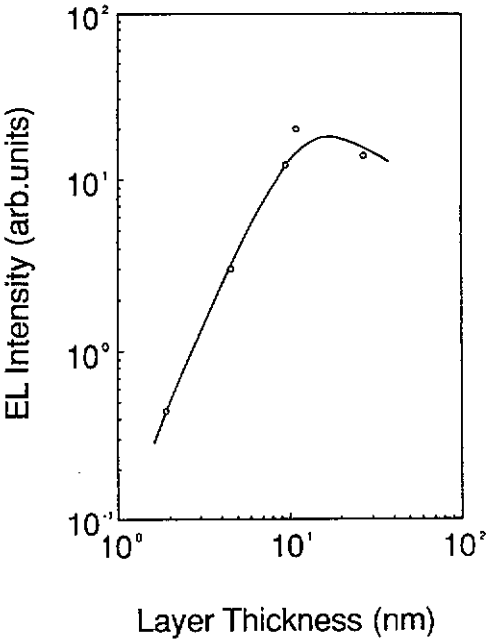


Figure 8. EL intensity of various multi-layer thicknesses under the same injection current.

layer structure of various Alq_3 layer thicknesses at the same injection current (40 μA). The EL intensity increases with increasing Alq_3 layer thickness. The EL intensity is the strongest for an Alq_3 layer thickness of around 9.5–27 nm in this experimental range, but more data points are needed to conclude that the emission peak exists at the layer thickness. A sufficiently high layer thickness of Alq_3 is needed for carriers to recombine with each other for the most efficient EL.

4. Conclusion

In conclusion, the experimental results are summarized as follows.

(1) An Alq_3/TPD organic multi-layer structure has been successfully fabricated using organic molecular beam deposition. The layer structure has been confirmed by small-angle x-ray diffraction.

(2) A quantum size effect has been observed in the PL emission from Alq_3. The peak emission energy shifts to a higher energy with decreasing layer thickness.

(3) Electroluminescent diodes with an Alq_3/TPD multi-layer structure have been fabricated. The EL intensity increases with increasing Alq_3 layer thickness up to 10–20 nm.

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