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Author(s)	Ohmori, Yutaka; Uchida, Masao; Morishima, Chikayoshi et al.
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Novel characteristics of electroluminescent diodes utilizing poly(3-alkylthiophene)s and organic molecules

Yutaka Ohmori, Masao Uchida, Chikayoshi Morishima, Akihiko Fujii
and Katsumi Yoshino

*Faculty of Engineering, Osaka University
Yamada-oka, Suita, Osaka 565 Japan*

ABSTRACT

Novel characteristics of visible electroluminescent (EL) diodes utilizing poly(3-alkylthiophene)s and organic molecules with superlattice structure have been presented. The diodes with poly(3-alkylthiophene)s emit red-orange light with a broad band emission at 640 nm. The EL diode has unique characteristics in temperature dependence of emission intensity.

Superlattice (SL) structure which consists of thin films of organic 8-hydroxyquinoline aluminum (Alq₃) and aromatic diamine (TPD) has been grown by organic molecular beam deposition. The SL structure was determined by X-ray diffraction, optical absorption and photoluminescence. Photoluminescence peak of Alq₃ shifts to higher energy with decreasing layer thickness, suggesting a quantum size effect. The EL diodes with SL structure emit green light at around 520 nm. Quantum size effect in the organic SL structure has been discussed.

1. INTRODUCTION

Conducting polymer has attracted much attention from both fundamental and practical viewpoints¹. Among various polymers, poly(3-alkylthiophene) has stimulated much interest, because it was the first fusible and even soluble conducting polymer² and it demonstrated novel characteristics such as thermochromism³ and solvatochromism⁴. Yoshino *et al.*⁵ reported the anomalous dependence of photoluminescence of poly(3-alkylthiophene) on temperature and alkyl-side-chain length.

Kaneto and Yoshino *et al.*⁶ reported many years ago on electroluminescence using polymer films. Recently, low-voltage-driven organic EL diodes^{7,8} have been fabricated using multilayer structure of dyes as light-emitting materials. More recently, light-emitting diodes based conducting polymers were reported⁹⁻¹³.

On the other hand, inorganic semiconductor superlattices¹⁴ and multi-quantum wells (MQWs) have substantially developed, and laser diodes with MQW structure^{15,16} 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.*^{17,18} reported fabrication and characteristics of crystalline organic MQWs by organic molecular beam deposition.

In this paper, we discuss novel characteristics of EL diode utilizing poly(3-alkylthiophene)s. We report fabrication and characteristics of organic multi-layer structure of tris(8-hydroxyquinoline) aluminum (Alq₃) and aromatic diamine (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine, TPD). The EL 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.

2. EXPERIMENTAL

Poly(3-alkylthiophene)s were prepared by chemical method utilizing FeCl₃ as a catalyst. The preparation and the synthesis of poly(3-alkylthiophene) were reported precisely by Yoshino *et al.*^{19,20} An EL diode with poly(3-alkylthiophene) was fabricated as follows. The EL diodes consist of an indium-tin-oxide (ITO)-coated glass substrate, an emitting layer of poly(3-alkylthiophene) and a magnesium containing indium

(Mg:In) electrode. The electrode area of the light-emitting diode was 2mm square. A thin layer of poly(3-alkylthiophene) was fabricated by spin coating onto an ITO-coated glass substrate using chloroform as a solvent. Poly(3-octadecylthiophene) (PAT-18) and poly(3-dodecylthiophene) (PAT-12) were mainly used for the emitting layer of the diode. However, other derivatives exhibited similar characteristics. The thickness of the emitting layer was about 100-200 nm. The emission spectrum and the light-intensity characteristics were measured by using JASCO CT-50 spectrometer with a photo-multiplier (R928 Hamamatsu Photonics Co.) or a Si photodiode. The Mg alloy electrode was vacuum-deposited on the spin-coated polymer film at a high vacuum ($\sim 10^{-7}$ Torr). The measurement was done under DC or pulsed current.

Organic multi-layer structure of Alq₃/TPD was deposited onto two kind of substrates. Quartz substrate was used for optical measurement and the ITO-coated glass substrate for EL diode, onto which layer structure was fabricated by organic molecular beam deposition. The base chamber pressure was under 10^{-6} Torr. The powders of Alq₃ and TPD were loaded to each separate Knudsen cell. The cells were subsequently heated up to sublimate at a growth rate of about 0.1nm/s which was determined by an oscillating quartz thickness monitor. A series of multi-layer samples consist of alternating layer of Alq₃ and TPD, whose layer thickness was changed from 1.9 to 27.1 nm. The layer structure of the MQW samples was determined by X-ray diffraction (Cu-K α line). Optical absorption and photoluminescence were measured at room temperature using conventional methods. The EL diode with multi-layer structure has been fabricated as same as that of poly(3-alkylthiophene) diode except for deposition of multi-layer structure.

3. RESULTS AND DISCUSSION

3.1 Poly(3-alkylthiophene) electroluminescent diode

Current-voltage dependence of poly(3-alkylthiophene) diode shows a typical rectifying characteristics. The forward bias current is obtained when the ITO electrode is positively biased and the Mg alloy electrode negatively. The emission intensity starts to increase drastically above 3 volts. The diode emits red-orange light at room temperature. The spectrum shows the peak intensity at 640 nm corresponding to the photon energy of 1.9 eV, which coincides with the band gap of poly(3-docosylthiophene)⁵ estimated from the absorption spectrum. This suggests that the emission occurs from the recombination of the electron-hole pairs in the bands or excitons.

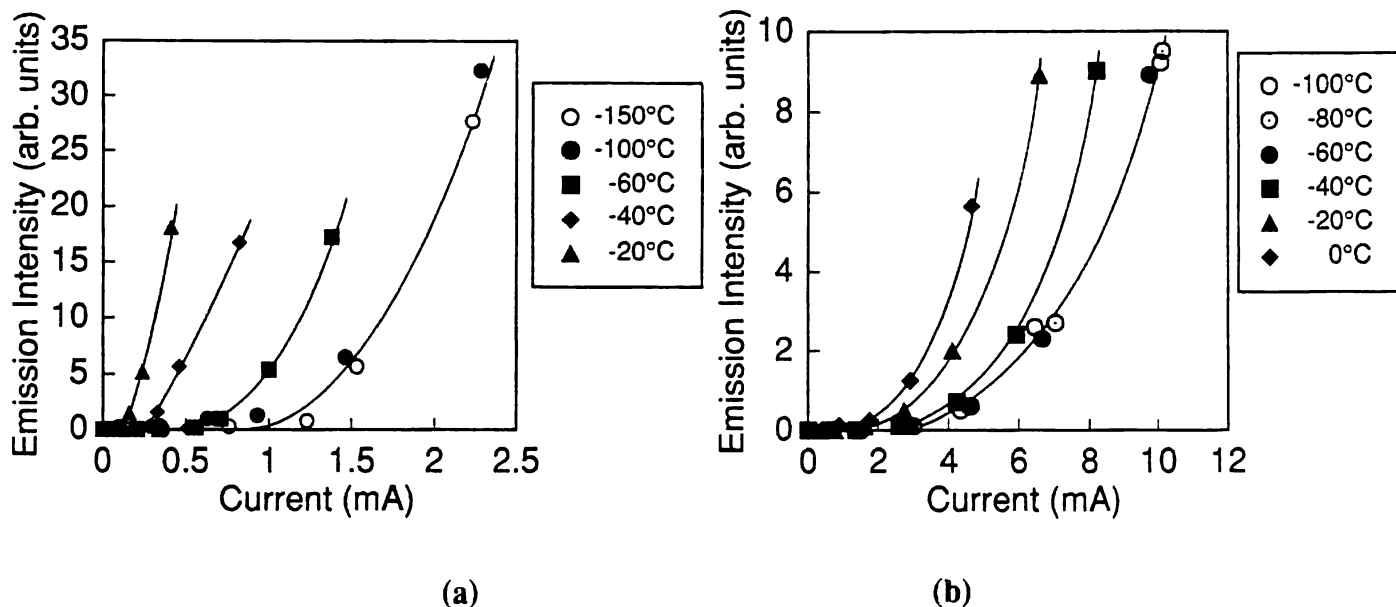


Fig. 1. Injection current dependence of EL intensity as a function temperature. (a) poly(3-octadecylthiophene), (b) poly(3-dodecylthiophene)

In Fig. 1, injection current dependence of emission intensity for poly(3-alkylthiophene) diodes at various temperatures below room temperature is shown. As evident in Fig. 1(a), the emission intensity from poly(3-octadecylthiophene) diode increases above -60°C . Below -100°C , the emission intensity remains constant value with the same injection current. In Fig. 1(b), the dependence of poly(3-dodecylthiophene) diode is shown. As shown in the figure, the emission intensity increases with increasing temperature above -40°C . Below -60°C , the emission intensity remains constant similar to that of poly(3-octadecylthiophene) diode. We have already reported temperature dependence of EL intensity on injection current above room temperature. EL emission intensity is reported to increase with increasing temperature²¹.

Comparing the temperature dependence of the two poly(3-alkylthiophene) diodes, the diode with poly(3-octadecylthiophene) shows the emission increase at lower temperature. The temperature difference coincides with the melting point or glass transition temperature difference of the two poly(3-alkylthiophene)s. Since the melting point² of poly(3-octadecylthiophene) is reported lower compared with that of poly(3-dodecylthiophene), the conformational change in poly(3-octadecylthiophene) should occur at lower temperature than that of poly(3-dodecylthiophene). At lower temperature, radiative recombination probability should increase with decreasing temperature. However, in this case of electroluminescence, the emission intensity remains constant value below a certain temperature. This may relate to the change in carrier injection processes or other carrier confinement process, but it is not clear at this stage of experiment. The result of the increase in luminescence intensity with increasing temperature is consistent with photoluminescence data⁵. The photoluminescence intensity of poly(3-alkylthiophene) was reported⁵ to increase with increasing temperature below melting point. The increase in photoluminescence intensity is explained by the change in effective conjugation length with temperature due to the change in polymer conformation in the main chain and the change in the nonradiative recombination probability. The super-linear increase in luminescence intensity with increasing injection current is observed for all the temperature range. This dependence is explained by the increase in temperature increase in the junction and the increase in luminescence intensity.

3.2 Optical characteristics of multi-layer structure of Alq₃-TPD

Structure of a multi-layer sample which consists of alternating layer of Alq₃ and TPD with the same thickness was determined by X-ray diffraction. Alq₃ and TPD layers deposited on substrates are reported microcrystalline (about 50nm crystal size)²² and non-crystalline, respectively. We have also observed no featured diffraction pattern from the deposited film in the diffraction angle from 2 to 60° . Nevertheless we have observed the diffraction pattern in the low angle position, which corresponds to the signal of the multi-layer structure. The X-ray diffraction pattern from the multi-layer of Alq₃/TPD corresponds to the signal which was reported for multi-layered thin film semiconductors, such as GaAs/AlAs thin film multi-layers²³. This fact shows that the diffraction from multi-layer structure with organic solid can also be obtained.

Photoluminescence measurement has been done for the sample with the multi-layer structure. The multi-layer samples exhibit strong fluorescence from Alq₃ layer (at around 510 - 520nm), which is indicated by an arrow, and rather weak emission from TPD layer (at around 400nm) as shown in the inset of Fig.2. The emission peak, which is originated from Alq₃ layer, shifts to higher energy according to the decrease in layer thickness of the Alq₃. Energy shift of the emission from Alq₃ is shown in Fig.2 as a function of layer thickness. The energy gap of Alq₃ and TPD was obtained from optical absorption edge, and are estimated as 2.6eV and 3.2eV, respectively. The work function of the Alq₃ and TPD have been determined by photoelectron emission spectroscopy and was reported as -5.7 eV and -5.5 eV, respectively. Therefore, energy band of the MQW has been found to be Type I' superlattice. Electrons in an Alq₃ layer are sandwiched by the TPD energy barriers, and the holes in a TPD layer by the Alq₃, separately. The energy barrier for the electrons in the Alq₃ layer is estimated as 0.8 eV, whereas the barrier for the holes in TPD is 0.2 eV. Since the conduction type of Alq₃ is reported to be n-type²², electrons in Alq₃ are localized by the TPD barrier. This is consistent with the fact that the peak emission from Alq₃ 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

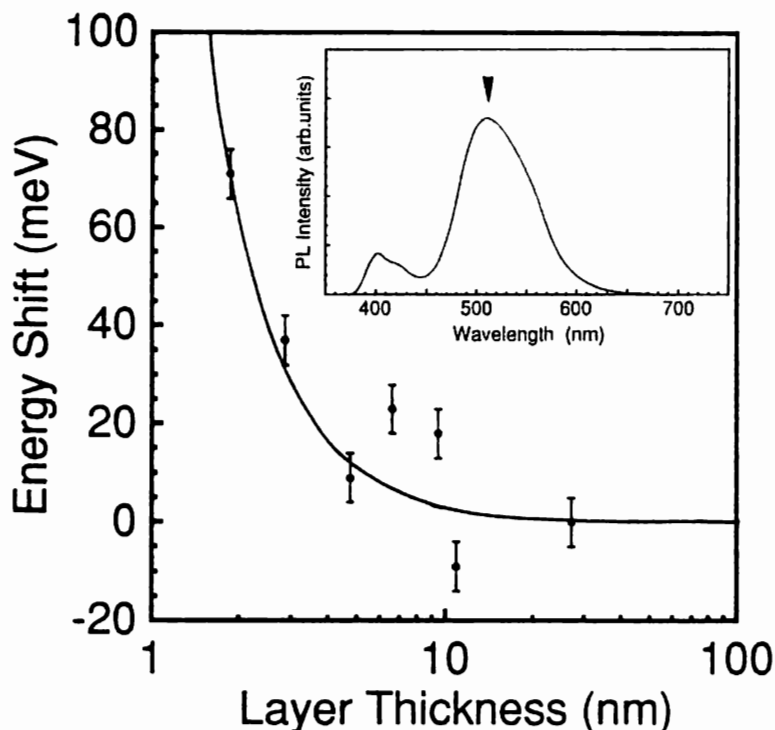


Fig. 2. Energy shift in photoluminescence peak of Alq3 in Alq3/TPD multi-layer structure. Inset figure shows photoluminescence spectrum of the multi-layer.

been confirmed due to the weak and broad emission band.

The energy shift is evaluated using 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 the solid line in Fig. 2, 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 calculation are needed to estimate the effective mass and to predict the energy level shift exactly.

3.3 Electroluminescent diode with Alq3/TPD multi-layer structure

Electroluminescent (EL) diodes have also been fabricated using the multi-layer structure. The EL diode consists of the multi-layer structure sandwiched by ITO-coated transparent electrode as positive bias side and the In-containing Mg (Mg:In) electrode as negative bias side. The Alq3 layer contacts to the Mg:In electrode and the TPD layer to the ITO electrode. The emission spectrum is shown in the inset figure of Fig. 3. The emission peak of EL spectrum has appeared at around 520 nm, whereas that of PL spectrum at 510-520 nm. This discrepancy may be explained by the difference in carrier injection and by the heating of the junction during carrier injection. The emission from TPD layer has not been observed or 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 Alq3 layer due to high energy barrier of the MQW structure as discussed in the former section.

In Fig. 3, dependence of EL intensity on layer thickness of the diode is shown as a function of layer thickness of the MQW structure. At the same injection current, EL intensity is the strongest at around 10-27 nm of Alq3 layer thickness. This is reasonable since the diffusion length of carriers in Alq3 are reported to be 20 nm²². This result shows that confinement of electrons in Alq3 layer of 10-20 nm in thickness is most efficient for the recombination of carriers to give electroluminescence.

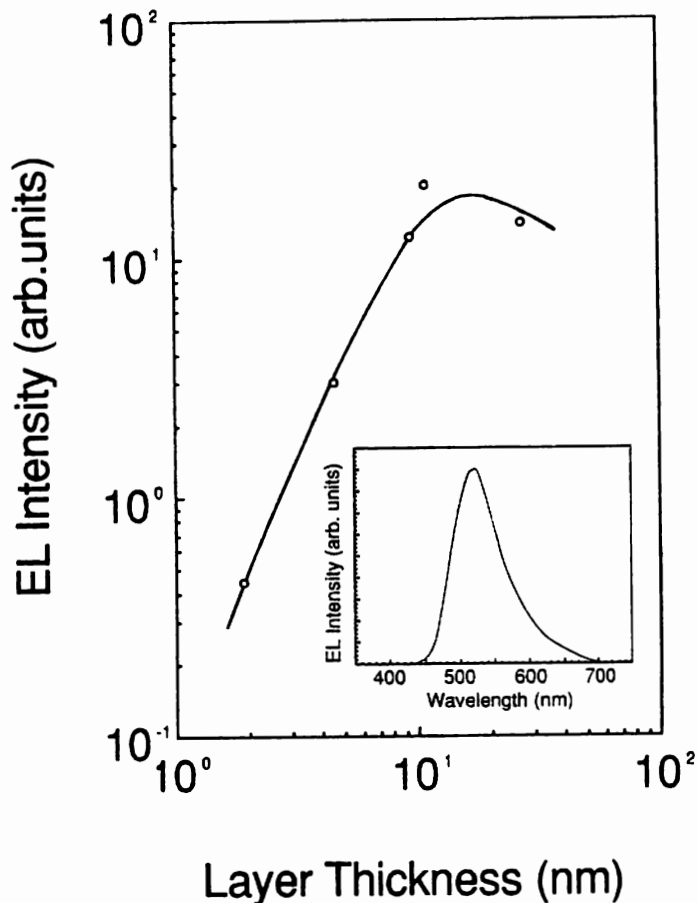


Fig.3. Dependence of EL intensity on layer thickness in the diode with Alq₃/TPD multi-layer structure. Inset figure shows electroluminescent spectrum.

4. CONCLUSIONS

The experimental results are summarized as follows.

- 1) The emission intensity of poly(3-alkylthiophene) electroluminescent diodes increases with increasing temperature above -60°C for poly(3-octadecylthiophene), whereas it remains constant below -100°C. The temperature dependence of luminescence in poly(3-alkylthiophene) depends on the alkyl-side-chain length; the longer the alkyl-chain-length is, the lower the temperature where the luminescence increases is.
- 2) Organic multiple quantum well structure of Alq₃ and TPD exhibited quantum size effect in the photoluminescence from Alq₃. The peak emission energy shifts to higher energy with decreasing layer thickness.
- 3) EL diodes of Alq₃/TPD MQW structure with Alq₃ of 10-20nm layer exhibited the most efficient emission characteristics.

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