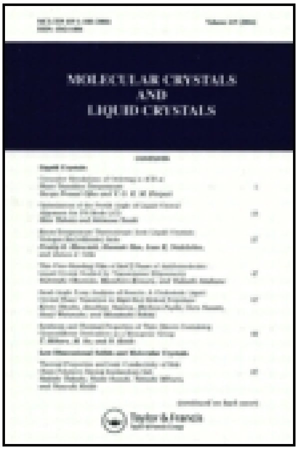

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Schottky Gated Field Effect Transistors and Visible Electroluminescent Diodes Utilizing Poly(3-alkylthiophene)s

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To cite this article: Yutaka Ohmori , Masao Uchida , Keiro Muro , Chikayoshi Morishima & Katsumi Yoshino (1993): Schottky Gated Field Effect Transistors and Visible Electroluminescent Diodes Utilizing Poly(3-alkylthiophene)s, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 227:1, 285-294

To link to this article: http://dx.doi.org/10.1080/10587259308030982

Mol. Cryst. Liq. Cryst. 1993, Vol. 227, pp. 285–294
Reprints available directly from the publisher

Printed in the United States of America

SCHOTTKY GATED FIELD EFFECT TRANSISTORS AND VISIBLE ELECTROLUMINESCENT DIODES UTILIZING POLY(3-ALKYLTHIOPHENE)S

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Abstract Fabrication and characteristics of Schottky gated field effect transistors (FETs) and visible electroluminescent (EL) diodes utilizing poly(3-alkylthiophene)s have been presented. The FETs show typical enhancement type metal-semiconductor FET characteristics. Large temperature dependence and gas-sensitivity have been found for poly(3-alkylthiophene) FETs. Visible red-orange poly(3-alkylthiophene) EL diodes have been successfully fabricated utilizing poly(3-alkylthiophene)s with long alkyl-side-chain. The emission intensity increases with increasing alkyl-side-chain length. Current-emission intensity characteristics show super-linear increase of the emission intensity with increasing injection current. Temperature dependence of emission intensity has been discussed. Carrier mobility has also been evaluated from the pulse response of the emission.

INTRODUCTION

Conducting polymer has attracted much attention from both fundamental and practical viewpoints [1]. Among various polymers, poly(3-alkylthiophene) has stimulated much interest, because it was the first fusible and even soluble conducting polymer [2] and it demonstrated novel characteristics such as thermochromism [3] and solvatochromism [4]. 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 reported [9-13]. We have also reported the fabrication and characterization of field effect transistors which have Schottky gated electrodes [14].

This paper presents the gas-sensitive and temperature-dependent characteristics of Schottky gated FETs using free-standing poly(3-alkylthiophene) films. We discuss the characteristics of visible light emission from EL diodes utilizing poly(3-alkylthiophene). From the pulse response of EL diodes the carrier transport has been discussed.

EXPERIMENTAL

Poly(3-alkylthiophene)s were prepared by two methods, chemically and electrochemically. The preparation and the synthesis of poly(3-alkylthiophene) were reported precisely by Yoshino *et al.*[15-16] Poly(3-alkylthiophene) films with thickness of 5-10 μm were prepared by casting chloroform solution on appropriate substrates.

Poly(3-alkylthiophene) FET was fabricated as follows. Two types of metals were used as electrodes. First, Au-Sn(20*wt%*) was vacuum-deposited onto poly(3-butylthiophene) films as source and drain electrodes, which are shaped in an inter-digitally placed comb shape configuration. Then Al metal was vacuum-deposited on the other side of the film to form gate electrodes. Al metal acts as Schottky contact to the polymer film. Fabrication of the field effect transistors has been reported precisely in our previous paper [14]. The measurement of the characteristics of the FETs was done in dark to avoid the effect of light under DC bias conditions. The water used in this experiment was deionized pure water, and the chloroform gas was dehumidified in vacuum.

EL diode 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) or zinc (Mg:Zn) 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-docosylthiophene) (PAT-22), 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 photomultiplier (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.

The pulse response of the emission intensity was measured by using boxcar averager (PAR model 4420) with a gate integrator (PAR model 4422) using the photomultiplier. The driving pulse generator was Hewlett Packard model 214B. The impedance of the measuring system was 50 ohm or 1k ohm. The pulse width of 200 μsec with the repetition rate of 1kHz was mainly used as the driving pulse.

RESULTS AND DISCUSSION

Gas-sensitivity and temperature-dependence of poly(3-alkylthiophene) FET characteristics

Schottky gated field effect transistor shows enhancement type metal-semiconductor FET characteristics. The current-voltage characteristics of the field effect transistors were discussed in terms of gas-sensitivity [17]. FET characteristics were found to depend strongly on the some sort of gases as shown in Fig.1. First, the FET characteristics in air were compared with that in vacuum. The source-drain current of FET in air increased by a factor of 5 compared with that in vacuum.

Carrier concentration N_A and carrier mobility μ have been estimated by the method used in Si FETs [18]. In this device configuration, the FET can be considered to be a long-channel FET. Estimation of N_A and μ has been predicted in our previous paper [14]. Carrier concentration N_A and mobility μ are estimated as $N_A = 5 \times 10^{13}$ cm^{-3} and $\mu = 2 \times 10^{-3}$ cm^2/V·s in vacuum.

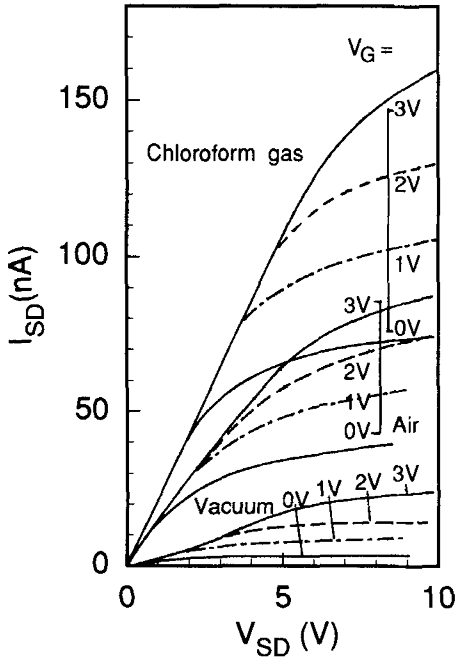

Fig.1. Current-voltage characteristics of poly(3-butylthiophene) FET under various kind of gases.

The increase in source-drain current is caused by the increase in carrier concentrations and carrier mobilities in the channel. In the case of air, water vapor exists as humidity. In this experimental condition, the humidity was 60%. We examined the effect of water vapor by introducing in vacuum. In the case of water vapor (H_2O gas) at 20 torr (saturated gas pressure at room temperature), the change in source-drain current of the FETs is similar to that in air. This suggests that the effect of air on the characteristics is originated in the effect of water. When the FET was exposed to the chloroform gas ($CHCl_3$) at 60 torr (the saturated gas pressure at room temperature), the source-drain current of the FETs increased drastically by a factor of about 10, as shown in Fig.1.

Carrier concentrations in air and in water vapor increased by about 40% and 60% of that in vacuum, respectively. Both the mobilities are about 3 times as large as that in vacuum. In the case of chloroform gas, the increase in carrier concentration is 40% of that in vacuum. On the other hand, the increase in the mobility is by a factor of 8. This shows that the increase in mobility in chloroform gas is much larger than that in other two gases, even if the increase in carrier concentration is nearly the same. This fact shows that the chloroform gas enhances the mobility of the FET. It seems that the enhancement of mobility relates to the conformation change in the main chain of poly(3-alkylthiophene) since the enhancement of mobility is not so large in other gases compared with that in chloroform gas. Poly(3-alkylthiophene) film is reported to show solvatochromism in chloroform, and is explained by the conformation change[4]. Although there is no direct relation between the solvatochromism and the mobility enhancement, the conformation change may occur in the poly(3-alkylthiophene) films in chloroform gas. Ethanol gas shows similar effect on the FET characteristics to that by water vapor. The change in FET characteristics by these gases is reversible. The change occurs in a few tens seconds but the recovery is slow. It needs few hours evacuation or a few days to recover to the initial characteristics when it is kept at room temperature, but it can recover in shorter hours at an elevated temperature. Poly(3-alkylthiophene)s with different alkyl-side-chain length show similar effect.

Temperature dependence of current-voltage characteristics of the field effect transistors has been measured. The observed temperature dependence of the poly(3-alkylthiophene) diodes suggests that the strong temperature dependence of mobility exists, whereas the carrier concentration remains in small change. The higher the temperature is, the larger the mobility of the poly(3-alkylthiophene) is observed. The change of characteristics by temperature is reversible. Hopping probability of carrier should be enhanced with increasing temperature, the conformation change of the polymer chain may suppress the enhancement of carrier mobility to some extent.

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. In Fig. 2, injection current dependence on emission intensity for poly(3-octadecylthiophene) diode at various temperatures is shown. As evident in the figure, the emission intensity increases super-linearly with increasing injected current. This dependence is quite anomalous in comparison with that in inorganic GaAs and InGaP LEDs in which EL intensity tends to saturate at high injected current, mostly due to the temperature increase of the junctions [19]. However, the super-linear increase in emission intensity of the poly(3-alkylthiophene) diode can be explained by the increase in the junction temperature with increasing injected current as shown in Fig. 2. This figure shows that the luminescence intensity increases with increasing temperature of poly(3-octadecylthiophene) in the temperature range between 20 and 80 oC. The other poly(3-alkylthiophene)s show similar characteristics. This is consistent with the photoluminescence data, since the photoluminescence intensity of poly(3-alkylthiophene) was reported to increase with increasing temperature below the melting point [5]. The increase in photoluminescence intensity with increasing temperature 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.

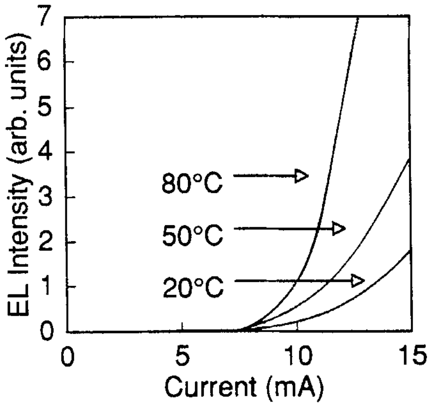

Fig. 2. Current-emission intensity characteristics of poly(3-octadecylthiophene) EL diode at various temperatures.

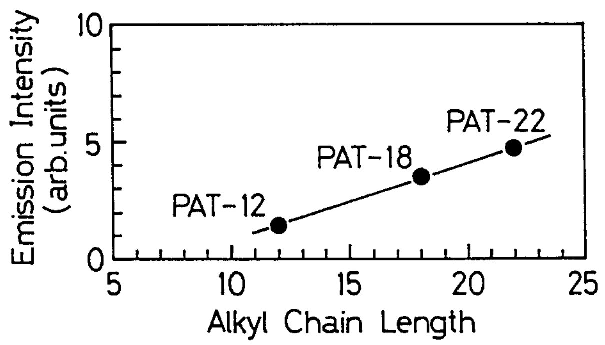

Fig. 3. Dependence of emission intensities on alkyl-side-chain length of poly(3-alkylthiophene) diodes.

In order to clarify the effect of the alkyl-chain length on the emission intensity, diodes of poly(3-dodecylthiophene), poly(3-octadecylthiophene) and poly(3-docosylthiophene) were prepared. In Fig. 3, comparison of emission intensitiy of the diodes at the same injection current (70mA) is shown. The longer the alkyl chain length is, the stronger the emission intensity is. This fact corresponds to the photoluminescence data of poly(3-alkylthiophene) with different alkyl chain length, since the higher photoluminescence intensity is obtained with increasing alkyl chain length. The emission intensity is enhanced by a confinement of carriers on a main chain with a long inter-chain distance caused by a long alkyl-side-chain.

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.

The emission is explained by the energy band diagram of the poly(3-alkylthiophene) diode, which is shown in Fig. 4. Injected electrons from Mg electrode are accelerated in the conduction band by the applied electric field, whereas injected holes in the valence band recombine with the electrons in the polymer film. This carrier recombination results in the light emission. There exists a barrier between the conduction band and the

Mg electrode. The band diagram shows the diode in the forward bias condition with the applied voltage V.

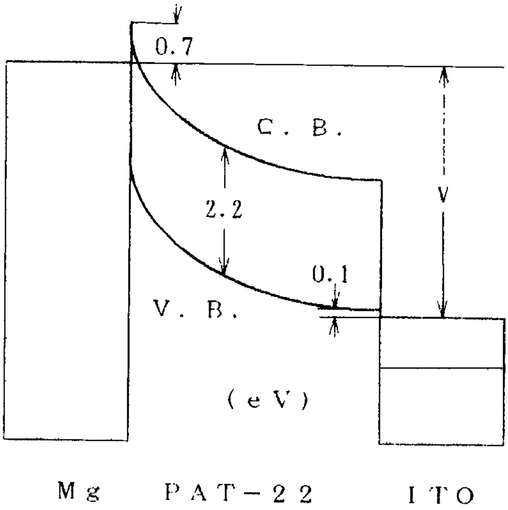

Fig. 4. Energy band diagram of poly(3-docosylthiophene) electroluminescent diode in the forward bias condition.

Pulse response of the electroluminescence

Figure 5 shows the pulse response of the emission from the poly(3-octadecylthiophene) diode driven with a rectangular pulse shaped injection current. In this case, voltage pulse of 6V in pulse height, 200 μsec in pulse width and 1kHz in repetition rate was used. The injection current to the diode shaped rectangular as same as the applied voltage.

The pulse response consists of two parts [20], that is, the fast rise and slow rise parts. The slow part becomes remarkable when the applied voltage is high. The fast response is interpreted to be due to the carrier transit between electrodes. Electrons and holes are injected from the electrodes to the emitting layer of the polymer film. The rise time decreased according to the increase in applied voltages. The shape of the pulse response is same as in the case of 50 ohm and 1k ohm independent of the measuring system. This means that the rise time is not restricted by the time constant of the measuring system or the capacitance of the diode. From the rise time of the emission, the carrier mobility is estimated. The recombination of encountered electrons and holes results in the luminescence. Transit time t_r of the carriers to recombine with each other is predicted

$$t_r = L / (<\mu> \times <E>) \qquad (1),$$

where L, $<E>$ and $<\mu>$ are the film thickness, mean electric field and mean mobility of carriers, respectively.

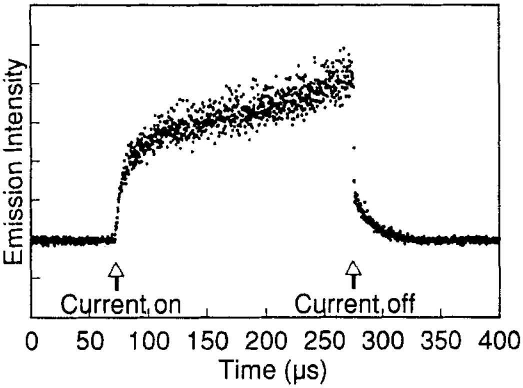

Fig. 5. Pulse response of EL intensity in poly(3-octadecylthiophene) diode.

In Fig. 6, transit time of the pulse response of the emission in EL diode is shown as a function of inverse applied voltage. As evident from Fig. 6, the transit time decreases with decreasing inverse of applied voltage. The relation between the transit time and the inverse applied voltage should be linear if the mobility is independent of applied voltage according to the eq.(1). In this case, however, the transit time is much decreased in the high applied voltage region. Carrier mobility increases with increasing temperature as estimated from FET [14]. The mean mobility of the carrier is estimated as $<\mu> = 1.4 \times 10^{-6}$ cm^2/V·s. The evaluated mobility is the averaged value of the carrier mobility. This is consistent with the value which is estimated from poly(3-alkylthiophene) FETs, because poly(3-alkylthiophene) with longer alkyl-side-chain length has smaller in mobility than poly(3-buthylthiophene).

As evident in Fig. 5, the slow response part is interpreted to be due to the temperature change in the junction. In poly(3-alkylthiophene) diodes the emission intensity increases with increasing temperature as discussed in the previous paragraph. Temperature dependence of the intensity of the poly(3-alkylthiophene) electroluminescent diodes is larger than that in longer alkyl-side chain.

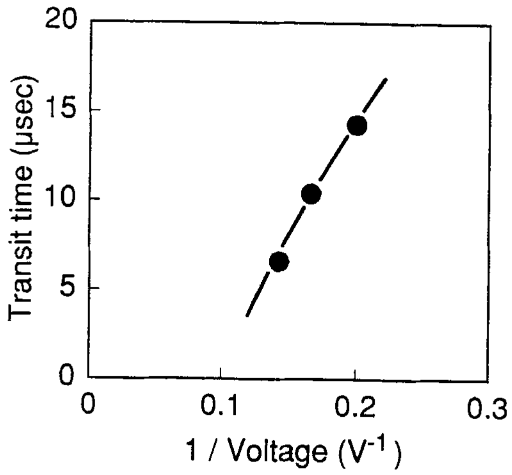

Fig.6. Transit time of poly(3-octadecylthiophene) EL diode as a function of inverse applied voltage.

SUMMARY

Present experimental results are summarized as follows.

1) Schottky gated poly(3-alkylthiophene) FETs are very sensitive to the atmospheric gases and temperature. The source-drain currents of the FETs are enhanced by gases. Air and water vapor increase the carrier concentration and the mobility in the polymer films, and the chloroform gas drastically enhances the mobility in the films. The change is reversible.

2) A visible (red-orange) EL diode utilizing poly(3-alkylthiophene) has been successfully realized. The light emission intensity increases super-linearly with increasing injected current, which is consistent with the enhancement of electroluminescence of poly(3-alkylthiophene) at higher temperature.

3) The emission intensity of poly(3-alkylthiophene) electroluminescent diodes depends on the alkyl chain length. Strong emission is obtained from a poly(3-alkylthiophene) diode of long alkyl-side-chain length.

4) From the pulse response of the electroluminescence in the poly(3-alkylthiophene) diodes, carrier mobilities are estimated.

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