

# Preparation of polythiophene thin films by UV laser-assisted deposition of 2,5-dichlorothiophene with a 248 nm excimer laser beam

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## Abstract

Polythiophene thin films are prepared by UV laser-assisted deposition (UV-LAD) of 2,5-dichlorothiophene (2,5-DCT) with a 248 nm (KrF) beam at several fluence values. Surface morphologies of the films depended strongly on laser fluence and deposition rate of the reactant. In the optimized conditions, mesh-like structures consisting of numerous fibers were observed. Electric conductivity of the film prepared by UV-LAD at  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  increased from less than  $10^{-7} \text{ S cm}^{-1}$  up to  $10^{-3} \text{ S cm}^{-1}$  on iodine doping. FT-IR, X-ray photoelectron spectroscopy (XPS) and ultra violet–visible (UV–vis) spectroscopy measurements show that, although sulfur atoms are eliminated to some extent, polymerization occurs basically at 2 and 5 positions of 2,5-DCT by effective elimination of halogen atoms to form polythiophene with various  $\pi$ -conjugation lengths. The film contained both soluble and insoluble components in tetrahydrofuran (THF) and acetonitrile (AN) solvents. Components with  $\pi$ -conjugation length corresponding to those of an oligothiophene with  $3 \pm 1$  thiophene units are dominant for soluble components. Optical band gap is estimated to be 2.93 eV for insoluble components in the film. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Polythiophene thin films; UV laser-assisted deposition

## 1. Introduction

Conducting polymer films have been playing an important role in a field of organic electronic and/or optical devices. Various preparation methods of conducting polymer films have been proposed so far, such as Langmuir–Blodgett (LB), spincoating, casting, chemical and electrochemical polymerization. Among them, chemical and electrochemical polymerization have been widely used as excellent methods for preparation of several conventional conducting polymers such as polypyrrole and polythiophene [1,2]. Almost all the preparation methods used hitherto for these conducting polymers are classified into wet processes. Only few attempts have been made at preparation of conducting polymer films in dry process. From a view point of application to hybrid electronic devices with inorganic material, which is expected as a near-future technology, it is desirable to prepare them in dry processes because of process-simplification and high-qualification. Plasma polymerization has been the only method for obtaining conducting polymers in dry process

[3]. Difficulty in energy control inherent in this method, however, prevents us from preparing organic films with well-organized structures.

In recent years, light-induced processing with UV lasers, such as a  $\text{N}_2$  laser, an excimer laser and the fourth harmonic of a Nd:YAG laser has attracted a great deal of attention as a promising new technology for synthesis or modification of polymers [4–8]. Above all, the excimer laser is considered to be excellent for the photochemical reaction and microscopic processing, making the best use of its high intensity, high photon energy (wavelength) selectivity as well as high spatial resolution [7].

In this paper, a method called UV laser-assisted deposition [9] (UV-LAD) is applied to preparation of conducting polymer films in dry process. Polythiophene films are prepared by UV-LAD of 2,5-dichlorothiophene (2,5-DCT) with an excimer laser beam at 248 nm (KrF) at several fluences.

## 2. Experimental details

Depicted in Fig. 1 is the experimental setup. Liquid 2,5-DCT was employed as a reactant. A molecular beam of the

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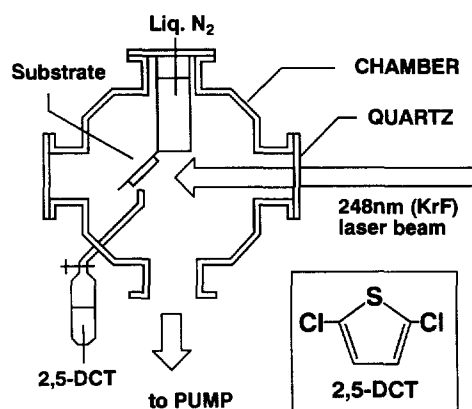


Fig. 1. Experimental setup. Inset: Chemical structure of 2,5-DCT.

reactant was continuously introduced into a reaction chamber by keeping the reactant at 0°C and deposited on a quartz or a KBr substrate settled at the angle of 30–60° to both directions of the laser beam and molecular beam. The typical flow rate of the reactant was fixed to 0.8 g h<sup>-1</sup> and 1.2 g h<sup>-1</sup>. Substrates were cooled between 210 and 240 K by liquid N<sub>2</sub> for effective deposition of 2,5-DCT. The reaction chamber was initially evacuated below 10<sup>-3</sup> Torr using rotary and mechanical booster pumps and kept between 10<sup>-2</sup> and 10<sup>-1</sup> Torr during UV-LAD. An excimer laser beam at 248 nm (KrF) was adopted as a light source for initiating polymerization, because the wavelength virtually coincided with the peak position of absorption band ( $\lambda_{\max}$ ) for 2,5-DCT (250 nm).

During deposition of the reactant on a substrate, the beam was radiated without optical lens to the substrate. Laser fluences were changed between 5 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup>. Repetition rate of the pulse laser was 5 Hz. After film formation, the substrate was heated up to 50°C to evaporate 2,5-DCT monomer deposited without polymerization. Iodine doping on the prepared films was performed by exposing them with I<sub>2</sub> vapor in a glass cell. The structures of the films prepared were investigated by scanning electron microscopy (SEM), FT-IR, X-ray photoelectron spectroscopy (XPS) and ultra violet–visible (UV–vis) spectroscopy.

### 3. Results and discussion

#### 3.1. Film formation by UV-LAD at various fluences—surface morphology and iodine doping effect on electric conductivity

UV-LAD of 2,5-DCT with 248 nm excimer laser beams at 5, 10 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> results in the formation of homogeneous yellow brown thin films on each substrate. The growth rate of the films prepared by UV-LAD depended on experimental conditions such as laser fluence, flow rate and vapor pressure of the reactant, and was typically 700 nm ± 300 nm for 1 h deposition. The surface morphologies of the films were dependent strongly on laser fluence and on flow rate of the reactant. In the optimized conditions, a mesh-

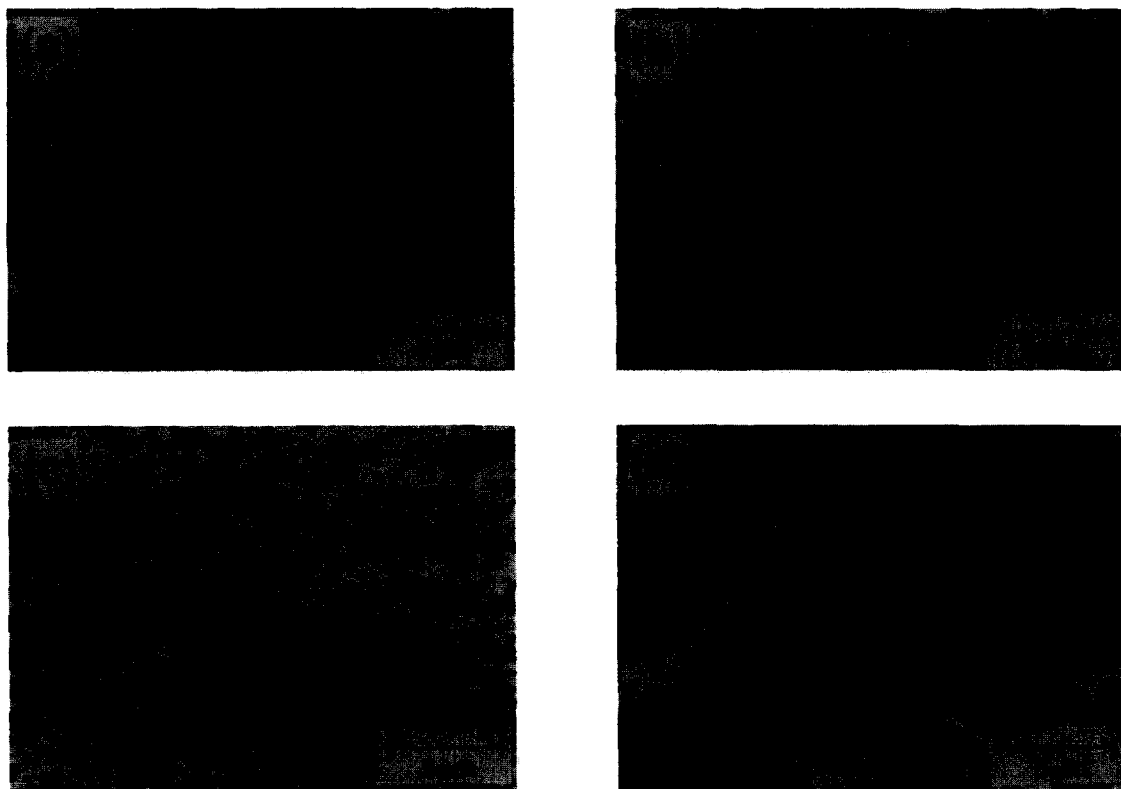


Fig. 2. Surface morphologies of the films prepared by UV-LAD at 248 nm with the flow ratio at 1.2 (a), 0.8 g h<sup>-1</sup> (b) (fluence at 10 mJ cm<sup>-2</sup> pulse<sup>-1</sup>) and those with fluence at 5 (c) and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> (d) (flow ratio at 0.8 g h<sup>-1</sup>).

like structure composed of a net with numerous fibers was observed. Fig. 2(a) and (b) show the surface morphologies of the films prepared by UV-LAD at 248 nm with the flow rate of 1.2 and 0.8 g h<sup>-1</sup>, respectively (fluence 10 mJ cm<sup>-2</sup> pulse<sup>-1</sup>). Although the morphology of the film prepared in the former condition is featureless and rather flat, the other one is characterized with stitch pattern consisting of fiber of about 0.5 μm in diameter. Some of the fibers have reached more than 10 μm in length. The diameter of the fibers increased with laser fluence as shown in Fig. 2(c) and (d) (fluences of 5 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, respectively). It should be noted that these peculiar structures are often observed for etching and modification of several polymer surface by laser ablation [4].

Iodine doping effect on electric conductivity for every film prepared by UV-LAD was investigated. Although the electric conductivities for the films prepared at 5 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> ranged between 10<sup>-5</sup> and 10<sup>-4</sup> S cm<sup>-1</sup>, the conductivity for the film at 10 mJ cm<sup>-2</sup> pulse<sup>-1</sup> was one order of magnitude higher, the maximum value of which reached almost up to 10<sup>-3</sup> S cm<sup>-1</sup>. This value is more than one order of magnitude higher compared with those of films prepared by plasma polymerization of polythiophene (10<sup>-5</sup>–10<sup>-4</sup> S cm<sup>-1</sup>) [3].

### 3.2. Studies on structure for the films prepared by UV-LAD at various fluences and estimation of their conjugation lengths by FT-IR and XPS spectroscopies

FT-IR spectra of the films prepared by UV-LAD of 2,5-DCT at 5, 15 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> are shown in Fig. 3. Peaks around 1510 cm<sup>-1</sup>, 1430 cm<sup>-1</sup> and 1210 cm<sup>-1</sup> ascribed to thiophene ring were detected in the spectra for the films prepared at 5 and 15 mJ cm<sup>-2</sup> pulse<sup>-1</sup>. Peaks around 1000 cm<sup>-1</sup> were assigned to C–H in-plane bending [10–12]. Presence of a peak at 794 cm<sup>-1</sup> assigned to C–H out-of-plane bending vibration related to β-H (H at 3 or 4 position) of thiophene [10–12] suggested that polymerization occurred predominantly at 2 and 5 positions of 2,5-DCT by eliminating halogen atoms. Peak around 1700 cm<sup>-1</sup> can be assigned to CO stretching of carbonyl groups formed through reaction of radicals created in the photochemical processes with oxygen atoms in reaction chamber or those in air, suggesting that structural defects also exist in the films. These defects may come from bond breaking of thiophene rings as well as from the link missing in polymerization. Peak intensity ratio between symmetric (1430 cm<sup>-1</sup>) and anti-symmetric (1510 cm<sup>-1</sup>) stretching vibration of thiophene ring gives us the information on the average conjugation length of the polymer [10]. According to such an analysis, average conjugation lengths *n* for the films prepared at 5 and 15 mJ cm<sup>-2</sup> pulse<sup>-1</sup> are estimated to 3 ± 1. Here we define *n* as conjugation length, which corresponds to the number of thiophene unit cells connecting each other with sp<sup>2</sup> hybrid orbitals of carbon atoms (C<sub>4</sub>H<sub>2</sub>S)<sub>*n*</sub>. FT-IR spectrum of the film prepared at 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> appeared quite differently from the above

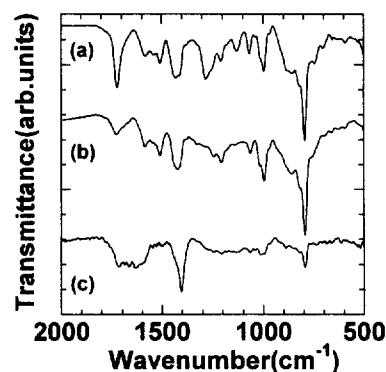


Fig. 3. FT-IR spectra of the films prepared by UV-LAD of 2,5-DCT at 5 (a), 15 (b) and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> (c).

two spectra. A broad band without any fine structures except for 1400 cm<sup>-1</sup> indicated that too much excess energy brought about undesirable reactions such as decomposition of thiophene rings to form amorphous carbon structure.

Content ratios of chloride and sulfur atoms against carbon atoms, Cl/C and S/C, and C<sub>1s</sub> peak positions of XPS for the films prepared at 5, 10 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> are listed in Table 1 together with those for 2,2':5',2''-terthiophene (TT) and 2,5-DCT monomer as references. The values of Cl/C for the films prepared at 10 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> mean that 80% of halogen atoms are successfully eliminated. C<sub>1s</sub> peak position for every sample shifts to lower energy region compared to that for sp<sup>3</sup> carbon atom (286 eV), suggesting π-conjugated structure with sp<sup>2</sup> carbon atoms in each film. According to a simple calculation from the Cl/C ratio on the assumption that polymerization occurs completely at 2 and 5 positions and the both ends of the chain are terminated by a chlorine atom, polymerization degrees of the films prepared at 5, 10 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> are to be 2.5, 5 and 5, respectively. The value for the films prepared at 10 mJ cm<sup>-2</sup> pulse<sup>-1</sup> is not the same with that estimated by FT-IR but a little bit larger. Undesirable structural defects such as bond breaking of thiophene rings are probably responsible for this discrepancy that polymerization degrees and average π-conjugation length disagree with each other. Actually, the value

Table 1

Cl/C, S/C and C<sub>1s</sub> peak position by XPS measurement for the film prepared at 5, 10 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> together with those for 2,5-DCT monomer and TT

Sample	Fluence (mJ cm <sup>-2</sup> pulse <sup>-1</sup> )	Cl/C	S/C	C <sub>1s</sub> peak position (eV)
Film by UV-LAD	5	0.2	0.18	284.4 ± 0.1
	10	0.1	0.14	284.3 ± 0.1
	20	0.1	0.12	284.1 ± 0.1
2,5-DCT		0.5 <sup>a</sup>	0.25 <sup>a</sup>	
TT			0.23 <sup>b</sup>	284.3

<sup>a</sup>Theoretical value.

<sup>b</sup>Sulfur atoms are eliminated, to some extent, in XPS measurement, resulting in smaller value (0.23) compared with theoretical one (0.25) for TT.

of S/C ratio is diminished compared to that for TT (0.23), suggesting bond breaking of thiophene rings. The value decrease with increasing fluence for UV-LAD. These structural disorders must impede the development of  $\pi$ -conjugated system. The actual extension of  $\pi$ -conjugation length  $n$  must be, therefore, somewhat shorter than the polymerization degree estimated from Cl/C. Comparison of  $C_{1s}$  peak position for the film prepared at  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  with that of TT allows us to conclude that  $n$  for this film is virtually equal to that for TT. This value is in good coincidence with the result from FT-IR measurement.  $C_{1s}$  binding energy for the film prepared at  $20 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  is barely lower than that at  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ . This may be due to formation of amorphous carbon structure with large amount of  $sp^2$  carbons. We will not discuss this subject any further since the film prepared at  $20 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  does not bear the slightest resemblance to polythiophene judging from the FT-IR spectrum.

### 3.3. Estimation of the optical band gap by UV-vis spectroscopy for insoluble components of the film prepared at $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$

Let us turn back our attention to the film prepared at  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ . It is hard to reconcile the high electric conductivity (more than  $10^{-3} \text{ S cm}^{-1}$ ) after iodine doping with the short conjugation length such as  $n = 3 \pm 1$ . It is suggested that components with larger  $n$  also existed in the film. Fig. 4 shows the UV-vis spectrum for the film prepared at  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  together with those for 2,5-DCT monomer and TT. The spectra for 2,5-DCT monomer and TT are measured by dissolving each monomer in methanol. Compared with 2,5-DCT monomer and TT, the film has a broad band. A shoulder is observed around 300–400 nm, at almost equal position to the band for TT. This spectrum supports the estimation of average  $n$  as described above. However the band edge extends to around 500 nm, indicating the presence of components with larger  $n$ . Actually, the film can be divided into soluble and insoluble components in some solvents such as tetrahydrofuran (THF) and acetonitrile (AN). A broad spectrum with several shoulders is observed in HPLC analysis for the soluble components of the film, although these could not be separated. Increase of electric conductivity on iodine doping is probably caused by the insoluble components with highly extended  $\pi$ -conjugation length. The average optical band gap ( $E_o$ ) for the insoluble components was estimated using following Eq. (1) (Mott plot) [13] in the range between 400 and 500 nm

$$\alpha(\omega)h\omega/2\pi = B(h\omega/2\pi - E_o)^m, \quad (1)$$

where  $\alpha(\omega)$  is the absorption coefficient,  $h\omega/2\pi$  is photon energy and  $B$  is a constant. It is well known that the absorption for many amorphous materials follows this relation assuming that energy bands are parabolic ( $m=2$ ) [14]. For organic conducting polymers with one-dimensional system, on the other hand, it has been claimed that  $m=1/2$  is applicable in

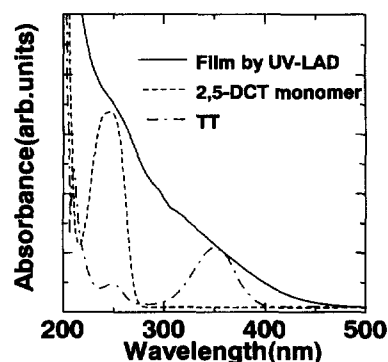


Fig. 4. UV-vis spectrum for the film prepared by UV-LAD of 2,5-DCT (—) together with those for 2,5-DCT monomer (---) and TT (-·-·).

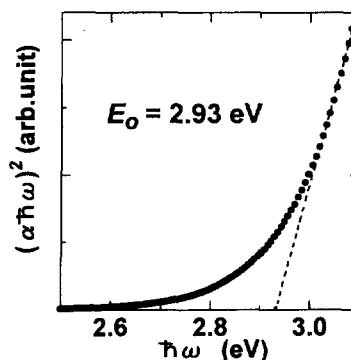


Fig. 5. The Mott plot for the insoluble components of the film prepared by UV-LAD.

Eq. (1) [15]. The plot for the film prepared at  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  is shown in Fig. 5. The  $E_o$  value estimated by this analysis with  $m=1/2$  is 2.93 eV. Although this value is larger than those for polythiophene prepared, for example, by chemical method reported by Kobayashi et al. [16], it is not inferior to those for the plasma-polymerized thiophene films (2.5–3.1 eV) [3].

## 4. Conclusion

Polythiophene thin films are prepared by UV-LAD of 2,5-DCT at 248 nm. Films prepared by UV-LAD possess fibrous structure. Electric conductivity of the film prepared at  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  has increased from less than  $10^{-7} \text{ S cm}^{-1}$  up to  $10^{-3} \text{ S cm}^{-1}$  on doping with iodine after UV-LAD. Although sulfur atoms are eliminated to some extent, polymerization occurs predominantly at 2 and 5 positions of 2,5-DCT by elimination of halogen atoms. The film consists of soluble and insoluble components with various conjugation length in some solvents. The average conjugation length  $n$  for the film prepared at  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  and the optical band gap for insoluble components are estimated to  $3 \pm 1$  and 2.93 eV, respectively. Detailed discussion on the polymerization mechanism under various conditions (wavelength, fluence, flow rate of reactant, etc.) and molecular design for reactant with suitable  $\lambda_{\text{max}}$  will lead to the films with longer

conjugation length without structural defects such as scarcity of sulfur atoms.

Along with these guidelines, UV-LAD at 248 nm of 2,5-dibromothiophene (2,5-DBT) and 2,5-diiodothiophene (2,5-DIT), in which side groups more easily eliminated [17], and UV-LAD at longer wavelength such as 308 nm and 351 nm of 5,5'-dibromo-2,2'-bithiophene (DBBT) and 5,5'-dibromo-2,2':5',2''-terthiophene (DBTT) which have  $\lambda_{\max}$  corresponding to these laser wavelengths are now in progress.

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