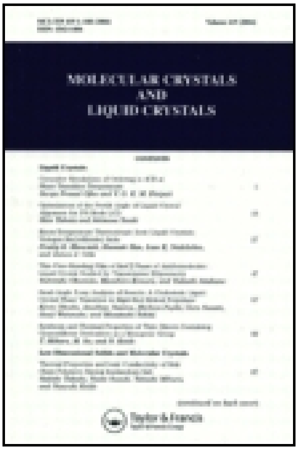

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Preparation of Conductingpolymer Thin Films by Excimer Laser Chemical Vapor Deposition

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PREPARATION OF CONDUCTING POLYMER THIN FILMS BY EXCIMER LASER CHEMICAL VAPOR DEPOSITION

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Abstract Organic thin films with laser induced periodic structures (LIPS) are prepared by excimer laser chemical vapor deposition (ELCVD) of two kinds of aromatic compounds, *p*-dichlorobenzene(DCB) and 5,5'-dibromo-2,2'-bithiophene (DBBT) with 193nm (ArF) and 308nm (XeCl) beams, respectively. The conductivity of the film from DBBT with 308nm beam has reached to 1×10^{-2} Scm^{-1} by doping with iodine after the ELCVD process.

INTRODUCTION

In recent years, UV light-induced processing with excimer laser beam has been developed as a new technology for polymerization or modification of polymers.[1-3] The excimer laser with high reaction selectivity and spatial control is considered to be an excellent tool for the photochemical reaction and microscopic processing.

In this report, conducting polymer thin films are prepared from two kinds of aromatic compounds, *p*- dichlorobenzene (DCB) and 5, 5' - dibromo-2, 2'-bithiophene (DBBT) by excimer laser chemical vapor deposition (ELCVD). Surface morphologies for the films prepared from DCB by ELCVD with a 193nm laser beam (DCB(193)) and from DBBT with a 308nm beam (DBBT(308)) are investigated. As for DBBT(308), the structure and physical property are studied by FT - IR, UV - vis., ESCA and electric conductivity measurements.

EXPERIMENTAL

The starting monomer, DCB or DBBT was deposited onto a quartz or KBr substrate under irradiation of an unfocused excimer laser beam in a reaction chamber evacuated below 10^{-3}Torr. 193nm(ArF) and 308nm(XeCl) laser beams are applied for the film preparation from DCB and DBBT, respectively. Substrate temperature was kept between 200 and 240 K with liq. N_2 during film preparation.

RESULTS AND DISCUSSION

SEM image of surface morphology of DCB(193) and AFM image of that of DBBT (308) are shown in Fig. 1(a) and (b), respectively. Both films have oriented structures consisting of numerous fibers. These structures are often observed in surface modification of polymers with polarized excimer laser beams and called laser induced periodic structures (LIPS).[4] For DCB(193), in particular, the fibers are about 200 nm in diameter and some of them reach more than 20 μm in length.

In FT-IR spectrum for DBBT(308), the peaks around 1500, 1415 and 1200 cm^{-1} related to thiophene ring stretching are observed. Peak at 790 cm^{-1} assigned to C-H out-of-plane bending for hydrogen atoms attached to thiophene rings at β positions is also

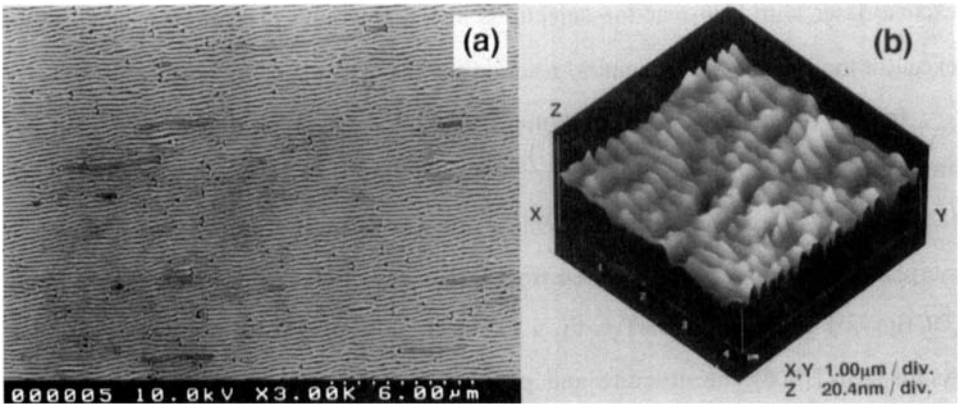

FIGURE 1 Surface morphologies of (a) DCB(193) and (b) DBBT(308).

observed, suggesting that polymerization occurs at α positions of thiophene rings successfully.

Content ratios of halogen and sulfur atoms against carbon atoms (X/C and S/C, respectively), and C1s peak position for DBBT(308) by ESCA measurement are listed in Table I together with those for α-terthiophene (3T) as a reference. Assuming a complete α, α'-bonded polymer, it consists of 7 - 8 thiophene ring units considering from the X/C ratio (0.07). Smaller value of S/C ratio (0.17) compared to that of 3T (0.23), however, suggests partial bond breaking of thiophene rings. This structural disorder must impede the development of π-conjugated system. C1s peak position for DBBT(308) is slightly lower (284.1eV) than that for 3T (284.2eV), indicating that π-conjugation length of the film is a little longer than that of 3T.

Figure 2 shows the UV-vis. spectrum for DBBT(308) together with that for 3T. Broad shape of the spectrum for DBBT(308) suggests that the film consists of several components with different π-conjugation length. Although the wavelength of the maximum peak position of the spectrum for DBBT(308) is slightly shorter than that for 3T, band edge of the spectrum comes up to 450 nm, corresponding to that for oligomer with 6 thiophene units.[5] The average π-conjugation length is, therefore, roughly estimated to be equivalent to that for oligomer with 3-5 thiophene units, which is not in contradiction with the ESCA results.

The conductivity of DBBT(308) has been increased up to 1×10^{-2} Scm^{-1} by doping with iodine after ELCVD. This value is more than two orders higher than those of polythiophene film prepared by plasma polymerization.[6]

TABLE I Content ratios of halogen atoms and sulfur atoms against carbon atoms, X/C and S/C, respectively, and C1s peak positions for DBBT(308).

Sample	X/C	S/C	C1s peak position (eV)
DBBT(308)	0.07	0.17	284.1
3T	-	0.23	284.2

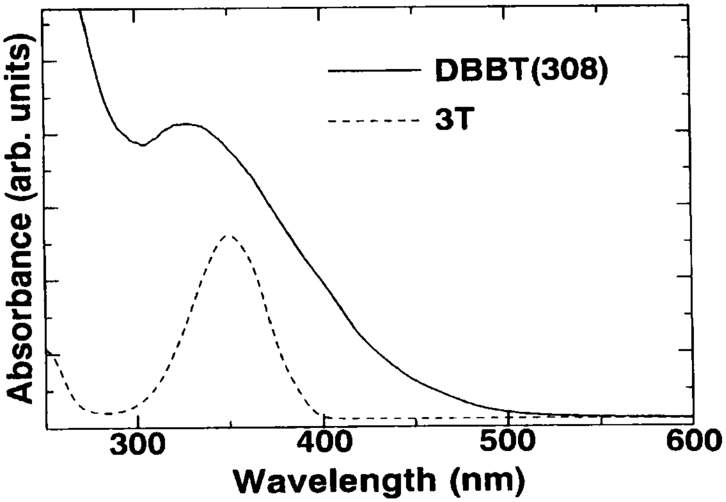

FIGURE 2 UV-vis. spectra of DBBT(308), DBBT monomer and 3T.

CONCLUSION

Organic thin films with LIPS are prepared by ELCVD of DCB and DBBT. The conductivity of DBBT(308) has reached to 1×10^{-2} Scm^{-1} by doping with iodine after the ELCVD process. For DBBT(308), FT-IR, UV-vis., ESCA measurements show that although sulfur atoms eliminate to some extent, oligomers with the π-conjugation length equivalent to that for oligomers with 3 - 5 thiophene units, on the average, are formed.

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