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CORRELATION BETWEEN DARK-CURRENT AND LIGHT ABSORPTION OF POLYIMIDES HAVING A TPA STRUCTURE

Teppei Chino, *Syo Fukuchi, Kazuhiro Takizawa,*
Shigeo Asai, Ryohei Ishige, and Shinji Ando

Department of Chemistry and Materials Science, Tokyo Institute of Technology,
Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo, 152-8552, Japan
E-mail: chino.t.aa@m.titech.ac.jp

INTRODUCTION

Polyimide (PI) is one of the super engineering plastics which shows excellent properties such as high mechanical strength, thermal stability and chemical resistance. Recently, studies on functional polyimides for optical and electrical applications have been increasingly reported. For instance, PIs having a triphenylamine (TPA) structure in the main chain were reported to show enhanced photoconductivity [1]. Electronic conduction in PI films is considered to occur in two steps. Firstly, charge transfer (CT) transition occurs between electron-donating diamine and electron-accepting dianhydride moieties, followed by generation of a pair of a hole and an electron. Secondly, the charges are dissociated into free carriers by external electric field. In a previous study, temperature dependence of electrical conductivity of PIs without light irradiation (dark-current) have been investigated [2] and PIs having TPA structure showed higher conductivity than the other PIs without TPA structure at higher temperatures (>100°C), where thermally assisted CT carrier generation were suggested. In this study, dark-current and optical absorption measurements were conducted for PI films synthesized from a TPA diamine unit and various dianhydrides (Fig. 1), and relations between CT interactions and electro-conductive properties are discussed.

EXPERIMENTAL

The chemical structures of the PIs used in this study are shown in Fig.1. PI films were prepared by spin-coating of poly(amic acids) (precursors of PI) solutions on ITO substrate and subsequent thermal imidization process at 300°C. The thickness of PI films were set to 1.5~2.2 μm. Silver electrode was deposited on a PI film by magnetron sputtering. Dark-current of PI films was measured by applying voltage between the silver and ITO electrodes at preset temperature in a shield box with a heater (Fig. 2). The preset temperatures were set at 40, 60, 90, 120, 150, 180, 210 and 230°C. And applied electrical field was 50 kV/cm. In such an electrical field, injection of carriers from the electrodes is considered to be difficult, and dark-current is dominated by intrinsic carrier conduction.

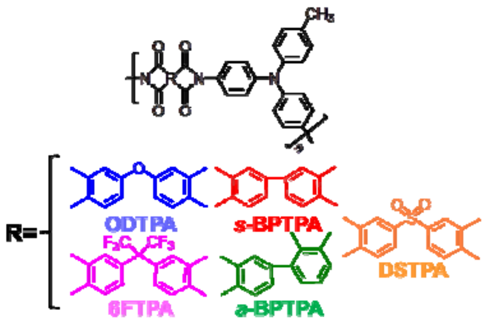

Figure.1 Chemical sturcture of PIs

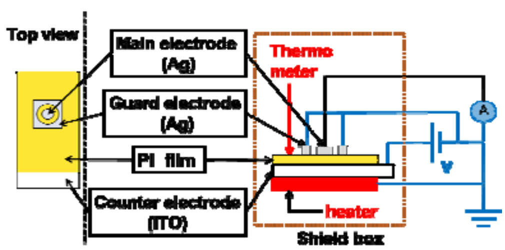

Figure.2 Experimental configuration for dark-current measurement.

RESULT AND DISCUSSION

Figs.3 (a) and (b) shows the results of dark-current measurement. In Fig.3 (a), (s-BPTPA, a-BPTPA and DSTPA), the temperature dependence of current density are changed at 60~90°C, and DSTPA shows a higher current density than s-BPTPA and a-BPTPA in a wide temperature range. In a previous study [2], the increase in the slope at higher temperatures was attributed to CT carrier excitation. For a-BPTPA and DSTPA, inflection points are also observed at higher temperatures (> ca.180°C). In general, current density is dominated by carrier density and carrier mobility. Tameev *et al.* reported constant temperature dependency of carrier mobility over relatively wide temperature range for a photoconductive PI [3]. If carrier mobility increases linearly with temperature, the inflection is attributable to a saturation of carrier density. On the other hand, in Fig.3 (b), ODTPA and 6FTPA show lower current densities than the other PIs even at higher temperatures, and no clear inflection points are observed. To investigate the relation between CT interactions and dark-current properties, UV-vis optical absorption spectra of the PI films were measured (Fig.4). The tailing of absorptions over 430 nm is assigned to CT absorption, and the activation energies for CT transitions are closely related with the optical bandgaps. Optical bandgaps can be evaluated from absorption spectra based on the following formula (1). (α: absorption coefficient, h: Planck constant, v: frequency, E_{opt}: optical bandgap)

$$(\alpha h v)^{1/2} \propto (hv - E_{opt}) \qquad (1)$$

A small bandgap corresponds to strong CT interactions. The results of Figs. 3 and 4 suggest that the current densities of the PIs increase at higher temperatures (120~180°C) with decreasing the bandgaps of PIs. In other words, CT carrier generation is a thermally assisted process at higher temperatures. In addition, ODTPA and 6FTPA show similar dark-current properties to those of the PIs without TPA structure, which indicates that CT carrier conduction is not a dominant mechanism for these PIs even at higher temperatures.

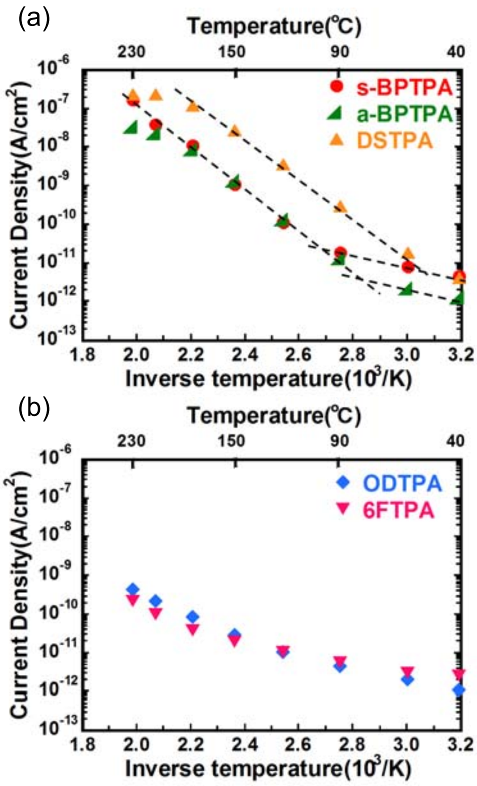

Figure.3 Temperature dependence of current density; (a) s-BPTPA, a-BPTPA and DSTPA, (b) ODTPA and 6FTPA

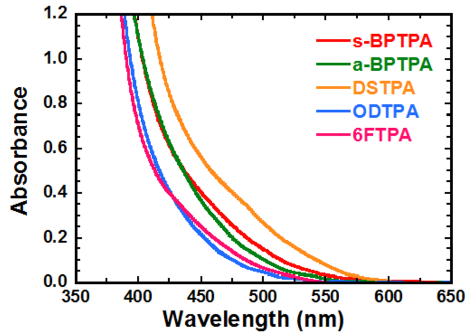

Figure.4 UV-vis absorption spectra of PIs

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