Correlation between Dark-current and Light Absorption of Polyimides having a TPA Structure

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I. INTRODUCTION

Recently, studies on functional polyimides (PIs) for optical and electronical applications have been increasingly reported. For instance, PIs having a triphenylamine (TPA) structure in the main chain were reported to show enhanced photoconductivity [1]. The electronic conduction of PIs is considered to occur in two steps. Firstly, charge transfer (CT) transition occurs between electron-donating diamine and electron-accepting dianhydride moieties, and a pair of hole and electron is generated. Secondly, they 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 PI having TPA structure showed higher conductivity than other PIs at higher temperatures, in which and 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, and the correlation between CT interactions and electro-conductive properties are discussed.

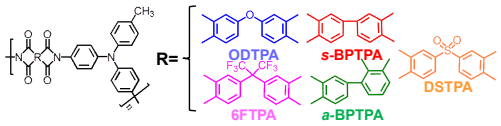

Figure 1. Chemical sturcture of the PIs

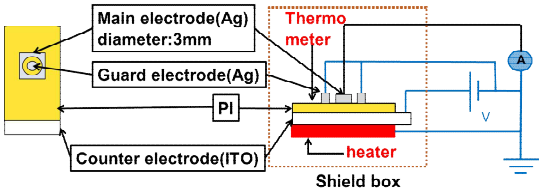

Figure 2. Experimental configuration for dark-current measurement

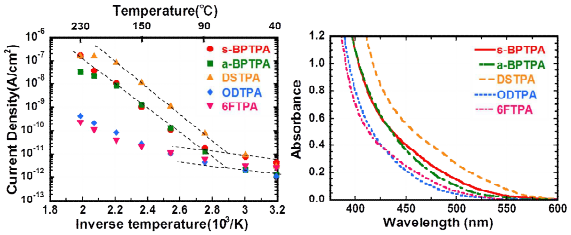

Figure 3. (a) Temperature dependence of current density and (b) UV-vis absorption spectra of the PIs

II. EXPERIMENTAL

The chemical structure 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 onto ITO substrate and subsequent thermal imidization process at 300°C. Silver electrode were deposited on the PI films by magnetron sputtering. Dark-current of the PI films was measured by applying voltage (50kV/cm) between silver and ITO electrode with heating at preset temperature in a shield box (Fig. 2). The measuring temperature were set to 40, 60, 90, 120, 150, 180, 210 and 230°C.

III. RESULT AND DISCUSSION

Fig.3 (a) shows the results of dark-current measurement. In *s*-BPTPA, *a*-BPTPA and DSTPA PIs, 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*-BPTPA and DSTPA, inflection points are observed again at higher temperatures (> ca.180°C), which could be attributable to a saturation of carrier density. On the other hand, ODTPA and 6FTPA shows lower current densities than the other PIs even at higher temperatures and apparent inflection points are not observed. To investigate the correlation between CT interaction and dark-current properties, UV-vis optical absorption spectra were measured (Fig.3 (b)). The gradually decreasing absorption at longer wavelength region corresponds to CT absorption, and the optical bandgap estimated from the spectra represents the activation energy of CT transition. A small bandgap corresponds to a strong CT interaction. Comparing the dark-current values and the optical bandgaps, current densities increase at higher temperatures (120~180°C) with decreasing the bandgap of PIs. These results imply that CT carrier generation is a thermally assisted process at higher temperatures. In addition, ODTPA and 6FTPA shows similar dark-current properties with the PIs without TPA structure, which indicates that CT carrier conduction is not a dominant mechanism in these PIs even at higher temperatures.

REFERENCES

[1] E.L. Aleksandrova, "Structural Properties of Polyimides and the Mechanism of Carrier Photogeneration in Polyimide-Based Molecular Complexes," *Opt. Spect.*, **93**, 118 (2002)

[2] K. Takizawa, S. Asai, S. Ando, "Temperature dependence of electric conduction in polyimides with main chain triphenylamine structures" *Polym., J.*, **46**, 201 (2014)