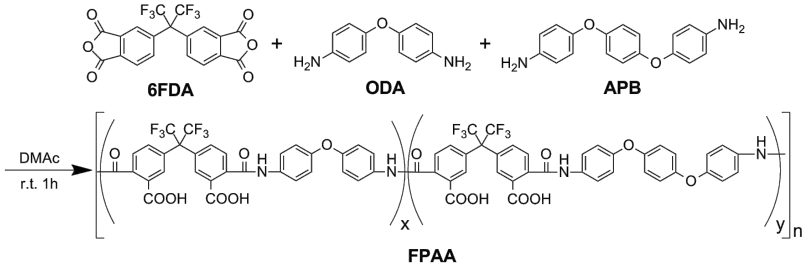
Alkaline-developable and Positive-type Photosensitive Polyimide based on Fluorinated Poly(amic acid) from Diamine with High Hydrophobicity and Fluorinated Diazonaphtoquinone

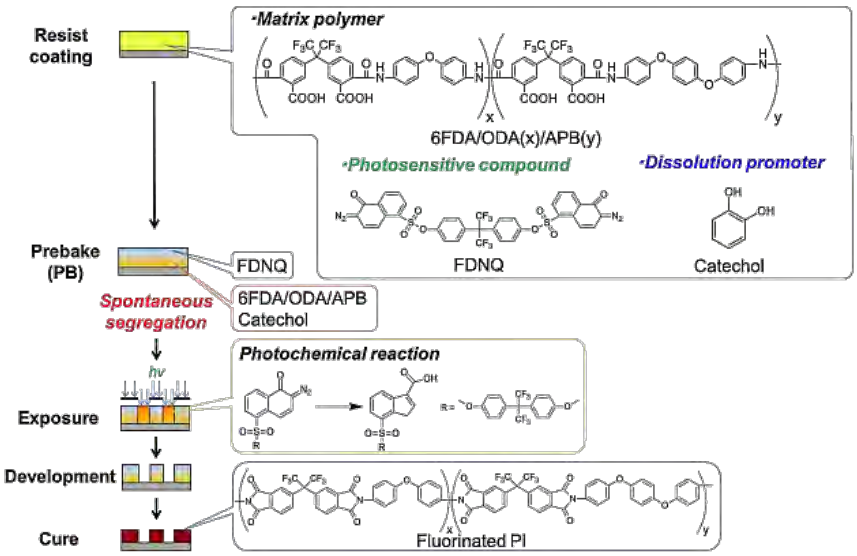
Yusuke Inoue[1](井上雄介), Yoshihito Ishida[3]（石田良仁）, Tomoya Higashihara[2](東原知哉), Atsushi Kameyama[3]（亀山敦）, Shinji Ando[1] (安藤慎治)and Mitsuru Ueda[3]（上田　充）

[1] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Japan [2] Department of Polymer Science and Engineering, Yamagata University, Japan [3] Department of Chemistry, Kanagawa University, Japan
mueda@kanagawa-u.ac.jp

An alkaline-developable positive-type photosensitive polyimide (**PSPI**) based on fluorinated poly(amic acid) (**FPAA**) and fluorinated diazonaphtoquinone (**FDNQ**) as a photoactive compound has been successfully developed as a promising material for use in microelectronics. The **FPAA** was prepared from 4,4'-(hexafluoroisopropylidene)diphtahlic anhydride and aromatic diamines, 4,4'-oxydianiline (80 mol%), and 4,4'-oxybis(4-phenoxyaniline) (20 mol%)(Scheme 1).



Scheme 1. Synthesis of **FPAA**



Scheme 2.　The photolithographic process

The solution of **FPAAx** and **FDNQ** is spin-coated on a silicon wafer and prebaked. The **FDNQ** rich top layer is spontaneously formed. The film is then exposed to the *i*-line through a photomask to produce an indenecarboxylic acid by a photochemical reaction. The indenecarboxylic acid is

extremely soluble in the alkaline aqueous developer. As a result, the dissolution rate of the exposed area to the 2.38 wt% TMAHaq increases and a positive image is formed.

The **PSPI** consisting of **FPAA**, catechol (3 wt% to **FPAA**), and **FDNQ** (25 wt % to **FPAA**) showed a high sensitivity of 45 mJ/cm^2 and a high contrast of 10 when it was exposed to a 365 nm line (*i*-line), and developed with 2.38 wt % TMAHaq for 10 seconds at room temperature (Fig. 1).

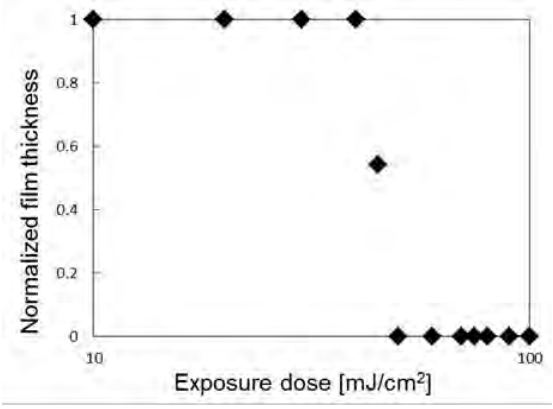


Fig. 1. Characteristic photosensitive curve of **PSPI**

A clear positive image of a 6-μm line and space pattern was printed on a film, which was exposed to 80 mJ/cm^2 of *i*-line by a contact printing mode and fully converted to the corresponding polyimide (PI) pattern upon heating at 350 °C, as confirmed by FTIR spectroscopy (Fig.2).

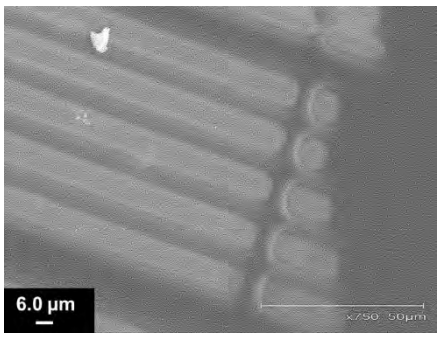


Fig. 2 SEM image of patterned **FPAA-2** in a 1.2-μm-thick film (**FPAA-2** and **FDNQ** (25 wt% to **FPAA2**)). The *i*-line exposure dose and PB condition were fixed to 80 mJ/cm^2 and 120 ºC for 2 min, respectively (3.0 kV x 1.30 k)

The new **PSPI** possesses several advantages over previous TMAHaq-developable and positive-type **PSPIs**, such as a higher sensitivity for the PI patterning and longer development time. Furthermore, the development is carried out with 2.38 wt% TMAHaq without using IPA. Thus, this system will be a good candidate for next generation **PSPIs**.