

# Vapor Deposition Polymerization of Polyimide Having Perylene Unit and its Characterization by Displacement Current Measurement

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## 1. Introduction

One of the key technologies for the development of polymer electronic devices is the formation of high-quality polymer thin films, multilayers, and microstructures. The conventional coating methods fail this purpose due to the problems coming from the solvent. This paper proposes the physical vapor deposition of polyimide thin films that have polycyclic unit in the main chain. Such a polymer has a possibility of showing semiconducting property as well as high stability inherent to polyimide. The vapor deposition polymerization [1] makes it possible to form uniform and high-purity thin films of such an insoluble polymer. This paper also reports the electrical property of the film characterized by the displacement current measurement.

## 2. Experiment

Figure 1 shows the reaction scheme of depositing polyimide that has perylene unit. The film formation process consists of two steps. 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and 1,12-diaminododecane (DADD) were co-evaporated in high vacuum from individual Knudsen sources onto a substrate kept at the room temperature. This forms a thin film of polyamic acid on the substrate. In the next step, the film was annealed in the air to form polyimide by dehydration. It is

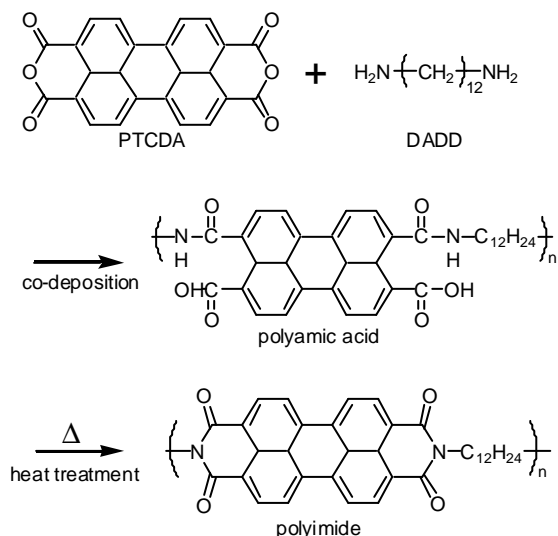


Fig. 1 Reaction scheme for the vapor deposition polymerization of polyimide having perylene unit.

important to optimize the evaporation and annealing conditions. The chemical structure of the films was characterized by the infrared (IR) absorption spectra measured by a reflection absorption method on Al surface.

The electrical property of the film was measured by the displacement current method. A 30-nm thick film of Teflon AF 1600<sup>(R)</sup> was evaporated [2] on an ITO-coated glass substrate, on which a 100-nm thick polyimide film was prepared as stated above. An aluminum top electrode was evaporated to form an MIS structure. The current flow through this cell was measured with a ramp voltage of 0.64 V/s at amplitude of 15 V.

## 3. Results and Discussions

### Deposition Polymerization

Figure 2 shows the IR absorption spectra of DADD (a) and PTCDA (b) monomers, the co-deposited film (c), and the film after annealing (d). When DADD was evaporated by itself, no film accumulated on the substrate. The co-deposited film had a structure largely different from the monomers. The carbonyl end group of PTCDA (1770 cm<sup>-1</sup>) and the amino end group of DADD (1600 cm<sup>-1</sup>) disappeared, but N-H and C=O bands of amide group appeared at 1550 and 1640 cm<sup>-1</sup>, respectively. This result indicates that the co-deposition of PTCDA and DADD yields polyamic acid in the as-deposited state. After

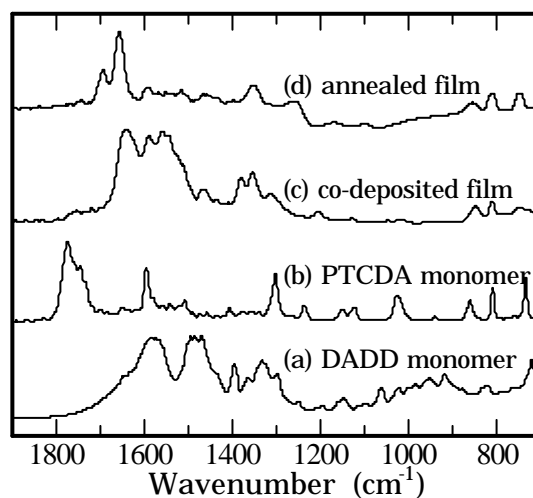


Fig. 2 IR spectra of DADD and PTCDA monomers (a and b), co-deposited film (c) and annealed film (d).

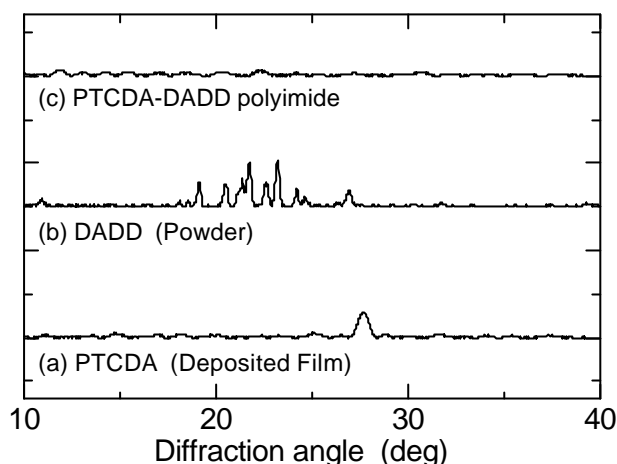


Fig. 3 X-ray diffraction pattern of DADD monomer (a), PTCDA deposited film (b), and deposition-polymerized polyimide film (c).

annealing this film for more than one hour at a temperature higher than 85 °C in the air, the amide band disappeared and the imide bands appeared at 1650 and 1690  $\text{cm}^{-1}$ . This indicates that polyimide can be deposited by co-evaporation of PTCDA and DADD followed by annealing.

#### Crystal Structure and Morphology

Figure 3 shows the x-ray diffraction patterns of PTCDA monomer film, DADD monomer powder, and the PTCDA-DADD polyimide film. The simple evaporation of PTCDA monomer produces polycrystalline thin films. Although the film has preferential crystal orientation, the film consists of small grains of crystallites, resulting in an inhomogeneous microstructure. On the other hand, the polyimide thin film had amorphous structure and gave no diffraction peaks. Figure 4 shows the optical micrographs of the PTCDA monomer and the polyimide films. Compared to the polycrystalline PTCDA film, the deposition-polymerized film is much superior in surface smoothness reflecting its amorphous microstructure.

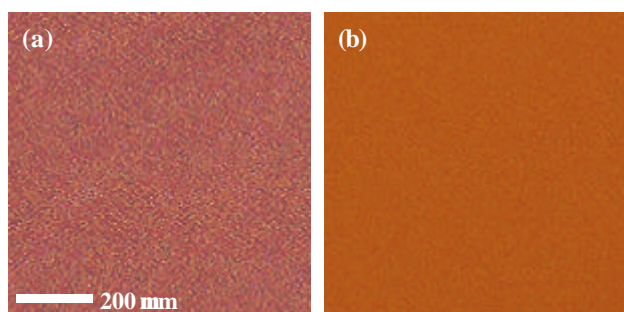


Fig. 4 Optical micrograph of PTCDA monomer film (a) and PTCDA-DADD polyimide film (b).

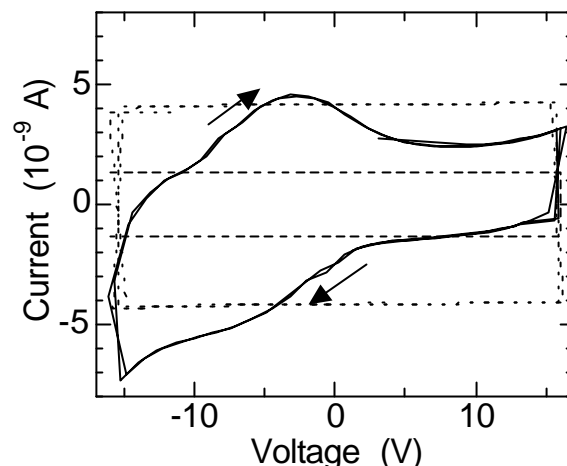


Fig. 5 Displacement current of MIS device consisting of Teflon AF insulator and PTCDA-DADD polyimide films.

#### Electrical Characteristics

Figure 5 shows the displacement current characteristics measured for the MIS diode of ITO/Teflon AF/PTCDA-DADD polyimide/Al. The dotted line represents the current for a MIM structure without the polyimide layer, and the dashed line shows the displacement current calculated from the dielectric constant of the MIS device. The current injection was observed when a negative voltage was applied on the Al electrode, suggesting that the PTCDA-DADD polyimide has the electron transport characteristics.

#### 4. Conclusions

It has been shown that the perylene-based polyimide thin films can be prepared by the physical vapor deposition polymerization of PTCDA and DADD. The polyimide films have uniform amorphous structure and have higher surface smoothness compared to the PTCDA monomer thin films. The displacement current measurement suggests that this polyimide thin film has electron-transporting characteristics. It is noteworthy that the vapor deposition polymerization was feasible for preparing multilayered polymer MIS device due to the solvent-free nature of the deposition process. It can be concluded from these results that the vapor deposition polymerization can be an attractive method for developing thin film polymer electronic devices.

#### References

- [1] H. Usui, *Thin Solid Films*, **365** (2000) 22.
- [2] H. Usui, R. Kojima, S. Horie, K. Tanaka and F. Ohishi, *Proc. 2001 Intern. Symp. Elect. Insulating Mat.* (2001) 570.