

# Vapor Deposition Polyimidization on Diamond Surfaces by p-Phenylene-diamine (PDA) and Pyromellitic Dianhydride (PMDA)

Masakatsu Kochi, Kaori Ohta, Yasushi Uehara, Rikio Yokota(1) and Toshihiro Ando(2)

Shizuoka Institute of Science and Technology, Toyosawa, Fukuroi-shi, Shizuoka 437, Japan. (1) The Institute of Space and Astronautical Science, Yoshinodai, Sagami-hara-shi, Kanagawa 229, Japan. (2) National Institute for Research in Inorganic Materials, Namiki, Tsukuba, Ibaraki 305, Japan.

## ABSTRACT

A new experimental apparatus for vapor deposition polymerization (VDP) was set up to permit monomers to deposit on a substrate from all directions. PDA was found to react with the oxidized surfaces of diamond powder. The successive evaporation of PMDA resulted in the imidization with the PDA coupled with the diamond surfaces. Diffuse reflectance FTIR spectra revealed that the imidized PDA-PMDA deposit tends to align perpendicular to the diamond surfaces.

## INTRODUCTION

Vapor deposition polymerization (VDP) is an attractive method for producing high performance polyimide (PI) thin films [1-3]. Vapor phase deposition is a dry process which does not require any use of solvents.

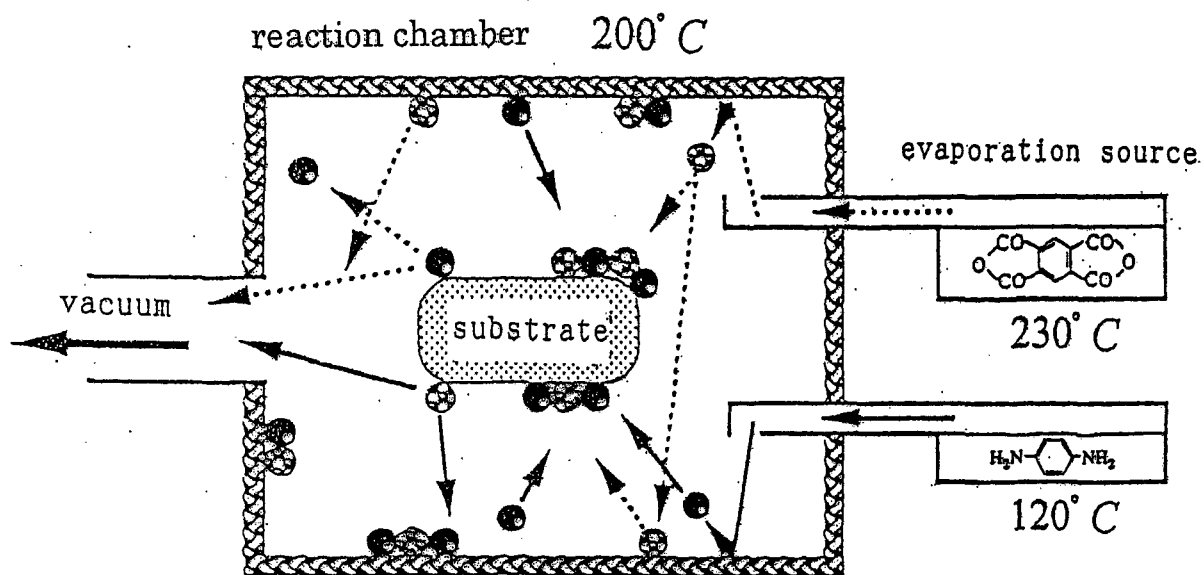


Figure 1. Schematic principle of the VDP from all directions

The rod-like conformation of polyimides is advantageous for realizing a polymer wire. We[4] have reported that the oxidized surface of diamond with carboxylic acid is expected to be a reactive anchor for vapor deposition polyimidization.

In this article the vapor deposition imidization by PDA and PMDA on the oxidized surfaces of diamond is studied by using a new VDP system permitting the monomers to deposit on a substrate from all directions( see Figure 1 ).

## EXPERIMENTAL

Commercially available synthesized diamond powder was fully hydrogenated and then oxidized at ca. 500°C in an O<sub>2</sub> environment[5].

PDA (T<sub>m</sub> = 140°C, Wako Pure Chemical Industries, Ltd.) and PMDA(T<sub>m</sub> = 275°C, TCI Ltd.) were used without further purification. PDA and PMDA were evaporated from the monomer sources at 120°C and 230°C, respectively, in a vacuum of ca. 2 x 10<sup>-5</sup> torr to react at 200°C in the reaction chamber.

Diffuse reflectance infra spectra and attenuated total reflection ( ATR ) spectra were obtained on an JASCO FT/IR 8300 at 2 cm<sup>-1</sup> resolution.

## RESULTS AND DISCUSSION

Figure 2 shows the diffuse reflectance FTIR spectrum of the oxidized diamond powder.

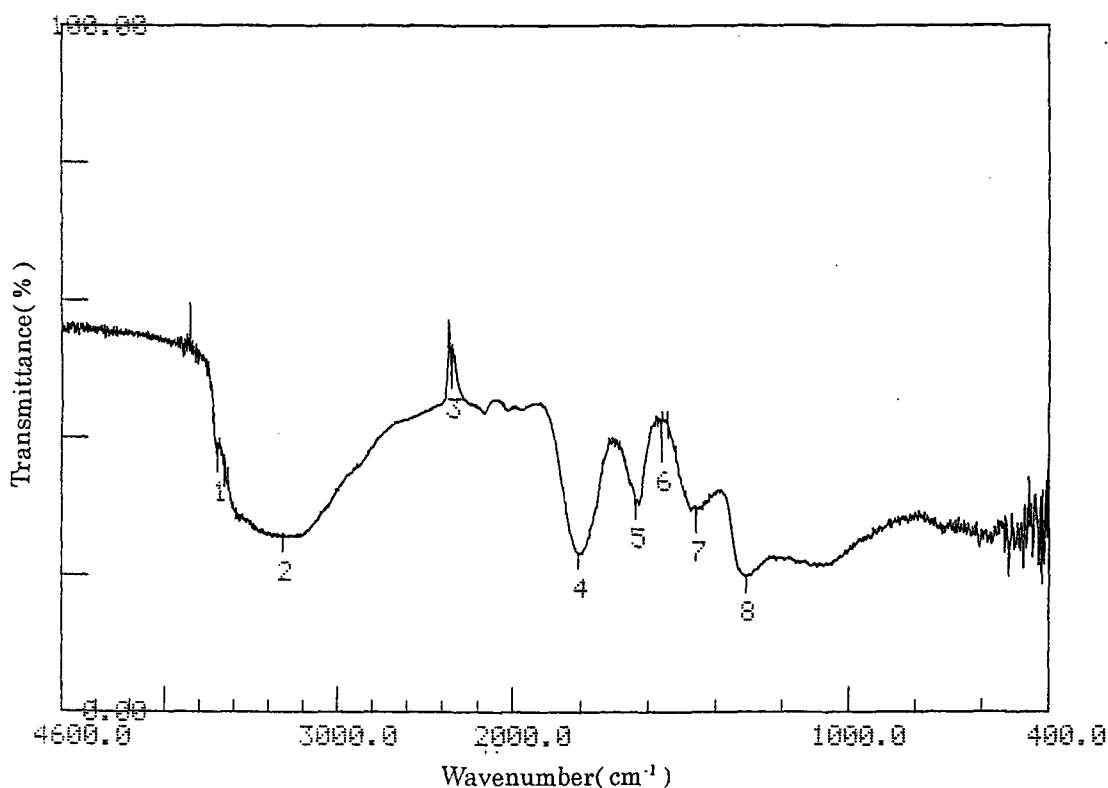


Figure 2. Diffuse reflectance FTIR spectrum of the oxidized diamond powder

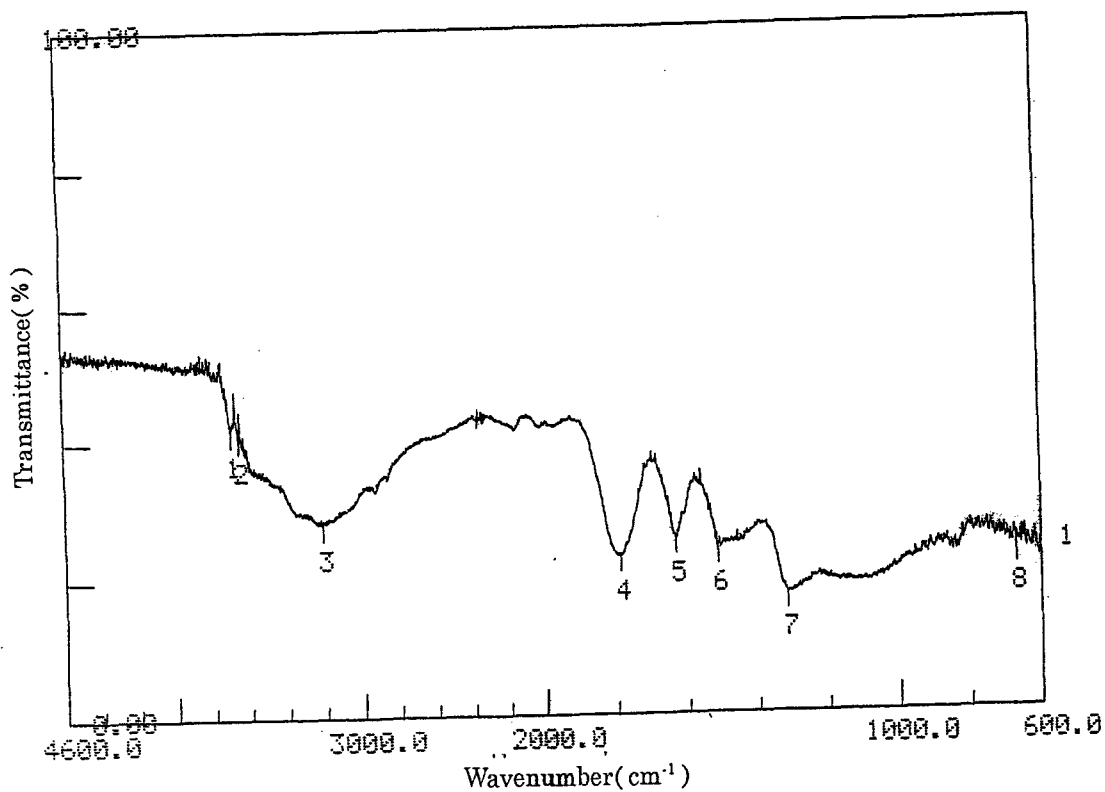


Figure 3. Diffuse reflectance FTIR spectrum of the PDA deposit on the oxidized diamond powder

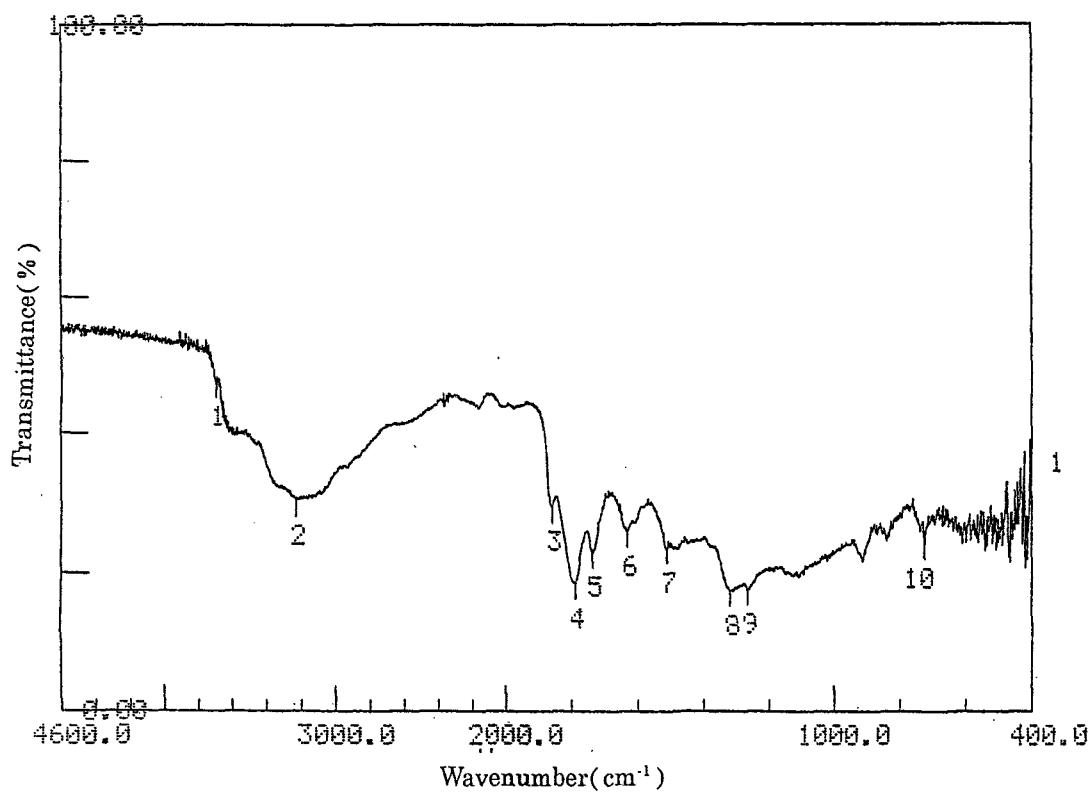


Figure 4. Diffuse reflectance FTIR spectrum of the PMDA deposit on the PDA coupled with the diamond surfaces

The characteristic absorption peaks due to carboxylic acid groups are found at  $3692\text{ cm}^{-1}$  ( No.1) and  $1637\text{ cm}^{-1}$  (No.5) in Figure 2. Ando et al. has reported that the hydrolysis of carboxylic anhydride structure on the oxidized diamond surfaces leads to formation of the carboxylic structure having new peaks at  $3710\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  assigned to the O-H and C=O vibrations, respectively. It is worth noting that the peak due to C=O stretching vibration is located at  $1806\text{ cm}^{-1}$ , while the similar peak due to C=O vibration is found at  $1778\text{ cm}^{-1}$  in the case of the commercial diamond powder[4]. Ando et al. [5] suppose that the C=O stretching vibration appearing in relatively high frequencies on the diamond surfaces oxidized at  $500^{\circ}\text{C}$  can be assigned to carboxylic anhydride structure, while the ones in relatively low frequencies correspond to lactone or cyclic ketone structures.

Figure 3 displays the diffuse reflectance spectrum of the PDA deposit on the oxidized diamond powder. The bands ascribed to PDA appear at  $1514\text{ cm}^{-1}$  ( No.6, C-H stretch of 1,4- $\text{C}_6\text{H}_4$  ) and  $3200 \sim 2800\text{ cm}^{-1}$  ( N-H stretch of aromatic amines ). This suggests that PDA forms an amide coupling with the carboxylic acid groups on the oxidized surfaces in analogy with the commercial diamond powder. The band due to C=O vibration at  $1806\text{ cm}^{-1}$  is shifted to  $1787\text{ cm}^{-1}$  through the vapor deposition of PDA. Subsequent thermal curing of the PDA deposit up to  $250^{\circ}\text{C}$  gave rise to desorption of the PDA deposit from the diamond surfaces.

Figure 4 shows the diffuse reflectance spectrum of the PMDA deposit on the PDA coupled with the diamond surfaces. The peak at  $1857\text{ cm}^{-1}$  ( No.3) is ascribed to the anhydride C=O stretch in the PMDA monomer. The formation of imide rings was confirmed by the appearance of the C=O symmetric stretch at  $1787\text{ cm}^{-1}$  ( No. 4 ) and the C=O asymmetric stretch at  $1736\text{ cm}^{-1}$  ( No.5). It should be noted that the ratio of the absorption peaks of the imide asymmetric stretch to that of the symmetric stretch in the figure reversed the same ratio in the PI(PMDA/PDA) film prepared by spin casting[6]. This indicates that the imidized PDA-PMDA deposit tend to align perpendicular to the diamond surfaces.

## REFERENCES

- 1 M. Iijima, Y. Takahashi, K. Inagawa and A. Itoh, *J. Vac. Soc. Jpn.* 28 (1985) 437.
- 2 J. R. Salem, F. O. Segunda, J. Duran, W. Y. Lee and R. M. Yang, *J. Vac. Sci. Technol.* A4, (1986) 369.
- 3 A. Kubono, H. Higuchi, S. Umemoto and N. Okui, *Thin Solid Films*, 232 (1993) 256.
- 4 M. Kochi, T. Shimomura, K. Kondo, R. Yokota and T. Ando, " Proceedings of Japan Polyimide Conference '98 ", (1999) 113.
- 5 T. Ando, K. Yamamoto, M. Ishii and Y. Sato, " Proceedings of The 4<sup>th</sup> NIRIM International Symposium on Advanced Materials (ISAM '97) ", (1997) 241.
- 6 S. E. Molis, " Polyimides: Materials, Chemistry and Characterization ", (1989, Elsevier ), 659.