

Parylene-C thin films deposited on polymer substrates using a modified chemical vapor condensation method

Hong Tak Kim, Taewook Koo, and Chinho Park[†]

School of Display and Chemical Engineering, Yeungnam University, Gyeongsan 712-749, Korea
(Received 13 August 2009 • accepted 11 November 2009)

Abstract—The properties of parylene-C thin films deposited on polymer substrates using a modified chemical vapor condensation technique were investigated. The configuration of the polymerization chamber was altered from horizontal to vertical and designed with a circular symmetry in the z -direction to improve the deposition rate. The growth rate of the thin films was improved 2-5 times in a vertical configuration compared to a horizontal configuration. Potential factors responsible for such an improvement include the effect of coincidence between the flow direction of the gases and the direction of the convection in the reaction tube due to buoyancy. The synthesized films have a high transparency (>90%) in the visible region, a smooth surface morphology ($R_s < 5.0$ nm), and amorphous phase structures with the presence of some crystalline domains.

Key words: Parylene, Chemical Vapor Condensation, CVC, Vertical Configuration, Polymer Substrate

INTRODUCTION

Parylene and its derivatives are widely used in many applications given its superior properties of high transmittance in the visible and IR regions, smooth surface morphology, high dielectric constant values, low refractive index, chemical stability, and water-resistive properties. As such, parylene films' applications include optical coating for spectral filters, moisture barrier coating, dielectric material for electronic circuits, and chemical resistive layers [1-3].

Parylene films are usually deposited by chemical vapor deposition [3,4], solution-coating deposition [5-7], and plasma-enhanced chemical vapor deposition [8,9]. The growth process of parylene is very clean and simple under these methods, because parylene itself is a self-initiated material that requires neither solvents nor catalysts. The growth mechanism of the film is composed of three steps: sublimation, pyrolysis, and polymerization. In the case of chemical vapor deposition, parylene dimers are sublimated upward and changed into the gaseous state above 80 °C, after which they are dissociated into monomers above 550 °C. Finally, monomers are condensed in a cold substrate and changed into a continuous polymer layer. A detailed illustration of this condensation process can be found in Fig. 1.

In this study, the growth properties of parylene-C films using a modified chemical vapor condensation technique were investigated. This method is similar to typical chemical vapor deposition techniques, except the configurations of the reactor were changed to allow for a more facile condensation process. First, the design of the modified system was changed from a horizontal to a vertical type. This change plays an important role in increasing the growth rate because of the coincidence between the stream direction of vaporized precursor, the flow direction of carrier gas, and the direction of the natural convection in the reactor. Second, the reactor system was designed to have a circular symmetry in the z -direction

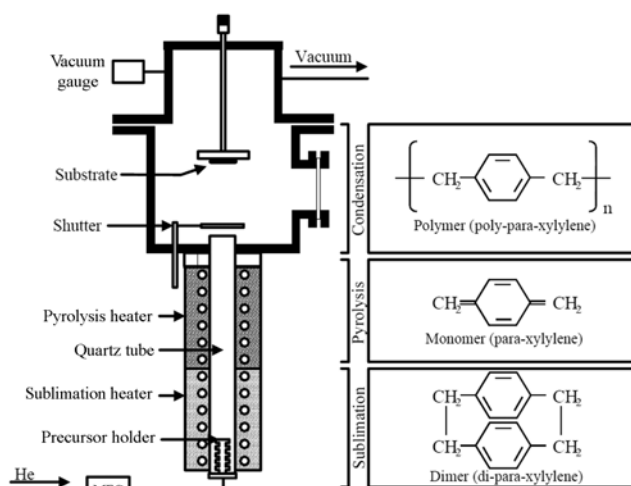


Fig. 1. Schematic diagram of the modified chemical vapor condensation system and polymerization process of parylene material.

capable of synthesizing more uniform films and reducing the effects of the process variables due to configuration simplicity. Using a modified chemical vapor condensation technique, the effect of the process variables such as carrier helium flow rate, sublimation temperature, and pyrolysis temperature on the growth rate was investigated. Film properties were also analyzed, including transmittance, surface roughness, crystallinity, and vibration modes.

EXPERIMENTAL DETAILS

The parylene-C films were deposited on polyethylene naphthalate (PEN) polymer substrates by a modified chemical vapor condensation technique. The condensation apparatus consisted of a polymer condensation chamber and a cylindrical quartz tube with heating

[†]To whom correspondence should be addressed.
E-mail: chpark@ynu.ac.kr

units. The quartz tube was composed of two parts: sublimation zone and pyrolysis zone. The condensation chamber was made of stainless steel with a radius of 30 cm and a height of 50 cm. The substrate holder, bearing a radius of 5.0 cm, could be moved along the z -direction. Reactor pressure was maintained at 1.0 Torr, and helium gas (99.9998%) was used as a carrier gas during the polymerization process of the parylene-C thin films. The pressure of the reactor and the flow rate of He were controlled by a thermocouple gauge and mass flow controller with the substrate temperature maintained at room temperature during the growth of the films. A schematic diagram of the apparatus for deposition of the films is shown in Fig. 1.

The thickness and structural properties of the parylene-C films were measured by a surface profilometer (Kosaka, Surfcomer ET3000) and X-ray diffractometer (PANalytical X'Pert PRO). Optical properties were measured with a UV-VIS-NIR spectrometer (Varian Cary500). The surface roughness of the films was measured by atomic force microscopy, and FT-IR spectrophotometry was used to investigate the vibration energy of bonding of the films.

RESULTS AND DISCUSSIONS

Fig. 2 shows the deposition rate as a function of sublimation temperatures. The deposition rate increased exponentially below the sublimation temperature of 130 °C and began to decrease at higher temperatures. The increase in the growth rate was related to the vapor pressure of the precursor material. The saturated vapor pressure of the precursor (P_p) can be described by:

$$\log P_p = A - B \frac{1000}{T} \quad (1)$$

where, A and B are coefficients determined experimentally and T is the sublimation temperature [10]. This equation directly represents the exponential relationship between vapor pressure and sublimation temperature. The decrease in growth rate above 130 °C can be explained by the collective behavior of precursor molecules and laminar vortices formed in the flow tube. Dushman suggested that the type of gas flow is characterized by $\lambda < 0.01d$ for viscous flow,

$0.01d < \lambda < d$ for transition flow, and $\lambda > d$ for molecular flow [11]. In this experiment, the total pressure was near 1.0 Torr; thus the flow in the reaction chamber was considered to be in a viscous flow region. The important property of a viscous flow is the collective behavior between particles moving along a stream due to internal friction. This inertial force is expressed by ρV^2 , where ρ is the fluid density, and V is the mean velocity of the fluid. When vapor pressure increases, ρ and V both increase, and then the interaction between the walls of the quartz tube and the collective flow of the vaporized molecules also increase. The results of this interaction can cause the flow patterns to develop in the reactor such as laminar eddies, vortices, and re-circulating flow patterns [12]. These phenomena are considered to be the important factors that reduce the growth rate in our study.

Fig. 3 shows deposition rate as a function of pyrolysis temperatures. This tendency is similar to the effect of a sublimation temperature. The concentration of pyrolyzed monomers also increased

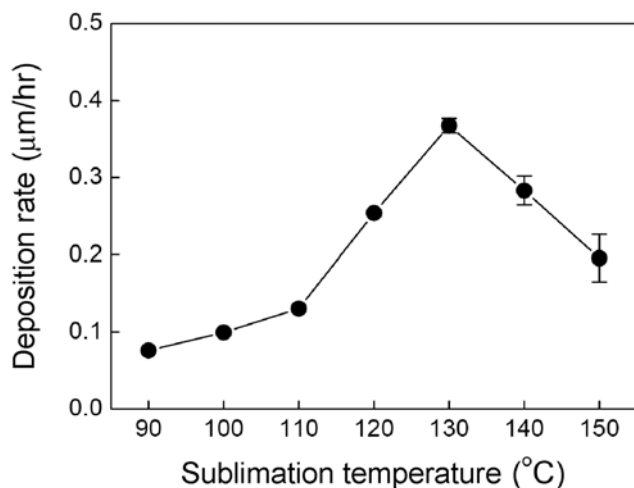


Fig. 2. Deposition rate as a function of precursor sublimation temperature (pyrolysis temperature=660 °C; He flow rate=75 sccm; total pressure=1.0 Torr).

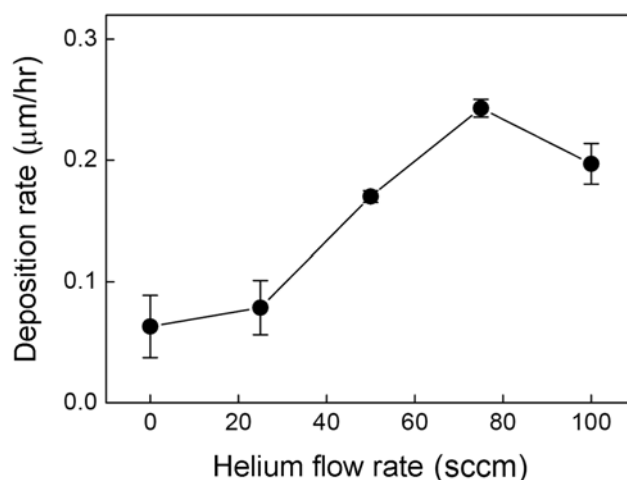


Fig. 3. Deposition rate as a function of pyrolysis temperature (sublimation temperature=120 °C; He flow rate=75 sccm; total pressure=1.0 Torr).

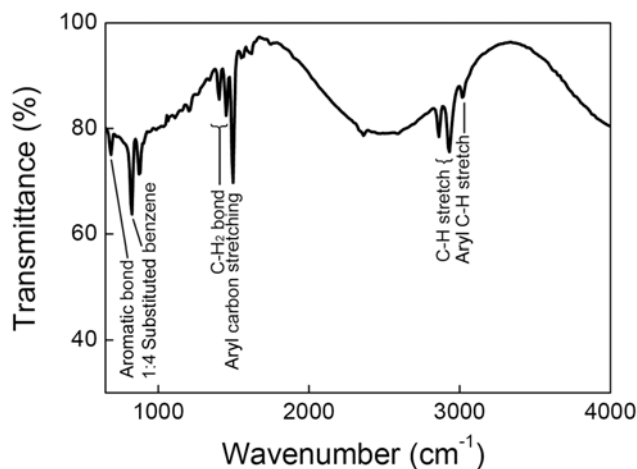


Fig. 4. Deposition rates of parylene-C films at different He flow rates (sublimation temperature=120 °C; pyrolysis temperature=660 °C; total pressure=1.0 Torr).

with respect to the rise in temperature. Generally, dimers from a sublimation zone are partially pyrolyzed under higher flow rates of the helium carrier gas and lower pyrolysis temperature. However, the pyrolysis processes of the dimers can easily take place when pyrolysis temperatures are sufficiently high. This fact is represented in that a higher growth rate can be obtained at higher pyrolysis temperatures under the high flow rate of the helium carrier gas.

Fig. 4 shows the deposition rate as a function of helium flow rates. The deposition rate increased below a flow rate of 75 sccm and then decreased at a higher helium rate. When the helium flow rate increased in the quartz tube, decomposed monomers could be efficiently transported from the quartz tube to the condensation chamber due to increasing internal friction between particles. However, a higher flow rate of helium gas can cause not only reduction in the effective concentration of the precursor materials due to the dilution effect of the helium gas itself, but also cooling effects of insufficiently pre-heated helium flow and an increase in the above-mentioned recirculation flow phenomena. The growth rate was strongly dependent on processing factors related to fluid flows in the quartz tube. The results also bear a similar tendency in that one is an exponential increase in the growth rate up to specific point and the other a decrease in the growth rate through this point. Therefore, these three factors play an important role in transporting precursor materials into the reaction chamber.

The deposition rate of the parylene-C thin films with optimized process conditions in this study (sublimation temperature of 130 °C, pyrolysis temperature of 660 °C and He flow rate of 75 sccm) was found to be 0.37 $\mu\text{m/hr}$, which is 2-5 times larger compared to that obtained from conventional type CVC system [3]. The thickness uniformity of the film represented a relatively low value. At the optimized condition above, the average film thickness and its standard deviation were 367 nm and 9.38 nm, respectively. The improvement of deposition rate was mainly attributed to the modified design of the newly developed reactor, favoring the gas flow, sublimation and condensation processes in the same and positive direction. The reactor is easily scalable, since the optimization conditions for the growth

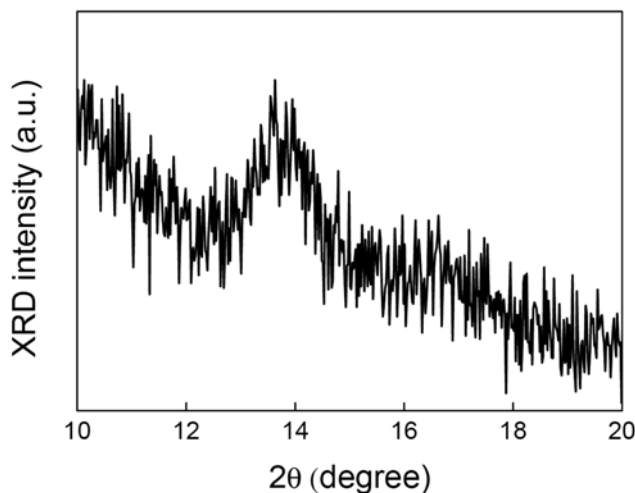


Fig. 5. FT-IR absorption spectrum of parylene-C films (sublimation temperature=120 °C; pyrolysis temperature=660 °C; He flow rate=75 sccm; total pressure=1.0 Torr).

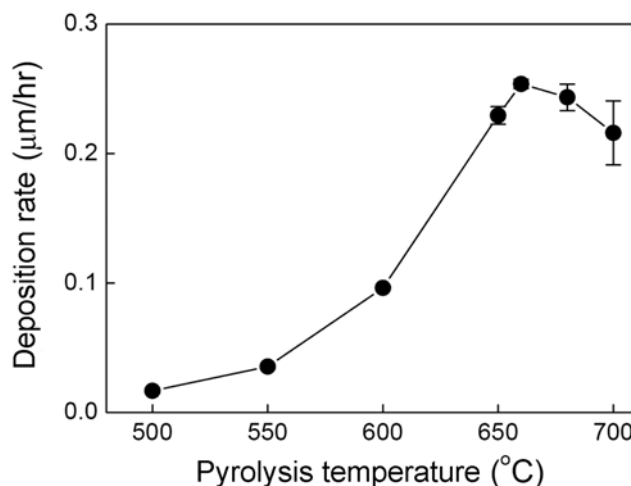


Fig. 6. X-ray diffraction patterns of parylene-C thin films (sublimation temperature=120 °C; pyrolysis temperature=660 °C; He flow rate=75 sccm; total pressure=1.0 Torr).

of films could be found easily through appropriate controls of the factors investigated in this study, when the deposition system needs scale-up.

Fig. 5 shows the FT-IR absorption spectrum of the parylene-C thin films. The FT-IR peaks from 2,800 to 3,100 cm^{-1} are characteristic of carbon-hydrogen stretching bond, and the peaks at 820 and 1,510 cm^{-1} are representative of 1:4 substituted benzene and aryl carbon stretching, respectively [13]. The FT-IR absorption spectrum of the films seldom changes with respect to considered growth conditions, including sublimation, pyrolysis temperature, and flow rate of helium gas. This implies that the process variables do not significantly affect the properties of the films and only play an important role in determining the growth rate of parylene-C films in a modified chemical vapor condensation reactor developed in this study.

Fig. 6 shows the X-ray diffraction pattern of parylene-C thin films. The X-ray diffraction peak of parylene-C appeared at 13.75 degrees with a broad shape [9,14]. This diffraction peak corresponds to the (020) preferred orientation of the monoclinic unit cell that is also referred to alpha phase of parylene-C [2]. From these results, there is some crystallization in the parylene-C film with the crystalline regions randomly dispersed in the amorphous phase. This is an important factor affecting film properties such as corrosion from chemical materials. The crystalline regions in the film are expected to possess more chemically resistive properties attributable to the cohesiveness of polymers derived from the linkages between the crystalline regions and polymer chain. The deposited parylene-C films showed a good transparency in the visible regions and low values of refractive index. For the experimental runs of this study, all the parylene-C films showed a high transmittance above 90% with a film roughness near 5.0 nm.

CONCLUSIONS

The properties of parylene-C thin films using a modified chemical vapor condensation method were investigated. To improve the deposition rate, the configuration of the condensation chamber was

modified from a horizontal type to a vertical type with circular symmetry. As a result, the growth efficiency of the parylene-C thin films increased 2-5 times compared to the conventional type CVD system. The stream of gases and vaporized reaction materials in the reaction tubes were mainly affected by the flow direction of the carrier gases, the convection of the gases due to thermal distribution of the tubes, pressure in reaction chamber, and interactions between the vaporized reaction gases and carrier gases. In this work, the effect of coincidence between the flow direction of the gases and the direction of the convection in the reaction tube due to gas buoyancy possibly played an important role in improving growth efficiency.

The properties of synthesized films represented a high transparency (>90%) in the visible region and bore a smooth surface morphology ($R_s < 5.0$ nm) and amorphous phase structures with some crystalline domains. However, the adhesion properties of the parylene-C films were deficient, particularly with inorganic substrates such as a glass and silicon.

ACKNOWLEDGMENTS

This research was supported by the Yeungnam University grants in 2008, and the researchers involved in this work were partially supported by the 2nd phase of the BK21 Program.

REFERENCES

1. G. P. Crawford, *Flexible flat panel display*, John Wiley & Sons, New York (2005).
2. J. B. Fortin and T.-M. Ju, *Chemical vapor deposition polymerization*, Kluwer Academic Publishers, New York (2004).
3. T. Lee, J. Lee and C. Park, *Korean J. Chem. Eng.*, **19**(4), 722 (2002).
4. W. Gorham, *J. Polym. Sci. Part A-1*, **4**, 3027 (1966).
5. M. Szwarc, *Discussions Faraday Soc.*, **2**, 46 (1947).
6. M. Szwarc, *J. Polym. Sci.*, **6**(3), 319 (1951).
7. M. Szwarc, *J. Chem. Phys.*, **16**(2), 128 (1948).
8. R. d'Agostino, *Plasma deposition, treatment, and etching of polymers*, Academic Press, New York (1990).
9. B. Mitu, S. Bauer-Gogonea, H. Leonhartsberger, M. Lindner, S. Bauer and G. Dinescu, *Surface Coatings Technology*, **174-175**, 124 (2003).
10. U. Göshel and H. Walter, *Langmuir*, **16**, 2887 (2000).
11. B. Chapman, *Glow discharge processes*, John Wiley & Sons, New York, 13-14 (1980).
12. J. Y. Hwang, C. Park, M. Huang and T. Anderson, *J. Cryst. Growth*, **279**, 521 (2005).
13. R. R. A. Callahan, K. G. Pruden, G. B. Raupp and S. P. Beaudoin, *J. Vac. Sci. Technol.*, **21**(4), 1496 (2003).
14. M. Beraa, A. Rivatona, C. Gandonb and J. L. Gardettea, *European Polymer Journal*, **36**, 1765 (2000).