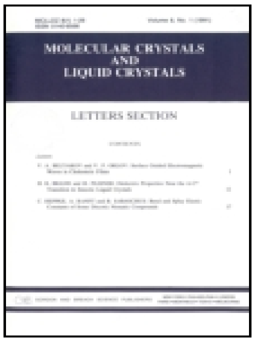

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Effects of Annealing Temperature on Parylene-C Films Formed by Chemical Vapor Condensation Method

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In this study, parylene-C films were deposited using vertically aligned-chemical vapor condensation (CVC) method and effects of post-annealing were investigated. The comparison results for as-deposited and post-annealed samples showed that the structural properties changed gradually with varying annealing temperature, while optical properties and surface morphology of the films seldom changed. The crystallinity, crystallite size, and d-spacing were changed from 60 to 87.2%, from 6.83 to 15.6 nm, and from 6.41 to 6.26 Å, respectively. The value of oxygen transmission rate (OTR) for the films was changed gradually from 3.22 to 1.53 cc/m^2•day after annealing process. However, the values of transmittance and surface roughness were 90% in the visible-near IR region and 5 nm without reference to annealing temperature. Consequently, the crystallization of parylene-C films was one of major effects without the change of optical properties and surface morphology after annealing process, and we believed that the enhancement of crystallinity caused to improve the property of OTR for parylene-C films.

Keywords Annealing temperature; Chemical vapor condensation; Oxygen transmission; Parylene-C; Para-xylylene

Introduction

Poly-para-xylylene based polymers, known as parylene, have been used in many applications given their superior properties of high optical transmittance, anti-moisture, high dielectric constant, and chemical stabilities [1]. These unique properties enable to apply to an optical coating for spectral filters, a moisture barrier coating, a dielectric material for electronic circuits, and chemical resistive layers [1,2–5]. Parylene has various derivatives depending on functional elements such as chloride and fluorine, and typical parylene derivatives are parylene-N (poly-para-xylylene), parylene-C (poly-chloro-para-xylylene), parylene-D (poly-dichloro-para-xylylene), and parylene-HT (tetrafluoro-poly-p-xylylene)

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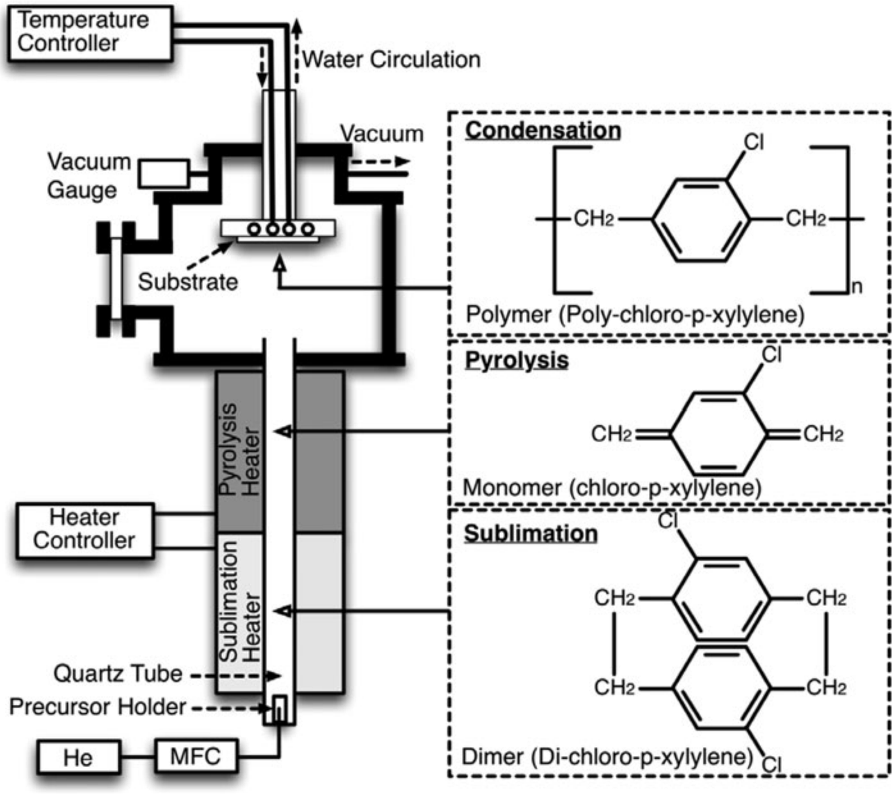

Figure 1. Schematic diagram of experimental setup for parylene-C film depositions using vertically aligned chemical vapor condensation (CVC) method.

[1]. Among them, parylene-C is the most popular due to its combination of barrier properties, cost, and other processing advantages. Parylene-C films have been formed using various deposition techniques [1,6–8] and commonly used technique is a chemical vapor condensation (CVC) method. This growth process for parylene films is very clean and simple technique, because parylene is a self-initiated material, which does not require any solvent and catalyst. The deposition mechanism for CVC method can be classified as sublimation, pyrolysis and polymerization [1,9]. In the case of CVC method, parylene dimers, as a precursor material for parylene film depositions, are sublimated and changed into gaseous phase above 80°C, after which they are dissociated into gaseous monomers above 550°C. These monomers are condensed in a cold substrate and formed continuous polymer films. This condensation process is illustrated in Fig.1.

In this study, parylene-C films were deposited using vertically aligned-CVC method, and the structural properties and oxygen transmission of post-annealed parylene-C films were investigated. This method is similar to typical CVC techniques, except the configurations of the reactor changed from a horizontal to a vertical type. The vertically aligned-CVC reactor is designed to have z-axis symmetry from precursor holder to cold substrate region, as shown in Fig. 1, and it is expected to allow a more facile condensation process 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.

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Table 1. Deposition conditions of parylene-C film using a vertical chemical vapor condensation (CVC) method

Parameter	Unit	Value
Sublimation Temperature	°C	130
Pyrolysis Temperature	°C	660
Flow Rate of Helium	sccm	75
Working Pressure	Torr	1
Base Pressure	Torr	5×10^{-3}
Deposition Time	Hr	2

Experimental Methods

Parylene-C films were deposited on glass substrate (Corning 7059) by vertically aligned-CVC and di-chloro-p-xyxlene (Aldrich, 98%) was used as a precursor for parylene film depositions. The reaction chamber was consisted of a polymer condensation chamber and a cylindrical quartz tube with two heating zones. The condensation chamber was made of stainless-steel with the radius of 30 cm and the height of 50 cm. The substrate holder with the radius of 5 cm could be moved in z-direction and the substrate temperature was kept at a room temperature under film depositions. The schematic diagram of vertically aligned-CVC apparatus for the film depositions is shown in Fig. 1. The base pressure was evacuated down to 5 mTorr and the pressure of reaction chamber was maintained at 1.0 Torr during the film depositions. The pressure was monitored by a thermo-couple gauge (Varian 531). Helium gas (99.9998%) was used as a carrier gas and the flow rate was controlled by a mass flow controller (KOFLOC, 3660). The deposition condition is summarized in Table 1. After parylene-C film depositions, the films were annealed in the range of 25 to 250°C for 30 minutes and rapidly cooled down to room temperature. The crystallinity and roughness of parylene-C films were measured by X-ray diffractometer (PANalytical, X'Pert PRO) and atomic forced spectrometer (DI Instrument, NanoScope IIIa). The thickness of parylene-C films was measured using a profiler-meter (Kosaka Lab., Surfcorder ET3000) and the optical properties of the films were analyzed by UV- Vis- NIR spectrometer (Varian, Cary500). The oxygen transmission rate (OTR) of parylene-C films was measured using an OTR tester (Mocon, OX-TRAN Model 2/21).

Results and Discussion

The X-ray diffraction patterns (XRD) of parylene-C films treated at different temperature conditions are shown in Fig. 2(a). The diffraction peak of parylene-C films was observed at around 14° and this peak was attributed to (020) phase of the monoclinic unit cell [4]. The position of (020) peak was shifted to higher angle with the increase of annealing temperature, as shown in Fig. 2(b), and the shift of this peak was closely related to d-spacing. The reason was thought that the release of residual stress due to a rapid cooling of the films caused the contraction of d-spacing after annealing process. The full width half maximum (FWHM) of (020) peaks decreased with increasing annealing temperature, as shown in Fig. 2(b). This meant that the folded and aligned regions in parylene-C films increased due to thermal motion, as the annealing temperature increased. Usually, crystallization process

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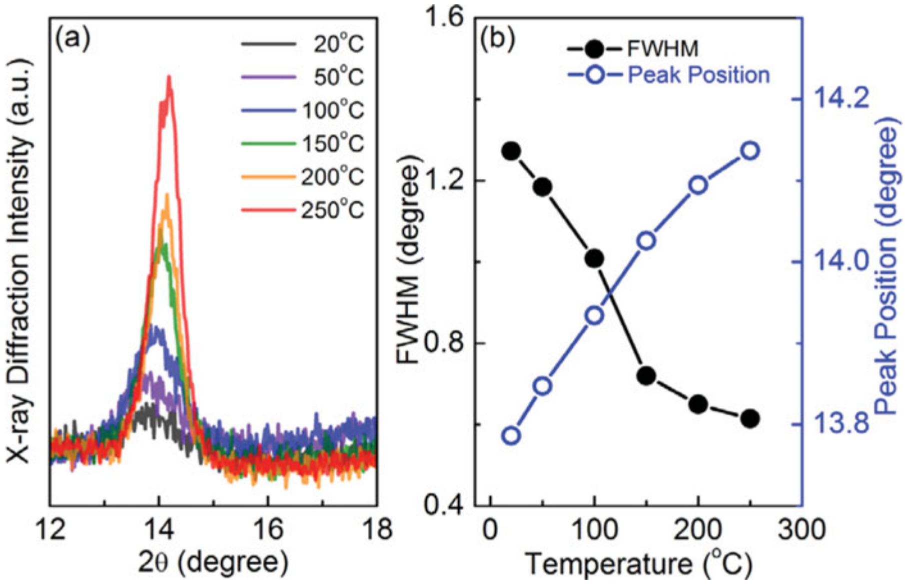

Figure 2. X-ray diffraction (XRD) patterns of parylene-C films at different annealing temperature; (a) XRD curves of the films from 12° to 18°, and (b) FWHM (solid circle) and peak position (open circle) at different annealing temperature.

in polymers is closely related to partial alignment of their molecular chains [10,11]. Long molecular chains are usually formed entangled and irregular shapes in polymers, and also the long chains are partially ordered in some regions. The molecular chains in this region are aligned and folded like crystal materials, and the crystallization of polymers strongly affected their properties. Thus, the rise of annealing temperature activated the thermal motion of polymer chains in parylene-C films and this led to the increase of aligned and folded regions in the films. In addition, the FWHM of parylene-C films was closely related to crystallite size and crystallinity of the films. The crystallite size of the films was evaluated from Scherrer's equation [12,13] and this equation is given by:

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

where, D is the crystallite size, λ is the wavelength of X-ray, B is the FWHM, and θ is the degree of diffraction peak. The crystallite size of parylene-C films increased from 6.83 nm to 15.6 nm, when the temperature increased. Furthermore, the sudden increase of crystallite size also exhibited in the range of 100 and 150 °C and it was conjectured that the activation temperature for the the growth of crystallite size is located in this temperature range, approximately. Consequently, the partial aligned regions in the parylene-C films increased with increasing temperature and it is expected that the increase of the crystallite size strongly affected the crystallinity of the films. The crystallinity of the films can be determined using Hermans method [14], where the crystallinity is defined as the ratio of the crystallized area to whole area in XRD curve. The calculated crystallinity of parylene-C films gradually increased, as shown in Fig. 3(c), and the value reached up to 87.2% with increasing annealing temperature. Fig. 3(b) shows the change of d-spacing of post-annealed parylene-C films and this values are calculated using Bragg's diffraction law ($2dsin\theta = n\lambda$).

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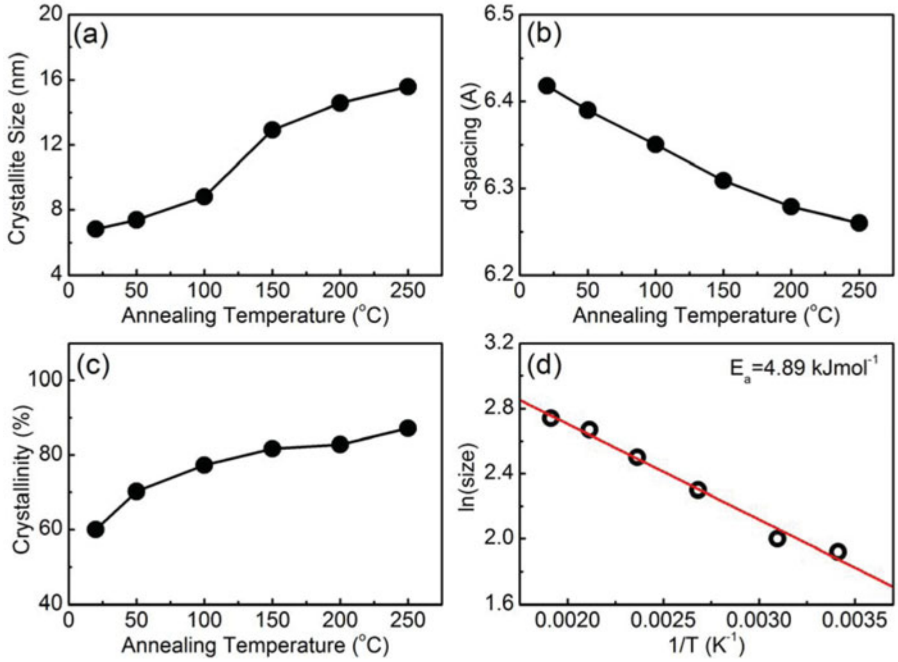

Figure 3. Structural properties of parylene-C films according to annealing temperature; (a) crystallite size, (b) d-spacing, (c) crystallinity of parylene-C films at different annealing temperature, and (d) Arrhenius plot for crystallite growth.

As mentioned above, this was strongly related to the peak position of diffracted peaks and the decrease of d-spacing represented the contraction of inter-planar spacing between two crystallite planes. Fig. 3(d) shows Arrhenius plot of ln(crystallite size) versus the inverse of annealing temperature. The activation energy (E_a) for the increase of crystallite size was

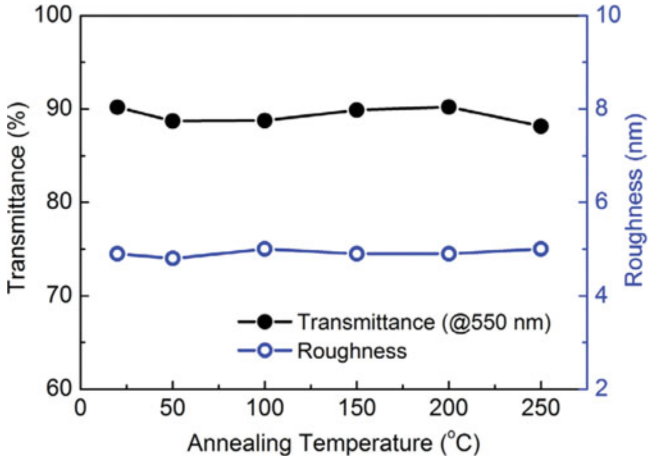

Figure 4. Transmittance (@550 nm) and roughness (Ra) of parylene-C films as a function of annealing temperature.

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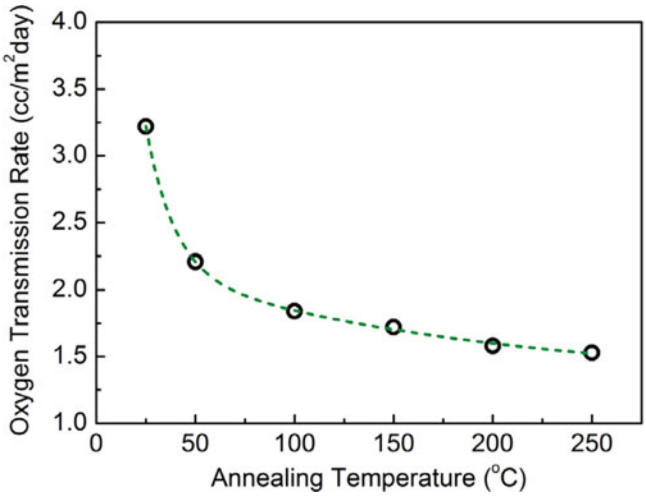

Figure 5. Oxygen transmission rate (OTR) of parylene-C films at different annealing temperature.

calculated from the slope of this plot [15] and the calculated value of E_a was 4.89 kJ/mol approximately.

Fig. 4(a) and 4(b) show the transmittance at the wavelength of 550 nm and roughness of parylene-C films according to annealing temperature. The transmittance at 550 nm was about 90% for all samples and also transmittance spectra of all films in the visible-IR region showed similar values (not shown here). This implied that the main effect of annealing process is not the chemical reaction between the polymer chains but the rearrangement of the polymer chains. Thus, the total transmittance of the parylene-C films seldom changed with varying the annealing condition. The surface roughness of parylene-C films was measured using AFM and the roughness of all samples was about 5 nm. Thus, it was concluded that the annealing process did not affect the optical properties and surface morphology.

Fig. 5 shows the OTR of parylene-C films according to annealing temperature. The OTR of the films exhibited an exponential relationship with the rise of annealing temperature. We believed that the OTR was strongly related to the crystallinity, and the crystallinity enhancement of parylene-C films due to thermal energy made oxygen molecules difficult to penetrate the films. Consequently, the OTR of parylene-C films decreased as the degree

Table 2. Properties of parylene-C films at different annealing temperature

Temperature [°C]	Crystallinity [%]	d-spacing [Å]	Crystallite size [nm]	R_s [nm]	T (@ 550nm) [%]	OTR [cc/m^2·day]
20	60	6.42	6.83	4.9	90.2	3.22
50	70.2	6.39	7.39	4.8	88.7	2.21
100	77.4	6.35	8.82	5.0	88.8	1.84
150	81.7	6.31	12.9	4.9	89.9	1.72
200	82.7	6.28	14.6	4.9	90.2	1.58
250	87.2	6.26	15.6	5.0	88.2	1.53

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of crystallization increased in the films. In addition, the optimum condition of annealing temperature might be more than 150°C to apply an oxygen barrier layer and the reason can be explained in terms of the low OTR value and the saturation value of the crystallinity. The properties of parylene-C films according to annealing temperature are summarized in Table 2.

Conclusion

In this study, parylene-C films were deposited using vertically aligned- CVC method and effects of post-annealing were investigated. The structural properties of parylene-C films such as crystallinity, crystallite size, and d-spacing were dramatically changed after annealing process. After annealing process, the value of crystallinity was varied from 60 to 87.2%, crystallite size was increased from 6.83 to 15.6 nm, and d-spacing was decreased from 6.41 to 6.26 Å. The value of OTR for the films was changed gradually from 3.22 to 1.53 cc/m^2•day after annealing process. However, the transmittance and roughness of the films seldom changed without reference to annealing process and the values were 90% in the visible-near IR region and 5 nm for transmittance and surface roughness, respectively. Consequently, the crystallization of parylene-C films was one of major effects without the change of optical properties and surface morphology after annealing process, and we believed that the enhancement of crystallinity caused to improve the property of OTR for parylene-C films.

Funding

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