

Promotion Effect of Iodine Treatment on Carbonization of Polymer Films for MEMS Chips

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In this paper we describe the promotion effect of iodine treatment on the carbonization of polymers at a low pyrolysis temperature for micro electromechanical systems (MEMS) and micro total analysis systems (μ TAS) applications. A higher pyrolysis temperature contributes to further carbonization. There is, however, a restriction of process temperature when applying pyrolyzed polymers to MEMS chips. We propose a unique technique for synthesizing pyrolyzed polymers to overcome this restriction. Through electrical and structural characterizations, it is confirmed that iodine treatment promotes further carbonization. The resistivity of a parylene C film was $2.0 \Omega\text{cm}$ after 12 h of iodine treatment followed by pyrolysis at 650°C , but only $3.4 \times 10^3 \Omega\text{cm}$ without iodine treatment. Furthermore, we present the potential of the proposed technique for electrochemical electrode applications.

1. Introduction

It is well known the pyrolysis of carbonaceous precursors such as polymer materials provides carbon materials.^(1–3) Regarding high temperature carbonization above 2000°C , many researchers have presented the carbonized polymers to synthesize amorphous and graphitelike carbons.^(4,5)

With regard to precursors, polymers utilized in the field of micro/nano-electromechanical systems (MEMS/NEMS) have the potential for use as carbonaceous precursors. Various polymers such as SU-8, polyimide and parylene C have been used as materials for MEMS/NEMS. Through polymer micromachining and a following pyrolysis, the microstructures of pyrolyzed polymers can be fabricated.⁽⁶⁾ Wang *et al.*, at the University of California at Irvine, reported a post array of pyrolyzed SU-8,

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provided by a multilayer photolithography technique for high-aspect-ratio carbon MEMS structures.⁽⁷⁾ Liger, at California Institute of Technology formed an all-pyrolyzed parylene C bolometer array.⁽⁸⁾

The pyrolysis temperature of polymers on MEMS chips is, however, limited by fabrication conditions as well as the melting point of the other materials used for MEMS. Decreasing the pyrolysis temperature is important for the combination of pyrolyzed polymers with MEMS. We previously reported a local heat-treatment method by multistep pyrolysis with the aim of decreasing the pyrolysis temperature in a furnace.⁽⁹⁾

In this work, we focus on the iodine treatment of precursor polymers for promoting further carbonization at a low temperature. Prior research has shown that the iodine treatment of coal tar pitch leads to high carbon yields due to dehydrogenative polymerization.⁽¹⁰⁻¹²⁾ In this paper, the effect of iodine treatment on the carbonization of polymers are discussed through electrical and structural characterizations. Furthermore, we discuss the application of the proposed technique to an electrochemical electrode. A pyrolyzed polymer treated with iodine is electrochemically characterized through cyclic voltammetry to examine the possibility of the electrode with high sensitivity.

2. Materials and Methods

2.1 Promotion mechanism of carbonization by iodine treatment

We applied the method of iodine treatment to polymer film pyrolysis for MEMS and μ TAS applications. Figure 1 shows a schematic of the mechanism by which iodine treatment promotes polymer pyrolysis. The mechanism, which promotes the

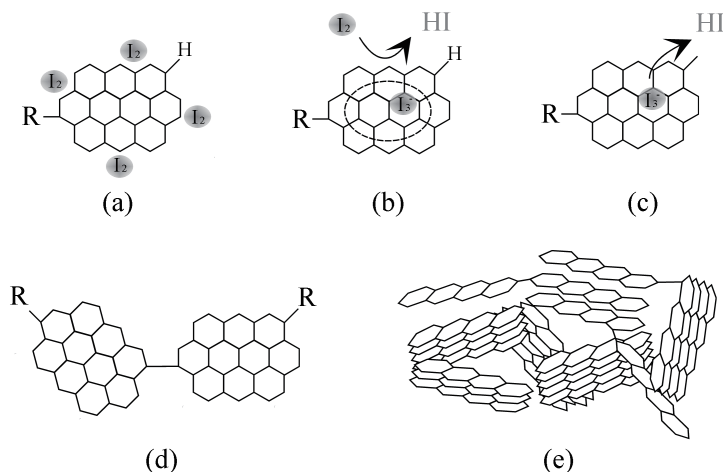


Fig. 1. Mechanism by which iodine treatment promotes polymer pyrolysis. (a) Iodine is adsorbed on the polymer film, (b) iodine accepts electrons from the benzene ring to form charge-transfer complexes, (c) dehydrogenation is accelerated by the decomposition of charge-transfer complexes, (d) polymerization (cross-linking) is promoted, and (e) carbonization is promoted.

carbonization of polymers, is as follows. Polymer films are exposed to iodine vapor in a closed system at the saturated vapor pressure of iodine for a desired period (See Fig. 1(a)). After the adsorption of iodine, it accepts electrons from the benzene ring of the polymer to form charge-transfer complexes. Here, the iodine ion, I_3^- , in the benzene ring is a component of the charge-transfer complexes. At this stage, the dehydrogenation occurs in the form of hydrogen iodide (HI), as shown in Fig. 1(b).

The charge-transfer complexes are heat-treated in an inert environment. The charge-transfer complexes are decomposed, and the dehydrogenation of the polymers in the form of HI is accelerated at low temperatures, as illustrated in Fig. 1(c), and leads to the polymerization or cross-linking, as shown Fig. 1(d). With increasing temperature, the carbonization of the polymers is promoted. As the result, a carbon film derived from the polymer can be obtained at low temperature (See Fig. 1(e)).

It is important to take account of the glass transition temperature, T_g , during the iodine treatment and the dehydrogenation. Poly-monochloroparaxylylene (commercially available as parylene C) is employed as a precursor polymer in this work. T_g for parylene C is from 80 to 90°C, which is relatively low compared with other polymer materials utilized in MEMS such as SU-8 and polyimide.^(13,14)

Parylene-pyrolyzed carbon is a new material for MEMS applications. Prior research has shown that the electrical characterization of parylene C changes with the pyrolysis temperature.⁽¹⁵⁾

2.2 Experimental procedure

The preparation of a parylene C sample is shown in Fig. 2. A pyrolyzed parylene C film was formed on four electrodes. The details of the sample preparation are as follows.

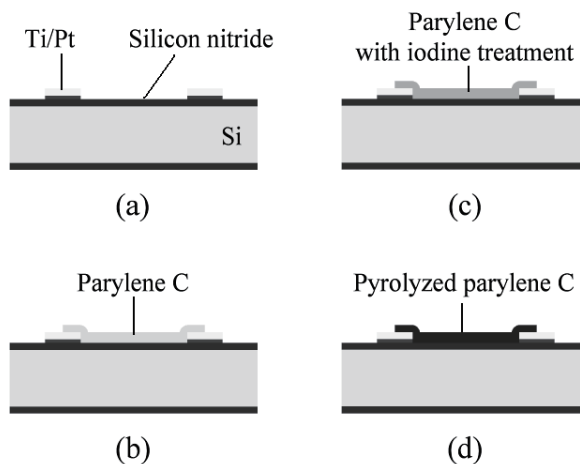


Fig. 2. Fabrication process of parylene C film on Ti/Pt electrodes. (a) Patterning of Ti/Pt by liftoff process on Si_3N_4/Si substrate, (b) parylene C coating and patterning, (c) iodine treatment and (d) pyrolysis at desired temperature.

Ti / Pt electrodes (20 nm / 100 nm) were patterned on a substrate with a silicon nitride insulating layer (200 nm) by the lift-off technique. The dimensions of each electrode were 2.0 mm × 2.0 mm. Next, parylene C was coated with 1.0 μm-thickness using a PDS2010 LABCOTER (SCS Cookson Electronics). A 50 nm-thick aluminum (Al) layer was deposited using a thermal evaporator (VPC-260, ULVAC), and patterned by photolithography and wet etching to form an etching mask of parylene C. Parylene C was then patterned by the oxygen (O₂) plasma etching using reactive ion etching equipment (RIE 10N, Samco, Inc.). The gas flow rate of O₂, the etching power and the etching time were 30 sccm, 150 W, and 3.0 min, respectively. The Al mask was removed using an Al etching solution. The dimensions of the patterned parylene C film were 5.0 mm × 5.0 mm.

The iodine treatment was executed continuously. Figure 3 shows the setup of the closed system used for the iodine treatment, which was executed at 90°C on account of the glass transition temperature of parylene C. The fabricated parylene C chip and 4.0 g of iodine powder (purity: 99.8%, Kanto Chemical Co., Inc.) tube were placed in a vacuum desiccator (Asone Corp.) and heated in a silicone oil bath, as shown in Fig. 3. When the temperature in the desiccator increased, the air was removed using a vacuum pump to generate iodine vapor. The pressure was about 400 Pa in the desiccator, which is the pressure of saturated iodine vapor. A cold trap using liquid nitrogen (N₂) was used to collect excess iodine. Iodine treatment was carried out for 6 or 12 h.

Finally, parylene C was pyrolyzed in a N₂ atmosphere in a quartz furnace (KTF050N-S, Koyo Thermo System Co., Ltd.) at a temperature range from 650 to 1000°C. The ramp-up and cooling rates were 10°C / min and 2.0°C / min, respectively.

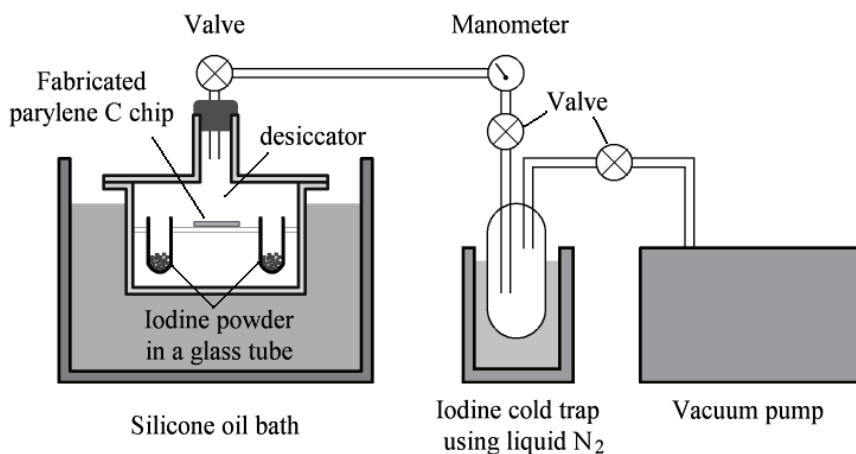


Fig. 3. Schematic diagram of experimental setup for iodine treatment.

2.3 Material characterization

The effect of iodine treatment on the carbonization of parylene C was characterized through electrical measurements and structural studies including Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements.

For electrical measurement, the resistivity of the obtained pyrolyzed parylene C film was evaluated from the sheet resistance and film thickness. The sheet resistance measurement was conducted by the Van der Pauw method. The film thickness was assessed using a surface profilometer (Alpha-Step, KLA-Tencor). The resistivity was determined from the average value of 4 samples.

Raman spectroscopy measurements were executed using a NRS-1000DT (JASCO Co.) with a green laser tuned to 532 nm. The resolution was approximately 4.5 cm^{-1} . The Raman spectra were recorded over the spectral region between 900 and 1800 cm^{-1} , which provides the most information on the microstructure of carbon materials.⁽¹⁶⁾

X-ray photoelectron spectroscopy (XPS) measurements were carried out using an AXIS ULTRA XPS (Shimadzu/Kratos) at C_{1s} peaks.^(17,18)

3 Results and Discussion

Figure 4 shows photographs of the fabricated chip with (a) the prepared parylene C film, (b) the film after iodine treatment and (c) the pyrolyzed film. The size of the chips was $10\text{ mm} \times 10\text{ mm}$. The thickness of parylene C did not appear to change significantly during the iodine treatment, while it decreased by 80% of its original value during the pyrolysis.

3.1 Electrical characterization

Figure 5 shows the electrical resistivity of pyrolyzed parylene C films for various pyrolysis temperatures after iodine treatment for 6 h and without iodine treatment. The resistivity of the parylene C film was $3.4 \times 10^3\ \Omega\text{cm}$ after 650°C pyrolysis, and decreased

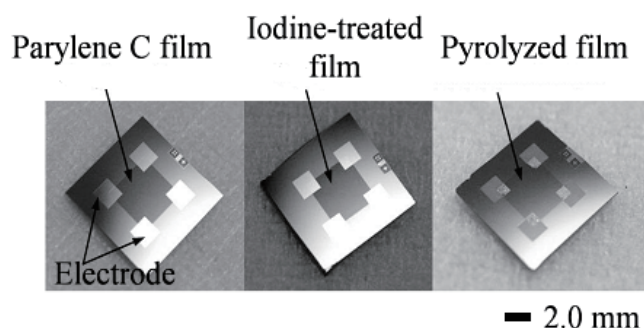


Fig. 4. Photographs of the fabricated parylene C chip with (a) prepared parylene C film, (b) iodine-treated film and (c) pyrolyzed film. The dimensions of the film are $5.0\text{ mm} \times 5.0\text{ mm}$.

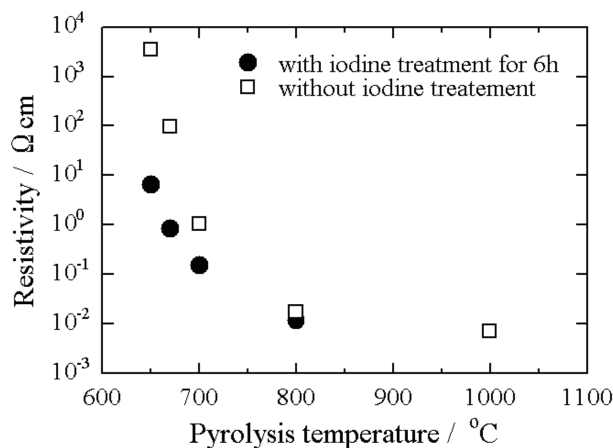


Fig. 5. Resistivity of pyrolyzed parylene C film for various pyrolysis temperatures with iodine treatment for 6 hours and without iodine treatment.

to $7.0 \times 10^{-3} \Omega\text{cm}$ after 1000°C pyrolysis. This means that we can obtain a wide range of resistivities by changing the pyrolysis temperature.

Table 1 shows the average and standard deviation of the resistivity of pyrolyzed parylene C after iodine treatment for 6 h. The resistivity after iodine treatment for 6.0 h at 650°C pyrolysis was $6.6 \Omega\text{cm}$. $\sigma_{\text{w/o}}$ and σ_{6h} are the resistivities of the pyrolyzed film without and with iodine treatment, respectively. The resistivity ratio of $\sigma_{\text{w/o}}$ to σ_{6h} ($\sigma_{\text{w/o}} / \sigma_{\text{6h}}$) after 650°C pyrolysis was 5.15×10^2 and decreased with increasing pyrolysis temperature, as shown in Table 1. This result suggests that iodine treatment is more effective at lower pyrolysis temperatures.

The dependence of iodine treatment time on the resistivity was also evaluated. The iodine treatment time was 6 or 12 h. The resistivity of parylene C pyrolyzed at 650°C after 6 h iodine treatment was $6.6 \Omega\text{cm}$, whereas the resistivity of pyrolyzed film without iodine treatment was $3.4 \times 10^3 \Omega\text{cm}$. The resistivity of the film pyrolyzed at 650°C after iodine treatment for 12 h was $2.0 \Omega\text{cm}$. This value is comparable to that of parylene C pyrolyzed at 700°C without iodine treatment.

3.2 Structural characterization

Figures 6 and 7 show the obtained Raman spectra of the parylene C film pyrolyzed at temperatures of 650 and 700°C , respectively. The two main features in the Raman spectrum are the D and G peaks at around 1360 and 1600 cm^{-1} , respectively. The G band corresponds to the symmetric E_{2g} vibrational mode in graphitelike materials, while the D band is activated in the first-order scattering process of sp^2 carbons by the existence of substitutional heteroatoms, vacancies, or other defects, all of which are consistent with disordered graphitic bonding within carbons.⁽¹⁶⁾

Table 1
Resistivity of pyrolyzed parylene C after iodine treatment for 6 h.

Pyrolysis temp. / °C	Average resistivity, $\rho_{6h}/\Omega\text{cm}$	Standard deviation	$\rho_{w/o}/\rho_{6h}$
650	6.64×10^0	2.56×10^{-1}	5.15×10^2
670	8.49×10^{-1}	1.23×10^{-2}	1.13×10^2
700	1.50×10^{-1}	3.27×10^{-3}	7.00×10^0
800	1.16×10^{-2}	6.54×10^{-4}	1.50×10^0

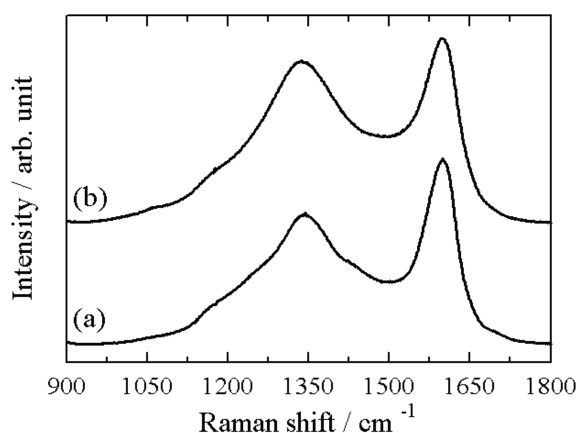


Fig. 6. Raman spectra of parylene C film pyrolyzed at 650°C. (a) Without iodine treatment and (b) with iodine treatment for 6 h.

The intensity ratios of the G/D band for 650°C pyrolysis with and without iodine treatment were 1.46 and 1.14, respectively. This result indicates that pyrolyzed parylene C after iodine treatment includes more disordered or amorphous carbons than untreated samples. The Raman spectra of polymers for different pyrolysis temperatures have been presented.^(19,20) The G/D ratios of the pyrolyzed photoresist decreased with increasing pyrolysis temperature, and the amount of disordered or amorphous carbons increased. From this result, we can conclude that iodine treatment promoted greater the carbonization of the parylene C film at a given pyrolysis temperature.

The G/D ratios for 700°C pyrolysis with and without iodine treatment were 1.28 and 1.10, respectively. The difference in the G/D ratio was smaller than for 650°C pyrolysis. These results correspond to the experimental results of the resistivity evaluation. It is likely that iodine treatment is more effective in promoting carbonization at lower pyrolysis temperatures.

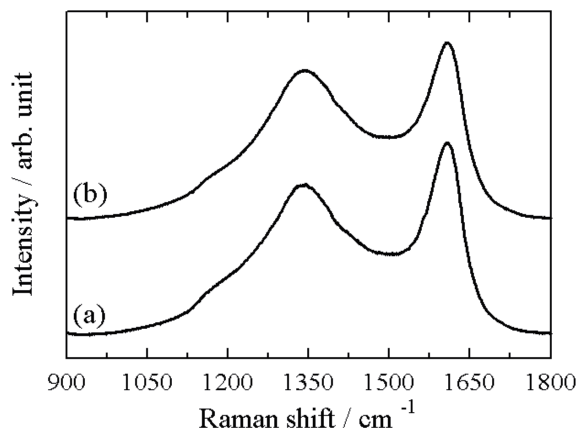


Fig. 7. Raman spectra of parylene C film pyrolyzed at 700°C. (a) Without iodine treatment and (b) with iodine treatment for 6 h.

Figure 8 shows the obtained XPS spectra for C_{1s} peaks. The binding energies at the peak for 650 and 800°C pyrolysis without iodine treatment were 280.8 and 281.6 eV, respectively. Peaks were shifted to the high-binding-energy region, and the intensities were reduced with increasing pyrolysis temperature. This result suggests that surface chemical structures were changed as the pyrolysis temperature increased. The binding energy at the peak for 650°C pyrolysis with 6 h iodine treatment was 281.7 eV. This result suggests that pyrolyzed parylene C includes different chemical structures of carbons after the iodine treatment.

3.3 Applications

One of the most attractive applications of pyrolyzed polymers is as a sensing electrode for electrochemical detection.⁽²¹⁾ Pyrolyzed parylene C with iodine treatment could be applied as an electrochemical electrode for μ TAS applications. In this study, pyrolyzed parylene C film was electrochemically characterized by cyclic voltammetry using an electrochemical analyzer (612A, BAS Inc.). 1mM K₃Fe(CN)₆ and 1M KNO₃ were used as an electrolyte and supporting electrolyte solution, respectively. The scan rate was 100 mV/s. Pt and Ag/AgCl were used as a counter and reference electrode, respectively.

Figure 9 shows the obtained cyclic voltammograms of pyrolyzed parylene C after 12 h iodine treatment and without iodine treatment. Pyrolysis was carried out at 670 °C. The oxidation and reduction peak separation, ΔE_p , of the electrode with iodine treatment was 225 mV, while that of the electrode without iodine treatment was 422 mV. This result indicated that pyrolyzed parylene C with iodine treatment is more sensitive to the electron transfers in the redox of the electrolyte at the electrode surface. It has been reported that a higher pyrolysis temperature could result in highly sensitive

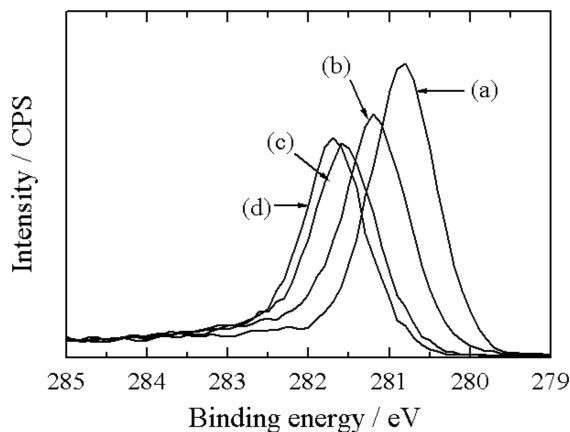


Fig. 8. C1s XPS spectra of pyrolyzed parylene C. Pyrolysis temperatures are (a) 650°C, (b) 700°C (c) 800°C and (d) 650°C with iodine treatment.

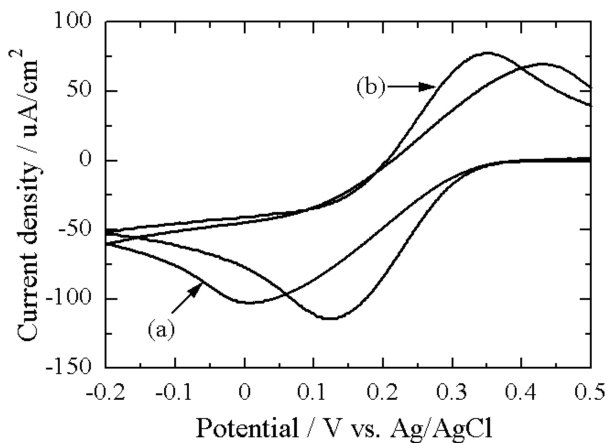


Fig. 9. Cyclic voltammograms of pyrolyzed parylene C film prepared at 670°C. (a) without iodine treatment and (b) with iodine treatment for 12 h.

electrochemical electrode, because the resistivity of pyrolyzed polymers decreases with increasing process temperature.^(22,23) As mentioned above, iodine treatment of the parylene C film contributes to a decrease in resistivity. It appears that the decrease in the resistivity results in the improvement of the electrochemical characteristics. The resistivity decrease in the pyrolyzed polymer films is due to the improvement of their carrier concentration and carrier mobility.⁽²⁴⁾ The electron transfers of the

electrochemical reaction between the pyrolyzed polymer electrode and the electrolyte became smooth; thus, the electrochemical characteristics of the pyrolyzed polymer were improved.

The developed technology can be used to provide a sensitive electrode of pyrolyzed polymer for electrochemical applications at a low process temperature.

4. Conclusion

In this paper, we presented the promotion effect of iodine treatment on the carbonization of parylene C at a low pyrolysis temperature. The prepared samples were characterized through electrical measurement, Raman spectroscopy and XPS measurements. The obtained results indicated that iodine treatment promotes the carbonization of polymers, particularly for pyrolysis at less than 700°C. The combination of sequential iodine treatment and pyrolysis can provide a carbon material with superior electrical characteristics at a lower carbonization temperature. The resistivity of pyrolyzed parylene C after iodine treatment for 12 h was 2.0 Ωcm. The use of iodine treatment to promote the carbonization of polymers has high potential for MEMS and μTAS applications.

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