Hydrophilic Patterning of Polymer Surfaces
Using a Scanning Microplasma Jet Source

Takuya Ideno* and Takanori Ichiki**

*Department of Electrical and Electronics Engineering, Toyo University,
2100 Kujirai, Kawagoe 350-8585, Japan
**Institute of Engineering Innovation, School of Engineering, The University of Tokyo,
2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan
***PRESTO, Japan Science and Technology Corporation, Kawaguchi Center Building,
1-8, Honcho 4-chome, Kawaguchi, Saitama 332-0012, Japan
ichiki@sogo.t.u-tokyo.ac.jp

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1. Introduction
Since the mid-1990s, intensive study has been carried out on microplasma sources confined to dimensions typically < 50 μm under high pressures, motivated by the practical applications of plasma display panel (PDP) and UV light sources [1-3]. Moreover, in recent years, several researchers have applied microplasmas to other fields like materials processing [4-9]. Thus microplasmas are now expected to be a promising basic technology that might lead to new practical applications. Authors’ group have developed on-chip microplasma jet sources for the portable analysis system [10], and have demonstrated localized and ultrahigh-rate silicon wafer etching using Ar/SF₆ microplasma jets [11]. Based on these studies, we recently developed a prototype of the scanning microplasma jet apparatus which is composed of an on-chip microplasma jet source and a numerically controlled scanner [12]. In this article, we have investigated fundamental characteristics of localized hydrophilic patterning on polymer surfaces using a scanning microplasma jet source. Hydrophilic patterning on polymer surfaces is attractive for biological applications. Furthermore, we discuss on effects of operation parameters on the improvement of minimum pattern dimensions and hydrophilicity.

2. Experimental
Figure 1 shows a schematic of the apparatus employed in this study. The compact plasma source is comprised with a 250-μm-thick copper antenna deposited on an alumina plate and a silica discharge tube with 0.9 mm inner diameter. A 100-MHz VHF power supplied to the plasma source was kept constant at 50 W. A fine argon plasma jet with the plasma density of 10¹⁴ cm⁻³ was emitted through the pinched end of the discharge tube which has an inner diameter of 0.1 mm. Another small cylindrical tube was connected to the end of the discharge tube for the introduction and subsequent dissociation of oxygen. The oxygen radical jet was emitted perpendicularly from the 0.1-mm-diameter hole opened at the bottom end of the oxygen introduction tube. The radical jet was horizontally scanned over the polycarbonate plate set on the grounded stage by numerically controlled stepping motors according to the CAD data. The distance between the end of radical source and the sample surface was adjusted at 3 mm. Contact angle profiles of treated polycar-

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Fig. 1. A schematic of the plasma treatment system using a scanning microplasma jet source.
bonate samples were evaluated from the shape of pure water droplets observed using a microscope with the long focal length.

3. Results and Discussion

Figure 2 shows a typical profile of the contact angle against pure water of the polycarbonate plate after the surface treatment in the line scan mode. The horizontal axis of the figure shows the distance measured from the center of the patterned line. The polycarbonate surface without any plasma treatment shows the water contact angle of 75 degree. It is found that the scanned area changed into hydrophilic surface. Moreover, it is noted that the contact angle profile has a core peak and a broad peak in its peripheral. For the characterization of such profiles, widths of sharp and broad peaks were defined as \( L_1 \) and \( L_2 \), respectively, as denoted in the figure. In addition, minimal contact angles of \( \theta_1 \) and \( \theta_2 \) were defined in the similar manner.

![Fig. 2. A typical profile of the water contact angle of the polycarbonate surface after the oxygen radical treatment using a scanning microplasma source. Ar and O\(_2\) flow rates were 180ccm and 20ccm, respectively. Scan speed of the microplasma source was 0.8 mm/s.](image)

First, effects of the oxygen flow rate on the hydrophilic line patterning were investigated. The argon gas flow rate and the scan speed were constant at 180 ccm and 5 mm/s, respectively. Line widths of \( L_1 \) and \( L_2 \) and the minimal contact angles of \( \theta_1 \) and \( \theta_2 \) were plotted against the oxygen flow rate in Fig. 3. At lower oxygen flow rates, hydrophilic profile did not show double peak structures. The gradual decrease in line width was observed with the increase of oxygen flow rate, and at oxygen flow rate of 40 ccm, rapid drop was observed in line width and contact angle. Further increase in oxygen flow rate results in the double peak profile. Since the change in oxygen flow rate directly causes the change of the oxygen radical density and flow speed of radical jet, its influence on the hydrophilic profile is rather large. Figure 4 shows the typical hydrophilic line profile at low oxygen flow rate. Although the minimum contact angle still remains at 40 degree, the line width is as fine as 0.4 mm. The experimental conditions were argon flow rate: 180 ccm, oxygen flow rate: 40 ccm and scan speed: 5 mm/s.

![Fig. 3. Effects of the oxygen flow rate on line widths of \( L_1 \) and \( L_2 \), and the minimal contact angles of \( \theta_1 \) and \( \theta_2 \).](image)

![Fig. 4. A typical profile of the narrow hydrophilic line patterned on the polycarbonate surface. Experimental conditions are argon flow rate: 180 ccm, oxygen flow rates: 40 ccm, and scan speed: 5 mm/s.](image)

Subsequently, effects of the scan speed on the hydrophilic line patterning were investigated. Here, experiments were carried out for the oxygen flow rates of 20 ccm (a) and 40 ccm (b), for comparison. Characteristic widths of \( L_1 \) and \( L_2 \) and the minimal contact angles of \( \theta_1 \) and \( \theta_2 \) were plotted against the scan speed in Fig. 5. The contact angle tends to show small value at low scan speed for both oxygen flow conditions, since the treatment time is inversely proportional to the scan speed. In addition, line widths of \( L_1 \) and \( L_2 \) tend to increase with the decrease of the scan speed, while \( L_1 \) hardly changed in the case of...
the oxygen flow rate of 40 ccm.

One might ask whether such effects of the scan speed on hydrophilic patterning are caused by the change in gas flow near the sample surface or the change in the treatment time. Therefore, additional experiment of repeated line scan was carried out at the fixed scan speed at 5 mm/s for oxygen flow rate of 40 ccm, as shown in Fig. 6. Gradual changes with the increase of treatment time and consequent saturation of line widths and contact angles are in good accordance with the results of Fig. 5. Hence, effects of the scan speed can be ascribed mainly to the change in the treatment time.

![Image](image.png)

Fig. 5. Line widths of L1 and L2, and the minimal contact angles θ1 and θ2 plotted against the scan speed. The argon flow rate was constant at 180 ccm, while the oxygen flow rate was 20 ccm and 40 ccm for (a) and (b), respectively.

![Image](image.png)

Fig. 6. Repetition time effects on line widths of L1 and L2, and the minimal contact angles of θ1 and θ2. Experimental conditions are argon flow rate: 180 ccm, oxygen flow rates: 40 ccm, and scan speed: 5 mm/s.

sample surface by the laminar gas flow, while the broad profile observed in its peripheral region may be due to the excess oxygen radicals which were not consumed on the polymer surface and diffused from the high-density region. For the similar reason, excess treatment time, namely too slow scan speed, should result in undesirable broad patterns. At present it is difficult to achieve both smallest line width and the smallest contact angle at the same time. In the future study, intensive control of the radical densities at both core and peripheral regions should be attempted for achieving thinner line patterns.

4. Conclusions

Hydrophilic patterning of polycarbonate surface has been studied using a scanning microplasma jet source. It is found that the water contact angle profile of the hydrophilic line was strongly dependent on the oxygen flow rate and the scan speed. As a result of the preliminary optimization of the operation conditions, patterning of a hydrophilic thin line with 0.4 mm width and the contact angle of 40 degree has been demonstrated.

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