Generation of a capacitively coupled microplasma and its application to the inner-wall modification of a poly(ethylene terephthalate) capillary

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A parallel-plate capacitively coupled microplasma excited by a conventional operating frequency of 13.56 MHz has been generated both in a quartz tube and in a capillary, whose cross section is 65–500 μm × 500–5000 μm, on a 20 mm × 20 mm quartz chip. To attain a plasma ignition at a low rf power without reflection, a π-type matching circuit was miniaturized and designed to satisfy the resonance condition with the excitation frequency, so that an atmospheric He discharge was obtained at an incident power of 1–3 W. The atomic excitation temperature in the atmospheric discharge was evaluated to be about 1900 K in terms of the atomic emission spectrum. Low-power (2–3 W) glow discharge of pure Ar was also attained at the pressure \( p \) given by \( (pd)_{\text{min}} = 0.5–0.8 \text{Torr cm} \), where \( d \) is a discharge gap. The microplasma was applied to the inner-wall modification of a poly(ethylene terephthalate) (PET) capillary to demonstrate the electro-osmosis flow (EOF) control on a microcapillary electrophoresis (CE) chip. We found that the mobility of the EOF (\( \mu_{\text{EOF}} \)) of the PET capillary treated by the downstream O\(_2\) plasma was \( 5.1 \times 10^{-4} \text{cm}^2/\text{N s} \), which is about three times larger than that of the untreated PET capillary. © 2002 American Vacuum Society. [DOI: 10.1116/1.1417541]

I. INTRODUCTION

In contrast with the development of the large-area (>\( \varnothing \)300 mm) and high-power (>1 kW) plasma sources, a small-scale and low-power plasma, i.e., microplasma, was studied to commercialize a plasma display panel and to create an on-chip plasma device as part of a miniaturized total (chemical) analysis system (\( \mu \)-TAS).\(^1\) For example, dc glow discharge,\(^2\) a 2.45 GHz microwave-induced plasma source based on a microstrip line technology,\(^3\) and an inductively coupled plasma source with a miniaturized spiral coil\(^4\) have been proposed to integrate a molecular emission detector of a gas chromatography on a chip. The typical dimensions of these plasma sources are from a few hundred \( \mu \text{m}^2 \) to about 10 mm.\(^5\) According to Paschen’s law, the operating pressure shifts toward high pressure with a reduced discharge space so that the mean free path of electrons is sufficiently smaller than the characteristic length of a discharge space. In fact, the plasma sources in Refs. 2 and 3 are able to operate at atmospheric pressure, thereby leading to the size reduction of the plasma sources because a vacuum pump is not used. On the other hand, the microplasma is applicable to the future microfabrication technologies of high-fidelity electronic devices and novel functional materials. For example, a scanning micro/nanonozzle plasma jet using the microplasma source was developed to induce the localized etching or deposition of materials, such as silicon, SiO\(_2\), and polymers.\(^5\) Moreover, a thin-film coating on the inner wall of a narrow tube (8–30 mm inner diameter, \( \geq 480 \text{ mm length} \)) was investigated using a coaxial magnetron pulsed or electron cyclotron resonance plasma.\(^6\)

In this article, a parallel-plate capacitively coupled microplasma (CCMP) source excited by a conventional operating frequency of 13.56 MHz is proposed. The CCMPs for various kinds of gases, such as He, Ar, and O\(_2\), are generated both in a quartz tube and in a capillary on the 20 mm × 20 mm quartz chips. An atmospheric discharge of He and Ar gas is attained, and the effect of O\(_2\) concentration on the maintenance of the on-chip atmospheric He+O\(_2\) plasma is also investigated. The application of the microplasma to the inner-wall modification of a capillary on a poly(ethylene terephthalate) (PET) chip is discussed to improve the mobility of the electro-osmosis flow (EOF) on a microcapillary electrophoresis (CE) chip.

II. EXPERIMENTAL APPARATUS

Figure 1 shows the schematic diagrams of the CCMP sources in a quartz tube (a) and in a capillary on a quartz chip (b). The quartz tube has an inner radius of 1 or 2 mm and an outer radius of 3 mm. The parallel-plate copper electrodes of 2 mm × 20 mm are held fast to the tube with adhesive tape so that a gas channel is sandwiched between two electrodes. Gas is introduced to a gas channel through a mass flow controller and is exhausted to a pump in low-pressure operation or to the air in atmospheric-pressure operation. On the other hand, the depth \( D \) and width \( W \) of a capillary on a chip are 65–500 and 500–5000 \( \mu \text{m} \), respectively. A chip with \( D \geq 150 \mu \text{m} \) is made of two quartz glass plates (20...
and a spacing glass plate (thickness of 150 or 500 μm) that are glued together. For D < 150 μm, a shallow groove is etched on a quartz glass plate using wet etching with hydrogen fluoride solution. The etched plate and a flat cover-glass plate are glued together to obtain a chip. The parallel-plate electrodes of 5 mm × 5 mm Cu are externally attached to a chip so that the capillary is sandwiched between the two electrodes. One electrode is connected to a 13.56 MHz rf generator via a matching circuit; the other is grounded. It was noted that plasma did not ignite without the grounded electrode. As shown in Fig. 1, the CCMP sources have a simple constitution. To generate plasma efficiently at a low incident power, a matching circuit was miniaturized and suitably designed to satisfy the resonance condition with the excitation frequency. Figure 2 shows the top view of a miniaturized π-type matching circuit (box size: 120 × 80 × 50 mm) with a microplasma chip. The capacitance C of the vacuum capacitors can be varied by sliding the upper electrode up and down. An important procedure is to determine the optimum value of inductance L in matching it with a small impedance load, such as microplasmas. Furthermore, the matching condition was seriously affected by parasitic capacitance between circuit elements in a matching box. A view port was opened on an electrode to extract the optical emission light. Emitted light was picked up by an optical fiber placed on top of the view port at intervals of 20 mm and observed using an optical emission spectrometer (PMA-11; Hamamatsu Photonics). The peak-to-peak voltage $V_{pp}$ between the electrodes was also measured using a digital storage oscilloscope.

III. RESULTS AND DISCUSSION

A. He microplasma

He plasma was ignited in various sizes of capillaries on a quartz chip in the range from subatmospheric to atmospheric pressure. Figure 3 shows the incident-power dependence of the emission intensity of a He I 667.8 nm line for various plasma volumes at atmospheric pressure. Cross sections ($D \times W$) of a capillary are 150 μm × 500 μm, 65 μm × 2800 μm, 150 μm × 5000 μm, and 500 μm × 5000 μm for the plasma volume of 0.38, 0.91, 3.75, and 12.5 μL, respectively. Plasma ignited at a low incident power of 1–3 W. Emission intensities monotonically increase with increasing incident power. Furthermore, emission intensity shows the tendency to increase with decreasing plasma volume, because the power density dissipated into a plasma increases with decreasing plasma volume at the same incident power. The $V_{pp}$ varied from 43 to 100 V with increasing incident power from 3 to 10 W. The $V_{pp}$ value is relatively small but close enough to the ionization energy of the He atom. The plasma generation under such a low voltage may be attributed to the effective acceleration mechanism of electrons, such as a wave riding effect due to the oscillating sheath, in a capacitively coupled rf discharge. In addition, the strongest peak line of He I of 706.5 nm was observed. This emission line corresponds to a $2^3S \rightarrow 2^3P$ transition. The $2^3P$ state finally transits to a metastable $2^3S$ state with a long lifetime of $6 \times 10^5$ s. Therefore, it seems that the metastable $2^3S$ state play an important role in sustaining the He microplasma. Assuming that the local equilibrium is satisfied in the microplasma, the He atomic excitation temperature $T_{exc}$ is estimated using the Boltzmann plot with the emission intensity distribution of He I lines (388.9, 471.3, 492.2, 501.6, 587.6, 667.8, 706.5, and 728.1 nm). Figure 4 shows the plasma volume dependencies of He excitation temperature at

![Figure 1](image1.png) Schematic diagrams of the experimental setup.

![Figure 2](image2.png) Top view of a miniaturized matching circuit. A microplasma chip (20 mm × 20 mm) is shown as a scale reference.
60 Torr and atmospheric pressure. The incident power is 5 W. At 60 Torr, $T_{\text{exc}}$ increases with decreasing plasma volume. The reason seems to be that electron temperature increases with decreasing plasma volume to maintain a discharge against the electron loss to the capillary wall. On the other hand, no obvious change in $T_{\text{exc}}$ can be observed with decreasing plasma volume at atmospheric pressure because of the energy loss due to frequent electron–neutral collisions. The $T_{\text{exc}}$'s were 1900–2300 and 1900 K at 60 Torr and atmospheric pressure, respectively. The result implies that a low-electronic-temperature plasma is generated.

B. Ar microplasma

Figure 5 shows the dependence of Ar plasma initiation power on the gas pressure for different cross sections of a gas channel. The pressure at which the plasma initiation power is minimum shifted toward high pressure with decreasing discharge gap $D$ between the two electrodes. In other words, Ar plasma ignited at an incident power of 2–3 W under the condition of $(pd)_{\text{min}} = 0.5–0.8$ Torr cm, where $p$ and $d$ are the gas pressure in a gas channel and the discharge gap. It is noteworthy that an atmospheric Ar discharge was attained at an incident power of 9 W in the capillary with $D$ of 65 $\mu$m. According to Townsend’s sparking voltage and breakdown relation:

$$ (pd)_{\text{min}} = \frac{2.718}{A} \ln \left( 1 + \frac{1}{\gamma} \right), $$

where $A = 13.6 \text{ cm}^{-1} \text{Torr}^{-1}$ for Ar gas, and the secondary-electron emission coefficient $\gamma$ by the ion bombardment onto a quartz plate is estimated to be 0.02–0.09.

C. O$_2$ microplasma

O$_2$ microplasma is available for oxidation or coating of various materials on the inner wall of a capillary. O$_2$ plasma has ignited both in a quartz tube and in a capillary on a quartz chip. The O$_2$ gas is 99.99% pure. Figure 6(a) shows the incident-power dependence of the emission intensity of O$_1$ 844.6 nm. The operating pressures are 20 and 45 Torr for a $\phi$1 mm quartz tube and a capillary with 500 $\mu$m $\times$ 5000 $\mu$m cross section, respectively. Plasma ignited at 3
and 5 W for a φ 1 mm quartz tube and a capillary (500 μm × 5000 μm) on a chip, respectively. The ignition power of O2 gas was somewhat higher than that of He and Ar gases. The reason seems to be that oxygen is an electronegative gas. Similar to Ar microplasma, a high incident power is required for plasma initiation if the condition of \((pd)_{\text{min}} = 0.5 - 2.5 \text{ Torr cm}\) is not satisfied. Emission intensities increased with increasing incident power. Figure 6(b) show the gas flow rate dependence of the emission intensity of O I 844.6 nm at an incident power of 5 W. Emission intensity decreases with increasing gas flow rate, because the residence time of the excited O atoms decreases.

It was difficult to attain an atmospheric O2 (100%) discharge at a low incident power (≤12 W). Therefore, to obtain oxygen radicals at a low power and atmospheric pressure, He dilution gas of O2 was used for O2 plasma ignition. Figure 7 shows the O2 concentration dependence of the emission intensities of He I 667.8 nm and O I 615.8 nm for the on-chip atmospheric He + O2 plasma, whose plasma volumes were 3.75 and 12.5 μL, respectively. Incident power and total gas flow rate were 7 W and 210 sccm, respectively. The emission intensity decreased with increasing O2 concentration and plasma extinguished at an O2 concentration above 15%. In addition, we can see that the reduction of plasma volume leads to the rapid decrease of emission intensity. This is because the number of electrons decreases with increasing O2 concentration due to electron attachment to O atoms and O2 molecules.

**D. Inner-wall modification of a PET capillary**

To demonstrate the EOF control on the micro CE chips, the microplasma is applied to the inner-wall modification of a PET capillary. Recently, CE chips were developed for various uses of a μ-TAS, for example, capillary electrophromatography and a chip for checking human health conditions. In the chips, the sample liquid to be analyzed is introduced into a capillary by the EOF pump. The EOF is characterized by the zeta potential, which corresponds to the electric potential of the interfacial electric double layer between the inner wall and the sample liquid. It is generally known that the zeta potential of the silica is larger than that of polymers, such as PET and Teflon. However, polymers have some advantages in the formation of complex capillary patterns and the integration of various chemical sensors on a chip. To enhance the zeta potential, the plasma treatment for the inner wall of a PET capillary has been carried out. In general, the capillary of a practical micro CE chip has a cross section of less than 50 μm × 50 μm; however, the present chip has a straight capillary of 500 μm × 500 μm cross section to primarily clarify the effect of the plasma treatment on a PET capillary. The schematic illustration of the experimental setup for the microplasma treatment is shown in Fig. 8. The chip is made of two PET plates of 20 mm × 20 mm. One plate has a groove molded with a Pt wire and the other has two holes to introduce the sample liquid into a capillary. Both plates are press bonded under the condition of 75 °C, 0.15 MPa, and 30 min, to obtain a capillary with a cross section of 500 μm × 500 μm and a length of 15 mm.

![Schematic illustration of the CCMP treatment on a PET capillary.](image)

**FIG. 7.** Emission intensity of an atmospheric on-chip He + O2 plasma as a function of O2 concentration at 7 W and total gas flow rate of 210 sccm.

**FIG. 8.** Schematic illustration of the CCMP treatment on a PET capillary.

**TABLE I.** Plasma treatment conditions for inner-wall modification of a PET capillary.

<table>
<thead>
<tr>
<th>Treatment conditions</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>He</td>
<td>He</td>
<td>He + O2 (3%)</td>
</tr>
<tr>
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<td>1 atm</td>
<td>1 atm</td>
</tr>
<tr>
<td>Gas flow rate</td>
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<td>144 sccm</td>
<td>150 sccm</td>
</tr>
<tr>
<td>rf power</td>
<td>6 W</td>
<td>6 W</td>
<td>6 W</td>
</tr>
<tr>
<td>Time</td>
<td>10 min</td>
<td>10 min</td>
<td>2 min</td>
</tr>
</tbody>
</table>
KH₂PO₄, 8 g/L NaCl, and 1150 mg/L Na₂HPO₄, in the capillary and adding monitor neutral particles (~1 μm beads) into the solution; (ii) inserting Pt electrodes into the holes and applying dc voltage between the electrodes; and (iii) estimating the average EOF velocity by tracing the beads’ motion. The schematic illustration of the EOF measurement is the inset in the top left corner of Fig. 9. The experimental results of the EOF velocity are shown in Fig. 9 as a function of the external electric field. The EOF velocity of the untreated PET capillary is shown as a reference. We found that the EOF velocity of the atmospheric-plasma treatment was larger than that of the low-pressure-plasma treatment. Furthermore, the 3% O₂ addition to He plasma enhanced the EOF velocity by a factor of 1.5 despite the short treatment time of 2 min. The result implies that introducing additional oxygen into the PET surface leads to an increase of the EOF velocity. Figure 10 shows the x-ray photoelectron spectroscopy (XPS) spectrum on the inner surface of the PET capillary before and after the plasma treatment. The treatment condition is the same as for case 3 in Table I. We found that the O 1s peak value increases and the C 1s peak value decreases after the plasma treatment. In addition, the difference spectrum by subtracting a dotted line (untreated) from a solid line (plasma treated) shows the signals of formation of the phenolic –OH and carboxylic acid end groups. The mechanism of the EOF enhancement due to the newly introduced –OH groups on a PET surface is as follows: the OH groups offer H⁺ cations to an electrolytic solution. Therefore, the residual O₂ bonds are arranged on the PET surface, and the inner wall is charged with negative electricity. As a result, the zeta potential on the PET inner wall increases.

Next, to expose the inner wall of a capillary to the O radicals in a simple manner, the downstream O₂ plasma treatment was proposed. The side view of the experimental setup for the PET inner-wall modification using the downstream O₂ microplasma source is shown in Fig. 11. A pure O₂ CCMP was generated in a quartz tube with an inner radius of 2 mm and a length of 20 mm. The PET chip to be treated was located about 12 mm below the CCMP source. The operating pressure, gas flow rate, and incident rf power were 13 Torr, 25 sccm, and 7 W, respectively. Figure 12 shows the dependence of the mobility of the EOF (μ_EOF) on the plasma treatment time with various treatment conditions. Each curve has a maximum value and then μ_EOF decreases with increasing treatment time. The decrease of μ_EOF is probably attributed to the PET surface etching by the O radicals. The μ_EOF obtained under the downstream O₂ plasma treatment for 3 min was 5.1×10⁻⁴ cm²/V s, which is about three times larger than that of the untreated PET capillary. Furthermore, we note that the wettability on the inner wall of a capillary increased after the He+O₂ (3%) and the downstream O₂
plasma treatment. The result confirms that the phenolic –OH and COOH acid groups were introduced to the inner wall of a PET capillary due to the free-radical oxidation mechanism.\textsuperscript{12}

Finally, we mention that there was an aging effect on the plasma-treated PET capillary: for example, the EOF decreased by a factor of 1.35 after 1 day.

### IV. CONCLUSION

A 13.56 MHz parallel-plate CCMP was generated both in a quartz tube with inner radius of 1 or 2 mm and in a capillary with a cross section of 65–500×500–5000 \( \mu \text{m} \) on a 20×20 mm quartz chip. The constitution of the CCMP source is very simple because of external plate electrodes. To attain a plasma ignition at a low rf power without reflection, a \( \pi \)-type matching circuit was miniaturized and suitably designed to satisfy the resonance condition with the excitation frequency so that an atmospheric He discharge was obtained at an incident power of 1–3 W, and the atomic excitation temperature was evaluated to be about 1900 K in terms of the atomic emission spectrum. Low-power (of 2–3 W) glow discharge of pure Ar was also attained at the pressure given by \( (pd)_{\text{min}}=0.5–0.8 \text{ Torr cm} \). Furthermore, an atmospheric Ar discharge was obtained at an incident power of 9 W in the capillary with a discharge gap of 65 \( \mu \text{m} \). The microplasma was applied to the inner-wall modification of a PET capillary to demonstrate the EOF control on a micro CE chip. We found that the \( \mu_{\text{EOF}} \) of the PET capillary treated by the downstream \( \text{O}_2 \) plasma was \( 5.1\times10^{-4} \text{ cm}^2/\text{V s} \), which is about three times larger than that of the untreated PET capillary.