Study on effect of introduced gas bubbles for the low channel damage in direct and alternating current liquid electrode plasma atomic emission spectrometry

Prasongporn Ruengpirasiri1, Phan Trong Tue2, Hidekazu Miyahara3, Akitoshi Okino4, and Yuzuru Takamura1

1School of Materials Science, Japan Advanced Institute of Science and Technology, Nomihodai, Ishikawa 923-1292, Japan
2Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology, 4259-835, Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan
3School of Science, The University of Tokyo, Bunkyo, Tokyo 113-0033, Japan
4FIRST, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503, Japan

E-mail: takamura@jaist.ac.jp

Received June 4, 2019; revised July 25, 2019; accepted August 4, 2019; published online August 21, 2019

1. Introduction

Heavy metals are found naturally in the Earth’s crust and become concentrated because of human activities. In developing countries with high population density and insufficient funds available for environmental restoration, low-cost and ecologically sustainable remedial options are required to monitor environment contamination in order to reduce associated health risks and make land available for agricultural production (to improve food security). Recently, many research groups have been developed to investigate miniaturized atmospheric pressure glow discharges,1–4 dielectric barrier discharge,5,6 atmospheric pressure liquid discharge,7,8 liquid electrode plasma (LEP)9,10 as excitation sources for optical emission spectrometry (OES) of dissolved analytes in liquids for analytical chemistry purposes.11–15 The standard methods for elemental analysis, such as inductively coupled plasma (ICP) OES, atomic absorption spectrometry, and ICP mass spectrometry are effective for chemical analysis of aqueous samples and are widely used for routine monitoring of personal exposure because of their high sensitivity, accuracy, and precision. However, these methods require large sample volume and are labor and time intensive. Low-cost, portable, real-time instruments for elemental analysis are needed to avoid these limitations.

Liquid electrode plasma atomic emission spectrometry (LEP-AES) was first introduced by Iiduka et al. in 2004.16 This emission spectrometry method uses microplasma as an excitation source and is suitable for various applications.17–22 Moreover, the use of LEP-AES in protein sensing studies employing Ag nanoparticle labeling was performed. The proposed technique has various promising applications in metal-nanoparticle-labeled biomolecule detection.23 This novel technique allows the plasma source to be miniaturized, as no plasma gas or high-power source is required, resulting in compact and portable systems. The device is inexpensive compared with the standard technologies mentioned above and requires minimal training to operate. In previous studies, LEP systems were developed that were driven by a direct current (DC) source; after repeated measurements, the narrow channel at the center of microchip was clearly deformed due to plasma damage, resulting in a channel width around 1.5 times larger than that in a new microchip.17 In LEP, high sensitivity and high accuracy are achieved by number of accumulation so that there is a tradeoff between sensitivity/accuracy and lifetime.12 Currently, such channel damage limits not only chip lifetime but also sensitivity and accuracy for repeated measurements.17,24,25

Recently, we demonstrated generation of LEP using alternating current (AC) in a new method called AC-LEP, which showed higher stability and significantly lower microchannel damage (1/3000) than DC-LEP.9 The plasma was continuously generated in a poly(dimethylsiloxane) (PDMS) chip for about 10 min without severe channel damage or expansion. These observations indicated that AC-LEP showed great potential for reducing channel damage, although the mechanism of this improvement was not clear. In conventional LEP, the plasma gas is generated from the sample solution itself by evaporation due to Joule heating at narrow channel. Thus, no external gas is required, which is the one of the most merits of LEP. In AC-LEP, however, we observed amount of accumulated gas bubbles at both electrodes. High-frequency AC electrolysis of water can occur if the current density is sufficiently high. Thus, it is considerable that the 20 kHz of AC signal caused the electrolysis of water, forming a gas product at the two electrodes.26,27 In AC-LEP, the accumulated bubbles at the electrode in upper stream flow into LEP and may affect the plasma generation. Therefore, in this study, various types of gases were introduced intentionally from outside into the AC- and DC-LEP and their effects on plasma generation and...
channel damage were investigated. For that purpose, a new chip design for the introducing gas into the channel was developed. Channel damage was compared in both DC-LEP and AC-LEP with and without gas introduction.

2. Experimental methods

The substrate of the chip was a glass slide, which was coated with a PDMS layer containing a microchannel. The pattern of the LEP chip set up for gas introduction consisted of two liquid inlets, one gas inlet, and one outlet. The plasma generation zone on the LEP chip was 100 μm in both depth and width at the narrowest part of the channel. In the case of the chip without gas introduction, the design described in our previous study was used.9)

The PDMS layer was made by molding and lithographic methods. The fabrication process is shown in Fig. 1. First, a silicon wafer was sequentially cleaned with acetone, ethanol, and then deionized (DI) water. Permanent epoxy negative photoresist SU-8 3050 was poured on a silicon wafer and spin coated at 1000 rpm for 30 s, then soft baked on a hotplate at 95 °C for 45 min, exposed to UV light for 30 s, and finally post-baked on a hot plate at 65 °C for 1 min and then 95 °C for 5 min. The silicon wafer was then cooled to room temperature and the channel pattern was developed with SU-8 developer, followed by rinsing with isopropanol. A PDMS monomer mixed with 10 wt% curing catalyst was poured onto the fabricated mold and cured at 75 °C for 90 min. The PDMS replica layer was peeled off and punched to make 2 mm diameter holes for the inlet and outlet. The obtained PDMS layer was bonded with the glass substrate by oxygen plasma bonding (75 W for 10 s). Finally, the as-fabricated chip was connected to tubes and connected to two platinum electrodes (0.3 mm diameter, 5 cm length).

The negative photoresist SU-8 3050 and developing solution were purchased from Nippon Kayaku, Japan. The PDMS monomer and curing catalyst were purchased from Dow Corning Toray. Pb standard solutions (1000 mg l \(^{-1}\), Kanto Chemical Co., Inc.) were used as a model analyte in both cases of DC-LEP and AC-LEP. Therefore, to compare the damage between AC-LEP and DC-LEP, it is important to choose the conditions giving the same strength. But it is not so easy because each parameter, such as voltage and exposure time have different meaning in DC-LEP and AC-LEP. In DC-LEP, plasma is not continuously and uniformly generated in the duration of one on-time of voltage. In one pulse of on-time, plasma repeats on and off many times along with the change of shape and position of the gas/liquid boundaries. Intensity also change very much. This situation is almost similar in AC-LEP case. For fair comparison of channel damage, both AC-LEP and DC-LEP conditions were optimized to give the same signal intensity (limit of detection, LOD) for Pb in 0.1 M nitric acid, having electric conductivity of 0.350 ± 0.005 mS cm \(^{-1}\). For AC-LEP, a liquid flow rate of 30 μl min \(^{-1}\) and Ar gas flow rate of 0.03 μl min \(^{-1}\) come together with carrier liquid flow rate of 30 μl min \(^{-1}\) (in case of gas introduction) were used. Average input power was 0.15 W during AC-LEP generation. Meanwhile, for DC-LEP, a liquid flow rate of 100 μl min \(^{-1}\) was introduced and 1400 V of applied voltage with 3 ms on-time and 2 ms off-time were applied. Emission spectra were acquired using the USB2000 spectrometer (Ocean Optics, USA). The exposure time of spectrometer for AC-LEP case is 1 s. For DC-LEP case, 50 ms exposure time of spectrometer, synchronized with the 10 pulses of applied voltage consists.

Fig. 1. (Color online) Schematic flow of chip fabrication. Negative photolithography was utilized for mold fabrication. After putting silicone tubes, all connection points were sealed by PDMS to prevent leakage.

© 2019 The Japan Society of Applied Physics 097001-2
The power was supplied by DC or AC power supplies. The emission spectra were acquired by a spectrometer controlled by a computer.

The gas outside the channel to be introduced into the channel.28–30) From these results, we concluded that the externally introduced bubble is important factor for plasma generation in the AC-LEP system, where hydrolysis of water occurs during the incubation time and the bubbles accumulate and move to the narrow channel with adequate flow rate. Here, the gas acts as seed bubble, AC-LEP is generated by lower powers. These results suggest that the lower damage in conventional AC-LEP without gas introduction also attributes to H₂/O₂ bubbles generated by hydrolysis at electrodes and consequently introduced into the LEP from outside of narrow channel.

As reduced channel damage was observed when introducing gas during AC-LEP, we proposed that it might have a similar effect during DC-LEP with gas introduction. Therefore, air and argon were introduced during DC-LEP and the voltage dependence of the signal intensity was investigated. Figure 6 illustrated the emission spectra in all cases. Next, Fig. 7 shows that the intensity of the Pb signal was higher when gases were introduced compared to the case of no gas at the same applied voltage, but no obvious difference between air and Ar was observed. This indicates

3. Results and discussion

3.1. Channel damage

Channel damage during LEP is the main factor limiting the physical lifetime of chips and measurement sensitivity, accuracy and reliability because it decreases the reproducibility of emission signals. We showed in our previous study30) that the novel AC-LEP significantly reduced channel damage. The microscopy images of a channel before and after AC-LEP [Fig. 3(A)] showed less channel damage compared to the DC-LEP sample [Fig. 3(B)]. The channel width increased over the duration of chip usage, resulting in a decrease in the signal intensity due to the lower excitation temperature at wider channel.31,32)

3.2. Investigation of effects of gas introduction

One of the advantages of LEP is that no plasma gas is required. However, in this part of the study, gas was intentionally introduced to study the mechanism of channel damage, as shown in Fig. 4. For the purpose, chips with a new design were fabricated to allow bubbles generated outside the channel to be introduced into the channel.28–30) The gas flow rate was optimized to facilitate plasma generation; high flow rates were avoided to prevent the introduced bubbles from disturbing plasma generation.31,32)

Air and argon gases were selected because Ar gas is known to facilitate easy plasma generation due to single atom gas, while air is the abundant gas easy to use and store. Figure 5 compares channel damage when different gases were introduced during DC-LEP and AC-LEP. The DC-LEP samples [Figs. 5(A) and 5(B)] showed less channel damage when gas was introduced. As before, the AC-LEP [Figs. 5(C) and 5(D)] samples showed much less channel damage than the DC-LEP ones, where the least damage was observed when argon gas was introduced. Figure 5(E) summarizes the volume percentage of channel expansion with and without gas introduction. There was an obvious difference between the huge channel expansion of the DC-LEP sample (69.1%) and small channel expansion of the AC-LEP sample (3.32%), with Ar gas introduced. In addition, DC-LEP samples showed no observable difference in the damage between air and Ar gas introduction.

Nitrogen and oxygen gas were selected as two further candidates for generation of bubbles; nitrogen gas can be produced from atomization of the nitric acid solvent, while oxygen is a product of the hydrolysis of water. In the case where no gas was introduced, the first plasma generation was observed after 15 s. On the contrary, plasma was generated almost immediately (less than 2 s) after turning on the power source when gas was introduced. In addition, for AC-LEP without gas introduction, adequate range of solution flow rate is narrow and low which is 30 μl min⁻¹. In contrast, DC-LEP shows higher signal stability at higher flow rate that is 100–1000 μl min⁻¹. From these results, we concluded that the externally introduced bubble is important factor for plasma generation in the AC-LEP system, where hydrolysis of water occurs during the incubation time and the bubbles accumulate and move to the narrow channel with adequate flow rate. Here, the gas acts as seed bubble, AC-LEP is generated by lower powers. These results suggest that the lower damage in conventional AC-LEP without gas introduction also attributes to H₂/O₂ bubbles generated by hydrolysis at electrodes and consequently introduced into the LEP from outside of narrow channel.

The microscopy images of a channel before and after chip usage, resulting in a decrease in the signal intensity due to the lower excitation temperature at wider channel.31,32)

3. Results and discussion

3.1. Channel damage

Channel damage during LEP is the main factor limiting the physical lifetime of chips and measurement sensitivity, accuracy and reliability because it decreases the reproducibility of emission signals. We showed in our previous study30) that the novel AC-LEP significantly reduced channel damage. The microscopy images of a channel before and after AC-LEP [Fig. 3(A)] showed less channel damage compared to the DC-LEP sample [Fig. 3(B)]. The channel width increased over the duration of chip usage, resulting in a decrease in the signal intensity due to the lower excitation temperature at wider channel.31,32)

3.2. Investigation of effects of gas introduction

One of the advantages of LEP is that no plasma gas is required. However, in this part of the study, gas was intentionally introduced to study the mechanism of channel damage, as shown in Fig. 4. For the purpose, chips with a new design were fabricated to allow bubbles generated outside the channel to be introduced into the channel.28–30) The gas flow rate was optimized to facilitate plasma generation; high flow rates were avoided to prevent the introduced bubbles from disturbing plasma generation.31,32)

Air and argon gases were selected because Ar gas is known to facilitate easy plasma generation due to single atom gas, while air is the abundant gas easy to use and store. Figure 5 compares channel damage when different gases were introduced during DC-LEP and AC-LEP. The DC-LEP samples [Figs. 5(A) and 5(B)] showed less channel damage when gas was introduced. As before, the AC-LEP [Figs. 5(C) and 5(D)] samples showed much less channel damage than the DC-LEP ones, where the least damage was observed when argon gas was introduced. Figure 5(E) summarizes the volume percentage of channel expansion with and without gas introduction. There was an obvious difference between the huge channel expansion of the DC-LEP sample (69.1%) and small channel expansion of the AC-LEP sample (3.32%), with Ar gas introduced. In addition, DC-LEP samples showed no observable difference in the damage between air and Ar gas introduction.

Nitrogen and oxygen gas were selected as two further candidates for generation of bubbles; nitrogen gas can be produced from atomization of the nitric acid solvent, while oxygen is a product of the hydrolysis of water. In the case where no gas was introduced, the first plasma generation was observed after 15 s. On the contrary, plasma was generated almost immediately (less than 2 s) after turning on the power source when gas was introduced. In addition, for AC-LEP without gas introduction, adequate range of solution flow rate is narrow and low which is 30 μl min⁻¹. In contrast, DC-LEP shows higher signal stability at higher flow rate that is 100–1000 μl min⁻¹. From these results, we concluded that the externally introduced bubble is important factor for plasma generation in the AC-LEP system, where hydrolysis of water occurs during the incubation time and the bubbles accumulate and move to the narrow channel with adequate flow rate. Here, the gas acts as seed bubble, AC-LEP is generated by lower powers. These results suggest that the lower damage in conventional AC-LEP without gas introduction also attributes to H₂/O₂ bubbles generated by hydrolysis at electrodes and consequently introduced into the LEP from outside of narrow channel.

As reduced channel damage was observed when introducing gas during AC-LEP, we proposed that it might have a similar effect during DC-LEP with gas introduction. Therefore, air and argon were introduced during DC-LEP and the voltage dependence of the signal intensity was investigated. Figure 6 illustrated the emission spectra in all cases. Next, Fig. 7 shows that the intensity of the Pb signal was higher when gases were introduced compared to the case of no gas at the same applied voltage, but no obvious difference between air and Ar was observed. This indicates
that it is possible to apply a lower voltage (100–200 V lower) and obtain a comparable signal intensity when gas is introduced, which should reduce channel damage. These facts also suggest that the voltage required for bubble generation by homogeneous nucleation is higher than that required for plasma generation, in these experimental setup and conditions. In conventional DC-LEP, a high-applied power is applied to generate bubbles, and then the identical and constant voltage still applied for following plasma generation, which some part of applied power is an excess power for plasma generation resulting the higher damage in conventional DC-LEP. Under AC power conditions, the plasma appeared in the bubble grown from the externally introduced seed bubble. This enables bubble formation with lower applied power, where plasma can be generated under milder conditions. Considering all of the experimental results, the proposed mechanism of low channel damage in AC-LEP is shown in Fig. 8. It can be seen that a gas bubble produced at an electrode or by the external gas generation system reaches the narrow channel. Next, LEP appears inside of the gas bubble as a result of the applied voltage. Finally, the elements in solution enter the plasma and emit their characteristic optical emission lines for quantitative analysis. In Fig. 6(C), no significant line of Ar was shown even though Ar was introduced. It seems simply because of small amount of Ar in water plasma bubble. Before plasma generation, bubble is formed as plasma gas. In Ar introduction case, the bubble was initiated by Ar bubble as nuclei, and then
expanded much by water evaporation. From the volume ratio of Ar nuclei and bubble after expansion, the molar ratio of Ar: water was estimated 1:500 in plasma gas. In addition, the part of excited Ar may be consumed to decompose molecules such as H₂O, N₂ and NO.

3.3. Long time stability of AC-LEP emission signal with various gases

Long time stability of emission signals is one of the important factors for developing reliable elemental analysis methods. Hence, we introduced different gases during AC-LEP while monitoring the emission signal over time. Figure 9 shows that, with gas introduction, the plasma could be generated for a longer time. Without gas introduction, the emission signal disappeared after around 40 min. When Ar gas was introduced, the emission signal showed the most stable average signal intensity. When other gases were used,
we observed signals for up to 1 h, although the signal stability was lower than for Ar. This indicates that gas introduction reduces channel damage, leading to longer chip lifetimes. Interestingly, when air was introduced, the emission signal seemed to disappear around 10 min, and from 26 to 40 min, fluctuations thereafter.

### 3.4. Analytical Performance of AC-LEP

The analytical performance of AC-LEP with the introduction of different gases was studied using Pb as a model heavy metal analyte. Pb concentrations of 0–100 ppm in 0.1 M nitric acid were investigated. Figure 10 shows the analyzed peak area as a function of Pb concentration, where the linear part of the curve for samples without gas introduction was shorter and became non-linear at Pb concentrations above 25 ppm. The slope of the calibration curve can be used to represent the detection sensitivity. The introduction of Ar gas resulted in the highest detection sensitivity, with a relatively low deviation and high coefficient of linear regression ($R^2$). Hence, we conclude that the introduction of gas bubbles facilitated the stability of plasma generation, while allowing the applied power to be reduced. Even though one of the advantages of LEP is that a gas does not need to be supplied, introduction of gas allowed us to elucidate some parts of the LEP mechanism and more clearly understand aspects of this novel plasma source for future applications.

### 4. Conclusions

The effects of external gas introduction into AC-LEP and DC-LEP were studied. In AC-LEP, the introduction of gas into the channel resulted in the plasma starting almost immediately after the voltage was applied, while it started after several seconds without gas introduction. In both case of AC-LEP and DC-LEP, the external gas bubbles facilitated stable and high sensitive plasma generation with lower power, which result in reducing channel damage and increasing the lifetime of the analysis chip. These effects are significant in Ar introduction and AC-LEP cases. The power for homogeneous nucleation of bubble in conventional DC-LEP is higher than that required for plasma generation, resulting in high channel damage. Those facts suggest that the lower damage in conventional AC-LEP without gas introduction is attributed to $H_2/O_2$ bubbles generated by hydrolysis at electrodes and consequently introduced into the LEP from outside of narrow channel.

**Acknowledgments**

The authors would like to thank Dr. Tamotsu Yamamoto (CEO) and other employees of Micro Emission Ltd for providing instrumentation and advice. The authors acknowledge Plasma Concept Tokyo, Inc. for lending a power-controllable AC power source for the experiments.

---

1) K. Greda, K. Swiderski, P. Jamroz, and P. Pohl, Anal. Chem. 88, 8812 (2016).
2) C. Yang, D. He, Z. Zhu, H. Peng, Z. Liu, G. Wen, J. Bai, H. Zheng, S. Hu, and Y. Wang, Anal. Chem. 89, 3694 (2017).
3) I. M. M. Rahman, M. Miyaguchi, A. S. Mashio, T. Maki, and H. Hasegawa, Sens. Actuators B 1001, 100 (2018).
4) Q. He, Z. Zhu, S. Hu, H. Zheng, and L. Jin, Anal. Chem. 84, 4179 (2012).
5) T. Krahling, A. Michels, S. Geisler, S. Florek, and J. Franzke, Anal. Chem. 86, 5822 (2014).
6) R. M. Hsiung, Z. L. Zhu, H. T. Zheng, Z. F. Liu, S. C. Zhang, and S. H. Hu, J. Anal. Atom Spectrom. 26, 1178 (2011).
7) A. Leng, Y. Lin, Y. Tian, L. Wu, X. Jiang, X. Hou, and C. Zheng, Anal. Chem. 89, 703 (2017).
8) K. Do Van, M. Hidekazu, Y. Tamotsu, T. Phan Trong, O. Akitoshi, and T. Yuzuru, Jpn. J. Appl. Phys. 55, 02BC23 (2016).
9) Y. Kohara, Y. Terui, M. Ichikawa, K. Yamamoto, T. Shirasaki, K. Kohda, T. Yamamoto, and Y. Takamura, J. Anal. Atom Spectrom. 30, 2125 (2015).
10) J. A. Broekaert, Anal. Bioanal. Chem. 374, 182 (2002).
11) J. Franzke, K. Kunze, M. Miclea, and K. Niemax, J. Anal. Atom. Spectrom. 18, 802 (2003).
12) V. Karanassios, Spectrochim. Acta B 59, 909 (2004).
13) J. Franzke and M. Miclea, Appl. Spectrosc. 60, 80A (2006).
14) M. Miclea and J. Franzke, Plasma Chem. Plasma Process. 27, 205 (2007).
15) A. Ishida, Y. Morita, E. Tamiya, and Y. Takamura, 8th Int. Conf. on Miniaturized Systems for Chemistry and Life Sciences, 2004, p. 423.
16) A. Kitano, A. Ishida, T. Yamamoto, Y. Urita, E. Tamiya, and Y. Takamura, Anal. Chem. 83, 9424 (2011).
17) Y. Kohara, Y. Terui, M. Ichikawa, T. Shirasaki, K. Yamamoto, T. Yamamoto, and Y. Takamura, J. Anal. Atom Spect. 27, 1457 (2012).
18) S. Bauru, I. M. M. Rahman, I. Alam, M. Miyaguchi, H. Sawai, T. Maki, and H. Hasegawa, J. Chromatogr. B 1060, 190 (2017).
19) V. K. Do, M. Yamamoto, S. Taguchi, Y. Takamura, N. Surugaya, and T. Kuno, Talanta 183, 283 (2018).
20) S. Bauru, I. M. M. Rahman, M. Miyaguchi, A. S. Mashio, T. Maki, and H. Hasegawa, Sens. Actuators B 272, 91 (2018).
22) D. Van Khoai, A. Kitano, T. Yamamoto, Y. Ukita, and Y. Takamura, Microelectron. Eng. 111, 343 (2013).

23) N. H. Tung, M. Chikae, Y. Ukita, P. H. Viet, and Y. Takamura, Anal. Chem. 84, 1210 (2012).

24) V. K. Do, T. Yamamoto, Y. Ukita, and Y. Takamura, Sens. Actuators B 221, 1561 (2015).

25) D. Van Khoai, T. Yamamoto, Y. Ukita, and Y. Takamura, Jpn. J. Appl. Phys. 53, 05FS01 (2014).

26) J. W. Shipley, Can. J. Res. 1, 305 (1929).

27) N. Shimizu, S. Hotta, T. Sekiya, and O. Oda, J. Appl. Electrochem. 36, 419 (2006).

28) A. Bulbul and H. Kim, Lab Chip 15, 94 (2015).

29) Z. Z. Chong, S. B. Tor, N. H. Loh, T. N. Wong, A. M. Ganan-Calvo, S. H. Tan, and N. T. Nguyen, Lab Chip 15, 996 (2015).

30) T. T. Fu and Y. G. Ma, Chem. Eng. Sci. 135, 343 (2015).

31) P. Garstecki, A. Gañán-Calvo, and G. M. Whitesides, Formation Of Bubbles And Droplets In Microfluidic Systems 2005, p. 361.

32) K. Wang, L. S. Xie, Y. C. Lu, and G. S. Luo, Chem. Eng. Sci. 100, 486 (2013).

33) Y. Takamura, T. Ozaki, A. Kato, H. Tokaihayashi, and T. Yamamoto, Japan Patent 5530222 (2014).