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Atomic Absorption Spectroscopy of Metal Atom from Liquid with in a DC-Pulsed Plasma with Electrolyte Electrode

電解質溶液を電極としたパルスDCプラズマにおける
液相由来金属原子の吸収分光計測

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Zinc (Zn) metal atom release from zinc sulfate electrolyte solution was observed by two-dimensional atomic absorption spectroscopy during irradiation of pulsed plasma (~5 μs) to the solution surface. Time-resolved measurement of Zn atom revealed that the Zn desorption rate monotonically increased with increasing the number of discharge repetition with a time-interval of 0.1 ms. Temperature of electrolyte solution surface was observed by a thermography camera and the temperature increase was also observed with the increase of the discharge repetition number. Correlation between the water desorption and Zn desorption suggests that Zn desorption is assisted not only by electric field of the discharge but also by thermal effect.

1. Introduction

Discharges in liquid or on liquid surface have attracted much attentions as a new plasma environment for a variety of materials processing such as surface coating, cleaning[1] and also for biomedical applications[2]. In these discharges, ions and radicals originated from solvent or solute are produced at plasma-liquid interface and such species strongly influences the processing performance. In this study, electrolyte solution is observed as an example and release behavior of alkaline atoms from liquid surface interacting with the plasma is investigated by atomic absorption spectroscopy. Furthermore, water temperature at a point of the plasma-water interaction is observed by a thermography camera and relation between the alkaline atom desorption and the water temperature.

2. Experimental

Figure 1 shows schematic of the experimental apparatus. A grounded stainless steel container with quartz windows was filled with 1 wt% $ZnSO_4$ solution and discharge gas (Ar, 200 sccm) was introduced into the small cell. A needle electrode was placed at 4 mm above the solution surface and positive or negative pulsed DC power (4 kV_{pp}, pulse FWHM 5 μs) at a repetition frequency of 10 kHz was applied to the needle electrode. To observe emission from Zn atom released from the liquid surface, emission from the plasma was measured by an ICCD camera through a band-pass filter at a center wavelength of 213.9 nm that corresponds to emission wavelength of Zn. Furthermore, Zn atom emission from a hollow cathode lamp was introduced into the cell and time-dependent two-dimensional distribution of Zn atom densities in the gas phase was measured using atomic absorption spectroscopy. From temporal development of the Zn atoms, Zn desorption rate was evaluated. During the discharge, water surface temperature at the point of the plasma-water interaction was measured by a thermography camera.

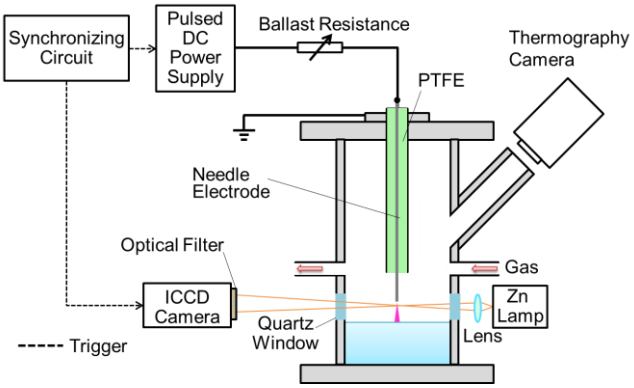

Fig.1. Schematic of experimental apparatus.

3. Results and Discussions

In our previous work, Zn emission from the plasma has been compared by changing the polarity of the DC voltage applied to the needle electrode, and Zn release has been clearly observed in the case of the negative voltage application to the needle electrode, but not in the case of the positive voltage[3]. The result indicates that the electric field is essential for the Zn release from the liquid surface. Next, temporal development of Zn atom into gas phase was observed by the two-dimensional ICCD atomic absorption spectroscopy with negative pulse application to the needle, as shown in figure 2. Zn atom expansion to the gas phase from the plasma-liquid interaction point was observed. From this two-dimensional absorption profile, total Zn atom number in the gas phase was evaluated using Lambert-Beer law, and Zn atom desorption rate was evaluated by differentiating the total Zn atom number by the repetition number.

Filled circles in figure 3 shows Zn desorption at one discharge pulse as a function of the discharge pulse repetition. The result indicates that Zn desorption is not constant during a series of the discharge pulse but shows monotonic increase with respect to the pulse repetition. The result suggests that there is strong interaction between the plasma irradiation and the Zn desorption.

To give an insight into the Zn desorption, surface temperature at the point of the plasma interaction was measured by the thermography camera. Figure 4 shows an example of the surface temperature, and the clear thermal spot was observed. Temperature decay time constant was evaluated after the plasma irradiation, and long decay time constant (~ 1s) compared to the pulse interval time (100 μs) was observed. This means that the water surface temperature increases step-by-step during a series of the pulse repetition. Open plots in figure 3 indicate H_2O desorption rate as a function of the pulse repetition number. The result suggests that the water desorption and Zn release shows strong correlation and, even though the Zn desorption is induced by the discharge current and electric field, Zn desorption rate is also influenced by the surface temperature or the water desorption.

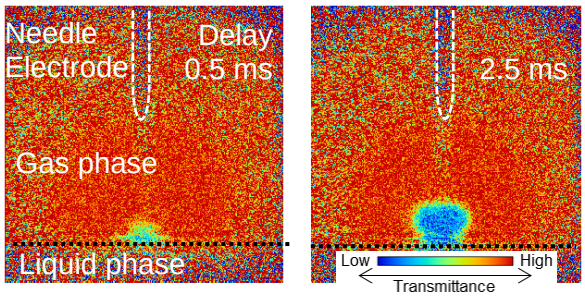

Fig. 2 Temporal variation of Zn absorption during the repetitive discharge pulse.

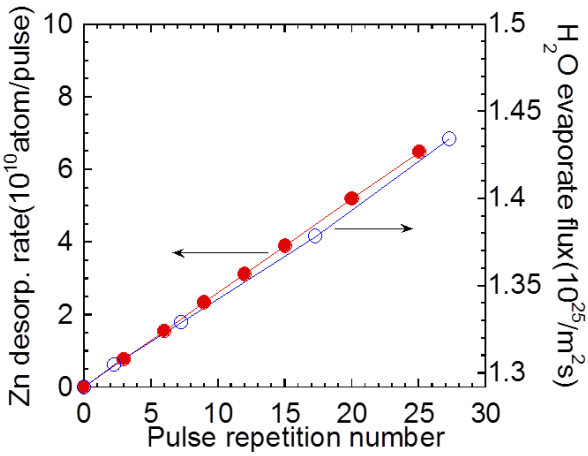

Fig. 3 Zn desorption rate (filled circles) and H_2O desorption rate (open circles) as a function of the discharge pulse repetition.

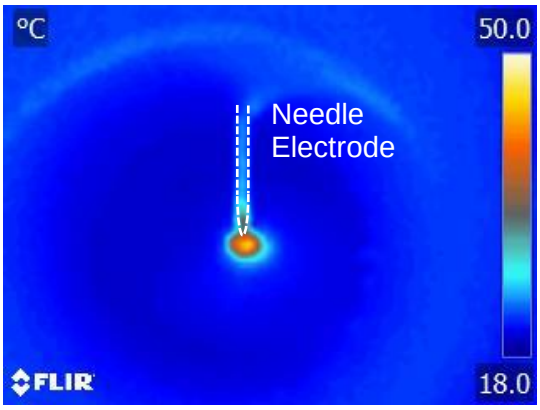

Fig. 4 Thermography image of the water surface temperature.

4. Summary

Zn desorption from zinc sulfate electrolyte solution was observed by two-dimensional atomic absorption spectroscopy. It was observed that the Zn desorption was not constant during a series of pulsed discharge and Zn desorption monotonically increased during the pulse repetition. Surface temperature also increased during the pulse repetition, suggesting that the Zn desorption was assisted not only by the electric field but also the water desorption.

References

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