STUDY ON ON-CHIP MASS SPECTROMETRY IN A LOW VACUUM OPERATION

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ABSTRACT

Aiming to realize low vacuum mass spectrometry on a chip, this paper reports a travelling feature of high molecular ions in a low vacuum, chip ion detector, and on-chip vacuum generation method. Pressure dependence on the ion current of high molecular samples was measured by the fabricated chip ion detector. On-chip vacuum generator integrated with a diaphragm pressure sensor demonstrates a reduction of the pressure in micro chamber to 8.5kPa by using gas-liquid phase transition of pure water.

KEYWORDS

Mass spectrometry, Chip ion detector, On-chip vacuum generation.

INTRODUCTION

Mass spectrometry is one of the most promising techniques for many biological analytical matters due to its outstanding sensitivity and resolution. Miniaturized mass spectrometer are very attractive because not only of their portability but also of their potential to develop state-of-art analytical concept. There are a few reports on the miniaturizations of mass spectrometry components [1-6]. These works studied about the miniaturizations of mass filter [1], ion sources [2, 3], faraday cup ion detector [4], and integration of each component [5]. However on-chip mass spectrometry integrated with a vacuum pump has not been realized despite its advantage of possibility to use it in a low vacuum [6]. Miniaturization of the vacuum pump is easily realized because high vacuum is not required thanks to shortening the flight distance of target ions in micro channel. This kind of miniaturized mass spectrometer has a potential to be used for point-of-care testing devices. Another issue to be solved is miniaturization of the high sensitive ion detector that can be integrated on a chip. In this paper, we studied the travelling features of high molecular ions in a low vacuum. To realize the integration of whole components of mass Spectrometer in to a chip, chip ion detector and on-chip vacuum pump were fabricated and demonstrated.

EXPERIMENTAL

Figure 1 shows the schematic of the experimental setup to investigate the travelling feature of high molecular ions in low vacuum. The experimental setup was composed of a tungsten filament for an electron impact ionizer, an ionization chamber, and a channeltron electron multiplier (Detector Technology Inc., Model 414, U.S.A.). In order to evaluate the feature of free flight of high molecular ions, detected peaks of poly ethylene glycol (PEG, M_w=200) ions were counted as a function of pressure. PEG was introduced on Si substrate in the vacuum chamber and heated up to 80 ^{O}C by a heater to evaporate.

We also developed the chip ion detector and tested it by using same ionizer. The conceptual diagram of the detector is shown in Fig. 2. Amplification of the ion signal by secondary electron emission was adapted to obtain high sensitive signal. Plain detection electrode for electron capturing and thermally grown SiO_2 thin layer (20 nm thickness) on Si substrate (20×20×0.5mm) faced each other with the gap of 1 mm by silicone rubber insulators. Accelerated positive ions by negatively biased mesh electrodes collide with the SiO_2 layer through a drilled hole. After that, generated electrons were captured by the electrode in positive electric field. The current was directly measured with a picoammeter (Keithley Instruments Inc., Model 6514, U.S.A.). Fabricated ion detector was placed instead of the channeltron electron multiplier with the gap of 30 mm between the ion source and the chip.

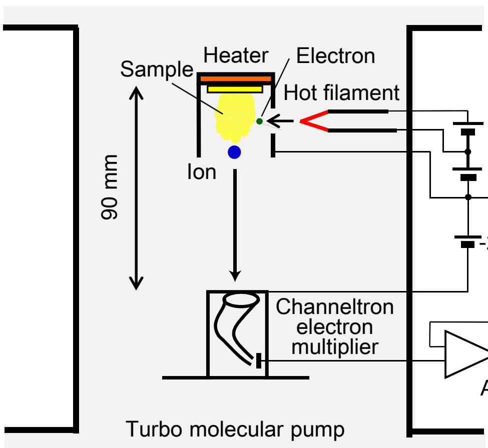

Figure 1: Schematic of experimental setup.

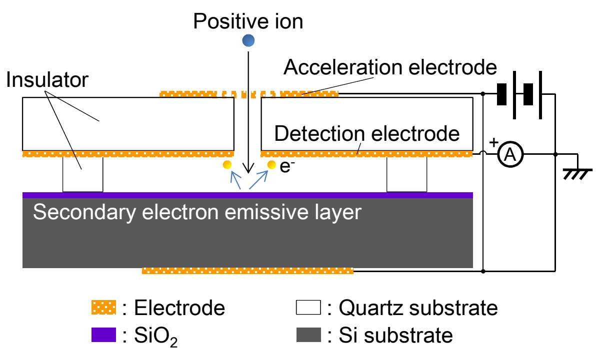

Figure 2: Schematic of fabricated chip ion detector.

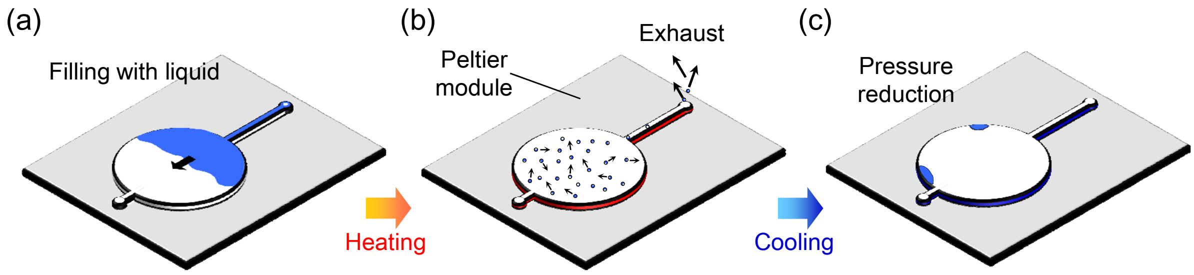

Figure 3: Procedure of the vacuum operation with the fabricated micro vacuum pump. Evacuation in the chamber is operated following process; (a) exchanging of initially occupying air by introducing the liquid sample, (b) vaporization of the liquid (c) adsorption and freezing onto the wall of the chamber by cooling.

For generation of the vacuum on a chip, the vacuum-tight chip with a micro chamber [7] was fabricated by etching and bonding of quartz substrates. The vacuum by the gas-liquid phase transition was generated in this chip. Figure 3 shows the procedure of the vacuum operation. Evacuation of gases from the chamber is carried out by two steps when existing gases in the chamber were replaced by the injected liquid and the liquid was vapored by temperature controlling. First, initially occupying air in the chamber was pushed out by introducing liquid sample. Then, most of the liquid was also evacuated by evaporation due to heating of the chamber. After that, the vapor of the liquid was removed from the working space in the chamber by adsorption and freezing onto the wall of the chamber by cooling. The pressure in the chamber was obtained to measure the diaphragm deflection by a laser displacement meter.

RESULTS AND DISCUSSION

Figure 4 shows the pressure dependence on detected peak frequency of high molecular ions. Ionized PEG by the electron impact ionizer was detected by the channeltron electron multiplier in the vacuum chamber. As shown in the waveforms in the inset of the figure, high intensity peaks were observed under 10^{-3} Pa. Detected peaks decreased with increasing the pressure. It means that free flight of PEG ions in 90 mm gap between the ion source and the detector was disrupted by residual gas molecules under lower vacuum than 2×10^{-2} Pa. As a result, it is expected that micro mass spectrometry with 100 µm channel is realized about 10 Pa, estimated by the theoretical relation of mean free path which follows inversely proportional to the pressure.

We also detected the current of the ions by using the chip ion detector and same ion source above the experiment. Figure 5 shows the pressure dependence on the detected current. The ion current was detected by fabricated chip detector. The detected ion current increased with increasing the pressure.

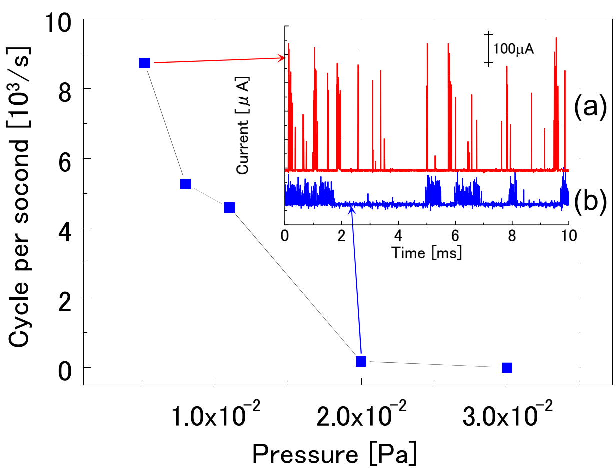

Figure 4: The pressure dependence on the detected peak frequency of PEG ions. Upper inset: obtained typical waveforms of the ion current converted to voltage by an amplifier at (a) 5.0×10^{-3} Pa and (b) 2.0×10^{-2} Pa.

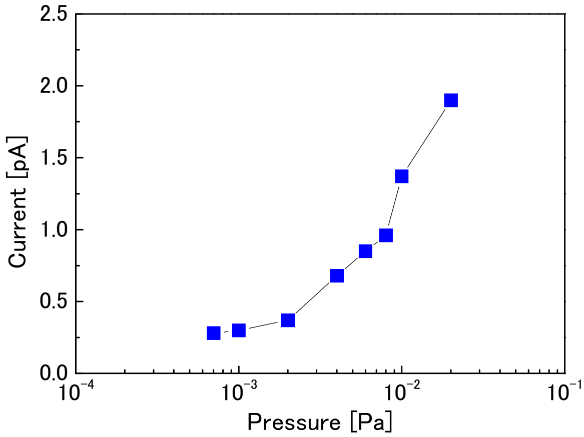

Figure 5: The pressure dependence on the detected ion current measured by the chip ion detector.

In order to make the low vacuum on a chip, phase transition by temperature alteration is effective because the highest performance of this vacuum pump attains to vapor pressure of introduced liquid. On the basis of the principle, on-chip vacuum generation was conducted. The pressure was monitored by the diaphragm pressure measurement with a laser displacement meter. The pressure reduced linearly as following the ideal gas law without phase transition. In the case of either diethyl ether or water, the pressure drastically reduced from boiling temperature. The lowest pressure was attained 8.5 kPa with phase transition of water.

CONCLUSIONS

Travelling feature of high molecular ions in low vacuum, fabrication of chip ion detector, and on chip vacuum generation were studied for aiming to realize mass spectrometry on a chip. Cleary peaks of free flight PEG ions in 90 mm gap between the ion source and the detector were detected at higher vacuum than 10^{-2} Pa. Detection of positive ion was demonstrated by the fabricated ion detector. Micro vacuum pump integrated with a diaphragm pressure sensor was fabricated by using conventional photo lithography techniques. Developed micro vacuum pump reduced the pressure in micro chamber to 8.5 kPa by using gas-liquid phase transition of pure water.

REFERENCES

[1] S. Wright, Shane O'Prey, Richard R. A. Syms, Guodong Hong, and Andrew S. Holmes, *Microfabricated Quadrupole Mass Spectrometer With a Brubaker Prefilter*, J. Microelectromech. Syst., 19, pp. 325-337, (2010).

[2] Luis Fernando Velasquez-Garcia, Blaise Laurent Patrick Gassend, and Akintunde Ibitayo Akinwande, *CNT-Based MEMS/NEMS Gas Ionizers for Portable Mass Spectrometry Applications*, J. Microelectromech. Syst., 19, pp. 484-493, (2010).

[3] S. Wright, R. Richard A. Syms, R. Moseley, Guodong Hong, Shane O'Prey, William E. Boxford, Neil Dash, and Peter Edwards, *MEMS-Based Nanospray-Ionization Mass Spectrometer*, J. Microelectromech. Syst., 19, pp. 1430-1443, (2010).

[4] R. B. Darling, A. A. Scheidemann, K. N. Bhat, and T.-C. Chen, *Micromachined Faraday cup array using deep reactive ion etching*, Sens. Actuators A, 95, pp.84-93, (2002).

[5] E. Wapelhorst, J.-P. Hauschild, and J. Muller, *Complex MEMS: a fully integrated TOF micro mass spectrometer*, Sens. Actuators A, 138, pp.22-27, (2007).

[6] P. Siebert, G. Petzold, A. Hellenbart, and J. Muller, *Surface microstructure/miniature mass spectrometer: processing and applications*, Appl. Phys. A, 67, pp. 155-160, (1998).

[7] K. Sugiyama, Y. Ukita, and Y. Takamura, *Development of on-chip vacuum generation by gas–liquid phase transition*, Sens. Actuators A, 176, pp.138-142, (2012).

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