

Invited paper

# Characteristics of Charged Droplet Beams Produced from Vacuum Electrospray

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Recently, various cluster ion beam sources have been studied with the aim of improving sensitivity in secondary ion mass spectrometry (SIMS) and achieving damage-free etching in X-ray photoelectron spectroscopy (XPS). Thus, compact gas cluster ion beam guns are now available for commercial SIMS and XPS instruments. The electrospray droplet impact (EDI) method was also developed as a new source for massive cluster beam, in which the charged droplet beams are produced from ambient electrospray and introduced into the vacuum system. The EDI method has been successful in achieving efficient ionization of organic molecules, soft etching of polymers, and nonselective etching of metal oxides. However, the current EDI method lacks adequate beam focusing and brightness for practical use. As a solution for these problems, we have proposed and developed a new method for producing a charged droplet beam and a stable electrospray of aqueous solutions under vacuum. In this study, the characteristics of ambient and vacuum electrospray were investigated with optical microscopy, and the ability of vacuum electrospray as the primary beam source will be discussed.

## 1. Introduction

Secondary ion mass spectrometry (SIMS) has been applied to a wide variety of materials. The study of organic materials by the static SIMS method was introduced by Benninghoven in 1969 [1]. Atomic ion probes, however, produce weak secondary ion signals for biomolecules and often damage them. Yields of secondary ions for organic molecules have been improved by using cluster primary ions such as  $C_{60}^{q+}$ ,  $Au_3^{q+}$  and  $Bi_3^{q+}$  ( $q=1,2$ ) [2–5]. These cluster ion beam guns are commercially available and their beams can be focused to less than 1  $\mu\text{m}$  in diameter. However, the secondary ion emission yield is still not enough, in particular for high spatial-resolution (below 1  $\mu\text{m}$ ) imaging mass spectrometry; therefore, there is a strong need to develop new cluster sources.

Techniques using massive cluster beams have been studied with the aim of increasing ionization efficiencies and achieving damage-free etching. Mahoney *et al.* pro-

duced a pioneering work in massive cluster ion beam for surface analysis using the massive cluster impact (MCI) method by the electrohydrodynamic emission of glycerol solutions [6]. In this method, massive clusters consisting of about  $10^6$  glycerol molecules and bearing about 200 electron charges on average are accelerated by a 10–20 kV high voltage [7]. Charged glycerol clusters can successfully produce soft desorption of peptides and proteins up to about 17000 u [8]. Despite its promising capabilities, this method was superseded before it received widespread acceptance, probably because of its limitation to low-volatility solvents.

The gas cluster ion beam (GCIB) system has been originally developed for surface modification by Yamada *et al.* [9], and later modified for application in SIMS by Matsuo *et al.* [10]. GCIB is produced by the ionization of neutral clusters formed by supersonic expansion of gaseous materials, and Ar GCIBs with a mean size of about 1000–5000 atoms/cluster have been frequently used.

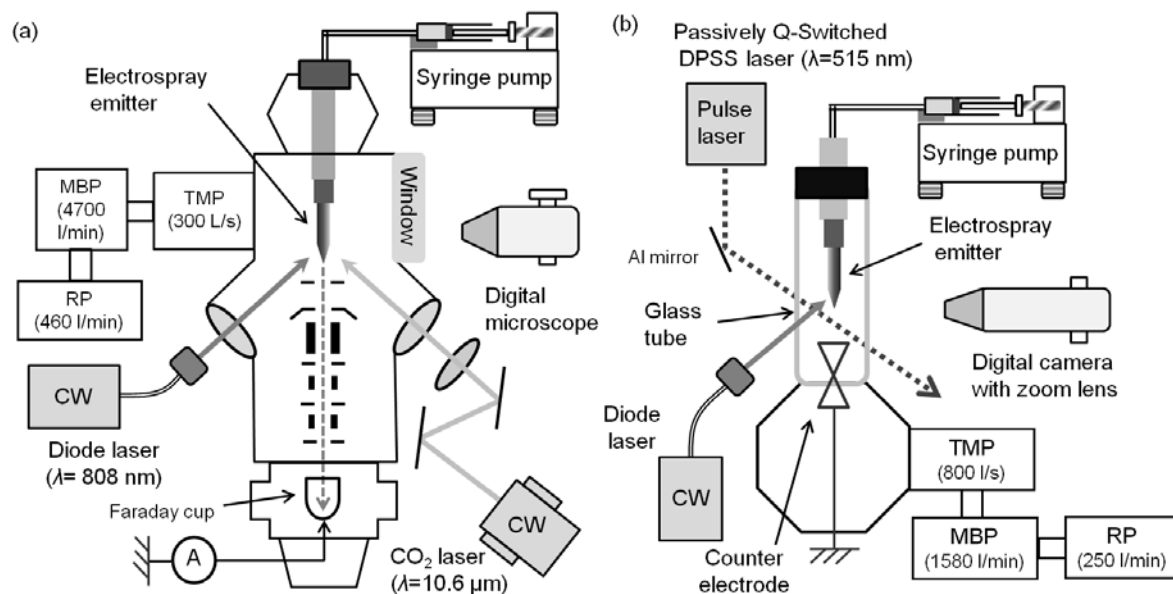


Fig. 1 Schematic views of a vacuum-type charged droplet beam gun (a) and of the optical microscopy setup (b).

Molecular depth profiling of organic films was successfully achieved with Ar GCIBs, because the chemical damage during etching is significantly suppressed [11, 12]. In addition, by using a similar supersonic expansion methodology as GCIB, water cluster beams have enhanced secondary ion yields on the order of 10 or more over Ar GCIBs for some organic molecules [13].

Recently, Durr *et al.* [14] have shown that surface impact of neutral SO<sub>2</sub> clusters from a supersonic beam can be employed as an alternative method for matrix-free and soft desorption and ionization of biomolecules (desorption/ionization induced by neutral clusters, DINeC). In the case of surface-adsorbed biomolecules, this method allows for desorption and ionization of oligopeptides at comparably low energy per cluster constituent without any fragmentation of the biomolecules. The ion-to-neutral ratio in desorption/ionization of oligopeptides by DINeC was quantified to be of the order of 10<sup>-3</sup> to 10<sup>-2</sup> [15].

The electro spray droplet impact (EDI) method based on the ambient electro spray technique was developed as a new massive cluster ion beam source by Hiraoka *et al.* [16]. The electro spray ionization (ESI) technique is one of the most important techniques for ionizing organic molecules [17, 18]. In mass spectrometry, samples ionized by elec-

tro spray are introduced into the vacuum chamber, and are transported to mass analyzers. In EDI, charged droplet beams are produced from ambient electro spray of 0.01 M trifluoroacetic acid (TFA) aqueous solution, and introduced into the vacuum system, where they are size-selected and transported by the ion guide. The EDI beam current on the target is typically 1 nA, and the beam diameter is about 2 mm without the object lens, and 0.2 mm with the object lens. The EDI method has been successful in achieving efficient ionization of organic molecules [16, 19], soft etching of polymers [20, 21], and nonselective etching of metal oxides [22, 23]. However, it lacks adequate beam focusing and intensity, and therefore it is not practical for use as a primary beam gun. These problems are attributed to the use of ambient electro spray as a beam source, because most of the charged droplets are lost by dispersion in air before entering the vacuum system. To solve these problems, we have proposed and developed a new method for producing a charged droplet beam using vacuum electro spray of aqueous solutions [24]. The present work is intended to apply vacuum electro spray to the EDI beam source to improve beam focusing and intensity.

## 2. Experimental

Figure 1 (a) shows the schematic view of a vacuum-type charged droplet beam gun, with a total length of 500 mm, the same size as a conventional liquid metal ion gun. An electro spray emitter was installed in the main vacuum chamber, and several commercially available electro spray emitters were tested in this study, i.e., metal-coated silica (internal diameter, (i.d.) 30  $\mu\text{m}$ , New Objective, Woburn, MA, USA) and stainless steel emitters (i.d. 30 and 50  $\mu\text{m}$ , New Objective, Woburn, MA, USA and Thermo Scientific, Waltham, MA, USA). Liquids were supplied to the emitters by using a syringe pump (PHD Ultra, Harvard Apparatus, Holliston, MA, USA) or a liquid chromatography (LC) pump (Micro-Flow pump MP710, GL Sciences, Tokyo, Japan). In this study, to prevent freezing of the liquid, the tip of the electro spray emitter was irradiated by a continuous wave (CW) infrared (IR) CO<sub>2</sub> laser (wavelength,  $\lambda = 10.6 \mu\text{m}$ , 20 W maximum power, FSV20KFB, Synrad, Mukilteo, WA, USA) or a CW near-IR diode laser ( $\lambda = 808 \text{ nm}$ , 3W maximum power, LFP-808W, Neoark, Tokyo, Japan) instrument. The vacuum electro spray was directly observed with an optical digital microscope system

(VH-5500 coupled with VH-Z50L lens; Keyence, Osaka, Japan). The beam current was measured with a Faraday cup and monitored by a picoammeter.

Figure 1 (b) shows another setup for optical microscopy to observe the properties of ambient and vacuum electro spray more clearly. The tip of the electro spray emitter was illuminated using a passively Q-Switched DPSS laser ( $\lambda = 515 \text{ nm}$ , 1.0 mJ maximum energy, Halo GN, InnoLight GmbH, Hannover, Germany) with a repetition rate of 10 Hz and with a pulse width of less than 10 ns. The electro spray generated from the emitter tip was visualized with this laser. The forward scattering light from the electro sprayed droplets was captured using a digital camera with a long working-distance lens, and the camera shutter was controlled in such a way that only one laser shot was recorded in each camera shot.

## 3. Results and discussion

Figure 2 presents the images of ambient and vacuum electro spray generated from the tip of the electro spray emitter with inner diameters of 30  $\mu\text{m}$ . Figure 2 (a) and (b) show the images of ambient electro spray observed with the digital microscope and the optical microscopy setup

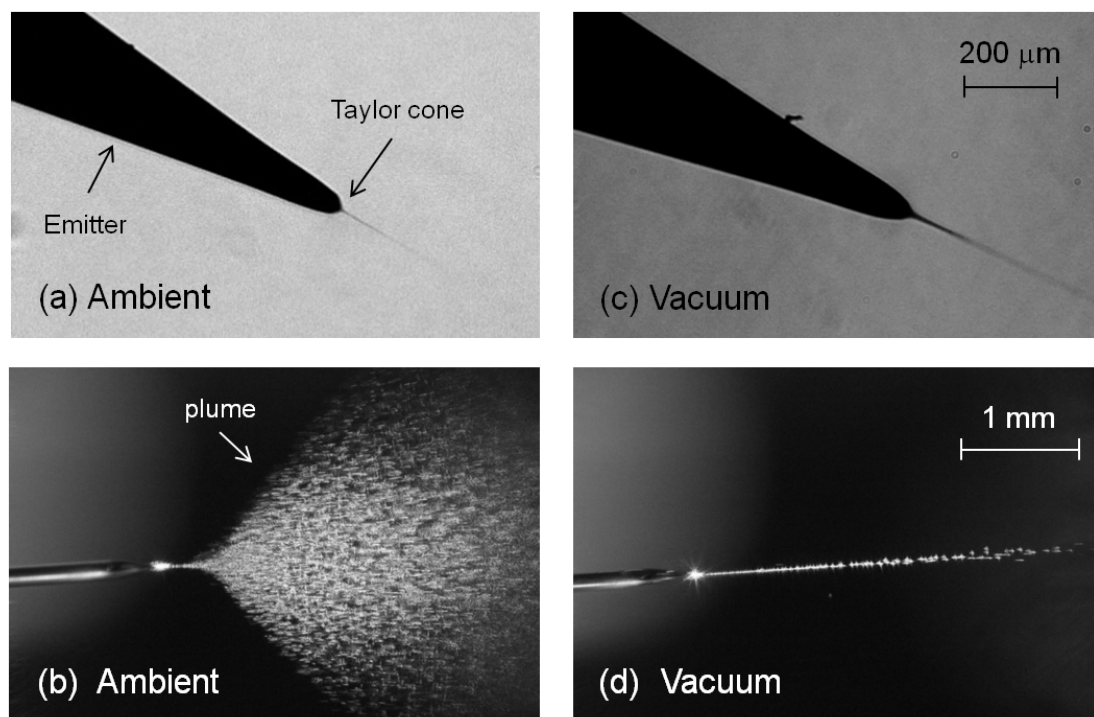


Fig. 2 Images of ambient electro spray observed with a digital microscope (a) and optical microscopy setup (b). Images of vacuum electro spray observed by the digital microscope (c) and optical microscopy setup (d).

setup, respectively. As shown in the Fig. 2 (a), a Taylor cone was formed at the exit of the emitter, and the jet emitted from this cone was also visible. The electro spray plume was not identified in the digital microscope image, whereas the plume was clearly visualized in the optical microscopy setup, as shown in Fig. 2 (b). This electro spray mode is termed “cone-jet mode” [25]. The modes of the electro spray changed as a function of bias voltage, and these trends are typical phenomena of electro spray [26], and the three typical modes of electro spray (pulsed cone-jet, cone-jet, and multi-jet) were observed. In general, for ambient electro spray, the charged droplets generated at the tip of the emitter shrink because of solvent evaporation, and break up into small droplets as a result of excess charge (The point at which this occurs is known as Rayleigh limit [27]). Simultaneously, these droplets are driven away from each other by Coulomb repulsion. From the reasons above, as clearly visualized in the Fig. 2 (b), the wide-angle plume is formed for ambient electro spray.

As already demonstrated in the previous studies, a stable vacuum electro spray of pure water and aqueous solutions can be realized by maintaining appropriate vacuum conditions to prevent the electric discharge and by heating the tip of the electro spray emitter with IR ( $\lambda = 10.6 \mu\text{m}$ ) CO<sub>2</sub> laser [24] or near-IR ( $\lambda = 808 \text{ nm}$ ) diode laser [28] to prevent freezing of these liquids. In the earlier study, the CO<sub>2</sub> laser was adopted to heat these liquids efficiently, because water absorbs this wavelength of light very well (the absorption coefficient in water is  $832 \text{ cm}^{-1}$  [29]). However, fine adjustment of the CO<sub>2</sub> laser irradiation position is too tedious under vacuum condi-

tions, mainly because the laser beam is not visible. On the other hand, the irradiation position of the diode laser in the visible range can be accurately observed with the optical microscope. The absorption coefficient in water at 808 nm is 4 orders of magnitude less than that at  $10.6 \mu\text{m}$  [29]. That is, these liquids are assumed to be indirectly heated by heat transfer from the tip of the electro spray emitter. Nevertheless, each laser can produce similar cone-jet mode of vacuum electro spray, and the effect of bias voltage on the electro spray current for the diode laser was also in good agreement with that found for the CO<sub>2</sub> laser.

Figure 2 (c) and (d) show the images of vacuum electro spray observed with the digital microscope and the optical microscopy setup, respectively. The near-IR diode laser was used to prevent freezing of the liquids in this study. The image of vacuum electro spray with the digital microscope (Fig. 2 (c)) was similar to that of ambient electro spray (Fig. 2 (a)), whereas the snapshots taken with the optical microscopy setup were dramatically different between ambient (Fig. 2 (b)) and vacuum electro spray (Fig. 2 (d)). In the ambient, the formation of the cone-like plume was observed away from the tip of the emitter. In contrast, under vacuum, the straight droplet beam was formed at least with the length of 3.5 mm from the tip of the emitter (Fig. 2 (d)). This must be caused by the fact that the space charge field effect became negligible for the charged droplets that were accelerated by the high electric field in vacuum. In addition, the velocity of the droplets should be sustained, because they rarely collide with residual gases. This is the rationale for the development of vacuum electro spray that

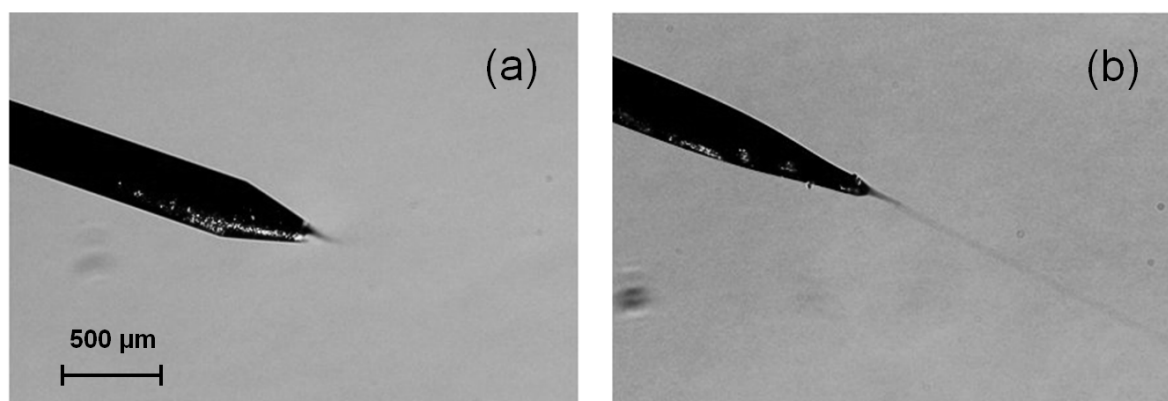


Fig. 3 Microscope images of vacuum electro spray emerging from the stainless steel emitters, with  $\sim 30^\circ$  (a) and  $< 10^\circ$  (b) taper angles.

is suitable for focusing of the beam leading to the high beam density.

The effects of the shape of the emitter on vacuum electrospray were also investigated. The Taylor cone and the resulting electrospray plume were compared for several commercially available electrospray emitters. Microscope images of the vacuum electrospray produced from the stainless steel emitters are shown in Fig. 3. In this study we used two emitters of 50 and 30  $\mu\text{m}$  i.d., respectively, a 0.01 M trifluoroacetic acid (TFA) aqueous solution, and the near-IR diode laser. The plume produced from the tip of the emitter with a taper angle of around  $30^\circ$  could not be identified away from the Taylor cone (Fig. 3 (a)). On the other hand, as clearly shown in Fig. 3 (b), the plume produced from the tip of the emitter with a taper angle below  $10^\circ$  was identified, indicating that the electrospray plume produced from an emitter with such a taper angle goes straight with little dispersion, making it suitable for a primary beam source.

#### 4. Summary

The characteristics of ambient and vacuum electrospray were compared by observing the Taylor cone and the resulting electrospray plume with optical microscopy. In ambient, the wide angle plume was observed away from the tip of the emitter, whereas under vacuum a straight droplet beam with the length of at least 3.5 mm from the tip of the electrospray emitter was clearly observed. The plume formation in vacuum depended on the shape of the emitter tip. An emitter with a taper angle below  $10^\circ$  has clearly produced a visible plume. This vacuum electrospray technique could be expected to be a high-intensity massive cluster beam source, and we are now evaluating the performance of the vacuum-type electrospray droplet beam gun using surface analysis (X-ray photoelectron spectroscopy (XPS) and SIMS).

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