Application of Electrospray Droplet Impact (EDI) to Surface Science

Kenzo HIRAOKA
Clean Energy Research Center, University of Yamanashi
Takeda-4, Kofu, Yamanashi 400-8511
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In Electrospray Droplet Impact (EDI), the charged liquid droplets formed by ambient electrospray are introduced through an orifice into vacuum, accelerated by 10 kV and impact the samples prepared on the metal substrate. The secondary ions are detected by an orthogonal-type time-of-flight mass spectrometer. EDI can afford soft ionization/desorption for various kinds of real-world samples such as biological tissues, dyes, pigments, synthetic polymers, and inorganic materials with no special sample preparation. EDI is capable of atomic- and molecular-level etching with leaving little damage on the etched surface. Moreover, the useful yield (total ions generated divided by the total atoms or molecules desorbed) was found to be larger than $10^{-2}$. Due to these unique natures, EDI may be promising for the next-generation nano-scale 3D imaging.

KEYWORDS : EDI, SIMS, surface analysis, imaging

1. Introduction

Secondary ion mass spectrometry (SIMS) is one of the most powerful techniques for material analysis. A number of studies have shown that the sputtering efficiency of secondary ions is improved by increasing the mass of the primary particles. For example, the $C_{60}^+$ ion enhances high-mass ion yields by factors $>10^3$ or more compared with Ga$^+$, and the damage accumulation rate is lower with C$_{60}^+$ than with Au$_3^+$ ion. Mahoney and coworkers made a pioneering work in generating multiple-charge massive glycerol clusters with the masses of $10^6$-$10^7$ u and the excess charges of $\sim$200 via electrohydrodynamic emission in vacuum using 1.5 M solution of ammonium acetate. Although this method was found to afford extremely soft ionization/desorption conditions for peptides and proteins, stable ion currents can only be obtained for several hours until the lens electrodes become contaminated by accumulated glycerol at which time source cleaning is necessary.

A gas cluster ion beam (GCIB) technology has been proposed by Yamada et al. as a surface smoothing technique. Gas clusters were generated by the supersonic gas expansion. For example, Ar$_n$ clusters with $n$ ranging from a few thousands to more than 10000 could be formed using Laval nozzle with a diameter of 0.1 mm and Ar stagnation pressure of $\sim 1 \times 10^6$ Pa. A characteristic feature of GCIB processing involves inherent surface smoothing effects.

Intrigued by the original work by Mahoney and coworkers, we have developed the electrospray droplet impact (EDI), that uses contamination-free water droplets generated by an ambient electrospray as a cluster source. In this article, the fundamental aspect and its application of EDI to surface analysis will be described.

2. Methodology

The conceptual experimental setup of EDI ion source coupled with an orthogonal time-of-flight mass spectrometer is displayed in Fig. 1. In brief, the charged liquid droplets generated by electrospraying 1 M acetic acid aqueous solution at atmospheric pressure are introduced into the first vacuum chamber through an orifice with a diameter of 400 µm. The voltages applied to the stainless steel capillary (inner diameter : 0.1 mm, outer diameter : 0.2 mm) are +2.2 V.
kV and −1.5 kV in the positive-and negative-mode electrospray, respectively. The charged droplets sampled through the orifice are transported into a 1st quadrupole ion guide for collimation, and accelerated by 10 kV after exiting the ion guide. The electrospray droplets (i.e. the multiply-charged massive clusters) are allowed to impact the solid sample prepared on a stainless steel substrate. The secondary ions formed by the droplet impact are transported into a 2nd quadrupole ion guide for collisional cooling and mass-analyzed by an orthogonal time-of-flight mass spectrometer (AccuTOF, JEOL, Akishima, Tokyo). The typical droplets are roughly represented as [(H\(_2\)O)\(_{100000}\) + 100H]\(^{100+}\). The kinetic energy of the droplet is about 10\(^6\) eV with the velocity of ∼12 km/s. The total current of the electrospray charged droplets irradiated on the target was measured to be ∼1 nA using a Faraday cup installed at the target position.

3. Comparison of EDI with other electrospray-based methods

Aksyonov and Williams developed the IDEM (impact desolvation of electrosprayed microdroplets) method.\(^{16}\) Analytes are dissolved in an electrolyte solution and then electrosprayed in vacuum, producing highly charged micron and submicron sized droplets. These microdroplets are accelerated through potential differences of ∼5–10 kV to velocities of several km/s and allowed to impact on a target surface. The energetic impacts vaporize some of the analyte molecules dissolved in the electrosprayed liquid. Oligonucleotides and peptides yield singly and doubly charged molecular ions with no detectable fragmentation. The basic methodology of the present EDI is similar to IDEM except that the charged droplets are formed by ambient electrospray and the samples are not dissolved in electrospray solution but are deposited on the metal target and ionized/desorbed by the droplet impact. Aksyonov and Williams found that the polarity of the microdroplets generated by positive-mode or negative-mode of electrospray is unrelated to ion formation in IDEM. This is also the case in EDI, that is, similar positive and negative EDI mass spectra were obtained regardless of the polarity of the charged droplets. This indicates that the mechanism for the formation of secondary ions by EDI is unrelated to the excess charges contained in the water droplet projectile.

In 2004, Cooks et al. developed a new desorption/ionization method called DESI (desorption electrospray ionization).\(^{21}\) The difference between DESI and EDI may be worth noting. As shown in Fig. 2, DESI is one of the ambient (atmospheric-pressure) ionization methods. Solid samples are partly dissolved by electrosprayed solvent droplets (methanol is mainly used), picked up by the electrospray charged droplets, ionized by the excess charges of the droplets, and gas-phase ions are generated from the charged droplets. The speed of the nebulized droplets is about 120 m/s. In EDI, the electrospray droplets are accelerated in vacuum by 10 kV and impact the sample placed on the metal substrate. The speed of the droplets is about 12 km/s. This value is about one order of magnitude larger than the sonic velocities of solids and thus \textit{supersonic collision} takes place upon collision with the surface resulting in unique ionization mechanism as described below. As such, the mechanisms for desorption/ionization of DESI and EDI are totally different.

4. Soft and high-sensitive ion formation

Analysis of large molecules by small-size particle
bombardment (e.g., Ar\(^{+}\), Ga\(^{+}\)) is typically characterized by low secondary ion yields, an intense chemical background, and extensive degradation of sample molecules. Thus the projectiles that make it possible to perform soft and high-sensitive ionization are highly demanded. We examined whether these demands are satisfied by EDI.\(^{18-20, 22-36}\) Figure 3 displays the EDI mass spectrum for 10 fmol gramicidin S deposited on the stainless steel substrate. The [M + H]\(^{+}\) ion could be detected as a major ion with S/N ratio of about 30. The left inset shows the ion intensity for [M + H]\(^{+}\) as a function of irradiation time. The ion [M + H]\(^{+}\) could be detected for as long as 30 min. Generally speaking, the sensitivity for EDI is about the same with that for MALDI. However, EDI does not need any special sample preparations, e.g., no matrix is necessary. The soft and high-sensitive ionization by EDI should be due to the high-momentum supersonic collision that induces vibronic excitation for molecules in the colliding interface.

5. Atomic-and molecular-level etching

EDI is a surface-sensitive method and only a very thin top layer of samples is ionized/desorbed.\(^{18, 22, 34}\) If the kinetic energy of the projectile is dissipated mainly as kinetic energies for the target atoms in the colliding interface, considerable sputtering and fragmentation of sample materials must take place. However, EDI is almost free from the serious damage of the sample materials after irradiation since molecular ions are observed as base peaks with much less fragment ions (see Fig. 3).

Figure 4 shows the EDI mass spectra for the self-assembled monolayer Au-(CH\(_2\))\(_6\)-NH\(_2\) as a function of irradiation time. At the beginning of the measurement (0.5 min), the ion abundances of [M + H]\(^{+}\), [2M + H]\(^{+}\), and [2M + Au]\(^{+}\) (M denotes HS-(CH\(_2\))\(_6\)-NH\(_3\)) are observed as major ions and that of Au\(^{+}\) is in the noise level. This clearly indicates that only the monolayer organic molecules are selectively ionized/desorbed. In Fig. 4 a gradual growth of Au\(^{+}\) is observed at the expense of [M + H]\(^{+}\), [2M + H]\(^{+}\), and [2M + Au]\(^{+}\) ions. Gold cluster ions Au\(_n^{+}\) were not detected for a prolonged EDI irradiation time. Only the appearance of Au\(^{+}\) clearly indicates that no ablation of gold substrate takes place by EDI. Namely, molecular-level desorption for SAM and atomic-level etching for Au substrate are realized by EDI.

As mentioned above, EDI is capable of soft
ionization with high-ionization efficiencies and of molecular-level surface etching. These characteristic features suggest that more or less adiabatic collision takes place between the water droplets and the solid surface, i.e., momentum transfer from the water droplets to the sample surface is suppressed to minimal. The H atoms in water droplet projectiles have the lightest mass among all the elements. Because of its lightest mass, the hydrogen atoms in the droplet surface are likely to backscatter in the supersonic collision with the surface atoms that have higher masses than hydrogen atom (forward scattering will result in surface damage). This may be envisaged by the backscattering of ping pong ball collided with the billiards ball. Right after the instant coherent collision (i.e., all the water molecules in the droplet have the same velocity and direction toward the surface), enormous pressure would be exerted at the colliding interface as the collective force due to the high-momentum water droplet impact. This induces the collective in-phase motion of atoms at the interface for collided water droplet and also for the sample. The in-phase motion will result in the shock wave propagation in the colliding systems. Since water droplets are composed of strong hydrogen bond networks, the efficient propagation of shock wave is anticipated in water droplet, i.e., the conversion of kinetic energy to dispersive shock wave in the colliding system. In a sense, the kinetic energy of water droplets is efficiently converted to internal energies in supersonic collision in EDI.

6. Application of EDI to inorganic, organic and biological samples

Some comparative studies were made for the surface characterization by XPS in Ar⁺ and EDI etching for inorganic and organic samples. Marked surface modification (e.g., selective etching) took place by Ar⁺ etching for all the samples examined. In contrast, no recognizable chemical modification was observed by EDI for all of the inorganic and organic materials investigated. As an example, experimental results obtained for indium phosphide (InP) will be shown.³⁴ For the surface analysis of InP by SIMS, it is of paramount importance to avoid the selective etching of P with respect to In and also to suppress the growth of etching cones on the surface. The surface topology of InP(111) etched by 3 keV Ar⁺ and EDI was examined by AFM. **Figure 5** (a)-(c) show the AFM images of InP(111) as received, etched by 3 keV Ar⁺ (etching rate : 2 nm/min as calibrated for SiO₂) for 30 min and etched by EDI (etching rate : ∼0.2 nm/min as calibrated for SiO₂) for 240 min, respectively. The etching depth for Ar⁺ impact and EDI are ∼60 and ∼48 nm, respectively, as calibrated for SiO₂. On the surface of InP(111) etched by Ar⁺ (Fig. 5 (b)), growth of etching cones is observed. The etching cones are known to be formed for InP when analyzed by conventional SIMS. The component on the top of the etching cone is mainly composed of In, i.e., phosphorus is preferentially sputtered by Ar⁺.³⁴ Compared with Fig. 5 (b), the surface of InP(111) etched by EDI is much smoother as shown in Fig. 5 (c). The average surface roughness (1.2 nm) after EDI etching (∼48 nm etching depth as calibrated for SiO₂) became only slightly greater than that of the sample as received (0.8 nm). In contrast, more than one order of magnitude greater roughness (16.7 nm) was observed for InP etched by 3 keV Ar⁺ (∼60 nm etching depth as calibrated for SiO₂).

The relative concentrations of In and P for InP etched by 3keV Ar⁺ and EDI were measured by XPS.

![AFM images (2 µm × 2 µm) for indium phosphide (InP). (a) As received; (b) etched by 3 keV Ar⁺ (etching depth of ∼60 nm as calibrated for SiO₂); (c) etched by EDI (etching depth of ∼50 nm as calibrated for SiO₂).](image-url)
The ratio of In to P (i.e., In/P) increased from 1 to 1.7 for 3 keV Ar⁺ etching. Apparently, P was etched more preferentially than In by 3 keV Ar⁺. In contrast, the ratio In/P was found to be 1.0 after EDI etching. Namely, preferential etching for InP does not occur in EDI. It was also found that the FWHM of In 3d_{5/2} and P 2p peaks for XPS spectra did not change before and after EDI etching. That is, crystalline structure of InP (111) is preserved and amorphatization does not take place by EDI. Similar results were obtained for SiO₂/Si and HF-treated Si. 34

EDI was applied to various synthetic polymers such as polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyimide (PI), polystyrene (PS), and polymethyl methacrylate (PMMA). 29, 32, 33, 35 The EDI mass spectra are found to be composed of fragment ions that reflect the molecular units of the polymer backbones. That is, random dissociation of polymer structure seems to be minor. In order to obtain more detailed information on the etching process by EDI, XPS was applied to the surface analysis for all the polymers investigated. As an example, the O 1s, N 1s, and C 1s XPS spectra of PI as a function of EDI irradiation time are shown in Fig. 6. 35 All the peaks for O, N, and C show little changes by EDI etching up to 120 min. That is, neither selective etching of oxygen and nitrogen nor accumulation of the radiation products on the sample surface takes place as far as the XPS measurements are concerned. In other words, surface damage if there is any formed on the surface is not detectable by the conventional XPS analysis. Similar results were obtained for all polymers investigated (PET, PVC, PS, and PMMA).

EDI/SIMS was applied to mouse brain as the biological tissue sample. In the positive-mode of operation, various kinds of PC (phosphatidylcholin) and GalCer (galactosylceramide) could be detected. In the separate experiments, MALDI measurements using DHB as a matrix were also made for comparison with EDI. The S/N ratios for positive-mode mass spectra obtained by EDI and MALDI were similar for PC and GalCer. That is, the sensitivities of EDI and MALDI are about the same. In contrast, negative-mode mass spectra obtained by EDI and MALDI have some distinct difference as shown in Fig. 7. While PE, PS, PI and ST are detected in EDI mass spectrum, PE and PS are absent in MALDI mass spectrum. That is, EDI is capable of more non-selective ionization for the biological molecules. The high efficiency of the formation of positive and also negative ions by EDI may be interpreted as follows.

7. Mechanism for the secondary ion formation

One of the characteristic features of EDI is its capability of formation of strong negative ions as well as positive ions for many organic compounds, e.g., amino acids, 22 peptides, 19 pigments, 23 etc. For example, both basic and acidic amino acids gave as strong negative ions [M−H]⁻ as the positive ions [M+H]⁺ with about equal ion abundances. 22 This suggests that EDI has some unique nature for the formation of secondary ions. The efficient formation of positive and also negative ions may be ascribed to the disproportionation proton transfer reaction of

Fig. 6. (color online). O 1s, N 1s, and C 1s XPS spectra of PI measured as a function of EDI irradiation time.

Fig. 7. Negative-mode mass spectra of homogenized mouse brain obtained by (a) EDI/SIMS, and (b) MALDI (matrix : 2,5-dihydrobenzoic acid (DHB)). PE : phosphatidylethanolamine, PS : phosphatidyserine, PI : phosphatidylinositol and ST : sulfatide. Insets : Enlarged mass spectra obtained by (a) EDI and (b) MALDI (matrix : DHB) for mouse brain in the range of m/z 750–950.
water molecules, i.e., the occurrence of electrolytic dissociation reaction of water molecules in the colliding interface.\textsuperscript{22–24)}
\[ H_2O + H_2O \rightarrow H_2O^+ + OH^- \quad (1) \]
Endoergic reaction (1) may be one of the primary routes for the energy dissipation of the colliding system. The $H_2O^+$, hydronium ion, is known to be a very strong acid, and likely to transfer its proton to the analyte to form protonated molecule $[M + H]^+$ in the colliding interface.
\[ H_2O^+ + M \rightarrow [M + H]^+ + H_2O \quad (2) \]
The occurrence of reaction (2) explains the strong appearance of $[M + H]^+$ for molecules that have larger proton affinities than $H_2O$ (691 kJ/mol).

The $OH^-$ in reaction (1) is also known to be a very strong base and it deprotonates from M to form $[M - H]^-$. \[ OH^- + M \rightarrow [M - H]^- + H_2O \quad (3) \]
In a sense, very strong acid $H_2O^+$ and also very strong base $OH^-$ are inherently incorporated in the supersonic collisional events in EDI.

In EDI mass spectra, some compounds give strong radical cations and anions (e.g., $C_{60}$, coronene, and organic pigments\textsuperscript{23)}) in addition to $[M + H]^+$ and $[M - H]^-$ ions. For example, in EDI mass spectra for $C_{60}$, $C_{60}^+$ and $C_{60}^-$ ions are observed with about equal abundances.\textsuperscript{20) We conjecture that these ions may be formed by the disproportionation electron transfer reaction (4) caused by the supersonic collision in EDI.\textsuperscript{23)}
\[ M + M \rightarrow M^+ + M^- \quad (4) \]

The MALDI mass spectrum in Fig. 7, PE and PS are not detected when DHB (a typical matrix for MALDI) is used. The ion formation mechanism for MALDI using DHB as a matrix may be ascribed to reaction (5). Here it should be recognized that DHB is one of the organic acids and acts as a protonating reagent.

\[ DHB + M \rightarrow [DHB - H]^- + [M + H]^+ \quad (5) \]
The $[DHB - H]^-$ ion, the reaction product in reaction (5), may act as the deprotonating reagent for the formation of negative ions of the analyte.

\[ [DHB - H]^- + M \rightarrow [M - H]^- + DHB \quad (6) \]
However, the basicity of $[DHB - H]^-$ is much weaker than that of $OH^-$ because the negative charge in $[DHB - H]^-$ is well delocalized in the whole molecular ions and the occurrence of reaction (6) is much less likely compared with reaction (3). This may explain the absence of the negative ions of PE and PS in the MALDI mass spectrum in Fig. 7.

8. High useful yields of EDI

In general, dyes and surface-active agents gave lower limits of detection (detectable with higher sensitivities) compared with neutral compounds because they have ionic forms and only desorption may give gaseous ion signals. As shown in Fig. 8, the limits of detection for rhodamine B and aerosol OT are 1 fmol and 100 amol, respectively. On the other hand, the limits of detection for neutral compounds are found to be about 10 fmol or less as shown in Fig. 3. The detection limit of $C_{60}$ was also found to be about 10 fmol. The lower limits of detection for neutral compounds are reasonable because ionization processes are necessary for the detection of neutral molecules as ion signals. In here, if one assumes that the desorption efficiencies are roughly the same for neutral compounds (e.g., gramicidin S and $C_{60}$) and ionic compounds (e.g., rhodamine B and aerosol OT) in EDI, useful yields (i.e., total ions generated divided by the total atoms or molecules desorbed) may be crudely estimated to be 0.01 (100 amol/10 fmol) or 0.1 (1 fmol/10 fmol). These values are about $10^3$ greater than the estimated values for other techniques (e.g., SIMS, cluster SIMS and MALDI), $10^{-5}$–$10^{-6}$. That is, EDI improves the useful yields by a factor of about $10^3$ compared with SIMS and MALDI. This unprecedented high value of the useful yield is mainly due to the two factors, one is the very high ionization efficiencies for neutral compounds and another is the molecular-level desorption of the sample molecules.

Fig. 8. EDI mass spectra for 1 fmol rhodamine B (positive-mode), and 100 amol aerosol OT (negative mode).
9. Summary

The characteristic features for EDI may be summarized as follows.

1. EDI utilizes the water droplet projectiles, typically represented as \([\text{H}_2\text{O}]_{10000}^+ + 100\text{H}\)^{+0}.

2. The kinetic energy of the droplet is about \(10^6\) eV with the velocity of \(\sim 12\) km/s. Since this velocity is about one order of magnitude higher than the sound velocities of solids, the supersonic collision takes place in EDI, resulting in the ionization/desorption of the sample atoms and molecules.

3. In general, the molecular ions are observed as base peaks with weaker fragment ions.

4. In EDI, atomic-and molecular-level etching take place with little damage left on the surface after EDI.

5. From the limits of detections for neutral and ionic compounds, the useful yields of EDI were estimated to be \(10^{-1}-10^{-2}\). These values are about \(10^6\) times higher than those for MALDI and conventional SIMS.

These unique natures of EDI are mainly ascribed to the efficient dissipation of kinetic energy of the projectile as the internal energies of the molecules in the colliding interface and also as the shock wave propagating through the hydrogen bonded water projectile.

If the diameter of the beam of the water droplet projectiles could be focused to submicron, EDI may be a useful method for 3D nano-imaging for organic and biological materials. A further investigation on this respect is in progress in our laboratory.

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