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Full Length Article

# ToF-SIMS analysis of an organic layer using toluene and its cluster ion beam projectiles generated by multiphoton ionization

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ABSTRACT

Secondary ion mass spectrometry (SIMS) has become a powerful tool for a chemical imaging of surfaces. In particular, cluster ion beams have been widely implemented with SIMS using spatial distributions of molecules as an analysis and imaging method for a sample composed of organic molecules. In this study, we developed a home-built time-of-flight (ToF)-SIMS instrument and generated organic molecular cluster ion beams ionized by multiphoton ionization (MPI) as a primary ion beam. Further, the sample stage loaded with rhodamine 6G was bombarded with size-controlled toluene cluster ions to produce secondary ions. Mass spectra of rhodamine 6G were acquired as a function of the size of toluene cluster ions. We plotted the fragments-to-parent ion ratio against each size of cluster ion, and we found that an intact rhodamine 6G signal would be observed with less fragmentations using $(\mathrm{Tol})_{n > 18}{}^{+}$. We expect this combination of the organic molecular cluster ion beam generated by MPI and ToF-SIMS to greatly expand the field of surface analysis.

## 1. Introduction

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is becoming an essential tool in the molecular and imaging analysis fields of mass spectrometry owing to its sensitivity and ability to monitor the distribution of elements or molecules [1–4]. SIMS has previously been used to explore the two-dimensional distribution of metallic atoms, small fragments, and rigid small molecules on surfaces because the primary ion beam has too-high energy to retain a whole molecule without any fragmentation. In addition, ToF-SIMS can be used to analyze surface depth information since a typical characteristic of the high-energy primary ion beam is the removal of elements from the sample surface [5–7]. With two-dimensional (2D) imaging coupled with depth profiling, three-dimensional (3D) distributions of sample components can be determined [8–12].

With increasing the concern about life sciences, 2D imaging of bio-samples determined by the distribution of an intact organic molecule is becoming an important techniques. Therefore, various kinds of cluster ion beams have been developed to avoid molecular damage or loss of information during the analysis of the intrinsic properties and structures of surfaces. In particular, these types of gas cluster ion beams (GCIBs) have been developed and applied as primary ion beams for bio-analysis, since GCIB is widely known [13]. Fletcher et al. showed that the higher energy and larger size of GCIBs were advantageous for ToF-SIMS applications in biology [14,15]. $CO_2$-GCIB-SIMS was applied for the imaging of lipids at sub-micrometer levels [16]. Further, water clusters also showed potential for a ToF-SIMS bio-applications due to the enhanced secondary ion yield from a bio-sample [17,18]. Multiple charged water droplets were used to produce protonated species from surfaces by using the electrospray droplet impact (EDI) ionization technique [19–21]. Thus, new types of cluster ion beam sources are being continuously developed to analyze organic molecules, including for surface bio-applications.

We proposed to utilize a size-selected primary ion beam generated by multiphoton ionization (MPI) applied for the organic molecular analysis based on ToF-SIMS here. This kind of photoionization (PI) traditionally used to produce molecular cluster ions in the gas phase [22] is more tractable since photons are not affected by the electric field. PI can be used to ionize weakly bound molecules retained by their cold internal temperature by virtue of a supersonic expansion because the photon energy used here has a smaller impact on the neutral species to be ionized than dose a typical electron impact ionization (EI) method. Our organic molecular cluster ion produced by PI can be easily broken when it collides with the surface due to its weak binding energy, which means it still possesses the advantages of a cluster ion beam, including a soft sputtering without subsurface damage. A cluster ion selected by mass gate with regard to its flight time has a narrower energy distribution than a commercial gas cluster ion beam selected by

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a Wien filter [23]. Thus, better mass resolution for the secondary ion mass spectrum is expected because a fairly well-defined $(Tol)_{10}^{+}$ brings us a better mass resolving power, compared to commercial Ar GCIB. In the present work, we developed a ToF-SIMS instrument with organic molecular cluster ion beam projectiles generated by PI. Mass spectra acquired by this instrument are shown. Ions of rhodamine 6G, which is a representative organic molecular dye, were produced from the surface and secondary ion signals and were monitored by changing the size of toluene clusters.

## 2. Materials and methods

A home-built ToF-SIMS instrument was developed with a source for primary ion beams produced by MPI. All components of our home-built ToF-SIMS were easily adapted in accordance with the purpose of the designed experiments.

Toluene was purchased from Sigma-Aldrich, used without further purification, and filled into a small chamber for vaporization by bubbling with Ar gas at a pressure of ~2 bars. The vapor was co-expanded through the orifice of a continuous nozzle. After the supersonic expansion of molecules, the neutral molecular beam passed through a skimmer with a 500 μm diameter. The 4th harmonic generation of the Nd: YAG laser (266 nm, 4 mJ/pulse, 3–4 ns pulse width, 10 Hz, Minilite, Continuum, CA, USA) was used to irradiate the molecular beam in the acceleration region to cause ionization. The molecule and its cluster ions produced by MPI were accelerated with 10 kV and focused them by using the 1st einzel lens. Focused ions were passed through the mass gate by applying a negative high voltage pulse (1.1 kV) at a specific time to control the size of a particular toluene cluster ion (see Table S2). Size-controlled toluene cluster ions were focused again using the 2nd einzel lens to prevent the diffusion of the ion beam and increase the number of ions per unit area. They were then investigated by using an on-axis double multichannel plate (MCP)-phosphor screen module that observed the cross-section of a selected molecular ion beam and checked the mass spectrum of a selected molecular ion beam by adding a photomultiplier tube (PMT).

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The sample stage mounted at the xyz manipulator (EC series, Thermionics, WA, USA) was lowered to block the primary ion beams produced by MPI. A size-controlled toluene and its cluster ions were accelerated to the sample stage to generate secondary ions. Therefore, the secondary ions sputtered by 10 keV toluene and its cluster ion projectiles were accelerated to the field free region of the ToF-MS by a 2 kV positive pulse. The timing of the acceleration pulse was determined by measuring the *m/Δm* value as a function of time. Further, the acceleration pulse timing at the maximum was plotted according to the square root of the mass-to-charge ratio (see Fig. S1) and this plot was well fitted for a linear equation that could be applicable for bigger toluene cluster ions. The cluster ions were observed using a 40 mm double MCP (see Fig. 1 in detail). All ion signals were digitized and averaged by a digital storage oscilloscope (MDO4104B-6, Tektronix, OR, USA). In this experiment, a rhodamine 6G dye [24–26] was painted directly on a stainless steel plate (6 × 6 mm, 1 mm thick) from the red pen composed mainly of rhodamine 6G. This plate was drawn with a single stroke of a pen and attached on the sample stage to evaluate the

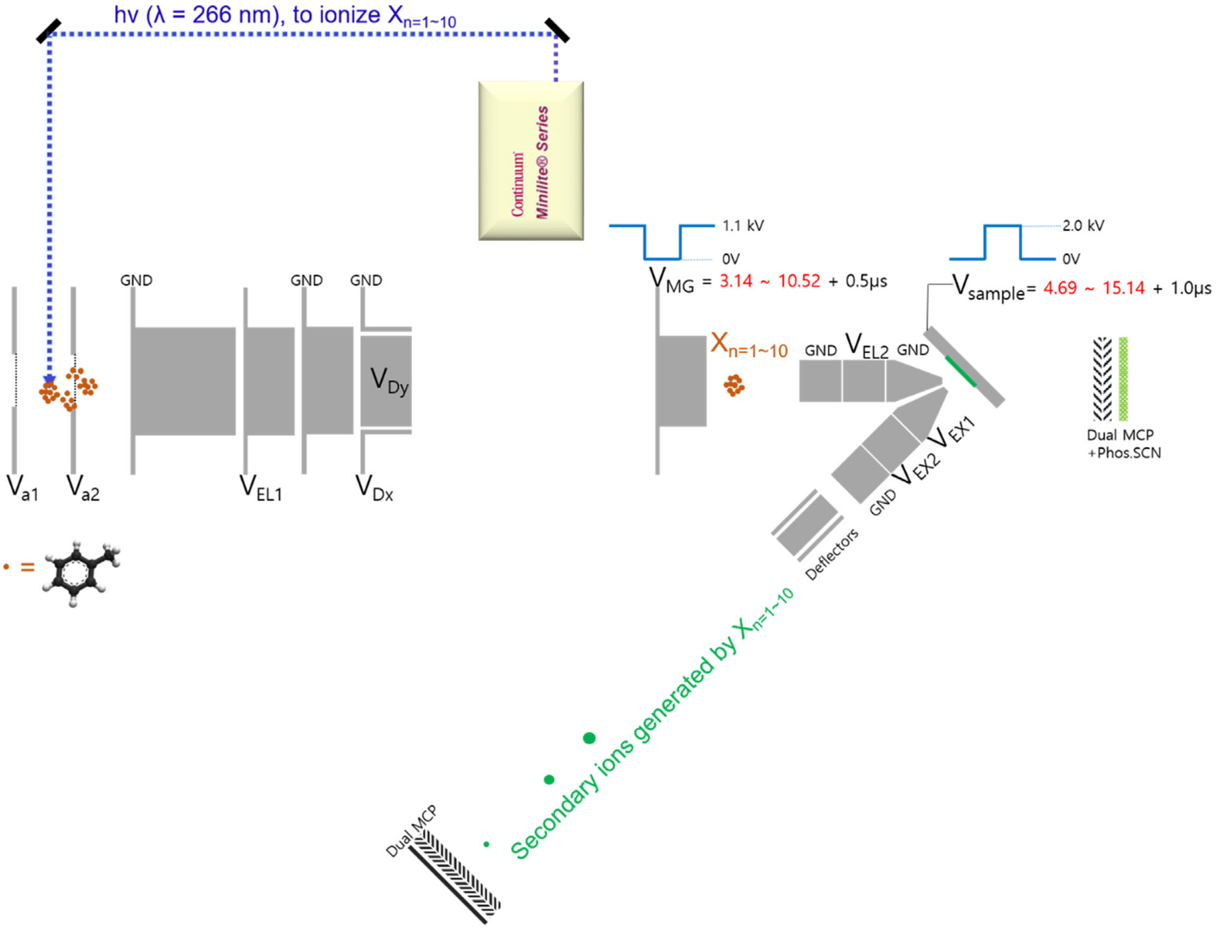

**Fig. 1.** General schematic diagram of the apparatus, consisting of acceleration electrodes ($V_{a1}$, $V_{a2}$, and grounded plate), 2 einzel lens sets ($V_{EL1}$ and $V_{EL2}$), 2 deflector sets ($V_{Dx}$ and $V_{Dy}$), a mass gate ($V_{MG}$), an on-axis detector for the primary ion beam, a sample stage ($V_{sample}$), extraction electrodes ($V_{EX1}$ and $V_{EX2}$), 2 deflector sets for the secondary ion (see Table S2 in detail).