Development of Mass Spectrometer Using Two Rotating Electric Fields for Separation of High-Mass Ions

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We developed a mass spectrometer with a novel mass-separation mechanism using two rotating electric fields (REFs). This mass spectrometer realizes a wide mass range with the continuous separation of ion beams. In principle, it has no limitation on the mass range. It can be operated stably for the detection of high-mass ions. To estimate the mass-separation ability, we directly introduced the mass spectrometer, which consists of two REFs, to a Ga focused ion beam column. The mass spectra of Ga isotopes were obtained by sweeping the frequencies of the REFs. The peaks of the Ga isotopes were clearly separated on the mass spectra.

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I. INTRODUCTION

Recently, Ar gas cluster ion beams (GCIBs) have been used as the primary ion beam in secondary ion mass spectrometry (SIMS). The irradiation of cluster ions increases the secondary ion yields of molecular ions and typical fragment ions [1]. Cluster ions decompose at the sample surface and distribute their own kinetic energies depending on the incident cluster sizes. Accordingly, fragmentation patterns, which depend on the irradiation energy, can be controlled by cluster-size filtering [2, 3]. However, existing mass filters are not suitable for cluster-size filtering, because of their focusing properties and mass resolution.

In this study, we developed a novel mass spectrometer that realizes a wide mass range with the continuous separation of ion beams. In principle, this mass spectrometer has no limitation on the mass range. It can be operated stably for the detection of high-mass ions.

Therefore, it is applicable to mass filters for massive cluster ion beams such as Ar-GCIB and water cluster ion beams. The mass spectrometer selects and separates a specific ion from other ions using two rotating electric fields (REFs) aligned on the same axis [4]. The phases of each REF are opposite for the selected ion. We control the cycle of the REF to be the travel time of the
selected ion in each REF. First, the ions enter the upstream REF. We define \( z \) as the direction of the ions; the trajectory of the selected ion resembles a cycloid in the \( x-y \) plane, as shown in Fig. 1. The cycloid spans from the center axis to the outside. Furthermore, the selected ion has opposite phases between the upstream REF and the downstream REF. It returns to the center axis and exits the downstream REF without velocity components in the \( x-y \) plane. We can select which ions return to the center axis by tuning the frequencies of the REFs.

We connected this mass spectrometer to a Ga focused ion beam (FIB) column and separated the Ga isotopes contained in the liquid metal ion source in order to estimate the mass-separation ability.

## II. PRINCIPLE OF THE MASS SPECTROMETER USING TWO REFS

### A. Operation method of REFS

In this mass spectrometer, two REFs are aligned on the same axis. We arrange cylindrical electrodes divided into eight pieces at symmetric positions. Figure 2 indicates that the cylindrical electrodes on the concentric circle generate a uniform REF inside the electrodes [5–7]. These electrodes are applied sinusoidal waves corresponding to each position. The sinusoidal waves \( \phi_i \) are as follows:

\[
\phi_i = V \cos(\omega t + \beta_i) \\
\beta_i = \frac{\pi}{4} i \tag{1}
\]

where \( \omega \) is the angular velocity of the sinusoidal waves, \( V \) is the amplitude of the sinusoidal waves, and \( t \) is time. The sinusoidal waves generate REFs with the same cycles. Therefore, we can control the cycles of the REFs by varying the cycles of the sinusoidal waves. We control the cycle of the REF to be the travel time of the selected ion in each REF. Assuming that the energy distribution of the selected ions is negligible, the cycle of the REF, \( \tau \), is given as

\[
\tau = \frac{1}{f} = L \sqrt{\frac{m}{2qV_{acc}}} \tag{2}
\]

where \( f \) is the frequency of the REF, \( L \) is the length of the REF, \( V_{acc} \) is the accelerating voltage of the selected ion, \( m \) is the mass weight of the ion for measurement, and \( q \) is the charge of the selected ion. \( m/z \) is given as

\[
\frac{m}{z} = \frac{2eV_{acc}}{f^2 L^2} \tag{3}
\]

where \( z \) is the valence number of the ion, and \( e \) is the quantum of electricity. If we define \( \alpha \) as the incident-angle distribution of the ions, \( m/z \) is given as

\[
\frac{m}{z} = \frac{2eV_{acc} \cos^2(\alpha)}{f^2 L^2} \tag{4}
\]

### B. Ion trajectory in REFs

We define \( z \) as the direction of the ions. Assuming that the field strength of the REF is constant, without dependence on the position of the selected ion, the motion equations for the selected ion in the upstream REF are as follows:

\[
m \frac{d^2x}{dt^2} = qE \cos(\omega t) \tag{5}
\]

\[
m \frac{d^2y}{dt^2} = qE \sin(\omega t) \tag{6}
\]

\[
m \frac{d^2z}{dt^2} = 0, \tag{7}
\]

where \( E \) is the field strength of the REF. Integration of these motion equations gives the velocity and the position of the selected ion, as follows:

\[
\frac{dx}{dt} = \frac{qE}{m_\omega} \sin(\omega t) \tag{8}
\]

\[
\frac{dy}{dt} = \frac{qE}{m_\omega} (1 - \cos(\omega t)) \tag{9}
\]

\[
\frac{dt}{dl} = \sqrt{\frac{2qV_{acc}}{m}} \tag{10}
\]

\[
x = \frac{qE}{ma^2} (1 - \cos(\omega t)) \tag{11}
\]

\[
y = \frac{qE}{ma^2} (\omega t - \sin(\omega t)) \tag{12}
\]

\[
z = \sqrt{\frac{2qV_{acc}}{m} l} \tag{13}
\]

Here, we assume that there are no velocity components of the ion in the \( x-y \) plane at \( t = 0 \). Equations (11) and (12) indicate that the ion trajectory resembles a cycloid in the \( x-y \) plane. Substituting \( \omega t = 2\pi \) in Eqs. (8), (9), (11), and (12) reveals that the selected ion exits the upstream REF at \( (x, y) = (0, EL^2/4\pi V_{acc}) \) without velocity components in the \( x-y \) plane. Therefore, the selected ion exits the upstream REF with the same trajectory, without dependence on its own mass, because of the frequency optimization. The trajectory of the selected ion between the upstream and downstream REF is parallel to the center axis. Other ions have different trajectories from the selected ion. Furthermore, the selected ion has opposite phases between the upstream REF and the downstream.
REF. The motion equations for selected ion in the downstream REF are as follows:

$$m \frac{d^2 x}{dt^2} = qE \cos(\omega t - \pi)$$

(14)

$$m \frac{d^2 y}{dt^2} = qE \sin(\omega t - \pi)$$

(15)

$$m \frac{d^2 z}{dt^2} = 0.$$  

(16)

Integration of these motion equations gives the velocity and position of the selected ion, as follows:

$$\frac{dx}{dt} = -\frac{qE}{m_0} \sin(\omega t)$$

(17)

$$\frac{dy}{dt} = \frac{qE}{m_0} (\cos(\omega t) - 1)$$

(18)

$$\frac{dt}{dt} = \sqrt{\frac{2qV_{acc}}{m}}$$

(19)

$$x = \frac{qE}{m_0} \cos(\omega t - 1)$$

(20)

$$y = \frac{qE}{m_0} (\sin(\omega t) - \omega t + 2\pi)$$

(21)

$$z = \sqrt{\frac{2qV_{acc}}{m}} t.$$  

(22)

The ion trajectory resembles a cycloid rotated $180^\circ$ from the upstream REF. Substituting $\omega t = 2\pi$ in Eqs. (17), (18), (20), and (21) reveals that the selected ion exits the downstream REF at $(x,y) = (0,0)$ without velocity components in the $x$-$y$ plane.

III. EXPERIMENTAL

We connected a mass spectrometer consisting of two REF units to a Ga-FIB column (FIB30, A&D Company, Ltd.), as shown in Fig. 3. The diameters and lengths of the REF units were 20 and 150 mm, respectively. The distance between the upstream REF unit and the downstream REF unit was 70 mm. An aperture unit, a Faraday cup, and a fluorescent screen were located behind the mass spectrometer. We used a fluorescent screen made of a glass substrates coated with $Y_2O_3:S:TB^{3+}$ [8]. The aperture unit and Faraday cup were movable. We switched between the image-observation mode on the fluorescent screen and the ion-beam current detection mode.

We introduced a direct digital synthesizer (DDS) to generate the sinusoidal waves for the REFs. The DDS output the sinusoidal waves with 16 different-phase channels. Each output sinusoidal wave was amplified by a high-frequency, high-voltage power amplifier and applied to an electrode of the REF unit.

The accelerating voltage of the Ga-FIB was 10 kV. The potential of each sinusoidal wave was 230 V (peak to peak). First, we set the image-observation mode and optimized the phase contrast between the upstream REF and downstream REF to make the phases of each REF mutually opposite for the selected ion. The phase contrast depended on the travel time of the selected ion between the upstream REF and the downstream REF. The selected ions converged to the center axis because of the optimized phase contrast. Then, we set the movable aperture unit and measured the ion-beam current. The diameter of the aperture was 50 $\mu$m. The mass spectra of Ga isotopes were obtained by sweeping the frequencies of the REFs from 1,120 to 1,090 kHz in steps of 1 kHz.

IV. RESULTS AND DISCUSSION

Figure 4(a) shows the mass spectrum assuming the lengths of the REFs to be 150 mm. The peaks of $^{69}\text{Ga}^+$ and $^{71}\text{Ga}^+$ were clearly separated; however, the peaks were shifted to the high-mass region. This peak shift was apparently caused by the fringing fields near the opening ends of the cylindrical electrodes. Figure 5 shows the numerical solution of the electric field near the opening end in the $x$-$z$ plane. The figure indicates that the effective lengths of the REFs were greater than the actual lengths of the cylindrical electrodes because of the fringing fields. Accordingly, we calibrated the effective lengths of the REFs to the precise positions of the peaks. Figure 4(b) shows the mass spectrum assuming the effective lengths of the REFs to be 150.34 mm. The peak area ratio of $^{69}\text{Ga}^+ : ^{71}\text{Ga}^+$ was 0.595 : 0.405. The relative error between this value and the natural abundance is

FIG. 3. Overview of the Ga-FIB column and two REF units. (a) Photo and (b) schematic of this system.

FIG. 4. Mass spectra of Ga isotopes. The $m/z$ values were calculated with (a) $L = 150$ mm and (b) $L = 150.34$ mm.
The mass resolution \( m/\Delta m \) was estimated to be 158 according to the full width at half maximum (FWHM). It appears that the mass resolution was affected by the energy distribution, the incident-position distribution, the incident-angle distribution, and the precision of the amplified sinusoidal waves. Generally, the FWHM of the energy distribution of Ga-FIB is lower than several electron-volts [9]. Under the condition that the potential of each sinusoidal wave was 230 V, the deflection of the selected ion by the REFs was constant. Therefore, the selected ion exits the REFs with the same trajectory, without dependence on the incident-position. In addition, the incident-angle distribution of this system was smaller than 0.02 mrad. Accordingly, we presume that the energy, incident-position and incident-angle distributions were small enough to be negligible. On the other hand, the standard deviations of the amplified sinusoidal waves were 2.24 and 1.66 V in the upstream REF and the downstream REF, respectively. This indicates that the precision of the amplifier was the main factor affecting the deterioration of the mass resolution.

V. CONCLUSION

We developed a mass spectrometer with a novel mass-separation mechanism using two REFs. We directly introduced this mass spectrometer to a Ga-FIB column and demonstrated its mass-separation ability. The mass spectrometer clearly separated Ga isotopes. Selected ions converged to the center axis as the frequencies of the REFs corresponding to each mass ion were tuned. A mass spectrum of Ga isotopes was obtained by sweeping the frequencies of the REFs. The mass separation was achieved at mass resolution of 158.

VI. FUTURE PERSPECTIVE OF REFs

The proposed mass spectrometer can separate Ar-GCIB for up to 1,500 atoms/cluster with a precision of 1% or less. The mass resolution is sufficient for cluster-size filtering. However, it is presently insufficient for application to secondary ion optics for SIMS. The mass resolution must be improved for many applications in mass spectrometry.

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