

Mass Separation of AuGe-LMIS Using a New Principle: Rotating Electric Fields

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Abstract

We have been developing a new principle type mass analyzer using two rotating electric fields (REFs). This mass analyzer can realize the continuous mass separation of ion beams with free mass range and simultaneous detection on two-dimensional (2D) plane. In this article, we aimed to mass separate AuGe liquid metal ion source (LMIS) on proper frequencies. Then, we simulated ion trajectories in REFs by theoretical calculations and identified the origins of each annular ring pattern. Finally, we confirmed the certainty of the theoretical calculations by time-of-flight secondary-ion-mass-spectrometry (TOF-SIMS) imaging of printed AuGe annular ring patterns on Si wafer.

Keywords: REF-MS; FIB; Ion implantation; AuGe-LMIS

Introduction

Characteristics

We have been developing a new principle type mass analyzer using two rotating electric fields (REFs). The principle is based on different ones from magnetic-sector, quadrupole or time-of-flight (TOF) type mass analyzers. The potentials of REF type mass analyzers have already been suggested by earlier studies [1,2]. According to those studies, they introduced simple TOF principle using a single REF geometry. However, the single REF slightly separate ion trajectories by m/Z . Our two REFs can realize mass separation with ion trajectorial differences continuously. Also, the mass separation of the REF-MS is performed on two-dimensional (2D) plane with simultaneous detection. The optical length of REF-MS can be assembled within only 40 cm, it is convenient to install and stand alone. It also can be applied for tandem use for fragment ions of biopolymers.

Principle

Figure 1 represents schematic diagram of REF-MS. REFs consist of the upstream REF and the downstream REF. Each REF is composed of eight small electrodes. AC voltages with a phase contrast of 45 degrees are applied on each electrode. First, ions are incident into the upstream REF. Then once a proper frequency is supplied for specific ion, the ion begins to draw cycloid trajectory and reaches the top on a half in the upstream REF. The ion draws a mirror trajectory and is converged to the initial axis by an opposite phase field in the downstream REF. The other ions draw each trajectory and form each concentric annular ring pattern within the REF-MS. The relationship between a proper frequency (f) and the mass electric charge ratio of the selected ion (m/Z) can be described by following the equation (1).

$$\frac{m}{Z} = \frac{2eV_{acc}}{f^2 L^2} \quad (1)$$

Where, L : the length of each REF electrode, e : the quantum of electricity and V_{acc} : the accelerating potential of the charged masses.

In our previous study, we directly introduced the REF-MS to a Ga-focused ion beam (FIB) column and succeeded in mass separation of Ga isotopes ($^{69}\text{Ga}^+$, $^{71}\text{Ga}^+$) [3,4]. In this article, we mass separated different kind of masses and isotopes of AuGe alloy and obtained the annular ring patterns on proper frequencies of REF-MS [5]. It is reported that many kinds of Au, Ge complete masses and isotopes are emitted from AuGe liquid metal ion source (LMIS) [6,7]. Moreover, we have simulated the ion trajectories emitted from AuGe-LMIS by theoretical calculations and printed annular ring patterns on Si wafer. The distribution of mass separated ions on Si wafer was analyzed by TOF-SIMS imaging. For these results, we identified the origin of each annular ring pattern and confirmed the certainty of the theoretical calculation results.

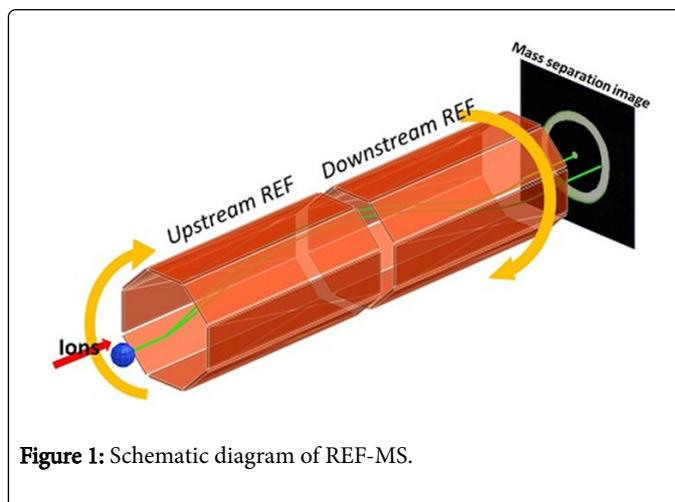


Figure 1: Schematic diagram of REF-MS.

Methods

Mass separation of AuGe-LMIS

In Figure 2, we introduced REF-MS to an AuGe-FIB column (FIB30, A & D Company, Ltd.). The diameters, lengths of each REF and the distance between the upstream REF and the downstream REF were 20, 150 and 70 mm, respectively. First, we installed micro channel plates (MCPs) with fluorescent screen behind REF-MS. Then sinusoidal waves for the REFs were generated by direct digital synthesizers (DDSs) with 16 channels shifted by 45 degrees. Each outputted sinusoidal wave was amplified by power amplifier (PA98A, Apex Micro technology, Inc) and applied on each electrode of the REFs. The potential of each sinusoidal wave was AC 210 V maximum (peak to peak). After that, we optimized the phase contrast between the upstream REF and the downstream REF to make the phases of each REF mutually opposite for the selected ion. Then, we installed the movable aperture unit. The accelerating voltage of the AuGe-FIB was 10 kV and the filament currents were kept at 3.0 A while the emission. We kept the ion beam current at about 5.2 nA. Finally, the annular ring patterns of AuGe-LMIS were observed on fluorescent screen by sweeping the frequencies of REFs from 290 to 1120 kHz at 5 kHz intervals.

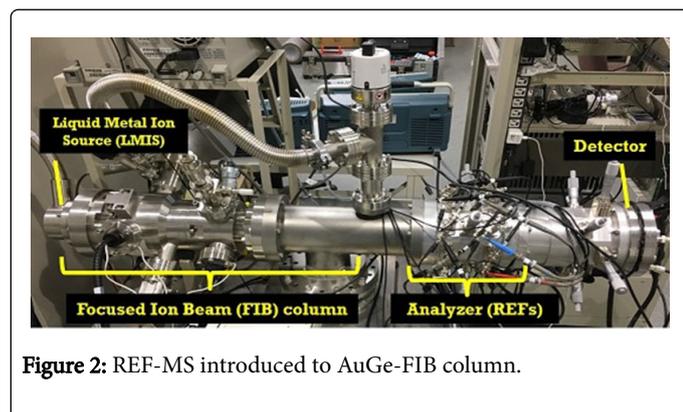


Figure 2: REF-MS introduced to AuGe-FIB column.

Trajectory simulation

We simulated ion trajectories in REF-MS for identifying the origins of each annular ring pattern by theoretical calculation (SIMIONTM, Scientific Instrument Services, Inc). This software can calculate the potentials of electric fields and simulate the trajectories of charged ions by Laplace's equations [8]. First, electric rotating fields were simulated by finite differential methods within the same potential array as REF-MS. Then, we set the frequency and AC voltage to the potential array of REFs. And the parameters of incident ions were input (i.e., amount, m/Z , incident position, direction and kinetic energy). The kinetic energy was set as 10 keV. Ions were assumed to be emitted from 20 mm

distance of the edge of REFs and the annular ring patterns were obtained at 20 mm behind. Finally, we obtained the annular ring patterns on the frequencies of 472, 668 and 956 kHz at the characteristic frequencies on equation (1).

Printing the annual ring patterns on Si wafer and TOF-SIMS imaging

We replaced Si wafer (a square 20 mm on a side) with MCPs and fluorescent screen. Therefore, mass separated ions were implanted onto the Si wafer. We kept emission of AuGe-LMIS at an accelerating voltage of 12.9 kV for 80 hours on the frequency of 956 kHz. We succeeded to obtain the annular ring patterns printed on the Si wafer. However, it is known that ion implanting process causes surface contamination by the ion bombardment. During ion implanting process by AuGe-LMIS, organic contaminations are piled up by ion assisted deposition [9,10]. Therefore, the organic contaminations were removed by plasma cleaning process by GV10x (ibss Group, Inc.). It can remove the contamination by three plasma species (ions, radicals and electrons) from plasma source [11,12]. The cleaned Si wafer was analyzed by TOF-SIMS (PHI TRIFT V nanoTOF, ULVAC-PHI, Inc.) imaging and the distributions of $^{70}\text{Ge}^+$, $^{76}\text{Ge}^+$, and Au^+ were imaged by stepping sample stage [13].

Results and Discussion

First, we succeeded in mass separation of AuGe-LMIS clearly. An ion converged to the initial axis and the other ions formed annular ring patterns on fluorescent screen were continuously moved by sweeping the frequencies of REFs from 290 to 1120 kHz at 5 kHz intervals. Furthermore, we obtained three characteristic annular ring patterns that bright spots were converged to the initial axis on the frequencies of 479, 680 and 956 kHz. Figure 3 represents the annular ring patterns of AuGe-LMIS obtained by using REF-MS. On Figure 3A, a kind of ion was converged to the initial axis and other masses and isotopes were observed as the annular ring patterns with different diameters from the center. On the other hand of Figure 3B, another ion was converged to the initial axis. Also, the ion converged to the initial axis on the frequency of 479 kHz, was disappeared from the fluorescent screen with increasing the frequencies of REF-MS. Asymmetric annular ring patterns were also observed near the edge of the fluorescent screen. We assume that it was attributed to the reflection within the wall of electrodes and formed fringed patterns. Because the fringed patterns drew the mirror trajectories from the annular ring patterns when the optical axis was shifted. On Figure 3C, another ion was also converged to the initial axis. The ions converged to the initial axis on the frequency of 680 kHz have moved from the center to the outside. Although ions converged to the initial axis on each frequency could be estimated by calculation using the equation (1), the origins of the ion and annular ring patterns located on the outside could not be identified certainly.

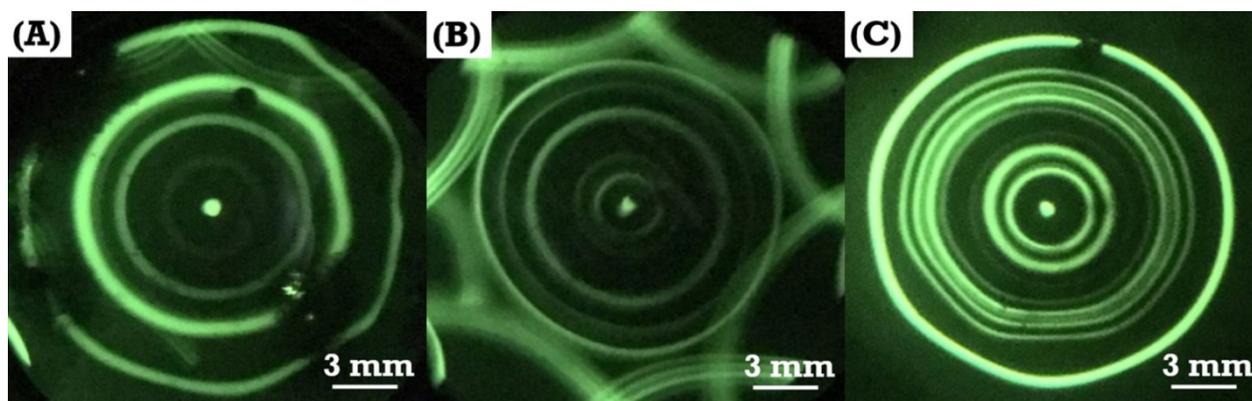


Figure 3: Annular ring patterns of AuGe alloy by mass separation of REF-MS. (A) $f=479$ kHz, (B) $f=680$ kHz, (C) $f=956$ kHz.

Figure 4 represents the results of trajectory simulations using theoretical calculations on the frequencies of 472, 668 and 956 kHz. Simulated annular ring patterns were appeared to be symmetrically equal to the initial axis. Therefore, we focused on only one quarter of the annular ring patterns including the initial axis. These patterns were revealed a cross-section of ion trajectories on fluorescent screen. On Figure 4A, it clarified that $^{197}\text{Au}_2^+$ ion was converged to the initial axis on the frequency of 472 kHz. The frequency was almost agreed with the estimation by equation (1). The annular ring patterns could be identified as Au_2Ge^+ and $\text{Au}_2\text{Ge}^{2+}$ ions from the center to the outside. The annular ring patterns near the edge were formed octagonal. We assume that these formed patterns were attributed to the geometry from eight small electrodes. On the other hand of Figure 4B, the ion converged to the initial axis was identified as $^{197}\text{Au}^+$ ion. Furthermore, annular ring patterns could be identified as $\text{Au}_3\text{Ge}^{2+}$, Au^{5+} , Au_4Ge^+ ,

Au_3^+ and Au_3Ge^+ ions from the outside to the center. In this trajectory simulation, Au_5^+ and Au_4Ge^+ were formed almost the same annular ring patterns. On Figure 4C, the ion converged to the initial axis could be identified as Au_4Ge^+ ion. Annular ring patterns could be identified as, Au_5^+ , Au_2^+ , Au_2Ge^+ , Au_3^+ , $\text{Au}^{76}\text{Ge}^+$, $\text{Au}^{74}\text{Ge}^+$, $\text{Au}^{73}\text{Ge}^+$, $\text{Au}^{72}\text{Ge}^+$, Au_3Ge^+ , $\text{Au}^{70}\text{Ge}^+$ and $\text{Au}_2\text{Ge}^{2+}$ ions from the center to the outside. The annular ring patterns derived from $\text{Au}^{73}\text{Ge}^+$ and $\text{Au}^{76}\text{Ge}^+$ ions could not be clearly observed in Figure 3C, because the abundance ratio of $^{73}\text{Ge}^+$ and $^{76}\text{Ge}^+$ ions is too small compared to major isotopes of Ge. However, they could be observed in Figure 4C. Furthermore, Au_3Ge^+ ion also overlapped with other annular ring patterns and could not be confirmed in Figure 3C. For these results, we succeeded to identify the most of origins of each annular ring pattern and clarify the behavior of ion trajectory in REF-MS.

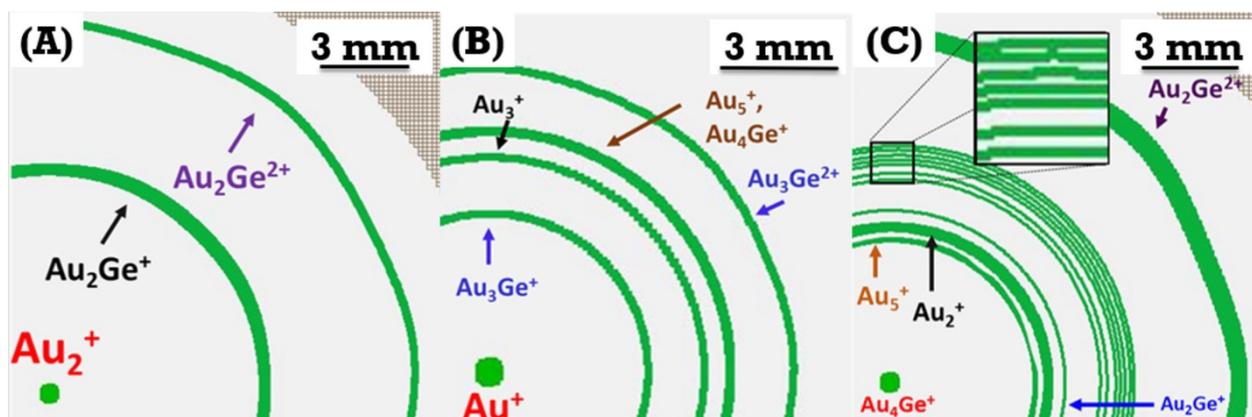


Figure 4: Annular ring patterns of AuGe-LMIS by theoretical calculation using SIMION™. (A) $f=472$ kHz, (B) $f=668$ kHz, (C) $f=956$ kHz.

Figure 5 represents the distribution of $^{76}\text{Ge}^+$, $^{70}\text{Ge}^+$, and Au^+ by TOF-SIMS imaging on the Si wafer (A) and theoretical calculation result (B) on the frequency of 956 kHz. On Figure 5A, $^{70}\text{Ge}^+$, $^{76}\text{Ge}^+$ and Au^+ are stood from outside to the inside on the implanted Si wafer.

Au^+ is stood inside Ge^+ isotopes and heavier Ge^+ isotope is stood inside lighter Ge^+ isotope. These results are certainly agreed with theoretical calculation result on Figure 5B. Therefore, we could confirm the certainty of the trajectory simulation result.

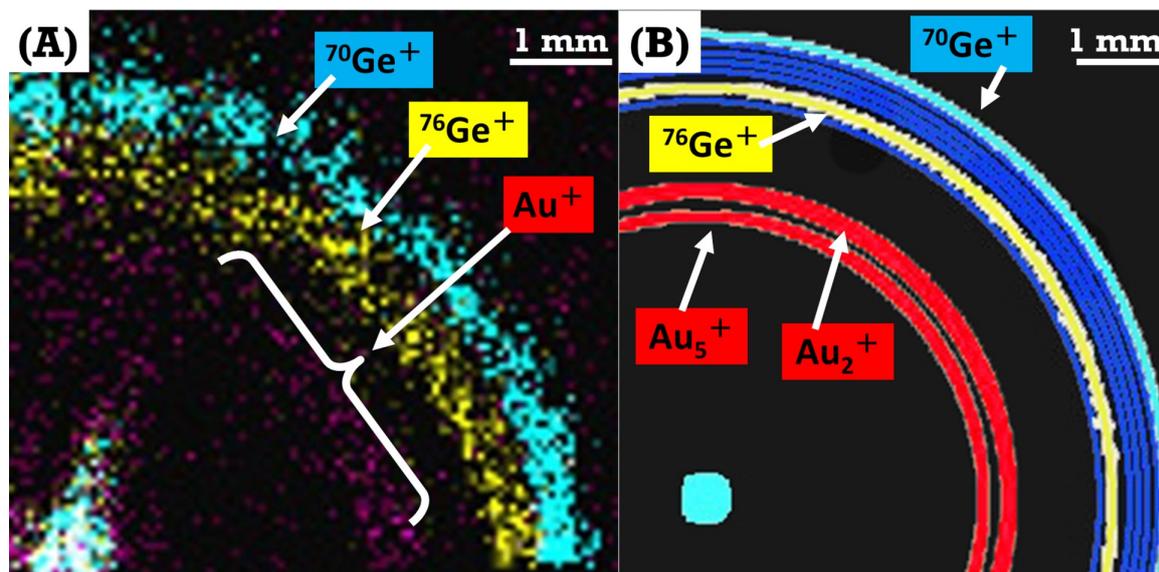


Figure 5: The distribution of $^{76}\text{Ge}^+$, $^{70}\text{Ge}^+$, and Au^+ by TOF-SIMS imaging of printed AuGe annular ring patterns on Si wafer. ($f=956$ kHz) (A) and theoretical calculation result ($f=956$ kHz) (B).

Conclusion

Consequently, the REF-MS can be highly developed to mass separate different ions on 2D plate continuously. By changing frequencies of REFs, we succeeded to make selected AuGe masses and isotopes converged to the initial axis and different annular ring patterns were obtained on the fluorescent screen. Furthermore, the origins of the ions and the annular ring patterns were identified by theoretical calculations (SIMIONTM). The certainty of these results was confirmed by TOF-SIMS imaging of printed AuGe annular ring patterns on Si wafer. This unique technique of REF-MS can be applied for rapid imaging mass spectrogram or industrial mass implantation process.

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