United States Patent

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[33] **Japan**
[31] **44/54506**

[54] **SCANNING-TYPE SPUTTERING MASS SPECTROMETER**
5 Claims, 16 Drawing Figs.

[52] **U.S. Cl.** .... **250/41.9 ME,**
250/41.9 SE, 250/49.5 P
[51] **Int. Cl.** **H01j 39/36**
[50] **Field of Search** .... 250/49.5 P,
41.9 SE, 41.9 ME

[56] **References Cited**

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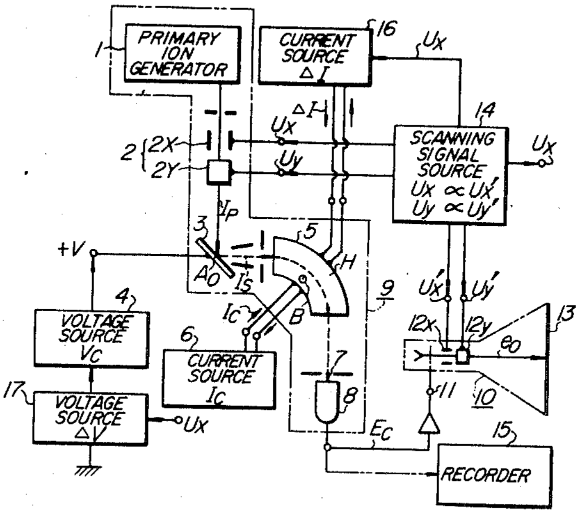
ABSTRACT: A scanning-type sputtering mass spectrometer comprising a primary ion-scanning unit including electrostatic-deflecting means and a secondary ion-analyzing unit including electrostatic-accelerating means, elecromagnetic-deflecting means and an ion collector. The accelerating voltage or the deflecting magnetic flux density is controlled in magnitude in synchronism with the scanning of the primary ion beam so as to let only ions of a particular mass-to-change ratio into the ion collector, irrespective of the displacement of the subject point of the secondary ion-analyzing unit.



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SHEET 1 OF 2

FIG. 1

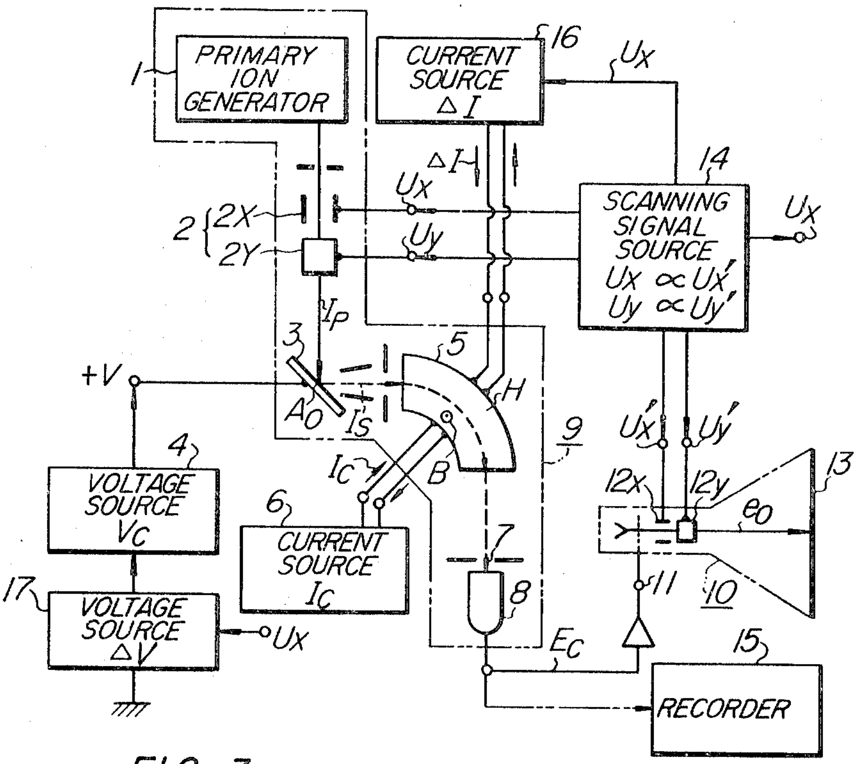

FIG. 3

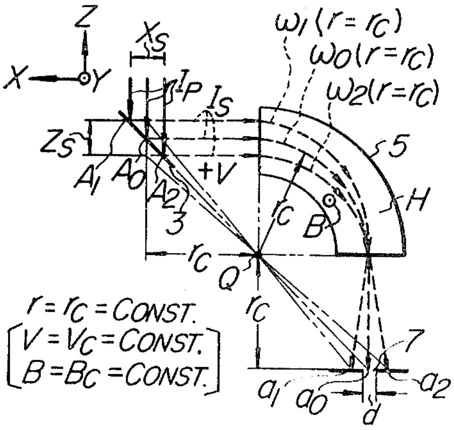

FIG. 4

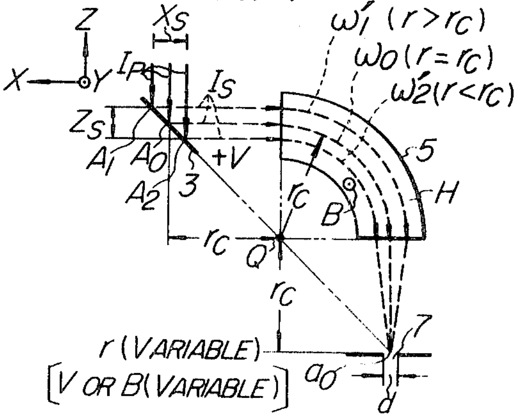

FIG. 2

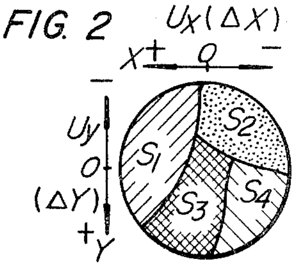

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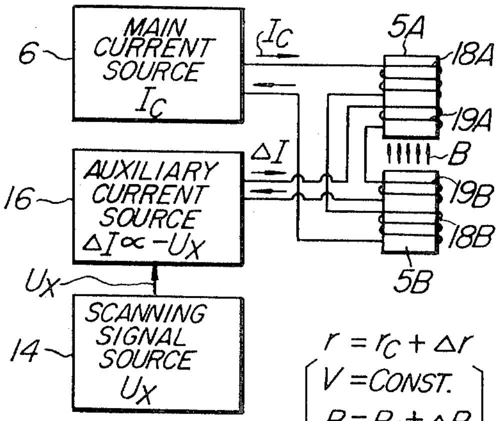
FIG. 5



$r = r_C + \Delta r$
$\left(\begin{matrix} V = \text{CONST.} \\ B = B_C + \Delta B \end{matrix} \right)$

FIG. 7a


FIG. 7b

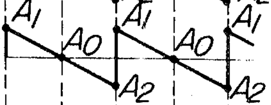

FIG. 7c


FIG. 7d

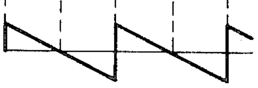
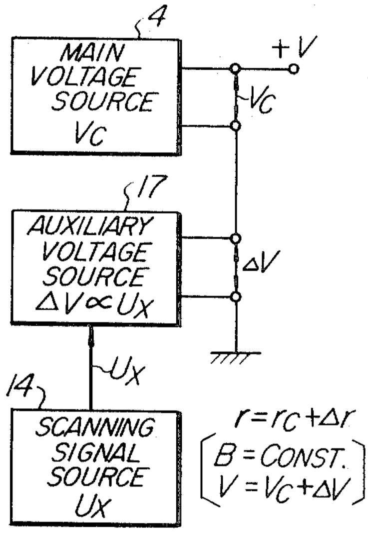

FIG. 7e


FIG. 6



$r = r_C + \Delta r$
$\left(\begin{matrix} B = \text{CONST.} \\ V = V_C + \Delta V \end{matrix} \right)$

FIG. 8a

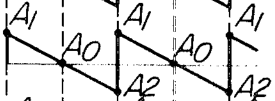

FIG. 8b


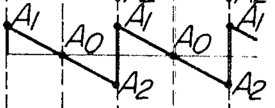
FIG. 8c


FIG. 8d


FIG. 8e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SCANNING-TYPE SPUTTERING MASS SPECTROMETER

This invention relates to a scanning type of sputtering mass spectrometer.

By the term "sputtering mass spectrometer" is meant a mass spectrometer in which a finely focused primary ion beam is directed onto the surface of a solid specimen to be analyzed and secondary ions (sputtered ions) emitted from this irradiated portion (analyzing spot) are analyzed through a mass spectroscopic system to provide the composition analysis of the specimen at said analyzed spot. This apparatus is also referred to as an ion microanalyzer.

In the case of analyzing the composition of a specimen at various points by the use of this apparatus, it is necessary to shift the irradiation spot of the primary ion beam from one desired position to another. Especially when it is used to find the concentration distribution of a certain element in the surface of a specimen, it is necessary to scan the irradiating spot of the primary ion beam in the plane of the specimen surface and to detect only such ions of a particular mass unit, or more strictly, the mass-to-charge ration *m/e*, among secondary ions emitted from the surface as traced by the scanning of the primary ion beam by an ion collector.

For shifting or scanning a primary ion beam on the surface of a specimen, it can firstly be thought of a method of shifting the specimen itself. In this method, however, an extremely precise and complicated structure is necessary for precisely shifting a specimen by a minute amount (of the order of microns), and there arise technical and economic difficulties in the manufacture.

Further, the consumption of manpower and time required for its operation is very large. Therefore, it is difficult to realize a rapid and precise shift or scan of an irradiation spot by this method.

Thus, generally the specimen has conventionally been fixed and the primary ion beam has been subjected to deflection scanning. Apparatus of this type is referred to as "a scanning type sputtering mass spectrometer". In such a system, since electrostatic or electromagnetic scanning of the primary ion beam can be employed, the irradiation spot can be shifted rapidly and accurately. However, the shift of the irradiation spot by the scanning of the primary ion beam, at the same time, causes the shift of the object point of the mass spectrometric system (i.e., emission point of the secondary ions). Thus, this type has a drawback in that the analyzing conditions of the mass spectrometric system are subjected to a change according to the scanning of the primary ion beam.

For example, in apparatus of the magnetic separation type, if the subject point is fixed which the magnitude of the accelerating voltage and the deflecting magnetic field for the secondary ions kept constant, the mass or more strictly the *m/e* ratio, of the ions collected by the ion collector is constant, but if the subject point is shifted by the scanning of the primary ion beam, the mass of ions injecting into the ion collector is changed accordingly. That is, a shift of the subject point causes a change of the starting position and hence the path of the secondary ions in the deflecting magnetic field, resulting in a shift of the focal point of ions of a particular mass.

Thus, in sputtering mass spectrometers of the magnetic separation type, so far as the accelerating voltage and the deflecting magnetic field intensity are kept constant, the mass of ions striking the ion collector is changed according to the scanning of the primary ion beam and it is impossible to detect the concentration distribution of a certain element in the specimen surface accurately.

This invention aims to eliminate the above drawback in a sputtering mass spectrometer.

An object of this invention is to improve the spectroscopic accuracy of a sputtering mass spectrometer by permitting ions of only a desired mass to enter into an ion collector, irrespective of the shift of the subject point accompanied with the scanning of the primary ion beam.

According to this invention, at least one of the accelerating voltage or the intensity of the analyzing magnetic field for the secondary ions is controlled to change in synchronism with the scanning of the primary ion beam to achieve the above-mentioned object.

Now, embodiments of the invention will be described with reference to the accompanying drawings in which:

FIG. 1 is a block diagram showing the principal structure of a scanning-type sputtering mass spectrometer according to the invention;

FIG. 2 schematically shows an example of an oscilloscope image of secondary ions emitted from a specimen surface;

FIG. 3 is a schematic diagram showing how the mass of ions going into an ion collector changes according to the displacement of the subject point in a conventional apparatus;

FIG. 4 is a schematic diagram showing how the mass of ions going into an ion collector is maintained constant irrespective of the shift of the subject point caused by the scan of the primary ion beam, in an apparatus according to this invention;

FIGS. 5 and 6 are block diagrams of central portions of an embodiments of the invention;

FIGS. 7*a* to 7*e* and 8*a* to 8*e* are waveforms for explaining the operation of the circuits of FIGS. 5 and 6, respectively.

FIG. 1 shows the schematic structure of a sputtering mass spectrometer of the magnetic field separation type in which ions forming the primary ion beam are emitted from an ion beam generating system 1, for example, comprising an ion gun such as a duo-plasmatron and an appropriate focusing lens and which are led to pass through a scanning system 2 comprising a pair of horizontal (X-axis) deflecting electrodes 2X and a pair of vertical (Y-axis) deflecting electrodes 2Y which are respectively supplied with deflecting electrodes U_x and U_y generated by a scanning signal source 14. The scanning primary ion beam thus formed, strikes a specimen 3 of interest applied with a secondary ion accelerating voltage V (usually several KV) by an accelerating voltage source 4, 17. Secondary ions are accelerated through the accelerating electric field of V and then pass through an analyzing magnetic field H (usually of several Killo-Gauss) established by an analyzing electromagnet 5 of sector shape energized by current sources 6 and 16. A collector slit 7 allows only ions of a certain mass, or more strictly *m/e* ratio, to pass through to activate an ion collector 8. Namely, the analyzing electromagnet 5, the slit 7 and the ion collector 8 form a mass spectrometric system of the magnetic field separation type. Reference numeral 9 indicates a vacuum housing the interior of which is kept to an appropriate vacuum by suitable exhausting means (not shown).

In such a structure, a finely focused primary ion beam I_p (usually of a diameter of from several to 10 add microns) emitted from the primary ion beam generating system 1, is irradiated onto a spot (analyzing spot) A_0 on the specimen surface to emit secondary ions (sputtering ions) I_s the components of which correspond to those of the elements of the analyzing spot A_0. These secondary ions are accelerated by the accelerating voltage V and are deflected and mass analyzed in the magnetic field H of flux density B according to the mass of the respective ions. The *m/e* ratio of the ion striking the ion collector 8 through the collector slit 7 provided at a fixed position is determined by the accelerating voltage V and the magnetic flux density B by the following formula:

$m/e \;\alpha\; r^2 \cdot B2/V$ .... (1) where, r is the radius of curvature of the path of ions in the magnetic field H. The fact that the subject point (emission point of the secondary ions) and the collector slit are fixed in position means that the radius of curvature is a constant, $r=r_c$ (constant).

Thus, ions of an arbitrary mass can be selectively detected by the ion collector 8 by suitably selecting the accelerating voltage V and/or the magnetic flux density B. When the value of V *and/or* B is continuously changed. the mass of ions striking the ion collector is also continuously changed, i.e., the mass spectrum of the specimen can be detected by recording the output voltage E_c of the ion collector 8 in a recorder 15.

From this mass spectrum, the composition of elements at the analyzing spot A_o can be determined.

On the other hand, when the primary ion beam I_p is scanned in the plane of the specimen surface by the ion beam-scanning system **2** (this is accompanied with the change in the radius of curvature of ions detected by the ion collector), and the accelerating voltage and/or the magnetic field is arranged to change so that ions of a certain mass always strike the ion collector, the emission distribution of ions of a certain mass in the specimen surface and hence the concentration distribution of a component element(s) of a certain mass can be detected. Provided that the output voltage of the ion collector is proportional to the concentration of a particular element in the specimen surface, a brightness-modulated image (secondary ion image) of the concentration distribution of a particular element in the specimen surface can be represented on the image screen **13** of a cathode-ray tube oscilloscope **10** by supplying the output voltage E_c of the ion collector **8** to the brightness modulation terminal **11** of said oscilloscope **10** and thus scanning the modulated image-forming electron beam e_o in synchronism with the scanning of the primary ion beams I_p. It will be apparent that the brightness variation in the image screen represents the concentration variation in the specimen surface. For the synchronous scanning, the pair of horizontal (X-axis) deflecting electrodes **12X** and the pair of vertical (Y-axis) deflecting electrodes **12Y** of the CRT oscilloscope **10** are respectively supplied with voltages U_x' (which is proportional to U_x) and U_y' (which is proportional to U_Y) by the scanning signal source **14**.

FIG. **2** shows a model of such a secondary ion image in which the concentration variation of a particular element in the specimen surface is represented as the brightness variation of regions S_1, S_2, S_3 and S_4. It is to be noted that the secondary ion image can represent the concentration distribution of a particular element in the specimen surface only when it is assured that the mass of ions striking the ion collector does not change.

However, according to the conventional system, even when the primary ion beams is scanned on a specimen surface, the accelerating voltage V and the magnetic flux B are kept constant and yet the secondary ion image formed by scanning the primary ion beam is treated as a representation of the concentration distribution of a particular element. In other words, variations in position of the subject point have been neglected.

FIG. **3** illustrates the principle of a conventional system in which a specimen **3** and a collector slit **7** are disposed in position as is shown in the figure with respect to the center Q of curvature of the standard path ω_o of ions in the sector shaped magnetic field H established by analyzing electromagnet **5**. The standard path ω_o has a radius of curvature r_c and the accelerating voltage V and the magnetic flux density B are kept constant ($V=v_c$, $B=B_c$). When the primary ion beam I_p is scanned in the X-axis direction with a scanning width X_s, the irradiation spot shifts on the specimen surface from A_1 to A_2 with a center at A_o and this will cause the displacement of the subject point of the mass spectrometer in the Z-axis direction to a width Z_s. As among the secondary ions emitted from point A_o, ions of a particular mass (m/e ratio) defined by equation (1) take the standard path ω_o (radius of curvature r_c) to focus onto spot a_o, ions of the same mass emitted from points A_1 and A_2 take the paths ω_1 and ω_2 (radius of curvature being both constant r_c) to focus onto spots a_1 and a_2 respectively. That is, if the emission position (i.e., subject position) is different, even ions of the same mass take different paths in the deflecting magnetic field and subsequently focus to different positions. Thus ions focusing on spots different from a_o cannot be correctly collected by the ion collector through the slit **7** having a slit width d. In another aspect, when the irradiation spot is shifted to a position A_1 or A_2 different from A_o, ions of some different mass than the desired mass are inevitably collected by the ion collector **8** to provide a detection result not true to the desired one.

This invention eliminates the above drawback by changing at least one of the accelerating voltage V and deflecting the magnetic flux density B in synchronism with the scanning of the primary ion beam so as to let ions of only the same mass go into the ion collector.

FIG. **4** illustrates the principle of this invention. When the irradiation spot of the primary ion beam is located at point A_o, ions emitted from there and having a certain mass take the standard path ω_o(radius of curvature being $r=r_c$) to focus onto spot a_o. When it is shifted to points A_1 or A_2, ions of said mass take path ω_1' (radius of curvature $r>r_c$) or ω_2' (radius of curvature $r<r_c$) to focus on the same spot a_o as before.

As is apparent from the figure, according to the invention, the accelerating voltage V and/or the flux density B of the analyzing magnetic field is varied in synchronism with the scan of the primary ion beam to compensate the displacement of the irradiation spot so as to always focus ions of a particular mass on a fixed spot. By such an arrangement, the ion collector always receives ions of a constant mass, irrespective of the scan of the primary ion beam.

Now, consideration will be given to the relation among the rates of variation for the mass of ions $\Delta m/m$, the radius of curvature of the path of ions $\Delta r/r$, the accelerating voltage $\Delta V/V$ and the magnetic flux density $\Delta B/B$. The differentiation of equation (1) approximately gives the following relation; $\Delta m/m=2\Delta r/r+2\Delta B/B-\Delta V/V$ .... (2)

For keeping the mass of ions striking the ion collector constant, the condition $\Delta m/m=0$ should be satisfied.

Thus, if the magnetic flux B is kept constant (i.e., $\Delta B=0$) the condition; $\Delta V/V=2\Delta r/r$ .... (3) results in $\Delta m/m=0$. And if the accelerating voltage V is kept constant ($\Delta V=0$) the condition of

$$\Delta B/B=-\Delta r/r$$

provides the result of $\Delta m/m=0$.

A displacement of the subject point of the mass spectrometer in the Z axis direction by ΔZ corresponds to a variation of the radius of curvature r of the ion path by ΔZ, namely $\Delta r=\Delta Z$. Further, displacement ΔZ is proportional to a displacement ΔX of the irradiation spot which is further proportional to the deflecting voltage U_x. Thus, in the region where ΔX is small, the following relations can be established from equation (3) and (4), $\Delta V \alpha \Delta x \alpha U_x$ .... (5) $\Delta B \alpha -\Delta x\ \alpha -U_x$ ....(6)

Namely, for keeping the mass of ions striking the ion collector constant, irrespective of the scanning of the primary ion beam, with the magnetic flux density B kept constant, it is sufficient to vary the accelerating voltage V in proportion to the deflecting voltage U_x. On the other hand, when the accelerating voltage V is kept constant, it is sufficient for keeping $\Delta m/m=$, to vary the magnetic flux density B in proportion, but in opposite polarity to the deflecting voltage U_x.

FIG. **5** shows an example of a circuit for the case of a constant accelerating voltage $V=V_c$ in which the magnetic flux density B is varied in the form of $B=B_c+\Delta B$. In the analyzing electromagnets **5A** and **5B**, primary windings **18A**, **18B** and auxiliary windings **19A**, **19B** are respectively provided. A constant current I_c is allowed to flow through the primary windings **18A** and **18B** by a primary current source **6** to establish a constant magnetic flux B_c. Through the auxiliary windings **19A** and **19B**, a current ΔI, the magnitude of which is proportional to the deflecting voltage U_x in opposite direction is allowed to flow from the scanning signal source **14** to establish a magnetic flux ΔB in proportion to the auxiliary energizing current ΔI. Thus, the total magnetic flux becomes $B+\Delta B$.

FIGS. **7***a* to **7***e* illustrate the operation of the circuit of FIG. **5**, in which FIG. **7***a* represents the variation of the deflecting voltage U_x for the primary ion beam, FIGS. **7***b* and **7***c* displacement distances ΔX and ΔZ of the irradiation spot and the subject point respectively, FIG. **7***d* the auxiliary energizing current ΔI, and FIG. **7***e* the variation Δr of the radius of curvature of the ion path in the magnetic field. As is apparent from this figure, the displacement ΔZ of the subject point is proportional to the deflecting voltage U_x, but since the auxiliary current ΔI is varied in proportion but in opposite polarity to the deflecting voltage U_x, the radius of curvature varies to cancel the displacement of the subject point, $\Delta r = \Delta Z$. Thus, the ion collector can receive only the ions of a particular mass.

Next, FIG. 6 shows another embodiment of a circuit for the case of a constant magnetic flux where $B = B_c$, in which the accelerating voltage is varied in the form of $V = V_c + \Delta V$. The circuit comprises a series connection of a main accelerating voltage source **4** and an auxiliary accelerating voltage source **17**. The main voltage source **4** supplies a constant voltage V_c and the output voltage ΔV of the auxiliary voltage source **17** is varied in proportion to the deflecting voltage from the scanning signal source **14**. Thus, an accelerating voltage of $V = V_c + \Delta V$ is applied to the specimen **3**. FIGS. **8***a* to **8***e* illustrates the operation of the circuit of FIG. **6**. The auxiliary accelerating voltage ΔV (FIG. **8***d*) is varied in proportion to the deflecting voltage U_x (FIG. **8***a*) to vary Δr in proportion to U_x, thus cancelling ΔZ with Δr.

In the above embodiments, the accelerating voltage V and/or the magnetic flux density B is varied corresponding to the X-axis deflecting voltage U_x. This corresponds to the case where the scanning in the Y-axis direction does not produce any displacement of the subject point in the Z-axis direction. If it does not, the voltage V and/or the flux B should naturally be varied in correspondence to the Y-axis deflecting voltage U_y. In a mass spectrometer of the magnetic field separation type, displacement of the subject point in a direction perpendicular to the deflection plane of ions is negligible and cause no problems, therefore, it is usually sufficient to vary either V or B corresponding to one deflecting voltage causing the displacement of the subject point in the Z-direction.

Further, in FIG. 1, it will be apparent that one of the auxiliary accelerating voltage source **17** and the auxiliary current source **16** is not necessary for a particular type of apparatus. It will be convenient for changing the mass of ions to be detected by the ion collector if the output voltage of the main accelerating voltage source or the output current I_o of the main energizing current source **6** is arranged to be variable.

As is apparent from the foregoing description, according to the present invention, the mass of ions striking an ion collector can be kept constant by a simple arrangement of varying at least one of the accelerating voltage V and the flux density B of the analyzing magnetic field for the secondary ions in synchronism with the scanning of the primary ion beam. Thus this invention is particularly useful for improving the spectroscopic accuracy when the concentration distribution of a particular element on a specimen surface is to be measured.

We claim:

1. In a scanning-type sputtering mass spectrometer including a primary ion generator having means for irradiating a finely focused primary ion beam on a surface of a solid specimen to be analyzed, scanning means for scanning said primary ion beam on the surface of said specimen to generate a secondary ion beam, electromagnetic means for generating a magnetic field to analyze said secondary ion beam emitted from said specimen as a result of irradiation of said primary ion beam thereon, an ion collector selectively positioned for collecting the analyzed ion beam derived from said electromagnetic means, an accelerating voltage source applying an accelerating voltage to said specimen, and an exciting current source supplying an exciting current to said electromagnetic means, the improvement comprising compensating means for varying at least one of the accelerating voltage and the exciting current synchronously with the scanning of said primary ion beam so as to direct ions of a predetermined mass to strike said ion collector irrespective of the position of the primary ion beam on said specimen.

2. A sputtering mass spectrometer according to claim **1**, wherein said scanning means is an electrostatic deflecting device, and said compensating means varies one of the accelerating voltage and the exciting current in proportion to the voltage energizing said electrostatic deflecting device.

3. A sputtering mass spectrometer according to claim **1**, wherein said compensating means varies the accelerating voltage synchronously with the scanning of said primary ion beam.

4. A sputtering mass spectrometer according to claim **1**, wherein said compensating means varies the exciting current synchronously with the scanning of said primary ion beam.

5. A sputtering mass spectrometer apparatus according to claim **1**, further comprising means for displaying the image of secondary ions through the output voltage of said ion collector.

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