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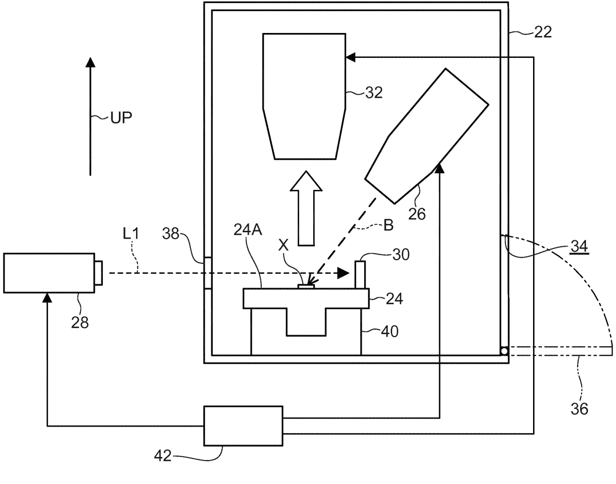
(54) MASS SPECTROSCOPE AND MASS SPECTROMETRY

(57) A mass spectrometer including a vacuum chamber, a sample stage disposed inside the vacuum chamber, an ion beam source configured to irradiate an ion beam onto a solid sample placed on the sample stage so as to eject atoms from the solid sample, a laser beam source configured to pass a laser beam above a region of the solid sample irradiated by the ion beam, a reflector disposed inside the vacuum chamber and configured to reflect the laser beam so as to cause the laser beam and a reflected beam to overlap above the irradiated region, and an analysis section configured to analyze a mass of atoms ionized by the laser beam and the reflected beam.

FIG.1



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Description

Technical Field

[0001] The present disclosure relates to a mass spectrometer and to a mass spectrometry method.

Background Art

[0002] Mass spectrometry methods are known as methods to analyze trace elements (see, for example, Japanese Patent Application Laid-Open (JP-A) No. 2001-108657). Mass spectrometry methods have the merit of enabling isotopic analysis to be performed due to measuring a mass of atoms (atomic mass). An example of an application of such mass spectrometry methods is radioisotope analysis of nuclear fuels, nuclear waste, and the like.

[0003] Measuring ratios of isotopes of radioactive elements contained in a given sample generally enables the time when the material was produced to be determined due to radioactive elements having different half-lives for each isotope. With respect to radioactive contamination resulting from the accident at the Fukushima No. 1 reactor, for example, mere detection of a radioactive substance is not proof that the radioactive substance comes from the nuclear accident. This is because there are various radioactive elements present at low concentrations and widely dispersed from fallout caused by past nuclear accidents and nuclear tests. However, for the same element having radioactive isotopes, the ratio of the isotopes to each other differ depending on the time produced. This is because the half-lives are different for each isotope, enabling when the radioactive substance was produced to be determined by utilizing this fact. However, the discrimination between fallouts in this manner is difficult in practice.

[0004] The present inventors have according developed an imaging mass spectrometer capable of analyzing components on a particle-by-particle basis for fine particles of a few micrometers in size or smaller. Although it is possible to perform isotopic ratio analysis for individual particles using such an imaging mass spectrometer, there is a demand for even higher sensitivity since generally the amounts of radioactive substance present are small.

[0005] Hitherto in imaging mass spectrometers, atoms have been ejected from the surface of a sample and ionized using irradiation by an ion beam alone. However, even high ionization rates in such methods are ionization rates of the order of a few %, and this is a limitation to increasing sensitivity. Methods of photo-ionization are accordingly being developed in which a high density laser beam is shone onto atoms ejected from the sample surface. Such methods are called sputtered neutral mass spectrometry (SNMS) methods. However, although a pulsed laser with a low repetition rate is employed in sputtered neutral mass spectrometry methods to achieve sufficient photon density, a laser with a high repetition rate (of about 10 kHz) required for imaging has a low pulse energy, and so an issue remains in that a sufficient ionization rate is not obtained.

SUMMARY OF INVENTION

Technical Problem

[0006] In consideration of the above circumstances, an object of the present disclosure is to provide a mass spectrometer and a mass spectrometry method with raised ionization rate for atoms ejected from a solid sample.

Solution to Problem

[0007] A mass spectrometer of a first aspect of the present disclosure includes a vacuum chamber, a sample stage disposed inside the vacuum chamber, an ion beam source configured to irradiate an ion beam onto a solid sample placed on the sample stage so as to eject atoms from the solid sample, a laser beam source configured to pass a laser beam above a region of the solid sample irradiated by the ion beam, a reflector disposed inside the vacuum chamber and configured to reflect the laser beam so as to cause the laser beam and a reflected beam to overlap above the irradiated region, and an analysis section configured to analyze a mass of atoms ionized by the laser beam and the reflected beam.

[0008] In the mass spectrometer of the first aspect, the atoms ejected from the solid sample (hereafter referred to as "sputter atoms" as appropriate) are ionized by the laser beam and the reflected beam. Due to causing the laser beam and the reflected beam to overlap with each other above the region of the solid sample irradiated by the ion beam (hereafter referred to as in the "ionization space" as appropriate), the photon density is increased in the region where the laser beam and the reflected beam overlap in the ionization space compared to, for example, configurations in which the laser beam and the reflected beam are not caused to overlap in the ionization space. This increases the probability of photons colliding with the sputter atoms. Namely, the ionization rate of the sputter atoms is raised. The mass spectrometry precision by the analysis section is raised by increasing the number of ionized sputter atoms in this manner.

[0009] A mass spectrometer of a second aspect of the present disclosure is the mass spectrometer of the first aspect, wherein the reflector is attached to the sample stage so that an optical axis of the laser beam and an optical axis of the reflected beam are coaxial.

[0010] Due to the optical axis of the laser beam and the optical axis of the reflected beam being coaxial in the mass spectrometer of the second aspect, the region where the laser beam and the reflected beam overlap in the ionization space is increased, further raising the ionization rate.

[0011] Moreover, in the mass spectrometer described above, the reflector is attached to the sample stage, and so an operation to align the optical axes of the laser beam and the reflector coaxially is easier than, for example, configurations in which the reflector is attached at a position separated from the sample stage.

[0012] A mass spectrometer of a third aspect of the present disclosure is the mass spectrometer of the first aspect, wherein a plurality of reflectors are attached to the sample stage such that reflected beams overlap with each other plural times above the irradiated region.

[0013] In the mass spectrometer of the third aspect, the region where reflected beams overlap with each other in the ionization space is increased due to at least reflected beams being overlapped with each other plural times in the ionization space by relaying the reflected beam using the plurality of reflectors, further raising the ionization rate thereby.

[0014] A mass spectrometer of a fourth aspect of the present disclosure includes a vacuum chamber, a sample stage disposed inside the vacuum chamber, an ion beam source configured to irradiate an ion beam onto a solid sample placed on the sample stage so as to eject atoms from the solid sample, a laser beam source configured to emit a laser beam parallel to a surface of the sample stage, the plurality of reflectors disposed inside the vacuum chamber and configured to reflect the laser beam so that reflected beams are caused to overlap with each other above a region of the solid sample irradiated by the ion beam, and an analysis section configured to analyze a mass of atoms ionized by at least reflected beams.

[0015] The atoms ejected from the solid sample are ionized by reflected beams in the mass spectrometer of the fourth aspect. Due to reflected beams being overlapped with each other above the region of the solid sample irradiated by the ion beam by reflecting the reflected beam using the plurality of reflectors, the photon density is increased in the region where reflected beams overlap with each other in the ionization space compared, for example, to configurations in which reflected beams are not overlapped with each other, thereby increasing the probability of photons colliding with the sputter atoms. Namely, the ionization rate of the sputter atoms is raised. The mass spectrometry precision by the analysis section is raised by increasing the number of sputter atom ionized in this manner.

[0016] A mass spectrometer of a fifth aspect of the present disclosure is the mass spectrometer of any one of the first aspect to the fourth aspect, wherein the laser beam source is capable of varying a wavelength of the laser beam according to a type of atom contained in the solid sample.

[0017] The mass spectrometer of the fifth aspect enables the sputter atoms to be resonant ionized by varying the wavelength of the laser beam according to the type of atom contained in the solid sample. This thereby raises the ionization rate of the sputter atoms further.

[0018] A mass spectrometer of a sixth aspect of the present disclosure is the mass spectrometer of any one of the first aspect to the fifth aspect, wherein the sample stage is detachably installed in the vacuum chamber, and an access port is provided at the vacuum chamber for extracting the sample stage.

[0019] The mass spectrometer of the sixth aspect enables the solid sample to be replaced by removing the solid sample from the vacuum chamber by extraction through the access port. The reflector can also be cleaned or replaced when removing the sample stage.

[0020] A mass spectrometry method of a seventh aspect of the present disclosure includes a process of disposing a sample stage having a solid sample placed thereon inside a vacuum chamber and placing the inside of the vacuum chamber in a state of vacuum, a process of irradiating an ion beam onto the solid sample so as to eject atoms from the solid sample, a process of passing a laser beam above a region of the solid sample irradiated by the ion beam so as to ionize atoms, a process of using a reflected beam, reflected so as to overlap with the laser beam to ionize atoms remaining un-ionized by the laser beam, and a process of analyzing a mass of atoms that have been ionized.

[0021] The mass spectrometry method of the seventh aspect of the present disclosure exhibits similar advantageous effects to those described above for the mass spectrometer of the first aspect.

[0022] The present disclosure enables the provision of a mass spectrometer and a mass spectrometry method capable of raising the ionization rate of atoms ejected from a solid sample.

BRIEF DESCRIPTION OF DRAWINGS

[0023]

Fig. 1 is a schematic diagram illustrating a configuration of a mass spectrometer according to a first exemplary embodiment.

Fig. 2 is close-up diagram illustrating an enlargement of relevant elements of the mass spectrometer of Fig. 1.

Fig. 3 is close-up diagram illustrating an enlargement of relevant elements of the mass spectrometer of Fig. 1 in a state in which a pulsed laser has been reflected by a reflector.

Fig. 4 is a plan view illustrating relevant elements of the mass spectrometer of Fig. 1 as viewed from above.

Fig. 5 is a plan view illustrating relevant elements of a mass spectrometer according to a second exemplary embodiment as viewed from above in a plan view of an outward path of a pulsed laser.

Fig. 6 is a plan view illustrating relevant elements of the mass spectrometer of Fig. 5 as viewed from above and illustrating a plan view of a return path of the pulsed laser.

Fig. 7 is a mass spectrum obtained by non-resonant ionization with reflection of the pulsed laser occurring once.

Fig. 8A is an explanatory diagram illustrating a process of ionization by non-resonant two-photon absorption in a sputter atom.

Fig. 8B is an explanatory diagram illustrating a process of ionization by resonant two-photon absorption in a sputter atom.

Fig. 9 is a graph illustrating a relationship between the wavelength of a pulsed laser and a number of ions of zirconium (Zr) detected.

Fig. 10 is a graph illustrating a relationship between the outward path wavelength and the return path wavelength of a pulsed laser against the number of ions of zirconium (Zr) detected.

Fig. 11A is an explanatory diagram to illustrate ionization ranges of a sputter atom group when a pulsed laser has passed once.

Fig. 11B is an explanatory diagram to illustrate ionization ranges of a sputter atom group when a pulsed laser has passed once and been reflected once.

DESCRIPTION OF EMBODIMENTS

First Exemplary Embodiment

[0024] Explanation follows regarding a mass spectrometer and a mass spectrometry method according to a first exemplary embodiment of the present disclosure, with reference to Fig. 1 to Fig. 4.

Mass Spectrometer

[0025] Fig. 1 is a schematic diagram illustrating a configuration of a mass spectrometer 20 according to the present exemplary embodiment.

[0026] The mass spectrometer 20 is an instrument that ejects atoms (neutral particles) contained in a solid sample X, ionizes the ejected atoms (hereafter referred to as "sputter atoms S" as appropriate) using a laser beam, and analyzes a mass of ionized atoms.

[0027] As illustrated in Fig. 1, the mass spectrometer 20 includes a vacuum chamber 22, a sample stage 24, an ion beam source 26, a laser beam source 28, a reflector 30, and an analysis section 32.

Vacuum Chamber

[0028] As illustrated in Fig. 1, the vacuum chamber 22 houses the sample stage 24, the ion beam source 26, the reflector 30, and the analysis section 32 therein. A non-illustrated pressure reduction circuit is connected to the vacuum chamber 22. The inside of the vacuum chamber 22 is placed in a state of vacuum by actuating the pressure reduction circuit.

[0029] An access port 34 for the sample stage 24 is provided at the vacuum chamber 22. The access port 34 is opened or closed by an openable door 36 provided at the vacuum chamber 22. Note that in the present exemplary embodiment the openable door 36 is a door that opens from one side, however the present disclosure is not limited to such a configuration. For example, a double-sided door may be provided or a sliding door may be provided for the openable door. There is no particular limitation to the direction in which the openable door opens.

[0030] Transparent glass 38 is fitted into a side wall of the vacuum chamber 22 at a position on the optical axis of a laser beam L1 being shone from the laser beam source 28. The laser beam L1 from the laser beam source 28 enters into the vacuum chamber 22 by passing through the transparent glass 38.

Sample Stage

[0031] As illustrated in Fig. 1, the sample stage 24 is detachably mounted to a base 40 provided at a lower portion of the vacuum chamber 22. A surface 24A of the sample stage 24 is configured by a flat face to place the solid sample X on. Note that the sample stage 24 includes a manipulator capable of adjusting the position of the solid sample X serving as the target as appropriate in order to adjust the irradiation position of the ion beam B.

Ion Beam Source

[0032] The ion beam source 26 is a beam source that irradiates the ion beam B onto the solid sample X placed on the sample stage 24 in order to eject atoms contained in the solid sample X. As an example, a readily available device such as a focused ion beam (FIB) device or the like may be employed for the ion beam source 26. In order to irradiate an ion beam onto the solid sample X, an ion beam may, for example, be extracted from a liquid metal gallium ion source, and after focusing the ion beam, the ion beam may then be irradiated as pulses onto the solid sample X at nanoscale precision.

[0033] Moreover, the ion beam source 26 may be configured so as to be movable, and the ion beam B then scanned over the surface of the solid sample X by moving the ion beam source 26. Such a configuration enables imaging to be performed at a micron scale by recording a signal value of the sputter atoms S in the region irradiated by the ion beam B. Note that the base 40 may be configured so as to be movable, and the ion beam B scanned over the surface of the solid sample X by moving the base 40.

Laser Beam Source

[0034] As illustrated in Fig. 1, Fig. 2, and Fig. 4, the laser beam source 28 is a device that emits a pulsed laser so that the pulsed laser (pulses of laser) passes above a region of the solid sample X irradiated by the ion beam B (hereafter referred to as the "ionization space" as appropriate). The incident beam of the pulsed laser is referred to below as the laser beam L1. The laser beam source 28 is positioned outside the vacuum chamber 22 and emits the laser beam L1 parallel to the surface 24A of the sample stage 24.

[0035] The laser beam source 28 ionizes the sputter atoms S by shining a pulsed laser of a predetermined wavelength and a predetermined laser intensity onto the sputter atoms S (atom group) ejected from the solid sample X.

[0036] There is no particular limitation to the wavelength of the pulsed laser shone from the laser beam source 28 and it may, for example, be 266 mm.

[0037] The atoms ejected from the solid sample X by the ion beam B are not isotropic and are dissipated as they fly off, so the laser beam L1 shone from the laser beam source 28 is preferably placed so as to emit the laser beam L1 from the laser beam source 28 onto the vicinity of the surface 24A of the sample stage 24. This approach enables the ejected sputter atoms S to be ionized efficiently. In cases in which the laser beam L1 is shone parallel to the surface 24A of the sample stage 24, a gap between the laser beam L1 and the surface 24A of the sample stage 24 is, for example, preferably about 1 mm.

[0038] A variable wavelength laser such as, for example, a commercially available ultraviolet laser generating device may be employed as the laser beam source 28.

Reflector

[0039] As illustrated in Fig. 1 and Fig. 3, the reflector 30 is attached to the surface 24A of the sample stage 24. The reflector 30 is disposed within 10 mm of the center of the solid sample X. The reflector 30 is attached to the surface 24A of the sample stage 24 so that the optical axis of the laser beam L1 (illustrated by the black arrow in Fig. 1 and Fig. 2) is coaxial with the optical axis of a reflected beam L2 (illustrated by the white arrow in Fig. 3). The laser beam L1 and the reflected beam L2 are thereby overlapped on each other in the ionization space. Note that the reflector 30 of the present exemplary embodiment is fitted into a recess (not-illustrated in the drawings) formed in the surface 24A of the sample stage 24.

[0040] The reflectivity of the reflector 30 is preferably close to 100%, however there is no particular limitation thereto.

Analysis Section

[0041] The analysis section 32 is a section for analyzing the mass of ionized atoms. Various devices are applicable as the analysis section 32 such as, for example, a magnetic sector mass spectrometer, a time-of-flight mass spectrometer (TOF-MS), a quadrupole mass spectrometer (QMS), or the like.

Control Section

[0042] A control section 42 performs control on each of the configuration elements provided in the mass spectrometer 20. Specifically, the control section 42 controls an irradiation timing with which the ion beam B is irradiated from the ion beam source 26, and controls the illumination timing with which the laser beam L1 is shone from the laser beam source 28. Next, explanation follows regarding a method by which each of the configuration elements is controlled using the control section 42.

[0043] The control section 42 controls the laser beam source 28 such that the laser beam L1 is shone into the ionization space into which the ejected sputter atoms S are ejected after a predetermined period of time has elapsed from when the ion beam B was irradiated onto the solid sample X. The sputter atoms S inside the ionization space are ionized by the laser beam L1 being shone into the ionization space. The sputter atoms S are also ionized by the reflected beam L2 reflected by the reflector 30 also passing through the ionization space. This enables the ionization rate to be raised.

Mass Spectrometry Method

[0044] Explanation follows regarding the mass spectrometry method of the present exemplary embodiment. Note that the mass spectrometer 20 is employed in the mass spectrometry method of the present exemplary embodiment.

[0045] First the solid sample X is placed on the surface 24A of the sample stage 24, and the sample stage 24 is passed through the access port 34 of the vacuum chamber 22 and attached to the base 40. The openable door 36 is then closed and the interior of the vacuum chamber 22 is placed in a state of vacuum by actuating the pressure reduction circuit referred to above.

[0046] Then the ion beam B is irradiated onto the solid sample X to eject atoms from the solid sample X.

[0047] Next, the laser beam L1 is shone through the ionization space above the region of the solid sample X irradiated by the ion beam B. Sputter atoms S inside the ionization space are thereby ionized.

[0048] The laser beam L1 that has passed through the ionization space is reflected by the reflector 30. The reflected beam L2 reflected thereby ionizes sputter atoms S not ionized by the laser beam L1. The wavelength of the pulsed laser is long, and a distance D from the center of the solid sample X to the reflector 30 is 10 mm or less. This means that a leading portion of the reflected beam L2 (a leading portion in the laser reflection direction) overlaps with a trailing portion of the laser beam L1 (a trailing portion in the laser incidence direction).

[0049] Atoms that have been ionized are then sucked into the analysis section 32, and analysis is performed on a mass of these atoms.

[0050] Next, description follows regarding the advantageous effects of the present exemplary embodiment.

[0051] In the mass spectrometer 20, the sputter atoms S ejected from the solid sample X are ionized by the laser beam L1 and the reflected beam L2. Due to the laser beam L1 and the reflected beam L2 being overlapped in the ionization space above the region of the solid sample X irradiated by the ion beam B (the range of the laser beam L1 is illustrated in Fig. 3 by the double-dot broken lines and the range of the reflected beam L2 is illustrated in Fig. 3 by the solid line). There is accordingly an increase in the photon density in the region where the laser beam L1 and the reflected beam L2 overlap in the ionization space, in comparison, for example, to configurations in which the laser beam L1 and the reflected beam L2 are not caused to overlap in the ionization space. This increases the probability of photons colliding with the sputter atoms S. Namely, the ionization rate is raised. The number of atoms ionized in this manner is thereby increased, raising the mass spectrometry precision using the analysis section 32.

[0052] The optical axis of the laser beam L1 and the optical axis of the reflected beam L2 are arranged in the mass spectrometer 20 so as to be coaxial. This increases the region where the laser beam and the reflected beam overlap in the ionization space, raising the ionization rate of the sputter atoms S even further.

[0053] Moreover, the reflector 30 is attached to the sample stage 24, facilitating an operation to align the optical axes of the laser beam L1 and the reflected beam L2 coaxially compared, for example, to configurations in which the reflector 30 is attached at a position separated from the sample stage 24.

[0054] Furthermore, in the mass spectrometer 20 the solid sample X can be replaced by removing the sample stage 24 from the vacuum chamber 22 by extracting the sample stage 24 through the access port 34. The reflector 30 can moreover be cleaned or replaced when removing the sample stage 24.

Second Exemplary Embodiment

[0055] Explanation follows regarding a mass spectrometer and a mass spectrometry method according to a second exemplary embodiment of the present disclosure, with reference to Fig. 5 and Fig. 6.

[0056] As illustrated in Fig. 5 and Fig. 6, a mass spectrometer 50 of the present exemplary embodiment is configured similarly to that of the first exemplary embodiment, except in configuration of a sample stage 52. The same reference numerals are appended to configuration similar to that of the first exemplary embodiment, and explanation will be omitted thereof.

[0057] There are plural (four in the present exemplary embodiment) grooves 54 formed to the sample stage 52 in a surface 52A. These grooves 54 extend from outer peripheral portions of the sample stage 52. A plurality of reflectors 30 are configured so as to be fitted into these grooves 54. Fitting reflectors 30 into the respective grooves 54 results in the laser beam L1 shone from the laser beam source 28 being reflected by the plurality of reflectors 30, so as to achieve a configuration in which reflected beams L2 overlap plural times in the ionization space as illustrated in Fig. 5 and Fig. 6.

[0058] Next, description follows regarding advantageous effects of the present exemplary embodiment.

[0059] In the mass spectrometer 50, the sputter atoms S that have been ejected from the solid sample X are ionized by the reflected beams L2. The reflected beams L2 reflected by the plurality of reflectors 30 in the ionization space above the region of the solid sample X irradiated by the ion beam B overlap with each other. The photon density in the region where the reflected beams L2 overlap with each other in the ionization space is thereby increased in comparison, for example, to configurations in which the reflected beams L2 do not overlap with each other, thereby increasing the probability of photons colliding with the sputter atoms S. Namely the ionization rate is raised. The number of atoms that are ionized is thereby increased, raising the mass spectrometry precision using the analysis section.

[0060] In the mass spectrometer 50 of the second exemplary embodiment, as illustrated in Fig. 5, the laser beam L1 shone from the laser beam source 28 is configured so as to not pass through the ionization space, however the present disclosure is not limited to such a configuration. The configuration of the sample stage 52 having the plurality of reflectors 30 attached thereto may be applied to the mass spectrometer 20 of the first exemplary embodiment. Configuration in this manner results in the laser beam L1 shone from the laser beam source 28 also passing through the ionization space, thereby raising the ionization rate of the sputter atoms S.

[0061] Moreover, although in the mass spectrometer 20 of the first exemplary embodiment the wavelength of the pulsed laser (laser beam L1) shone from the laser beam source 28 is fixed, the present disclosure is not limited to such a configuration. For example, the laser beam source 28 may be configured such that the wavelength of the laser beam L1 is variable according to the species of atoms contained in the solid sample X. Such a configuration enables resonant ionization of the sputter atoms S to be achieved by being able to vary the wavelength of the laser beam according to the species of atoms contained in the solid sample X. The ionization rate of the sputter atoms S can be raised thereby. Note that a configuration in which the wavelength of the laser beam L1 is variable may also be applied to the mass spectrometer 50 of the second exemplary embodiment.

Experiments

Confirmation of Advantageous Effects of Present Disclosure

[0062] Description follows regarding advantageous effects of raising the ionization rate using the present disclosure. Note that there are two mechanisms operating under different principles to achieve the ionization rate raising advantageous effect of the present disclosure, and so mechanism will be described in turn.

(1) Advantageous Effect of Increased Photon Density from Overlap Between Incident Beam and Reflected Beam of Pulsed laser (Non-Resonant Ionization)

[0063] Fig. 7 illustrates a mass spectrum for an experiment in which one reflector is employed to obtain an increase effect from reflection once. An indium (In) plate is employed as a solid sample. The laser employed as the laser beam source has a wavelength of 266 nm, a repetition rate of 2 kHz, and a pulse width of about 7 ns. A polished silicon wafer is employed as the reflector. The reflectivity of the silicon wafer to the laser beam was found to be 63% in prior measurements. An increase of 1.8 times was observed in the results for the peak area intensity of $^{115}In^+$ ions compared to with no reflection. Due to the reflectivity of the reflector being 63%, an increase effect of 1.63 times would have been expected from the combination of the outward path and the return path of the laser (the incident beam and the reflected beam of the laser). However, an advantageous effect actually obtained exceeded this expectation.

[0064] This can be explained by reference to Fig. 8A and Fig. 8B. The pulse width of the laser employed was 7 ns, and the pulse length exceeded 2 meters.

[0065] Due to the closeness from the center of the solid sample to the reflector being 10 mm or less, the reflected beam and the incident beam overlapped above the sample stage. The ionization of indium atoms with a laser wavelength of 266 nm is non-resonant two-photon absorption ionization, and the ionization rate is theoretically proportional to the square of the photon density.

[0066] Theoretically the advantageous effect obtained should be $(1 + 0.63)^2 = 2.66$ times. However, considering that in reality there is a slight misalignment between the optical axes, and that any atoms that had already be ionized by the incident beam would not be counted in this advantageous effect, although the increased rate in experiment did not reach 2.66 times, this did, however, explain why the increased rate was greater than simply 1.63 times.

[0067] Thus a single occurrence of reflection demonstrated that an advantageous effect of raised ionization rate was obtained that exceeded the simple sum of the outward path and the return path of the laser as expected from the reflectivity under the condition of the optical axes of the outward path and the return path of the laser overlapping with each other.

[0068] Note that although precision placement is performed for the reflector, due to the distance D between the center of the solid sample and the reflector being about 10 mm, as illustrated in Fig. 2, for a thickness of optical axes of the laser of about 0.2 mm, a geometric computation would estimate that an advantageous effect would be obtained as long as coaxial alignment with the incident beam was achieved to an angle of 1 degree or smaller.

(2) Increase Effect from Passing Laser (Incident Beam and Reflected Beam) Twice in Different Directions (Resonant Ionization)

[0069] A case of a further high increase in rate has been discovered for a method employing reflection once. As illustrated in Fig. 8A and Fig. 8B, the processes in which ionization occurs by atoms absorbing light includes both "non-resonant ionization" and "resonant ionization".

[0070] Non-resonant ionization corresponds to the experiment on indium described above. Namely, corresponds to a case in which the ionization potential is reached by the simultaneous absorption of two photons from a laser beam of a given wavelength. Cases such as this occur with a probability that both a first photon is absorbed and a second photon is absorbed, and so the ionization rate is proportional to the square of the photon density.

[0071] However, by employing light of a wavelength tuned to an internal potential (excitation level) of an atom, as illustrated in Fig. 8A, ionization is achieved when a second photon is absorbed during an interval of the order of several nanoseconds in which the atom remains in an excited state after being excited by a first photon.

[0072] Namely, in a resonant process there is an extended period of time of a few nanoseconds during which to absorb the second photon, such that the ionization rate increases dramatically when the laser beam is matched to the resonant wavelength. This phenomenon is called resonant ionization. The laser beam source employed for resonant ionization should have a variable wavelength, and so an implementable laser system specification in terms of repetition rate, energy, and the like of the laser is even more difficult to achieve in practice than for a non-resonant laser system. This means that there is also demand with laser resonant ionization methods for a method employing a wavelength variable laser at a given repetition rate and energy to obtain the maximum advantageous effect (ionization rate).

[0073] Fig. 9 illustrates the results when zirconium (Zr) is employed as the solid sample.

[0074] The wavelength of the laser is shown on the horizontal axis, and an increase effect of an increased number of ions arising from resonance is observed in a region from 737.69 nm to 737.72 nm centered on a wavelength of fundamental wave of 737.705 nm (since it is the second harmonic wave of the fundamental wave that is employed herein, the wavelength of the laser beam is actually half this wavelength).

[0075] In the experiment respective signals are split out for the incident direction and the reflection direction of the laser (respectively referred to as the outward path and the return path), and these signals are plotted in Fig. 9. An aluminum coated mirror having a reflectivity of 90% was employed as the reflector.

[0076] As illustrated in Fig. 9, when the number of ions detected are substantially the same on the return path as on the outward path, an advantageous effect obtained is about a doubling at the resonance central wavelength (737.705 nm) for the relative increase for the total value of the outward path and the return path.

[0077] The resonant ionization process proceeds, as stated above, first via the excitation level, and so the relationship between the ionization rate and the photon density is not the ionization rate being proportional to the square power of the photon density, and is rather proportional the single power thereof (i.e. a linear relationship). In this case the reflectivity is 90%, and so the ionization rate is the simple sum of the outward path and the return path, i.e. 1.9 times.

[0078] In practice an advantageous effect of 2 times was obtained, exceeding the simple sum, albeit only slightly. The following is an interpretation of this phenomenon. In the resonant ionization process the excited state is achieved by absorbing the first photon. Although the excited state differs according to which element is employed and the excitation levels thereof, the excited state generally has a life in the order of nanoseconds.

[0079] Thus even suppose that excitation occurred due to the laser on the outward path, then even if this was not immediately followed by absorption of a second photon, the process of second photon absorption might still proceed due to action of the laser on the return path. Namely, an increase in the increased rate was demonstrated of an amount commensurate with this extra effect in resonant ionization over the simple sum from the overlap of the incident beam and the reflected beam by the reflection once.

[0080] Moreover, sometimes a Doppler effect is seen in the resonant ionization process.

[0081] Atoms are ejected in various directions and at various kinetic energies from a point where the ion beam is irradiated so as to form a sputter atom group. When a laser is incident from one direction onto the sputter atom group, some atoms are flying off in the direction toward the laser incidence direction, and some atoms in the direction away from this direction. The frequency of the laser appears different for these respective atoms. This phenomenon is referred to as the Doppler effect. A broadening accordingly arises in the wavelengths at which the resonance effect appears due to the sputter atom group being a group of atoms of various kinetic directions and energies. This is referred to hereinafter as Doppler broadening. Suppose that the width of wavelengths in Doppler broadening are wider than the line width of the laser, then only the atoms in the sputter atom group for which the Doppler shift lies inside the line width of the laser would undergo resonant ionization. This would result in a reduction in the ionization rate. In an ideal method the line width of the laser would be variable so that the line width matched the Doppler broadening, however, it is generally difficult to change the line width of the laser in such cases.

[0082] The resonant ionization by reflection once in the present disclosure achieves an advantageous effect as follows even when such Doppler broadening occurs. Fig. 10 is a simplified chart of the same data as in Fig. 9, wherein only the signal strength of the incident beam (outward path) and the reflected beam (return path) of the laser are illustrated. From Fig. 10 it is apparent that the resonance peak wavelengths are slightly displaced from each other in the outward path and the return path of the laser (the laser is shifted to the short wavelength side on the outward path, and the laser is shifted to the long wavelength side on the return path).

[0083] The laser beam source employed in this example has a line width of about 0.005 nm, and the line width is not as narrow as the Doppler broadening. However, a shift appears in the resonant wavelength depending on whether the laser is on the outward path or the return path, i.e. depending on the direction the laser is passing along, and it is apparent that this acts to give different Doppler shift bands on the outward path and the return path of the laser. This effect means that an increase effect can be expected particularly in situations in which the line width of the laser can only be set in a narrow range with respect to the Doppler broadening, as illustrated in Fig. 11A and Fig. 11B. For example, when the laser is incident from the left as illustrated in Fig. 11A, atoms are ionized in the ranges illustrated by the bold lines where the central wavelength of the laser is tuned to vertical direction components in the sputter atom group that experience no Doppler shift. However, stated in reverse, there is a large Doppler shift in ranges outside thereof (ranges illustrated by the fine lines), and these ranges fall outside resonant conditions.

[0084] In contrast thereto, as illustrated in Fig. 11B, ionization is performed by utilizing the reflected beam and setting the central wavelength of the laser to the shorter wavelength side by half a line width. Doing so results in resonant ionization for the atom group ejected toward the left side of the vertical direction when the laser is incident (on the outward path of the pulsed laser), and results in resonant ionization for the atom group ejected toward the right side when the direction is changed during reflection (on the return path of the laser).

[0085] Namely, resonant ionization can be induced for a wider width of Doppler broadening than with a single pass. Although the experiment results illustrated in Fig. 9 and Fig. 10 include the advantageous effect referred to above, the line width of the laser was not that narrow with respect to the Doppler broadening. Thus the experimental results can be interpreted as being due to only the effect of overlapping the optical axes of the outward path and the return path of the laser, as described above. Note that the method illustrated in Fig. 11B is more effective when the line width of the laser is narrower.

[0086] Although an exemplary embodiment of the present disclosure has been described above, the present disclosure is not limited thereto, and obviously various modifications other than those described above may also be implemented within a range not departing from the spirit of the present disclosure.

[0087] The entire disclosure of Japanese Patent Application No. 2017-054691 filed on March 21, 2017 is incorporated by reference in the present specification.

[0088] All publications, patent applications and technical standards mentioned in the present specification are incorporated by reference in the present specification to the same extent as if each individual publication, patent application, or technical standard was specifically and individually indicated to be incorporated by reference.

Claims

1. A mass spectrometer comprising:

a vacuum chamber;
a sample stage disposed inside the vacuum chamber;
an ion beam source configured to irradiate an ion beam onto a solid sample placed on the sample stage so as to eject atoms from the solid sample;
a laser beam source configured to pass a laser beam above a region of the solid sample irradiated by the ion beam;
a reflector disposed inside the vacuum chamber and configured to reflect the laser beam so as to cause the laser beam and a reflected beam to overlap above the irradiated region; and
an analysis section configured to analyze a mass of atoms ionized by the laser beam and the reflected beam.

2. The mass spectrometer of claim 1, wherein the reflector is attached to the sample stage so that an optical axis of the laser beam and an optical axis of the reflected beam are coaxial.

3. The mass spectrometer of claim 1, wherein a plurality of reflectors are attached to the sample stage such that reflected beams overlap with each other a plurality of times above the irradiated region.

4. A mass spectrometer comprising:

a vacuum chamber;
a sample stage disposed inside the vacuum chamber;
an ion beam source configured to irradiate an ion beam onto a solid sample placed on the sample stage so as to eject atoms from the solid sample;
a laser beam source configured to emit a laser beam parallel to a surface of the sample stage;
a plurality of reflectors disposed inside the vacuum chamber and configured to reflect the laser beam so that reflected beams are caused to overlap with each other above a region of the solid sample irradiated by the ion beam; and
an analysis section configured to analyze a mass of atoms ionized by at least reflected beams.

5. The mass spectrometer of any one of claim 1 to claim 4, wherein the laser beam source is capable of varying a wavelength of the laser beam according to a type of atom contained in the solid sample.

6. The mass spectrometer of any one of claim 1 to claim 5, wherein:

the sample stage is detachably installed in the vacuum chamber; and
an access port is provided at the vacuum chamber for extracting the sample stage.

7. A mass spectrometry method comprising:

a process of disposing a sample stage having a solid sample placed thereon inside a vacuum chamber and placing the inside of the vacuum chamber in a state of vacuum;
a process of irradiating an ion beam onto the solid sample so as to eject atoms from the solid sample;
a process of passing a laser beam above a region of the solid sample irradiated by the ion beam so as to ionize atoms;
a process of using a reflected beam, reflected so as to overlap with the laser beam, to ionize atoms remaining un-ionized by the laser beam; and
a process of analyzing a mass of atoms that have been ionized.

FIG.1

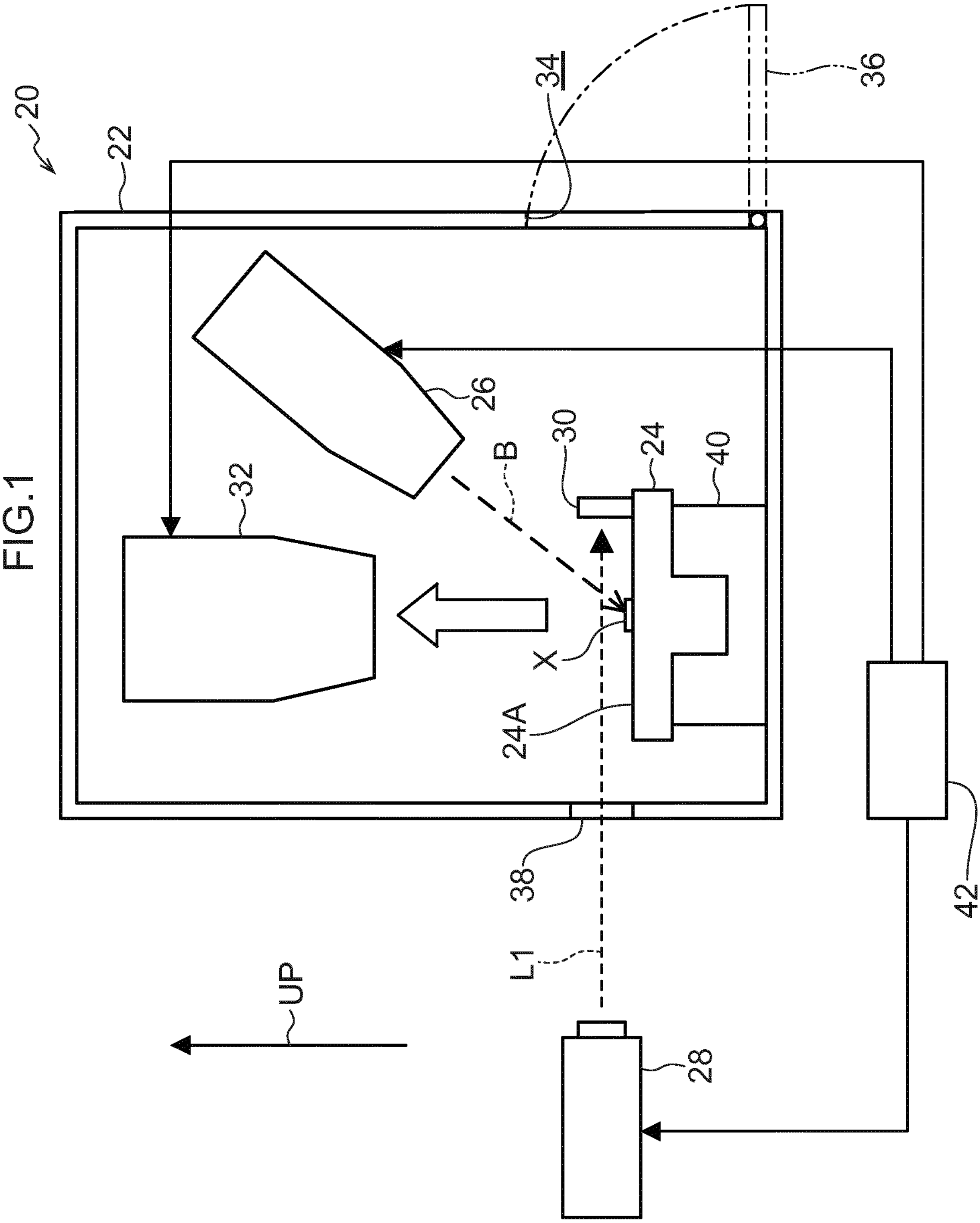


FIG.2

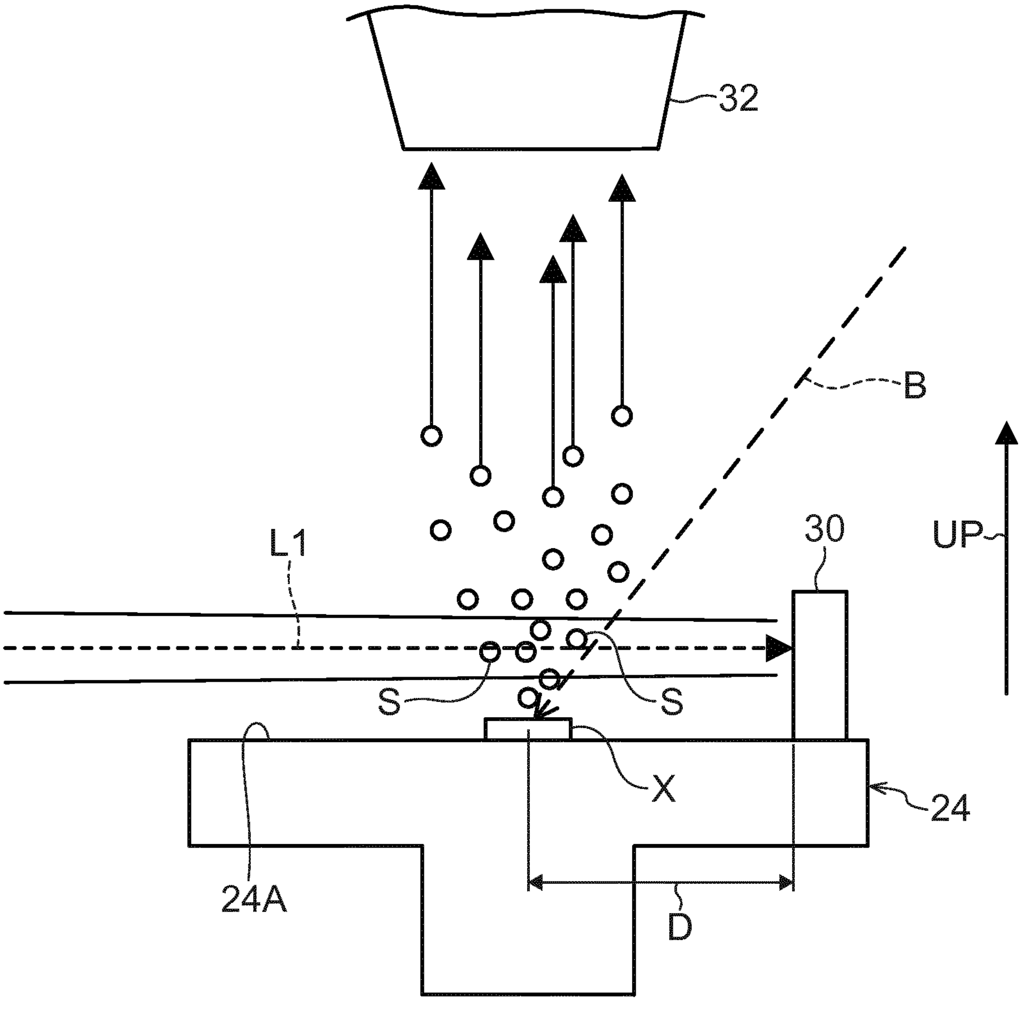


FIG.3

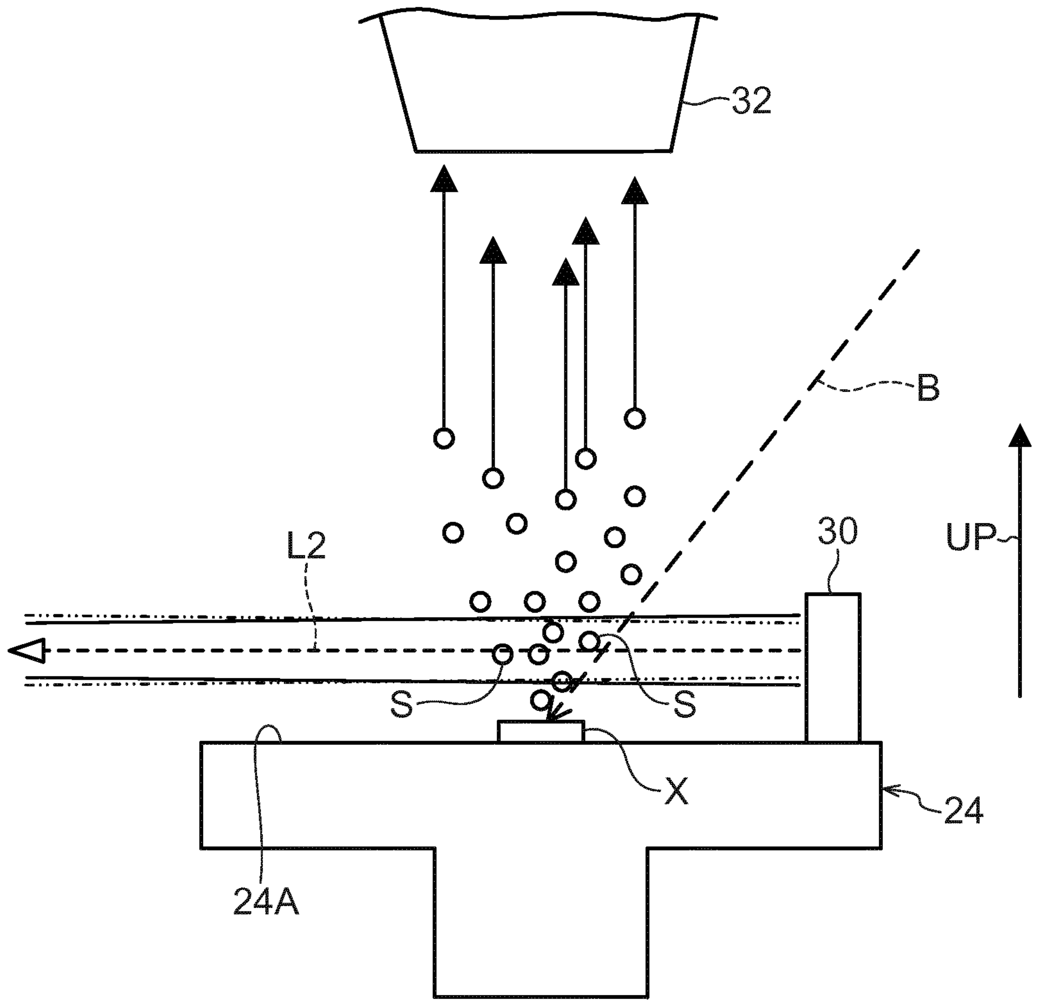


FIG.4

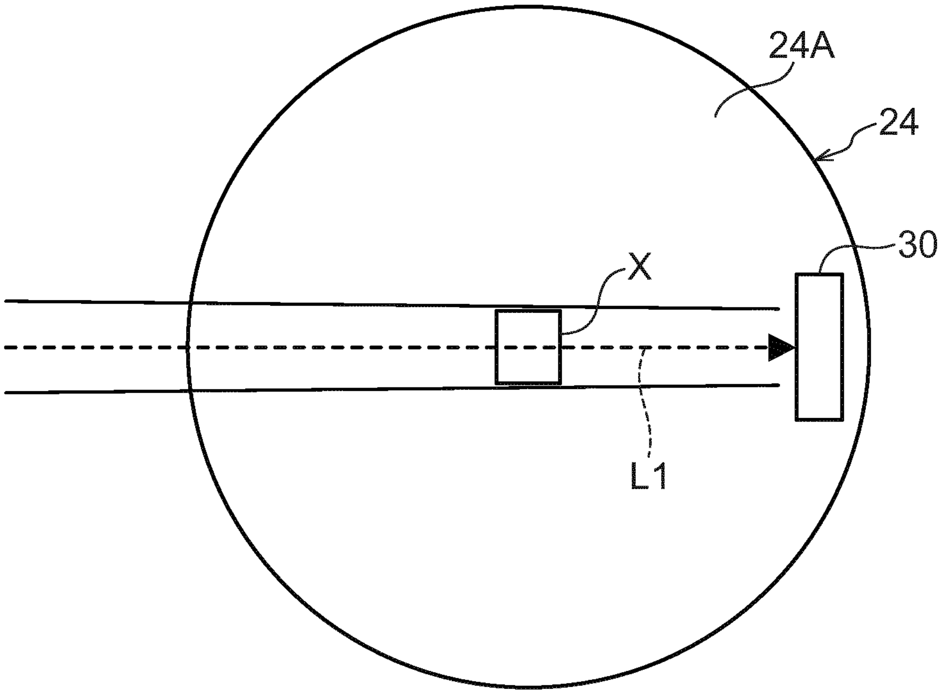


FIG.5

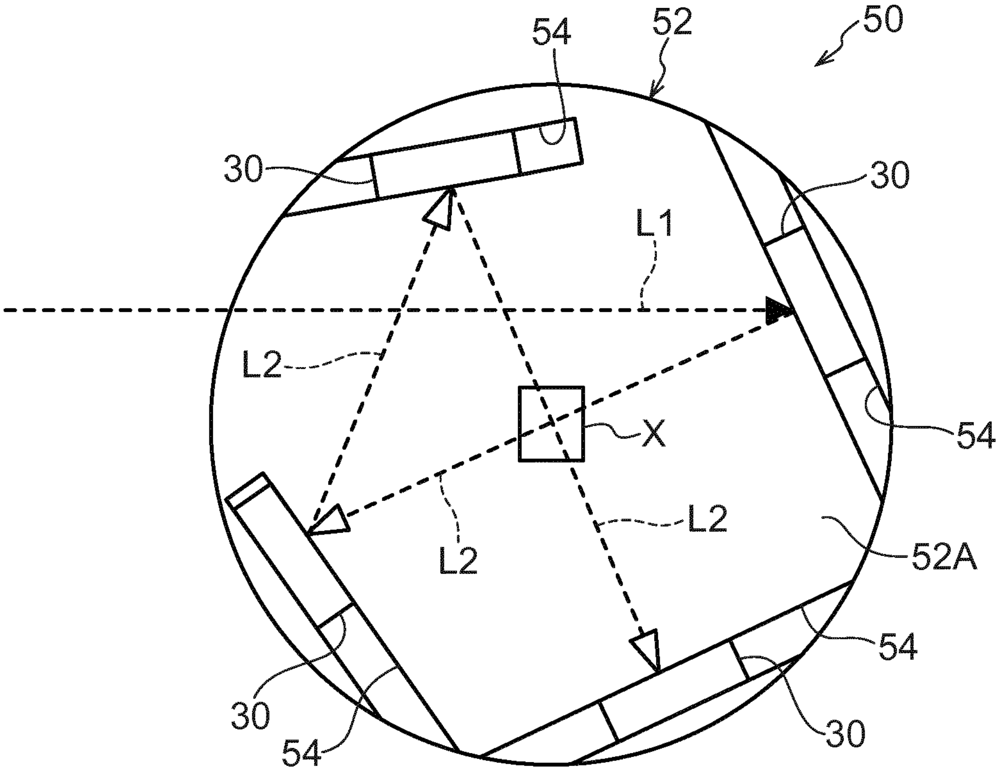


FIG.6

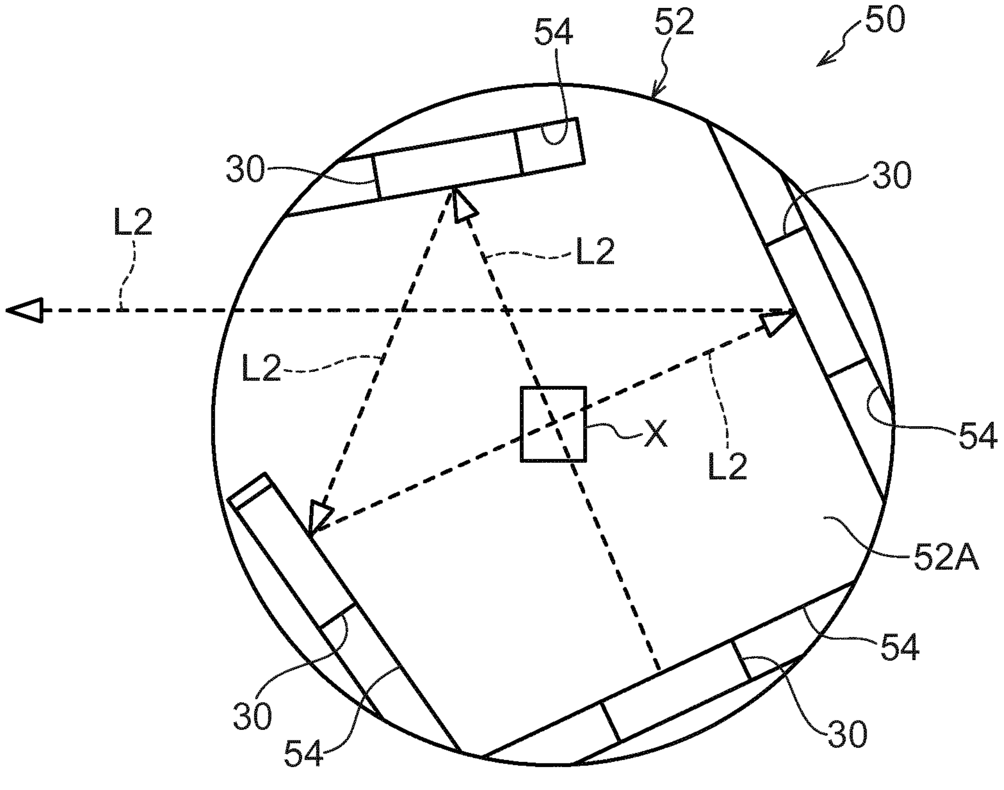


FIG.7

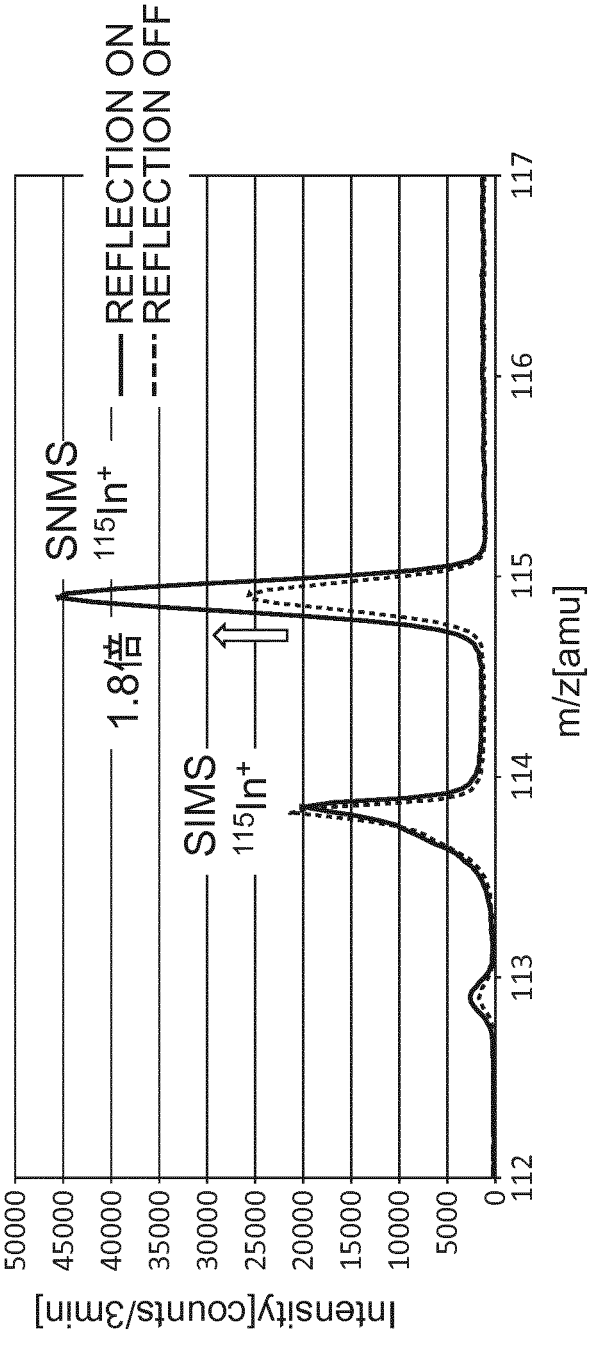

Intensity[counts/3min]
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
112
113
114
115
116
117
m/z[amu]
SIMS
^{115}In^{+}
SNMS
^{115}In^{+}
1.8倍
REFLECTION ON
REFLECTION OFF

FIG.8A

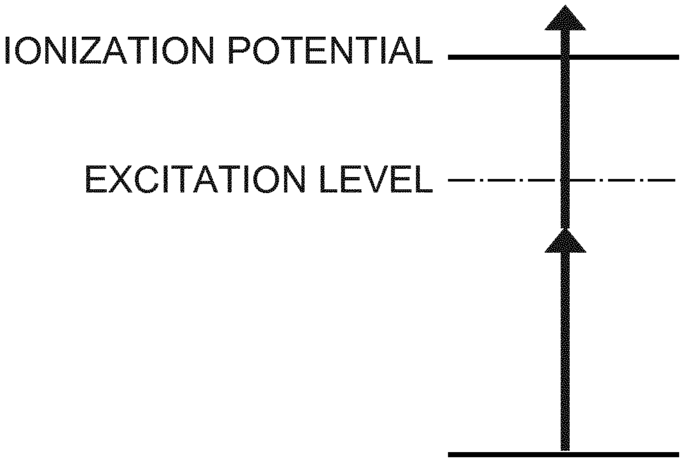

IONIZATION POTENTIAL
EXCITATION LEVEL

FIG.8B

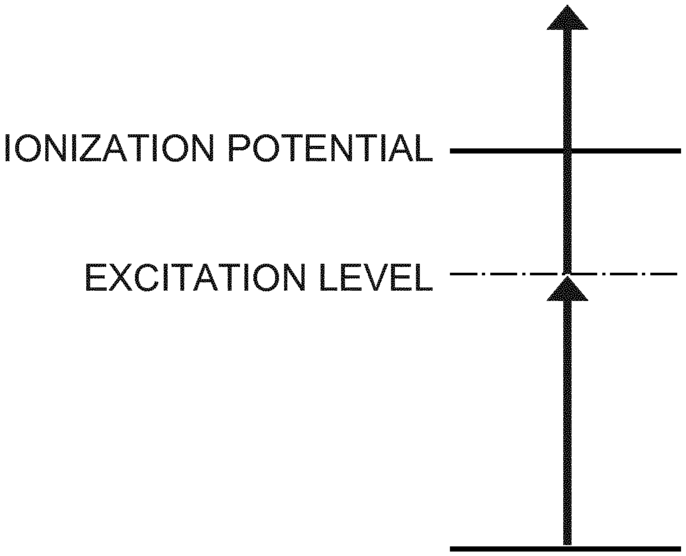

IONIZATION POTENTIAL
EXCITATION LEVEL

FIG.9

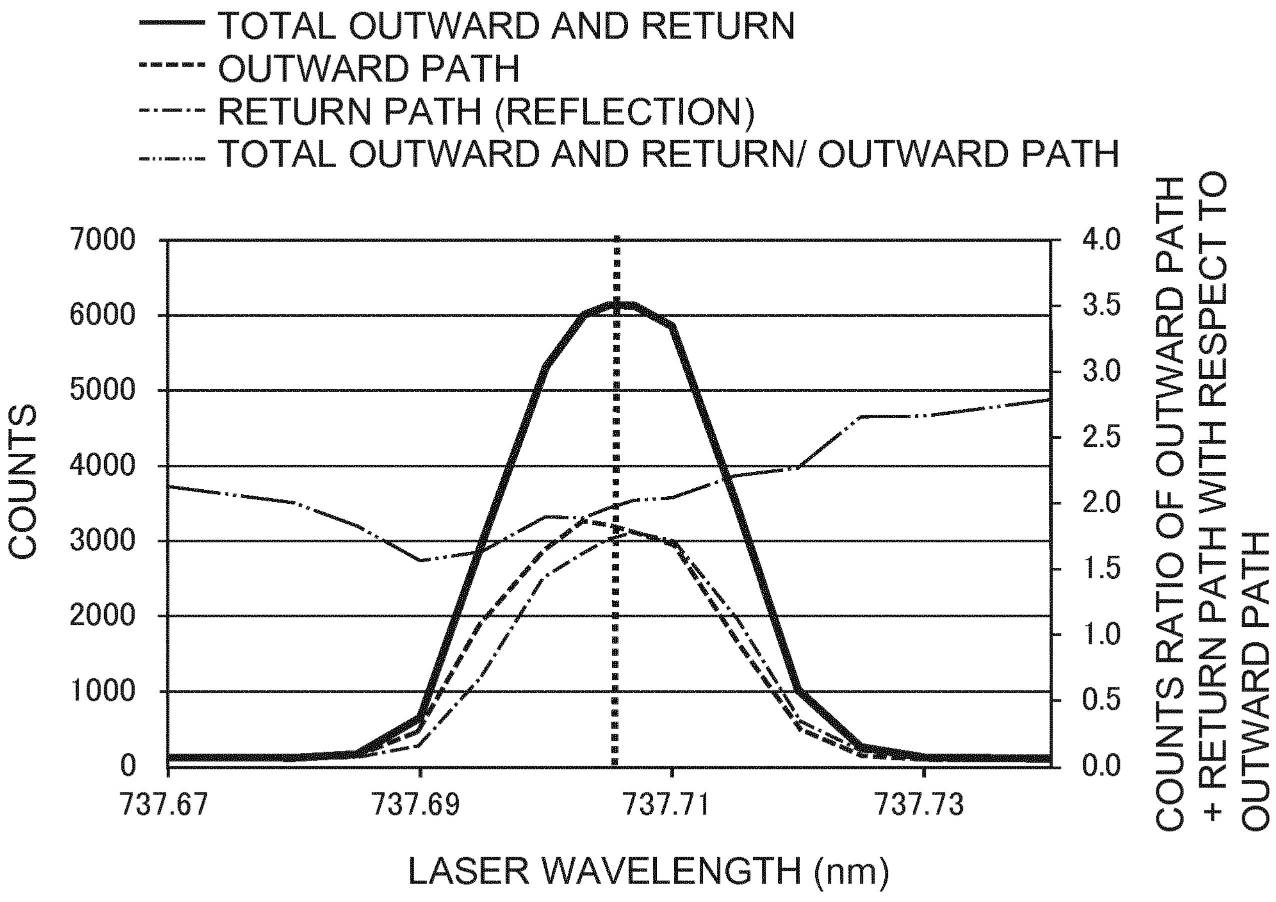

TOTAL OUTWARD AND RETURN
OUTWARD PATH
RETURN PATH (REFLECTION)
TOTAL OUTWARD AND RETURN/ OUTWARD PATH
COUNTS
7000
6000
5000
4000
3000
2000
1000
0
737.67
737.69
737.71
737.73
LASER WAVELENGTH (nm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
COUNTS RATIO OF OUTWARD PATH + RETURN PATH WITH RESPECT TO OUTWARD PATH

FIG.10

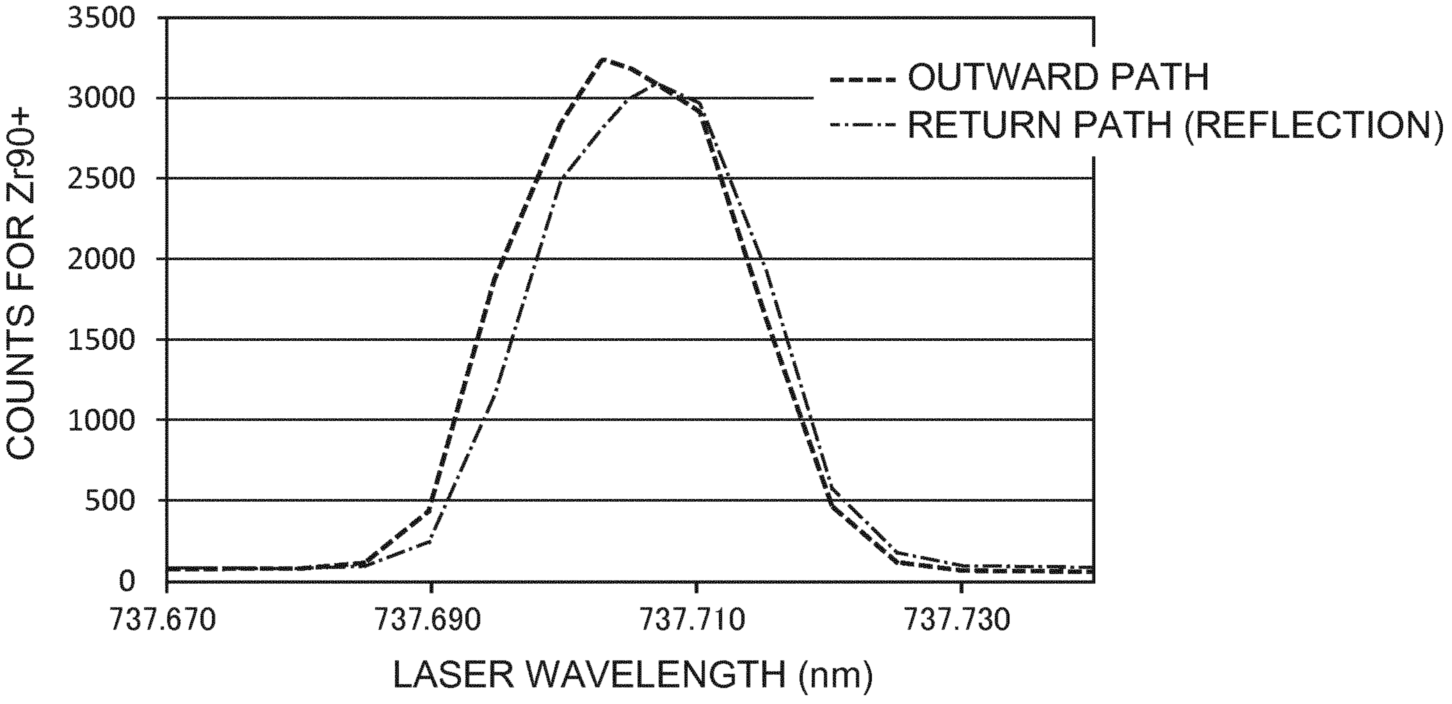

COUNTS FOR Zr90+
3500
3000
2500
2000
1500
1000
500
0
737.670
737.690
737.710
737.730
LASER WAVELENGTH (nm)
OUTWARD PATH
RETURN PATH (REFLECTION)

FIG.11A

Y-Z (SIZE OF CIRCLE INDICATES MAGNITUDE OF DOPPLER SHIFT, ONE PASS)

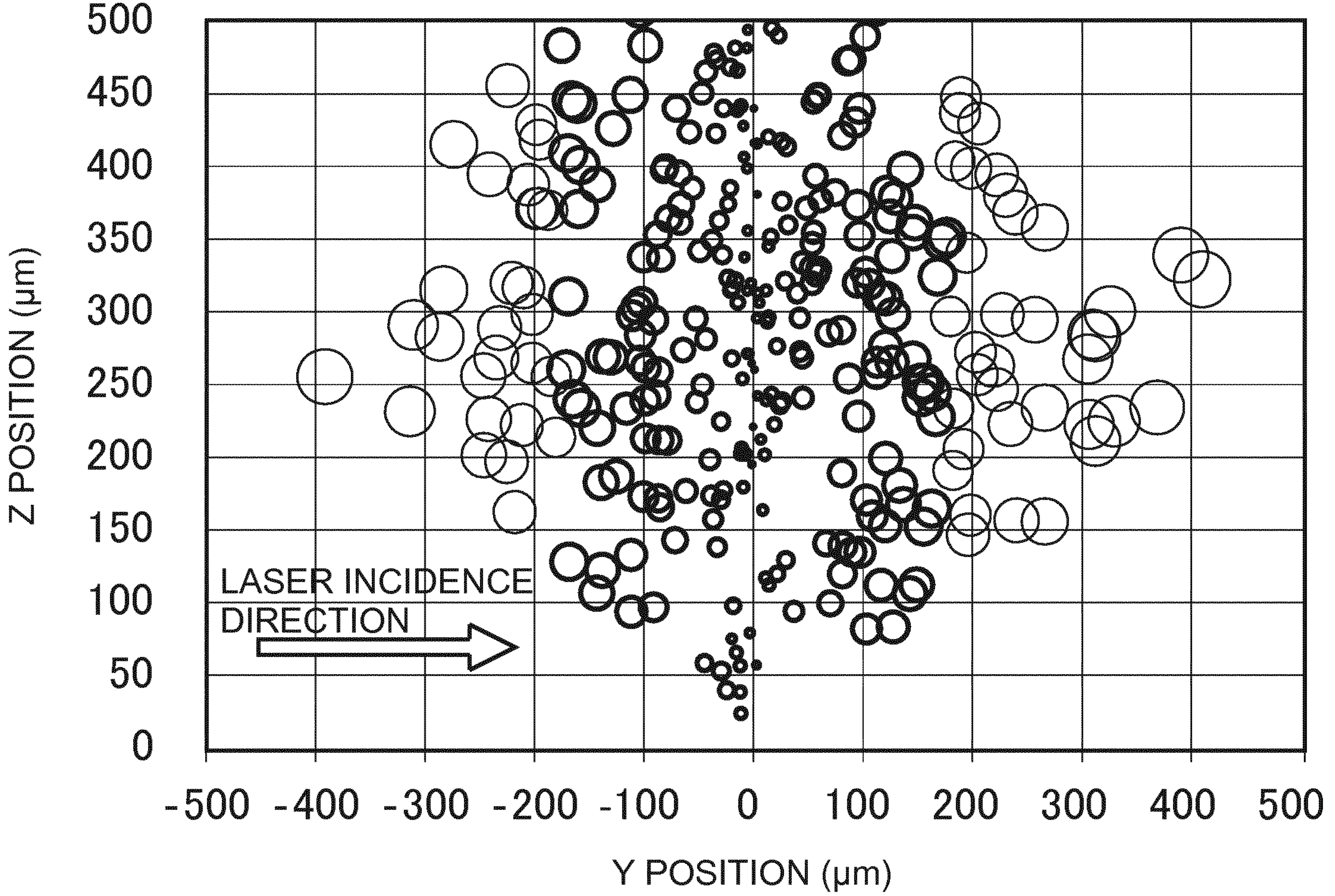
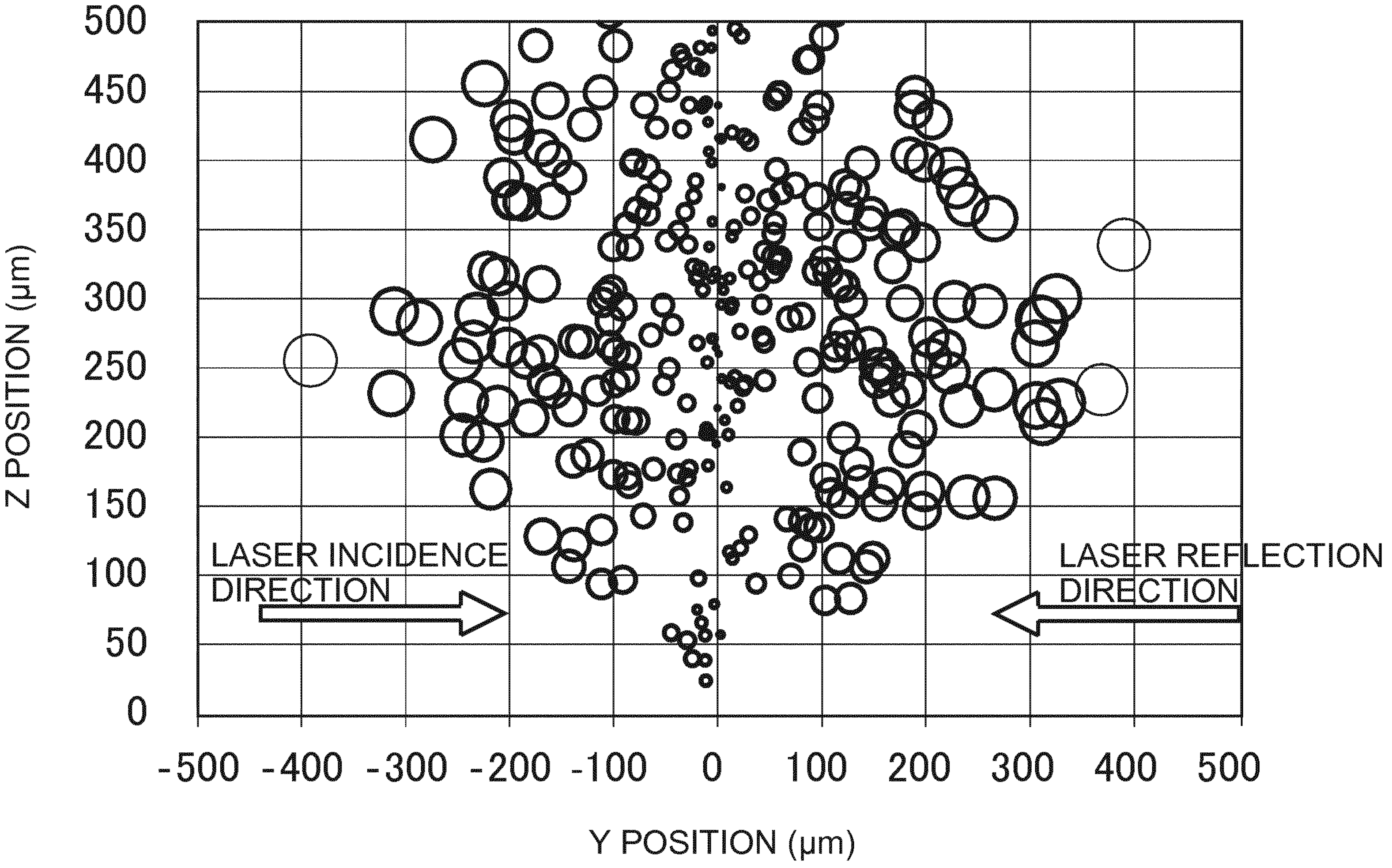


FIG.11B



Y-Z (SIZE OF CIRCLE INDICATES MAGNITUDE OF DOPPLER SHIFT, REFLECTION ONCE)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/010332

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. H01J49/10(2006.01)i, G01N27/62(2006.01)i, G01N27/64(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. H01J49/10-49/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 10-149795 A (HITACHI, LTD.) 02 June 1998, abstract, paragraphs [0013], [0021], [0022], fig. 10, 11 (Family: none)	1-4, 6-7 1-7
Y	Microfilm of the specification and drawings annexed to the request of Japanese Utility Model Application No. 106890/1988 (Laid-open No. 29151/1990) (JEOL LTD.) 26 February 1990, examples, fig. 1 (Family: none)	1-2, 5-7

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
30.03.2018

Date of mailing of the international search report
10.04.2018

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/010332

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 10-334847 A (HITACHI, LTD.) 18 December 1998, abstract, paragraphs [0016]-[0022], fig. 1, 6 (Family: none)	1-7
Y	JP 2016-24992 A (KOGAKUIN UNIV) 08 February 2016, paragraph [0036] (Family: none)	5-6
Y	JP 2000-162164 A (HITACHI, LTD.) 16 June 2000, paragraph [0045] (Family: none)	5-6

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2001108657 A **[0002]**
- JP 2017054691 A **[0087]**