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Description

The present invention relates to a sample holder for a glow discharge mass spectrometer. The invention is applicable to a sample holder which holds a sample to be analyzed by glow discharge mass spectroscopy for analyzing trace element(s) contained in a highly pure sample such as a metal, semiconductor or ceramic sample and electrically insulates the sample from an anode.

A sample holder is known from "Glow-discharge mass spectrometry - Technique for determining elemental composition profiles in solids" by Coburn et al, published in Journal of Applied Physics, vol. 45, no. 4, April 1974, pp 1779-1786.

In the glow discharge mass spectrometer, an insulating sample holder, which is preferably in the form of a cone, is made of an insulating material for electrically insulating a sample which acts as a cathode from an anode. As the insulating material, polytetrafluoroethylene (hereinafter referred to as "PTFE") is preferably used, since it is easy to process and has good insulating properties and chemical resistance to a chemical used for cleaning a surface of the holder such as an acid.

Fig. 1 shows a cross sectional view of a typical glow discharge source, which comprises an insulating sample holder 1, a sample 2, an anode 3, a metal chuck 4, an ion exit slit 5 and a gas inlet 6. Glow discharge is generated in a gap between the sample which is held by the metal chuck 4 and acts as the cathode and the anode 3. By the insulating sample holder 1, the anode 3 is electrically insulated from the metal chuck 4 and the sample 2. Ion generated by glow discharge exhausts from the ion exit slit 5 into a mass spectrometer (not shown).

As described above, the sample holder 1 is conventionally made of PTFE.

When the glow discharge source is used, the atmosphere is evacuated to high vacuum of about 1 to 5 x 10^{-8} Torr. before discharge. Thereafter, a very small amount of argon gas is supplied from the gas inlet 6 into the glow discharge source and then the discharge is started. In Fig. 1, when the sample holder is made of PTFE, air or some other gas is trapped in pores of the PTFE material even after the glow discharge source is evacuated for a long time since the PTFE material is very porous. Therefore, for a long time from the start of glow discharge, ion species of residual gasses such as N^+, O^+ and CO^+ are detected with high intensity. Since these ions may cause interferences in analysis, it is necessary to wait till the intensities of the residual gasses decrease in case of analysis of trace elements such as S, Si and Fe. Such waiting time decreases efficiency of the analysis. Since PTFE contains fluorine atoms, fluorine-containing ion species such as $^{19}F+$ and $^{31}CF^+$ are generated and cause interferences in analysis like the above described ion species.

In addition, after repeat of the measurement, the tip end of the sample holder is severely damaged to form large unevenness. Therefore, deposited materials on the tip end are not removed by washing with an acid and remain on the surface of the sample holder. Further, whisker-like materials are formed on the surface which cause abnormal discharge during measurement.

An object of the present invention is to provide a sample holder for a glow discharge mass spectrometer, which overcomes the above described problems of the conventional sample holders and enables efficient and accurate analysis.

According to the invention, there is provided a sample holder for a glow discharge mass spectrometer, which comprises a sample holder body, characterized by a coating film of i-carbon or crystalline diamond covering the surface of the sample holder body.

For a better understanding of the invention, and to show more clearly how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, in which:

Fig. 1 is a cross sectional view of a known glow discharge source;

Fig. 2 is a cross sectional view of one embodiment of a sample holder of the present invention;

Figs. 3 and 4 are graphs showing intensity changes of interference ions with time when the sample holder of the present invention having an insulating film of i-carbon and the conventional PTFE sample holder are used, respectively; and

Fig. 5 is a graph showing intensity changes of interference ions with time when the sample holder made of quartz not being an embodiment of the present invention is used.

In an example not being an embodiment of the present invention, the sample holder 1 may be made of quartz. Since quartz glass is non-porous, the defects of the PTFE made sample holder can be overcome.

However, when the sample holder made of quartz glass is used for trace analysis of silicon (Si) by the glow discharge mass spectroscopy, quartz glass is also sputtered so that contamination due to Si which is one of the constituent elements of quartz glass occurs. In elemental analysis of trace impurity elements contained in a highly pure material, particularly in purity analysis of a compound semiconductor such as GaAs and InP or a raw material for such semiconductor, Si is often one of important elements to be analyzed, and its analytical accuracy should be in the order of ppm or less. Therefore, a sample holder which causes no or substantially no contamination due to Si is desired.

Accordingly, in an embodiment of the present invention, very dense i-carbon or crystalline diamond is used as insulating material for coating the sample holder. For forming the i-carbon or crystalline diamond thin film, plasma CVD (chemical vapor deposition), particularly low temperature plasma CVD is preferably used.

The thickness of the insulating film depends on other analysis conditions and the like. Generally, it is from 0.1 to 1 µm.

When a base material of the sample holder is PTFE, PTFE is heated to a temperature not higher than 100 °C during the formation of the insulating film by the above preferred methods, any problem such as deformation of PTFE is not caused.

By using the sample holder of the present invention which is coated by the i-carbon film, evacuation time for degassing the glow discharge source can be greatly shortened. During discharge, not only the sample but also the sample holder are sputtered. While from the conventional PTFE made sample holder, ion species consisting of carbon and/or fluorine atoms are generated, from the i-carbon insulated sample holder, ion species consisting of carbon atoms are generated since only the i-carbon film is sputtered. Thereby, the number of interfering ion species is decreased and, in turn, the efficiency of analysis is increased.

In another preferred embodiment of the present invention, the sample holder is made of quartz glass coated with the insulating film. When such insulated sample holder is used, contamination due to Si does not occur since the quartz glass is not sputtered. This type of the sample holder is particularly useful for the analysis of Si in the sample.

Fig. 2 schematically shows a cross sectional view of the typical sample holder of the present invention, which comprises a sample holder body 7 made of PTFE or quartz glass and an insulating film 8 made of the i-carbon or crystalline diamond.

The present invention will be illustrated further in detail by following Examples.

Example 1

A sample holder made of the quartz glass material 7 and the insulating film 8 of the i-carbon having a thickness of 0.5 µm as shown in Fig. 2 was produced and used for glow discharge mass spectroscopy of highly pure GaAs crystal by means of the VG 9000 glow discharge mass spectrometer (manufactured by VG Isotopes Ltd., England) under following glow discharge conditions:

Discharge voltage: 1 kV
Discharge current: 2 mA
Discharge gas: 6N argon

Changes of intensities of interfering ion species generated from the residual gasses were measured with time after the initiation of glow discharge. The results are shown in Fig. 3.

Comparative Example 1

For comparison, by using a sample holder made of PTFE having no insulating film, the glow discharge mass spectroscopy of the same sample as used in Example 1 was carried out under the same conditions as in Example 1.

The results are shown in Fig. 4.

In Figs. 3 and 4, for designating the ion species, the numerals indicate mass numbers of the ion species.

From Fig. 3, it is understood that, in Example 1, the intensities of all the ion species $^{14}N^+$, $^{54}ArN^+$, $^{28}CO^+$ and $^{16}O^+$ are stabilized within about 20 minutes from the start of the glow discharge. On the contrary, in Comparative Example 1, it is apparent from Fig. 4 that more than 3 hours from the start of glow discharge was required for stabilizing the intensities of the ion species. This means that, by the sample holder of the present invention, a time before the start of analysis is shortened to about one ninth of that in Comparative Example 1.

Example 2 and Comparative Example 2

To evaluate the contamination due to silicon from the sample holder, the mass spectroscopic analysis of highly pure GaAs was carried out in the same manner as in Example 1 but using the quartz made sample holder having the i-carbon coating film having a thickness of 0.5 µm on the surface (Example 2) or a quartz glass made sample holder (Comparative Example 2). Detected amounts of silicon in each run are shown in Table.

Table

Run No.	Example 2	Comparative Example 2
1	<0.001 ppma	5.8 ppma
2	<0.001 ppma	4.9 ppma
3	<0.001 ppma	4.6 ppma

As is apparent from the results of Table, the contamination due to silicon in Example 2 is less than one thousandth of that in Comparative Example 2.

The lower limits of detection of various elements in this Example were as follows:

Element	Lower limit of detection (ppba)
B	<0.3
Na	<0.4
Mg	<0.5
Al	<0.4
Si	<0.8
P	<0.5
S	<0.2
Ti	<0.6
V	<0.4
Cr	<0.5
Mn	<0.2
Fe	<0.3
Co	<0.4
Ni	<0.6
Cu	<0.2
Zn	<0.3
Cd	<0.6
Sb	<0.7
I	<0.4

Comparative Example 3

In the same manner as in Example 1 but using a sample holder made of quartz glass, the glow discharge mass spectroscopic analysis of the highly pure GaAs crystal was carried out. The result is shown in Fig. 5.

Claims

1. A sample holder (1) for a glow discharge mass spectrometer, which comprises a sample holder body (7), characterized by a coating film (8) of an insulating material of i-carbon or crystalline diamond covering the surface of the sample holder body (7).

2. The sample holder (1) according to claim 1, wherein the sample holder body (7) is made of polytetrafluoroethylene.

3. The sample holder (1) according to claim 1, wherein the sample holder body (7) is made of quartz glass.

Patentansprüche

1. Probenhalter (1) für ein Glimmentladungs-Massenspektrometer, der einen Probenhalterkörper (7) umfaßt, **gekennzeichnet** durch einen Beschichtungsfilm (8) aus einem isolierenden Material aus i-Kohlenstoff oder aus kristallinem Diamant, der die Oberfläche des Probenhalterkörpers (7) bedeckt.

2. Probenhalter (1) nach Anspruch 1, dadurch gekennzeichnet, daß der Probenhalterkörper (7) aus Polytetrafluorethylen hergestellt ist.

3. Probenhalter (1) nach Anspruch 1, dadurch gekennzeichnet, daß der Probenhalterkörper (7) aus einem Quarzglas hergestellt ist.

Revendications

1. Porte-échantillon (1) pour un spectromètre de masse à décharge incandescente, qui comprend un corps (7) de porte-échantillon, caractérisé par un film de revêtement (8) d'un matériau isolant en diamant de carbone i ou en diamant cristallin recouvrant la surface du corps (7) du porte-échantillon.

2. Porte-échantillon (1) selon la revendication 1, dans lequel le corps (1) du porte-échantillon est constitué de polytétrafluoroéthylène.

3. Porte-échantillon (1) selon la revendication 1, dans lequel le corps (7) du porte-échantillon est en verre quartzeux.

Fig. 1

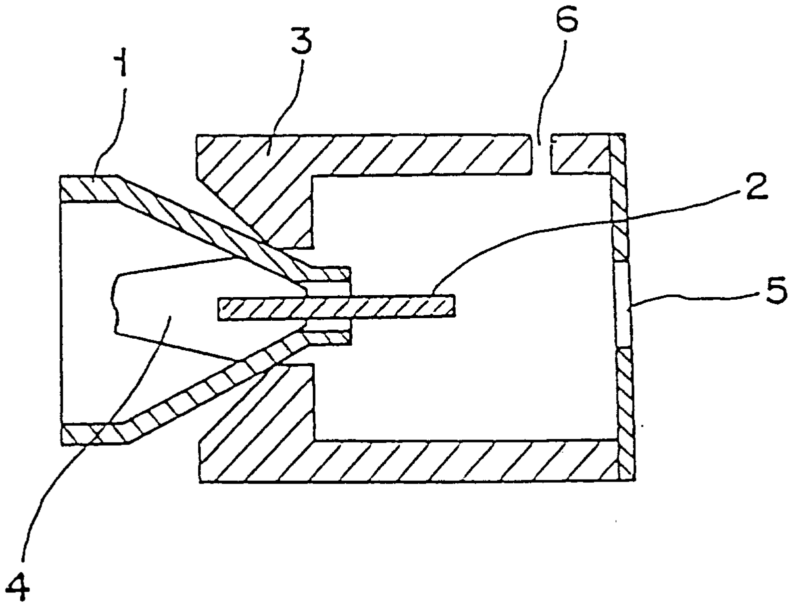


Fig. 2

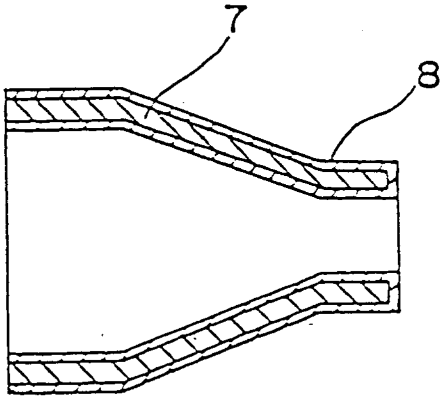


Fig. 3

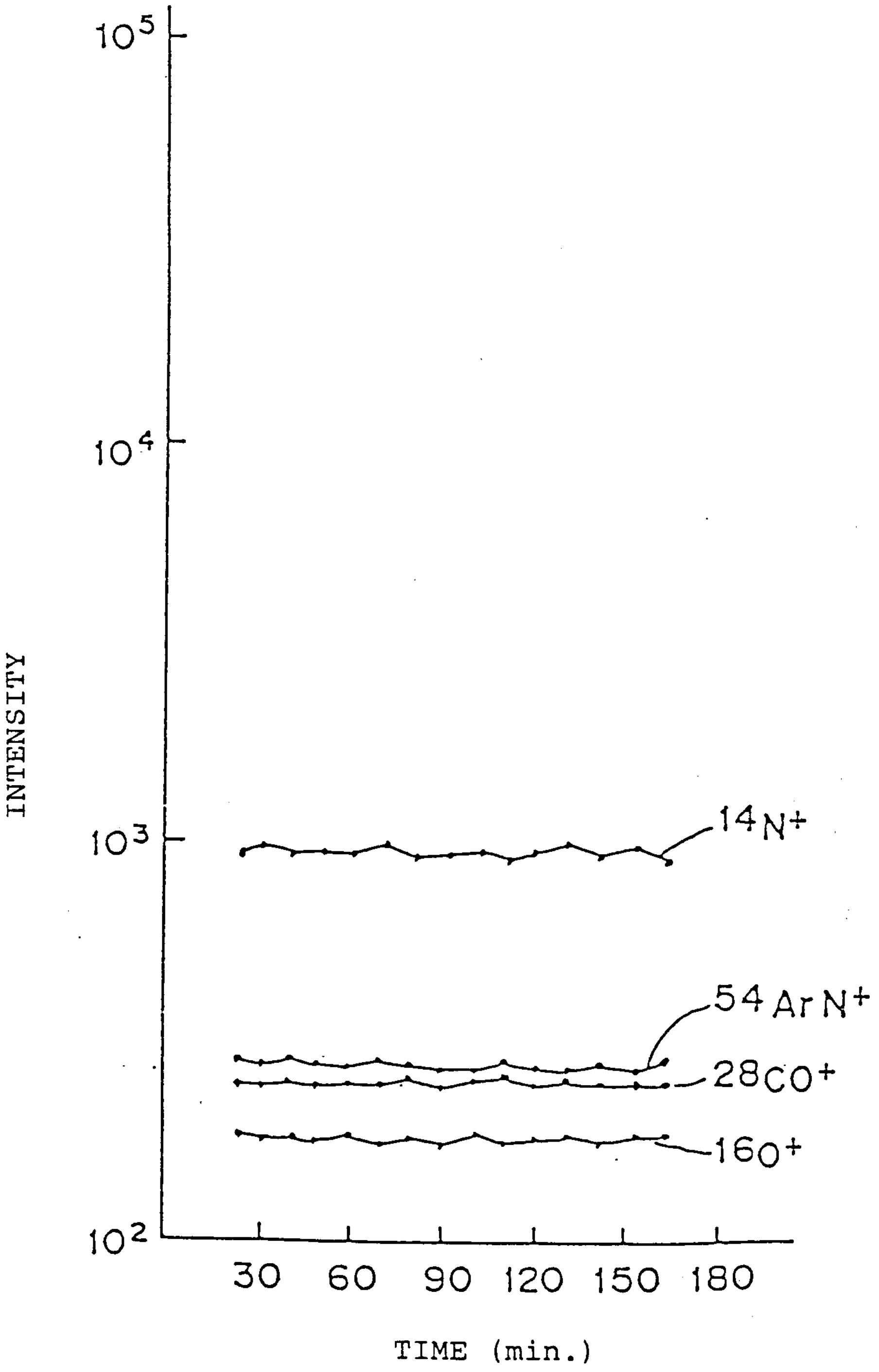

INTENSITY
10^5
10^4
10^3
10^2
$^{14}N^+$
$^{54}ArN^+$
$^{28}CO^+$
$^{16}O^+$
30
60
90
120
150
180
TIME (min.)

Fig. 4

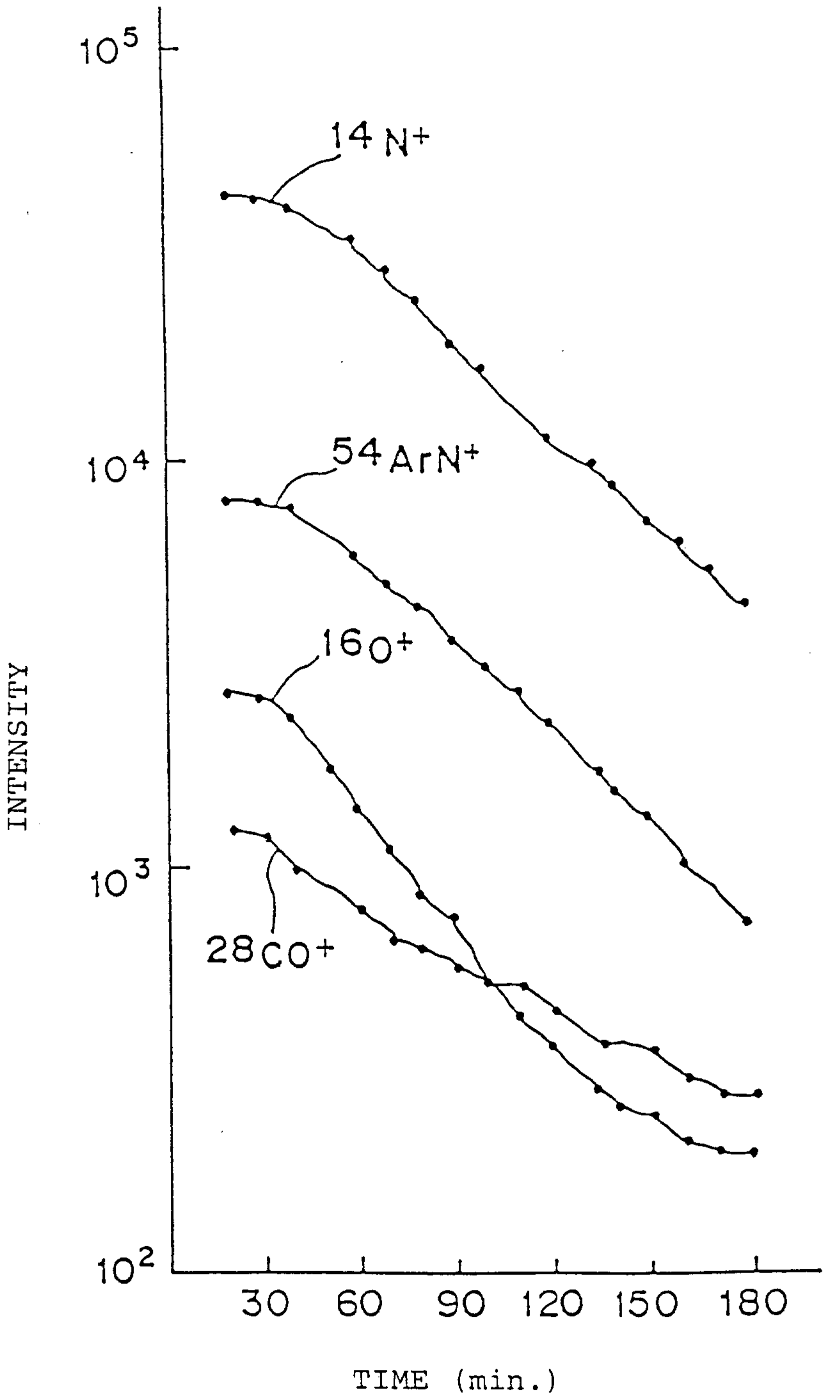
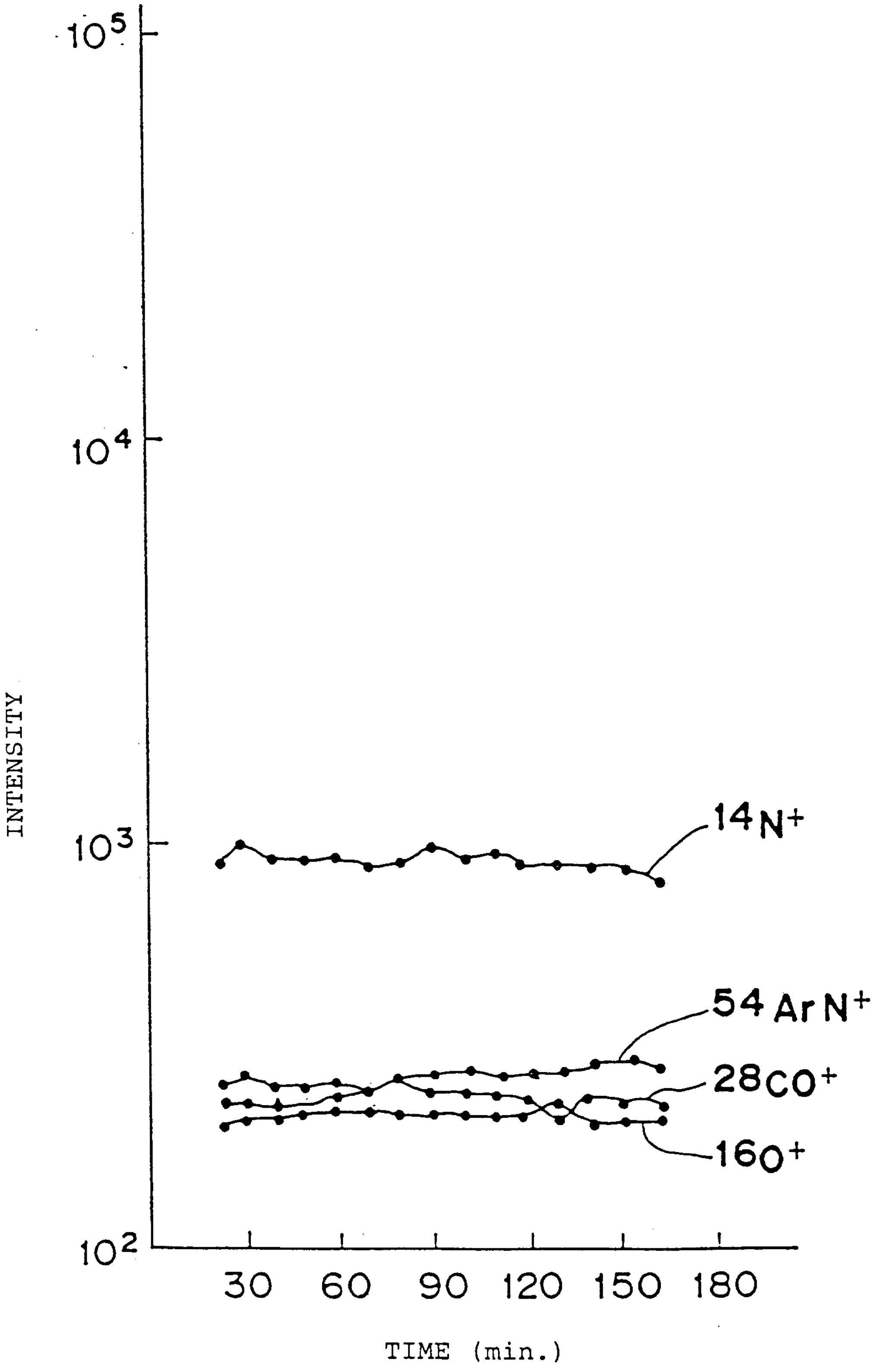

10^5
10^4
10^3
10^2
INTENSITY
$^{14}N^+$
$^{54}ArN^+$
$^{16}O^+$
$^{28}CO^+$
30
60
90
120
150
180
TIME (min.)

Fig. 5


10^5
10^4
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INTENSITY
$^{14}N^+$
54 ArN+
$^{28}CO^+$
$^{16}O^+$
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60
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TIME (min.)