

A SMALL CYCLOTRON FOR USE IN ION BEAM ANALYSIS

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SUMMARY

This paper describes the construction of a small cyclotron that is used to characterize electrical materials such as semiconductors and fibers in relation to light elements. Ion beam analyses is used to do this. At first, charged particle activation analysis for the determination of trace light elements is confirmed by non-destructive and chemical separation methods. A substoichiometric separation is introduced into light elements determinations. Total time to accomplish the chemical separation is 20 minutes and 110 minutes for nitrogen and fluorine. Finally, 1 ng/g (ppb) of carbon and oxygen in gallium arsenide can be determined in these procedures. Further improvements to cyclotron should results in other ion beam analysis such as Rutherford backscattering spectroscopy.

INTRODUCTION

Trace characterizations of light elements and crystallographic characterizations of thin film have become very important in the development of new electrical materials and devices such as large scale integration (LSI), gallium arsenide integrated circuits (GaAs IC) and optical fibers. For these purposes, ion beam analyses are used because they are highly sensitive and have unique ion channeling characteristic.

The charged particle activation analysis in ion beam analysis, is most sensitive in the determination of light elements. In comparison, Rutherford backscattering spectroscopy is useful in measuring depth profiles of elements and of ion channeling phenomenon. Ion beams from 1 to 20 MeV are used for both type of analyses. In order to establish accurate and precise methods, it is necessary to use the machines for long periods of time. More over, an ion accelerator which is able to accelerate ions in the range of 1 to 20 MeV has been necessary for this type of research.

In this paper, a compact and conventional cyclotron for use in ion beam analyses is described. It was constructed in NTT Electrical Communication Laboratories. Its use in determination of light elements by charged particle activation analysis and its applications to Rutherford backscattering spectroscopy are also described.

Cyclotron For Ion Beam Analysis

Nuclear reactions, such as $^{10}\text{B}(d,n)^{11}\text{C}$, $^{12}\text{C}(d,n)^{13}\text{N}$, $^{14}\text{N}(p,\alpha)^{11}\text{C}$, $^{16}\text{O}(^3\text{He},p)^{18}\text{F}$, are employed in the determination of light elements by charged particle activation analysis. The maximum ion energy required is approximately 15 MeV for protons¹. For

this purpose, a compact and conventional cyclotron has been constructed.

The accelerated ions and energy and maximum extracted current of the cyclotron are shown in table 1.

Table 1 Initial performance of the cyclotron

	energy(MeV)	current (A)
p	16	50
d	8	20
^3He	21	10
^4He	16	10

The acceleration energy is fixed and four kinds of ions are accelerated at maximum fields of 15.4 kG and extracted radius of 375 mm with two alternating RF frequencies of 47 MHz and 31.3 MHz. The beam was extracted and focused on the object through the beam line. Charged particle activation analysis of light elements deals with short half-life nuclides. Examples of these are nitrogen-13 of 10 minutes, Carbon-11 of 20 minutes, and fluorine-18 of 110 minutes, Therefore, its sensitivity depends on irradiation current and rapid handling after irradiation.

Large currents generates heat in the surface region of a sample and damage it. Sample was cooled with water and helium gas during irradiation. Then it was automatically transferred between the target position in the cyclotron room and the inlet and outlet position in the experimental room. This allowed the radioisotope with a short half-life to be easily handled.

Lower acceleration energies and highly collimated beams are necessary for the use of the cyclotron to Rutherford back scattering spectroscopy. The magnetic field was decreased to 5 kG for the lower energy acceleration. The magnetic field of the cyclotron was tuned by addition of three circular trimming coils and fine adjustment of the pole gap. This made it possible to obtain isochronous fields from 100 to 375 mm in radius for 16 MeV protons and 130 to 375 mm for 1.8 MeV with first harmonics of less than 4 G. Acceleration energies were attained with alternating use of RF frequency and acceleration modes, as shown in table 2. Highly collimated beams were obtained by using collimator and slits. The beam current of 1.8 MeV proton increased to 10 nA on the target, even when the beam divergence was set below 0.1 degree. It is good enough for Rutherford backscattering spectroscopy and ion channeling measurement. Other intermediate energies were also used for charged particle activation analysis in special cases where nuclear interference was expected. Lower energy activation avoids nuclear interference by using different threshold energy levels of the reactions and reducing produc-

tion of fast neutrons.

Table 2 Acceleration energy of cyclotron (MeV)

Frequency	47 MHz		31.3 MHz	
	2-nd	4-th	2-nd	4-th
p	16	4	7.2	1.8
d		8		3.6
³ He		12	21	5.4
⁴ He		16		7.2

Charged Particle Activation Analysis

Metal impurity have already been removed from semiconductor and optical fiber materials. The impurities in light elements such as oxygen and carbon of 1 ng/g (ppb) will affect property of these materials. For trace analysis of carbon and oxygen, contamination from ambient circumstance is very significant. In charged particle activation analysis, surface radioactivity produced from surface contamination can be completely removed after irradiation.

The nuclear reactions for determination of carbon and oxygen are shown in Table 3. The left column in table 3 shows main reactions and right column shows interference from nuclear reaction.

Table 3 Nuclear reaction for light elements

reaction	Q-value (MeV)	interference	Q-value (MeV)
¹² C(d,n) ¹³ N	-0.3	¹⁴ N(d,t) ¹³ N	-4.3
		¹⁶ O(d,n) ¹³ N	-7.4
¹² C(³ He,α) ¹¹ C	1.9	¹⁰ B(³ He,d) ¹¹ C	3.2
		¹⁶ O(³ He,2α) ¹¹ C	-5.3
¹³ C(p,n) ¹³ N	-3.0	¹⁴ N(p,d) ¹³ N	-8.3
		¹⁶ O(p,α) ¹³ N	-5.2
¹⁶ O(³ He,p) ¹⁸ F	2.0	¹⁹ F(³ He,α) ¹⁸ F	10.4
¹⁸ O(p,n) ¹⁸ F	-2.4	¹⁹ F(p,d) ¹⁸ F	-8.2

Deuteron and helium-3 activation are most sensitive to carbon determination. The selection of two reactions is judged by co-existing elements and matrices. In the helium-3 activation, if boron co-exists, then it causes nuclear interference in carbon determination. Nuclear interference will not occur if the activation energy of the deuteron is below 4.3 MeV.

While helium-3 activation is most sensitive to oxygen determination, fluorine interferes with oxygen determination. For the sample containing fluorine, 7.2 MeV proton activation is used. Small quantities of carbon and oxygen isotopes are also important because these enriched isotopes are used as doping agents. This process distinguishes the flowing elements from each other: the elements intrinsically existing in the

sample, the elements that are contaminated from ambient circumstances, and the doping agents.

Non-destructive Method

The non-destructive method has the advantage that elements are determined only by measurement of radioactivity. Also, the analysis is repeatable. Boron and carbon in gallium arsenide were determined simultaneously by deuteron activation.

The nuclides produced from light elements are positron emitters and can not be distinguished by gamma-ray energies. Each activity is calculated by the analysis of the decay curve of 511 keV annihilated gamma rays. The decay curve which consists of multi-nuclides is written as equation 1:

$$A(t) = \sum_{i=1}^n a_i X_i + b \quad \text{--- (1)}$$

$$X = \exp(-\lambda_1 t)$$

A is total radioactivity, t is the time after the irradiation, a is the radioactivity of each nuclide at the end of the irradiation, λ is the decay constant and b is long life component included with natural back ground. The radioactivity a_i is calculated from the measured decay curve by using the least square method.

A pair of gamma-rays were emitted in opposite directions at the annihilation of the positron. Their selective detection is possible by a coincidence counter of two gamma-ray detectors. In the determination of boron and carbon in gallium arsenide by deuteron activation, induced radioactivities of gallium-72 and arsenic-76 interfere with the measurement of carbon-11 and nitrogen-13. These nuclides are multi-gamma-ray emitters, so interferences can not completely be removed even using coincidence technique with high energy resolution detectors such as germanium semiconductor detectors. however, it reduced interference by a factor of approximately 30 in comparison to ordinary gamma-ray measurement.

The dependences of thick target yields on irradiation energy were measured in order to improve the lower detection limit. Figure 1 shows the ratio of thick target yields of nitrogen-13 in graphite to gallium-72 and arsenic-76 in gallium arsenide. It shows that irradiation with lower energy is feasible for determination of carbon.

Figure 2 shows the measured decay curve of gallium arsenide with deuteron bombardment. The straight lines are analyzed components of nitrogen-13, carbon-11 and gallium-72. The curved line in figure 2 is the synthesized decay curve of these three components. The curve supports the experimental points. By this method, boron and carbon are simultaneously determined.

The boron and carbon interfere with each other. The detection limit of carbon with the co-existence of boron was estimated by Monte Carlo simulation. The expected decay curve with no fluctuations is calculated from equation 1 with known concentrations of carbon and boron in gallium arsenide. Then, the decay curve with statistical fluctuation was obtained by the generation of random numbers with gaussian distribution characteristics. The standard deviation of the gaussian distribution was calculated from the square root of the expected count with no fluctuations in the decay curve. The 100 fluctuating decay curves were analyzed at one boron concentration level where concentration of carbon was 0. The detection limit of

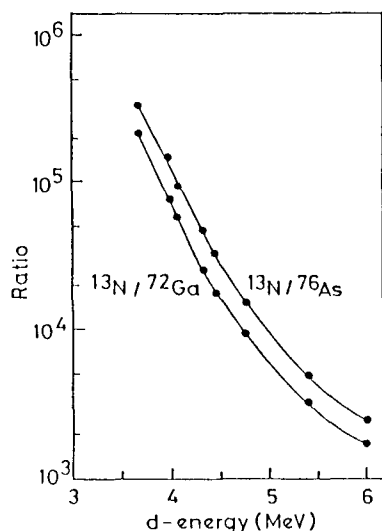


Fig. 1. Ratio of thick target yields

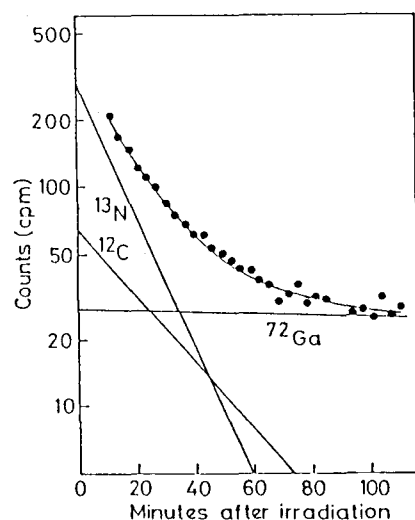


Fig. 2. Decay curve of gallium arsenide

carbon at this boron concentration is calculated at three standard deviation of mean analyzed carbon concentration. The results are shown in Fig. 3. Below 100 ppb of the boron concentration, the detection limit of carbon is about 30 ppb and gets larger with boron concentration. If there is no boron in the sample, the detection limit decreases to 10 ppb.

Method With Chemical Separation

Substoichiometric separation

Objective nuclides are chemically separated and only radioactivity is measured when other radioactivities interfere. Chemical separation must be accomplished in a short time because the half-lives of light elements are very short. Thus, substoichiometric separation is one of the best chemical separation

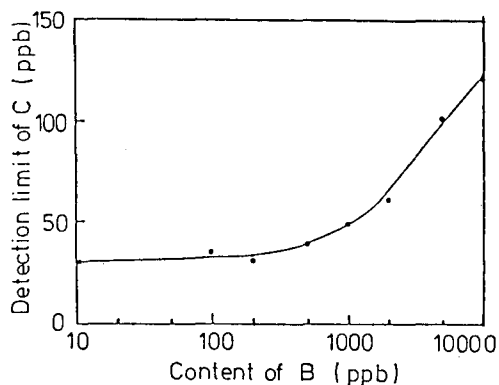


Fig. 3. Detection limit of carbon

methods. It has many excellent advantages such as no yield correction in chemical separation process as well as being time efficient.

Table 4 shows the chemical species and reagents for substoichiometric separation in the determinations of carbon and oxygen.

Table 4 Chemical species and reagents for substoichiometric separation

Element	Nuclide	Chemical species	Substoichiometric reagent
Carbon	¹³ N	NH ₄ ⁺	Tetra Phenyl Borate (TPB)
Oxygen	¹⁸ F	F ⁻	La

For example, a large and known amount (M) of ammonium carrier (1 mmol) is added to the solution of nitrogen-13, and chemical species of nitrogen change into ammonium ion. Then 0.2 mmol to 1 mmol of tetraphenyl borate (TPB) is added to these solutions. This causes the creation of ammonium tetraphenyl borate precipitate. Figure 4 shows the relation between ammonium tetraphenyl borate precipitate and the tetraphenyl borate. The amount of ammonium tetraphenyl borate is proportional to that of the added TPB. That is, a known and smaller amount (m, m < M) of TPB is added and a known and substoichiometric amount (m) of ammonium can be separated. From the activity (a) of ammonium tetraphenyl borate precipitate, the original activity of nitrogen-13 (A) is calculated by equation 2.

$$A = (M/m)a \quad \text{--- (2)}$$

Fluorine can be substoichiometrically separated in the same way.

Chemical procedure of carbon and oxygen determination in GaAs

Carbon and oxygen were determined by deuteron and helium-3 activation. In the former, gallium-72 and

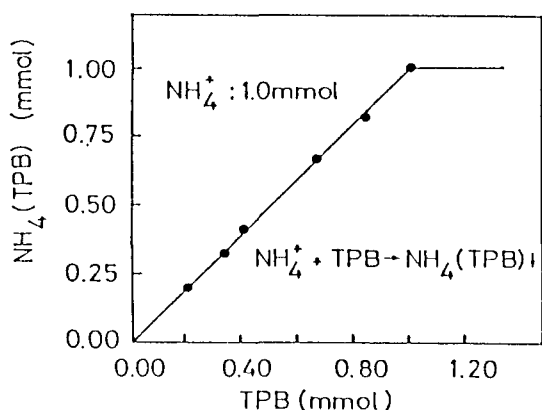


Fig. 4. Substoichiometric separation of ammonium

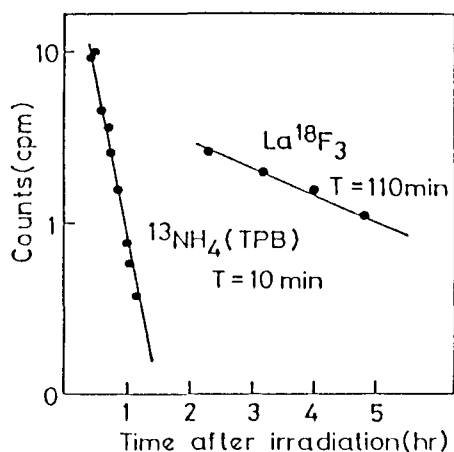


Fig. 5. Decay curve of precipitate

arsenic-76 from the matrix and carbon-11 from boron impurities are produced. In the latter, arsenic-70 and bromine-76 are produced from the matrix. These radionuclides interfere with the trace determination of oxygen and carbon. To avoid these interferences, distillation was used for pre-separation of nitrogen and fluorine. Nitrogen was converted to ammonium ion before distillation. The interferences decreased below 10 and the chemical yields of ammonium and fluorine were above 70%. In the final step, ammonium and fluorine were precipitated substoichiometrically.

The decay curve of the precipitate is shown in figure 5. The decay curves of ammonium tetraphenyl borate and lanthanum fluoride agree with the decay curves of 10 minutes and 110 minutes, respectively. Therefore, only nitrogen-13 and fluorine-18 were separated. The concentration was calculated by comparing the radioactivity of test and standard samples by average cross section method. Graphite and quartz were used for standard samples. The elapsed time was 20 minutes for determination of carbon and 110 minutes for oxygen. Carbon and oxygen levels as low as 1 ppb could be determined.

the oxygen concentration was also the same order.

Table 5 Analytical result of boron, carbon and oxygen in GaAs

sample	analytical result (ppb)		
	boron	carbon	oxygen
LEC (C-dope)	550*	226 250*	-
LEC (undope)	1200*	13 < 60*	4 - 16
HB	<60*	18 20*	10 - 36

Determination of Light Element In Gallium Arsenide

Non-destructive methods were applied to the determination of boron and carbon in gallium arsenide and destructive methods were applied to the determination of carbon and oxygen. Table 5 show the analytical results of boron, carbon and oxygen in gallium arsenide. The values with asterisks were determined by non destructive methods. The samples were gallium arsenide crystals, grown by the Liquid Encapsulated Czochoralsky method (LEC) and the Horizontal Bridgmann method (HB). Carbon doped crystals grown by LEC were also used. The concentration of boron in the LEC crystals was higher than in the HB crystals and was about 1000 ppb. Boron in the LEC crystal comes from the liquid encapsulated material. The carbon concentrations of both non-destructive and destructive methods were close to each other. The HB crystal may not have contained boron which affected the determination of carbon by the non-destructive method. The carbon concentration of undoped crystal was about ten ppb and

CONCLUSION

A compact and conventional cyclotron has been constructed for the exclusive use of ion beam analysis. Charged particle activation analysis by both non-destructive and substoichiometric chemical separation methods were successfully used for determination of boron, carbon and oxygen in gallium arsenide down to level of 1 ppb. The cyclotron was able to accelerate 1.8 MeV protons with a beam property which is useful for Rutherford backscattering analysis.

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