DETERMINATION OF CARBON IMPURITY
IN GALLIUM ARSENIDE CRYSTALS
BY PHOTON ACTIVATION ANALYSIS

A. YOSHIOKA,* K. NOMURA,* O. KAWAKAMI,* K. SHIMURA,*
K. MASUMOTO,** M. YAGI***⁺

*Central Research Institute. Mitsubishi Metal Co.,
1-297 Kitabukuro. Omiya, Saitama 330 (Japan)
**Laboratory of Nuclear Science, Tohoku University,
Mikamine, Taihaku, Sendai 982 (Japan)
***Institute for Materials Research, Tohoku University,
Katahira, Aoba, Sendai 980 (Japan)

Determination of carbon impurity in GaAs crystals has been investigated by photon activation analysis using the $^{12}C(\gamma, n)^{11}C$ reaction. Chemical isolation of the radiocarbon as CO_2 was carried out by the combustion method using Pb_3O_4 as a fusing agent and/or oxidizing accelerator in a high flow rate of oxygen stream. The CO_2 was then collected by passing through a double trap containing NaOH solution, and precipitated finally as $BaCO_3$. By measuring positron annihilation gamma-rays due to the isolated radiocarbon, it was proved that determination of the above carbon impurity can be achieved easily and favourably. On the basis of the results obtained, a conversion factor for the LVM absorption of carbon at room temperature in Fourier-transform infrared spectroscopy was found to be $1.4 \cdot 10^{16}$ atoms $\cdot$ cm^{-1}.

Introduction

Electrical properties of high purity gallium arsenide crystals are influenced considerably by the carbon impurity, because it exists predominantly on the arsenic lattice site, and acts as an acceptor.[1] In order to improve the manufacturing processes of gallium arsenide crystals, therefore, it is required that concentration of the carbon impurity can be determined accurately, precisely and easily.

Although the most sensitive determination method of carbon impurity is Fourier-transform infrared spectroscopy due to the local vibrational mode (LVM) of carbon, determination of the absolute carbon concentration by this method is needed to establish the conversion factor for the LVM absorption given by $f = N/\alpha\Delta$, where N

⁺Author for correspondence.

is the carbon concentration, α the peak absorption coefficient and Δ its full width at half height. As values for f, some results differing from each other have been reported.[2-4] The cause for the above discrepancy may be attributed to the difficulty in determination of the absolute carbon concentration in the standard material.

Determination of carbon impurity in a wide variety of materials has been tried extensively by using non-nuclear and nuclear methods. Unfortunately, the former methods have the serious disadvantage that reagent and equipment blank and surface contamination cannot be eliminated. On the contrary, the latter methods have striking characteristics that the above problems can be solved completely.

In the nuclear methods, however, only charged-particle and photon activation analyses make it possible to determine carbon impurity at extremely low concentration levels. Determination of carbon impurity in gallium arsenide crystals due to the $^{12}C(d, n)^{13}N$ reaction has been carried out by NOZAKI et al.[5] and SHIKANO et al.,[6] whereas that due to the $^{12}C(\gamma, n)^{11}C$ reaction has not yet been examined. In comparison with the former reaction, the latter possesses the great advantage that the activation area of the sample is relatively uniform and not restricted by thickness of the sample because of large penetrating power of photons, and that the radiocarbon produced as a positron emitter has a half-life longer than that of ^{13}N. In the case of the latter, however, determination of carbon impurity is often interfered by positron emitters induced from other components of the sample, by analogy with the case of the former. Accordingly, radiocarbon must be isolated from those interferences as soon as possible. The best way to isolate the radiocarbon can be achieved easily and quickly by oxidizing to CO_2 by either combustion of the sample in an oxygen stream,[7,8] or by fusion in an oxidizing bath.[8-15]

In the present study, determination of carbon impurity in gallium arsenide crystals has been examined by photon activation analysis using 30 MeV bremsstrahlung. Chemical isolation of the radiocarbon as CO_2 was performed by the combustion method using Pb_3O_4 as a fusing agent and/or oxidizing accelerator in a high flow rate of oxygen stream. From the results obtained for systematically prepared samples, furthermore, determination of the conversion factor for the LVM absorption of carbon has also been tried.

Experimental

Materials and chemicals

A Japanese standard of high purity iron, JSS-003-1 containing 0.0011% carbon, furnished by the Iron and Steel Institute of Japan was used as a comparative standard to determine the concentration of carbon impurity. Since the above standard was supplied in small chips, about 0.5 g was pressed into a pellet of 1 cm in diameter.

Samples used for the present analysis were 10 undoped gallium arsenide crystals, grown by the liquid encapsulated Cyochralski technique, ranging in carbon concentration form $1 \cdot 10^{15}$ to $4.4 \cdot 10^{16}$ atoms $\cdot$ cm^{-3}. Among them, 8 samples were distributed by Japan Electronic Industry Development Association as standards for Fourier-transform infrared spectroscopy and charged-particle or photon activation analysis, and the other two were obtained from a metal corporation in Japan.

After all samples were cut into thin slices ($7 \times 9 \times 2$ mm^3), they were etched with a dilute $H_2SO_4 - H_2O_2$ mixture to remove the surface contamination of carbon, and rinsed twice with bi-distilled water and acetone before weighing. For irradiation, the sample prepared as above was wrapped in a pure aluminium foil.

All the other chemicals used in the present study were of analytical reagent grade.

Irradiation

The samples were irradiated separately with the bremsstrahlung of the Tohoku University Electron Linear Accelerator. The linac was operated at an electron energy of 30 MeV with a beam pulse length of 3 μs and a repetition rate of 300 Hz.

The sample was placed perpendicularly at a distance of about 2 cm behind a platinum converter of 0.71 radiation length (2 mm), and cooled by running tap water. Most irradiations were performed under an average beam current of 150 μA for 20 minutes. In order to monitor the density of photon flux, two nickel foils were used by placing on both sides of the sample. The details of such an irradiation have been described elsewhere.[16]

Isolation of radiocarbon by the combustion method

The irradiated sample was etched with a HCl–HNO$_3$ mixture to remove the surface contamination of carbon, and rinsed with bi-distilled water and acetone. By this etching, the etched thickness of the surface layer was found to be about 50 μm.

Isolation of radiocarbon was carried out as follows, using the apparatus shown in Fig. 1. At first, the sample was introduced in an alumina crucible containing 0.150 g of BaCO$_3$ to provide CO$_2$ carrier, and covered with about 0.8 g of Pb$_3$O$_4$ to support the fusion and oxidation. The crucible was then heated at 1350 °C in an electric furnace under an oxygen flow rate of 500 cm^3 per minute. The gases were passed successively through a quartz-wool filter to remove the generated fine solid particles, a SCHUTZE reagent column (I$_2$O$_5$ on silica gel) to oxidize completely the CO produced, a washing bottle containing conc. H$_2$SO$_4$ to trap the other volatile species, and a double collector containing 0.1 N NaOH and excess BaCl$_2$ to collect

and precipitate thoroughly the generated CO_2. By using a suction pump, the precipitated $BaCO_3$ was then filtered off rapidly on a small filter paper of 35 mm in diameter, and washed with ethanol. Finally, the resulting precipitate was transferred
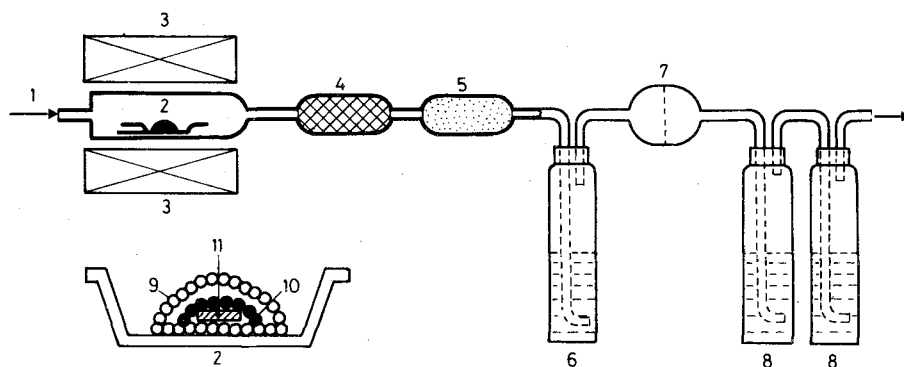

Fig. 1. Apparatus for radiocarbon isolation by the combustion method; 1 — oxygen, 2 — alumina crucible, 3 — electric furnace, 4 — quartz-wool filter, 5 — SCHUTZE reagent, 6 — washing bottle, 7 — Teflon filter, 8 — collector bottle, 9 — Pb_3O_4, 10 — $BaCO_3$, 11 — sample

into a polyethylene bag together with the filter paper to measure the radioactivity under a constant geometry.

Radioactivity measurement

Using a computerized gamma-ray spectrometer connected to a high resolution germanium detector with a relative efficiency of 31% and a resolution of 1.87 keV at the 1332 keV ^{60}Co gamma-ray, radiocarbon in the resulting precipitate was measured for 20 minutes after at least 20 minutes cooling to allow the above chemical isolation. In order to convert completely the positron from the radioacarbon, the sample bag was sandwiched by Lucite plates of 1 cm in thickness.

Results and discussion

Combustion of gallium arsenide crystal

In preliminary experiments, it was found that complete combustion of the gallium arsenide crystal in an oxygen stream is rather difficult in the absence of a fusion agent. Since it is well known that determination of the carbon impurity in metals

204

is carried out effectively by the fusion method using a Pb_3O_4 oxidizing bath,[14] its application to the gallium arsenide crystal was examined fundamentally. As samples for the above examinations, powdered gallium arsenide, Pb_3O_4 and $BaCO_3$ were used. According to the present combustion method, the above samples were ignited

Table 1

Chemical forms of the products in the residues ignited at various temperatures

Temperature, °C			
500	600	800	>1200
GaAs	GaAs**		
Pb_3O_4	Ga_2O_3	Ga_2O_3	Ga_2O_3
$BaCO_3$	As_2O_3 *	As_2O_3 *	As_2O_3 *
$+O_2$	$Pb_3As_2O_8$	$Pb_3As_2O_8$	$Pb_3As_2O_8$
	$Pb_8As_2O_{13}$	$Pb_8As_2O_{13}$	$Pb_8As_2O_{13}$
	Pb*	Pb**	
	PbO	PbO	PbO
	$BaCO_3$ **		
	$Ba_3As_2O_8$ *	$Ba_3As_2O_8$ *	$Ba_3As_2O_8$ *

*Small amount.
**Trace amount.

in oxygen stream at the range of 500 to 1350 °C, and then chemical forms of the products in the residues were identified by X-ray diffraction method. The results obtained are shown in Table 1.

As can be seen in Table 1, the sample used is decomposed completely at above 600 °C, and converted into stable oxides. From these results, it was apparent that Pb_3O_4 is a suitable material as a fusion agent and/or oxidizing accelerator for gallium arsenide, and that $BaCO_3$ is also adequate as a generator of CO_2 carrier.

Since the practical samples in the present study were cut into thin slices, all combustions were carried out at 1350 °C. In a similar manner as above, it was also comfirmed that the products in the above residue were identical to those shown in Table 1.

Recovery yield of the radiocarbon

In the present combustion method, 0.150 g of $BaCO_3$ was used as a generator of CO_2 carrier. Hence, the recovery yield of radiocarbon can be determined easily by gravimetric analysis of the $BaCO_3$ precipitate collected finally for the radioactivity

measurement. It was demonstrated that the recovery yields were given in the range of 85 to 91%, and that the reproducibility in the yields was rather poor. From these facts, the recovery yields of radioacarbon were measured individually, and each radioactivity of the radiocarbon was necessarily corrected by the above recovery yield.

Interferences

In order to realize high sensitivity with minimum interference, all samples were irradiated with 30 MeV bremsstrahlung for 20 minutes. In such irradiations, however, it is predicted that the same radiocarbon is induced by the $^{14}N(\gamma, t)$ reaction, and/or the $^{16}O(\gamma, \alpha n)$ reaction. Using the data reported by ENGELMANN,[17] amounts of nitrogen and oxygen leading to the same radiocarbon as a 1 μg of carbon at 30 MeV are found to be about 50 and 500 μg, respectively. Hence, the above interference reactions are negligible.

On the other side, the irradiated standard iron is obliged to contain a positron-emitter of ^{53}Fe (8.512 m) due to the $^{54}Fe(\gamma, n)$ reaction, while the irradiated gallium arsenide is also forced to contain ^{68}Ga (1.1355 h) and ^{74}As (17.783 d) due to the $^{69}Ga (\gamma, n)$ and the $^{75}As (\gamma, n)$ reactions, respectively. In order to check these interferences, the decay curves of the annihilation gamma-rays in the collected $BaCO_3$ precipitates were measured for the former and the latter samples. The curve due to the former showed a half-life of 20.4 minutes for period up to 150 minutes after the end of irradiation, whereas that due to the latter also showed 20.5 minutes for about 100 minutes. These facts indicate that the radionuclidic purity in the final precipitate was sufficiently high, and that the present chemical isolation method was satisfactory.

Determination of carbon impurity in the gallium arsenide crystals

Determinations of carbon impurities in 10 gallium arsenide crystals were carried out comparing with those determined similarly by the use of iron standard. The results obtained on multiple runs are tabulated in Table 2.

As indicated by the values given in Table 2, the concentrations of carbon impurities in the levels above $7 \cdot 10^{15}$ atoms $\cdot$ cm^{-3} were determined with a relative standard deviations of within $\pm 10\%$, whereas those at the levels below $5 \cdot 10^{15}$ atoms $\cdot$ cm^{-3} were determined with about $\pm 20\%$. As possible sources for the above large errors in the latter case, the following two reasons may be pointed out: (1) carbon impurity in the gallium arsenide crystal was distributed nonuniformly; (2) the concentration levels of carbon impurity were close to the detection limit.

The former may be supported by the fact that the sample cut out from different positions in an identical crystal resulted in the isolated value. The detection limit in the latter can be calculated on the basis of the relation $N = 3B^{1/2}$, where B is the

Table 2
Concentrations of carbon impurity in the GaAs crystals

Sample No.	Concentration of C, $\times 10^{15}$ atoms $\cdot$ cm^{-3}	Average, $\times 10^{15}$ atoms $\cdot$ cm^{-3}
A–1	1.13	1.10 ± 0.04
A–2	1.07	
B–1	1.77	
B–2	1.46	1.74 ± 0.27
B–3*	1.99	
C–1*	13.4	
C–2	14.3	13.9 ± 0.5
C–3	14.0	
D–1	3.41	
D–2	3.14	3.06 ± 0.39
D–3*	2.64	
E–1	3.54	
E–2	3.92	4.16 ± 0.77
E–3*	5.03	
F–1	51.1	
F–2	47.9	51.8 ± 3.5
F–3	51.6	
F–4	56.4	
G–1	7.29	7.85 ± 0.78
G–2	8.40	
H–1	<1	<1'
I–1	37.7	36.3 ± 2.0
I–2	34.9	
J–1	14.6	14.8 ± 0.3
J–2	15.0	

*The sample was cut out from different positions of an identical crystal.

number of counts in the background and N the minimum number of counts under the photopeak of annihilation gamma-ray. As a value corresponding to N in the present study, it was found to be $1 \cdot 10^{15}$ atoms $\cdot$ cm^{-3}. If a figure of merit is defined as a ratio of the average concentration of carbon impurity to the above

detection limit, a value close to unity would involve a large error. The figures of merit for the samples A, B, D and E are less than 5, so that their concentrations determined will involve serious errors.

Relationship between the concentrations of carbon impurity and the LVM adsorptions

The LVM adsorptions of carbon in the above gallium arsenide crystals were also determined at room temperature by Fourier-transform infrared spectroscopy. Figure 2 shows the relationship between the concentrations of carbon impurity (atoms · cm^{-3}) resulting from the present photon activation analysis and the LVM adsorption
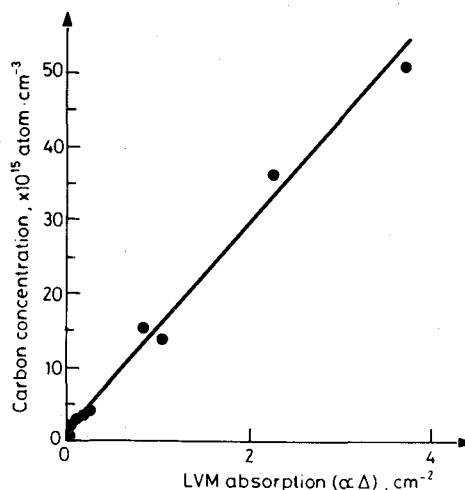

Fig. 2. Relationship between the concentrations of carbon impurity and the LVM absorptions of carbon at room temperature

($\alpha\Delta$, cm^{-2}) measured as above. As is seen in the figure, both bear a linear relationship to each other. The conversion factor (f) obtained by the least-squares method of the above relationship was found to be 1.4 · 10^{16} atoms · cm^{-1}. Although this value is much smaller than that reported by BROZEL,[2] it is also slightly larger than that obtained by HUNTER.[3]

If the above conversion factor is used in Fourier-transform infrared spectroscopy, accurate and precise determination of carbon concentration in the gallium arsenide crystals would be achieved reasonably and favourably.

*

References

1. W. M. THEISE, K. K. BAJAJ, C. W. LITTON, W. G. SPITZER, Appl. Phys. Lett., 41 (1982) 70.
2. M. R. BROZZEL, J. B. CLEGG, R. C. NEWMAN, J. Phys. D, 11 (1978) 1331.
3. A. T. HUNTER, H. KIMURA, J. P. BAUKUS, H. V. WINSTON, O. J. MARSH, Appl. Phys. Lett., 44 (1984) 74.
4. Y. HOMMA, Y. ISHII, T. KOBAYASHI, J. OSAKA, J. Appl. Phys., 57 (1985) 2931.
5. T. NOZAKI, Y. ITOH, Y. OHKUBO, T. KIMURA, H. FUKUSHIMA, Japan J. Appl. Phys., 24 (1985) L801.
6. K. SHIKANO, H. YONEZAWA, T. SHIGEMATSU, J. Radioanal. Nucl. Chem., 111 (1987) 51.
7. A. YOSHIOKA, K. NOMURA, M. TAKEYA, K. SHIMURA, K. MASUMOTO, M. YAGI, J. Radioanal. Nucl. Chem., 122 (1988) 42.
8. G. REVEL, J. Radioanal. Chem., 3 (1969) 421.
9. G. J. LUTZ, L. W. MASTERS, Anal. Chem., 42 (1970) 948.
10. V. I. RODIONOV, V. N. SAMOSYUK, B. A. CHAPYZHNIKOV, G. REVEL, M. FEDOROFF, Radiochem. Radioanal. Lett., 18 (1974) 379.
11. M. FEDOROFF, C. LOOS-NESKOVIC, G. REVEL, Radiochem. Radioanal. Lett., 22 (1975) 283.
12. M. FEDOROFF, C. LOOS-NESKOVIC, G. REVEL, J. Radioanal. Chem., 38 (1977) 107.
13. C. LOOS-NESKOVIC, M. FEDOROFF, V. N. SAMOSYUK, B. A. CHAPYZHNIKOV, Radiochem. Radioanal. Lett., 45 (1980) 185.
14. M. FEDOROFF, C. LOOS-NESKOVIC, G. REVEL, J. Radioanal. Chem., 55 (1980) 219.
15. M. FEDOROFF, C. LOOS-NESKOVIC, J. C. ROUCHAUD, V. N. SAMOSYUK, B. A. CHAPYZHNIKOV, J. Radioanal. Nucl. Chem., 88 (1985) 45.
16. M. YAGI, K. KONDO, J. Radioanal. Chem., 36 (1977) 247.
17. CH. ENGELMANN, J. Radioanal. Chem., 6 (1970) 399.