PROTONS ACTIVATION UP TO 30 MeV FOR TRACE ANALYSIS IN HIGH PURITY MATERIALS

E.H. Bakraji, M.T. Bajard, M.F. Barthe, G. Blondiaux, J.L. Debrun, G. Ducouret, A. Giovagnoli

C.N.R.S.-C.E.R.I., 3A, rue de la Férollerie
45071 - ORLEANS CEDEX 02 (France)

ABSTRACT

Activation analysis with 20 to 30 MeV protons, either instrumental or after radiochemical separations, was applied to the determination of trace elements in pure Si, InP and ZrF_4. Experimental detections limits are ✖ppb in most cases.

INTRODUCTION

Charged particle activation is mostly useful for the analysis of ubiquitous elements like C, N and O, at trace level (<ppm) in metals and semiconductors (see for instance, reference 1).

This method is also of interest in the case of the analysis of heavier elements, as a complement to other existing methods or as another independent method for the certification of reference samples.

This paper describes some of the work done at the CERI with the cyclotron in the field of trace analysis, for medium Z elements. Three differents matrices will be considered: Si, InP and ZrF_4.

I. ANALYSIS OF TRACE ELEMENTS IN SILICON BY DIRECT GAMMA-RAY SPECTROMETRY

This type of analysis was used as a help during the development of the metallurgy of polycrystalline silicon ingots for photovoltaic applications. Although neutron activation is used with success for the analysis of silicon, proton activation is superior in this particular case for the determination of important metallic elements (Ti, Fe, Ni...) and at the same time allows the control the doping element (B).

EXPERIMENTAL

Samples thicker than the proton range were irradiated in the air; the particle beam emerges from the vacuum through a 25 µm titanium foil. The samples are irradiated for 3 hours at 5 µA, with 20 MeV protons.

Cooling is achieved with air cooled by liquid N_2. After irradiation, ~30 µm are etched all over the samples, using a mixture of acids (3 HF + 5 HNO_3 + 3 CH_3COOH), to eliminate surface contaminations.

Counting of the solid samples is performed with a Ge; for quantitative analysis, the average crosssection method is used (2). Instrumental analysis is possible because the radioisotopes obtained by irradiation of Si are short-lived or possess a low specific activity.

RESULTS

Table I presents actual results obtained for a "normal" sample and for a sample that had been contamined by the wetting agent placed at the surface of the graphite crucible used for crystal growth. The presence of Ca and Ti, usually undetected, is obvious; this can be correlated with bad electrical characteristics.

Element	Concentration in "normal sample (ppb/weight)	Concentration in contamined sample (ppb/weight)
B	95	80
Ca	< 0.2	80
Ti	< 0.15	2.5
Cr	< 0.4	< 0.2
Fe	< 0.9	< 0.9
Co	< 1	< 0.6
Ni	< 7	< 9
Cu	< 3	< 3
Zn	< 0.1	< 0.1
Ge	1	0.6
Zr	< 0.03	< 0.03

TABLE I
Instrumental analysis of silicon samples after activation with 20 MeV protons.

II. ANALYSIS OF TRACE ELEMENTS IN INDIUM PHOSPHIDE

This material is used in optoelectronics, mostly as a semi-insulating substrate. A high degree of purity is required for the final crystal obtained by the Czochralski method. As a cross-checking with other analytical methods (SIMS and SSMS), we have developed the analysis

of Cr, Fe, Ni, Cu and Zn in InP and in the starting material In. In this case, the analysis is complicated by the fact that the matrix activity is high and must be eliminated using radiochemical separations.

EXPERIMENTAL

Samples are 15 x15 mm and 1 mm thick. They are thinner than the proton range at the energies used. The energy is 26 MeV for the analysis of undoped InP and of In, and 21 MeV for Fe doped InP (in order to render the interfering reaction ^{56}Fe (p, α n)^{52}Mn negligible). The samples are "thin" to obtain high sensitivities while limiting the amount of energy absorbed. Irradiation takes place in the air, at 5 µA, for 2 hours. The backside of the samples is in contact with a metal cooled by liquid nitrogen, and the front side is cooled by a stream of cold air. The matrix activity is mainly due to radioactive indium produced by nuclear reactions with protons (isotopes 111 and 114 m) or with secondary neutrons (113 m, 114 m, 115 m, 116 m), to radioactive tin (113), and to radioactive cadmium (111 m). InP is dissolved in HI (3.5 M); Sn and In are extracted in diisopropylether (HI, 1.5 M), Cd is later retained on Dowex 1 x 10 (HBr 0.1 M). The radioisotopes of interest, ^{52}Mn(Cr) - ^{55}Co(Fe) - ^{57}Ni(Ni) - ^{62}Zn(Cu) and ^{66}Ga(Zn) are then separated on Dowex 1 x 10 (HCl, HNO_3).

Gamma-ray spectrometry is effected on the various fractions obtained.

RESULTS

	Undoped InP (26MeV) (ppb/weight)	Fe doped InP (21MeV) (ppb/weight)
Cr	< 2	8
Fe	1	500
Ni	< 0.6	< 8
Cu	< 0.6	< 3
Zn	6	20

TABLE II

Analysis of Cr, Fe, Ni, Cu and Zn in InP crystals (seed end of the crystals).

Results are given in Table II for a Fe doped InP crystal and for an undoped crystal. In the doped crystal, the Fe concentration was found to vary from 2.5×10^{16} at/cm^3 at the seed end to 2×20^{17} at/cm^3 at the tail end of the ingot.

A good agreement with SIMS and SSMS was found for Fe at high levels (doped crystal); both SIMS and SSMS could not obtain the low detection limits of proton activation for the analysis of Cr, Fe, Ni, Cu and Zn in InP.

III. ANALYSIS OF IMPURITIES IN ZrF_4

This product is the main component of the fluoride glasses to be used in the future for the making of low-loss optical fibres at 2.55 µm. Extrinsic losses in the fibres are due to impurities; the starting materials (ZrF_4, AlF_3, LaF_3, BaF_2, NaF) must be purified and controlled. We have studied the analysis of Fe, Co, Cu and Ni in ZrF_4; these elements possess signifiant absorption coefficients at 2.55 µm. Proton activation was studied because there is no other suitableanalytical method at the moment, except neutron activation whose application is very delicate in the present case (3).

EXPERIMENTAL

ZrF_4 is irradiated as a powder in a titanium container sealed by an ultrapure Al foil (50 µm); another Al foil is placed on the bottom of the container to avoid direct contact between Ti and ZrF_4. The container is irradiated in the air; it is water cooled at the rear and air cooled at the front. 30 MeV protons are used and the apparent powder density is such as the particles emerge from the powder at $\sim$20 MeV.

The sample is thus "thin" ($\sim$ 4 mm), for the same reasons as for InP. Irradiations last 2 hours at 0.5 µA.

After irradiation, ZrF_4 is dissolved in HF 5 N. Radioisotopes of Zr-Nb and Y are obtained from the matrix, Zr and Nb are retained on Dowex 1 X 10 (HF 5N) and Y is coprecipited with LaF_3. $^{55,56}Co$(Fe), ^{58}Co(Co), ^{57}Ni(Ni) and ^{62}Zn-(Cu) are then separated on Dowex 1 x 10 (HCl). Changing the medium from HF to HCl and the precipitation of LaF_3, leads to an effective elimination of ^{18}F (from $^{19}F(p,pn)^{18}F$). Direct gamma-ray spectrometry thus possible immediately after the separation on Dowex 1 x 10 (HCl).

RESULTS

ZrF_4 powders of different purities were analyzed: technical grade, high-purity (commercially available) and high purity (purified in laboratory). The results appear in Table III.

	Fe	Co	Cu	Ni
Technical grade	200 ± 10	_	60 ± 4	7 ± 1
Purified commercially available (BDH)	0.8	< 0.007	< 0.015	0.06
Purified in laboratory (L.d.M.)	0.1 ±0.015	< 0.009	0.03±0.01	0.01±0.008

TABLE III

Analysis of ZrF_4 of various purities, using 30 MeV protons (ppm/weight)

The level of purity attained in laboratory (L.d.M. Marcoussis), is sufficient taking into account the extrinsic losses in the fibres at the moment.

CONCLUSION

Charged particle activation, especially proton activation, is well suited for the analysis of medium Z trace elements in a variety of matrices. The analysis can be very simple in all respects in a few cases, like for silicon; in general though, the analysis necessitates radiochemical separations after irradiation.

The irradiation of powders is possible, but is a complication, considering the risks of contamination and the problem of heat dissipation. The use of "thin" targets for 20 to 30 MeV proton activation is interesting, because we are in a domain were (p,2n) and (p,pn) reactions of analytical interest, present their maximum value and also present rather flat cross-sections.

Although well suited for the analysis of medium Z elements at trace level, charged particle activation is not (generally speaking) a fast and a routine method. It is more and more in competition with other analytical techniques (e.g. GDMS, ICP-MS with laser ablation, RIMS). Its use should therefore be restricted to "difficult" cases (for other methods) and in any case limited to a small number of samples. On another hand, it remains a valuable independent method for the elaboration of standards.

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