

APPLICATION OF NEUTRON ACTIVATION ANALYSIS IN
THE FIELD OF SILICON TECHNOLOGY FOR THE MODERN ELECTRONIC
INDUSTRY

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The specific application of neutron activation analysis in the research on the preparation of silicon integrated circuits is discussed. The high flux irradiation facility for large silicon wafers (up to 15 cm diameter) was used, the analytical procedure, and some typical results will be described.

Introduction

In materials research for the fabrication of integrated circuits the determination of very small amounts of impurities and dopants plays an important role /1/. If we want to discuss where neutron activation analysis is used in this field of research, we must realize that our Radiochemical Department is a part of a rather large analytical group in which almost all current analytical techniques are available. Consequently we are only applying NAA to those analytical problems which cannot be solved better with other methods. But then immediately the question arises: what is better? And so one arrives at the greatest strength of neutron activation analysis: the multielement character in combination with very low limits of detection, at least if the matrix elements only produce nuclides with a short half life or low specific activity, and the high reliability.

Another important feature is the possibility that oxide layers, epitaxial layers etc. can be removed after irradiation by etching (usually with carriers of the expected impurities added to the solutions). By measuring either the remaining sample or the solution or both the impurities can be localized.

Silicon as a matrix element is favourable: the activity of ^{31}Si produced is relatively low, its half life is only 2.62 hours and also its γ ray abundance is only 0.07%.

In this paper we describe how neutron activation analysis is used for the determination of very low bulk concentrations, concentration gradients, surface contaminations etc. Of the topics which are treated, we mention:

- a. Impurity and dope concentrations in silicon rods and wafers.
- b. Contaminations from handling by mechanical equipment such as stainless steel parts or graphite susceptors, which may occur during electrical measurements, numbering or marking, ion implantation, scanning electron microscopy, reactive ion etching and rapid thermal annealing.

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- c. Contaminations introduced during epitaxial growth.
- d. Contaminations introduced during cleaning and etching procedures.
- e. Contaminations from the furnace during high temperature treatments such as oxidation, annealing after implantation and diffusion processes.
- f. Contaminations during medium temperature treatments such as deposition of layers (Si_3N_4 , polycrystalline Si and SiO_2).
- g. Gettering of metals, e.g. in high doped regions.

Irradiation facilities

For high flux irradiations of bulk samples of up to 5 gram the reactors BR2 at Mol, Belgium (distance 45 km), HFR at Petten, Netherlands (180 km), and FRJ2 at Juelich, FRG (140 km) were used, with thermal neutron flux densities of about 2×10^{14} n/cm².s. Usual irradiation times were 24 or 48 hours.

In order to prevent contaminations by cutting the silicon wafers into small pieces before irradiation we prefer to put the entire wafers in the reactor, which was possible in the reactor FRJ1 at Juelich until the end of 1984 for wafers up to 10 cm diameter. Since the middle of 1985 we have at our disposal a specially constructed irradiation facility in the HFR at Petten, in which it is possible to irradiate up to 30 silicon wafers of up to 15 cm diameter simultaneously /2/. The hermetically sealed silica glass container with the wafers is put in an aluminium drum; this drum is perforated for water cooling and is rotated slowly during irradiation.

The thermal neutron flux is about 4×10^{13} n/cm².s and irradiation times are 72 or 96 hours.

PACKAGING PROCEDURE

It is evident that the packaging of the samples before the irradiation must be carried out under carefully controlled conditions in order to prevent contaminations. The procedure starts with the cleaning of all silica glass parts of the container in the vapour of fuming nitric acid, rinsing with ultrapure water and drying. The outer part of the container has a diameter of about 165 mm for the 15 cm wafers (115 mm for 10 cm wafers, etc.) and a wall thickness of about 2 mm, see Fig. 1. The initial height is 250 mm. On the bottom a silica glass spring washer is placed to prevent breaking of the samples during transport, and also two 0.1% Co in Al wire flux monitors (sealed in silica glass). Up to 20 samples with a thickness of about 0.5 mm each are placed on the spring washer. To prevent cross contaminations, pure dummy wafers are used under the first and above the last sample, and also between wafers of different contamination levels. A second spring washer is placed on the top of the upper dummy wafer. All handling is carried out in a dust free box with silica glass vacuum tweezers. The inner part of the container (height 50 mm) is telescoped into the outer one. Then the upper end of the outer

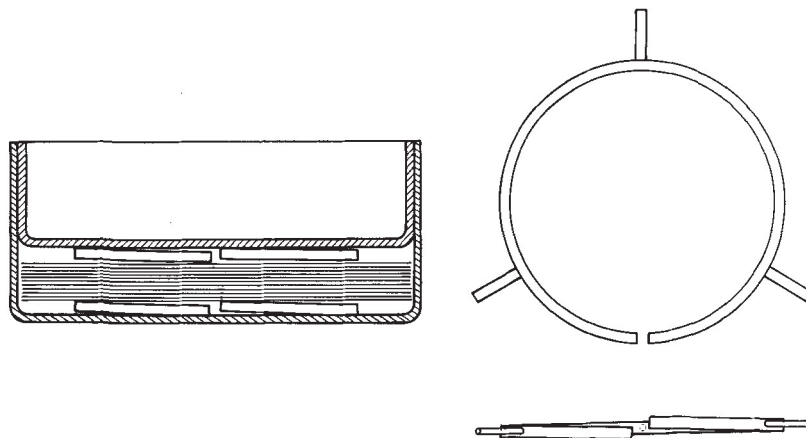


Fig. 1. The sealed irradiation container with silicon wafers between spring washers (left) and a spring washer (right); material: silica glass

part is connected to a vacuum system, via a filter, and temporarily closed. With a flame the outer and the inner parts are fixed at a few places. After that the container is flame sealed while rotating in a lathe. During this sealing operation the bottom of the container is cooled in order to keep the temperature of the silicon slices low. Finally the upper part of the container is removed by sawing; the remaining height is about 70 mm.

Spectrum measurement and evaluation

In order to obtain the lowest possible limits of detection a large (high efficiency) germanium detector and long measuring times (e.g. 8 or 16 hours) are needed. The consequence of this is that the number of samples determines the number of detectors: we use eight Ge(Li) detectors of 100 to 150 cm³, connected to a Nuclear Data ND6600 system with two terminals, hard disks, magnetic tape and a line printer.

We apply the monostandard method with Co as flux monitor and employ a nuclear library with the data of 127 nuclides, in which the k_0 - and Q_0 -values of De Corte and Simonits /3/ are used.

Measuring geometries are standardized as described before /4/, but now also for circular samples such as silicon wafers. Pulse pileup correction /4/ as well as subtraction of the annihilation background peak is applied. The software is organized as follows:

- a. Spectrum processing such as peak search etc. is carried out with the Nuclear Data system.
- b. If only one spectrum of a sample is measured, the further evaluation can be performed with the Nuclear Data system as well, because all detector efficiency parameters and the library with nuclear data are stored on a hard disk. The programs are written in FORTRAN-IV.
- c. If we want to make the most of an analysis, however, a sample is measured 3, 4 or even 5 times during a month after irradiation. In this case the reduced spectra

are sent to an IBM computer, with which up to five reduced spectra of a sample can be evaluated simultaneously. This means that the half lives are also used for the identification. The program, which is written in PASCAL, also performs a number of corrections: γ cascade summation, burn-up, ^{235}U fission interference, ^{64}Cu interference by ^{24}Na and ^{199}Pt - ^{199}Au interference by ^{199}Au from ^{198}Au . In a print-out the impurity contents, the detection limits and the possible interfering nuclides are listed.

Examples of analysis

The untreated wafer

It should be understood that the wafers used as starting material are very pure. In Table 1 we give an analysis of a 10 cm wafer which has only been rinsed in water after irradiation for removing possible silica glass dust from the container. The impurities found (Cu, As, Br, Sb, W, Au) are below the (ng/g) ppb level. It must be emphasized that the contents are supposed to be homogeneously distributed in the wafer,

Table 1

Contents of the impurities found (***) and limits of detection of the other elements (<) in pg/g for a very pure silicon wafer, diameter: 10 cm, weight 10 g; irradiation: 72 hrs in $4.9 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$; measured 2 times on a lead shielded 130 cm^3 Ge(Li) detector: 1) decay time: 2 days, measuring time: 16 hrs, 2) decay time: 10 days, measuring time: 66 hrs

Na @ < 500	Se < 2	Te < 4	Tm < 3
Si ***	Br *** 2.4	I < 8000	Yb < 0.2
K < 150	Rb < 10	Cs < 0.5	Lu < 0.04
Ca < 10000	Sr < 150	Ba < 60	Hf < 0.3
Sc < 0.03	Y < 200000	La < 0.15	Ta < 0.5
Ti < 3000	Zr < 150	Ce < 0.9	W *** 25
Cr < 2	Nb < 15000	Pr < 6	Re < 0.3
Mn < 15000	Mo < 6	Nd < 10	Os < 0.7
Fe < 300	Ru < 1.5	Sm < 0.03	Ir < 0.004
Co < 0.5	Pd < 60	Eu < 0.07	Pt < 4
Ni < 150	Ag < 3	Gd < 6	Au *** 1.6
Cu *** 560	Cd < 15	Tb < 0.1	Hg < 0.6
Zn < 15	In < 4	Dy < 300000	Tl < 3000
Ga < 1.5	Sn < 200	Ho < 3	Pb < 300000
Ge < 1000	Sb *** 180	Er < 40	Th < 0.2
As *** 33			U < 1

@ see text

which is not always the case. Depending on the element, its concentration and the presence of other impurities, the accuracy is about 5 to 25%, which is acceptable for these extremely low amounts.

As always, an apparent Na content was found, caused by the $^{28}\text{Si}(n,\alpha p)^{24}\text{Na}$ reaction /5/, in this case it was 550 pg/g. It can be seen that the detection limits for some elements are relatively high due to rapid decay (Mn, Dy), or due to the fact that (n,p)- or (n,2n)-reactions have to be used (Ti, Y, Nb, I, Tl, Pb).

Contaminations from handling during implantation

At one time in the device fabrication process, yield problems arose and the As implantation step was one of the suspected process steps. A number of analyses were carried out (Table 2, only the conspicuous impurities are given) to investigate this problem.

It appears that during the whole implantation procedure most probably a contamination from stainless steel occurs (a). In the implantation machine, indeed, the wafers glided over a stainless steel plate during transport into the implantation chamber. After replacement of this plate by an aluminium one with an Al_2O_3 coating, analysis of the wafers showed a decrease in impurity contents (b). The question arises, whether the transport mechanism only is responsible for the contamination. The results of the next experiment (c) show that this is really the case. It must be emphasized that not all stainless steel parts have been removed:

Table 2
Metal contents in ng in 10 cm diameter wafers (10 g)
due to handling in an implantation apparatus

Sample treatment	Cr	Fe	Co	Ni	Mo
a) Total implantation procedure (original)	38	190	0.20	150	-
b) Total implantation procedure, but now stainless steel plate replaced by aluminium	14	72	0.12	14	-
c) Only transport, no implantation (Al plate)	15	76	0.12	13	0.16
d) The same as (c), but with lacquer on front side of the wafer	3.5	17	.024	2.3	.063

springs etc. are still present and they may cause the remaining contamination. As is shown in experiment (d), contaminations still occur on the surface of the wafer by transport. In this experiment a lacquer layer is provided on the front side, which is removed after irradiation. The metal contents are found to be again much lower.

The numbers given in Table 2 are the average of two wafers. In the experiments (c) and (d) the transportations were carried out 10 times in order to enhance the effect; the results given relate to one transportation.

Contamination during epitaxial growth

It has been established that during growth of an epitaxial layer on 10 cm wafers in one of our silicon reactors the wafers showed a Ni contamination (see Table 3, other elements were not significantly increased). From the results it can be seen that this Ni contamination is present in the backside layer of the wafers. It might be possible that the graphite susceptor had been responsible. Indeed, after using a new cleaned susceptor in the same reactor no Ni (<10 ng/wafer) could be found.

Table 3
Nickel contents in ng in 10 cm diameter wafers (9.75 g) after
epitaxial growth; determination by means of the $^{58}\text{Ni}(n,p)^{58}\text{Co}$ reaction

Wafer number -->	1	2	3
Successive treatments after irradiation:			
1. Rinsed in water	530	580	550
2. Etched 12 microns from the front side; backside covered during etching	540	570	540
3. Etched 10 microns from the backside and also 10 microns from the front side	< 10	< 10	< 10

< means: not detected, number is limit of detection

Contaminations by photolithic processes

On the surface of a silicon substrate with a thermal oxide often a photolithic process is applied for structuring the oxide. During this process Na and K can get into the oxide which may cause problems. It was our task to look for these and possible

other impurities in oxide layers. The wafers under investigation had a diameter of 10 cm and a SiO_2 layer of $0.6 \mu\text{m}$, grown at 1200°C . Two kinds of treatments were applied (table 4). After irradiation (76 hours in $4.3 \cdot 10^{13} \text{ n/cm}^2\text{s}$) the wafers were cleaned in HCl/HNO_3 with carriers. The oxide was removed with HF .

It may be concluded that processes as mentioned in Table 4 may cause serious Na and K contaminations of the oxide layer. Other elements, not listed here, did not show significant differences between the processed and the unprocessed wafers.

Table 4
Na and K contents in ng in the oxide layer of 10 cm
diameter wafers (10 g) due to photolithic processes

Sample	treatment after irradiation	Na ng	K ng
Untreated sample	cleaned	9.8	2.7
	oxide removed	5.0	< 3
Photoresist applied, exposed, developed in alkaline solution, washed, unexposed resist removed in oxygen plasma	cleaned	17	19
	oxide removed	5.2	< 5
Photoresist applied, exposed, developed in alkaline solution, washed, unexposed resist removed at 500°C in O_2	cleaned	72	4.7
	oxide removed	5.1	< 5

Conclusion

With this four examples the application of neutron activation analysis has shown to be crucial in the resolution of a number of problems in integrated circuit technology. It is foreseen that its role will even become more important in the future.

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