(1988).
3. L. Meites, "Handbook of Analytical Chemistry", 1st ed. McGraw Hill Co., Inc. (1963).
4. C. C. Torardi, J. C. Calabrese, K. Lázár, and W. M. Reiff, *J. Solid State Chem.*, **51**, 376 (1984).
5. G. E. Pake, and T. L. Estle, "The Physical Principles of Electron Paramagnetic Resonance" 2nd ed., W. A. Benjamin, Inc. (1973).
6. C. C. Torardi, W. M. Reiff, K. Lázár, and E. Prince, *J. Phys. Chem. Solids*, **47**, 741 (1986).
7. Y. Tanabe, and S. Sugano, *J. Phys. Soc. Jpn.*, **753**, 766 (1954).

A Study on the Characterization on Some Semiconductor Materials by Neutron Activation Analysis. Characterization of Semiconductor Silicon

Chul Lee*, Oh Cheun Kwun, Ho Kun Kim, Jong Du Lee†, and Koo Soon Chung‡

Department of Chemistry, Hanyang University, Seoul 133-791
†Korean Advanced Energy Research Institute, Seoul 139-240
‡Department of Chemistry, Sogang University, Seoul 121-742. *Received July 22, 1988*

Traces of nine elements, gold, arsenic, cobalt, chromium, copper, europium, hafnium, sodium and antimony in commercially available silicon crystals were determined by the instrumental neutron activation analysis using the single comparator method. The values of the concentrations of these elements in both single and polycrystals were found to decrease significantly to a low limiting level by simply washing and etching surface contaminants having been introduced during various steps of sample preparation and irradiation. However, the chromium levels in polycrystals were not easily decreased, these depending upon the cutting tools employed. The Sb-doped content in each semiconductor has been compared with the associated quantities such as the concentration and the conductivity range given by the sample donor. Uncertainty in the sodium analysis due to the fission neutron reaction by silicon itself was discussed.

Introduction

Trace impurities are believed to play a significant role in determining the mechanical and electrical properties of semiconductor silicon. However, in the majority of cases it is not possible to estimate theoretically the effects of different impurities on these properties. For this reason, ideally the semiconductor silicon should be free of all of the elements so as to meet requirements of "absolute purity" placed on the silicon.[1,2] Such requirements need survey analysis methods, which enable a maximum number of impurities or some of the dopant components to be determined. In addition, the purity of ultra pure semiconductors as well as the contents of some dopants are further checked by electrophysical methods which offer a means of estimating performance characteristics.

Silicon semiconductors which meet requirements of "absolute purity" would be ideal samples for instrumental neutron activation analysis (INAA). The matrix has a small activation cross-section, enabling analysis of silicon to be performed for 40-45[1,3] elements. The ideality of INAA for ultra pure silicon remains valid even for the analysis of some dopant components.

The purpose of the present work was to estimate the possibility of using INAA for the survey analysis of ultratrace impurities and some dopants in semiconductor grade silicon crystals of different origins. An attempt has also been made to determine some differences of impurity contents between doped and undoped silicon samples due to possible contamination during the doping processes. The extrinsic conductivity of Sb-doped semiconductors has been estimated by analytical data and compared with that obtained by the electrophysical method.

In the present investigation, nondestructive neutron activation analysis was carried out by the single comparator method with a Ge gammaray spectrometer as descrived previously[4,5]. The method is advantageous for the simultaneous determination of various elements in samples and its reliability is similar to that of the relative method[4,5].

Experimental

Apparatus. Gamma-counting was done with a Ge detector of 70cc volume coupled to a 4096 channel analyzer and a PDP-11 computer system. The system resolution was better than 1.9 KeV (FWHM at 1.33 MeV) with a peak-to-Compton ratio of 40:1. The data for the spectra were computed for the decay-corrected peak areas as described previously.[6]

Sample Preparation. The silicon samples analysed were either bulk or sliced. The bulk samples were cut to the weight of ca. 3g from a single-or polycrystal silicon rod. The slice samples were cut similarly from wafers. The bulk and slice samples were washed in a teflon beaker with trichloroethylene, acetone and deionized water, etched with a mixture of nitric and hydrochloric acid (1:3) and etched again with a mixture of nitric and hydrofluoric acid (10:1). The samples were then rinsed in deionized water and ethanol. The samples were weighed and sealed in a silica glass vial which had been treated similarly.

Neutron Activation Analysis. A known amount of Au

Table 1. Impurity Concentration in Semiconductor Grade Silicon Crystals. Figures in Parentheses are Percentage Errors, *ppm, **Calculated from the Sb Content. CZ = Czochralski's. PC = Poly Crystal

Sample No.	Process	Type	Resistivity (ohm-cm)	Elements determined, ppb								
				Au	As	Co	Cr	Cu	Eu	Hf	Na	Sb
1	CZ	N	1-2	0.0061(±8.2)	0.011 (±30)	1.3 (±3.5)	0.039(±24)	0.048(±62)	0.010 (±24)	0.87 (±6.8)	0.87(±10)	0.054(±25)
2	"	—	—	0.013 (±9.1)	0.026 (±43)	0.65(±4.8)	0.20 (±52)	0.37 (±37)	0.11 (±12)	0.058 (±6.5)	3.2 (±5.9)	0.012(±51)
3	"	P	1-2	0.0068(±13)	0.068 (±22)	1.5 (±3.4)	0.33 (±48)	0.038(±69)	0.26 (±6.2)	0.18 (±16)	1.7 (±16)	0.065(±22)
4	"	P	1-2	0.0080(±9.4)	0.064 (±18)	0.32(±7.5)	0.25 (±12)	0.15 (±43)	0.0088(±29)	0.19 (±9.5)	0.92(±10)	0.022(±37)
5	"	N	1-2	0.0048(±9.0)	0.0022(±48)	0.98(±5.7)	0.14 (±15)	0.071(±45)	0.0078(±62)	0.10 (±15)	0.81(±10)	0.031(±30)
6	"	N	—	0.011 (±6.7)	0.033 (±34)	1.0 (±4.2)	0.63 (±24)	0.35 (±38)	0.14 (±8.4)	0.040 (±10)	1.7 (±7.3)	0.041(±28)
7	PC	—	—	0.0021(±23)	0.018 (±23)	0.67(±4.0)	15 (±2.9)	0.30 (±37)	0.098 (±9.0)	0.043 (±8.9)	0.85(±9.3)	0.017(±35)
8	CZ	N	3-9	0.0018(±8.2)	0.0083(±16)	0.21(±4.8)	0.54 (±19)	—	0.015 (±15)	0.0024(±21)	0.58(±12)	—
9	CZ	N	0.006-0.02 $(4.3\times10^{-4**}$ (±12))	—	—	—	—	—	—	—	—	*209(±14)

Table 2. Impurity Concentration in Semiconductor Grade Silicon Crystals, % Errors are Same as in Table 1. * : 10^{16} atoms / cm^3, ** : Calculate from the Sb Content, *: Given by the Sample Dornor.**
CZ = Czochralski's. PC = Poly Crystal

Sample No.	Process	Type	Resitivity (ohm-cm)	Elements determined ($\times10^{13}$ atoms/cm^3)								
				Au	As	Co	Cr	Cu	Eu	Hf	Na	Sb
1	CZ	N	1-2	0.0045	0.021	3.2	0.11	0.11	0.0095	0.71	5.5	0.064
2	"	—	—	0.0095	0.050	1.6	0.56	0.84	0.10	0.047	20	0.014
3	"	P	1-2	0.0050	0.13	4.0	0.93	0.086	0.25	0.15	11	0.077
4	"	P	1-2	0.0059	0.12	0.78	0.71	0.34	0.0084	0.16	5.8	0.026
5	"	N		0.0035	0.0043	2.4	0.39	0.16	0.0074	0.082	5.1	0.037
6	"	N	—	0.0081	0.064	2.0	1.8	0.79	0.13	0.033	11	0.049
7	PC	—	—	0.0015	0.035	1.6	42	0.68	0.093	0.035	5.4	0.020
8	CZ	N	3-9	0.0013	0.016	0.51	1.5		0.014	0.0020	3.7	—
9	CZ	N	0.006-0.02 $(4.3\times10^{-4**})$	—	—	—	—	—	—	—	—	$2.5\times10^{2*}$ ***$(0.15\text{-}1.0\times10^{3})$

and Co was attached to the surface of each silica glass vial as single comparators. The use of two nuclides with different nuclear properties facilitates the evaluation of the effective activation cross section of all nuclides involved in activation for a given irradiation condition[8].

The vials irradiated in the rotary specimen rack of the TRIGA MARK III reactor for about 24 hrs. The thermal neutron flux was 5×10^{13} neutrons $cm^{-2}sec^{-1}$ at the irradiation point. After irradiation the samples were allowed to cool for 2 days and the surface of each silica vial was cleaned with dilute nitric acid and distilled water. The vials were opened and the bulk or slice samples were washed in a teflon beaker as described above under the "sample preparation". Each sample was accurately weighed and packed in a polyethylene bag for counting. The bag was placed at 1 cm distance from the Ge detector and counted for 2,000 sec. The same bag was counted again for 40,000 sec. for the longer-lived nuclides after 2 weeks' cooling.

Gamma-ray energy and peak areas were calculated by the PDP-II computer system. The calculation of elemental contents was carried out using the flux index at the irradiation point[4,5], the nuclear data given elsewhere[7,8] and the counting efficiency curves at given counting geometries.[4,5]

Table 3. Characteristic Gamma-ray Used for the Determination

Element (nuclide)	Half-life	Selected energy (KeV)
Au (^{198}Au)	64.7 h.	411.8
As (^{36}As)	26.3 h.	559.1
Co (^{60}Co)	5.27y.	1332
Cr (^{51}Cr)	27.70d	320.0
Cu (^{64}Cu)	12.70h.	511
Eu (^{152}Eu)	12.7 y.	1408
Hf (^{181}Hf)	42.4 d.	482.0
Na (^{24}Na)	15.0 h.	1368
Sb (^{124}Sb)	60.2 d.	1691

Result and Discussion

Impurity Concentration. Table 1 and 2 show the mean values of impurity concentration in the crystals of different origins. The nuclear data pertinent to the present work are shown in Table 3.

As shown in Table 1 and 2, nine elements, gold, arsenic, cobalt, chromum, copper, europium, hafnium, sodium and antimony were detected and determined. Among these, five elements, gold, cobalt, copper, sodium and antimony are the same elements determined by Fujinaga *et al.*[3]; using the same chemical treatment before and after irradiation, *i.e.*, the samples were cut, washed, etched and rinsed before and after irradiation. These authors had shown that arsenic, chromium and some lanthanides decreased easily below the detection limits or to relatively low limiting levels upon washing or etching.

In the present work, the washing and etching procedures were repeated several times after irradiation so as to determine whether the four elements, arsenic, chromium, europium and hafnium in addition to the five elements estimated by Fujinaga *et al.* originated from surface contamination or from impurities in the silicon bulk. The fact that the radioactivity of the elements decreased to low limiting levels and was not decreased further after thrice washing and etching indicated that these elements originated from impurities in the silicon bulk. However, the radioactivity of chromium in polycrystals did not easily decrease to a limiting level and the chromium levels seem to depend upon the tools employed for cutting. The higher contents in polycrystals given in Tables 1 and 2 were due to contamination during cutting and the difficulty of decontamination by the present washing and etching procedures.

It was found from Table 1 that cobalt, chromium, copper and sodium were contained in all single crystals at 0.04-3 ppb and arsenic, europium, hafnium and antimony were contained in all samples at 0.002-0.2 ppb. Gold, which has a very high sensitivity, was found to be in the concentration levels of 0.002-0.01 ppb.

The figures in parentheses in Table 1 show the estimated total uncertainties, including statistical and systematic errors for the quantitative determination.[9] In the analysis of sodium, ^{24}Na could be produced from the sodium impurity by (n, γ) reaction as well as from the silicon sample itself by $(n, \alpha\, p)$ reaction[11] because the ratio of thermal to fission neutron flux[12], which was 3.8 at the present work, is comparable with 4.0 given by Niese[11]. The origin of sodium content (ca. 1 ppb) in Table 1 was found to be attributable to two reactions, as estimated by the ratio[12] of σ_{th}/σ_f, *i.e.*, $5.0 \times 10^{-25}/1.8 \times 10^{-33} \approx 10^9/4$. Therefore, the sodium content in Tables 1 and 2 should be accepted with an additional uncertainty.

Dopant Concentration. It is interesting to note that the impurity concentrations determined in the present work can be associated with the resistivity and conduction type of single crystals. For this purpose, the extrinsic conductivity σ_{ex} of a Sb-doped semiconductor, *i.e.*, the sample No. 9 in Tables 1 and 2, was estimated by the following equation, neglecting the intrinsic conductivity,

$$\sigma_{ex} = n_d \cdot q \cdot \mu_n,$$

where n_d, q and μ_n are the number of carrier electrons, charge of an electron and the mobility of electron, respectively. Since Si crystal has eight atoms per unit cell like diamond and Sb has one carrier electron per atom σ_{ex} can be estimated after calculation of the number of carrier electron, n_d, as follows[10].

$$n_d = \left[\frac{8 \text{ Si atoms}}{(\text{lattice constant of Si})^3}\right] \left[\frac{10^{-7} \text{ Sb atoms}}{\text{Si atoms}}\right]\left[\frac{1 \text{ carrier}}{\text{Sb stom}}\right]$$

The calculated conductivity was found to be much less than the value given by the sample donor as shown in Tables 1 and 2. However, the concentration of antimony obtained in this work was found to be within the range given by the sample donor as shown in Table 2. Other impurity contents in the sample could not be estimated because of high background due to antimony.

For other samples, no features linking impurity concentrations with the resistivity and conduction type of single crystals were observed because dopants used, such as boron, phosphorus and oxygen, are difficult subjects for INAA method adopted in the present work. No difference of impurity contents due to contamination during the doping process was found in Tables 1 and 2.

Acknowledgements. The authors thank the Ministry of Education for supporting the present work by the Basic Science Research Institute Program, 1987. The authors are also grateful to Dr. Suk-Ki Min, Korea Advanced Institute of Science and Technology, and Dr. Dong-Sung Ma, Korea Electronics and Telecommunications Research Institute, for their kind supply of samples.

References

1. Yu. A. Zolotov and M. Grasserbauer, "Trace Analysis of Semiconductor Materials, Part A: Bulk Analysis". Pure and Appl. Chem., **57**(8), 1133-1152 (1985).
2. M. Grasserbauer, Yu. A. Zolotov and G. H. Morrison, "Trace Analysis of Semiconductor Materials, Part B: Distribution Analysis". *ibid.*, 1153-1170 (1985).
3. K. Fujinaga and K. Kudo, *J. Radional. Chem.*, **52**, 411 (1979).
4. C. Lee, *J. Kor. Nucl. Soc.*, **5**, 137 (1973).
5. N. B. Kim, "A Study on Neutron Activation Analysis for the Determination of Contents of Impurities in Reactor Materials" Ph. D. Theses, Seoul Nat. Univ., 1983.
6. C. Lee, N. B. Kim, I. C. Lee and K. S. Chung, *Talanta*, **24**, 241 (1977).
7. J. I. Kim, I. Fiedler, H. J. Born and D. Lux, *Intnat. J. of Environ. Anal. Chem.*, **10**, 135 (1981).
8. J. I. Kim, *J. Radioanal. Chem.*, **63**, 121 (1981).
9. L. A. Currie, *Anal. Chem.*, **40** (3), 586 (1968).
10. L. H. Van Vlack, "Materials Science. for Engineers", Addison-Wesley Pub. Co., 1971.
11. S. Niese, *J. Radioanal. Chem.*, **38**, 37 (1977).
12. H. I. Bak, C. Lee and N. B. Kim, *New Physics (Korean Physical Soc.,)* **41**, 199 (1974).