Standardization of Nitrogen Analysis in CZ-Si by Charged Particle Activation Analysis

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Introduction

Nitrogen doping is becoming a key technology for preparing high performance bulk CZ silicon for ULSI. Hence, JEITA (Japan Electronics & Information Technology Association) organized a working group for the standardization of nitrogen concentration of CZ silicon, which consists of experts of IR, PL, SIMS and CPAA (charged particle activation analysis)[1] [2].

As well known, CPAA is suited for the bulk analysis of ultra-trace amount of nitrogen without the effect of its chemical state and the surface contamination [3] [4]. CPAA has been recommended as one of the definitive method directly linked with SI-unit. However, analytical procedure should be carefully examined for each element and each matrix, in order to obtain reliable data. For the standardization project of JEITA, we tried to use the cyclotron of NMCC and SHIEI to check the accuracy of CPAA of 10^{14} atoms/cm^3 level of nitrogen. Two different analytical procedures were carefully checked and applied to CPAA of silicon respectively at the above facilities.

Experimental

The $^{14}N(p,\alpha)^{11}C$ reaction was used for the determination of nitrogen. Silicon samples of 2×2×0.2 cm size were bombarded with 15 MeV protons.The beam current and irradiation time were set 5μA and 20 min. A disk of aluminum nitride was used for the standard. The beam current and irradiation time were set 0.1μA and 0.5 min.

Two rapid chemical separation methods, i.e. oxidizing fusion method and wet chemical separation method have been examined and used for the separation of ^{11}C, which is a positron emitter with 20 min half-life. In fusion method, ^{11}C was separated from silicon as CO_2 by heating with an induction furnace and trapped with Ascarite. In wet method, samples were decomposed with NaOH and ^{11}C was oxidized to carbonate by adding $KMnO_4$ and heating in a microwave oven. After oxidation, CO_2 was generated by adding H_2SO_4 and finally collected as Li_2CO_3. The recovery of ^{11}C after chemical separation was obtained by weighing a precipitate of Li_2CO_3.

The annihilation radiation from ^{11}C was measured by a coincidence counting system composed of two NaI or BGO scintillation detectors facing each other. Samples and standard were set between two detectors and radioactivity was measured continuously to confirm the radiochemical purity. The difference of proton range between sample and standard was corrected.

Results and discussion

The recovery yields of ^{11}C separation were 80% and 70% for the oxidizing fusion and the wet chemical separation, respectively. Impurity boron in silicon causes severe interference, also giving ^{11}C by the $^{11}B(p,n)^{11}C$ reaction. Then, the degree of interference caused by boron has been also examined. It was confirmed that the activity of ^{11}C from equal content of N and B is almost same. For the CZ sample, B correction was performed. The analytical results of several CZ and FZ samples are summarized in Table 1, together with the results of SIMS obtained by two laboratories. Good agreements, in general, are shown among the results of CPAA with two different methods as well as of SIMS. It was confirmed that nitrogen of 10^{14} atoms/cm^3 can be measured by the present technique.

References

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Table 1. Analytical results of nitrogen in CZ silicon (10^{14} atoms/cm^3)

Sample	CPAA(SEI)	CPAA(NMCC)	SIMS(Lab1)	SIMS(Lab2)
C1	1.9 2.0	-	1.1	0.6
C2	9.7	5.7 4.7	6.0	5.0
C3	10.8	9.7 7.4	9.0	
C4	16.2 15.2	11 10.6	16.0	11.0
F1	-	3.9 4.9	6.6	
F2	10.6	4.4 8.1	8.6	
F3	12.6	3.8 10.3	12.7	

Sample name Cn and Fn means CZ and FZ silicon, respectively.