II. 1 Determination of Oxygen Concentration in Silicon by $^3$He Activation Analysis

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Impurity oxygen atoms are known to affect the electrical and the mechanical properties of silicon crystal remarkably. Oxygen atoms are introduced into silicon crystals grown by the Czochralski technique at the time of crystal growth from fused quartz crucibles. A Czochralski-grown silicon crystal usually contains impurity oxygen atoms of a concentration of order of $10^{18}$ cm$^{-3}$ which become super-saturated in the temperature range below about 1200°C. Such super-saturated oxygen atoms turn to donors of electrons by clustering upon annealing at relatively low temperatures$^{1,2}$ and also develop atmospheres around dislocations, resulting in a severe reduction in the density of active dislocation sources$^{3-5}$. Thus, the determination as well as the control of oxygen concentration in silicon is very important from the view point of device technology.

Oxygen atoms dissolved in silicon crystal are on interstitial sites and active in the absorption of infra-red light of a wave length of 9 μm. Thus, the concentration of interstitially dissolved oxygen atoms in silicon crystal can be determined from the absorption coefficient at 9 μm provided that the absorption due to free carriers is negligibly small compared with that due to the local oscillation of the oxygen atoms. This technique is now widely used to determine the concentration of dissolved oxygen atoms in silicon crystal. The above technique, however, is not applicable to silicon crystals having resistivities lower than about 1.0 Ω cm at room temperature since the absorption due to free carriers prohibits the transmission of the infra-red light through the crystals. The purpose of this work is thus, to determine the concentrations of dissolved oxygen atoms in a series of Czochralski-grown silicon crystals doped with various impurities by means of $^3$He activation analysis.

The following nuclear reactions were utilized in the analysis:

$$^{16}O(^3He,p)^{18}F\xrightarrow{\beta^+}^{18}_0 \text{min}$$

$$^{16}O(^3He,n)^{18}Ne\xrightarrow{\beta^+}^{18}_F\xrightarrow{\beta^+}^{18}_0 \text{min}$$

The above two reactions occur simultaneously, resulting in the increase in the sensitivity of the activation analysis. The decay in the intensity of 0.511 MeV γ-ray generated by the annihilation radiation of $\beta^+$ in Eq. (1) was measured.

The determination of the oxygen concentration was done by the comparison method using a reference sample of quartz. The concentration of oxygen atoms $N_i$
is given by the following equation;

\[ N_l = \frac{C_0 f \bar{\gamma}_s R_s \left[ 1 - \exp(-\lambda \tau_s) \right] \exp \left( -\nu_s \frac{d_s}{s} \right) N_s}{C_0 S f \bar{\gamma}_s R_s \left[ 1 - \exp(-\lambda \tau_i) \right] \exp \left( -\nu_i \frac{d_i}{i} \right) N_s} \]  

(2)

where \( C_0 \) is the \( \beta^+ \) activity at the end of the irradiation period, \( f \) the number of incident \( ^3 \)He ions per unit time, \( \bar{\gamma} \) the average reaction cross section, \( R \) the range of the \( ^3 \)He ions, \( \lambda \) the decay constant, \( \tau \) the irradiation time, \( \nu \) the attenuation coefficient for annihilation radiation, \( d \) the sample thickness, \( S \) and \( s \) refer to the silicon and the quartz samples, respectively. \( N_s \) is the concentration of oxygen atoms in quartz, being \( 5.5 \times 10^{22} \) cm\(^{-3} \). The average radiation cross sections were calculated by the method of Ricci and Hahn\(^6\) who adopted the straight-line fitting of excitation function.

Four types of Czochralski silicon crystals having different dopants were subjected to the activation analysis of oxygen. Sample 1 was intrinsic, sample 2 doped with phosphorus of a concentration of approximately \( 1 \times 10^{19} \) cm\(^{-3} \), sample 3 doped with boron of a concentration of approximately \( 1 \times 10^{19} \) cm\(^{-3} \), and sample 4 doped with carbon of a concentration of approximately \( 1 \times 10^{17} \) cm\(^{-3} \). The samples had the shape of disk with a diameter of 10 mm and a thickness of 2 mm. The surface of the silicon sample was finished by chemical polishing with CP-4 etchant. \( ^3 \)He beams with an energy of 15 MeV were irradiated on the silicon samples at a beam current of about 1 \( \mu \)A for 10 minutes and on the reference quartz sample at about 0.5 \( \mu \)A for 3 minutes while the samples were cooled with running water. Prior to the measurements of the radioactivities of the irradiated silicon samples, the surface layers of a thickness of about 20 \( \mu \)m were polished out chemically in order to avoid the over-counting due to the oxide films formed on the surfaces.

Figure 1 shows an example of the relation between the count rate of 0.511 MeV \( \gamma \)-ray and the time \( t \) after the end of the irradiation of \( ^3 \)He for a reference sample. It is seen that the decay with a half-life of 110 minutes appears in the period 2.5-5 hr after the irradiation. The counting was done three or four times for each sample. The values of \( C_0 \)'s were obtained by the extrapolation of the curves to time zero. Table 1 shows the concentration of oxygen atoms thus determined for the silicon samples together with the ratios of various parameters in Eq. (2). All the Czochralski-grown silicon samples are known to contain oxygen atoms the concentrations of which are of the same order of magnitude in agreement with expectation. An infra-red absorption measurement on the intrinsic silicon sample (sample 1) with the use of the Kaiser-Keck calibration curve\(^7\) gave a concentration of oxygen atoms of \( 7.4 \times 10^{17} \) cm\(^{-3} \) which was lower than that obtained by the activation analysis by a factor 0.6. Such discrepancy may be due to the fact that the infra-red absorption measurement detects only interstitially dissolved oxygen atoms while the activation analysis all oxygen atoms in the sample including those in precipitates and also to the possible inaccuracy
of the Kaiser-Keck calibration curve.

References


Table 1. Results of activation analysis of oxygen in Czochralski-grown silicon crystals together with relative magnitudes of various parameters

| Sample | $f_s/f_i$ | $C_{o,i}/C_{o,s}$ | $S_i/S_{i}$ | $R_{e}/R_{i}$ | $1 - \exp(-\lambda r_s)$ | $\exp(-\lambda r_i)$ | $N_i (10^{17} \text{ cm}^{-3})$
|--------|----------|------------------|-------------|---------------|-----------------------|---------------------|------------------|
| 1      | 0.448    | 1.7x10^{-4}      | 0.931       | 1.08          | 0.31                  | 0.995               | 13
| 2      | 0.418    | 2.3x10^{-4}      | 0.972       | 1.03          | 0.31                  | 0.997               | 16
| 3      | 0.457    | 1.2x10^{-4}      | 0.917       | 1.09          | 0.31                  | 0.997               | 9.2
| 4      | 0.469    | 1.6x10^{-4}      | 0.917       | 1.09          | 0.31                  | 0.996               | 12 |
Fig. 1. Decay curve of 0.511 MeV γ-ray for a $^3$He irradiated reference sample.