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# Introduction of high oxygen concentrations into silicon wafers by high-temperature diffusion

The RD48 Collaboration

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**Abstract**

The tolerance of silicon detectors to hadron irradiation can be improved by the introduction of a high concentration of oxygen into the starting material. High-resistivity Floating-Zone (FZ) silicon is required for detectors used in particle physics applications. A significantly high oxygen concentration ( $> 10^{17}$ atoms $cm^{-3}$) cannot readily be achieved during the FZ silicon refinement. The diffusion of oxygen at elevated temperatures from a $SiO_2$ layer grown on both sides of a silicon wafer is a simple and effective technique to achieve high and uniform concentrations of oxygen throughout the bulk of a 300 μm thick silicon wafer. 

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## 1. Introduction

The damage caused to silicon detectors by the intense hadron fluxes predicted in the future experiments of particle physics [1,2] can lead to the failure of these devices before the end of the experimental programme. The radiation tolerance of silicon can be improved by a deliberate introduction of impurities into the silicon crystal [3,4]. The impurity atoms can react with the primary-induced defects (vacancies and interstitials) and effect the formation of electrically active centres. Certain impurities can thus influence the changes of the electrical parameters of the devices, such as an increase of the full depletion voltage due to the changes in the effective spatial charge in irradiated detectors. In particular, oxygen atoms can capture vacancies, reducing the rate of formation of $V_2O$, di-vacancy (or multivacancy) complexes and thereby limiting the rate of degradation of the electrical properties of silicon detectors.

Oxygen is present in low-resistivity Czochralsky silicon with a concentration up to $\sim 10^{18}$ atoms $cm^{-3}$, but concentrations of only $\sim 10^{15}$ $cm^{-3}$ are

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found in the high-grade and high-resistivity Floating-Zone (FZ) silicon.

The high-temperature diffusion technique can be used to enhance the oxygen concentration in the 250–300 μm thick silicon wafers produced from FZ grown ingots.

## 2. Impurity diffusion in silicon

Impurities can diffuse into the silicon crystal through vacancy or interstitial sites. The isotropic diffusion process is described in terms of the diffusion coefficient $D$, as defined by the first Fick's law [5]

$$\bar{j} = -D\nabla N \tag{1}$$

where $\bar{j}$ is the current of the diffusing atoms and $N$ is the impurity concentration. The silicon devices are fabricated on large area wafers (7.5–15 cm in diameter) with thickness ranging between 200 and 500 μm. If the diffusing atoms enter the silicon wafer homogeneously through the surface, then the analysis can be limited to the simple one-dimensional case. By applying the continuity equation to Eq. (1) we obtain, for the one-dimensional case:

$$\frac{\partial N}{\partial t} = D\frac{\partial^2 N}{\partial x^2}. \tag{2}$$

In order to maintain a constant concentration at the surface plane ($x = 0$) for the diffusing impurities, the boundary conditions are

$$N(x > 0, t = 0) = 0 \quad \text{and} \quad N(x = 0, t \geq 0) = N_0. \tag{3}$$

Solving Eq. (2) gives

$$N(x,t) = N_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right). \tag{4}$$

This solution describes reasonably well an impurity diffusing into the silicon from a gas or a vapour phase.

Considering a "rectangular" box at $t = 0$ with thickness $h$, and with a constant concentration $N_0$ of the impurity in a semi-infinite body, the solution of Eq. (2) is

$$N(x,t) = \frac{N_0}{2}\left[\operatorname{erfc}\left(\frac{x-h}{2\sqrt{Dt}}\right) - \operatorname{erfc}\left(\frac{x+h}{2\sqrt{Dt}}\right)\right]. \tag{5}$$

The Taylor's series expansion of Eq. (5) about $x/2\sqrt{Dt}$ is

$$\begin{aligned} N(x,t) &= \frac{N_0 h}{\sqrt{\pi Dt}} \exp\left[-\left(\frac{x}{2\sqrt{Dt}}\right)^2\right]\left[1 + \frac{1}{3!}\left(\frac{h}{2\sqrt{Dt}}\right)^2 \times H_2\left(\frac{x}{2\sqrt{Dt}}\right) + \frac{1}{5!}\left(\frac{h}{2\sqrt{Dt}}\right)^4 \times H_4\left(\frac{x}{2\sqrt{Dt}}\right) + \cdots\right]. \end{aligned} \tag{6}$$

where $H_n$ is the Hermite polynomials of order $n$.

This solution is used to describe an impurity introduced into the silicon bulk before the diffusion.

## 3. The oxygen diffusion experiment

The velocity of the diffusion depends on the coefficient $D$, and the maximum concentration depends on the solubility of the impurity in silicon. The value of $D$ as a function of temperature is

$$D(T) = D_0 \exp\left(-\frac{E_d}{k_B T}\right) \tag{7}$$

where $D_0$ is the limit value of $D$ for infinite temperature and $E_d$ is the activation energy.

Table 1 lists the values of the diffusion parameters of oxygen in silicon reported by many groups. The value of the solubility of oxygen in silicon is $\sim 8.4 \times 10^{17}$ at 1250°C [6].

The oxygen diffusion tests have been performed at the Technion University in Haifa (Israel) using $1 \times 1\ \text{cm}^2$ and 300 μm thick samples of standard silicon produced by POLOVODICE.[1] Layers of silicon oxide $\sim 3000$ Å in thickness were grown on

[1] POLOVODICE,Vovodvorská 994, 142 21 Praha 4 (CZ).

Table 1
Diffusion parameters for oxygen in silicon [6]

| $E_d$ (eV) | $D_0$ ($cm^2\ s^{-1}$) | $D$(1150°C) ($cm^2\ s^{-1}$) | $D$(1200°C) ($cm^2\ s^{-1}$) |
|---|---|---|---|
| 3.5 | 135 | $5.44\times10^{-11}$ | $1.43\times10^{-10}$ |
| 2.55 | 0.21 | $1.96\times10^{-10}$ | $3.97\times10^{-10}$ |
| 3.5 | 83 | $3.35\times10^{-11}$ | $8.82\times10^{-10}$ |
| 2.4 | 0.091 | $2.88\times10^{-10}$ | $5.60\times10^{-10}$ |
| 3.15 | 22.6 | $1.58\times10^{-10}$ | $3.78\times10^{-10}$ |
| 2.44 | 0.07 | $1.60\times10^{-10}$ | $3.15\times10^{-10}$ |
| 2.77 | 1.5 | $2.33\times10^{-10}$ | $5.01\times10^{-10}$ |
| 2.54 | 0.17 | $1.72\times10^{-10}$ | $3.47\times10^{-10}$ |
| 2.51 | 0.11 | $1.42\times10^{-10}$ | $2.85\times10^{-10}$ |
| 2.43 | 0.033 | $8.19\times10^{-11}$ | $1.60\times10^{-10}$ |
| 2.53 | 0.14 | $1.54\times10^{-10}$ | $3.10\times10^{-10}$ |

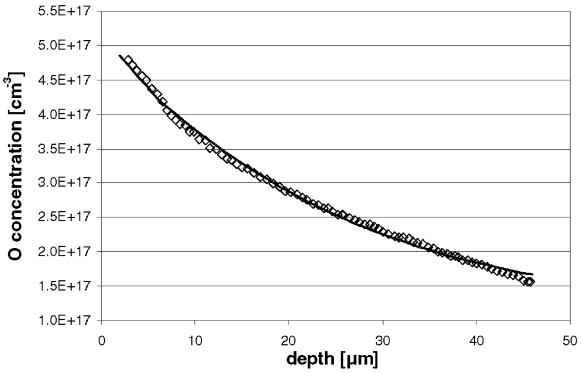


Fig. 1. Oxygen concentration profile, measured by SIMS, in a silicon sample diffused for 20 h at 1150°C in an $N_2$ ambient from a 3000 Å layer of $SiO_2$.

both sides using the dry oxidation technique. The samples were then heated to 1150°C in an inert ($N_2$) ambient to allow the dissociation of oxygen from the $SiO_2$ at the interface, and its diffusion into the silicon bulk. The samples were maintained at 1150°C for 20 h. Fig. 1 shows the oxygen profile obtained as a function of the depth, as measured by the Secondary Ion Mass Spectroscopy (SIMS) technique, by the Evans Europa Company. The value of $D$ and $N_0$ (maximum concentration at the surface) obtained by fitting the data are $2.25\times10^{-10}\ cm^2\ s^{-1}$ and $5.6\times10^{17}\ cm^{-3}$, respectively. The $SiO_2$ layer disturbs the SIMS signal for the shallower points, which have been excluded from the fit.

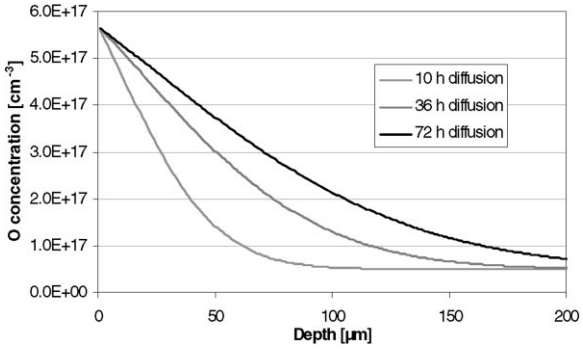


Fig. 2. Oxygen concentration as a function of depth in silicon calculated for three different diffusion times at 1150°C. The diffusion parameters have been obtained from the fit shown in Fig. 1.

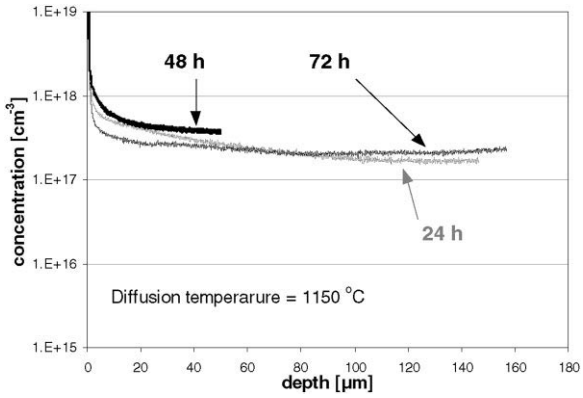


Fig. 3. SIMS measurements of the oxygen concentration profile as a function of depth in silicon after different diffusion times from $SiO_2$ surface layers grown on both sides of the silicon wafer. The diffusion times are 24, 48, and 72 h at a temperature of 1150°C.

Fig. 2 shows the oxygen concentration as a function of the depth in the silicon wafer. It is calculated using the fitted parameters for three different diffusion times at 1150°C. The high-temperature diffusion technique was used to introduce oxygen into 3″ n-type silicon wafers, 300 μm thick, with initial resistivity of $\sim 2.5\ k\Omega\ cm$. The single-crystal wafers were provided by POLOVODICE and were diffused by ITE[2] for 24, 48 and 72 h at 1150°C.

[2] ITE, Institute of Electronic Materials Technology, Al. Lotnikóv 32/46, 02-688 Warsaw (PL).

Fig. 3 shows the profile of the oxygen concentration as a function of the depth in the silicon, measured by SIMS. A certain enhancement of the obtained oxygen concentration compared with predictions is observed in the 24 h diffusion.

ITE processed the oxygen-diffused wafers to produce $5 \times 5\,mm^2$ diodes. The resistivity of the diffused material, as measured using the capacitance–voltage technique, was found to be between 2.2 and 2.7 kΩ cm. This range of fluctuations is normally found for FZ wafers and the resistivity after diffusion is comparable to the initial value. This indicates that the formation of small clusters of oxygen atoms, forming in silicon at $\sim 450°C$ and acting as double thermal donors [7] is relatively negligible.

## 4. Conclusion

High-temperature diffusion is an effective technique to introduce fast diffusing impurities into silicon. A high oxygen concentration ($\sim 2 \times 10^{17}\,cm^{-3}$) in 300 μm thick silicon wafers is obtainable with diffusion times in the range 24–48 h at 1150°C from $SiO_2$ layers grown on both surfaces of the wafers. An oxygen concentration value of $\sim 1.5 \times 10^{17}\,cm^{-3}$ is found in the middle of the wafer (150 μm) after a diffusion time of 24 h and an almost homogeneous value of $\sim 2.5 \times 10^{17}\,cm^{-3}$ all over the silicon bulk after 48 h diffusion time. This technique also guarantees optimal radial homogeneity of the oxygen concentration.

The changes induced by the thermal cycle for the diffusion process on the initial resistivity are negligible. This technique is therefore suitable for the introduction of oxygen in the high-resistivity silicon required for the fabrication of detectors for high-energy physics.

## 5. Additional remarks

The negligible change of the initial resistivity measured after the oxygen diffusion implies low formation of O-related thermal donors. This result is achieved avoiding long periods of annealing around 450°C during the decreasing temperature cycle after diffusion. The wafers should be removed from the furnace when the temperature has reached 600–700°C.

After diffusion, the deposited silicon oxide is removed. This can be obtained by chemical etching or by polishing. Polishing probably leads to a better quality of the surface of the wafer, removing the $Si–SiO_2$ interface layer that could otherwise present a high density of defects after the high-temperature treatment.

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