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Intentional thermal donor activation in magnetic Czochralski silicon

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Abstract

We have made a quantitative study about the thermal activation of thermal donors in high resistivity magnetic Czochralski silicon. The thermal donor activation has been performed through a thermal treatment at 430 °C up to a total time of 80 min. The space charge density after each annealing step has been extracted from capacitance–voltage measurements. If the starting material is boron-doped p-type high-resistivity Czochralski silicon, the thermal donor generation process can be utilized in order to produce $p^+/n^-/n^+$ detectors. The last thermal process step, i.e. the sintering of aluminum, is intentionally carried out at the temperature where thermal donors are created. According to our results, we have improved the previously reported model of the thermal donor generation.

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Keywords: Silicon particle detectors; Czochralski silicon; Thermal donors; Material engineering

1. Introduction

It is well known that the aggregation of oxygen atoms leads to the formation of electrically active defects, commonly named thermal donors (TDs) [1,2]. The TDs are probably among the most studied defects in semiconductors. The TDs are shallow donor levels below the conduction band [3]. The formation of TDs depends strongly on the temperature and the oxygen concentration in the silicon material. In high resistivity silicon, a heat treatment between 400 and 600 °C can yield a TD concentration comparable with the initial doping concentration. The formation of TDs has often been explained to be due to the so-called anomalously fast diffusing species (FDS). Oxygen dimers (O_2) and trimers (O_3) among other oxygen complexes have been proposed to be such FDS [4]. Additionally, a third-power dependence of the TD formation rate (d/dt NTD) on the oxygen concentration has widely been quoted.

The purpose of this work is to utilize TDs in our detector process and to characterize and to model the TD formation in a high resistivity magnetic Czochralski (MCz) silicon (MCz-Si) material. The motivation arises from the lately developed application of the MCz as a very radiation hard particle detector material for high-energy physics applications. The sensors used in particle-tracking systems must be fully depleted at reasonably low operating

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voltages, typically less than 100 V. Therefore, the silicon sensors have traditionally been fabricated on wafers grown by the float zone (FZ-Si) crystal growth method. The FZ-Si method ensures high purity and sufficiently defect-free silicon crystals that are the basic requirements for the production of high-resistivity silicon substrates for detector applications. On the other hand, FZ-Si has characteristically a low oxygen concentration because of the contactless, crucible-free crystal growth technique. Low oxygen concentration in FZ-Si is a drawback for radiation hardness [5,6].

Although Cz-Si is the basic raw material for the microelectronics industry, high resistivity ($>1\,\mathrm{k\Omega cm}$) MCz-Si wafers suitable for detector fabrication have become available only recently [7]. Oxygen is dissolved into silicon from the quartz crucible during crystal growth. A major part of the oxygen is dissolved as silicon monoxide and is flushed away by argon gas. Furthermore, the resulting oxygen concentration depends on the velocity of the silicon melt flow as well as on the rate of oxygen evaporation from the melt. These parameters can be influenced in order to obtain the desired oxygen concentration in the silicon ingot. The application of a magnetic field is an especially effective way to moderate and control the melt flow, since the silicon melt is an electrically conductive liquid [8].

In this paper, we describe a detector fabrication process, measurement and characterization of TDs in MCz-Si substrates, propose an empirical model for TD formation and discuss the benefit and applications of TDs in particle detectors.

2. Samples

All samples used in this study have been processed on p-type MCz-Si [8]. The starting material of the detectors was 4″ diameter double-side polished $300\pm2\,\mu\mathrm{m}$ thick $\langle 1\,0\,0\rangle$ silicon wafers. The nominal resistivity of the wafers measured by the four-point probe method is $1800\,\Omega\mathrm{cm}$, which corresponds to the boron concentration $7.38\times10^{12}\,\mathrm{cm^{-3}}$. The oxygen concentration was measured by Fourier transformation infrared (FTIR) spectroscopy from a thick reference wafer. The following oxygen concentrations were measured: 4.95×10^{17} (center), 4.89×10^{17} (right), 4.93×10^{17} (left) and $4.93\times10^{17}\,\mathrm{cm^{-3}}$ (bottom) [9].

Two types of detectors were processed by our group at the Micro and Nanofabrication Centre of Helsinki University of Technology. The active implanted pad area of all the diodes is $5\times5\,\mathrm{mm^2}$. The first set of samples was the $p^+/p^-/n^+$-diode structures, i.e. the pad had been implanted by boron and backside by phosphorous. The active area is surrounded by one wide guard ring (100 μm) and 16 small guard rings (each 16 μm wide). The distance between the active area implant and the first guard ring is 10 μm. A 1 mm diameter round opening in the front metallization was left for transient current technique (TCT) measurements [10]. The second set of samples was the $n^+/p^-/p^+$ structures processed with a different mask set. An additional mask level and a boron ion implantation were required because of the electron accumulation at the SiO_2/Si surface. Surface inversion was terminated by boron-implanted guard rings. One 100 μm wide and eight 16 μm wide p^+ guard rings were processed between n^+ rings. Boron field implantation (often referred as p-spray) was not done on these samples.

The $p^+/p^-/n^+$ and the $n^+/p^-/p^+$ process contain two and three thermal oxidations, respectively. The oxidations were done at 1100 °C. All existing TDs were killed during oxidation steps. After the oxidations, the temperature was ramped down at the rate of 4 °C/min. The pull-out of the wafers took place at 700 °C. Thus the wafers were cooled as fast as possible in order to avoid TD formation temperature range 400–600 °C. After metallization, all detectors were protected with approximately 60 nm thick patterned silicon nitride (Si_3N_4) film grown by the plasma-enhanced chemical vapor deposition (PECVD) method. The deposition temperature of PECVD Si_3N_4 was 300 °C [9].

The last process step of these detectors was aluminum sintering. In order to study the TD generation, the detector wafers were sintered at 430 °C for different times, i.e. 35, 45, 60, 70 and 80 min. The thermal profile of sintering is push-in 2 min followed by 10 min stabilization while the furnace settles again at the annealing temperature (the furnace door is open during the push-in). After heating at the annealing temperature the wafers were pulled out in 2 min. An $n^+/p^-/p^+$ reference wafer was processed and sintered at 370 °C.

After processing, the wafers, containing 80 pad detectors each, were diced. The diodes were characterized at the probe station by capacitance–voltage (CV) and current–voltage (IV) measurements.

Formation of the TDs depends not only on the oxygen concentration but also on the temperature

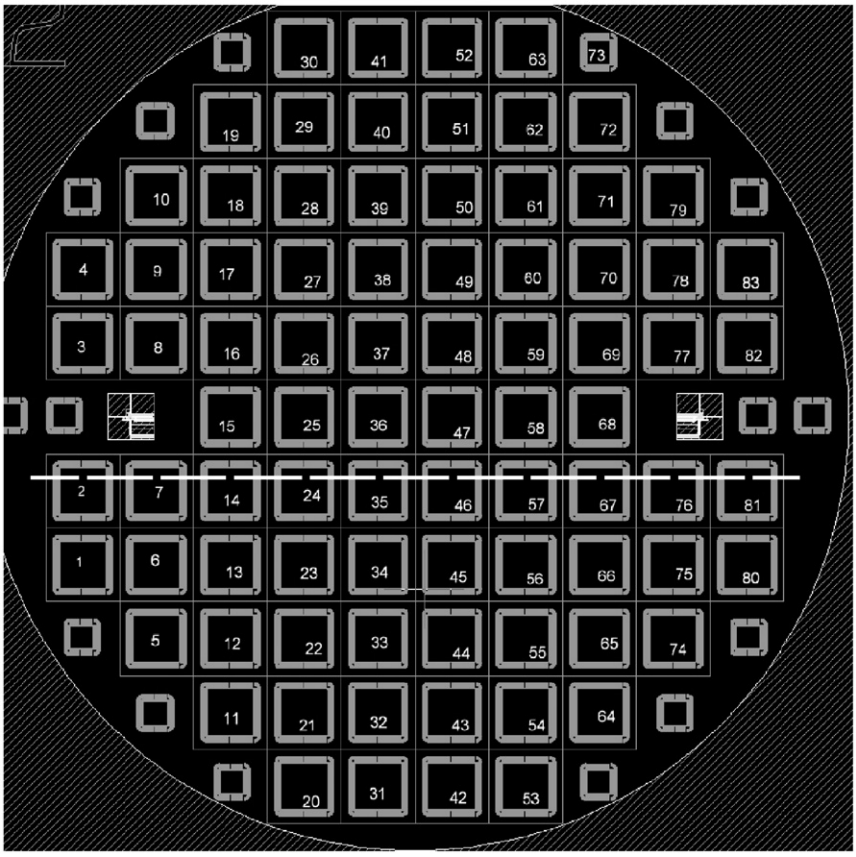

Fig. 1. Position on the wafer of the pad detectors used in this study.

and on the amount of hydrogen used in the detector-manufacturing process [11]. In order to study the spatial uniformity of the full depletion voltage, V_{fd}, 10 diodes along the wafers diameter were picked for the CV measurements as shown in Fig. 1.

3. Measurements

When a detector is reverse biased, the electric field extends towards the backside of the detector. With sufficiently high reverse bias, the space charge region exists through the entire bulk, i.e. the detector is fully depleted and the capacitance signal saturates. V_{fd} of the devices was extracted from the CV curve measured at room temperature and with the 10 kHz frequency. The effective doping concentration (N_{eff}) is calculated from

$$N_{eff} = \frac{2\varepsilon\varepsilon_0 V_{fd}}{qd^2}, \quad (1)$$

where d is the thickness of the detector, q is the elementary charge and ε is the dielectric constant of the silicon. The concentration of TDs is obtained from

$$N_{TD}^0 = |N_A - N_{eff}|,$$
$$N_A = 4.38 \times 10^{12}\,\mathrm{cm}^{-3}, \quad (2)$$

where N_A is the boron doping concentration of the wafers. The value for N_A was obtained from the depletion of as-processed p-type devices that took place at 300 V. It corresponds to a resistivity of approximately 3000 Ωcm, which differs from the 1800 Ωcm value provided by the wafer manufacturer. It is therefore obvious that boron doping has been to some extent compensated during detector processing.

4. Results and modeling of TD generation

The results of the CV measurements are shown in Fig. 2. The sign of the space charge is obtained from TCT measurements reported in Ref [12].

It can be seen that the TD formation is almost linear. It is therefore obvious that the empirical models, claiming 3 [2] or 3.4 [13] power dependence

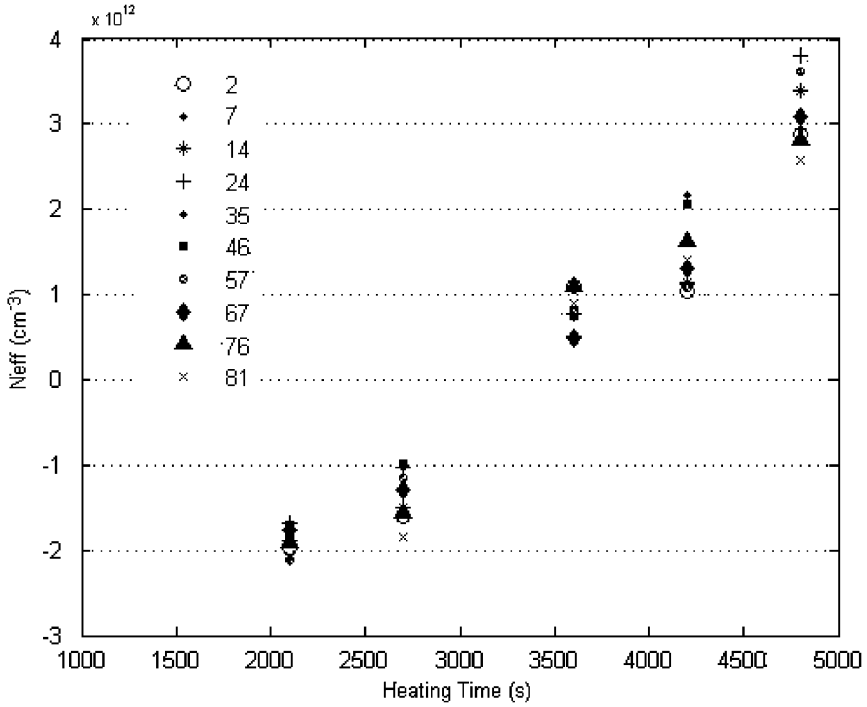

Fig. 2. Effective doping concentration (N_{eff}) with respect to heating time at 430 °C. The individual symbols correspond to the diode numbering presented in Fig. 1.

on the oxygen concentration for the TD formation rate, cannot explain our experimental results. We have made an effort to improve the existing models by following the time and temperature-dependent equation with two fitting parameters.

$$N_{\text{TD}}(t,T) = a(1 - \mathrm{e}^{-xt}) + N_{\text{TD}}(0,T), \tag{3}$$

where t is the time, T is the absolute temperature and a is given by

$$a = c \times O_{\text{i}}^{\chi}, \tag{4}$$

where c is a fitting constant, O_{i} is the concentration of the interstitial oxygen and χ is the reaction order, i.e. the exponent to where oxygen concentration is to be raised. The x in Eq. (3) is given by

$$x = bO_{\text{i}}D_{\text{i}}, \tag{5}$$

where b is a fitting parameter and D_{i} is the diffusion coefficient of the interstitial oxygen given by

$$D_{\text{i}}(T) = 0.13\mathrm{e}^{-(E_{\text{A}}/kT)}\ (\text{cm}^2/\text{s}),$$
$$E_{\text{A}} = 2.53\,\text{eV}, \tag{6}$$

where k is the Boltzmann's constant and E_{A} is the activation energy, which is found in Ref. [2]. Fitting of the model to the experimental data is shown in Fig. 3.

The fitting gives the following results:

$$N_{\text{TD}}(t,T) = 6.82 \times 10^{-20} O_{\text{i}}^{1.89}(1 - \mathrm{e}^{-6.61\times10^{-6}D_{\text{i}}O_{\text{i}}t}) + N_{\text{TD}}(0). \tag{7}$$

In the literature, a 3 or 3.4 power dependence of the TD formation rate (d/dt NTD) on the oxygen concentration has widely been quoted [2,3,13]. There are, however, experimental observations based on the infrared absorption method that claim strong deviations from this dependence. With lower temperatures, at e.g. 430 °C, the exponential dependence in the formation has been reported to be very close to our finding 1.89. Additionally, Lee et al. have shown by total energy calculations in Ref. [14,15] that the TD formation is not due to the so-called FDS and report a reaction order close to 2.

5. Conclusions

There is a good agreement between the calculations of the Eqs. (1)–(7) and the experimental data,

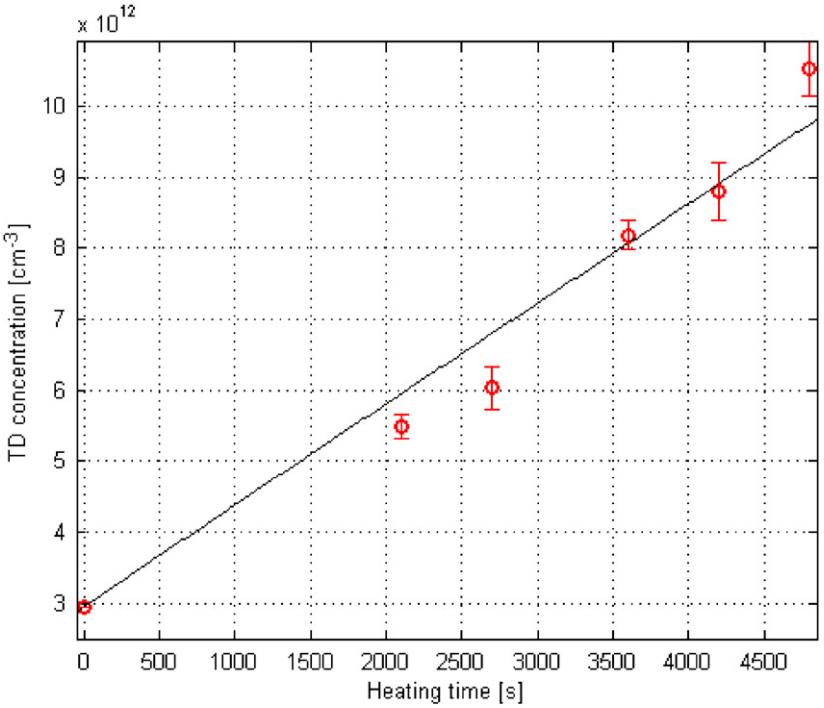

Fig. 3. Exponential fit of the proposed model to the experimental data. The data points correspond to the average of the measurements of N_{eff}.

based on measurement of V_{fd}, if the TD formation is assumed to obey NTD O_{i} 1.89 dependence on the oxygen concentration.

The shallow donors have twofold influence on the macroscopic properties of the detectors. First, shallow oxygen TDs can be utilized during the fabrication process in order to manipulate the effective doping concentration (N_{eff}) of the silicon bulk [16]. This is important in order to tailor the full depletion voltage (V_{fd}). Second, the shallow donors interact with the radiation defects and influence the radiation hardness of the detectors [17]. With TD generation method, it is possible, with low cost and with a process of low thermal budget, to fabricate detectors with high oxygen concentration that can be depleted at voltages less than 100 V.

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