Thermal donors formation via isothermal annealing in magnetic Czochralski high resistivity silicon

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A quantitative study about the thermal activation of oxygen related thermal donors in high resistivity p-type magnetic Czochralski silicon has been carried out. Thermal donor formation has been performed through isothermal annealing at 430 °C up to a total time of 120 min. Space charge density after each annealing step has been measured by transient current technique. The localized energy levels related to thermal double donors (TD) have been observed and studied in details by thermally stimulated currents (TSC) in the range of 10−70 K, and activation energies E and effective cross sections σ have been determined for both the emissions TD0/+(E=75±5 meV, σ =4×10−14 cm2) and TD+/+(E=170±5 meV, σ =2×10−12 cm2). The evolution of the space charge density caused by annealing has been unambiguously related to the activation of TDs by means of current deep level transient spectroscopy TSC, and current transients at constant temperature i(t, T).

Our results show that TDs compensate the initial boron doping, eventually provoking the sign inversion of the space charge density. TD’s generation rate has been found to be linear with the annealing time and to depend critically on the initial interstitial oxygen concentration, in agreement with previous models developed on low resistivity silicon. © 2006 American Institute of Physics. [DOI: 10.1063/1.2192307]

I. INTRODUCTION

Float zone (FZ) silicon is used in several applications where a semiconductor material with both high crystalline quality and high resistivity is required.1−3 Recently, Czochralski (Cz) silicon with high crystalline quality and resistivity of the order of 1 kΩ cm has become commercially available.4−6 The growth procedure can include the application of an external magnetic field to stabilize the melt flow during the crystal growth, thus improving the crystal quality and yields.7 In this case the material is called magnetic Czochralski (MCz) silicon.

In the Cz technique silicon is grown in a quartz crucible,5 and the material is naturally enriched with interstitial oxygen (Oi), which is present in concentrations up to [Oi]~1018 cm−3 (while in float zone, [Oi]~1015 cm−3). It is well known that in oxygen enriched silicon ([Oi] >1017 cm−3) the formation of a significant amount of thermal double donors (usually indicated as TD or TDD) may occur. TDs are small clusters of atoms formed at the early stages of oxygen aggregation.8−10 It has been widely shown that in Cz silicon TDs formation is activated by heat treatments in the temperature range of 400−500 °C.11−13 Shallow thermal donors (STD) with ionization energies in the range of 30−40 meV can be activated in the same temperature range14 too. STDs are believed to have a structure similar to TD, but incorporate a hydrogen atom or other impurities.

Formation of thermal donors is a critical issue in high resistivity Cz Si. In fact, the concentration of TDs generated by typical processing temperatures of microelectronic devices can be high enough to critically change the local resistivity along the wafer.15 Nonetheless, up to now the problem of TD formation has been studied mainly only in low resistivity (typically 1−100 Ω cm) Cz silicon,11,12

This paper reports a quantitative study of TD activation in MCz samples with resistivity ranging from 1 kΩ cm to quasi-intrinsic. TDs activation has been performed through thermal treatments at 430 °C in six steps, up to a total time of 120 min. In Refs. 11 and 12, where the samples resistivity was typically of the order of 10 Ω cm, the TD concentration was determined by four-probe measurements at room temperature. Since this technique cannot detect a change of conductivity type, we simultaneously determined resistivity and conductivity type by transient current technique (TCT).16 Starting with a high resistivity p-type material, an inversion of the conductivity type has been measured after the last annealing step.

In this work, the evolution of space charge density caused by annealing is unambiguously related to TDs activation by thermal spectroscopy techniques such as current deep level transient spectroscopy17−19 (I-DLTS) and thermally stimulated currents (TSCs).20 The TDs activation energies and effective cross sections21 have been measured, and evi-
of Poole-Frenkel effect\textsuperscript{22,23} is advantageously used to
determine the charge state of these energy levels. Further
information about the energy levels responsible for the space
charge sign inversion are deduced from current transient
measurements at constant temperature \(i(t, T)\). Finally, the
models of TD formation proposed in older works are dis-
cussed within the perspectives opened by our results.

II. EXPERIMENTAL PROCEDURE

The samples used in this study are \(p^+\slash p\slash n^+\) devices (active
area 0.25 \text{ cm}^2, \text{ thickness } W=300 \mu \text{m}) made from (100)
MCz \(p\)-type Si wafers by Okmetic, Finland, with a resistivity
of about 1 \text{ \Omega cm}. The diodes have been processed by the
Helsinki University of Technology, Finland, from 4 in. wa-
fers. Secondary-ion-mass spectroscopy (SIMS) measure-
ments gave indication that [O\textsubscript{i}] \(\approx (4.6\pm0.2)\times10^{17} \text{ cm}^{-3}\).\textsuperscript{24} The
\(p^+\) implant (boron) on front surface is surrounded by a set
of guard rings, while the back \(n^+\) contact is made with a
P implant on the whole wafer surface. Two windows have
been cut in the Al layer at back and front electrodes to allow
optical excitation via a laser beam. The distribution of the six
investigated diodes along the wafer size is shown in Fig. 1.
The samples belong to two sets: diodes 7, 8, and 17 have
been cut from the central part of the wafer (set A), while
diodes 46, 57, and 58 have been cut from a peripheral region
(set B).

Details about diode processing can be found in Ref. 15.
After processing, an isothermal annealing has been per-
formed using a nitrogen-controlled atmosphere oven, by
heating all the diodes in different time periods ranging from
45 to 120 min at 430 °C. Heating treatments and TCT mea-
surements have been performed at the Brookhaven National
Laboratory, Upton, NY. After each annealing step, full deple-
tion voltage \(V_T\) and space charge concentration have been
determined by TCT.\textsuperscript{25} In the TCT setup the sample is ac
coupled with a 500 MHz oscilloscope (Tektronix TDS-445)
by a coaxial cable. Nonequilibrium carriers were generated
on the surface of the crystal by laser pulses with 660 nm
wavelength and about 1 ns duration. The diameter of the
laser spot on the detector was about 2 mm. Laser pulses were
flashed repeatedly either on the front or the rear contact,
while a reverse voltage in the range of 0–400 V was applied
to the device by means of a Keithley 238 \textit{II/V} source.

TSC, \(i(t, T)\), and \(i(t, T)\) measurements have been per-
formed at Dipartimento di Energetica, Università di Firenze
(DEF), Italy. The experimental setup is described in details
in Ref. 26. The sample is cooled by immersion in liquid
helium vapor. The initial temperature is thus determined by
the sample holder height above the He surface. A heating
resistance, allocated inside the sample holder, increases the
sample temperature during thermal scans. The temperature
sensor is a silicon diode (Lake Shore DT-470-CU11), mea-
sured by a temperature controller (Lake Shore DRC91C). In
\(i(t, T)\) experiments, the reverse bias \(V_R\), and the forward voltage pulses \(V_f\) for sample excitation are provided by a pulse generator (Systron Donner 110D), and the current
transients \(i(t, T)\) are measured using a custom readout circuit.
It converts the current into voltage, ensuring adequate values
of transresistance \((r=0.5–2 \times 10^6 \times V/A)\), input resistance
\((R_{in}=2.2 \text{ k}\Omega)\), and bandwidth (BWD=1 MHz). The readout
circuit output is monitored by a 500 MHz digital oscillo-
scope (Tektronix TDS520D) which samples the current
transients. During each current transient acquisition the tem-
perature is kept constant. The \(i(t, T)\) spectra \(S(T)\) are extracted
from current transients as \(S(T)\)\(=i(t_1, T)\times i(t_2, T)\), where \(t_1\) and
\(t_2\) are two fixed sampling times. In TSC experiments, reverse
biasing and current reading are provided by a Keithley 6517
electrometer. During the excitation stage, a forward bias is
applied to the diode in order to saturate the concentration of
filled states.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. TCT measurements

The TCT technique has been used to determine the full
deployment voltage \(V_T\), the sign of the space charge \((\eta
=\pm 1)\) and the effective doping concentration \(N_{eff}\). According
to this notation, the space charge density \(\rho=\eta N_{eff}\) (in
elementary charges per unit volume). As an example, the
results of the measurements carried out on one of the samples
(no. 46) before any thermal treatment are reported in Fig. 2.
The small picture inside the plots depicts a cross section of
the device indicating the relative position of the laser beam
and of the sample. Deposition region and electrodes are indi-
cated by shaded and black areas, respectively. As the device
is a \(p^+\slash p\slash n^+\) junction \((\eta=-1)\), the depletion region develops
from the back electrode. When the reverse bias \(V_R\) is in-
creased, the depletion depth \(x_d\) increases as well, reaching
the device thickness at full depletion. For this reason, when
the laser is pulsed on the front electrode a significant charge
is collected only when \(V_R\approx V_T\) [Fig. 2(a)]. On the contrary,
a non-negligible charge collection is always measured when
the laser is pulsed on the back electrode [Fig. 2(b)].

Figure 3 shows the collected charge \(Q\) obtained by in-
tegrating the TCT current signal, as a function of \(V_R\). The
linear fits (before and after full depletion) of the \(Q(V_R)\)
measurement carried out with the laser pulsing on the front side are shown too. \( V_{fd} \) is determined as the abscissa of the intersection point of these fits. \( V_{fd} = 233 \pm 5 \) V for this sample. Prior to any thermal treatment no correlation has been found between \( N_{eff} \) and the position of the diode along the wafer. For all the samples we estimate a space charge density of \( \rho = -3.5 \pm 0.4 \times 10^{12} \) cm\(^{-3}\).

The TCT measurements have been repeated for each diode after five different annealing treatments at 430 °C. The total duration of these treatments were 0, 45, 60, 90, and 120 min. The charge collection measurements carried out on one of the samples (No. 46) are reported in Fig. 4(a). Before annealing and up to 60 min of annealing the total collected charge drops to zero if \( V_{rev} < V_{fd} \) when laser hits the front side, because the sign of the space charge is \( \eta = -1 \). A decrease of the full depletion voltage to values of the order of few volts can be easily explained considering that the annealing procedure activates TD energy levels, which compensate the shallow boron present in the starting material. Very high resistivity values, up to \( \rho \sim 10^{-30} \) k\( \Omega \) cm, are achieved in this way after 45–60 min of annealing. After annealing times of 90 and 120 min, the signal saturation at full depletion can be evidenced only if the laser beam hits the sample on the back side, as shown in Fig. 4(b). This indicates that the activated TD has overcompensated the boron doping, the conductivity type of the bulk has become \( n \) type, and, correspondingly, the space charge region has shifted close to the front electrode. After the last annealing step (120 min) a positive space charge density (\( \eta = +1 \)) is measured in all the six diodes.

Full depletion voltages measured by TCT for all the six diodes are shown in Fig. 5 as a function of the annealing time. We observe that samples which were close to each other along the wafer (see Fig. 1) exhibit a similar trend of \( V_{fd} \): the final full depletion voltage values of the two groups A and B differ by about 100 V.

**B. TSC and DLTS measurements**

Emissions from localized energy levels have been studied by TSCs and I-DLTS, and the results of our analysis have been compared with literature. TD centers comprise a family of more than 16 double donors.\(^{13,27}\) However, DLTS is unable to resolve the energy levels of individual TD species. As a consequence, only two TD-related emissions, with zero-
field activation energies of 0.07 eV (TD<sup>0/+</sup>) and 0.15 eV (TD<sup>/++</sup>), have been detected by DLTS in Czochralski silicon. These lines represent the total response of the whole distribution of cluster sizes. The identification of these defects can in principle also be performed through different spectroscopic techniques, such as TSC. As a matter of fact, the feasibility of the TSC technique to perform measurements at temperatures lower than 20 K has been recently demonstrated by the investigation of shallow levels in FZ high resistivity silicon.

Note that at the very early stage of annealing studied in this work, the thermal double donor species TD0, TD1, and TD2, which are bistable, should be the dominant ones. They can exist in two configurations: one (A) is associated with the double donor discussed above, while the other (B) is neutral. In configuration (B) the electrons are strongly bound to the center and the ionization energy exceeds the energy gap. Only configuration (A) can be observed by DLTS, and the fraction of TDs frozen in this configuration depends on the Fermi level position during the cooling procedure. Configuration (B) becomes stable only in n-type silicon if <i>E_F</i> &gt; <i>E0</i>/++ (i.e., <i>E_F</i> &gt; 0.45, 0.32, and 0.22 eV in the case of TD0, TD1, and TD2, respectively). In this work we deal only with high resistivity samples whose starting material is <i>p</i>-type and whose effective doping never exceeds <i>N</i> &lt; ~5 x 10<sup>12</sup> cm<sup>-3</sup>, even after type inversion. Moreover cooling procedures are always carried out with an applied reverse bias, thus depleting the junction from free carriers. As a result we can expect almost all the TDs to emit from configuration (A) during TSC and 1-DLTS measurements.

The TSC spectra of a diode (No.57) before any annealing and after 120 min heating at 430 °C are shown in Fig. 6. After the annealing treatment two intense peaks are observed at 25 K and 55 K, corresponding to emissions TD<sup>0/+</sup> and TD<sup>/++</sup>, respectively. On the contrary, before the thermal treatment, the same peaks are visible but with very weak amplitudes.

Various TSC spectra measured with different reverse biases are shown in Fig. 7. It is evident that the peaks shift at lower temperatures when <i>V</i><sub>rev</sub> is increased, according to the Poole-Frenkel (PF) barrier lowering. Corresponding to each peak we can calculate the activation energy <i>E</i> by a best fit procedure, thus obtaining the energy shifts ∆<i>E</i>=<i>E0</i>−<i>E</i> being the extrapolated zero-field activation energy. An example of peak fitting is shown in Fig. 8. As a first approximation, the energy shifts ∆<i>E</i> are related to the electric field <i>F</i> at the donor site by the following relation:

\[ \Delta E(F) = \left( \frac{Zq^2F}{\pi\varepsilon_0\varepsilon} \right)^{1/2} = \alpha F^{1/2}. \]  

Here Z is the charge state of the emitting center: Z=1 for TD<sup>0/+</sup> transition and Z=2 for TD<sup>/++</sup>. According to this equation, \( \alpha \approx 0.22 \text{ meV/(cm/V)}^{1/2} \) if \( Z=1 \), and \( \alpha \approx 0.31 \text{ meV/(cm/V)}^{1/2} \) if \( Z=2 \). This simple formula accounts for one dimensional enhanced emission, which somewhat overestimates the barrier lowering of a three dimensional Coulombic well. According to this model, the plot of \( \Delta E \) vs \( F^{1/2} \) should give a straight line with slope \( \alpha \). In our analysis, the average value of electric field in the depleted region has been obtained as \( F = V_{rev}/x_d \), where \( x_d \) is the depletion depth. The resulting TDs signatures and \( \alpha \) values are in good agreement with the existing literature. For TD<sup>0/+</sup> we found \( E_0 = 75 \pm 5 \text{ meV, } \alpha = 4 \times 10^{-14} \text{ cm}^2, \) and \( \alpha = 0.3 \text{ meV/(cm/V)}^{0.5} \). For TD<sup>/++</sup> we found \( E_0 = 170 \pm 5 \text{ meV, } \sigma = 2 \times 10^{-12} \text{ cm}^2, \) and \( \alpha = 0.2 \text{ meV/(cm/V)}^{0.5} \).

Figure 9 shows the 1-DLTS measurements carried out on the same diodes of Fig. 6, before and after 120 min of annealing. Before annealing the only visible spectral component is the one related to boron. After the thermal treatment the two TD peaks are clearly observed. TD signatures obtained by TSC analysis are consistent with these measurements too.

Evidence of space charge sign inversion due to overcompensation of boron with TDs can be obtained by measuring the current transients at different temperatures. Nonmonotonic current transients are in fact produced by type inversion of the space charge, which can take place during the emis-
sion from an energy level such as those related to TDs. When this happens, if \( V_{\text{rev}} < V_{\text{sd}} \), the active volume increases during the transient, reaches the total volume, and then decreases, producing a nonmonotonic current pulse shape. By measuring the temperature range in which the current transient shape is nonmonotonic, it is possible to infer quite precisely which energy level is responsible for type inversion. We have investigated our diodes with this technique in the temperature range close to the two TD peaks. Before thermal treatments, current transients are monotonic in the entire temperature range investigated by us. This means that the space charge, which is initially negative, as it is settled by boron, does not change sign during electron emissions TD\(^{0+/+}\) and TD\(^{+/++}\). After the last thermal treatment, the current transient exhibits a nonmonotonic shape if the temperature is close to the value \( T = 65 \) K, in proximity of the emission TD\(^{+/++}\). Results are shown in Fig. 10, and can be explained as follows: when the temperature is close to \( 65 - 70 \) K, immediately after the filling pulse, TD levels are filled with electrons, and \( \rho \) is negative, due to boron doping. Subsequently, within few milliseconds, TDs become doubly ionized and produce a positive dominant contribution to the space charge, which determines the space charge sign inversion. This experimental evidence demonstrates that the second ionization TD\(^{+/++}\) is responsible of the change of \( \rho \) sign observed by TCT. This also implies that the thermal donor’s concentration \( n_{\text{TD}} \) is still smaller than the boron concentration \( [B] = 2 \times 10^{12} \) cm\(^{-3}\) (otherwise sign inversion would take place during TD\(^{0+/+}\) emission), and that \( n_{\text{TD}} \) is larger than \( [B]/2 \) (otherwise sign inversion would never appear): \( [B] > n_{\text{TD}} > [B]/2 \).

In principle, information about the concentration of emitting levels can be obtained from the amplitude of TSC or I-DLTS spectra. This can be easily accomplished if the active volume is constant during the emission. This is not our case, because carrier emission from TD levels causes a huge modification of \( N_{\text{eff}} \), resulting in a change of depletion depth and active volume. In addition, the occurring of field enhanced emission introduces additional uncertainty on the relationship between peak amplitude and center’s population. Nevertheless, it is possible to explain qualitatively the amplitude

![FIG. 7. TSC spectra measured with different reverse biases, showing peaks related to TDs emissions. The two temperature ranges corresponding to the TDs peaks are shown.](image)

![FIG. 8. TSC spectra showing Poole-Frenkel effect and TD\(^{+/++}\) peak fitting. The measurements are denoted by solid lines, and fits by dashed lines. Thick lines refer to \( V_{\text{rev}} = 100 \) V and thin lines to \( V_{\text{rev}} = 50 \) V. Fits have been calculated according to standard TSC analysis, and the discrepancy with respect to the measured spectra is due to the space charge modulation occurring during carrier emission.](image)

![FIG. 9. I-DLTS spectra measured before (lower plot) and after a 120 min thermal treatment (upper plot). Sampling times are \( t_1 = 20 \) ms and \( t_2 = 90 \) ms, the reverse bias is \( V_{\text{rev}} = 10 \) V, and the deep level excitation is obtained by a forward pulse of \( t_{\text{fill}} = 10 \) ms duration.](image)
of the low-field TSC peaks related to TDs. The amplitude of the TD$^{0/+}$ and TD$^{+/++}$ peaks is proportional to the concentration of those donors populated by low temperature injection (which is the same for the two peaks) and to the volume of the depleted region. The amplitude of the TD$^{+/++}$ peak at 55 K is higher than the amplitude of the TD$^{0/+}$ one because $N_{\text{eff}}$ diminishes after the TD$^{0/+}$ emission at 25 K, thus determining an increase of the active volume. Such an explanation does not hold for I-DLTS peaks because the current transient due to TD$^{+/++}$ emission is nonmonotonic. As discussed in detail in Ref. 26 this effect produces a strong distortion of the TD$^{+/++}$ peak which makes any comparison meaningless with the amplitude of the TD$^{0/+}$ one.

C. Thermal donor’s formation rate

Our results give a direct proof of the TD’s activation via isothermal annealing in MCz Si. In this paragraph, we wish to discuss TD’s formation rate as a function of annealing time and initial oxygen concentration by comparing earlier works on low resistivity silicon with our results. According to these studies, the initial rate of donor formation ($dn_{\text{TD}}/dt$) at 450 °C is almost linear with annealing time and proportional to the fourth power of the grown-in interstitial oxygen concentration [$O_i$]. Using simple kinetic arguments, this result was considered to provide evidence that the core of TD defects contains four oxygen atoms. In Ref. 11 a simplified aggregation model of oxygen thermal donors is described, based upon existing experimental data. The concentration of thermal donors is given by the law:

$$n_{\text{TD}}(t) = k_1 \left[ O_i \right] \left[ 1 + 2/3 D_i [O_i]^{2/3} \right]^{-2/3} t^{1.02},$$

with $D_i$ diffusivity of interstitial oxygen, $t$ annealing time, and $k = 4.61 \times 10^{-52}$. The proportionality of $n_{\text{TD}}$ with $t^{1.02}$ is discussed in detail in Ref. 43, where this model has been tested with low resistivity Cz Si ([O$_i$] $\approx 7 \times 10^{17}$ cm$^{-3}$), doped with 2–8 $\times$ 10$^{14}$ cm$^{-3}$ P or B and annealed at 450–470 °C. For annealing times up to $6 \times 10^5$ s, the TD concentration was found to increase almost linearly with increasing annealing time. In more recent works, these measurements have been extended to a wider range of temperatures (350 °C < $T$ < 500 °C) and modeling have been further improved. These latter results showed that in the range of 350–400 °C a second-power dependence ($x=2$) is more appropriate, suggesting that the dominant mechanism controlling the formation of TDs is presumably limited by the rate of oxygen dimer’s ($O_2^+$) formation. At higher temperatures, oxygen agglomerates would tend to dissociate on a time scale close to that required to cause a measurable increase of $n_{\text{TD}}$ and this would bring a superlinear increase of the power exponent $x$. The values $x=3.5$ and 9 were estimated, respectively, at 450 and 500 °C.

Our measurements of TCT, coupled with TSC and DLTS analyses, show that a space charge sign inversion occurs in the initially $p$-type Si material due to the formation of TD aggregates. The initial decrease of $V_{\text{id}}$ with time shown in Fig. 5 is actually due to the compensation of boron with an increasing concentration of the TDs. This decreasing trend is followed by a $V_{\text{id}}$ increase when the TDs start to overcompensate the B doping and the inversion of the space charge sign occurs. We note that samples, cut from the same wafer regions, show a similar trend of $V_{\text{id}}$. To evidence this effect $N_{\text{eff}}$ has been evaluated from the mean value of full depletion voltage ($V_{\text{id}}$), measured for samples of the same group, as $N_{\text{eff}} = 2 \varepsilon (V_{\text{id}})/(qW^2)$. In this formula $\varepsilon$ indicates the absolute dielectric constant, and $W$ is the thickness of the sample. The plot of $\rho = N_{\text{eff}} \eta$ as a function of the annealing time is shown in Fig. 11. The linear increase of $\rho$ from negative to positive values can be explained considering that, in agreement with Ref. 43, the concentration of TDs is increasing almost linearly with annealing time, up to the overcompensation of the B dopants.

The two sets A and B are characterized by different activation rates: samples from the central part of the wafer have a slope value 30% higher than those cut closer to the wafer periphery. To discuss this effect we simulated the $\rho(t)$ curves by means of Eq. (2). The effective density in the space charge has been calculated as

$$\rho = \eta N_{\text{eff}}(t) = 2n_{\text{TD}}(t) - N_B.$$

The interstitial oxygen diffusivity $D_o$, which appears in Eq. (2), has been calculated as $D_o = D_{e} e^{-E_a/kT}$, with $D_{e}$
=0.13 cm²/s and $E_a=2.53$ eV, in agreement with Ref. 11. The interstitial oxygen concentration [O_i] is used as the free parameter. The possibility of small temperature variations ($±0.5$ °C) around the nominal value of 430 °C has been taken into account, and the value of the exponential factor $x$ has been varied with temperature according to Ref. 12. The two best fits of the curves shown in Fig. 11 have been obtained with same annealing temperature (429.5 °C), slightly lower than the nominal one, using [O_i]=4.4×10¹⁷ cm⁻³ (for samples coming from set A) and [O_i]=4.8×10¹⁷ cm⁻³ (for samples coming from set B). Thus, at this temperature, the different trends of samples from sets A and B can be well accounted for by the ±0.2×10¹⁷ cm⁻³ uncertainty in the initial oxygen concentration measured by SIMS analysis.²⁴

Note that, according to Eq. (3), the $N_{eff}$ value determined from TCT measurements gives a TD concentration ranging from $n_{TD}=2.3×10^{12}$ cm⁻³ in the peripheral region to $n_{TD}=2.8×10^{12}$ cm⁻³ in the central region. These values fit well to those found with TSC and DLTS measurements, which gave $n_{TD}=2–4×10^{12}$ cm⁻³.

By concluding this section we wish to note that, as the formation of TD is very sensitive to the precise value of the exponential factor $x$, which in turn depends critically on the annealing temperature $T$, even small variations of the annealing temperature might influence dramatically the rate of TD formation. This phenomenon deserves further investigations in order to assess the procedure of TD activation outlined in this work.

IV. CONCLUSIONS

This work presents a thorough study of thermal donor activation via isothermal annealing at 430 °C, up to 120 min, on high resistivity magnetic Czochralski silicon. The study has been carried out on diodes made from initially $p$-type material. Transient current technique (TCT) has been used to measure the full depletion voltage, effective doping concentration, and sign of the space charge after process and at each annealing step. Thermal donors have been directly observed by means of current deep level transient spectroscopy (I-DLTS) and by thermally stimulated currents (TSCs). Activation energies and effective cross sections have been evaluated for single and double emissions: TD⁺⁺⁺ (E =75±5 meV, $\sigma=4×10^{-14}$ cm²) and TD⁺⁺ (E =170±5 meV, $\sigma=2×10^{-12}$ cm²). Our results evidence that the activation of TDs is responsible for the progressive compensation of the boron doping during annealing. After the longest thermal treatment, overcompensation occurred and a change of the space charge sign was observed. At the longest annealing time, thermal donor concentrations estimated by us are $n_{TD}=2.3–2.8×10^{12}$ cm⁻³. Consistently, current transient measurements revealed that the second ionization of thermal donors TD⁺⁺⁺ is indeed responsible for the inversion of space charge sign.

We used our experimental data to validate a model of thermal donor formation rate proposed in earlier works for low resistivity (1–100 Ω cm) Cz silicon.¹¹,¹² Our results confirm this model, showing that it can be extended to the 1–100 kΩ cm resistivity range. Our work also demonstrate that the annealing procedure is a simple and effective way to obtain very high resistivity MCz Si both of $n$ and $p$ types from the same starting low resistivity material. Nonetheless, we showed that a strict control of the annealing parameters and of the initial interstitial oxygen concentration is necessary to obtain reproducible results. In fact, small fluctuations in the initial interstitial oxygen concentration along the wafer size, or slight changes in the annealing temperature, can introduce significant uncertainties in the rate of thermal donor formation.

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²³J. Frenkel, Phys. Rev. 54, 647 (1938).