Peculiarities of electron emission from high-density deep levels of nanodefects in oxygen-implanted silicon

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Abstract. The peculiarities of electron emission from electronic states of nanodefects formed at the early stages of oxygen precipitation in oxygen-implanted silicon annealed at 700°C were investigated with a combination of capacitance and current transient spectroscopy of the space charge region (SCR) in semiconductors. It was established that the particular properties of acceptor-like states are due to their high density and their localization at the back side of the implanted region. A model is suggested that explains an apparent emission rate slowdown and the appearance of an unexpected sign of capacitance relaxation signal as a result of the non-monotonic shape of the potential of the Schottky-diode.

1. Introduction
The engineering of oxygen precipitates (OPs) in silicon is widely used in the processing of modern microelectronics due to their ability to getter metallic impurities and, in this way, to clean the device active regions (so-called “internal gettering”) [1, 2]. This has stimulated extensive studies of OP structural, electric and recombination properties that began in the middle of the last century. Most of the published results were obtained on “big” OPs, i.e. with sizes in the micrometer range. It was established that OPs possess an embedded positive charge and their composition is nonhomogeneous: the stoichiometric SiO$_2$ core is surrounded by a nanometer SiO$_2$ shell [3, 4]. In addition, a correlation between OP size and the charge was established: the embedded positive charge of the OPs decreased with an increase in their size [5, 6], which gave evidence that the charge is formed by dangling bonds of the SiO$_2$ shells.

The mechanism of formation and the properties of small OPs, which are also called OPs nuclei, have been much less investigated [7, 8]. In our recent work [6], it was found that a high density of acceptor-like states was formed in oxygen-rich samples at early precipitation stages in the interstitial-rich region, in addition to the positive charge in the near surface vacancy-rich region. Unusual behavior of the capacitance and current transient spectroscopy (DLTS & I-DLTS) signals due to electron emission from these states was revealed but its origin was not clearly established.

In this work, additional experimental investigations were performed to find an explanation of the above mentioned results.

2. Experimental
The sample preparation process was identical to that presented in previous studies [5]. Cz-Si wafer with a phosphorus doping concentration of about $10^{15}$ cm$^{-3}$ was implanted with oxygen sequentially with energies of 350/225/150 keV and with doses of $1.5 \times 10^{15}/0.9 \times 10^{15}/0.7 \times 10^{15}$ cm$^{-2}$, respectively, to
create a nearly constant oxygen distribution profile at depths from 300 to 800 nm from the surface. After implantation, the wafer was annealed at 700°C for 0.5 h in a chlorine-containing atmosphere [9]. Schottky diodes were fabricated by thermal evaporation of gold. Ohmic contacts were created by InAl eutectic rubbing. Thin cross-section foils for TEM investigations were fabricated by mechanical polishing followed by low-energy Ar ion milling.

3. Results and discussions
The cross-sectional transmission electron microscopy (TEM) image shown in figure 1(a) demonstrates the point-like contrasts of unknown defects with an average size of several nanometers in the near-surface region of the wafer. The black line in figure 1 represents the oxygen concentration profile calculated with SRIM software. One can see that the contrast depth distribution correlates well with the implant depth profile being evenly distributed between 300 nm and 800 nm. This correspondence indicates the participation of oxygen in the defects responsible for the TEM contrasts.

**Figure 1** a) Cross-section dark-field TEM image of the defect structure in the near-surface region of the sample. The calculated oxygen profile distribution is represented by the black line. b) A set of DLTS spectra measured at various filling pulse voltages from 0 to +4 V (the rate window is 0.5 kHz; the pulse duration and period are 1 ms and 50 ms, respectively).

Figure 1(b) shows the DLTS spectra measured under a reverse bias voltage of -4 V bias and filling pulse voltage levels from 0 to +4 volts. The spectra consist of two narrow peaks at temperatures of about 150 K and 260 K, denoted in the figure as E150 and E260. The Arrhenius plots corresponding to these DLTS peaks are shown in figure 3(a).

According to our previously reported DLTS results [6], the height and temperature position of the E260 peak did not depend on the magnitude of the filling pulses in the selected range, and the corresponding electronic levels were localized in the near-surface implantation region. The activation energy and capture cross-section of the levels were determined to be E<sub>a</sub> 0.59 eV and 5x10<sup>-16</sup> cm<sup>3</sup>, respectively, being close to those reported for deep vacancy-related KD-complexes [10]. According to ref. [11], such complexes can form nanoscale voids (noids) in silicon at similar annealing temperatures, which, in turn, can become nucleation sites for OP nuclei. Such OP-related nanodefects appear to be responsible for the point-like TEM contrasts (see figure 1) and for the formation of an embedded positive charge of local concentration of 10<sup>17</sup> cm<sup>-3</sup> in the implanted region [5].

The second DLTS peak E150 had unusual behavior: an increase in the refilling pulse voltage from 0 V to +4 V led both to an increase in the magnitude of the DLTS peak by about 8 times and to a
temperature shift of about 20 K to high temperatures. Moreover, the DLTS signal in the low-
temperature tail of the peak did not change upon the refilling pulse variation and a weak positive
signal above the high-temperature tail of the DLTS peak caused by the non-monotonic character of the
capacitance transient shown in figure 2(a).

![Capacitance relaxation kinetics measured at 150 K for the selected filling pulses levels shown in the legend.](image1)

![Temperature dependences of capacitance measured at testing voltage frequencies between 40kHz and 1MHz.](image2)

Figure 2 a) Capacitance relaxation kinetics measured at 150 K for the selected filling pulses levels shown in the legend. b) Temperature dependences of capacitance measured at testing voltage frequencies between 40kHz and 1MHz.

The Arrhenius plots derived from the E150 DLTS peak temperature behavior exhibited a
monotonic shift with an increase in refilling pulse levels (solid squares in figure 3(a)), but without a
significant change in the slope. As a result, the activation energy for electron emission was determined
to be about E_c-0.28 eV, and the capture cross-section varied in the range between 10^{11} and 10^{15} cm^{-3}
. The emission parameters at equilibrium occupancy of the defect states were obtained from the
temperature dependences of the capacitance step measured at testing voltage frequencies between 40
kHz and 1 MHz (see figure 2(b)). The corresponding Arrhenius plot data are shown in figure 3(a) by
open squares giving the values E_c-0.26 eV and σ=10^{-15} cm^{-3}, respectively.

![Arrhenius plots obtained from the DLTS data (solid circles and squares) and from the C(T, ω) data in figure 2 (b) (open squares).](image3)

Figure 3 a) Arrhenius plots obtained from the DLTS data (solid circles and squares) and from the C(T, ω) data in figure 2 (b) (open squares). b) E150 deep level concentration (left scale) and the diode depletion region width (right scale) on the refilling pulse level and applied bias, respectively.

The dependence of the E150 DLTS peak magnitude on the refilling pulse voltage is shown in
figure 3(b) together with the dependence of the depletion region width (DRW) on the applied bias
voltage recalculated from C(V) characteristics measured at 150K. From a comparison of these dependences, one can recognize that the most rapid increase in the DLTS signal of deep levels takes place in the range of forward bias pulse voltage from $+1$ to $+4$ V, which corresponds to a DRW of about 0.9 to 1 μm. The fact that the apparent DRW remains rather big at pulse voltages well above the built-in voltage of the diode (0.7 V) indicates a significant voltage drop across the deeper part of the implanted region. That might be explained by the presence of deep acceptor-like states of sufficiently high density to form a barrier and its own depletion region (DR), similar to the grain boundary. The DRW of the plane-like distributed states which pin the Fermi level at $E_c - 0.26$ eV can be estimated to be of about 0.5 μm at each side, which correlates with the total DRW of about 1 μm of a DRW plateau at $+3 - +4$ V forward bias in figure 3(b). Thus, the obtained data indicate that the states are confined in a narrow layer at a depth of 800-900 nm from the surface, i.e. at the back-side of the implanted region. As suggested in [6], the discussed acceptor-like states can be ascribed to rod-like interstitial defects. While the existence of a barrier at forward bias voltages follows from the DRW width values, as well as from the current-voltage (IV) saturation at 100K, clearly seen in figure 4(a) (see also ref. [6]), its presence at reverse bias voltage was obtained from the results of current transient spectroscopy (I-DLTS) depicted in figure 4(b).

In a conventional Schottky diode, the emission current flows in the direction of the reverse current, which is independent on the latter value, and decreases with the trap emptying. The first remarkable feature of the current transient in the investigated diode was the signal sign opposite to the expected one, i.e. the current increased with time after the end of the refilling pulse. In addition, the I-DLTS peak appeared above a certain reverse bias voltage, and then increased rapidly with voltage, which was accompanied by its shift to higher temperatures.

![Figure 4](image)

**Figure 4** a) Current-voltage characteristics of the sample at 100K and 200K. b) I-DLTS spectra measured at a 0.5 kHz rate window and reverse bias/pulse level voltages shown in the legend.

The appearance of a positive sign of the I-DLTS signal might be explained by reverse current modulation by the barrier to current flow with the help of the band diagram in figure 5, as follows. Under application of a forward refilling pulse voltage of $+4$ V the voltage drops at the barrier of a plane-like acceptor-like defect due to Fermi level pinning with a high density of traps (upper diagram in figure 5). The absence or a low value of the I-DLTS signal at low reverse bias voltages indicates that all conduction and displacement currents in the structure compensate each other. Such a situation can take place in an electric symmetrical structure surrounding electron-emitting centers. This can take place when the DR barrier at the edge of the implanted region does not overlap with that of the diode forming a valley between them, as shown in the bottom diagram of figure 5(b) with a dashed line. In this case, the electron emission currents from the states in the barrier center flow in both directions and
are compensated by the correspondent displacement currents caused by decreases in DRW from each side of the barrier.

With increasing reverse bias, the DRs of the diode and the trap-related barrier overlap (figure 5(b), solid line). In this case, the barrier height with respect to the quasi-neutral base of the diode increases drastically [15], and part of the applied voltage will drop at the first one, providing modulation of the reverse current when recharging the defect deep levels. This explains the bias voltage dependence of the I-DLTS signal as the reverse current in the investigated sample increases drastically with the voltage, which is shown in figure 4(a).

**Figure 5** The band-bending diagram of a Schottky diode with a barrier due to the plane distribution of acceptor-like states at a depth of $x_d$ under forward (figure 5(a)) and reverse (figure 5(b)) bias. Solid/dashed lines in figure 5(b) correspond to a high/low occupancy of the traps, respectively.

The high-temperature shift of the DLTS and I-DLTS peaks indicates an apparent slowdown in the emission rate with time. These properties are opposite to the well-known band-like behavior, often observed when studying extended defects in silicon [12-14], which is characterized by a low-temperature shift of the DLTS peak with increasing trap occupancy. To explain the high-temperature shift of the I-DLTS peak, one has to note that the current relaxation ends when the DRWs of the diode and the barrier are again separated, as just discussed above. The smaller is the reverse bias voltage and the corresponding DRW at the surface, the bigger is the final refilling grade when the overlap of surface and defect-related DRs ceases. As a result, the apparent emission rates measured with the I-DLTS method decrease with an increase in the reverse bias voltage, which leads to a shift of the I-DLTS peak to higher temperatures.

Capacitance transients are rather not sensitive to the current ones. Instead, they are sensitive not only to the charge value within the DRW, but also to its spatial location. In this way, a particular situation occurs when the potential minimum between the barriers in figure 5 is quite low, so that a significant density of free electrons, $n_{QX}$, may be localized within that valley. The change in their concentration or/and in the position of the localized free carriers led to an additional contribution to the DR width and the measured capacitance relaxation. As was shown in [15-17], a change in the concentration of free carriers localized between two barriers could be caused by several processes: (i) free carrier exchange over the barrier in the semiconductor bulk, (ii) lateral diffusion from the Schottky contact region, and (iii) the shift of the potential minimum position upon trap refilling (compare the dashed and solid line in the diagram of figure 5). The first two processes were accompanied by an increase in capacitance, but had a different relaxation time constant. The last one might cause a capacitance decrease during electron emission.

To assess the effect of lateral spreading of the carriers, an additional Schottky diode with circular gold contacts with a 3 times smaller diameter was fabricated. DLTS results did not show significant changes in the position or magnitude of the DLTS signal. That indicates the absence of a significant effect of lateral spreading of carriers.

Thus, the emission rate slowdown detected with DLTS is rather similar to I-DLTS. The relaxation process ends with the state when the DRWs of the defect and the diode become close to be separated. This can be associated with both the moving of the valley with free electrons toward the bulk accompanied an increase in their density due to the electron flow over the barrier from the bulk. Both processes result in a decrease in the capacitance, providing a positive contribution to the
conventionally negative capacitance transients, which become dominant at the end of the relaxation, as was shown in figure 2(a). A strict description of these processes required solving the Poisson equation in the presence of free carriers, which can only be done numerically and is beyond the scope of this paper.

4. Conclusions
Particular properties of electron emission from high-density acceptor-like states formed after 700°C annealing of oxygen-implanted silicon were investigated. A DLTS peak E150 caused by emission from such states increased and shifted towards higher temperatures with increasing state filling grade. Furthermore, the I-DLTS signal measured under reverse bias corresponded to the apparent forward current flow and exhibited a high temperature shift as well as a rapid growth with increasing reverse bias voltage. The non-monotonic character of the capacitance transient due to the emission and a correlation between the leakage current and the I-DLTS signal were established, which indicated the presence of a barrier for the current flow within the depletion region of the Schottky diode.

The particular features of the DLTS and I-DLTS signals were qualitatively explained in the framework of the model, which assumes the formation of a depletion region near the high-density acceptor-like states spatially confined in a narrow layer at the back side of the implanted region, which results in a non-monotonic character of the potential profile.

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References
[1] Gilles D, Weber E R and Hahn S 1990 Phys Rev Lett 64 196-9
[2] Kissinger G, Kot D, Klingsporn M, Schubert M A, Sattler A and Muller T 2015 Ecs Journal of Solid State Science and Technology 4 N124
[3] Kot D, Kissinger G, Schubert M A, Klingsporn M, Huber A and Sattler A 2015 Phys Status Solidi-R 9 405
[4] Kot D, Kissinger G, Schubert M A and Sattler A 2017 Ecs Journal of Solid State Science and Technology 6 N17
[5] Danilov D, Vyvenko O, Trushin M, Loshachenko A and Sobolev N 2019 J. Phys.: Conf. Ser 1190 012016
[6] Danilov D, Vyvenko O, Loshachenko A and Sobolev N 2019 Phys. Status Solidi A
[7] Antonova I V, Popov V P and Shaimeneev S S 1998 Physica B 253 123
[8] Kot D, Mchedlidze T, Kissinger G and von Ammon W 2013 Ecs Journal of Solid State Science and Technology 2 P9
[9] Vdovin V I, Sobolev N A, Emel'yanov E M, Gusev O B, Shek E I and Yugova T G 1997, ed G Davies and M H Nazare pp 1521
[10] Schmidt D C, Svensson B G, Seibt M, Jagadish C and Davies G 2000 J Appl Phys 88 2309-17
[11] Frewen T A and Simno T 2006 Appl Phys Lett 89
[12] Danilov D V, Vyvenko O F, Sobolev N A, Vdovin V I, Loshachenko A S, Shek E I, Aruev P N and Zabrodskiy V V 2015 Solid State Phenom 242 368-73
[13] Schrotter W, Kronewitz J, Gnauert U, Riedel F and Seibt M 1995 Phys Rev B 52 13726
[14] Bondarenko A and Vyvenko O 2018 Journal of Electronic Materials 47 4975
[15] Vyvenko O 2005 phys. status solidi c 2 1917
[16] Schmalz K, Yassievich I N, Collart E J and Gravesteijn D J 1996 Phys Rev B 54 16799
[17] Schmalz K, Yassievich I N, Rucker H, Grimmeiss H G, Frankenfeld H, Mehr W, Osten H J, Schley P and Zeindl H P 1994 Phys Rev B 50 14287