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Peculiarities of thermoannealing in n-Si and n-Ge crystals with oxygen impurity

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Abstract. Investigated in this work were changes in the concentration of charge carriers n_e and their mobilities μ, which occur under the influence of thermoannealing of $\mathrm{n-Si}$ and $\mathrm{n-Ge}$ crystals grown by the Czochralski method. Thermoannealing of $\mathrm{n-Si}$ samples was carried out both at 450 °C and 650 °C. The results of the influence of two-stage (combined) thermoannealing have been presented. In the first series of experiments, the annealing was performed at 450 °C with varied duration (from 5 to 45 h) at the beginning, and then it was carried out for 40 hours at 650 °C. The second series of experiments was as follows: the annealing at 450 °C for 45-hour duration, then the annealing at 650 °C, which was carried out for various periods of time (5, 10, 20, 45, 66 hours). The observations for changes of n_e and μ were carried out both at the temperature 300 and 77 K. It is ascertained that changing the main parameters (n_e and μ) in $\mathrm{n-Ge}\langle\mathrm{As}\rangle$ heavily doped single crystals, as a result of the series of thermoannealings (duration 30 min in each case) within the temperature range from 540 to 900 °C, is non-monotonous due to transformation of the thermodonors $\mathrm{TD-I}$ into $\mathrm{TD-II}$.

Keywords: silicon, germanium, oxygen, thermoannealing, thermodonor, the Hall effect, carrier concentration, mobility.

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1. Introduction

It is known [1] that the thermal treatment of silicon crystals doped with oxygen within the temperature range 350 to 550 °C leads to formation of donor centers and change in the resistance of samples. Having learned the kinetics of thermodonor formation, Kaiser et al. [2, 3] concluded that these centers have oxygen nature and represent a complex containing four atoms of oxygen (SiO_4). The thermodonor properties were described in detail in the review [4]. Investigations of the thermodonor properties [1, 2] showed that their donor activity disappears after a short annealing at the temperatures above 550 °C. It was also observed [5] that the further thermal treatment at higher temperatures (550…800 °C) leads to the appearance of donor activity again. In [6] it was shown that these donor centers (the authors call them "new donors") differed in many properties from the thermodonors that are formed in a lower temperature range (350…550 °C).

In the literature [7], the low-temperature thermodonors are called the thermodonors –I ($\mathrm{TD-I}$), and the "new donors" – the thermodonors –II ($\mathrm{TD-II}$).

In [6, 8–12], the influence of carbon impurities, as well as the preliminary annealing of samples at 400…500 °C, on the formation of $\mathrm{TD-II}$ was studied. It follows from the works [6, 8–11] that the preliminary annealing at 400…500 °C of Si single crystals with the low carbon content ($N_C < 10^{16}\,\mathrm{cm}^{-3}$), as well as the presence of this impurity in the bulk of silicon in the

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appreciable amounts ($N_C < 2\cdot10^{16}\,\text{cm}^{-3}$), promotes the process of the formation of $\text{TD}-\text{II}$. On the other hand, the high content of carbon impurities in Si ($N_C > 2\cdot10^{16}\,\text{cm}^{-3}$) complicates the generation of $\text{TD}-\text{I}$ [13]. In addition, the reduction of the ionization energy of $\text{TD}-\text{I}$ with increasing the annealing time was found [14].

For the last few decades, scientists of the world have been shown great interest to the properties of Si crystals doped with oxygen. And these studies have been still far from completed. For a long time the thermodonors have been actively studied using different techniques: the Hall effect [10, 14–16], the electron paramagnetic resonance (EPR) [7, 17, 18], deep level transient spectroscopy (DLTS) [19–21], infrared spectroscopy [22, 23], photoluminescence [15] and others. However, despite the large number of studies [24], up to date an exact model of the donor center, which could describe all the existing experimental data, has not been developed.

2. Experimental

For the experiments with thermoannealing (TA) the dislocation-free single crystals of $\text{n}-\text{Si}$, doped with phosphorus and grown by the Czochralski method, were used. The content of doping and residual impurities in the investigated crystals is presented in Table 1.

A higher concentration of oxygen in the ingot 2 provided a higher concentration of $\text{TD}-\text{I}$ (as compared to the ingot 1) after the thermoannealings at 450 °C ($\text{TA}-\text{I}$) of equal duration (see Table 2) as well as in the growing process itself. The resistivity ρ in the ingot 2 was 10 Ohm·cm just when the growing process had been over, however, proceeding from the calculation of the quantity of added phosphorus as electrically active impurity, it could have been expected about 35 Ohm·cm. After the 16-h annealing of the ingot 2 at 450 °C, the carrier concentration increased up to $n_{300K} \approx 5.7\cdot10^{15}\,\text{cm}^{-3}$ ($\rho_{300K} \approx 0.9$ Ohm·cm). To achieve the value of $n_{300K} \approx 1.5\cdot10^{14}\,\text{cm}^{-3}$ ($\rho_{300K} \approx 28$ Ohm·cm, which is close to the calculated ρ value), the ingot 2 needed to be annealed for 1 hour at 650 °C. This value $n_{300K} \approx 1.5\cdot10^{14}\,\text{cm}^{-3}$ was taken as the initial one and related to the phosphorus dopant in the ingot 2.

Table 1. The content of main impurities in the crystals of n – Si. *T* = 300 K.

Ingot	Doping concentration N, cm^{-3}		
	Phosphorus	Oxygen	Carbon
1	2.45×10^{14}	5.1×10^{17}	3.8×10^{16}
2	1.50×10^{14}	9.5×10^{17}	3.0×10^{16}

The carrier concentration (n_e) in the ingot 1 corresponded to the calculated value. This fact and, perhaps, a lower concentration of oxygen in the ingot 1 (in comparison with that of the ingot 2) provided a higher stability of the ingot 1 with respect to the thermoannealing at 650 °C ($\text{TA}-\text{II}$) (see Table 2), although the carbon content in both ingots was almost identical.

3. Two-stage thermoannealing of n-Si samples with a different content of oxygen impurity

The abovementioned thermal stability of the ingot 1 with respect to $\text{TA}-\text{II}$ (at 650 °C) was lost after its preliminary annealing (during 10–45 h) at 450 °C (see Tables 3 and 4). These results show that, at lower concentration of carbon atoms in the crystal ($N_C \le (3-4)\times10^{16}\,\text{cm}^{-3}$), the $\text{TD}-\text{I}$, which are formed during the low-temperature annealing of silicon crystals (doped with oxygen) at the temperature about 450 °C, most likely serve as the nucleation centers of $\text{TD}-\text{II}$. Indeed, as seen from the Table 3, a significant change in the concentration of n_e is observed after the thermoannealing for 10 h at 450 °C

The two-stage thermoannealing changes not only the concentration of the electrically active thermodonors, which is evidenced by the change in the carrier concentration n_e as compared with n_e in the initial sample, but with the increase of $\text{TA}-\text{I}$ time qualitative changes occur in the characteristic of newly-formed thermocentres, as it is evidenced by the change in their ability to ionization with increasing the $\text{TA}-\text{I}$ time, as well as the growth of the ratio $n_e(300\,\text{K})/n_e(77\,\text{K})$ from 1 to 1.14 (see Table 3).

The appearance and growth of EPR-activity in thermodonors with increasing the $\text{TA}-\text{II}$ time is also of great interest (see the data in column 7 of Table 4). This fact also indicates that the increase of the $\text{TA}-\text{II}$ time (which followed the $\text{TA}-\text{I}$, Table 4) led not only to quantitative but also to qualitative changes of the thermodonors, which arose (and formed) as a result of the combined thermal treatments [($\text{TA}-\text{I}$) + ($\text{TA}-\text{II}$)].

The latent period for the formation of the nucleation centers of $\text{TD}-\text{II}$ at low-temperature annealing (at the temperature close to 450 °C) is no less than 5 h, as seen from the Table 3. While EPR-activity in the studied samples appeared only after $\text{TA}-\text{II}$, the duration of which was $t \ge 10$ hours (see Table 4, columns 6 and 7).

It should be noted that $\text{TD}-\text{I}$ under the normal conditions (i.e., when the crystal is free of any impurities) do not show EPR-activity, which is evidently explained by the presence of their double charge. In contrast with $\text{TD}-\text{I}$, $\text{TD}-\text{II}$ show the EPR-activity that is clearly seen from the data of Table 4.

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Table 2. Influence of the annealing at various temperatures on the electrophysical properties of n – Si samples. The time of thermoannealings (I and II) is approximately the same.

Ingot	Annealing time (hour)	Annealing at 450 °C (TA-I)				Annealing at 650 °C (TA-II)			
		300 K		77 K		300 K		77 K	
		n_e×10^{-14}, cm^{-3}	μ×10^{-3}, cm^2/(V·s)	n_e×10^{-14}, cm^{-3}	μ×10^{-3}, cm^2/(V·s)	n_e×10^{-14}, cm^{-3}	μ×10^{-3}, cm^2/(V·s)	n_e×10^{-14}, cm^{-3}	μ×10^{-3}, cm^2/(V·s)
I	0	2.55	1.790	2.58	18.2	2.56	1.790	2.58	18.2
	1	3.07	1.790	2.72	17.8	2.22	1.310	2.31	17.6
	5	4.01	1.720	2.92	18.0	2.44	1.740	2.47	18.2
	10	6.08	1.770	3.66	17.9	2.47	1.660	2.46	17.6
	20	8.61	1.630	4.37	16.4	2.35	1.790	2.40	18.2
	45	12.70	1.550	5.43	15.0	2.44	1.740	2.47	18.2
	66	19.00	1.140	6.82	12.3	–	–	–	–
II	0	1.5	1.590	1.20	17.4	1.5	1.590	1.26	17.4
	1	3.18	1.480	1.98	15.2	1.87	1.670	1.79	15.7
	2	5.16	1.440	2.70	14.5	2.81	1.530	2.17	15.5
	3	8.66	1.330	3.49	14.4	3.22	1.430	2.56	14.6
	5	12.8	1.430	4.7	14.3	8.45	1.300	5.32	13.2
	10	24.9	1.400	7.11	14.0	16.9	1.320	8.73	12.0
	15	38.8	1.220	10.5	11.66	25.0	1.350	7.80	12.0
	45	83.6	1.180	18	10.6	33.6	1.170	7.14	10.8
	101	–	–	–	–	32.0	1.160	6.40	10,6

Table 3. Influence of the time of preliminary annealing on the results of the two-stage thermal treatment of n – Si samples prepared from the ingot 1.

Time of 1-st stage of TA at 450 °C, hour (TA-I)	Time of 2-nd stage of TA at 650 °C, hour (TA-II)	300 K n_e×10^{-14}, cm^{-3}	77 K n_e×10^{-14}, cm^{-3}	300 K Δn×10^{-13}, cm^{-3}
5	40	2.44	2.44	0
10		2.87	2.80	4.2
20		3.07	2.85	6.2
45		3.35	2.95	9.0
Initial sample		2.45	2,45	–

4. Influence of thermoannealings (at T_{ann} = 540…900 °C) applied to heavily doped single crystals of n – Ge ⟨As⟩ on the change in concentrations of charge carriers and their mobilities

The investigation of changes in the concentrations of charge carriers n_e and their mobilities μ as a result of thermoannealings of $n-\mathrm{Ge}\langle\mathrm{As}\rangle$ single crystals grown by the Czochralski method at various temperatures (when the annealing time in all the cases was 30 min) was carried out. Cooling the crystals to room temperature was achieved by simple turning-off the heat source. The obtained results that are summarized in Table 5 showed that changes of the main parameters (n_e and μ) in the heavily doped samples of $n-\mathrm{Ge}\langle\mathrm{As}\rangle$ with an increase of T_{ann} from 540 up to 900 °C are not monotonous. Certainly, because after some decrease of n_e, related to the thermoannealing within the range 600…725 °C of $\mathrm{TD-I}$, formed in the crystal with the residual oxygen impurity at the temperature range 500…540 °C, the concentration n_e begins to increase due to transition into the temperature range ~830…900 °C. In this range, the so-called $\mathrm{TD-II}$ are formed from atomic oxygen appeared as a result of $\mathrm{TD-I}$ decay. This transformation of $\mathrm{TD-I}$ into $\mathrm{TD-II}$ is observed in oxygen impurity rich crystals (exactly these samples were used in these experiments).

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Table 4. Data obtained after two-stage thermal treatment of n – Si. The samples were prepared from the ingot 1.

Stage of TA	T_{ann}, °C	Time of TA t, hour	300 K $n_e \times 10^{-14}$, cm^{-3}	77 K $n_e \times 10^{-14}$, cm^{-3}	N_{TD}^{EPR} $\frac{N_{TD}^{EPR}}{N_P^{EPR}}$	N_{TD}^{EPR} $N_{TD}^{EPR} \times 10^{-3}$ cm^{-3}	300 K $\Delta n \times 10^{-13}$, cm^{-3}
1	2	3	4	5	6	7	8
Initial sample	–	–	3.0	3.0	0	0	0
Stage 1	450	45	12.7	5.43	0	0	97
Stage 2	650	5	3.02	2.76	0	0	0.2
		10	3.05	2.79	0.02	0.6	0.5
		20	3.62	3.10	0.165	5.0	6.2
		45	4.75	3.33	0.423	13.0	17.5
		66	6.19	3.06	–	–	31.9

Table 5. Changes in the concentrations of charge carriers n_e and their mobilities μ as a result of thermoannealings of heavily doped samples of n – Ge⟨As⟩ grown by the Czochralski method at various temperatures (the annealing time in all the cases was 30 min).

Number of sample	State of sample: Initial (In) / Conditions of TA: T_{ann}, °C; t = 0.5 h	Charge carrier concentration $n_e \times 10^{-19}$, cm^{-3}	Charge carrier mobility μ, cm^2/(V·s)	Changes of n_e after TA: n_0 / Changes (±), no changes (0)
1	In	3.57	322	n_0
	540 °C	3.57	310	no changes (0)
2	In	3.85	286	n_0
	600 °C	3.51	300	decreases (–)
3	In	3.90	270	n_0
	640 °C	3.15	290	decreases (–)
4	In	4.00	278	n_0
	725 °C	4.00	263	no changes (0)
5	In	4.02	272	n_0
	800 °C	4.56	246	increases (+)
6	In	4.00	280	n_0
	830 °C	4.87	230	increases (+)
7	In	3.88	292	n_0
	900 °C	4.68	248	increases (+)

Note. Temperature of measurements was 293…300 K.

It should be noted that the atoms of background impurities (oxygen, hydrogen, nitrogen or helium) in the lattice of silicon and germanium are the defects that can directly or indirectly (due to creating the local mechanical strains) affect the properties of crystals. The significant concentration of oxygen impurity ($N_O \sim 5\times10^{17} - 2\times10^{18}\,\text{cm}^{-3}$) in the ingots, pulled out from the melt, as well as the ability of this impurity to transform into the electrically active state during thermoannealing, led to the need to study in detail the behaviour of the TD – I and TD – II.

5. Conclusions

In the oxygen-containing single crystals n – Si and n – Ge, transformation of thermodonors TD – I into TD – II during the change of thermoannealing regimes, which are widely used in the manufacture of semiconductor devices, was investigated.

In crystals n – Si that were characterized by the different concentration of dopant (phosphorus) and residual (oxygen and carbon) impurities, the influence of low-temperature (450 °C) and high-temperature (650 °C)

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thermoannealings on the change in the carrier concentration was studied. It is shown that the results of high-temperature thermoannealings (at 650 °C) with different time duration depend significantly on the initial state of the investigated crystals and on the specific parameters of the low-temperature thermoannealing (at 450 °C), which was applied to the crystal before its high-temperature thermal treatment.

In crystals of $\mathrm{n-Ge}$, it was found that changing the main parameters (concentrations of charge carriers n_e and their mobilities μ) in heavily doped single crystals of $\mathrm{n-Ge}\langle\mathrm{As}\rangle$, grown by the Czochralski method, as a result of the series of thermoannealings (for 30 min in each case) within the temperature range from 540 up to 900 °C is non-monotonous due to transformation of $\mathrm{TD-I}$ (appearing within the range 500…540 °C and are annealed at 600…725 °C) into $\mathrm{TD-II}$, which were formed from atomic oxygen appearing as a result of $\mathrm{TD-I}$ decay during transition within the temperature range ~830…900 °C.

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