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Magnetic susceptibility of p-Si(B) single crystals grown in "vacancy" regime at presence of thermodonors created by thermal treatments at 450 °C

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Abstract. By using the Faraday method and complex of electro-physical studies (Hall effect, ESR, etc.) the features of magnetic susceptibility (χ) of *p*-Si(B) crystals grown in "vacancy" regime and annealed at 450 °C are studied. It is demonstrated that the presence of deep thermodonors with the ionization energy $E_i \geq 200$ meV in these samples contributes to the appearance of a paramagnetic constituent with the magnetic susceptibility (χ^{par}) even at 300 K. χ^{par} in this material does not depend on temperature in the range of 77 - 300 K that can testify on the Van-Fleck origin of this magnetic susceptibility component. Absence of nonlinearities in the dependence $\chi(H)$ within the interval 0.3-4 kOe shows uncooperative character of magnetism found out.

Keywords: diamagnetism, magnetic susceptibility, thermodonor, thermal treatment.

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1. Introduction

The first attempt to find out the possibility of application of magnetic susceptibility method along with a complex of galvano-magnetic measurements to study properties of semiconductor Si crystals with oxygen-containing thermodonors (TDs) was made in [1]. The paramagnetic component of magnetic susceptibility (MS) in the samples of *n*-Si(P) with thermodonors was established and responsibility of doubly-charged TDs in the one-fold ionized state $(TDs)^+$ for appearance of this MS component was proposed. Authors [1] explained the nonlinear field dependences of MS on the magnetic-field $\chi(H)$ by the magnetic arrangement of doubly-charged TDs due to exchanged interaction between TDs in their local accumulations caused accordingly by the microaccumulations of interstitial oxygen in the initial Si crystals.

It is known that in the process of thermal treatment at 450 °C in the crystals *n*-Si(P) except of doubly-charged TDs singly-charged shallow thermodonors (STDs) appear, too [2] with ionization energies within the range 31.3-37.4 meV [3, 4]. Paramagnetic properties of STDs in *n*-Si(P) are detected by the electron spin resonance (ESR) method [3]. Certainly, within the experimental conditions reported in [1], these centers couldn't show their paramagnetic properties because of they were in the ionized state.

In contrast, for the samples prepared from the crystals *p*-Si(B), grown in "vacancy" regime (at the speed of growth of $\upsilon = 2$ mm/min $> \upsilon_{cr}$), besides doubly-charged TDs, the deep TD-centers (DTDs) appear with the ionization energy $E_i \geq 200$ meV [5]. Galvano-magnetic studies (Hall effect and temperature dependences $n_e = f(T)$) along with measurements of ESR spectra and low-temperature (at 4.2 K) photoluminescence on the samples with DTDs enabled simply to establish that DTDs are singly-charged donor-centers which represent oxygen complexes containing one atom of boron [5]. Presence of deep singly-charged donor-centers DTDs with the ionization energy $E_i \geq 200$ meV, which are in not ionized state within the range of 77-300 K, assists to study paramagnetic properties of these centers by the method of magnetic susceptibility even at room temperatures.

Taking into account the different nature of doubly-charged TDs and DTDs, it is important to investigate the magnetic susceptibility features in the *p*-Si(B) samples in comparison with *n*-Si(P) ones determined only by the presence of doubly-charged TD-centers in the certain charged state. It is the aim of this research.

2. Experimental

The Czochralski-grown crystals *p*-Si(B) and *n*-Si(P) without dislocations were used for this study. The amount of doped (B and P) and ground (O and C) impurities was as follows:

Sample No. 1: $N_B = 10^{15}\,cm^{-3}$; $N_P = 2\cdot10^{13}\,cm^{-3}$; $N_O = 7.2\cdot10^{17}\,cm^{-3}$; $N_C = 7.5\cdot10^{16}\,cm^{-3}$.

Sample No. 2: $N_P = 10^{14}\,cm^{-3}$; $N_B = 10^{12}\,cm^{-3}$; $N_O = 9.5\cdot10^{17}\,cm^{-3}$; $N_C = 3\cdot10^{16}\,cm^{-3}$.

The single crystal *p*-Si(B) was grown in the "vacancy" regime. After preparation, the vacancy-type microdefects are usually dominant in these crystals. Beside doubly-charged TD-centers, the DTDs were also detected in this crystal [5]. In the crystals *p*-Si(B) grown at $\upsilon<\upsilon_{cr}$ (with the same amount of B and O impurities), the DTDs did not appear showing that presence of B and O is a necessary condition but insufficient to form DTDs.

Thermal treatment of the samples No. 1 and No. 2 were performed at 450 °C in air. After annealing, the samples were chemically polished. The samples for MS measurements were of 10×1.5×1 mm size. The measurements of $\chi(H)$ dependences were performed at the temperatures of 300 and 77 K within the range of magnetic fields (0.3-4.0) kOe on the modernized equipment [6] based on the Faraday method. The relative error for MS measurements did not exceed 1 %. The Hall effect was studied in the initial and thermally-treated samples within the temperature range of 20 up to 450 K. In order to explain the MS results obtained, the experimental data more early published in [5, 7, 8] on the ESR spectra in the temperature range of 20-50 K and low temperature (at 4.2 K) photoluminescence for the investigated samples thermally annealed at 450 °C were used in this work.

3. Results and discussion

Thermal treatment of the samples *p*-Si(B) at 450 °C during $t \geq 4$ hours results in conversion of conductivity from *p*-type to *n*-type. Fig. 1 shows the typical temperature dependences for the concentration of electrons of conductivity for three samples from the crystal No. 1. On these temperature dependences two areas can be seen: (i) on the left side from the dotted line, where ionization of DTDs with the energy $E_i \geq 200$ meV is easily detected and (ii) on the right side from the dotted line, where doubly-charged TD-centers are clearly observed. In particular, two levels are fixed on the right side in Fig. 1: curve 1 – the level $E_2 \approx$ 140 meV of one-fold ionized doubly-charged TDs in the state $(TDs)^+$; and curve 2 – more shallow level $E_1 \approx$ 64 meV of doubly-charged TDs in the state $(TD)^0$.

It is easy to calculate the concentrations of DTDs for all samples thermally treated (taking into consideration singly-charged defects of these ones) for every annealing period (4–46 h) from dependences of $n_e = f(T)$. These data are presented in Table and Fig. 2 (curve 1).

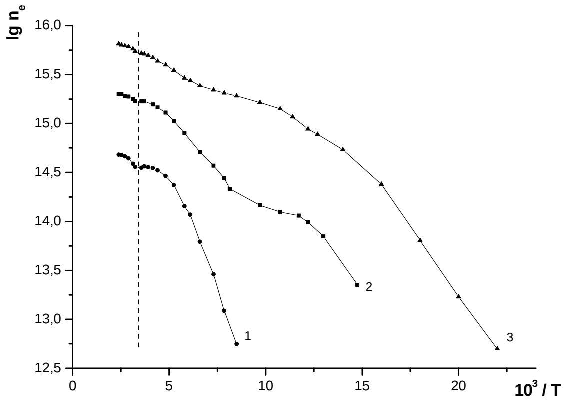

Fig. 1. Temperature dependences of the electron concentration of sample conductivity taken from the crystal No. 1 depending on time of annealing at 450 °C: *1* – 4; *2* – 15; *3* – 57 h.

To identify TD-centers and establish nature of DTDs which were detected in the samples *p*-Si(B) thermally treated at 450°C, the several adequate methods such as the Hall effect, ESR and low temperature photoluminescence were applied [5, 7, 8]. Let us remind two important results of these studies. By using ESR method, it was established that with rising of annealing period of the samples *p*-Si(B) at 450 °C from 4 to 240 hours in the ESR spectra measured at 20-50 K besides the spectrum of TD-centers, the spectrum from the ground phosphorous impurity appears beginning from $t \geq 50$ h. In the initial sample, the ESR spectrum from the P impurity was observed only at illumination of the sample in a resonator by light band-gap. Such behavior of the ESR spectrum in the initial and annealed samples can be explained by the appearance of TD-centers with the ionization energy less than one of P impurity or when an acceptor B impurity is transformed into electrically non-active state with increasing the annealing period. These hypotheses were successfully confirmed by using the low temperature photoluminescence method [5, 7].

Table.

Annealing period, h	$n_e \equiv N_{DTDs}$, 10^{14} cm $^{-3}$	lg (N_{DTDs})	χ^{par}, 10^{-8} cm^3 g^{-1}
4	1.19	14.08	0.56
8	2.81	14.45	
10	3.03	14.48	0.94
15	2.90	14.46	1.07
20	3.05	14.484	
46	7.01	14.846	2.02
57	10.29	15.01	
100	9.68	14.99	
150	10.05	15.002	
240	10.00	15.00	

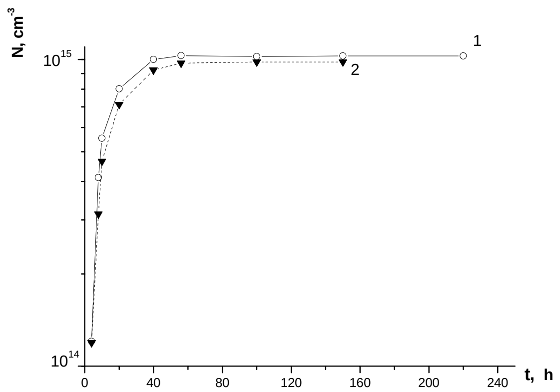

Fig. 2. Accumulation kinetics of deep thermodonors (*1*) and transition of boron from the electrically active acceptor-type state (*2*).

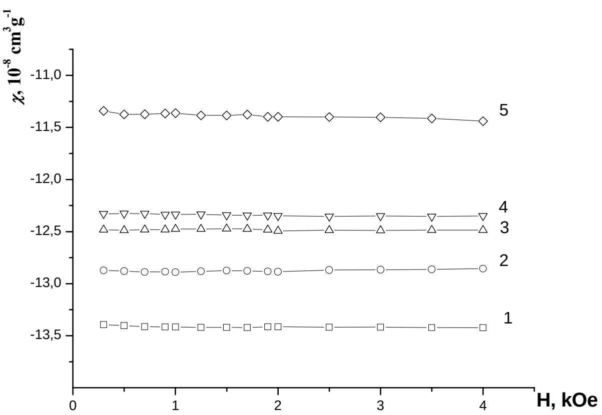

Fig. 3. Dependence of the magnetic susceptibility of $\chi(H)$ at 300 K inherent to p-Si(B) samples annealed at 450 °C: *1* – 0; *2* – 4; *3* – 10; *4* – 15; *5* – 46 h.

By analyzing the photoluminescence spectra in a non-ground region for the samples of p-Si(B) (crystal No. 1) for different annealing periods at 450 °C, authors [7] concluded that the concentration of B decreases in the interstitial cite with acceptor properties or B remains in interstitial cite but is included into a complex with the loss of its acceptor properties. By studying kinetics of saturation of DTDs (Fig. 2, curve 1) and transition of B from electrically active acceptor state (Fig. 2, curve 2) for the p-Si(B) sample, it is seen that these both kinetics are very similar. It can be concluded that B atoms take part at the formation of the DTDs. One of early models of TD-centers for p-Si(B) was proposed in [9] which foresees the implantation of boron atom (in the interstitial cite) into the complex with 4-atoms of oxygen. As a result, the complex becomes of the donor type.

Let us dwell now on the peculiarities of the magnetic susceptibility of p-Si(B) single crystals (samples No. 1) and n-Si(P) single crystals (samples No. 2). After thermal treatment of these samples at 450 °C in the first of them, except for doubly-charged TD, the deep singly-charged donor-type centers (DTD) appear with the energy of ionization $E_i \geq 200$ meV and in the second doubly-charged TDs appear with the energies of ionization $E_1 \approx 70$ meV and $E_2 \approx 140$ meV.

First let us consider the results of the performed researches of the magnetic susceptibility for the initial and annealed at 450 °C samples of p-Si(B) (crystal No. 1), which contain different concentrations of DTD. The measured results are presented in Fig. 3. Obvious is the fact that the magnetic susceptibility of the observed samples does not depend on the strength of the magnetic field. In the samples which were treated at 450 °C (i. e., in the samples which contained singly-charged DTD) a decrease of diamagnetism (χ^{dia}) has been found out. If this decrease χ^{dia} is caused by the appearance of the MS (χ^{par}) paramagnetic constituent, we come to the doubtless conclusion that there is a good correlation between the size χ^{par} and concentration of deep TD-centers created in the process of thermal treatment (Fig. 3, Table).

Let us take the value of diamagnetic susceptibility of initial crystal No. 1 as the susceptibility of crystal lattice, and let us consider that MS of the lattices of the observed crystals

$\chi_L = -(13.4\pm0.2)\cdot10^{-8}\,\mathrm{cm}^3\,\mathrm{g}^{-1}$.

As χ^{par} does not depend on the magnetic-field strength it is predetermined by dispersed paramagnetic centers, or by those being in less dense clusters and do not pass to the magnetic ordered state in the researched temperature ranges ($77\,\mathrm{K} \leq T \leq 300\,\mathrm{K}$) and magnetic fields ($0 < T \leq 4$ кOe). Independence of this paramagnetism from the temperature testifies to its Van-Fleck origin. It should be noted that paramagnetism is observed already at the ambient temperatures, which was to be expected, as at $T \approx 300$ K all the DTDs are not ionized. The $\chi(H)$ curves at 77 K for the same samples that were measured at $T = 300$ K are within errors of the experiment and repeat the result presented in Fig. 3 which testifies to the independence of χ from the temperature.

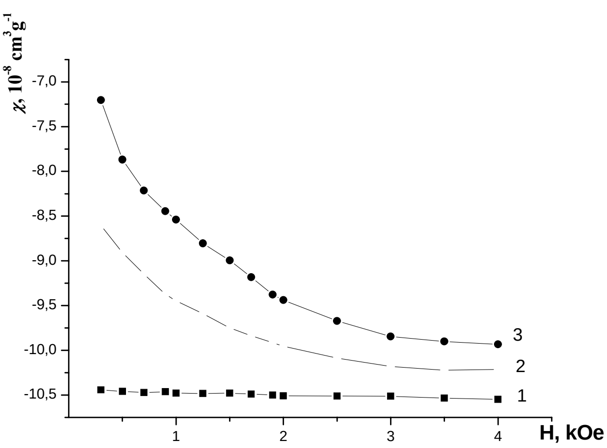

Fig. 4. Dependence of the magnetic susceptibility of $\chi(H)$ at 77 K inherent to n-Si(P) samples annealed at 450 °C: *1* – 0; *2* – 40; *3* – 303 h.

Taking into account the suppositions and remarks, the expression which describes experimentally observed MS of the studied crystals can be presented in the following way:

$\chi(H) \equiv \chi_{exp} = \chi_L + \chi^{par}$.

Typical dependences of MS on the magnetic-field strength H obtained for the samples from the n-Si(P) crystal No. 2 (both for the initial and annealed ones) are presented in Fig. 4. Nonlinear dependences $\chi(H)$ can be described as in [1] by a presence together with χ_L of χ^{par} and χ^{ord} constituents which is typical for the TD-centers of the cooperative type, which in [1] were considered as doubly-charged TD-centers in the singly ionized state $(TD)^+$.

4. Conclusion

Researches of the MS of p-Si(B) samples with different contents of deep thermodonors show that paramagnetic constituent of MS (χ^{par}) increases in the samples proportionally to the DTD content. Lack of dependence of χ^{par} size from the temperature (in 77 to 300 K range) is probably predetermined by its Van-Fleck origin. It has been also found out that DTD paramagnetism does not show the nonlinearities on $\chi(H)$ dependences both at 77 and 300 K, which, in our opinion, testifies to the uncooperative character of discovered paramagnetism. Thus, comparison of results, obtained during research of $\chi(T)$ and $\chi(H)$ of n-Si(P) and p-Si(B) single crystals with TD-centers present in them, created by thermal treatment at 450 °C confirms the different origin of doubly-charged and deep thermodonors.

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