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MODELLING OF CHANGES IN THE RESISTIVITY OF SEMI-INSULATING MATERIALS

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Abstract

Electrical properties of semiconductor materials depend on their defect structure. Point defects, impurities or admixture contained in a semiconductor material, strongly affect its properties and determine the performance parameters of devices made on its basis. The results of the currently used methods of examining the defect structure of semiconductor material are imprecise due to solution of ill-posed equations. These methods do not allow for determination of concentration of the defect centers examined. Improving the resolution of the obtained parameters of defect centers, determining their concentration and studying changes in the resistivity of semi-insulating materials can be carried out, among others, by modelling changes in the concentration of carriers in the conduction and valence bands. This method allows to determine how charge compensation in the material affects the changes in its resistivity. Calculations based on the Fermi-Dirac statistics can complement the experiment and serve as a prediction tool for identifying and characterizing defect centers. Using the material models (GaP, 4H–SiC) presented in the article, it is possible to calculate their resistivity for various concentrations of defect centers in the temperature range assumed by the experimenter. The models of semi-insulating materials presented in the article were built on the basis of results of testing parameters of defect centers with high-resolution photoinduced transient spectroscopy (HRPITS). The current research will allow the use of modelling to determine optimal parameters of semi-insulating semiconductor materials for use in photoconductive semiconductor switches (PCSS).

Keywords: resistivity, semiconductor, gallium phosphide, silicon carbide.

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1. Introduction

The resistivity of semiconductor materials depends on the concentration of defect centers, which are imperfections of crystals consisting in point or layered breaking of the regularity of their lattice. As part of the defect centers, we can distinguish point native defects and admixtures [1]. Native point defects are disturbances in the crystal structure that occur in regions of the crystal with dimensions on the order of the interatomic distance (10^{-8} cm). The native point defects include, among others, the lack of an atom in a network node (Schottky defect, called the gap) or

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the shift of a nodal atom to an inter-node position (Frenkel defect). Admixtures are foreign atoms introduced into the crystal lattice, which can be in the nodal position (substitution admixtures) or in the inter-nodal position (inter-nodal admixtures). The substitution admixture is generally characterized by high electrical activity.

Research on defect centers in semi-insulating materials is an important problem in the development of electronics. These materials are increasingly used for the production of semiconductor devices with better characteristics [2–5]. Additionally, thanks to the defect structure engineering, appropriate doping of the material will allow to obtain new properties [4, 6–8]. The results of testing the properties of semi-insulating semiconductor materials have a significant impact on improvement of operating parameters of electronic devices designed on their basis. One of the methods of studying the defect structure of semiconductor materials is *high-resolution photoinduced transient spectroscopy* (HRPITS). Unfortunately, due to the solution of ill-posed equations, the results of the parameters of defect centers obtained on the basis of this method are imprecise [9, 10].

Among of the devices for which tests of properties of semi-insulating materials are performed are photoconductive semiconductor switches (PCCSs) in power engineering and power electronics. These elements have the potential to replace the currently used electronic devices [11]. Research related to modelling the structure of a photoconductive semiconductor switch will allow to determine the relationship between the properties of materials (determined by concentrations, types of defect centers and issues related to defect compensation) and the performance parameters of a PCSS. For this purpose, simulations of various models should be performed. The analysis of the results will allow for the selection of the optimal structure PCSS depending on its design purpose.

The aim of the article is to present a simulation method for determining the resistivity of a material, depending on the concentration of assumed defect centers with different parameters. This method has previously been used to study the effect of laser power on changes in photoconductivity of the 4H–SiC material and was described in [12]. Defect centers concentration is important from the point of view of insulation properties of a PCSS in the blocking state [13]. As a result of simulation calculations, the influence of defect centers concentration on the 4H–SiC and GaP resistivity was determined. The simulations performed also confirmed the experimental tests to determine the parameters of defect centers in these materials.

2. Description of the procedure for calculating the resistivity of semiconductor materials

Figure 1 shows a functional diagram of calculation of resistivity characteristics of semiconductor materials as a function of any parameter.

In Step 1 of the procedure, it is necessary to select the material for which the calculations will be performed. For a given material, the temperature dependencies of the forbidden gap width E_g and the equations of the density of the states of the conduction band N_C and valence band N_V should be assumed.

In Step 2 of the procedure, a specific number of defect centers (donors and acceptors) should be assumed for the selected material, specifying their activation energy and concentration. These parameters can be selected on the basis of the knowledge base or on the basis of the parameters of defect centers determined experimentally, *e.g.* with the HRPITS method. The properties of defects, depend on the degree of disturbance of periodicity of the crystal lattice potential. These disturbance results in formation of localized energy states of electrons, located at different depths in the forbidden gap.

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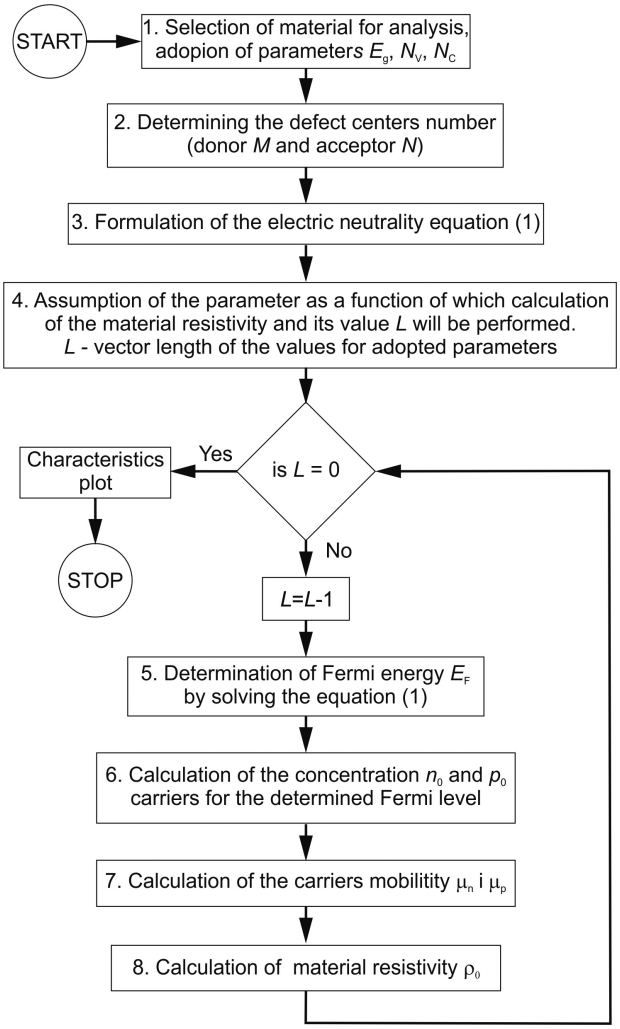

Fig. 1. Scheme of the procedure for determining the resistivity of semiconductor materials.

For a specific material model, in Step 3, the electric neutrality (1) should be formulated where n_0 and p_0 is the equilibrium concentration of electrons and holes in the conduction and valence bands given by (2) and (3) [14].

$$n_0 - \sum_{m=1}^{M} N_{Dm}^{+} = p_0 - \sum_{n=1}^{N} N_{An}^{-}, \tag{1}$$

$$n_0 = N_C \exp\left(-\frac{E_C - E_F}{k_B T}\right), \tag{2}$$

$$p_0 = N_V \exp\left(-\frac{E_F - E_V}{k_B T}\right), \tag{3}$$

where N_{Dm}^{+} is the concentration of ionized m-th donor center, and N_{An}^{-} is the concentration of ionized n-th acceptor center assumed in the calculations. The coefficient E_F is the energy at the Fermi level, k_B is the Boltzmann constant, and T is the absolute temperature. Assuming that $E_V = 0$ and $E_C = E_g + E_V = E_g$, N_{Dm} and N_{An} are total concentrations of a given defect center and E_{Dm} and E_{An} are the activation energies of these centers, the concentrations of ionized centers can be determined using the Fermi–Dirac formula

$$N_{Dm}^{+} = \frac{N_{Dm}}{1 + 2\exp\left(\dfrac{E_F - \left(E_g - E_{Dm}\right)}{k_B T}\right)}, \tag{4}$$

$$N_{An}^{-} = \frac{N_{An}}{1 + \dfrac{1}{2}\exp\left(\dfrac{E_{An} - E_F}{k_B T}\right)}. \tag{5}$$

The presented procedure makes it possible to calculate the characteristics of changes in material resistivity as a function of any parameter (temperature or concentration of the selected defect center). In Step 4, this parameter must be set and the vector of changes in its values must be assumed (L vector length). If there is no need to perform calculations when changing several values for the assumed parameter, then $L = 1$.

In Step 5 of the procedure, for the assumed temperature value, the neutrality equation (1) should be solved by calculating the Fermi energy E_F for which this equation is satisfied.

For the determined value of the Fermi level, in Step 6, the concentration of electrons in the conduction band (2) and of holes in the valence band (3) should be calculated. Additionally, it is also possible to calculate the concentration of charge carriers in the defect center adopted for the analysis.

In the next step, the mobility of carriers μ_n and μ_p) should be determined. The mobility values may depend on the temperature or the concentration of the carriers in the bands. The literature describes formulas on the basis of which their values can be determined. For example, for 4H–SiC using the Masetti model they can be described by the equations [8]:

$$\mu_n = \frac{947 \times \left(\dfrac{T}{300}\right)^{-2}}{1 + \left(\dfrac{n_0}{1.97 \times 10^{17}}\right)^{0.61}} \quad \left[\frac{\mathrm{cm}^2}{\mathrm{V \cdot s}}\right], \tag{6}$$

$$\mu_p = 15.9 + \frac{124 \times \left(\dfrac{T}{300}\right)^{-2}}{1 + \left(\dfrac{p_0}{1.76 \times 10^{19}}\right)^{0.34}} \quad \left[\frac{\mathrm{cm}^2}{\mathrm{V \cdot s}}\right]. \tag{7}$$

In the last step of the procedure, based on the determined mobility and concentration of carriers in the bands, changes in the resistivity ϱ_0 of the material can be determined using the commonly used formula:

$$\rho_0 = \frac{1}{\sigma_0} = \frac{1}{q(n_0\mu_n + p_0\mu_p)}, \tag{8}$$

where q is the electron charge.

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3. Properties of materials selected for calculations

Calculations of resistivity changes will be performed for two materials, *i.e.* 4H–SiC and GaP. Figure 2 shows the energy models of materials used in the calculations. It should be noted that the material models presented so far in the literature are limited to a small number of defects [14, 15].

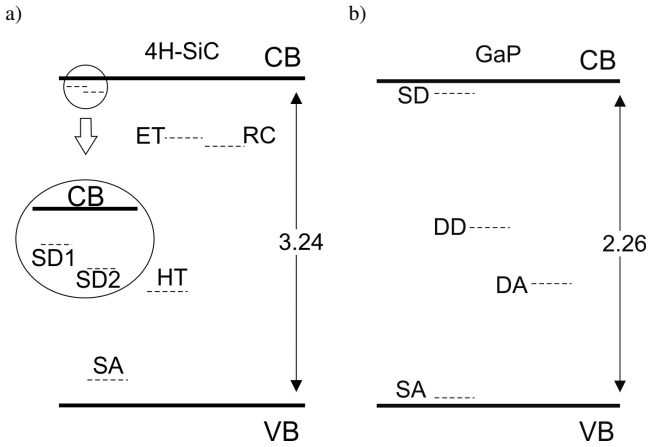

Fig. 2. Energy models of materials adopted in testing of the procedure 4H–SiC a) and GaP b). The labels SD1, SD2, SA, ET, HT and RC mark levels of two types of shallow donors as well as the levels of shallow acceptor, deep electron trap, deep hole trap, recombination centre in 4H–SiC, respectively. For Gap, labels SD, SA, DD and DA mark levels of shallow donor, shallow acceptor, deep donor and deep acceptor, respectively. The arrow marks the energy gap width of the material at the temperature of 300 K.

3.1. Silicon carbide (4H–SiC)

In the presented procedure, it is necessary to know the band gap width. The change of its width as a function of temperature for 4H–SiC in the range of 200–600 K is described by the equation [7]:

$$E_g = 3.29 - \frac{3.3 \times 10^{-2} T^2}{T + 1 \times 10^5} \text{ [eV]}. \tag{9}$$

Taking into account the density of electrons and holes in the effective mass states of this material: $m_{dn} = 0.77\, m_0$ and $m_{dp} = 1.0\, m_0$, the densities of the states can be described as $N_C = 3.27 \times 10^{15} \times T^{3/2}$ and $N_V = 4.83 \times 10^{15} \times T^{3/2}$ cm^{-3}.

For the purposes of simulation studies, a model consisting of six defects was proposed. In the adopted model, two shallow donors (SD1, SD2) are associated with the presence of nitrogen atoms in the semiconductor material which replace the carbon atoms for the first donor in the hexagonal (h) and for the second donor in the cubic (k) structure of the 4H–SiC crystal lattice. Shallow acceptors SA are boron atoms that replace silicon atoms present in both hexagonal (h) and cubic (k) structures of the semiconductor crystal lattice [16]. The ID9 center observed in SiC, which was classified as a native defect, was adopted as the electron trap [17]. The properties of the recombination center adopted in the model are identical to the $Z1/2$ center. $Z1/2$ centers are characteristic for the analysed material and are probably related to double gaps: no carbon in h structure and no silicon in the k structure of the crystal lattice, or no carbon in k structure and no silicon in h structure [16, 18]. HK3 centers, the properties of which were observed by the

method of electron resonance (EPR), were assumed as hole traps [17, 19]. Table 1 presents the parameters of the defect centers used in the calculations.

Table 1. Properties of defect centers adopted for 4H–SiC resistivity modelling.

Defect label	Defect type	Activation energy [eV]	Concentration [cm^{-3}]	Identification
SD1	Shallow donor	$E_c - 0.050$	5×10^{15}	N_C in h site [16]
SD2	Shallow donor	$E_c - 0.092$	5×10^{15}	N_C in k site [16]
ET	Electron trap	$E_c - 0.555$	5×10^{14}	ID9 [16]
RC	Recombination center	$E_c - 0.630$	8×10^{14}	$Z_{1/2}$ centre [16, 18]
HT	Hole trap	$E_v + 1.125$	7×10^{14}	ID9 centre [17], HK3 trap [19]
SA	Shallow acceptor	$E_v + 0.285$	1×10^{16}	B_{Si} in both h and k sites [16]

3.2. Gallium phosphide (GaP)

In simulations for gallium phosphide, a model was adopted in which four defect levels were taken into account, *i.e.* one level for shallow donor, shallow acceptor, deep donor and deep acceptor. The shallow donor is located 0.085 eV from the bottom of the conduction band. This level corresponds to the ionization energy of silicon atoms in the gallium (Si_{Ga}) sub-lattice, which can be identified as the main donors in the GaP single crystal [20, 21]. The shallow acceptor is located 0.055 eV from the top of the valence band. This level corresponds to the ionization energy of carbon atoms in the phosphorus sub-lattice (C_P), which are the dominant acceptors in GaP single crystals grown by the Czochralski method [20, 22]. A defect with an energy of 1.02 eV against the bottom of the conduction band was assumed as a deep donor, which can be attributed to the double-ionized state of the antibacterial phosphorus $P_{Ga+/2+}$ [20, 22]. The defect located at the level of 0.85 eV above the top of the valence band observed by various laboratories was assumed as a deep acceptor [23]. It is worth noting that the deep acceptor centers in GaP are poorly understood and the origin of the 0.85 eV level remains unknown. The equation of temperature changes of the band gap width is given in the form [21, 24]:

$$E_g = 2.34 - \frac{6.6 \times 10^{-4} T^2}{T + 460} \ \text{[eV]}. \tag{10}$$

Taking into account the density of effective masses of electron states and holes $m_{dn} = 0.79 m_0$ and $m_{dp} = 0.83 m_0$, the densities of the conduction and valence band states are respectively $N_C = 3.392 \times 10^{15} \times T^{3/2}$ and $N_V = 3.653 \times 10^{15} \times T^{3/2}$ cm^{-3}. Table 2 presents the parameters of the defect centers used in the calculations.

Table 2. Properties of defect centers adopted for GaP resistivity modelling.

Defect label	Defect type	Activation energy [eV]	Concentration [cm^{-3}]	Identification
SD	Shallow donor	$E_c - 0.085$	5×10^{15}	Si_{Ga} [20, 21]
DD	Deep donor	$E_c - 1.02$	5×10^{14}	$P_{Ga+/2+}$ [20, 22]
DA	Deep acceptor	$E_v + 0.85$	8×10^{14}	Unidentified [23]
SA	Shallow acceptor	$E_v + 0.055$	1×10^{16}	C_P [20, 22]

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4. Results of simulation

The verification of the model of materials accepted for simulation (4H–SiC, GaP) was based on a comparison of simulation results with experimental data, *i.e.* a series of measurements of dark resistivity of materials at different temperatures. The measurements were performed by a group of scientists led by prof. Paweł Kamiński at the Łukasiewicz Research Network – Institute of Microelectronics and Photonics. In the case of 4H–SiC, the measurements were carried out at the temperatures of 540–770 K with a step of 10 K. In the case of GaP, the measurements were performed in the temperature range of 440–550 K with the same step value. The tested materials were made in a planar structure with dimensions of $4 \times 9 \times 0.38$ mm. On the top of the material sample, two ohmic contacts with dimensions of 2.5×2.5 mm, separated by a 0.7 mm gap, were made. The resistivity was determined both experimentally and simulated in a temperature range appropriate for a given material and the results were compared as shown in Figs. 3 and 5. The resistivity was experimentally determined on the basis of measurement of the dark current which was performed with a Keithley 428 picoammeter. The measurements were carried out with the material sample supplied with the source voltage of 30 V, applied to the ohmic contacts of the material in the assumed temperature range. The resistivity was then determined using the formula $\rho = R \cdot S/l$, where R is the ratio of the voltage set on the source to the measured current, S is the cross-sectional area calculated as the product of the ohmic contact width and the plate thickness, and l is the distance between the ohmic contacts.

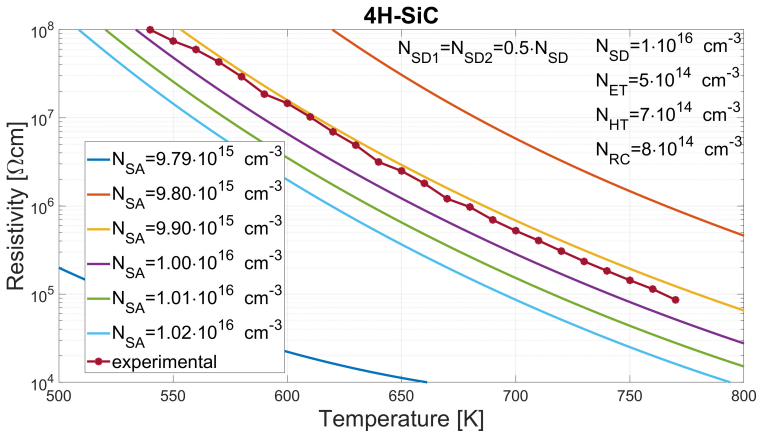

Fig. 3. Comparison of results of measurements and simulation of 4H–SiC resistivity in the temperature range from 540 to 770 K with 10 K step [12].

The simulations of the influence of temperature changes on 4H–SiC resistivity (Fig. 3) were carried out for six different values of shallow acceptor concentrations $N_{SA} = (0.979, 0.98, 0.99, 1.00, 1.01, 1.02) \times 10^{16}$ cm^3 and assumed parameters of the material model defects ($N_{ET} = 5.00 \times 10^{14}$ cm^{-3}, $N_{HT} = 7.00 \times 10^{14}$ cm^{-3}, $N_{RC} = 8.00 \times 10^{14}$ cm^{-3}, $N_{SD} = 1.00 \times 10^{16}$ cm^3, where $N_{SD1} = N_{SD2} = 0.5 \times N_{SD}$). It can be seen that the experimental results coincide much, over a wide temperature range, with simulated resistivity for $N_{SA} 1.00 \times 10^{16}$ cm^{-3}, but for $N_{SA} = 0.99 \times 10^{16}$ cm^{-3}. Nevertheless, the described material model for 4H–SiC can still be considered a good representation of the physical semiconductor material because errors in the measurement of only defect concentrations are well above the difference between 1.01×10^{16} to 1.00×10^{16} cm^{-3}.

Figure 4a shows the simulation results related to the change in the concentration of electrons in the conduction band and resistivity at 400K due to changes in boron concentration (shallow acceptor center SA). An increase in boron concentration from 9×10^{15} to 9.7×10^{15} cm^3 reduces the concentration of electrons in the conduction band from 6.12×10^{11} to 1.98×10^{10} cm^3. A further increase in boron concentration causes the concentration of electrons in the conduction band to drop practically to zero. In the analysed range of changes in boron concentration, material resistivity increased from 1.91×10^4 Ωcm to 5.93×10^5 Ωcm. The maximum material resistivity greater than 1×10^{10} Ωcm occurs for a boron concentration of $0.98 \div 1.04 \times 10^{16}$ cm^{-3}. In this range, the Fermi energy (Fig. 4b) shifts to the half of the forbidden gap. A further increase in boron concentration above 1.06×10^{16} cm^{-3} makes it a p-type material, while for concentrations smaller than 0.9×10^{16} cm^{-3} it is n-type material.

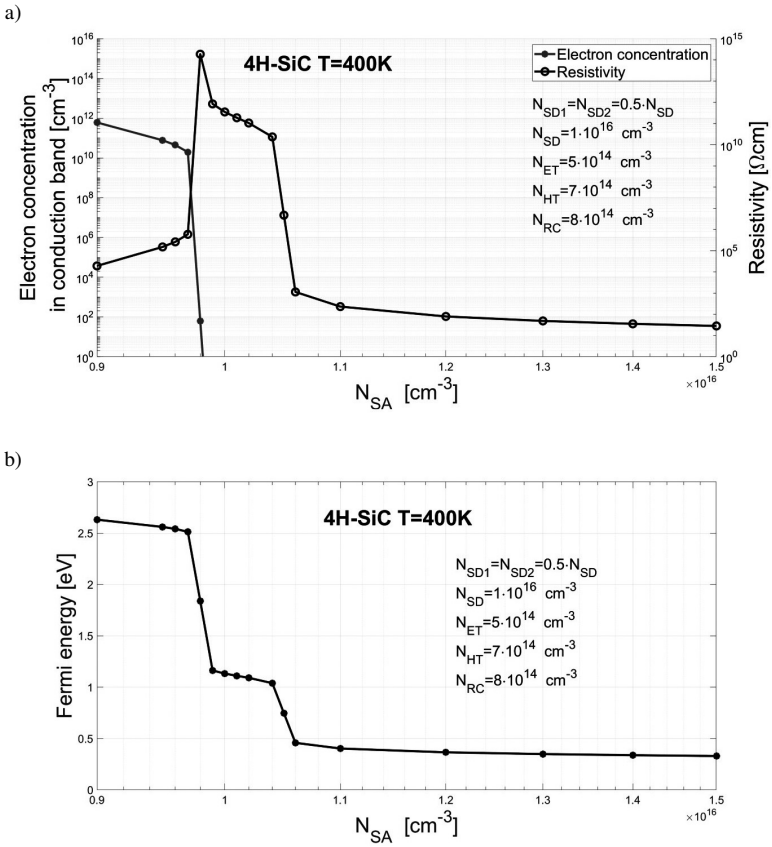

Fig. 4. Simulated changes in the concentration of electrons in the conduction band and resistivity a) and changes in the Fermi level b) for SI 4H–SiC at the temperature of 400 K caused by changes in the concentration of shallow donor centers NSA at the assumed concentrations for the remaining defects $N_{SD1} = N_{SD2} = 5 \times 10^{15}$ cm^{-3}, $N_{ET} = 5 \times 10^{14}$ cm^{-3}, $N_{HT} 7 \times 10^{14}$ cm^{-3} and $N_{RC} = 8 \times 10^{14}$ cm^{-3}.

Figure 5 shows the simulation results of temperature changes in resistivity for gallium phosphide (GaP). The simulation results were compared with the measurement results. The simulations were performed for the assumed concentration of defects ($N_{SD} = N_{DD} = 3 \times 10^{16}$ cm^3, $N_{SA} = 2 \times 10^{16}$ cm^{-3}) and also five slightly different concentrations of shallow acceptors

$N_{SA} = (1, 2, 3, 4, 5) \times 10^{15}$ cm^{-3}. The simulation results show convergence with the results of the experiment. The adopted model can be considered as well suited to the physical semiconductor material because of the concentration of shallow acceptors at the level of 2×10^{15} cm^{-3}.

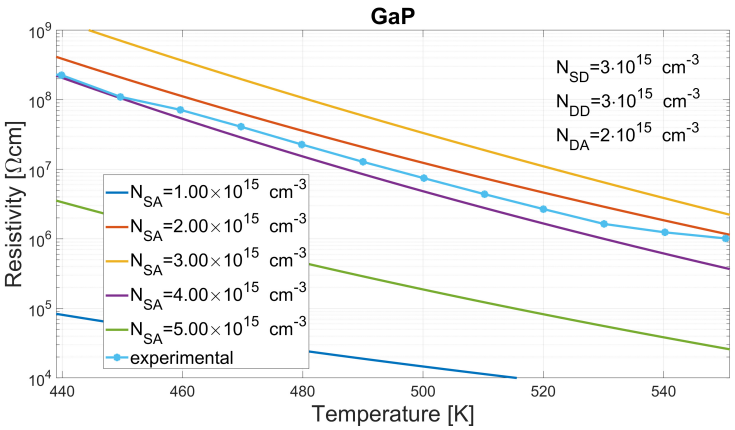

Fig. 5. Comparison of results of measurements and simulation of GaP resistivity in the temperature range from 540 to 770 K with 10 K step.

For the material model confirmed in the verification process, simulations were made of the impact of changes in the concentration of the shallow acceptor N_{SA} (carbon atoms in the phosphorus subnetwork) on changes in the concentration of carriers in the bands (left axis, Fig. 6a) and resistivity (right axis, Fig. 6a). The calculations were made for the temperature 300 K. Based on the data presented in the figure, a significant increase in the resistivity of the material can be observed from 2.52×10^2 to 1.36×10^{13} Ωcm with an increase in N_{SA} concentration from 0.9 to 1.1×10^{15} cm^{-3}. For an N_{SA} concentration of 3.9×10^{15} cm^{-3}, the resistivity reaches the maximum value of $\sim 8 \times 10^{15}$ Ωcm. A further increase in the concentration of the shallow acceptor reduces the resistivity of the material. For N_{SA} concentrations bigger than 6×10^{15} cm^{-3}, the material resistivity is lower than 5×10^2 Ωcm and it decreases with its increase. The increase in N_{SA} concentration to 0.9×10^{15} cm^{-3} causes a gradual decrease in the concentration of electrons in the conduction band ($n_0 \gg p_0$). In the range of N_{SA} concentration (0.9 to 1.1) $\times 10^{15}$ cm^{-3}, the concentration of electrons in the conduction band significantly decreases from 9.9×10^{15} to 1.8×10^3 cm^{-3}. A further increase of the N_{SA} value causes a further decrease in n_0 which for an N_{SA} of 3.9×10^{15} cm^{-3} is zero. For N_{SA} concentrations bigger than 3.9×10^{15} cm^{-3}, the holes in the valence band increase, and for N_{SA} equal to 1×10^{16} cm^{-3}, their concentration is $\sim 4 \times 10^{15}$ cm^{-3}.

Figure 6b shows the changes in the location of the Fermi level associated with changes in N_{SA} concentration, as shown in Fig. 6a. For N_{SA} concentrations lower than 0.9×10^{15} cm^{-3}, the Fermi level is in the upper part of the band gap. This means that this material is of the n type, with the concentration of electrons much higher than the concentration of holes ($n_0 \gg p_0$). For a shallow acceptor concentration ranging from 0.9 to 6×10^{15} cm^{-3}, the Fermi level is in the middle of the band gap which proves the compensation of impurities to be related to shallow acceptors. In this range, the resistivity of the material increases. A further increase in the concentration of shallow acceptors lowers the Fermi level to the lower part of the band gap. For these concentrations, the material is of the p type.

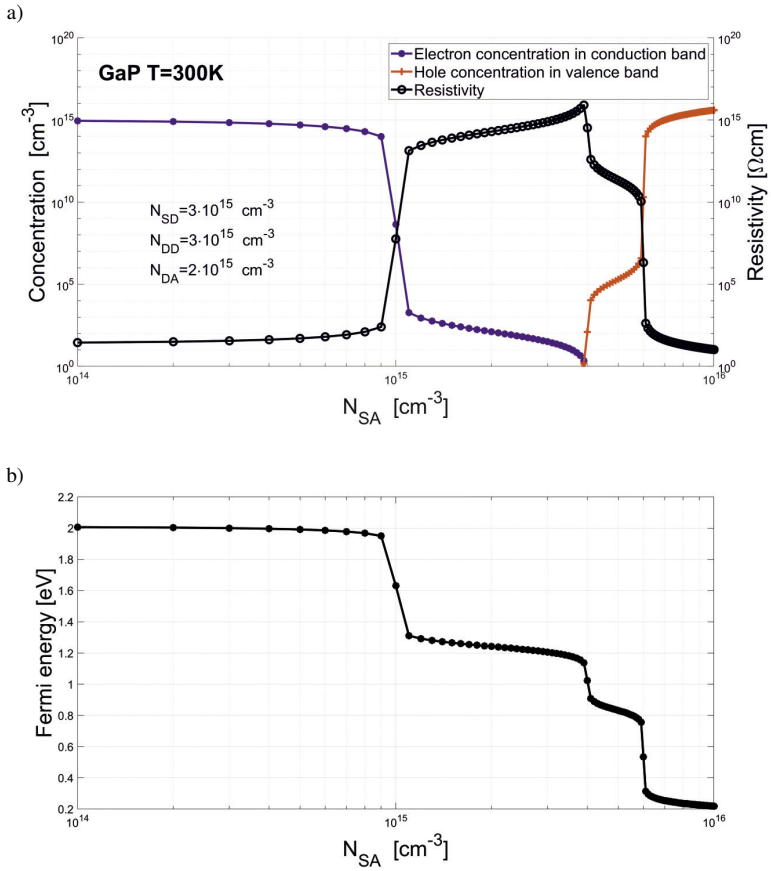

Fig. 6. Simulated changes in the concentration of electrons in the conduction band and resistivity a) and changes in the Fermi level b) for GaP at the temperature of 300K caused by changes in the concentration of shallow donor centers N_{SA}.

5. Conclusions

The article presents a procedure for determining the resistivity of semiconductor materials. This procedure was tested for two materials, *i.e.* silicon carbide 4H–SiC and gallium phosphide GaP. The models adopted in the calculation of material resistivity have been verified with experimental data. The procedure for modelling semiconductor materials presented in the article allows to determine the conditions, allowing to achieve very high resistivity of undoped single crystals of materials (SiC and GaP).

On the basis of the research, it has been found that the SiC resistivity depends on boron concentration. The results of the calculations for 4H–SiC silicon carbide show that in the analysed case, the maximum material resistivity is possible at the boron concentration of $\sim 1 \times 10^{16}$ cm^{-3}. The same calculations for the GaP gallium phosphide have shown that the change in the concentration of carbon impurities in the range $(1.1 \div 5.9) \times 10^{15}$ cm^{-3} results in the material resistivity bigger than 10^{10} Ωcm.

On the basis of the conducted research, it can be concluded that the simulation calculations are useful for the verification of the concentration of defect centers in silicon carbide and gallium phosphide. For simulation, it is sufficient to know the parameters E_G, N_V, N_C of the studied

material. The adoption of appropriate parameters of the defect centers determines the adjustment of the model to actual material. Changing the concentration of centers adopted will determine the resistivity of the material involved. Without verification, simulation can be performed in order to investigate the effect of changing the concentration of the selected defect center. The procedure presented in the article can be successfully used in research of other materials.

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