DETERMINATION OF TRANSPORT PROPERTIES OF SILICON ELECTRON GAS

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Abstract. The paper discusses the results of mathematical modeling of characteristics of electron gas of silicon with intrinsic conductivity. The properties of electronic subsystem are determined within the framework of the continuum approach using the quantum statistics of electron gas and Fermi-Dirac integrals in an arbitrary degeneracy range of the electron gas with a temperature change from 300K to 2000K. When modeling the properties of the electronic subsystem, the effect of narrowing the band gap under the conditions of sufficiently strong heating of the intrinsic semiconductor and carrier degeneracy is taken into account. The properties of electron gas, such as carrier concentrations in the conduction and valence bands, mobility of carriers, electrical conductivity, and the coefficient of ambipolar diffusion are determined. Numerical and graphical information on obtained properties and comparison results with experimental data are presented.

1 INTRODUCTION

In the past few decades, technological applications related to the laser processing of semiconductors with short pulses have been rapidly developing. The wide spectrum of technologies associated with this direction includes such as the generation of nanoparticles and nanostructures [1, 2], the creation of metamaterials [3], modification of the surface of semiconductors by laser pulses [4]. The development of technologies related to laser action on semiconductors, activates research on the fundamental mechanisms underlying such processes as ultrafast melting, ablation, which are still the subject of active scientific discussions [5]. In this connection, knowledge of the properties of semiconductors, in particular silicon, at temperatures close to the melting and evaporation temperature is of decisive importance.

Traditionally, the properties of semiconductors, like metals, are determined experimentally. In the literature, the experimental values of the equilibrium thermophysical properties of silicon obtained for different temperature ranges (up to the melting point) are reported [6-9]. These data, mainly relating to thermal conductivity and electrical conductivity, differ markedly from each other. There are also methods for measuring the equilibrium thermophysical properties of semiconductors in a molten state [9]. The data obtained by measurements, in the course of experiments, are widely used for testing theoretical dependencies. Despite this, the experimental approach has a number of limitations, primarily on a range of measurement conditions, especially in the field of melting.

In the problems of laser action on semiconductors the knowledge of equilibrium properties is insufficient. Laser heating of semiconductors (silicon) as well as of metals is nonequilibrium and proceeds with a large separation of the temperatures of current carriers

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from the lattice; therefore, in problemsof laser action on silicon it can be considered as an object consisting of two interacting subsystems, electronic and phonon. At the same time, for each of the subsystems it is necessary to determine thermophysical, optical and thermodynamic characteristics that vary over a wide temperature range. In view of limited possibilities of the experimental approach in determining the properties of the electron gas of silicon, in this paper we propose to use the theoretical approach and the possibilities of mathematical modeling. For theoretical determination of the properties of electronic subsystem, the present paper uses the quantum statistics of electron gas, i.e. distribution functions and Fermi-Dirac integrals [10, 11]. Numerous experiments [5-8] have shown that in the process of melting in silicon covalent bonds are destroyed, with a change in the short-range order accompanied by a sharp increase in the concentration of conduction electrons and leading to the transition of silicon to the metallic state. The behavior of the electronic subsystem of silicon under phase transition conditions is decisive for laser impact problems. The most important characteristic of the phase transition, along with the temperature dependence of the carrier concentration, is the fundamental characteristic of silicon - band gap. Under the conditions of temperature increase, the band gap *Eg(T)* narrows, having a significant effect on the increase in the carrier concentration reaching high values of $N(T) \approx 10^{18}$ cm^{-3} and higher, which is confirmed by experimental studies [13,14].

The article presents numerical and graphical information about some characteristics of the electronic subsystem of silicon with intrinsic conductivity, determined by means of mathematical modeling. Such electron gas properties as electron concentration *Ne(T)*, holes concentration *Nh(t)*, Fermi energy $E_F(T,N)$, band gap $E_g(T,N)$, carrier mobility $\mu(T,N)$, electrical conductivity $\sigma(T,N)$, ambipolar diffusion coefficient $D_a(T,N)$ are determined within the framework of quantum statistics in an arbitrary range of electron gas degeneracy with a temperature change from 300K to 2000K. The results are compared with the experimental data.

2 CALCULATION OF PROPERTIES OF ELECTRONIC SUBSYSTEM OF SILICON

The calculation of the properties of electronic subsystem of silicon is based on the use of statistics of electron gas of semiconductors. Central to this approach is the charge carrier distribution function for energy states. Electrons in the conduction band and holes in the valence band of silicon can be considered as an ideal Fermi gas. For an ideal Fermi gas, the probability of an electron filling a state k with energy E at a temperature T is found using the Fermi-Dirac distribution [10-12]:

$$f(\mathrm{E},\mathrm{T}) = \frac{1}{\left(1+\exp\left(\dfrac{E-E_F}{k_B T}\right)\right)} \tag{1}$$

where E_F is the Fermi energy, determined from the electroneutrality condition, k_B is the Boltzmann constant.

For electron gas, the value of Fermi energy coincides with the value of chemical potential at T = 0 K and is defined as the amount of energy needed to change the number of particles in the system per unit volume.

An important characteristic of semiconductors, which is necessary for determining the majority of the thermophysical properties of silicon, is the concentration of charge carriers. In intrinsic semiconductors, unlike metals, the number of charge carriers and their mobility depend on temperature.

The electron $N_e(T)$ and holes $N_h(T)$ concentrations at the temperature T in conduction band under thermodynamic equilibrium conditions are determined

$$N_e(T) = \int_{E_C}^{\infty} N_C f(\mathrm{E}) dE \qquad N_h(T) = \int_{-\infty}^{E_V} N_V f(\mathrm{E}) dE \tag{2}$$

where E_C is energy of the bottom of conduction band, E_V - energy of the top of valence band, $N_C = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2}$, $N_V = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2}$ – effective densities of states in conduction band and valence band, ħ is the Planck constant, $m_e = M^{2/3}\left(m_l \cdot m_t^2\right)^{1/3}$ – effective mass of the density of states of electrons in conduction band, taking into account the number of equivalent energy minima in conduction band M (for silicon $M=6$) [10-12], m_l, m_t – the longitudinal and cross-section masses, m_h is the effective mass of hole density of states in the valence band, and $f(E)$ is Fermi-Dirac distribution function (1). For an intrinsic semiconductor that does not contain impurities, equality of concentrations holds

$$N_e(T)=N_h(T)=N(T). \tag{3}$$

The integrals in (2) can be represented in the form

$$N_e(T) = N_C \cdot \mathcal{F}_{1/2}(\eta_e) \qquad N_h(T) = N_V \mathcal{F}_{1/2}(\eta_h) \tag{4}$$

where $\mathcal{F}_{1/2}(x)$ is Fermi-Dirac integral of order $j=1/2$, a representative of the family of integrals that play an important role in determining the properties of semiconductors

$$\mathcal{F}_j(\eta_c) = \frac{1}{\Gamma(j+1)} \int_0^{\infty} \frac{\varepsilon^j}{1+exp(\varepsilon-\eta_c)} d\varepsilon \tag{5}$$

where $\Gamma(x)$ – Gamma function, j is order of Fdermi-Dirac integral, $c=e$ for electrons and $c=h$ for holes, ε is reduced electron (hole) energy, reduced Fermi energy for electrons and holes

$$\eta_e = \frac{E_F - E_C}{k_B T} \qquad \eta_h = \frac{E_V - E_F}{k_B T}. \tag{6}$$

where E_C is energy of the bottom of conduction band, E_V - energy of the top of valence band.

At low temperatures in semiconductors, the concentration of conduction electrons is so small that they behave like a gas of noninteracting particles, the electron gas is nondegenerate. In this case, the Fermi level E_F lies below the bottom of conduction band (E_C-E_F>0) in band gap E_g and distribution function (1) easily reduces to the classical Maxwell-Boltzmann distribution function and the calculation of carrier concentration (4) reduces to

$$N_e(T) = N_C \exp\left(\frac{E_F - E_C}{k_B T}\right) \qquad N_h(T) = N_V \exp\left(\frac{E_V - E_F}{k_B T}\right) \tag{7}$$

Taking into account the intrinsic conductivity *N(T)*

$$N_e(T) = N_h(T) = N(T) = \frac{1}{4}\left(\frac{2k_B T}{\pi \hbar^2}\right)^{3/2} (m_e m_h)^{3/4} \exp\left(-\frac{E_g}{2k_B T}\right) \qquad (8)$$

In the computational context, determination of carrier concentrations will not be difficult. As the temperature rises, the situation changes. Hot electrons give energy to the lattice, while the band gap decreases and concentration of free charge carriers in the conduction band increases. The Fermi level penetrates either to the conduction band (E_C-E_F<0) or to the valence band (E_F-E_V<0), the electron gas degenerates and the classical statistics become unfair, and (7) is not valid. Therefore, it becomes necessary to use quantum statistics and expressions (4) for carrier concentrations. This immediately leads to computational difficulties, since the integral (5) with the exception of an integral with order $j=0$ can not be calculated analytically. The computational difficulties associated with the use of Fermi-Dirac integrals arise not only in determining the carrier concentrations, but also in determining the properties of electron gas such as electrical conductivity, carrier mobility, the ambipolar diffusion coefficient and others, where were used Fermi-Dirac integrals with integer and half-integral orders, as a rule, not high $-1/2 \le j \le 7/2$ and $-1 \le j \le 3$. In [15,16] for Fermi-Dirac integrals of orders j=-1/2, 1/2, 1, 3/2, 2, 5/2, 3 and 7/2 continuous analytical expressions have been obtained for each single order in a wide range of degeneracy

$$\mathcal{F}_j(\eta_c) = \exp\left(\sum_{i=0}^{m} a_i \eta_c^i\right), \; c = e,h, \quad m = 5 \div 7, \qquad (9)$$

Which in this paper were used to calculate the properties of an electron gas. To calculate integrals with order j=1/2, for example, an approximating function with $m = 7$ is used (9).

As the temperature in the semiconductor increases, process of thermal excitation of electrons from valence band to conduction band proceeds continuously, electrons recombine from the conduction band to the valence band. In the intrinsic semiconductor these processes are balanced, and electron and hole concentrations are the same. From the electroneutrality condition, we can find the temperature dependence of Fermi energy E_F, using (4) and (9) for $j=1/2$, we obtain

$$N_C \cdot exp\left(\sum_{i=0}^{7} a_i \eta_e^i\right) = N_V \cdot exp\left(\sum_{i=0}^{7} a_i \eta_h^i\right) \qquad (10)$$

The band gap of silicon Eg, like other semiconductors, with increasing temperature and increasing concentration of charge carriers, tends to narrow [10-14].

The effect of narrowing the band gap is due to three main mechanisms: thermal expansion of the lattice, electron-lattice interaction and collective interactions of carriers. Thermal expansion with increasing temperature together with the enhancement of the electron-lattice interaction causes a shift in the relative positions of the conduction and valence bands. The total manifestation of the first two mechanisms of narrowing of the band gap is described by a semiempirical relationship [17]

$$E_g(T,N) = E_{g,0} - \alpha T^2 / (T + \beta), \qquad (11)$$

where $E_{g,0} = 1.169$ eV is band gap at temperature 0°K, α and β are constants, whose experimental estimates for silicon: $\alpha = 7.021\times10^{-4}$ eV/T, $\beta = 1108K$.

The third mechanism of narrowing of the band gap is associated with the effects of collective interactions of carriers, which become dominant at sufficiently high concentrations. The influence of quantum effects becomes noticeable at a carrier concentration of $N\approx10^{18}$ cm^{-3} and is formulated in a complex manner [18]. The most significant contribution to the narrowing of the band gap is made by the exchange interaction estimated by the empirical dependence of the form $\Delta E_g(N)\sim\gamma\times N^{1/3}(T)$ [19], where γ is the fitting parameter used for combining theoretical estimates with the experimentally determined values of the narrowing of the band gap in various semiconductors. For silicon at a temperature of $T\approx300K$ and carrier concentration $N=10^{17}\div10^{19}$ cm^{-3}, the value of the parameter γ is in the range of $(1.0\div3.6)10^{-8}$ eV×cm [18, 20].

An estimate of narrowing of Si band gap taking into account all mechanisms at high temperatures and carrier concentrations $N\approx10^{18}\div10^{21}$ cm^{-3} can be performed within a semiempirical relationship [21, 22]

$$E_g(T,N) = E_{g,0} - \alpha T^2/(T+\beta) - \gamma N^{1/3}(T), \qquad (12)$$

where the value $\gamma = 8.35\times10^{-8}$ $eV\times cm$ – was chosen from the condition that the band gap should be zero at equilibrium melting point $E_g(T_m)=0$ [22]. Figure 1 shows temperature dependences giving a clear picture of the shape and velocity of narrowing of the band gap $E_g(T,N)$ and the position of Fermi energy level $E_F(T)$ calculated with quantum statistics relative to the edges of valence $E_V(T)$ and conduction $E_C(T)$ bands and intrinsic Fermi level in the middle of the band gap. With increasing temperature, Fermi energy $E_F(T)$ deviates from its own level toward the edge of valence band $E_V(T)$, which is determined by lower effective mass of density of states of the valence band. For silicon, the ratio of effective masses of states of electron and hole is $m_{de}/m_{dh}=1.89$. Because of this, the degeneracy of hole gas $(E_V-E_F<k_bT,\ \eta_h\approx-4)$ occurs earlier than the degeneracy of electron gas at a temperature $T=1000K$ which is much lower than equilibrium melting point.

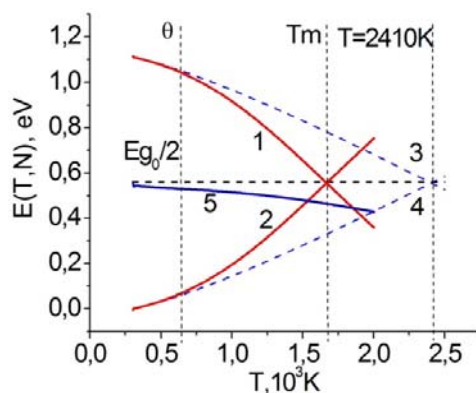

Figure 1. Temperature dependences of the edges of conduction $E_C(T)$ and valence $E_V(T)$ bands taking into account: (1), (2) -thermal and quantum effects; (3), (4) - thermal effects. (5) - Fermi energy $E_F(T)$.

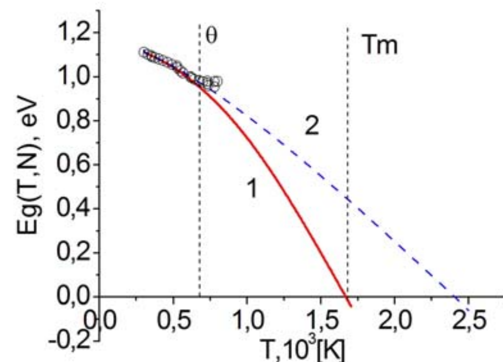

Figure 2. The temperature dependence of the band gap with regard to: (1) - thermal and quantum effects; (2) - thermal effects. The markers show experimental data [23].

Figure 2 shows the band gap computed taking into account quantum and thermal (12) and only thermal (11) effects. In the temperature range from 300 ° K to θ where influence of quantum mechanisms is weak the band gap is equally well approximated by both dependences and completely coincide with experiment [23]. Above Debye temperature, the contribution of collective interaction mechanisms to band gap becomes appreciable which causes a stronger narrowing of band gap by means of the dependence (12) taking these effects into account.

Figure 3 shows temperature dependences of the carrier concentration calculated with quantum statistics and band gap (12) and classical Maxwell-Boltzmann statistics and the constant value of band gap $E_g=1.12$ eV at *300K*.

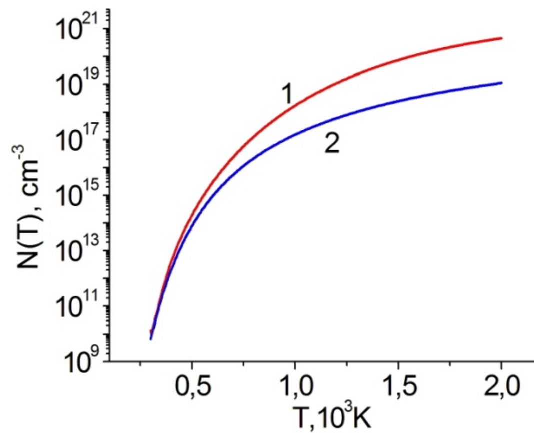

Figure 3. Temperature dependences of carrier concentrations calculated using statistics: (1) - Fermi-Dirac, (2) - Maxwell-Boltzmann, $E_g = 1.12\ eV$.

2.1 Mobility of carriers

Mobility is an important transport characteristic of a semiconductor. Using quantum statistics the mobility of carriers is determined by following expression

$$\mu_c(T,N) = \mu_c^0(T)\frac{\mathcal{F}_0(\eta_c)}{\mathcal{F}_{1/2}(\eta_c)}\bigg|_{c=e,h} \tag{13}$$

where $\mu_c^0(T)$ is mobility of carriers for a nondegenerate semiconductor, $\mathcal{F}_{1/2}(\eta_c)$, $\mathcal{F}_0(\eta_c)$ $(c=e,h)$ are Fermi-Dirac integrals of orders $j=1/2$ and $j=0$.

In [24] was given method for calculating the mobility of nondegenerate charge carriers taking into acoount electron-hole scattering which was used to calculate μ_c^0. In this approach, it is assumed that the mobility of electron or hole is a function of the following three components: mobility of lattice, mobility of impurity scattering and mobility of electron-hole scattering.

Figure 4 shows temperature dependences of the mobilities of electrons and holes. With increasing temperature, the mobility of carriers decreases which is due to the enhancement of electron-lattice interaction and effects of collective interactions acting at sufficiently high carrier concentrations and degeneracy of electron gas. Figure 4 also provides reference [25] and experimental [26, 27] data in temperature range $T=300K\div600K$.

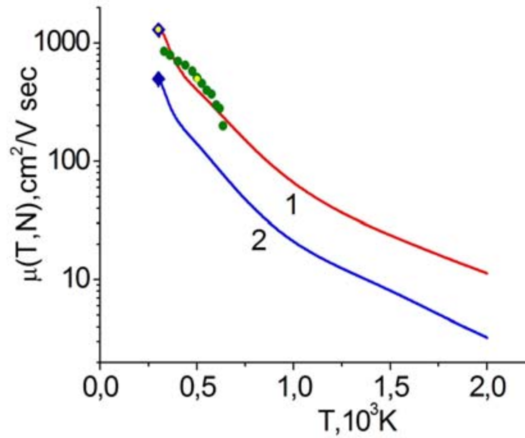

Figure 4. Temperature dependences of mobilities (1) - electrons, (2) - holes, (3) - total calculated with quantum statistics, markers: blue - reference data [25], light green - experimental data [26], dark green markers – experimental data [27].

In the region of low temperatures $T<600K$ as can be seen from Fig. 4, obtained temperature dependences of carrier mobilities show good agreement with reference and experimental data. In the high-temperature region $T > 600K$ (near the melting point), experimental values of carrier mobility are absent.

2.2 Ambipolar diffusion coefficient

As the mobility of carriers the ambipolar diffusion coefficient is important transport semiconductor characteristic. When laser action on a semiconductor, in the near-surface layer the concentration of free carriers sharply increases which diffuse deep into the sample. As the temperature increases, carrier concentration increases reaching at equilibrium melting temperature $T=Tm=1687K$ the value of 1.7×10^{20} cm^{-3} (Fig. 3), with that diffusion rate decreasing due to an increase in frequency of electron-electron and electron-phonon collisions. This process is characterized by the ambipolar diffusion coefficient $D_a(T,N)$ which depends both on temperature and on carrier concentration. In arbitrary range of electron gas degeneracy using quantum statistics the ambipolar diffusion coefficient is determined [28]

$$D_a(T,N)=\frac{k_BT}{e}\frac{\mu_e(T,N)\mu_h(T,N)}{\mu_e(T,N)+\mu_h(T,N)}\left(\frac{\Im_{1/2}(\eta_e)}{\Im_{-1/2}(\eta_e)}+\frac{\Im_{1/2}(\eta_h)}{\Im_{-1/2}(\eta_h)}\right), \tag{15}$$

where $\mu(T,N)$ is total mobility (14), $\mathcal{F}_{1/2}(\eta_c)$, $\mathcal{F}_{-1/2}(\eta_c)$ $(c=e,h)$ are Fermi-Dirac integrals of orders $j=1/2$ and $j=-1/2$. Approximating functions for Fermi-Dirac integrals from [15, 16] were used in the simulation. It is seen that $D_a(T,N)$ depends on carrier concentration and temperature, electron $\mu_e(T,N)$ and hole $\mu_h(T,N)$ mobilities, degeneracy of electron gas.

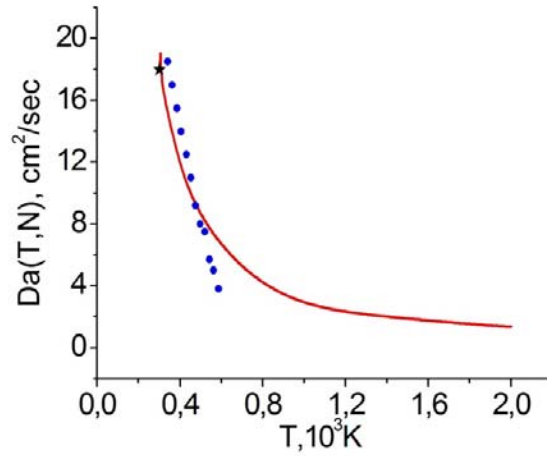

Figure 5. Temperature dependence of ambipolar diffusion coefficient Da(T,N) (solid line) calculated with quantum statistics. Black markers denote reference data [25], blue - experimental [27].

Figure 5 shows temperature dependence of coefficient $D_a(T,N)$ calculated from equation (15). Comparison of calculated data with experimental data in the temperature range *300K÷600K* [25, 27] and reference value at a temperature of *300K* showed good agreement up to the temperature *T=500K*. In the region of higher temperatures *T>600K* the comparison was not carried out because of the lack of experimental data.

2.3 Electrical conductivity

In calculating the temperature dependence of specific electrical conductivity taking into account the degeneracy of electron gas we also used quantum statistics (Fermi-Dirac integrals). Electron and hole electrical conductivities are determined [10-12]

$$\sigma_c(T,N) = qN_c(T)\mu_c(T,N), \quad c = e,h \tag{16}$$

where μ_c is carrier mobility (13).

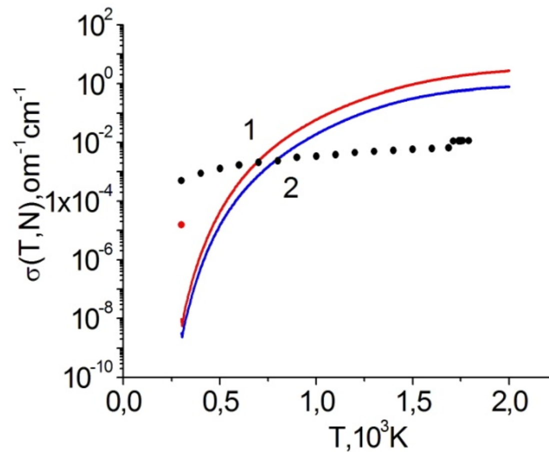

Figure 6. Temperature dependences of electrical conductivity of electrons (1), holes (2) calculated with quantum statistics. Experimental data are marked with black markers [7], red marker is reference value [25].

Figure 6 shows electron and hole electrical conductivities of silicon calculated using quantum statistics, experimental data and reference values are indicated by markers [7, 25].

Concentration of charge carriers Ne(T) and Nh(T) makes the main contribution to temperature dependence of electrical conductivity of semiconductors. Therefore, temperature way of electrical conductivity in basic features repeats temperature dependence of concentration of charge carriers (Fig. 3) and qualitatively coincides with experimental dependence (Fig. 6).

4 CONCLUSION

The properties of electron subsystem of silicon are calculated in the framework of continuum approach using quantum statistics and Fermi-Dirac integrals in an arbitrary range of electron gas degeneracy with temperature change from 300K to 2000K. Such characteristics of electron subsystem of silicon with intrinsic conductivity as carrier concentration and mobility, coefficient of ambipolar diffusion, electrical conductivity are calculated. When modeling the properties of electron subsystem, the influence of narrowing of band gap under conditions of sufficiently strong heating of intrinsic semiconductor and carrier degeneracy is taken into account. The results of calculations are compared with the results of experiments. A comparison of calculated data with experimental ones showed acceptable quantitative agreement between band gap, electron and hole mobilities and ambipolar diffusion coefficient and qualitative coincidence of electrical conductivity. Numerical and graphical information on the properties obtained and comparison results with experimental data are presented.

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