Electrical properties of diluted n- and p-$Si_{1-x}Ge_x$ at small x

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Hall effect and conductivity measurements are taken on $Si_{1-x}Ge_x$ of n- and p-type at $x \leq 0.05$. Much attention is given to electrical measurements over a temperature interval of 25 to 40 K where the mobility of charged carriers is strongly affected by alloy scattering. The partial mobility of electrons and holes due to this scattering mechanism is estimated for n-$Si_{1-x}Ge_x$ and p-$Si_{1-x}Ge_x$ at small x. Together with this, an effect of the presence of Ge atoms upon the ionization energy of phosphorus and boron impurities is investigated. Some points related to an inhomogeneous distribution of Ge atoms in $Si_{1-x}Ge_x$ are discussed.

1. Introduction

Besides their technical applications in various fields, silicon–germanium alloys are of keen interest to scientists, too, because of their electrical properties. First of all, the disturbance of the periodic potentials of the host crystal lattice due to the presence of isoelectronic atoms of different size is expected to produce remarkable effects upon the scattering of charge carriers, thus giving rise to their decreasing mobility. This so-called alloy scattering introduces an additional scattering mechanism, together with such well-known scattering mechanisms of charge carriers due to acoustic and optical phonons, ionized and neutral centers and so on; see e.g. [1]. The first attempt to describe the alloy scattering of charge carriers in a direct band gap semiconductor was made by Brooks assuming a homogeneous distribution of lattice atoms of two kinds; see in [1]. In this case the temperature-dependent mobility appears to be inversely proportional to $\sqrt{T}$. In the ensuing years the model of alloy scattering was considerably improved taking into account the complex structures of the conduction and valence bands in Si and Ge [2–6] as well as non-uniform distributions of both species [7]. The improved models make it possible to fit reasonably well the electron- and hole mobility measured in $Si_{1-x}Ge_x$ alloys at $x \geq 0.1$ at room temperature [8]. At $x < 0.1$ there are no reliable experimental data, since the scattering of charge carriers at $T = 300$ K is mostly defined by acoustic and optical phonons. Under these conditions it is impossible to extract any information concerning the alloy scattering. Electrical measurements on strongly diluted $Si_{1-x}Ge_x$ at cryogenic temperatures, when the phonon scattering is of minor importance, should help one to shed light on the alloy scattering of charge carriers in such materials. The purpose of the present paper is aimed at bridging the existing gap in our knowledge.

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2. Experimental

A couple of n- and p-$Si_{1-x}Ge_x$ ingots at $x < 0.1$ were grown by the Czochralski technique. Square-shaped samples doped with phosphorus in concentrations of $1.0 \cdot 10^{16}$ to $1.5 \cdot 10^{16}$ cm^{-3} or boron in concentrations of $2.1 \cdot 10^{16}$ to $2.8 \cdot 10^{16}$ cm^{-3} were cut for electrical measurements.

Electrical measurements of the concentrations of electrons and holes, n and p, as well as their mobility, μ_n and μ_p, respectively, were taken with the aid of the Van der Pauw technique over a wide temperature range of $T \approx 25$ K to 300 K. Curves of n, $p(1/T)$ were then analyzed by means of relevant equations of charge balance allowing one to determine the total concentrations of donor and acceptor centers, N_D and N_A; see for instance [9,10]. In the case of materials of p-type the equation of charge balance is modified replacing $n \to p$, $N_D \to N_A$, $N_A \to N_D$, and $N_C \to N_V$ where N_C and N_V are the effective density-of-states in the conduction and valence band, respectively. The degeneracy of the valence band at $\boldsymbol{k} = 0$ as well as an increase in the density-of-states effective mass of holes at $T > 70$ K were taken into account. In this way a contribution of the third split-off valence band to $p(1/T)$ was considered, too. In most samples the compensation ratios of doping impurities, $K = N_A/N_D$ and $K = N_D/N_A$ in n- and p-materials, respectively, were found to be very small, being less than 2%. The total concentrations of compensating acceptors in the n-$Si_{1-x}Ge_x$ samples were estimated as $N_A < 1 \cdot 10^{14}$ cm^{-3} and the total concentrations of compensating donors in the p-$Si_{1-x}Ge_x$ samples were less than $N_D < 2 \cdot 10^{14}$ cm^{-3}. It should be noted that in weakly compensated materials the scattering of charge carriers by ionized centers doesn't play a leading part in the charge carrier mobility over a temperature range of interest, $25 < T < 40$ K. In this range $n, p \ll N_D$, N_A and the concentration of ionized centers being equal to $N_{ion} = 2N_A$ and $2N_D$ in n-type and p-type samples, correspondingly, turned out to be relatively small.

3. Results and Discussion

As an illustration, two curves of $n, p(1/T)$ in the n-$Si_{1-x}Ge_x$ and p-$Si_{1-x}Ge_x$ at $x \approx 0.05$ are depicted in Fig. 1 and Fig. 2. The effective ionization energy of shallow donors defined from an exponential part of $n(1/T)$ was found to be $E_D = (42.0 \pm 0.5)$ meV at $x = 0.048$, compared to $E_D = (43.0 \pm 0.5)$ meV for the reference sample without intentional doping with Ge. In the reference sample the decrease in the ionization energy of shallow donors, compared to an ionization energy of 45 meV in lightly doped n-Si : P, is certainly caused by the well-known effect associated with a high doping level of phosphorus at $N_D \approx 1.5 \cdot 10^{16}$ cm^{-3}; see for instance [11,12]. This effect results from a noticeable overlapping of the wave functions of electrons localized at shallow donor centers. Therefore, the effect of alloy disorder upon E_D at small x is barely detected by Hall effect measurements. In actual fact, a considerable decrease in the concentration of shallow donors down to $\sim 1 \cdot 10^{15}$ cm^{-3} in the n-$Si_{1-x}Ge_x$, even at $x = 0.064$, leads to $E_D = (44.0 \pm 0.5)$ meV, thus showing an importance of the first effect as against the effect of Ge doping. Of course, infrared spectroscopic techniques make it possible to provide useful information on this point. An inhomogeneous broadening of the spectral lines of substitutional phosphorus and boron in n-$Si_{1-x}Ge_x$ and p-$Si_{1-x}Ge_x$, respectively, has been reported in [13,14].

A similar situation is observed in p-$Si_{1-x}Ge_x$ doped with boron in concentrations about $2 \cdot 10^{16}$ cm^{-3}. The effective ionization energy of shallow acceptors defined from an exponential part of the $p(1/T)$ curve in Fig. 2 was found to be $E_A = (44.0 \pm 0.5)$ meV in the p-$Si_{1-x}Ge_x$ at $x = 0.049$, being equal to that for the reference sample without intentional doping with Ge. Therefore, an effect of alloy disorder upon E_A appears to be even smaller than that observed in n-$Si_{1-x}Ge_x$. Again, a considerable decrease in the concentration of shallow acceptors down to $\approx 3.4 \cdot 10^{14}$ cm^{-3} in the p-$Si_{1-x}Ge_x$ at $x = 0.024$ leads to $E_A = (45.0 \pm 0.5)$ meV, thus very close to the value known for lightly doped p-Si : B [11]. This casts doubt on the data on E_A in p-$Si_{1-x}Ge_x$ published earlier [15] where the authors reported the relation between the ionization energy of boron and mole fraction of Ge, $E_A = (44.4 - 108x)$ meV. In accordance with this relation, the ionization energy should drop to $E_A = 39$ meV at $x = 0.049$. This is in sharp contrast to the $p(1/T)$ curve shown in Fig. 2, beyond any possible errors in our measurements. It should be recalled that a noticeable discrepancy between Hall effect data and photoconductivity spectra in p-$Si_{1-x}Ge_x$ was also mentioned in [14].

Several factors may be responsible for such a discrepancy in electrical data. The density-of-states effective mass of holes is set constant in the equations of charge balance over the whole temperature range studied in [15], what is known to be not the case in p-Si; see [16]. Together with this, the authors [15] believed that the Ge distribution in p-$Si_{1-x}Ge_x$ is random at $0 < x < 0.13$. They tried approximating a

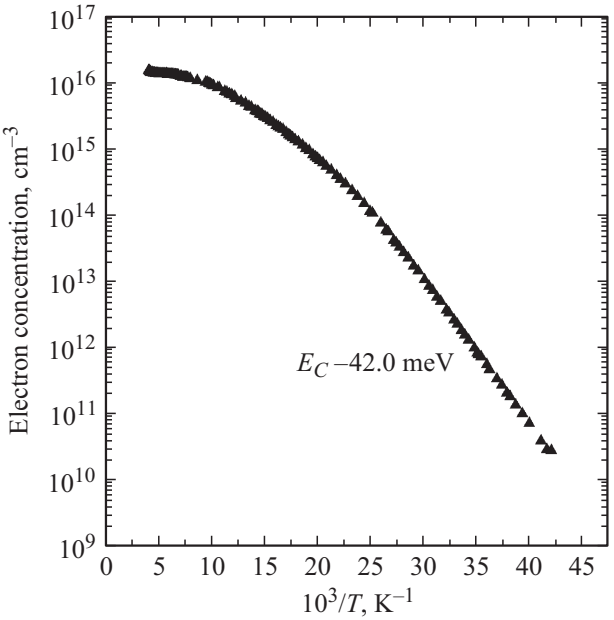

Figure 1. Charge carrier concentration versus reciprocal temperature for the n-$Si_{1-x}Ge_x$ at $x = 0.048$. Points, experimental. Effective ionization energy of shallow donors is indicated.

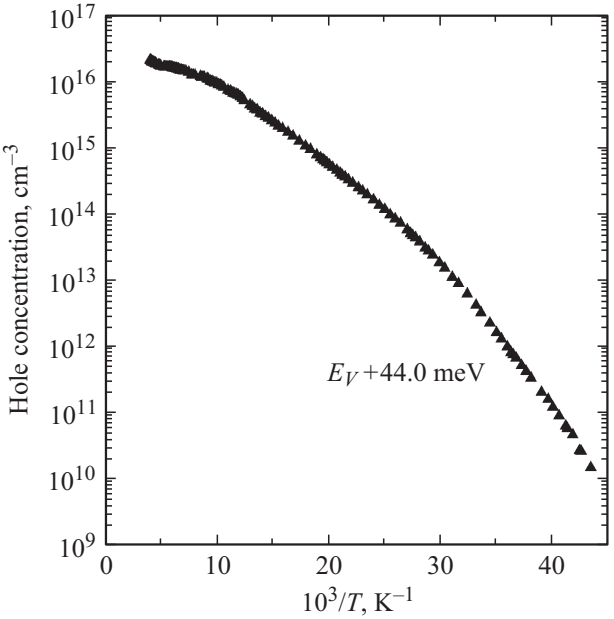

Figure 2. Charge carrier concentration versus reciprocal temperature for the p-$Si_{1-x}Ge_x$ at $x = 0.049$. Points, experimental. Effective ionization energy of shallow acceptors is indicated.

relation of $E_A(x)$ from small x, despite the scattered data on $E_A = (44 \pm 1)$ meV even for reference samples of p-Si. In their later paper the authors [14,15] left room for an inhomogeneous distribution of Ge atoms and alloy fluctuations. In actual fact, studies of EPR lines of substitutional phosphorus in n-$Si_{1-x}Ge_x$ at $0 < x < 0.057$ [17] provided experimental evidence that the non-uniform Ge distribution

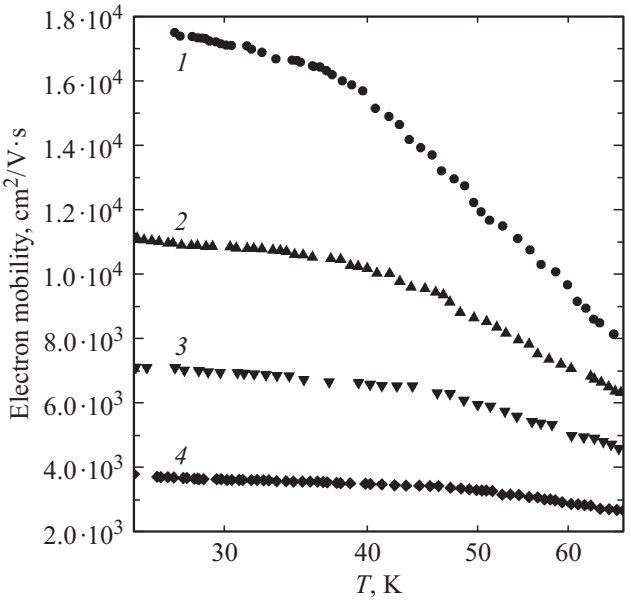

Figure 3. Charge carrier mobility versus temperature for the n-$Si_{1-x}Ge_x$ at $x < 0.05$. Points, experimental: $x = 0$ (*1*); $x = 0.008$ (*2*); $x = 0.019$ (*3*); $x = 0.048$ (*4*).

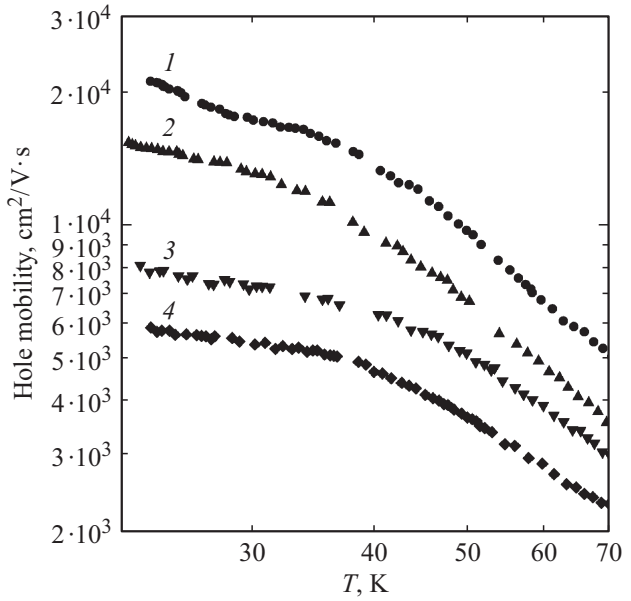

Figure 4. Charge carrier mobility versus temperature for the p-$Si_{1-x}Ge_x$ at $x < 0.05$. Points, experimental: $x = 0$ (*1*); $x = 0.008$ (*2*); $x = 0.02$ (*3*); $x = 0.049$ (*4*).

starts changing in character at $x \geq 0.024$. Therefore, the relation of $E_A(x)$ should be approximated in two intervals of x. In doing so, the trend towards the decreasing $E_A(x)$ in p-$Si_{1-x}Ge_x$ at larger $x > 0.04$ [15] may be reliable. Besides, some remarks concerning the Hall factor in electrical measurements will be given below.

The mobility of charge carriers in $Si_{1-x}Ge_x$ samples at $x \leq 0.05$ studied in the present work is shown in Fig. 3 and Fig. 4. The charge carrier mobility at low cryogenic temperatures displays a clearly defined feature characteristic for the alloy scattering, μ_n, $\mu_p \propto T^{-1/2}$. The higher is the mole fraction of Ge in $Si_{1-x}Ge_x$, the more pronounced is this behavior. At $x \leq 0.05$ the temperature range where the contribution of alloy scattering to the mobility makes its appearance spans an interval of $25 < T < 40$ K. The next question is how this contribution can be extracted from $\mu(T)$ curves. Generally speaking, a direct way is to calculate partial contributions to the scattering of charge carriers due to acoustic phonons, charged and neutral centers as well as alloy disorder. The alloy disorder arising from aperiodic atomic potentials and aperiodic atomic positions in $Si_{1-x}Ge_x$ is characterized by the alloy scattering potential ΔE_{alloy} used as a mere fitting parameter while comparing calculated and experimental $\mu(T)$ data. This pathway was taken in [15] but there are some weak points to be recalled, together with a fitting parameter ΔE_{alloy}. First of all, the scattering of charge carriers by ionized centers at very low cryogenic temperatures should be properly treated by the partial-wave phase-shift formalism [18,19], for the Conwell-Weisskopf or Brooks-Herring models [20] based on the Born approximation cannot provide an accurate description. Besides, in low-resistivity p-$Si_{1-x}Ge_x$ samples [15] the scattering of holes due to neutral shallow acceptors being present in sizeable concentrations about $1.5 \cdot 10^{16}$ cm^{-3} was not taken into consideration at all, although this scattering mechanism in moderately doped Si is known to assume substantial importance [18,19].

Trying to solve this problem in the present work n-$Si_{1-x}Ge_x$ and p-$Si_{1-x}Ge_x$ samples as well as reference ones were so selected that they have very similar concentrations of shallow donors or shallow acceptors, respectively. Along with this, the compensation ratios were very small in all the samples, as indicated above in Section 2. Then the partial mobility of charged carriers due to alloy disorder can be estimated taking into account the experimental μ_n, $\mu_p(T)$ curves for the reference n-Si and p-Si over a temperature interval of $25 < T < 40$ K. In this way one can circumvent the difficulties in calculating the combined mobility of charge carriers due to scattering by acoustic phonons as well as charged and neutral centers, having very different power laws of T. The partial mobility of electrons and holes associated with alloy scattering is displayed in Fig. 5 and Fig. 6. It is seen that the partial mobility of charge carriers in n-$Si_{1-x}Ge_x$ and p-$Si_{1-x}Ge_x$ at $x \approx 0.02$ starts decreasing at a much lesser rate. It is believed that this is because of some strong changes in an inhomogeneous distribution of Ge atoms. This way of reasoning is in line with [17]. It is interesting to note that at $x < 0.02$ the partial mobility of holes turned out to be considerably higher than the mobility of electrons. Based on an atomistic approach to alloy scattering in $Si_{1-x}Ge_x$ the authors [7] came to the conclusion that electrons in these solid solutions are scattered more due to bond variation while holes are scattered more due to atom variation. It may mean that in strongly diluted n-$Si_{1-x}Ge_x$ the first factor plays

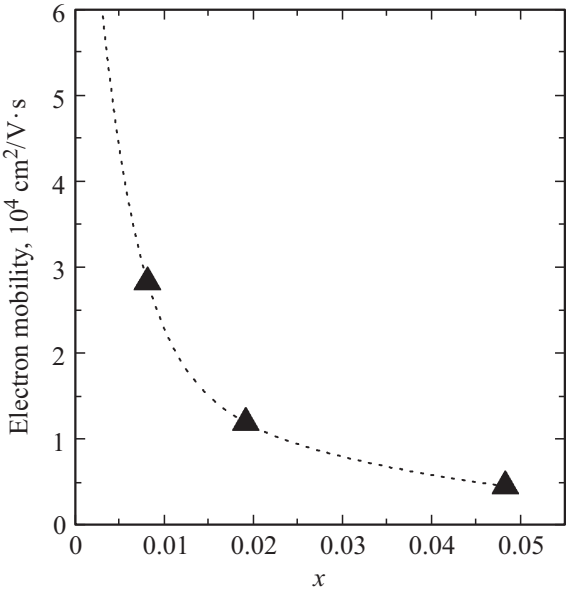

Figure 5. Partial mobility of electrons due to alloy scattering at $T \approx 28$ K versus mole fraction of Ge atoms x in the n-$Si_{1-x}Ge_x$ at $x < 0.05$. The dashed line is shown as the eye guide.

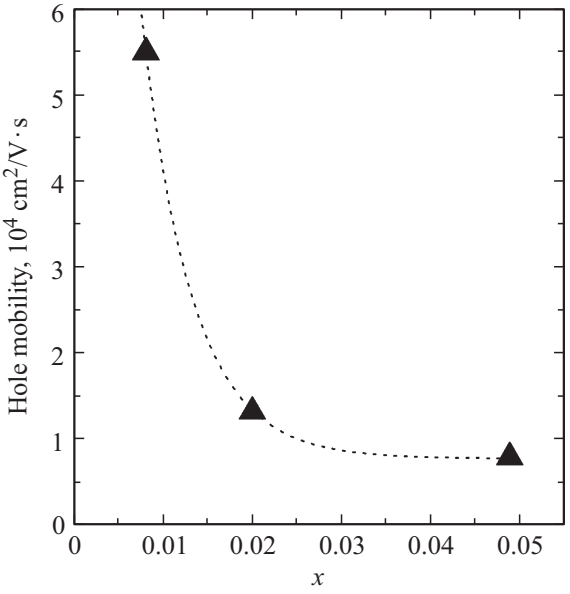

Figure 6. Partial mobility of holes due to alloy scattering at $T \approx 28$ K versus mole fraction of Ge atoms x in the p-$Si_{1-x}Ge_x$ at $x < 0.05$. The dashed line is shown as the eye guide.

a leading role in the alloy scattering. Changes in an inhomogeneous distribution of Ge atoms with increasing x result in disappearance of this disparity.

Some remarks should be made in the connection with the Hall factor. Generally, this point should be taken into consideration for conversion of the charge carrier mobility determined from Hall effect and conductivity measurements to the drift mobility. Data obtained for p-$Si_{1-x}Ge_x$ samples at $x \leq 0.13$ allow one to conclude that the Hall factor at room temperature is close to $r_H = (0.8 \pm 0.1)$ and it doesn't significantly depend on x [15]. The Hall mobility of holes at cryogenic temperatures $25 \leq T < 40$ K increases considerably, at least by an order-of-magnitude as compared to that observed at room temperature. As a result, the Hall factor should also increase, being close to unity. Because of this it was set $r_H = 1$ at cryogenic temperatures [15], so we also do for n-$Si_{1-x}Ge_x$ and p-$Si_{1-x}Ge_x$ samples at $x \leq 0.05$ in the present work. A possible weak dependence of $r_H(T)$ shouldn't produced any pronounced effect upon n, $p(1/T)$ curves, since the concentration of charge carriers increases by several orders-of-magnitude over the temperature interval indicated above; see Fig. 1 and Fig. 2.

4. Conclusion

Electrical measurements were taken on n-$Si_{1-x}Ge_x$ and p-$Si_{1-x}Ge_x$ at $x \leq 0.05$ as well reference samples of n-Si and p-Si. An effect of the presence of Ge atoms upon the ionization energy of substitutional phosphorus and boron was found to be weak. There is experimental evidence that the Ge distribution in SiGe solid solutions is inhomogeneous and not totally random, as often suggested in earlier papers. Moreover, an inhomogeneous distribution starts changing at $x > 0.024$. This characteristic feature also makes its appearance in the alloy scattering of charge carriers. The partial mobility of electrons and holes due to the alloy scattering in n-$Si_{1-x}Ge_x$ and p-$Si_{1-x}Ge_x$ at $x \leq 0.05$, respectively, has been estimated.

References

[1] L. Makowski, M. Glicksman. J. Phys. Chem. Solids, **34**, 487 (1973).
[2] S. Krishnarmurthy, A. Sher, A.-B. Chen. Appl. Phys. Lett., **47**, 160 (1985).
[3] C.B. Van der Walle. In: *Properties of Silicon Germanium and SiGe: Carbon*, ed. by Erich Kasper and Klara Lyutovich (London, INSPEC, 2000), p. 149.
[4] S. Joyce, F. Murphy-Armando, S. Fahy. Phys. Rev. B, **75**, 155 201 (2007).
[5] F. Murphy-Armando, S. Fahy. Phys. Rev. B, **78**, 035 202 (2008).
[6] F. Murphy-Armando, S. Fahy. Phys. Rev. B, **86**, 079 903 (2012).
[7] S.R. Mehrotra, A. Paul, G. Klimeck. Appl. Phys. Lett., **98**, 173 503 (2011).
[8] G. Busch, O. Vogt. Helv. Phys. Acta., **33**, 437 (1960).
[9] J.S. Blakemore. *Semiconductor Statistics*. (Pergamon, 1962).
[10] V.V. Emtsev, N.V. Abrosimov, V.V. Kozlowskii, G.A. Oganesyan. Fiz. i Tekhn. Poluprovodn., **48**(11), (in press) (in Russian) (2014) [Semiconductors, **48**, in press (2014)].
[11] A.K. Ramdas, S. Rodriguez. Rep. Progr. Phys., **44**, 1297 (1981).
[12] N.A. Penin, B.G. Zhurkin, B.A. Volkov. Phys. Sol. State., **7**, 3188 (1965).

[13] S.A. Lynch, G. Matmon, S.G. Pavlov, K.L. Litvinenko, B. Redlich, A.F.G. van der Meer, N.V. Abrosimov, H.-W. Hübers. Phys. Rev. B, **82**, 245 206 (2010).
[14] M. Franz, K. Pressel, P. Gaworzewski. J. Appl. Phys., **84**, 709 (1998).
[15] P. Gaworzewski, K. Tittelbach-Helmrich, U. Penner, N.V. Abrosimov. J. Appl. Phys., **83**, 5258 (1998).
[16] H.D. Barber. Sol. St. Electroncs, **10**, 1039 (1967).
[17] A.I. Veinger, A.G. Zabrodskii, T.V. Tisnek, S.I. Goloshchapov, N.V. Abrosimov. Semiconductors, **41**, 666 (2007).
[18] J.R. Meyer, F.J. Bartoli. Phys. Rev. B, **23**, 5413 (1981).
[19] J.R. Meyer, F.J. Bartoli. Phys. Rev. B, **24**, 2089 (1981).
[20] J.S. Blakemore. *Solid State Physics* (Cambridge, London, New York, New Rochelle, Melbourn Sydney: Cambridge University Press, 1985).

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