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Finding Singular Points of the Concentration Curve of Doped Semiconductors

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Abstract | **Original Research Article**

The paper continues to consider the state of a system consisting of a crystalline semiconductor doped with donor and acceptor impurities. Based on the general equation of state of the system that we derived earlier and its solution, a method for calculating the singular points of the system's state is proposed. These singular points include equivalence points and points of maximum buffer capacity. This development can find practical application in the design of semiconductor devices and equipment, as well as for assessing changes occurring in semiconductor crystals due to diffusion and electro-diffusion of impurities.

Keywords: Semiconductor, Silicon, Germanium, Electron Concentration, Hole Concentration, Equivalence Points, Points of Maximum Buffer Capacity.

INTRODUCTION

When creating semiconductor devices, a certain amount of electron-acceptor (p) or electron-donor (n) type impurities is introduced into a pure semiconductor crystal, forming p- and n-type semiconductors (Electrons and Holes in Semiconductors. 2020). At the point of contact between p and n semiconductors, mutual diffusion of impurities from one semiconductor to another occurs (Microelectronic Materials and Processing. 1989). Our previous work (Yefimov S. 2024) is devoted to the problem of determining the concentration of charge carriers in a doped semiconductor. This work considers the determination of the singular points of the concentration dependence, namely, the equivalence points of charge carriers of opposite signs, and the points of maximum buffer capacity. The identity of the equations derived here, and the equations derived for aqueous solutions (Yefimov S. 2023) is indicated.

MATERIALS AND METHODS

The basis of the calculations is the General Equation of State of a doped semiconductor that we derived. We derived the equations for the singular points of semiconductors by analogy with the derivation made for determining the singular points of aqueous solutions of electrolytes (Yefimov S. 2023). The Microsoft EXCEL spreadsheet was used for calculations and the creation of graphs.

RESULTS AND DISCUSSION

The General Equation of State for a doped semiconductor, which we use here to find singular points, is presented in Table 1. The derivation of these equations is given in (Yefimov S 2024).

Table 1: Polynomial coefficients of the General Equation of State. A semiconductor is doped with a donor and a fully ionizing acceptor ***

Max. degree.	The mix of two-stage ionizing donor D1(K1, K2) and one-stage ionizing donor. D2(K3). $n^5 + a*n^4 + b*n^3 + c*n^2 + d* n + e = 0$	Three-stage ionizing donor. $n^5 + a*n^4 + b*n^3 + c*n^2 + d* n + e = 0$	Two-stage ionizing donor. $n^4 + a*n^3 + b*n^2 + c* n + d = 0$	One-stage ionizing donor $n^3 + a*n^2 + b* n + c = 0$	Completely ionizing donor. $n^2 + a* n + b = 0$
n^5	1	1	0	0	0
n^4	A + K1+K2+K3	A + K1+K2+K3	1	0	0

n^3	K1*K2 + K1*K3 + K2*K3 + A*(K1 + K2 + K3) – S – D1*K1 - D2*K3	K1*K2 + K1*K3 + K2*K3 + A*(K1 + K2 + K3) – S – D*K1	A + K1 + K2	1	0
n^2	K1*K2*K3 + A*(K1*K2 + K1*K3 + K2*K3) – S*(K1 + K2 + K3) – D1*(2*K1*K2 + K1*K3) - D2*(K1*K3 + K2*K3)	K1*K2*K3 + A*(K1*K2 + K1*K3 + K2*K3) – S*(K1 + K2 + K3) – D*(2*K1*K2 + K1*K3)	A*(K1 + K2) + K1*K2 - S – D*K1	A + K1	1
n	A*K1*K2*K3 – S*(K1*K2 + K1*K3 + K2*K3) – 2*D1*K1*K2*K3 – D2*K1*K2*K3	A*K1*K2*K3 – S*(K1*K2 + K1*K3 + K2*K3) – 3*D*K1*K2*K3	A*K1*K2 – S*(K1 + K2) - 2*D*K1*K2	A*K1 – S – D*K1	A - D
n^0 (const.)	-S*K1*K2*K3	-S*K1*K2*K3	-S*K1*K2	-S*K1	-S

***Note 1**: The equation of state of a semiconductor doped with a stepwise ionizing acceptor and a fully ionizing donor is symmetrical to this [***]. The donor ionization constants are replaced by the acceptor ionization constants, D is replaced by A, A is replaced by D, and n is replaced by p—the molarity of holes in the semiconductor.*

The dependencies pn=f(A, D, $_{Ge,\ K1,\ K2})_T$, obtained by solving the General Equation of State (Yefimov S, 2024) are shown in Figure 1. We are interested in the position of the singular points of the curve, which include the equivalence points (the concentrations of n and p are equivalent) and the points of maximum buffer capacity, at which small variations in the impurity concentration led to minimal variations in the concentration of charge carriers.

In our case, the singular points of the curve are the inflection points. In the simplest case, the curve has one inflection point which can be visually determined (Figure 1a). In general, to find the inflection points, you need to differentiate the function whose graph we are considering twice, equate the second derivative to zero, and solve the resulting equation.

The function pn=f(A, D, $_{Ge,\ K1,\ K2})_T$, whose graph we are considering, is continuous and monotone (Figure 1 a, b, c), which means that the inverse function A=A(pn) is also continuous and monotone and has the same inflection points. The inverse function (its analytical expression) can be obtained directly from the equation of state (see below) because the terms A and D are presented in the General Equation of State in the first degree (Table 1). The inverse function A=A(pn) inflection points are easier to find (Yefimov S. 2023), so we will work with this inverse function.

Here is an example of the transformation of the function P = f(n, A, D) = 0 into the inverse function A = A(n, D): $P = n^4 + (A + K1 + K2)*\mathbf{n^3} + (A*(K1 + K2) + K1*K2 - S – D*K1)*n^2 +(A*K1*K2 – S*(K1 + K2) - 2*D*K1*K2)*n -S*K1*K2 = 0$, so, we can express A as function of n and D:

$A = [(S*K1*K2 – n^4 - n^3*(K1 + K2) – n^2*(K1*K2 – S – D*K1) + n*(K1*S + K2*S + 2*D*K1*K2)]/(n^3 + n^2*(K1 + K2) +n*K1*K2)$. Replacing n with pn we obtain the desired function A = A(pn) or, more simply, use a logarithmic scale for the o-n axis to display A=A(n).

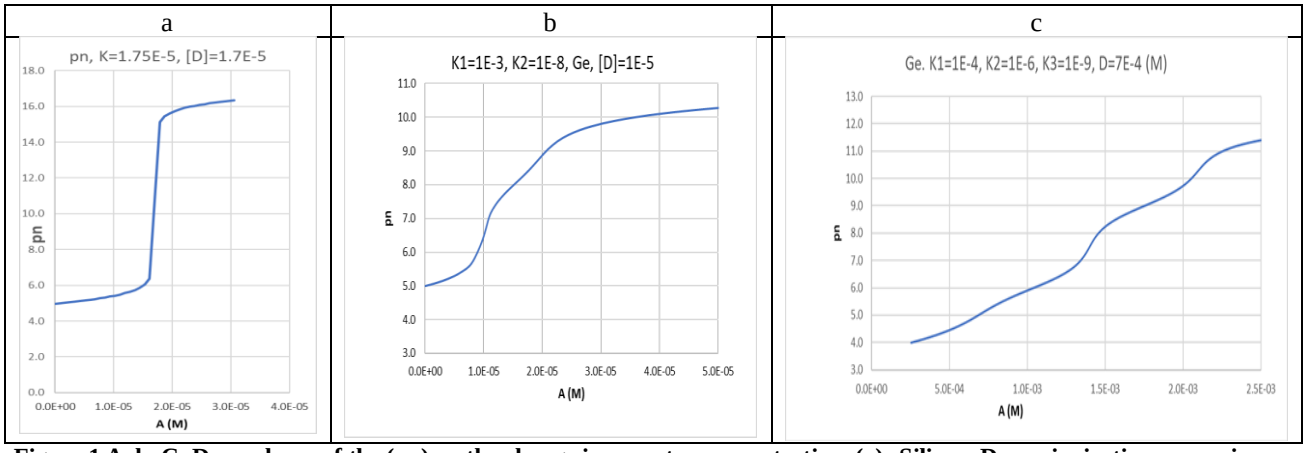

Figure 1 A, b, C: Dependence of the (pn) on the change in acceptor concentration. (a) -Silicon. Donor ionization occurs in one stage with the constant K1. (b) – Germanium. Donor ionization occurs in two stages with the constants K1 and K2. (c) - Germanium. The General Equation of State contains three ionization constants K1, K2, and K3 (Yefimov S. 2024)

Determination of equivalence points by double differentiation of the equation of state. The equivalence point corresponds to the inflection of the curve (A=A(pn)). To find this point, we need to calculate the second derivative (A") concerning pn of the equation of state A=A(n), equate it to zero, and find the roots of the resulting equation (BYU'S Inflection point 2023). Finding the roots of equation A"=0 is somewhat easier than finding the roots of the Equation of State (Yefimov S 2023) since we only need the numerical values of the singular points, that is, we can use any numerical method, for example, Newton's *root-finding algorithm*. Here we will apply an illustrative method of finding the roots, the Scaling Method. We will not calculate anything, but we will scale the plot of A" =A"(pn) and find the coordinate of the point of intersection of the curve with the O-pn axis.

To find out the first and second derivative of A, let's make a change of variables: $\mathbf{n=10^{-y}}$, where **y=pn**.
The derivative of **n** concerning **y** is equal to $\mathbf{-10^{-y}*ln(10)}$, i.e. **n'= -n*&**, where **&=ln(10)**.
The procedure for finding derivatives consists of 5 consecutive operations:

1) From the equation of state in normal form ($P=0=n^5 + a*n^4 + b*n^3 + c*n^2 + d*n + e$) extract A=A(n).
2) Find the first derivative of P concerning pn, given that **n'= -n*&.**
3) Extract A'=A'(n)
4) Find the second derivative of P concerning pn, given that **n'= -n*&**
5) Extract the desired second derivative: A"=A"(n)

Silicon. Completely ionizing donor and acceptor.
$n^2 + (A - D)*n - S = P=0$. (here we use the silicon constant (S))
$A=(S + n*D - n^2)/n = S/n + D – n$
$P'_{(y)} = -2*n^2*\& - n*A_{(y)}*\& + A'_{(y)}*n + n*D*\& \rightarrow$
$A'_{(y)}/\& = 2*n + A_{(y)} – D$ (first derivative)
$P''_{(y)} = 4*n*\&^2 + n*A_{(y)}*\&^2 – 2*n*(A'_{(y)}/\&)*\&^2 + n*A''_{(y)}*\&^2 – n*D*\&^2 \rightarrow$
$A''_{(y)}/\&^2 = D- A_{(y)} + 2*(A'_{(y)}/\&) – 4*n$ (second derivative)
$A''_{(y)}/\&^2 = S/n – n$

One singular point is the point of equivalence. $A''_{(y)}/\&^2 = 0 = S/n – n$, $n= \pm \sqrt{S}$, We choose positive root; $n = \sqrt{S}$, and $pn= -\text{Log10}(n)=10.6$. The Scaling Method (Figure 2 c) gives us the same result pn=10.6.

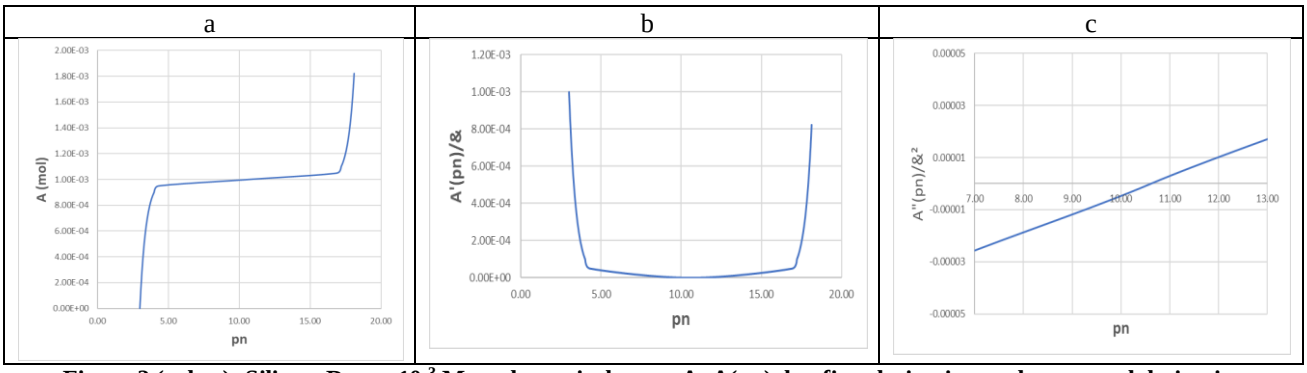

Figure 2 (a, b, c): Silicon. Donor 10^{-3} M, a- theoretical curve A=A(pn), b – first derivative, and c – second derivative

Silicon. One-stage ionizing donor with the constant K.

The equation of state, its first and second derivatives look like this: $P=n^3+n^2*(A+K)+n*(A*K-W-D*K)-S*K=0$, extract A: $A = (S*K + n*(S + D*K) – n^2*K – n^3)/(n^2 + K*n)$. $P'= -3*n^3*\&-2*n^2*(A+K)*\&+n^2*A'-n*(A*K-S-D*K)*\&+n*A'*K=0$, extract A':
$A'/\&= (A * (2n^2 + K*n) + 3n^3 + 2n^2*K - n*(S+ D*K))/(n^2 + K*n)$

$P''=9*n^3*\&^2+4*n^2*(A+K)*\&^2-4*n^2*A'*\&+A''*n^2+n*(A*K-S-D*K)*\&^2-2*n*A'*\&+A''*n*K=0$, extract A'':
$A''/\&^2= (A'/\& *(4*n^2 + 2*n*K) - A*(4*n^2 +n*K) - 4*K*n^2 - 9*n^3 + n*(S + D*K))/(n^2 + n*K)$

The estimated pn in the equivalence point by Scaling Method is 10.7 (Figure 3 c).

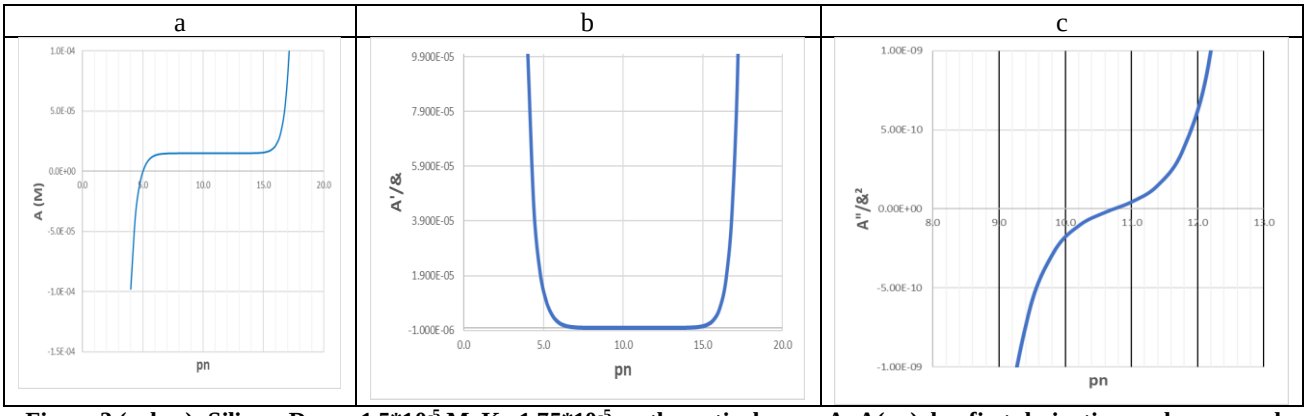

Figure 3 (a, b, c): Silicon. Donor $1.5*10^{-5}$ M, K= $1.75*10^{-5}$. a- theoretical curve A=A(pn), b – first derivative, and c – second derivative

Germanium. Two-stage ionizing donor with the constants K1 and K2, $P=n^4 + a*n^3 + b*n^2 + c* n + d = 0$.

$P= n^4+ A*n^3+n^3*(K1+K2) + A*a^2*(K1+K2) +n^2*(K1*K2 -Ge - D*K1) + A*n*K1*K2 - n*((K1+K2)*Ge+ 2*D*K1*K2) - Ge*K1*K2 = 0$, extract A:

$A=(-n^4-n^3*K1-n^3*K2- n^2*(K1*K2-S-K1*D)+n*((K1+K2)*Ge+2*D*K1*K2)+Ge*K1*K2)/(n^3+ n^2*(K1+K2)+n*K1*K2)$

$P'= -4*n^4*\& - 3*A*n^3*\&+ A'*n^3 - 3*n^3*(K1+K2)*\& - 2*A*n^2*(K1+K2)*\& + A'*n^2*(K1+K2) – 2*n^2*(K1*K2 -Ge - D*K1)*\& - A*n*K1*K2*\&+ A'*n*K1*K2 + n*((K1+K2)*Ge+ 2*D*K1*K2)*\& = 0$ extract A':

$A'=(4*n^4+3*n^3*(K1+K2)+2*n^2*(K1*K2-Ge-D*K1)-n*(Ge*(K1+K2)+2*D*K1*K2)+A*(3*n^3+2* n^2*(K1+K2)+n*K1*K2))/(n^3+ n^2*(K1+K2)+n*K1*K2)$.

$P''= 16*n^4*\&^2 + 9*n^3*A*\&^2-6*A'/\&*n^3*\&^2 + A''*n^3 + 9*n^3*(K1+K2) *\&^2 + 4*n^2*A*(K1+K2) *\&^2 - 4*A'/\&*n^2*(K1+K2) *\&^2 + A''*n^2*(K1+K2) + 4*n^2*(K1*K2-Ge-D*K1) *\&^2 + n*A*K1*K2*\&^2 - 2*A'/\&*n*K1*K2*\&^2 + A''*n*K1*K2 - n*(Ge*(K1+K2)+2*D*K1*K2) *\&^2= 0$, extract A'':

$A''/ \&^2 = (-16* n^4-9* n^3*(K1+K2)-4* n^2*(K1+K2-Ge-D*K1)+n*(Ge*K1*K2+2*D*K1*K2)+A'/\&*(6*n^3+4* n^2*(K1+K2)+2*n*K1*K2)-A*(9*n^3+4* n^2*(K1+K2)+n*K1*K2))/(n^3+ n^2*(K1+K2)+n*K1*K2)$.

The Scaling Method is used to find the roots of the equation $A''/\&^2=0$ (Figure 4 c). We have three roots corresponding to two equivalence points corresponding to the first and second ionization stages, respectively, pn = 6.4 and pn =8.8, and one inflection point located between them (pn=8.1). This last point corresponds to the state of the system in which a change in the impurity concentration in the semiconductor leads to the smallest change in the concentration of free charge carriers. By analogy with aqueous solutions, we will call it the point of maximum buffer capacity.

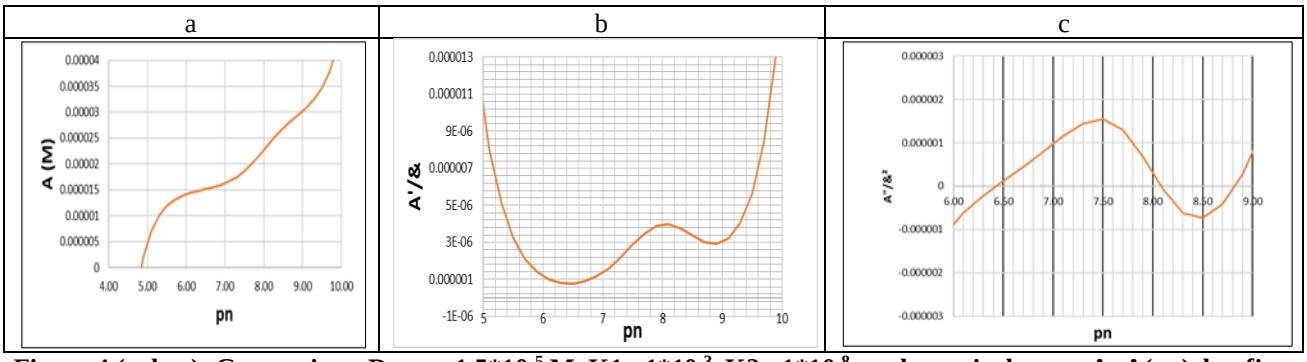

Figure 4 (a, b, c): Germanium. Donor, $1.5*10^{-5}$ M, K1= $1*10^{-3}$, K2= $1*10^{-8}$. a- theoretical curve A=A(pn), b – first derivative, and c – second derivative

Germanium. Three-stage ionizing donor with the constants K1, K2, and K3. $P= n^5 + a*n^4 + b*n^3 + c*n^2 +d* n + e = 0$ (Table 1).

To reduce the length of formulas, we introduce the following notation:

a=K1+K2+K3

b=K1*K2+K1*K3+K2+K3

c=K1*K2*K3

d=b-Ge-D*K1

e=c-Ge*a-D*(2*K1*K2+K1*K3)

f=Ge*b+3*D*c

g=Ge*c

Equation of state:

$P=n^5+n^4*(A+a)+n^3*(A*a+d)+n^2*(A*b+e)+n*(A*c-f)-g=0$. extract A:

$A= (-n^5-n^4*a-n^3*d-n^2*e+n*f+g) / (n^4+n^3*a+n^2*b+n*c)$

Remember: n'=-n*&

P'= -5*n^5*&-4*n^4*(A+a)*&+n^4*A'-
3*n^3*(A*a+d)*&+n^3*A'*a-2*n^2*(A*b+e)*&+n^2*A'*b-
n*(A*c -f)*&+ n*A'c= 0. extract A':
A'/&= [A*(4*n^4+3*n^3*a+2*n^2*b+n*c)
+5*n^5+4*n^4*a+3*n^3*d+2*n^2*e-n*f)] /
(n^4+n^3*a+n^2*b+n*c)
P"=25*n^5*&2+16*n^4*(A+a)*&2-
8*n^4*A'*&+n^4*A"+9*n^3*(A*a+d)*&2-
6*n^2*A'*a*&+n^3*A"*a+ 4*n^2*(A*b+e)*&2-
4*n^2*A*b*&+n^2*A"*b+n*(A*c-f)*&2-
2*n*A'*c*&+n*A"*c=0. extract A":

A"/&^{2}= [2*A'/&*(4*n^4+3*n^3*a+2*n^2*b+n*c)-
A*(16*n^4+9*n^3*a+4*n^2*b+n*c)-25*n^5-16*n^4*a-
9*n^3*d-4*n^2*e+n*f)] / (n^4+n^3*a+n^2*b+n*c)

The Scaling Method finds the roots of the A"/&2=0 equation (Figure 5 c). We have four roots corresponding to two points of equivalence and two points of maximum buffer capacity between them. The equivalence points are 5.0 pn, 7.5 pn, and 10.3 pn. The points of the maximum buffer capacity are pn=6.0 and pn=9.0.

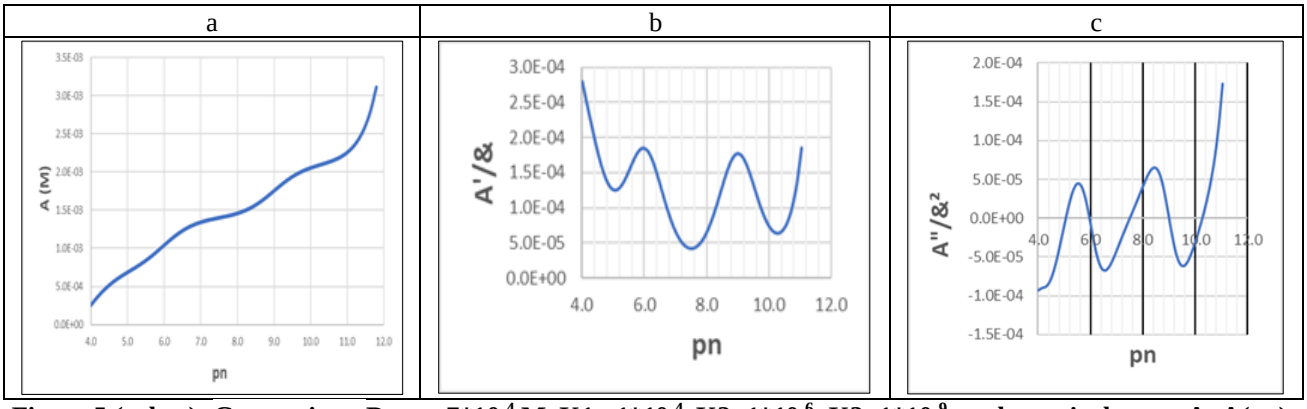

Figure 5 (a, b, c): Germanium. Donor 7*10^{-4} M, K1= 1*10^{-4}, K2=1*10^{-6}; K3=1*10^{-9}, a- theoretical curve A=A(pn), b – first derivative, and c – second derivative

Figure 6 shows a fragment of the EXCEL spreadsheet used to determine the singular points.

A = [Ge*K12*K2*K3 – n^5-n^4*(K1 + K2 + K3) – n^3*(K1*K2 + K1*K3 + K2*K3 – Ge – D*K1) – n^2*(K1*K2*K3 – Ge*(K1 + K2 + K3) – D*(2*K1*K2 + K1*K3)) + n*(W*(K1*K2 + K1*K3 + K2*K3) + 3*D*K1*K2*K3)]/(n^4 + n^3*(K1 + K2 + K3) + n^2*(K1*K2 + K1*K3 + K2*K3) + n*K1*K2*K3)

Ge=	1.60E-15	a=	0.000101	f=	2.1E-22
K1=	1.0E-04	b=	1.001E-10	g=	1.6E-34
K2=	1.0E-06	c=	1E-19	pK1=	4
K3=	1.0E-09	d=	-6.99E-08	pK2=	6
D=	7.00E-04	e=	-1.4E-13	pK3=	9

#	n(mol)	pn	A (M)	A'/&	A"/&²
1	1.00E-04	4.0	2.5E-04	2.8E-04	-9.3E-05
2	7.08E-05	4.2	3.4E-04	2.5E-04	-9.0E-05
3	5.01E-05	4.3	4.3E-04	2.2E-04	-8.8E-05
4	3.55E-05	4.5	5.0E-04	1.9E-04	-8.1E-05
5	2.51E-05	4.6	5.6E-04	1.6E-04	-6.8E-05
6	1.78E-05	4.8	6.1E-04	1.4E-04	-4.8E-05
7	1.26E-05	4.9	6.5E-04	1.3E-04	-2.5E-05
8	8.91E-06	5.1	7.0E-04	1.3E-04	-1.2E-06
9	6.31E-06	5.2	7.4E-04	1.3E-04	2.0E-05
10	4.47E-06	5.4	7.9E-04	1.4E-04	3.7E-05
11	3.16E-06	5.5	8.4E-04	1.5E-04	4.5E-05
12	2.24E-06	5.7	8.9E-04	1.7E-04	4.2E-05
13	1.58E-06	5.8	9.5E-04	1.8E-04	2.6E-05
14	1.12E-06	6.0	1.0E-03	1.9E-04	2.2E-06
15	7.94E-07	6.1	1.1E-03	1.8E-04	-2.5E-05
16	5.62E-07	6.3	1.1E-03	1.7E-04	-4.9E-05
17	3.98E-07	6.4	1.2E-03	1.5E-04	-6.3E-05
18	2.82E-07	6.6	1.2E-03	1.3E-04	-6.8E-05
19	2E-07	6.7	1.3E-03	1.0E-04	-6.3E-05
20	1.41E-07	6.9	1.3E-03	8.3E-05	-5.4E-05
21	1E-07	7.0	1.3E-03	6.6E-05	-4.2E-05
22	7.08E-08	7.2	1.4E-03	5.4E-05	-2.9E-05
23	5.01E-08	7.3	1.4E-03	4.6E-05	-1.6E-05

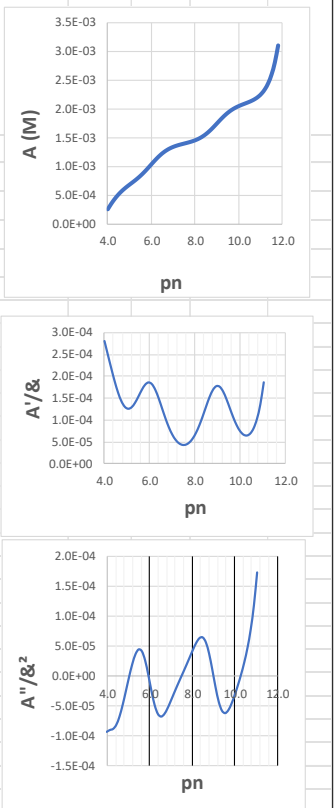

Figure 6: An example of an EXCEL spreadsheet for calculating A, A'/&, and A"/&2

CONCLUSION

This paper completes a series of two papers devoted to quantitative regularities of the state of charge carriers in doped semiconductors. The results of these studies may be useful to developers of semiconductor devices. For practical application of the obtained theoretical regularities, it is necessary to supplement them with experimentally determined values of the diffusion constants, electro diffusion, and impurity ionization constants. Having a complete set of data, it is possible to model the behavior of semiconductor devices, determine the limits of their applicability, and predict their lifetime.

Abbreviations:

K1, K2, and K3 – dopant ionization constants.
A – a molar concentration of acceptor in crystal.
D – a molar concentration of donor in crystal.
n – a molar concentration of electrons in the conduction band.
p - a molar concentration of holes in the conduction band.
S – the Silicon Constant ($S= n*p = 2.25*10^{20}$ cm^6 = $6.25*10^{-22}$ M^2)
Ge – the Germanium Constant ($Ge= n*p = 16*10^{-16}$ M^2)
$pn = - \log_{10}(n)$
P – normal polynomial.
&=ln(10) – constant.

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