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Equations for nonlinear diffusion

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Abstract. The diffusion is the result of Brownian movement and occurs with a finite velocity. We presented the nonlinear diffusion equation, with diffusion coefficient directly proportional to the impurities concentration. Analytical solutions, showing that the maximum displacements of diffusing particles are proportional to the square root of diffusion time like for Brownian movement, was obtained. For small concentrations of impurities, nonlinear diffusion equation transforms to linear.

Keywords: diffusion, diffusion coefficient, nonlinear diffusion equation, analytical solutions.

1 Introduction

This paper is stimulated by author's scientific investigations about period of thirty years. In late 1982 author proposed nonlinear diffusion equation with diffusion coefficient directly proportional to the impurities concentration. This equation corresponds to the diffusion process which can occur with a finite velocity. This statement is not satisfied in Fick's first and second laws or linear diffusion equation. The experimental profiles of boron and phophorus in crystal silicon were successfully approximated by the theoretical solutions of this nonlinear equation. The nonlinear diffusion equation was solved for temperature and for the diffusion coefficient depending on time in a special way. The temperature function $T(t)$ has a singularity at an arbitrarily chosen time moment t_0. The obtained analytical solutions describe the diffusion in the case of excited systems when the vacancies and the impurity atoms are not in thermal equilibrium with the lattice. The possibility of superdiffusion is shown considering the connection between the presented temperature function and the excited state population for atoms surrounding vacancies. The excited charged vacancies at room temperature in Si crystals were obtained by irradiation of the sample with soft X-rays. Diffusion coefficients for that excited vacancies are about 10^4 times large than diffusion coefficients of vacancies obtained by thermal heating. These excited vacancies we used for fast introducing Boron and Phosphorus at room temperature in crystal silicon. The obtained technologies can be used in production of new microprocessors and new devices.

In the result of a external perturbations the system can be transferred to no equilibrium state where distribution of temperature, pressure and concentration depends on coordinates $\vec{r}$ and are characterized by appropriate gradients $\nabla T(\vec{r}) \neq 0$, $\nabla n_i(\vec{r}) \neq 0$. The force of movement descended by these gradients generates the diffusion fluxes of mass and heat for i component of system

$$\vec{J_i} = -\alpha_i^{\mu} \nabla n_i - \alpha_i^T \nabla T. \tag{1}$$

Here α_i^{μ} and α_i^T proportionality coefficients, n_i concentration of i-th component of diffusing impurities. Using (1) for isothermical case we obtain diffusion flux density

$$J_i = -D_i \nabla n_i, \tag{2}$$

with diffusion coefficient D_i which depends on temperature, concentration of all components and chemical potential. Eq. (2) coincides with phenomenological Fick's first law published in 1855.

2 Models for the nonlinear diffusion

We discuss the properties of the nonlinear diffusion equation with the diffusion coefficient directly proportional to the concentration of the impurities presented in [7, 10, 3].

The diffusion coefficient must be equal zero in the region where the impurities are absent. In [7] the following nonlinear diffusion equation was proposed,

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial n}{\partial x}\right), \qquad j = -D \frac{\partial n}{\partial x}, \tag{3}$$

with the diffusion coefficient directly proportional to the impurities concentration

$$D(t, n) = D_n n(x, t). \tag{4}$$

Eqs. (3), (4) was proposed [7] as a new more physically motivated diffusion equation. This model includes the physically realistic model according to which the impurities flux (3) j, rewritten by the discretization method, differs from zero at the point $x + \Delta x$

$$J(x + \Delta x, t) \approx -D_n n(x, t) \frac{n(x + \Delta x, t) - n(x, t)}{\Delta x}$$

only if impurities present at the point x.

Physically, the latter equation means that the length of the jump of diffusing particles from the point x to $x + \Delta x$ in the diffusion process is not greater than Δx and jump is possible only when a diffusing particle exists at the point x. In this model, the maximum penetration depth of diffusing impurities has finite value, and it grows with finite velocity.

For nonlinear diffusion [7] in solids

$$D_n = \frac{D_0}{N_a} e^{\frac{-E}{kT}}, \tag{5}$$

where D_0 is the pre-exponential factor, E is the activation energy and N_a is nonlinearity coefficient.

Later (3) was presented in [10] as the diffusion equation for a high-concentration of boron and phosphorus which included effects such as lattice vacancy generation and the internal electric field. In this case the diffusion coefficient was expressed in the form [10]

$$D = D_i\left(\frac{2\beta}{1+\beta}\right)\frac{n}{n_{ie}}, \tag{6}$$

where D_i is the intrinsic diffusivity, n_{ie} is the intrinsic carrier concentration and β is a phenomenological constant.

The offer (4) has been made by very common theoretical assumption that diffusion is result of Brownian movement and diffusion must occur with finite velocity.

Now we will consider similarity solution of the nonlinear diffusion equation (3) with boundary

$$n(0, t \geqslant 0) = N_s, \qquad n(\infty, t) = 0 \tag{7}$$

and the initial

$$n(x, 0) = 0, \quad x > 0 \tag{8}$$

conditions. Introducing the similarity variable [3]

$$\xi = \frac{x}{\sqrt{D_s t}}, \qquad D_S = D_n N_s, \tag{9}$$

and

$$n(x, t) = N_s f(\xi), \tag{10}$$

into (3) we can get the nonlinear ordinary differential equation

$$2\frac{d}{d\xi}\left(f\frac{d}{d\xi}f\right) + \xi\frac{d}{d\xi}f = 0. \tag{11}$$

We can express the solution of the nonlinear equation (11) in the power series

$$f(\xi) = \sum_{n=0}^{\infty} a_n \xi^n. \tag{12}$$

From the boundary conditions (7), (9), (10) we obtain $a_0 = 1$. Substituting (12) into (11) we obtain the system of equations [7, 3]

$$\begin{gathered} 2\sum_{m=0}^{n}(n+1-m)(m+1)a_{n+1-m}a_{m+1} + 2\sum_{m=0}^{n} c_{nm} + n a_n = 0, \\ c_{nm} = (n+2-m)(n+1-m)a_{n+2-m}a_m, \quad n = 1, 2, 3 \ldots. \end{gathered} \tag{13}$$

Taking in (12) a finite number of coefficients and solving the system of equations (13) we obtain the second approximate solutions for (11)

$$\begin{gathered} N_4 = N_s\left(1 - 0.4439\xi - 0.09855\xi^2 - 6.754\times10^{-3}\xi^3 + 3.582\times10^{-4}\xi^4\right), \\ 0 \leqslant \xi \leqslant \xi_{04}, \quad \xi_{04} = 1.615, \quad x_{04} = 1.615\sqrt{N_s D_n t}, \quad 0 \leqslant x \leqslant x_{04}, \end{gathered} \tag{14}$$

$$\begin{aligned} N_5 = N_s\big(&1 - 0.4436\xi - 0.09837\xi^2 - 6.671\times10^{-3}\xi^3 + 4.002\times10^{-4}\xi^4 \\ &+ 2.157\times10^{-5}\xi^5\big), \quad \xi_{05} = 1.617, \quad x_{05} = 1.617\sqrt{N_s D_n t}, \quad 0 \leqslant x \leqslant x_{05}. \end{aligned} \tag{15}$$

The obtained approximate solutions satisfy boundary (7) and initial (8) conditions. Obtained maximum penetration depts of impurities (14), (15) are proportional to $\sqrt{t}$ and coincide with Brownian movement theory [8]. Substituting ξ_{04} into N_4 we get 1.71×10^{-3}, whence we see that the roots ξ_{04} and the solutions N_4 are obtained with sufficient accuracy. Solutions (14) and (15) approximately coincide. If $N_a = N_s$ we can obtain from (15) that the maximum penetration depth of an impurities into the solids is

$$\xi_0 = 1.617\sqrt{D_s t}. \tag{16}$$

In this case the diffusion coefficient at the surface D_s attains the standard meaning. On the frontier of diffusion for $x = x_0$ the concentration of impurities and diffusion coefficient (4) is decreasing to zero. x_0 defines the maximum penetration depth of impurities which approximately equals square root from the mean-square displacement [8]

$$\sqrt{x^2} = \sqrt{2D_c t}, \quad D_c = \frac{\varDelta^2}{2\tau}, \tag{17}$$

where $\varDelta$ is a atom jump and τ is the average time between the elementary jumps. From this we can draw the conclusion that D_s approximately equals D_c. The proof of (17) is based on the equality of the probability jumps in the positive and negative directions. The atom can diffuse by the vacancy mechanism. A vacancy must occupy the nearest neighbour positions of a diffusing atom and the number of free vacancies in positive direction must be larger and $D_s > D_c$.

Theorem 1. *The diffusion coefficient for nonlinear diffusion* (5) *multiplied by impurities concentration at the source is aprohimately equal to the diffusion coefficient for the linear diffusion.*

We will prove this theorem considering diffusion on the frontier, including fact about diffusion with finite velocity. For the one-dimensional case the flux density expression in the point x_0 can be written as

$$j = \frac{\varDelta}{2\tau}\left[\rho\left(x_0 - \frac{1}{2}\varDelta\right) - \rho\left(x_0 + \frac{1}{2}\varDelta\right)\right]. \tag{18}$$

On the frontier of diffusion

$$\rho\left(x_0 + \frac{1}{2}\varDelta\right) = 0. \tag{19}$$

Taking into account (17) and (18) can be approximated with reasonable accuracy,

$$j = -\left(\frac{\varDelta^2}{2\tau}\right)\frac{\rho(x_0)}{\rho(x_0 - \frac{1}{2}\varDelta)}\left(\frac{\varDelta\rho}{\varDelta}\right)_{x_0}, \qquad \frac{\varDelta\rho}{\varDelta} = \frac{d\rho}{dx}. \tag{20}$$

From the formulaes (20) and (19) we find that the flux density on the frontier

$$j = -\frac{D_c}{\rho(x_0 - \frac{1}{2}\varDelta)}\rho(x_0)\left(\frac{d}{dx}\rho\right)_{x_0} \tag{21}$$

satisfies the nonlinear diffusion equations (3), (4).

Comparing (21) with (3)–(5) we obtain

$$\frac{D_c\rho(x_0)}{\rho(x_0-\frac{1}{2}\Delta)}=\frac{D_0e^{-\Delta E/kT}n}{N_a}. \tag{22}$$

We can define the linear diffusion coefficient D of impurities in standart form

$$D_c\approx D=D_0e^{-\Delta E/kT} \tag{23}$$

on the frontier of diffusion from (4) and (23) we have

$$N(x_0)=N_a\frac{\rho(x_0)}{\rho(x_0-\frac{1}{2}\Delta)}. \tag{24}$$

This condition is satisfied near the surface $N_a=N_s$. We obtained that $D_s=D_0N_s=D$ and theorem is proved. Using this result we can compare theoretical prifiles of impurities in crystal with experiment [9, 2].

We assume that the process of spreading of impurities is similar to other diffusion processes and, in the nonlinear case, can be described by nonlinear flow density I. In the case of three dimensions when the frequencies of the jumps depends upon the particle coordinates and the time variation of the impurities concentration $n(x,y,z,t)$ we have [1]

$$\begin{aligned}
&\frac{\partial n}{\partial t}=I_x+I_y+I_z,\\
&I_x=v(x+L,y,z)n(x+L,y,z)+v(x-L,y,z)n(x-L,y,z)-2vn,\\
&I_y=v(x,y+L,z)n(x,y+L,z)+v(x,y-L,z)n(x,y-L,z)-2vn,\\
&I_z=v(x,y,z+L)n(x,y,z+L)+v(x,y,z-L)n(x,y,z-L)-2vn,
\end{aligned} \tag{25}$$

Here, L is the average free path of the particles of smoke or molecules of impurities in gases, or the length of the jump of molecules or atoms from one equilibrium position to another in fluids and solids; v are the frequencies of these collisions or jumps [5, 6].

Using sufficiently exact [5] expanding (25) in the power series and including three main terms in the expansions of v and n, we obtain the following nonlinear equation:

$$\frac{\partial n}{\partial t}=L^2v\Delta n+2L^2(\operatorname{grad}v)(\operatorname{grad}n)+L^2n\Delta v=L^2\Delta(v,n). \tag{26}$$

We here used the frequency of collisions the same like in [5].

$$v(x,y,z,t)=\frac{1}{2}\sigma n(x,y,z,t)\cdot u\sqrt{2}.$$

Theorem 2. *When diffusion coefficient is appointed on the frontier the diffusion process must be definited by nonlinear equation* (3), (4)*.*

Taking into account that experimental diffusion coefficients are usually defined on the front of diffusion profiles, we can replace $\operatorname{grad}v$ by (27) $\operatorname{grad}v_f$ on the right side of (26) where [5] $v=\sigma Nu\sqrt{2}$, $D=\sqrt{2}L^2\sigma un$ we obtain the following nonlinear equation

$$\frac{\partial n}{\partial t}=D_n\big[n\Delta n+(\operatorname{grad}n)^2\big],\quad D_n=\frac{D}{N_s} \tag{27}$$

which coincide with nonlinear diffusion equations (3), (4). Theorem 2 is improved.

This Theorem 2 and nonlinear diffusion equation (27) is very important for diffusion in solids [7, 10, 3], when diffusion occure through vacancies in lattice, because in electronic devices production by diffusions processes the densites of introduced impurities in semiconductors are the same oder like density of vacancies.

Theorem 3. *When diffusion coefficient depends only on density of solvent gas the diffusion equation* (26) *transforms to linear diffusion equation or second Fick's law.*

This theorem we improve substituting in (26) the average frequencies of collisions in solvent gas [5] or impurities atoms jumps in solids. This situation can occure only for small concentration impurities diffusion when impurities can not introduce any changes in solvent gas and ν become constant.

It is interesting to consider the presented nonlinear equations and decide which kind of obtained nonlinear diffusion equations conform with Fokker's–Plank's equation. At first was proposed first nonlinear diffusion equations [7, 3], (3), (4) and we can present the second nonlinear diffusion equation for diffusion of impurities by interstitials in solids [6]

$$\frac{\partial n}{\partial t} = \frac{\partial^2}{\partial x^2}\big[D(x)n\big]. \tag{28}$$

The equations (3) and (28) can be rewritten using method of finite differences

$$\frac{\partial n}{\partial t} = \frac{1}{L^2}\big(D_{k+1/2}(n_{k+1} - n_k) - D_{k-1/2}(n_k - n_{k-1})\big), \tag{29}$$

$$\frac{\partial n_k}{\partial t} = \frac{1}{L^2}(D_{k+1}n_{k+1} - 2D_k n_k + D_{k-1}n_{k-1}). \tag{30}$$

In the equations (3), (29) diffusion coefficient is defined between two sites of lattice and depends on its states. This nonlinear diffusion equation did not fit to Fokker's-Planck's equation and can describe the diffusion through vacancies or in excited states [4]. In the nonlinear diffusion equations (28), (30) diffusion coefficient depends only on coordinate of equilibrium place and probability of jump like for Brownian movement is independent on direction. Nonlinear equation (28) can be applied to interstitial diffusion.

3 Conclusions

The obtained in [6] nonlinear diffusion equation (26) can be transformed in to the nonlinear equations (3), (4) when introduced diffusion coefficient is proportional to the impurities concentration and was definited in the region where density of impurities are equal half density of solvent. When concentration of impurities is small and diffusion coefficient depends only on solvent parameters the equation (26) transform to simple linear diffusion equation or to second Fick's law.

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REZIUMĖ

Netiesinės difuzijos lygtys

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Straipsnyje pateiktos netiesinės difuzijos lygtys aprašančios priemaišų difuziją vykstančią baigtiniu greičiu. Įvestas netiesinės difuzijos koeficientas proporcingas priemaišų koncentracijai. Gauti analiziniai netiesinės difuzijos lygties sprendiniai parodantys kad maksimalus priemaišų įsiskverbimo gylis yra proporcingas kvadratinei šakniai iš difuzijos laiko kaip ir Brauno judėjimo atveju. Dėl mažų priemaišų koncentracijų netiesinė lygtis virsta tiesine.

Raktiniai žodžiai: difuzija, difuzijos koeficientas, netiesinė difuzijos lygtis, analiziniai sprendiniai.