https://doi.org/10.46813/2024-149-099

UDC 539.2:620.18

MATHEMATICAL MODELLING OF IMPURITY MOTION ATOMS IN THE GRADIENT PRESSURE FIELD OF MELTS

V.O. Skachkov, O.R. Berezhna, H.V. Karpenko
Zaporizhzhia National University, Zaporizhzhia, Ukraine
E-mail: abkarpenko2017@gmail.com

The paper explores the feasibility of purifying semiconductor materials by removing impurity atoms within a hydrostatic pressure gradient field. The study employs a computational experiment using a rapidly rotating disc with a slot-type internal cavity filled with an alloy melt containing impurity atoms as a model. To perform the calculations, a differential equation is formulated and solved, describing the movement of impurity atoms in response to the pressure gradient generated by the disc's rotation. The speed of movement of impurity atoms in the radial direction and the time of movement of atoms were determined by calculation.

INTRODUCTION

To execute these calculations, an algorithm and a program were developed within the TurboPascal environment. The calculations yielded results, including the velocities of impurity atom movement along the radial direction and the maximum duration of atom movement along the inner and outer walls of the slot cavity of the disc.

At present, a large number of methods and technologies for deep purification of semiconductor materials for electronic elements, solar energy and other scientific and technical areas have been developed.

Wide application of high-purity materials implies further increase of economic efficiency of their obtaining, improvement of functional characteristics and increase of the yield of the final product.

Physical methods of obtaining high-purity materials are often enough used. A review of such methods is presented in [1]. These methods are realised in solid, solid-liquid and liquid phases [2–5].

The distribution of impurity atoms in heterostructures allows controlling a number of properties of semiconductor systems. The most efficient distribution of impurity atoms is possible by the method of its fixation from the metal melt by crystallisation [6].

One of the important characteristics of melts responsible for atomic transport is viscosity. Models for estimating the kinetic parameters of melts are discussed in [7–9].

Diffusion processes are no less important mechanisms evaluating the redistribution of impurity atoms in the metal melt. Bulk diffusion processes are described in [10], diffusion mechanisms in disordered systems are presented in [11], diffusion coefficients of liquid metals are defined in [12]. Diffusion mechanisms allow us to determine the migration of impurity atoms in the volume of metal melt.

The pressure gradient causes some movement of melt atoms. The interaction of bodies and liquid is considered in [13]. In this paper, the ultimate ratios for determining the flow of a liquid in circular rotation are obtained, and it is established that a homogeneous liquid rotates as a solid body.

Purpose of the work. To develop a mathematical model and estimate quantitative parameters of the impurity atoms motion of different grades in the gradient pressure field of multicomponent melts.

MODEL DEVELOPMENT

We consider a melt consisting of a matrix medium with density of ρ_m and N impurity atoms with density ρ_i ($i = \overline{1.N}$). Part of impurity atoms have density below ρ_m, the rest of atoms have density above ρ_m.

The mathematical model is developed under the assumption that:

1. The volume density of the melt is weakly dependent on the presence of impurity atoms. The number of impurity atoms is small enough.
2. Impurity atoms are uniformly distributed throughout the melt volume.
3. The electrochemical interaction of atoms is assumed to be small enough and is not taken into account.
4. Atoms do not form chemical compounds.
5. Diffusion rates of atoms are assumed to be sufficiently small and are not taken into account.
6. The hydrostatic pressure is equal-dimensional along the thickness of the melt layer.
7. The melt layer is sufficiently small. Under hydrostatic pressure, the melt layer rotates like a solid.

The density of the melt ρ_p is determined by the mechanical mixture rule and is calculated by the formula:

$$\rho_p = \sum_{i=1}^{N} P_i \rho_i ,$$

where P_i – is the volume content of atoms of variety i.

The density of atoms of variety i is determined by

$$\rho_i = (\frac{4}{3}\pi r_i^3)^{-1} \cdot M_i ,$$

where r_i – is the radius of atoms of variety i; M_i – atomic mass of atoms of variety i.

A gradient pressure field is realised in a thin layer of a rotating disc with melt at a speed of n revolutions per

minute. Under these conditions, the centrifugal force F_i^c acting on the atoms of variety *i* is determined by:

$$F_i^c = \frac{4}{3}\pi r_i^3 (2\pi n)^2 \rho_i \left(R_i^0 + S_i\right), \quad (1)$$

where R_i^0 – is the initial position along the radius of atoms of variety *i*; S_i – the length of the path of motion of atoms of variety *i*; ρ_i – the density of impurity atoms of variety *i*; r_i – the radius of impurity atom of variety *i*; *n* – the number of revolutions of the rotating disc with the melt.

Power of friction resistance during the movement of atoms in the melt:

$$F_i^R = -6\pi\mu \frac{\partial S_i}{\partial t} r_i, \quad (2)$$

where F_i^R – is the frictional resistance force at the movement of atoms of variety *i*; μ – is the dynamic melt viscosity.

The melt viscosity in (2) can be given by the ratio, which takes into account the changes due to the creation of a hydrostatic pressure gradient in the melt:

$$\mu = \mu_0 = (1 + \frac{4}{3} k\pi\rho_m r_m^3 (2\pi n)^2 (R_i^0 + S_i), \quad (3)$$

where μ_0 – is the dynamic viscosity of the melt in the free condition; *k* – is the coefficient determining the change of the melt viscosity depending on the pressure value.

The value of hydrostatic pressure of the melt at the point (R_i^0 + S_i):

$$F_i^h = \frac{4}{3}\left(\pi\rho_m r_m^3\right)(2\pi n)^2 (R_i^0 + S_i), \quad (4)$$

where F_i^h – is the force of hydrostatic pressure of the melt; ρ_m – is the density of matrix melt atoms; r_m – is the radius of a matrix melt atom.

The inertial forces acting on the moving atoms of grade i are defined by:

$$F_i^{in} = \frac{\partial^2 S_i}{\partial t^2} \cdot \frac{4}{3}\pi r_i^3 \rho_i, \quad (5)$$

where F_i^{in} – is the inertial force acting on the atoms of variety *i*.

Considering (1), (2), (3), (4), and (5) the general equation for the motion of atoms of sort i in the melt along the radius direction will be:

$$\frac{\partial^2 S_i}{\partial t^2} \cdot \frac{4}{3}\pi r_i^3 \rho_i = \frac{4}{3}\pi r_i^3 (2\pi n)^2 \rho_i (R_i^0 + S_i) - \\ - 6\pi\mu_i \frac{\partial S_i}{\partial t} r_i - \frac{4}{3}\pi (2\pi n)^2 \left(r_m^3 \rho_m\right)(R_i^0 + S_i). \quad (6)$$

After algebraic transformations, equation (6) will be written in the form:

$$\frac{\partial^2 S_i}{\partial t^2} + \alpha \frac{\partial S_i}{\partial t} - \beta (R_i^0 + S_i) = 0, \quad (7)$$

where $\alpha = \frac{9}{2} \frac{\mu_0 \left(1 + 4\pi k (2\pi n)^2 \rho_m r_m^3 \frac{R_i^0}{3}\right)}{\rho_i r_i^2}$;

$$\beta = (2\pi n)^2 \left(1 - \frac{r_m^3 \rho_m}{r_i^3 \rho_i}\right).$$

Equation (7) must satisfy the boundary conditions:

$$S_i\big|_{t=0} = R_i^0; \quad (8)$$

$$\left.\frac{\partial S_i}{\partial t}\right|_{t=0} = 0. \quad (9)$$

The solution of equation (7), taking into account conditions (8) and (9), will have the form:

$$S_i = \frac{2R_i^0 k_2}{k_2 - k_1} e^{k_1 t} + \frac{2R_i^0 k_1}{k_1 - k_2} e^{k_2 t} - R_i^0, \quad (10)$$

where

$$k_1 = -\frac{\alpha}{2} - \sqrt{\frac{\alpha^2}{4} + \beta}; \\ k_2 = -\frac{\alpha}{2} + \sqrt{\frac{\alpha^2}{4} + \beta}.$$

The speed of motion V_i

$$V_i = \frac{dS_i}{dt} = \frac{2k_1 k_2 R_i^0}{(k_2 - k_1)} \left[e^{k_1 t} - e^{k_2 t}\right]. \quad (11)$$

The motion of atoms along the radius direction from the center or towards the center of rotation gives rise to the Coriolis acceleration, which is defined in the form:

$$\overrightarrow{W_k} = \vec{\varpi} \times \vec{V}, \quad (12)$$

where $\vec{\varpi}$ – the vector of rotation velocity; $\vec{V}$ – the velocity of atoms moving along the radius.

The Coriolis force is defined by:

$$F_i^C = \vec{W}_k \frac{4}{3}\pi r_i^3 \rho_i. \quad (13)$$

The Coriolis force ensures the motion of the atoms of grade i along the direction of the circumferential coordinate. When moving along the circumferential coordinate, there is no hydrostatic pressure gradient and the atoms of sort i are influenced only by the force Coriolis (12) and the frictional resistance force of type (2). In this case, the equation of motion of atoms of sort i along the circumferential direction in scalar form can be written:

$$\pm \frac{2\pi n}{60} \frac{dS_i}{dt} \cdot \frac{4}{3}\pi r_i^3 \rho_i = 6\pi\mu_i \frac{dS_i^\varphi}{dt} r_i, \quad (14)$$

where S_i^φ – is the path of motion of atoms of variety *i* along the circumferential direction.

In (14), the "+" sign is for atoms moving from the center of rotation, and the "-" sign is for atoms moving towards the center of rotation.

By transforming equation (14) taking into account (11), the ratio determining the speed of atoms moving along the circumference is obtained:

$$\frac{dS_i^\varphi}{dt} = \frac{2\pi n r_i^2 \rho_i k_1 k_2 R_i^0}{135(k_2 - k_1)\mu_i} \left[e^{k_1 t} - e^{k_2 t}\right]. \quad (15)$$

Integration of equation (15) over time from 0 to t results in the solution in the form:

$$S_i^{\varphi} = \frac{\eta}{k_2}(1-e^{k_2 t}) - \frac{\eta}{k_1}(1-e^{k_1 t}), \qquad (16)$$

where $\eta = \frac{2\pi n r_i^2 \rho_i k_1 k_2 R_i^0}{135(k_2-k_1)\mu_i}$.

The total velocity V_i^{Σ} of motion of atoms of variety *i* along the radial-circumferential direction is written:

$$V_i^{\Sigma} = \frac{dS_i^{\Sigma}}{dt} = \sqrt{V_i^2 + (V_i^{\varphi})^2}, \qquad (17)$$

where V_i, V_i^{φ} – are the velocities of motion of atoms of variety *i* along the radius and circumferential directions, respectively.

The relation (17), taking into account (11) and (15), will be written as:

$$\frac{dS_i^{\Sigma}}{dt} = \frac{2k_1 k_2 R_i^0}{(k_2-k_1)_i}\left(e^{k_1 t} - e^{k_2 t}\right)\sqrt{1+\left[\frac{\pi r_i^2 \rho_i n}{135\mu_i}\right]^2}. \qquad (18)$$

By integrating (18) over *S* from 0 to S_i^{Σ} and over time from 0 to *t*, the length of the total path travelled by an atom of variety *i* in time *t* is obtained:

$$S_i^{\Sigma} = \frac{2k_1 k_2 R_i^0}{(k_2-k_1)_i}\left[\left(\frac{1}{k_1}(e^{k_1 t}-1) + \frac{1}{k_2}(1-e^{k_2 t})\right)\right] \times$$

$$\times\sqrt{1+\left[\frac{\pi r_i^2 \rho_i n}{135\mu_i}\right]^2}. \qquad (19)$$

The tangent of the angle of inclination of the circumferential velocity vector to the radial velocity vector will be:

$$tg(\phi) = \frac{V_i^{\phi}}{V_i} = \frac{\pi r_i^2 \rho_i n}{135\mu_i}. \qquad (20)$$

The value of the angle of inclination of the circumferential velocity to the radial velocity follows from relation (20):

$$\varphi = arctg\left(\frac{\pi r_i^2 \rho_i n}{135\mu_i}\right). \qquad (21)$$

Ratio (21) shows that the angle of inclination of the circumferential velocity vector to the radial velocity vector depends on the rotational velocity *n* and remains constant for atoms of variety i along the whole trajectory of their motion.

CALCULATION RESULT

To realise the calculation experiment, a silicon melt with uniformly distributed impurity atoms was used. The component composition of silicon melt and the characteristics of impurity atoms for the calculations are presented in Table [14].

As a working unit of the experimental unit a horizontally collapsible disc rotating on an axis is chosen, consisting of hermetically assembled lower and upper halves, in the inner flat cavity of which there is silicon melt.

The impurity atoms of carbon, chromium and cobalt have density higher than the density of silicon atoms and they move in the direction from the inner radius of the disc cavity to the outer one (curves 1–3, Fig. 1). The density of phosphorus and boron atoms is lower than the density of silicon atoms. These atoms move in the direction from the outer radius of the disc cavity wall to the inner radius (see curves 4 and 5, Fig. 1).

Initial data for calculations [14]

N	Atom	Radius of atoms, $r_i 10^{-9}$, m	Atomic mass, $M_i \cdot 10^{-27}$, kg	Melt content, % wt.	Initial position, R_0, m
1	C	0.077	12.011	0.05	0.290
2	B	0.091	10.810	0.03	0.283
3	Cr	0.127	51.996	0.04	0.058
4	Co	0.125	58.933	0.02	0.057
5	F	0.130	30.974	0.06	0.060
6	Si	0,134	28.986	the rest	0.050…0.29

The upper and lower halves of the disc are in a temperature field, which provides a given temperature of the melt. The radius of the inner wall of the disc cavity is 50 mm and the radius of the outer wall is 300 mm. The motion of impurity atoms was calculated both from the inner wall to the outer wall and from the outer wall to the inner wall. The calculation was carried out using the developed program in TurboPascal language

Fig. 1 shows the trajectories of impurity atoms motion as a function of process time. The calculated speed of disc rotation was taken as 30000 rpm.

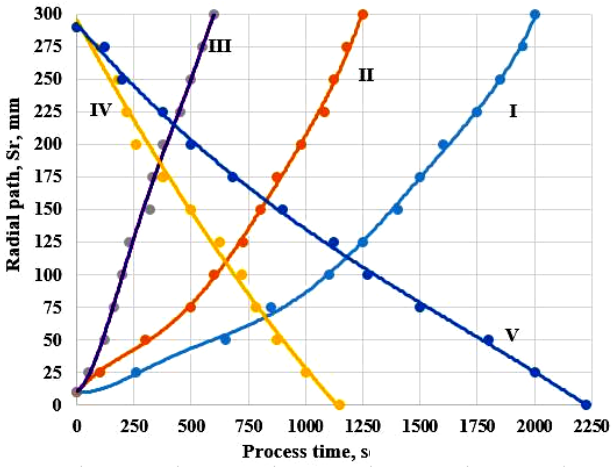

Fig. 1. Trajectory of impurity atoms movement as a function of process time (I – carbon atoms; II – chromium atoms; III – cobalt atoms; IV – phosphorus atoms; V – boron atoms)

Fig. 2 shows the curves of change of radial velocity of impurity atoms depending on the travelled path from the beginning of the process (I – carbon atoms; II – chromium atoms; III – cobalt atoms; IV – phosphorus atoms; V – boron atoms).

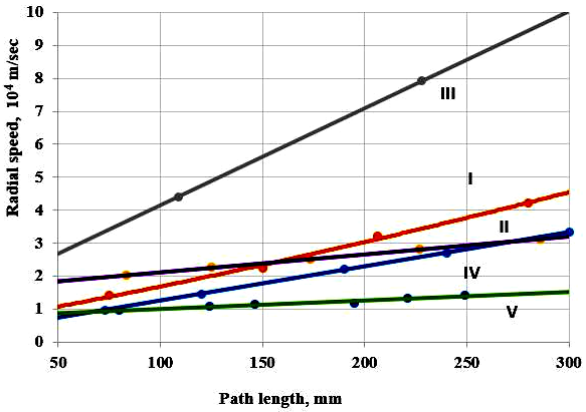

Fig. 2. Changes in radial velocity of impurity atoms depending on the travelled path from the beginning of the process

The velocities of impurity atoms depending on their density at the maximum radius of 300 mm change from $1.5 \cdot 10^{-4}$ m/s (boron) to $13.5 \cdot 10^{-4}$ m/s (cobalt).

The velocities of impurity atoms, depending on their density at the minimum radius of 50 mm, vary from $0.64 \cdot 10^{-4}$ m/s (carbon) to $2.5 \cdot 10^{-4}$ m/s (cobalt).

Carbon and boron atoms have a negative velocity that is directed towards the center of rotation.

CONCLUSIONS

The final formulae for calculating the motion of impurity atoms in the melt along the radius direction, along the circumferential direction and the calculated physical trajectory have been obtained. Quantitative calculations have been carried out to determine the time of motion of impurity atoms with density above the density of the matrix melt from the radius of 50 mm to the radius of 300 mm and impurity atoms with density below the density of the matrix melt from the radius of 300 mm to the radius of 50 mm.

REFERENCES

1. V.M. Azhazha, G.P. Kovtun, I.M. Neklyudov. Complex approach to obtaining high-purity materials for microelectronics // *Technology and Design in Electronic Equipment*. 2002, N 6, p. 3-6.

2. V.M. Azhazha, G.P. Kovtun, G.F. Tikhinsky. Obtaining and Metallophysics of Highly Pure Metals // *Metallophysics and New Technologies*. 2000, v. 22, N 2, p. 21-35.

3. V.A. Skachkov, O.R. Berezhnaya, T.V. Kritskaya. Modelling of impurity atoms transfer in inhomogeneous field of microvoltages of polycrystal // *Nauki notatki*. Lutsk, LNTU, 2013, issue 41, part 1, p. 237-241 (in Ukraine).

4. V.T. Tolok, V.G. Padalka. Development and implementation of new methods of vacuum-plasma technology of high energies // *Bulletin of the Academy of Sciences of the Ukrainian* SSR. 1979, N 4, p. 40-50.

5. Y.G. Krivonos, V.G. Pisarenko, I.A. Varava. Modelling of intelligent control of crystallization of metallic melts // *Artificial Intelligence*. 2009, N 3, p. 234-241.

6. Ya.N. Frenkel. *Kinetic theory of liquids*. M.: Publishing House of the Academy of Sciences of the USSR, 1945, 424 p.

7. V.V. Brazhkin, A.G. Lyapin. Universal growth of viscosity of metallic melts in megabar pressure range // *Uspekhi physicheskikh nauk*. 2003, v. 170, N 5, p. 535-551 (in Russian).

8. V.I. Lesin, S.V. Lesin. Fractal formula of dependence of viscosity of non-Newtonian liquid on velocity gradient // *Oil economy*. 2012, N 3, p. 46-48.

9. V.N. Chuvildeev, E.S. Smirnova. Mechanisms of volume diffusion at “high” and “low” // *Physics of Solid State*. 2011, v. 53, N 4, p. 727-732.

10. D.K. Belashchenko. Mechanisms of diffusion in disordered systems (computer modelling) // *Uspekhi physicheskikh nauk*. 1999, v. 169, N 4, p. 380-382 (in Russian).

11. A.A. Vostryakov, E.A. Pastukhov, N.I. Sidorov, I.S. Sipatov. Diffusion in Ta, Nb and Zr melts // *Mathematical modelling. Metallurgical processes*. 2012, v. 30, N 5, p. 20-24.

12. A.Ya. Milovich. Theory of dynamic interaction of bodies and liquid // *State Energy Publishing House*. Moscow-Leningrad, 1940, 240 p.

13. V.S. Urusov. *Theoretical Crystallochemistry*. M.: Izd. MSU, 1987, 275 p.

14. V.A. Rabinovich, Z.Ya. Khavin. *Brief chemical reference book.* Leningrad: “Khimiya”, 1991, 432 p.

Article received 02.10.2023

МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ РУХУ ДОМІШКОВИХ АТОМІВ У ГРАДІЄНТНОМУ ПОЛІ ТИСКУ РОЗПЛАВІВ

В.О. Скачков, О.Р. Бережна, Г.В. Карпенко

Показано можливість очищення напівпровідникових матеріалів від домішкових атомів у градієнтному полі гідростатичних тисків. В якості моделі для розрахункового експерименту використовується диск, що обертається, з внутрішньою порожниною щілинного типу, який заповнений розплавом сплаву з домішковими атомами. Для розрахунку побудовано та вирішено диференціальне рівняння, яке описує рух домішкових атомів під дією градієнтного тиску у сплаві, що виникає при обертанні диска. Розрахунковим шляхом визначено швидкості руху домішкових атомів за радіальним напрямом та час переміщення атомів.