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COMPUTER MODELING OF HYDROGEN INDUCTED MASS TRANSFER IN SEMICONDUCTORS

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In connection with the widespread use of copper conductors in microelectronics, the problem arises of modeling the processes that occur when active gases act on the substrate surface. The situation is further complicated by the circumstance that in order to obtain the final result facing a specific process, individual parts of the system are specifically placed under the influence of an external force. This complicates the thermodynamic modeling of systems in which both the location of the phase boundaries and the distribution of substances over the volume are essential. Based on thermodynamic principles, a model is proposed for the behavior of copper penetration into germanium from spots on the surface under the action of sprayed hydrogen. It has been suggested that some of the energy that is released on the surface is transferred to the crystal lattice and copper atoms and causes a shift in equilibrium. A differential equation is derived that describes the propagation of deviations from the equilibrium composition, and a method for compiling boundary conditions for it is also shown. The results of modeling the hydrogen-germanium-copper system are presented, and the dependence of the concentration of diffused copper on the concentration of superequilibrium atomized hydrogen is obtained. It has been proven that an increase in hydrogen atomization ensures an increase in the number of copper atoms in germanium. Thus, the stationary state of a chemical heterophase system, caused by a point source of perturbation of the chemical composition, is described using the minima of the functionals corresponding to the shift of the Gibbs free energy from the equilibrium value into the elementary cells of the system, the distribution of which over the system is described by differential equations of the form. In this case, due to the consideration of zones (elementary cells) bordering the phase boundary, not only the dissolution of an impurity in a solid body, but also sorption phenomena are described. The results of applying the model in an extended reactor for the H-H_2 system are also presented, and the correspondence of the results to the classical scheme for solving the problem using mass transfer equations is shown.

Key words: *thermodynamics, equilibrium concentration, mass transfer.*

Сгадов С. О. Комп'ютерне моделювання індукованого воднем масопереносу у напівпровідніках

У зв'язку з широким використанням мідних провідників у мікроелектроніці постає проблема моделювання процесів, що відбуваються при дії активних газів на поверхню підкладки. Ситуація ускладнюється ще й тією обставиною, що для отримання кінцевого результату в конкретному процесі окремі частини системи спеціально піддаються впливу зовнішньої сили. Це ускладнює термодинамічне моделювання систем, в яких істотне значення має як розташування меж фаз, так і розподіл речовин за об'ємом. На основі термодинамічних принципів запропоновано модель поведінки проникнення міді в германій з плям на поверхні під дією розпиленого водню. Було припущено, що частина енергії, яка вивільняється на поверхні, передається кристалічній решітці та атомам міді та викликає зміщення рівноваги. Виведено диференціальне рівняння, яке описує поширення відхилень від рівноважного складу, а також показано метод складання для нього граничних умов. Наведено результати моделювання системи водень-германій-мідь і отримано залежність концентрації дифундованої міді від концентрації надрівноважного розпиленого водню. Доведено, що збільшення розпилення водню забезпечує збільшення числа атомів міді в германію. Таким чином, стаціонарний стан хімічної гетерофазної системи, викликаний точковим джерелом збурення хімічного складу, описується за допомогою мінімумів функціоналів, що відповідають зсуву вільної енергії Гіббса від рівноважного значення в елементарні комірки системи, розподіл яких по системі описується диференціальними рівняннями виду. У цьому випадку завдяки врахуванню зон (елементарних осередків), що межують з межею розділу фаз, описується не тільки розчинення домішки в твердому тілі, а й сорбційні явища. Також наведено результати застосування моделі в розширеному реакторі для системи H-H_2 та показано відповідність результатів класичній схемі розв'язання задачі за рівняннями масопереносу.

Ключові слова: *термодинаміка, рівноважна концентрація, масоперенос.*

Introduction. Processing of surfaces with the activated gas phase finds a wide application in the technologies connected by cleaning, oxygenating, nitridation of a surface of solid bodies, their etching, sedimentation on a surface of various coverings [1, 2]. Such processes, for the purpose of modeling, are usually described by methods of chemical kinetics [3]. So way they receive systems of the differential equations (most often nonlinear and non-uniform) containing parameters which are selected empirically from a condition of coordination of results of modeling with experimental data for each case. Along with methods of chemical kinetics equilibrium thermodynamics methods have wide distribution for studying of structure of systems [4]. Such methods use thermodynamic parameters which are derived on the basis of independent experimental data, are reliably established and tabulated.

However the considered systems in principle are non-uniform and therefore are nonequilibrium. The situation is complicated also by that circumstance that for obtaining the end result facing concrete process, separate parts of system are specially taken away under the influence of external power. It complicates thermodynamic modeling of systems in which both the arrangement of borders of phases, and distribution of substances on volume is essential.

As the majority of above-mentioned processes are conducted in the stationary modes, the author made attempt to apply thermodynamic methods to the description of processes of interaction of the activated gases with a surface of a solid body.

Due to the wide use of copper conductors in microelectronics there is a problem of modeling of processes which happen at impact of active gases on a substrate surface. In this work the behavior model of the copper getting in germany of the islands of copper applied on the surface of the semiconductor in the form of fragments of a thin film at influence of the atmosphere of atomized hydrogen on the basis of thermodynamics methods is considered.

Mathematical model. The most general, i.e. not demanding strict specification, approaches are thermodynamics methods on the basis of optimization of thermodynamic potentials, for example, Gibbs’s function. It will allow do not consider concrete mechanisms of migration of atoms of copper in germany. Then the task is formulated as a research of amount of the dissolved substance in a substrate depending on concentration of atomic hydrogen.

Thus, the considered system includes:

H2, H, Ge (gas) – a gas phase;

Cu – in the form of a film,

Ge (кр), Cu in Ge, H in Ge – as components of solid solution.

Using of such model assumptions of structure of system allows to find a conditional minimum of energy of Gibbs look like:

$$G(\vec{n},\vec{N})=\sum_{i=1}^{I} n_i\left(c_i+\ln\frac{n_i}{\sum n_i}\right)+\sum_{k=1}^{K} N_k c_k \qquad (1)$$

where

$$c_i=\frac{\Delta_{f,0}H_i}{RT}-\frac{\Phi_i^*}{R}+\ln p,\quad c_k=\frac{\Delta_{f,0}H_k}{RT}-\frac{\Phi_k^*}{R} \qquad (2)$$

corresponds to individual substances in the gas and condensed phase.

$\Delta_{f,0}H$ – their enthalpies of education, Φ^* – their specified thermodynamic potential (Massye – Planck’s function), defined from experimental data [5], p – the general pressure in the atmospheres.

The material balance is considered by restrictions look like

$$\sum_{i=1}^{I} a_{ji} \mathrm{n}_i + \sum_{k=1}^{K} a_{jk} \mathrm{N}_k = b_j, \quad \mathrm{j} = 1..\,\mathrm{J} \quad n_i > 0, \quad N_k \geq 0 \text{ for all } i \text{ and } k\,. \tag{3}$$

Function (1)–(3) have been minimized analytically by method of multipliers of Lagrange [4]

$$\begin{cases} \ln \dfrac{n_i}{P} = \sum\limits_{j} a_{ji} \lambda_j - c_i, \quad (\mathrm{i}=1..\mathrm{I}), \\ \sum \mathrm{a}_{\mathrm{jk}} \lambda_j - c_k = 0, \quad (\mathrm{k}=1..\mathrm{K}), \\ \sum\limits_{\mathrm{i}} a_{ji} n_i + \sum\limits_{k} a_{jk} N_k - b_j = 0, \quad (\mathrm{j}=1..\mathrm{J}) \end{cases} \tag{4}$$

and (missing intermediate calculations) we receive expression for a share of the dissolved copper in germanium:

$$\omega_{Cu_{Ge}} = \exp\left(c_{Cu(\text{кр})} - c_{Cu_{Ge}}\right). \tag{5}$$

As in the received formula the copper's part in solution has no obvious dependence on concentration of monohydrogen, the author make the assumption that some part from energy of $Q = K\Delta_{\text{рек}} H[H]^2$ which is allocated at a hydrogen recombination for surfaces is transferred to a crystal lattice and atoms of copper. At the same time subexponential expression changes at a inteface

$$\phi = \frac{\beta Q}{RT} = \frac{\beta K \Delta_{\text{рек}} H[H]^2}{RT}, \tag{6}$$

where $\beta \approx \dfrac{n_{Cu}}{n_{Ge} + n_{Cu}}$ – a part of the transferred copper film of energy of a recombination of hydrogen and K-coefficient characterizing experimental conditions and speed of reaction,

$\Delta_{\text{рек}} H$ – hydrogen recombination enthalpy, $[H]$ – its concentration.

Finally we receive a part $\omega^*_{Cu_{Ge}}$ of superequilibrium copper in Germanium

$$\omega^*_{Cu_{Ge}} = \exp\left(\frac{n_{Cu}}{n_{Ge} + n_{Cu}} \frac{K\Delta_{\text{рек}} H[H]^2}{RT}\right) \exp\left(c_{Cu(\text{кр})} - c_{Cu_{Ge}}\right). \tag{7}$$

Finally we have:

$$\omega^*_{Cu_{Ge}} = \omega_{Cu_{Ge}} \exp\left(\frac{n_{Cu}}{n_{Ge} + n_{Cu}} \frac{K\Delta_{\text{рек}} H[H]^2}{RT}\right) \exp\left(c_{Cu(\text{кр})} - c_{Cu_{Ge}}\right), \tag{8}$$

where n_{Cu} – amount of copper in a film, n_{Ge} – quantity germanium in a near-surface layer in moths, $\Delta_{\text{рек}} H$ – a specific enthalpy of a recombination of atomic hydrogen, and [H] – its concentration, K – the empirical coefficient reflecting experimental conditions.

For accounting of transfer of products of chemical reactions between cells we will write down the continuity equation look as:

$$D_i \frac{\partial^2}{\partial x^2} n_i = F_i(n,x) \tag{9}$$

where $F_i(n,x)$ – considers interaction of *i*-go of substance with borders.

The amount of the substance nim = n(xm) has to satisfy to differential equation (9). Therefore substituting n(x) in the form of

$$n_{im} = P_m \exp\left(\sum_{j=1}^{J} a_{ji} \lambda_{jm} - c_{im} - \varphi_{im} \right) \tag{10}$$

in the equation (9) we receive the equation for distribution of perturbation in the system:

$$-\frac{\partial^2 \phi_i}{\partial x^2} + \left(\frac{\partial \phi_i}{\partial x} \right)^2 + \frac{\partial \phi_i}{\partial x} f_i(x) + g_i(x) = \varpi_i, \tag{11}$$

where

$$f_i(x) = 2(c_i' - \sum_j a_{ji} \lambda_j' - \frac{P'}{P}),$$

$$g_i(x) = (c_i')^2 - 2c_i' \sum_j a_{ji} \lambda_j' + \left(\sum_j a_{ji} \lambda_j' \right)^2 + 2\frac{P'}{P}\left(c_i' - \sum_j a_{ji} \lambda_j' \right) - c_i'' + \sum_j a_{ji} \lambda_j'' + \frac{P''}{P},$$

$$\omega_i = F_i / \left[D_i P \exp\left(\sum_j a_{ji} \lambda_j - c_i - \varphi_i \right). \right] \tag{12}$$

value ϖ_i considers influence of boundary conditions and power exchange on borders of the cell and in case of two and more measured boundary-value problems it is most often equal to zero since in this case it is considered by boundary conditions. For example, for the recombination case on walls $F_i = \frac{\gamma_i \, \mathrm{v}_i n_i}{2r}$ therefore from (11) we receive $\omega_i = \frac{\gamma_i \, \mathrm{v}_i}{2rD_i}$ where r – the cross size of the system, γ_i and Vi – the recombination coefficient and thermal speed of molecules respectively. Generally speaking, boundary conditions for (11) can be received from boundary conditions for the equation of the mass transfer (10) according to the scheme:

$$n_i(x_0) = n_i^o \rightarrow \phi_i \big|_{x=0} = -\ln \frac{\mathrm{n_i}}{\mathrm{n_i}\,*},$$

$$n_i'(x_0) = \Pi_i \rightarrow \phi_i'(x_0) = \sum_j a_{ji} \lambda_{jm} + \frac{P_m}{P} - c_{im} - \frac{\Pi_i}{P n_i(x_0)}$$

where $\mathrm{n_i}\,*$ – equilibrium concentration.

Values $\phi_{im} = \phi_i(x_m)$ and λ_{jm} are also interdependent therefore it is reasonable to use the Zeydel method, having separated process of the solution of the system (4) and differential equation (11) substituting in turn the received values ϕ_{im} in the system (4) and received from it λ_{jm} in coefficients and local conditions of the equation (11).

If the considered process is in steady state, then it is possible to demand performance of the principle of detailed balance in sense of constancy of amount of atoms in each unit cell and in volume in general. On the other hand as a result of chemical reactions atoms do not disappear and do not arise, and there is their regrouping both between substances, and in space. And from here follows that if the system contains J grades of atoms, then for them conservation law in the form of the law of continuity, for concentration of j-go atoms of the grade b_j which for the case of fixed diffusion constants (i.e. not depending from x) can be written down in the look has to be carried out b_j:

$$\nabla^2 b_j = 0, \quad \text{j=1..J}. \tag{13}$$

The solution of the corresponding boundary-value problem for these equations on the differential grid is the sizes b_{jm} which are logging in. (4). Thus, steady state of the system is generally described by the solution of the system of the nonlinear equations (4) and boundary-value problems of differential equations.

The considered system is separated into three parts: the gas phase with possible deposits of the besieged (condensed) phases of individual substances, the thin near-surface zone which corresponds to the substance adsorbed by the surface and solid solution behind the phase boundary. The model received above allows to describe solution as the perfect gas (approach which works in many cases, especially at low impurity concentrations, besides, not ideality can be considered introduction of activities that is quite trivial within this model). Therefore it is easy to broadcast the description of transfer in the gas phase on the description of distribution of impurity in the solid body, having considered it also as set of unit cells. For this purpose it is necessary to write the condition for approval of two parts of the system for the decision of differential schemes of differential equations (13) and (12).

Let's consider the interphase boundary. Let's consider at the same time that the interphase boundary passes on border between σ and σ+1 a cell. The cell has to correspond to a layer thickness of h of an adsorbed gas. The following cell (m=σ+1) corresponds to a near-surface layer of a solid body h1 thickness. As both phases differ with chemical composition, on border diffusion constants suffer jump. At the same time, as penetration of a diffusant goes through an adsorption stage, for substance flows at the left and on the right surfaces for the same substance in a type of the principle of detailed balance the ratio has to be carried out:

$$D_- \frac{\partial \mathrm{n}}{\partial x}\Big|_- = D_+ \frac{\partial \mathrm{n}}{\partial x}\Big|_+ , \tag{14}$$

where D_-, D_+ – diffusion constants for this substance in gas and in a solid body of the same substance. Having separated both parts (14) on D_+ and, having used determination of amount of atoms in bjm cell, we receive a ratio for the near-surface site:

$$\frac{\partial b_j}{\partial x}\Big|_+ = \sum_i a_{ji} \frac{D_-}{D_+} \frac{\partial \mathrm{n}}{\partial x}\Big|_- . \tag{15}$$

If to enter differential operators Δ+ and Δ- defined as finite differences

$$\Delta_- y = y_\sigma - y_{\sigma-1} , \qquad \Delta_+ y = y_{\sigma+1} - y_\sigma , \tag{16}$$

then (13) it is possible to write down in the form of the differential scheme:

$$\Delta_+ b_j = \frac{h}{h_1}\sum_i a_{ji}\frac{D_-}{D_+}\Delta_- b_j . \qquad (17)$$

Considering n, c as functions of coordinate x, we will substitute expression (10) in (14), having expressed the last in terms of finite differences (16). After some transformations we will receive:

$$\frac{D_- h_1}{D_+ h}\left(1-\frac{P_{\sigma-1}}{P_\sigma}\exp(-\sum_i a_{ji}\Delta_-\lambda_j+\Delta_-\phi_i+\Delta_- c_i)\right)=\frac{P_{\sigma+1}}{P_\sigma}\exp(\sum_i a_{ji}\Delta_+\lambda_j-\Delta_+\phi_i-\Delta_+ c_i)-1. \qquad (18)$$

Thickness of layers of h and h1 are chosen so that cells σ and σ+1 could be considered in mutual thermodynamic equilibrium separately from volume, that is would become possible to apply to them a condition of equality of chemical potentials which in this case can be formulated through the parameters λ_{jm} making sense of chemical potential on atom in a look:

$$\lambda_{j\sigma} = \lambda_{j\sigma+1} \qquad (19)$$

Neglecting composed under an exponent in comparison with 1 and considering that the total quantity of substance in a cell P_σ is proportional to its size and also a ratio (19) from (18) we receive the equation:

$$\frac{P_{\sigma+1}}{P_\sigma}\exp\left(-\Delta_+\phi_i-\Delta_+ c_i\right)=1+\frac{D_-}{D_+}\frac{h_1}{h}\left(1-\frac{\Delta x}{h}\right). \qquad (20)$$

As a rule, the cell size in a gas phase Δx> h and therefore that the equation (20) had the decision, has to will be executed a ratio

$$\left|\frac{D_-}{D_+}\frac{h_1}{h}\left(1-\frac{\Delta x}{h}\right)\right|<1, \qquad (21)$$

h reached by selection, h1 and Δx. Then we receive expression for jump of size ϕ_{im} on border:

$$\Delta_+\phi_i \approx \ln\frac{P_{\sigma+1}}{P_\sigma}-\Delta_+ c_i-\frac{D_-}{D_+}\frac{h_1}{h}\left(1-\frac{\Delta x}{h}\right) \qquad (22)$$

or, neglecting last composed in (22) rather others we will receive:

$$\Delta_+\phi_i \approx \ln\frac{P_{\sigma+1}}{P_\sigma}-\Delta_+ c_i . \qquad (23)$$

Thus, the stationary state of a chemical heterophase system caused by a point source of perturbation of chemical composition is described by means of minima of the functionalities of a look (4) corresponding to the shift of a Gibbs free energy from equilibrium value in unit cells of a system which distribution on a system is described by differential equations of a look (8). Influence of border, is considered by introduction of jump of shift (23) for approval of a mass transfer in a gas and condensed phase.

At the same time due to consideration of zones (unit cells), border to a phase boundary, not only dissolution of impurity in a solid body, but the sorption phenomena is described. It is important to note in this sense that the size $\Delta_+ c_i$ corresponding to jump of free energy a surface – solution describes change of energy of an unbound particle in the course of implementation in surface layers of a solid body

Results of modeling and discussion. Results of calculations for the above-mentioned algorithm for the sequence of temperatures are given in Table 1 and on graphics (fig. 1) in the form of dependence of concentration of copper on concentration of hydrogen. Atomization of hydrogen was modelled by temperature increase.

Table 1

Composition of the system

p, atm	T, K	H2 GAS, atm	H GAS, atm	GE GAS, atm	GE SOL, mol	H in GE, mol	Cu in GE, molar shares	Cu film
1.E-05	300	1.00E-05	1.25E-33	2.16E-03	2.00	1.52E-29	3.80E-18	5.00E-01
	350	1.00E-05	3.38E-28	2.25E-85	2.00	9.24E-26	1.17E-15	5.00E-01
	400	1.00E-05	4.05E-24	2.55E-72	2.00	6.31E-23	8.60E-14	5.00E-01
	450	1.00E-05	6.09E-21	1.95E-62	2.00	1.01E-20	2.43E-12	5.00E-01
	500	1.00E-05	2.13E-18	1.08E-54	2.00	5.79E-19	3.53E-11	5.00E-01
	550	1.00E-05	2.59E-16	1.81E-48	2.00	1.59E-17	3.15E-10	5.00E-01
	600	1.00E-05	1.42E-14	2.36E-43	2.00	2.49E-16	1.95E-09	5.00E-01
	650	1.00E-05	4.24E-13	4.49E-39	2.00	2.56E-15	9.12E-09	5.00E-01
	700	1.00E-05	7.81E-12	1.92E-35	2.00	1.87E-14	3.42E-08	5.00E-01
	750	1.00E-05	9.79E-11	2.54E-32	2.00	1.05E-13	1.08E-07	5.00E-01
	800	1.00E-05	8.98E-10	1.31E-29	2.00	4.72E-13	3.02E-07	5.00E-01

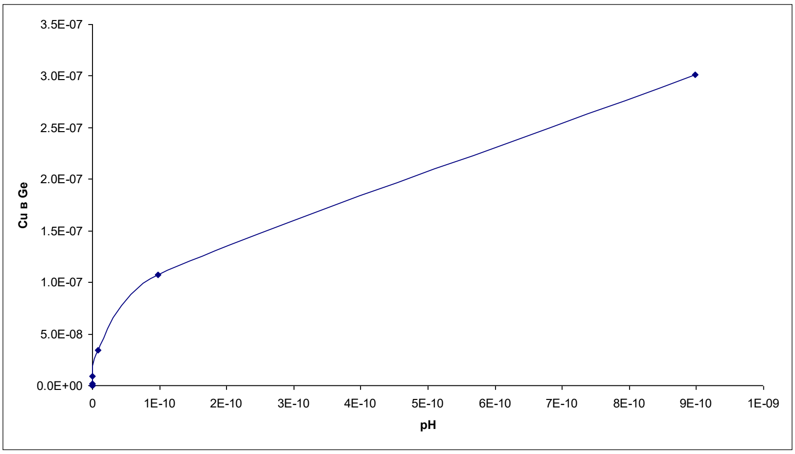

Fig. 1. Dependence of concentration of copper on the partial pressure of hydrogen

Let's apply the model received above to the one-dimensional problem of the recombination of atomic hydrogen on reactor walls the radius of r and long L at the set shift and recombination coefficients γ1 and γ2 on reactor walls and on the sample respectively. And for simplicity we will not consider influence of structure of the sample on gas, and we will consider distribution of atomic hydrogen.

For this task the right part of differential equation (11) $F=\frac{\gamma\nu n}{2r}$ therefore from (12) we receive $\omega=\frac{\gamma\nu}{2rD}$. As a result of numerical experiments it is revealed that the f (x) and g (x) functions are small therefore at. (11) it is possible to rewrite in the look

$$-\frac{\partial^2\phi_i}{\partial x^2}+\left(\frac{\partial\phi_i}{\partial x}\right)^2=\varpi_i$$

(analytical solution of which could be easily received).

Calculations of the reactor L=0.25m, r = 0.0125 m, p=10 containing hydrogen with the pressure were made 4 atm, and average temperature of T=600K. Dependences for different values of recombination coefficients on the sample are by results constructed. At the same time the recombination coefficient on walls was accepted by equal 10^{-3}.

For comparison calculations for the formulas received at the analytical solution of differential equation (11) at the same coefficients were carried out:

$$\frac{n}{n_0}=\frac{k\,\mathrm{ch}\,k(L-x)+\beta\,\mathrm{sh}\,k(L-x)}{k\,\mathrm{ch}\,kL+\beta\,\mathrm{sh}\,kL},\ \text{ã ä å}\quad k=\sqrt{\varpi},\quad \beta=\gamma_2/4D.$$

Calculation results are given Tab. 2. and Tab. 3.

Table 2

x, м	**n(x)/n$_0$**	**n$_{\text{etalon}}$(x)/n$_0$**
0.00E+00	1.00E+00	1.00E+00
1.30E-02	9.08E-01	9.08E-01
2.50E-02	8.25E-01	8.24E-01
3.80E-02	7.50E-01	7.48E-01
5.00E-02	6.82E-01	6.80E-01
6.30E-02	6.21E-01	6.18E-01
7.50E-02	5.66E-01	5.62E-01
8.80E-02	5.16E-01	5.12E-01
1.00E-01	4.71E-01	4.67E-01
1.10E-01	4.31E-01	4.26E-01
1.30E-01	3.95E-01	3.89E-01
1.40E-01	3.63E-01	3.56E-01
1.50E-01	3.34E-01	3.27E-01
1.60E-01	3.09E-01	3.00E-01
1.80E-01	2.86E-01	2.77E-01
1.90E-01	2.67E-01	2.56E-01
2.00E-01	2.50E-01	2.38E-01
2.10E-01	2.35E-01	2.22E-01
2.30E-01	2.22E-01	2.08E-01
2.40E-01	2.12E-01	1.96E-01

Table 3

x,м	**n(x)/n$_0$**	**n$_{\text{etalon}}$(x)/n$_0$**
0.00E+00	1.00E+00	1.00E+00
1.30E-02	9.03E-01	9.04E-01
2.50E-02	8.15E-01	8.16E-01
3.80E-02	7.34E-01	7.37E-01
5.00E-02	6.61E-01	6.64E-01
6.30E-02	5.94E-01	5.98E-01
7.50E-02	5.33E-01	5.38E-01
8.80E-02	4.77E-01	4.83E-01
1.00E-01	4.26E-01	4.32E-01
1.10E-01	3.78E-01	3.86E-01
1.30E-01	3.35E-01	3.44E-01
1.40E-01	2.95E-01	3.05E-01
1.50E-01	2.57E-01	2.68E-01
1.60E-01	2.23E-01	2.35E-01
1.80E-01	1.90E-01	2.04E-01
1.90E-01	1.59E-01	1.74E-01
2.00E-01	1.30E-01	1.47E-01
2.10E-01	1.03E-01	1.20E-01
2.30E-01	7.65E-02	9.54E-02
2.40E-01	5.15E-02	7.12E-02

Thus, the author relaying on methods of thermodynamics has received the dependence describing dissolution of copper in the semiconductor under the influence of atomized hydrogen. It is proved that with a growth of atomization of monohydrogen the number of copper quantity of atoms, difused in a substrate, grows. The simple formula (8) describing concentration of superequilibrium copper in Germany is received. The received model can be expanded on the basis of a hypothesis of local balance on a diffusion picture if to consider the sample thickness as a set of elementary cells.

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