Defect and Diffusion Forum Vols 258-260 (2006) pp 32-38 Online: 2006-10-15
© (2006) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/DDF.258-260.32

On the Atomistic Dynamic Modelling of Simultaneous Diffusion of Dopant and Point Defect (B, V, I) in Silicon Material

Dao Khac An[1,a], Phan Anh Tuan[1,b], Vu Ba Dung[2,c] and Nguyen Van Truong[3,d]
[1]Institute of Materials Science, VAST, Vietnam
[2]Mining and Geology University, Ha Noi, Vietnam
[3]Le Quy Don University, Ha Noi, Vietnam
[a]andk@ims.vast.ac.vn

Keywords: atomistic simulation, simultaneous diffusion of B, point defects.

Abstract. Understanding the atomic movements of simultanous diffusion of dopant (B) and point defects (V, I) in silicon is of great importance for both experimental and theoretical diffusion studies. This paper presents the atomistic dynamic diffusion modelling of boron (B), self-interstitial (I) and vacancy (V) process in silicon based on simultaneous diffusion of boron dopant and point defects based on a previous developed theory. The simulation is based on the random walk theory with three main diffusion mechanisms: namely vacancy, interstitial and interstitialcy mechanism. The migration frequencies of dopant and point defects have been programmed based on the experimental diffusion data of boron, vacancy and Si self-interstitial. This simulation procedure can be seen very clearly about the atomic movements, the interactions between dopant and point defects via three diffusion mechanisms. The diffusion depth of B, V, I in very short time can be estimated from the simulation picture on the screen. The simulation results reflect the simultaneous diffusion as well as the interaction of boron and point defects via the three diffusion mechanisms. The point defects (V, I) were generated during the dopant diffusion and they diffused further into the depth as shown in the results of the simulation as well as in the previous published experimental findings.

Introduction

Any theory on atomic diffusion must begin with the consideration of the diffusion mechanisms and a fundamental question has to be answered: how does a particular atom move from one position to another? The diffusion of impurities in silicon materials is a result of many small jumps of atoms [1-6]. Due to the interaction between impurity and the crystal lattice, the impurity diffusion process in silicon often gives rise to point defects which are diffused simultaneously with the impurities [7-16]. This means that a dopant diffusion process in silicon is a complex diffusion process which is consisting of the simultaneous diffusion of multi-species including impurities, point defects (V, I), environmental gas atoms in the diffusion system such as N_2, O_2, different diffusivities, ... So far, the dopant diffusion is mainly investigated by Fick's law with continuous approach. Nowadays, the atomistic approach is more and more developed and used but mainly for single diffusion processes. The theoretical and experimental problems of the simultaneous diffusion of multidiffusion species including the diffusion of multidopants and point defects have not been developed widely; of course that there are a few results published. In order to theoretically investigate the diffusion of multi-species, the use of a powerful theory, i.e. the irreversible thermodynamic theory for the investigation of multidiffusion species system has been proposed by many authors [18,19,20...]. We have developed some theoretical aspects of simultaneous diffusion of B-Au, B-P, B-As and point defects in silicon semiconductors using the irreversible thermodynamic theory [21,22] and recently we have been dealing with atomic movements or simulation of three diffusion species (B, V, I) and four diffusion species (As, B, I and V).

All rights reserved. No part of contents of this paper may be reproduced or transmitted in any form or by any means without the written permission of Trans Tech Publications, www.ttp.net. (ID: 132.174.255.116, University of Pittsburgh, Pittsburgh, USA-04/05/15,18:06:34)

Basic Theory

As known, a dopant in a semiconductor may diffuse by several diffusion mechanisms but the dopant in silicon usually diffuse mainly by three diffusion mechanisms: namely vacancy, interstitial and interstitialcy mechanisms. The dopant diffusion mechanism via vacancy mechanism or interstitial mechanism has been discussed for a very long time. So far the dopant diffusion in Silicon semiconductors has been accepted via both vacancy and interstitial diffusion mechanisms in terms of mixture diffusion mechanism, sometimes called as interstitialcy mechanism. The vacancy diffusion mechanism and interstitial diffusion mechanisms have been considered as relative two aspects of diffusion process depending on the semiconductor lattice structure, dopants size and many other factors such as diffusion temperature, pressure [3,4,5,7,8,9,10,11,12,13,14...].

In the case of a multispecies diffusion system, the image of diffusion is more complex. The diffusion fluxes or the diffusion equations system of multispecies using irreversible thermodynamic theory in the semiconductor material can be written [14,15,16,17,18]. As known, the irreversible thermodynamic theory and Fick's diffusion theory are compatible. Based on this point, the diffusion equation system for simultaneous diffusion of three diffusion species (B, I and V) using irreversible thermodynamic theory in combination with Fick's diffusion theory can be written in the following form [22, 23]:

$$\frac{\partial C_B}{\partial t}=\frac{1}{2}\frac{\partial}{\partial x}\left[\left(2D_B+D_V+\frac{D_BC_B-D_IC_I}{C_V}\right)\frac{\partial C_B}{\partial x}\right]+ \\ +\frac{1}{2}\frac{\partial}{\partial x}\left[\left(D_V-D_I+\frac{D_VC_V-D_BC_B}{C_I}+\frac{D_BC_B-D_IC_I}{C_V}\right)\frac{\partial C_I}{\partial x}\right] \tag{1a}$$

$$\frac{\partial C_I}{\partial t}=\frac{1}{2}\frac{\partial}{\partial x}\left[\left(2D_I+D_V+\frac{D_IC_I-D_BC_B}{C_V}\right)\frac{\partial C_I}{\partial x}\right]+ \\ +\frac{1}{2}\frac{\partial}{\partial x}\left[\left(D_V-D_B+\frac{D_VC_V-D_IC_I}{C_B}+\frac{D_IC_I-D_BC_B}{C_V}\right)\frac{\partial C_B}{\partial x}\right] \tag{1b}$$

$$\frac{\partial C_V}{\partial t}=-\left(\frac{\partial C_B}{\partial t}+\frac{\partial C_I}{\partial t}\right) \tag{1c}$$

In order to solve these equations numerically, the following initial and boundary conditions are chosen [23]:

$$C_B(x<0,t)=C_{B0},\ C_I(0,0)=C_{I0},\ C_V(0,0)=C_{V0} \tag{2.a}$$
$$C_B(\infty,t)=0,\ C_I(\infty,t)=C_{I0},\ C_V(\infty,t)=C_{V0} \tag{2.b}$$
$$C_B(x>0,0)=0;\ C_I(x>0,0)=C_{I0};\ C_V(x>0,0)=C_{V0} \tag{2.c}$$

Here, we show as examples the calculated results for two cases in Fig 1, where the distributions of B, I and V have been shown in Fig 1a) for the case of a short diffusion time (the diffusion depth is in the range of nano-size) and distributions of B, I and V in Fig 1.b for the case of a longer diffusion time with very large diffusion depth.

From the results in Fig 1.a,b) we can see that distributions of B, V, I during simultaneous diffusion containing mutual interaction of dopant and point defect where the point defect are generated during diffusion and diffused further into the depth due to the diffusivities of V, I are larger then that of boron dopant. The higher the temperature and the longer the diffusion time is, the

more point defects are generated and go to greater diffusion depths. Many experimental results have shown this fact but theoretical developments and simulations about it have not been demonstrated.

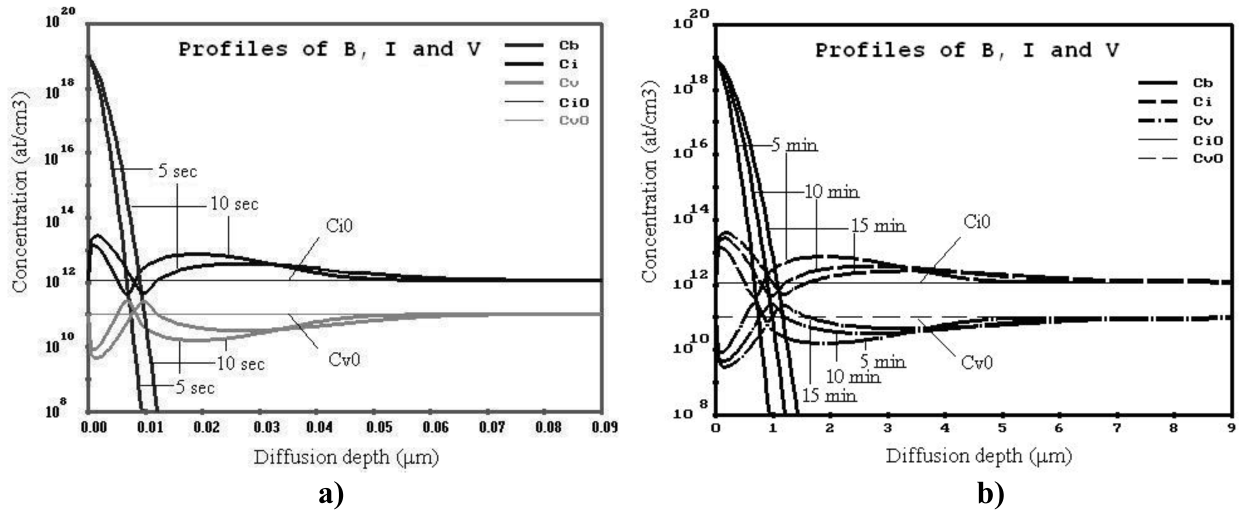

Fig. 1: *The calculated profiles of B, I and V concentration for 5 sec, 10 sec diffusion times at 800 °C diffusion temperature a) and for 5, 10 15 minutes diffusion timesat 1000 °C at 1000 °C diffusion temperature b)*

If we limit the simultaneous diffusion of B, I and V to three mechanisms: namely vacancy, interstitial and interstitialcy diffusion mechanisms and, in addition, if we accepted that the dopant is fully ionized as well as the interactions between B and point defects via the Watkins reaction and Kick-out mechanism and Coulomb interaction then the interaction between B, I and V can be written in the following reactions [3, 4, 7,8,9,10,11,12, 14, 22]:

$$B \leftrightarrow B- + e+ \quad (3)$$

$$B + Si \leftrightarrow B + I \quad (4)$$

$$I + V \leftrightarrow Si \quad (5)$$

$$B- + V+ \leftrightarrow B- V+ \quad (6)$$

Here, we would like to note that Eq. 3 shows the ionization of B in the silicon lattice, and the last equations shows the interaction of B with I, V via Watkins, Kick –out and Coulomb interaction.

Dynamic Simulation of B, I and V in Silicon

So far there have been many authors that have dealt with numerical calculation, modelling and simulation of impurities in semiconductor materials [1,2,11,12,14,15,16,19, 23, 26, 27, 28] but here we deal with the atomistic movements of the simultaneous diffusion of B, I and V. The diffusion of dopants and point defects in silicon crystal are the processes in which the atoms and point defects (I, V) are jumping from one site to another. In a gradient diffusion process of dopant in silicon semiconductors, the jumps mainly occur in one direction. The point defects (I, V) generated via the Watkins reaction, Kick-out mechanism and Coulomb interaction during dopant diffusion also diffuse mainly in the same direction of dopant into the depth of silicon lattice.

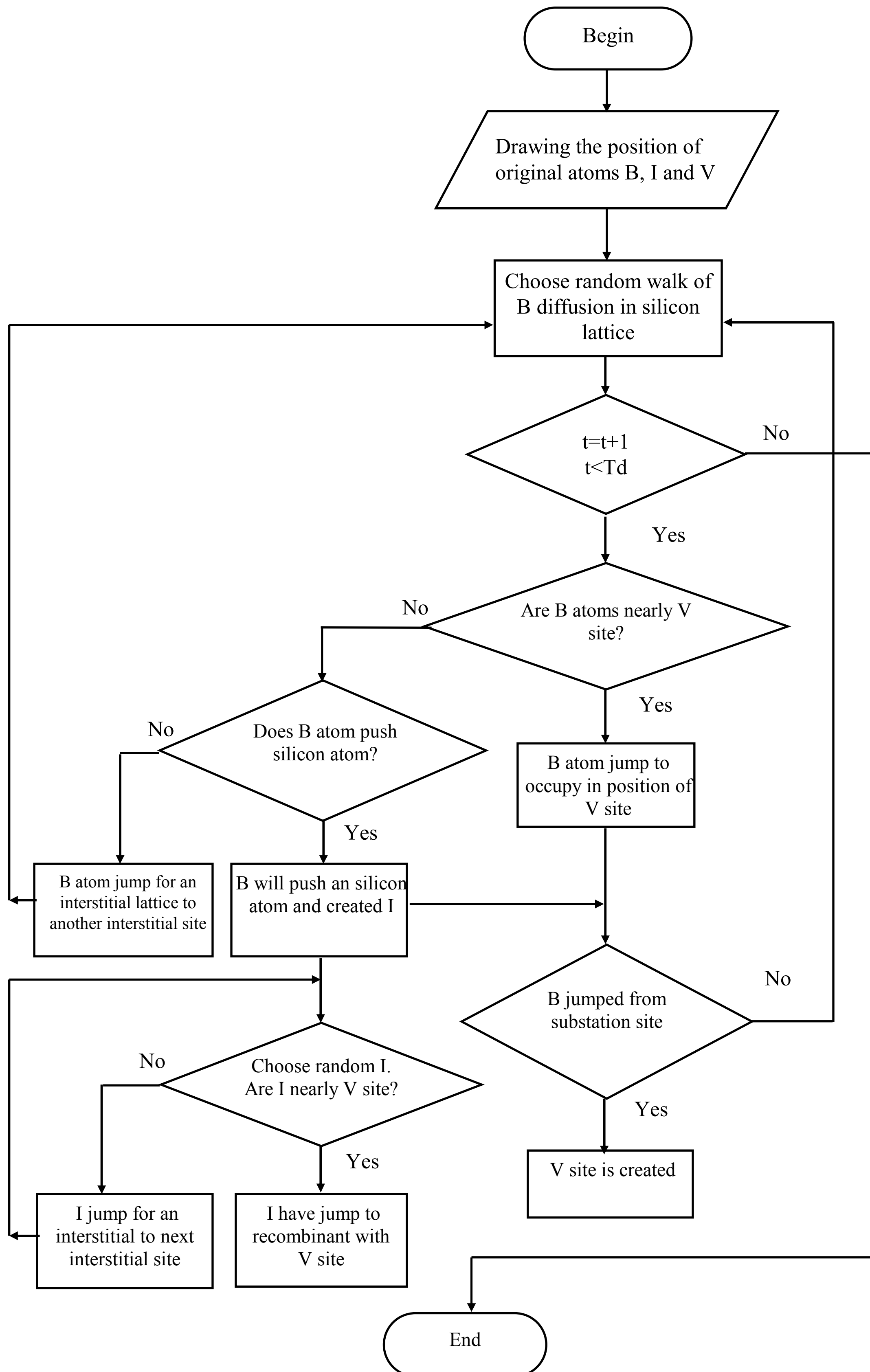

Fig 2. The algorithmic chart of the dynamic simulation program for simultaneous diffusion of B, I and V in silicon material

Here we also would like to note that a self Si interstitial meeting a vacancy will become a Silicon site. This means that both V and I disappeared. In addition, diffusivities of boron dopant, vacancy and self Si interstitial are different. We chose the diffusivities of B, I, and V in the following way [7]:

$$D_B = 30\exp[-3,4\ (eV)/kT] \quad (7a)$$
$$D_I = 1.03.10^{-5}\exp[-1,73(eV)/kT] \quad (7b)$$
$$D_V = 0.1\exp[-2,97(eV)/kT] \quad (7c)$$

The factors of interstitialcy mechanism and vacancy mechanism can be described as [7]:

$$f_I = 0{,}96\exp(-0{,}193eV/kT) \quad (8)$$
$$f_V = 1 - f_I \quad (9)$$

But in order to simulate the atomic movements of B, I and V, we must choose a jump distance in a simple way as in the following manner:

$$L_B = \sqrt{D_B t},\ L_I = \sqrt{D_I t} \text{ and } L_V = \sqrt{D_V t} \quad (10)$$

The time steps can be chosen as the following:

$$\Delta t = \frac{L^2}{2nD} \quad (11)$$

We get a two-dimensional crystal lattice which has a dimension of 20 × 30 atomic layers. The indefinite diffusion source of B is located on the silicon crystal surface. The diffusion temperature can be chosen at certain diffusion temperature. From a given diffusion temperature and the above questions [7,8,9,10,11], we can calculate the equilibrium concentrations of C_{vo}, C_{Io}, diffusivities, jump distances for each step. Based on these data, an atomic simulation program has been written in the Macromedia Flash language. The flow chart can be seen in Fig 2.

Results and discussions

We cannot choose the real diffusion of dopant for our simulations because the lattice dimension and time step would lead to a too high program complexity. Here, we choose a very small two-dimensional crystal lattice with a dimension of 20 × 30 atomic layers with a diffusion time for some seconds. Fig.3.a) shows the positions of B, I and V at the t = 0 diffusion time (with V and I equilibrium concentration at given temperature). Fig.3.b) shows the positions of B, I and V after the first 22 jumps of the simultaneous diffusion process. The results show that the diffusion depths of B are very small, about 6-7 atomic lattice layers, meanwhile the point defect (V, I) that are generated exceed the equilibrium concentrations, they diffused further into the material in comparison with Boron. In a live running simulation program, we can observe very clearly the atomic movements of B, V, I in the small Si lattice as well as interactions between B and point defects via three mechanisms.

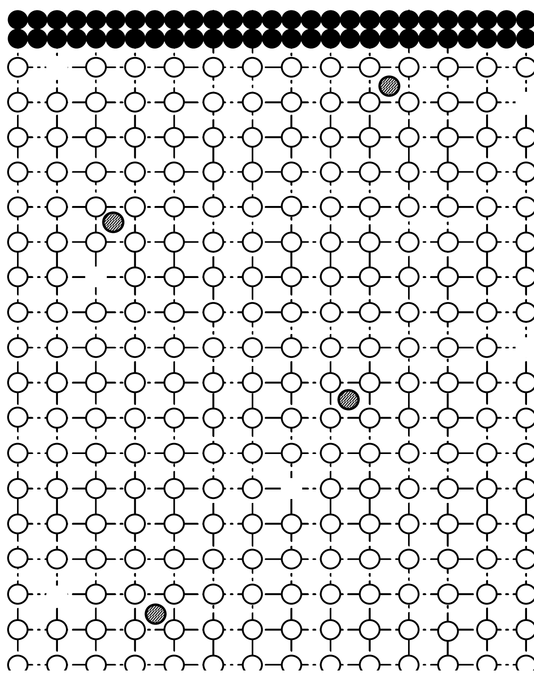

Fig. 3.a) The positions of B, I and V at diffusion time t = 0

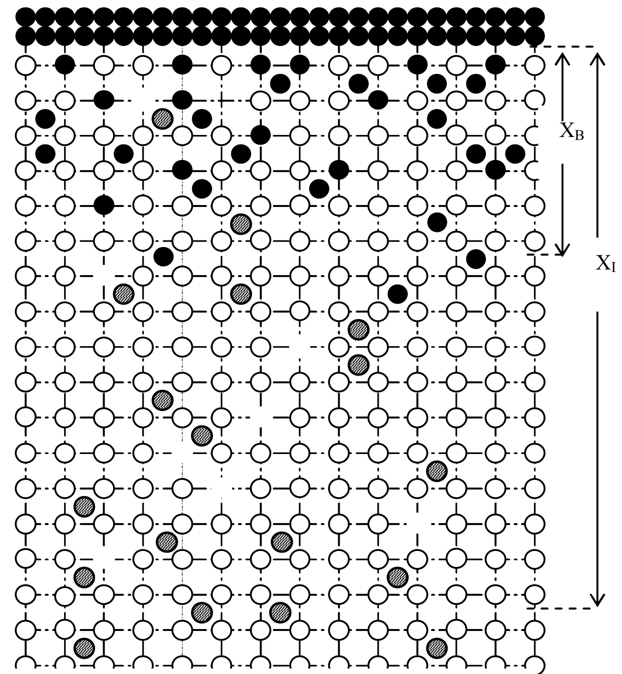

Fig. 3.b) Dynamic positions of B, I and V at diffusion time t =12 s at 800 oC

Conclusion

A simulation program of dynamic movements of B, I and V has been developed. The obtained results of the simulation reflect the simultaneous diffusion of B, I and V containing the mutual interaction of boron dopant and point defects V, I in silicon semiconductors. The movements of boron and point defects can be seen visually via three diffusion mechanisms. We can also observe the point defects generated over equilibrium concentrations and diffused further under the boron diffused layer. Our obtained results via both numerical calculation and dynamic simulation reflect the good agreement with the observed experimental phenomena of the dopant diffusion and point defects distribution in the material.

Acknowledgement. The Authors are very thankful for funding of the State Basic Research Program in the stage of 2006-2007 for this research project.

Reference

[1] D. Shaw: *Atomic Diffusion in Semiconductors* (Plenum Press, London and New York 1973).

[2] J. Crank: *The Mathematics of Diffusion,* (Oxford at the Clarendon Press (1956), Chapter: V, VIII, IX, X, XII).

[3] G. D. Watkins: Lattice Defects in Semiconductor, Inst. Phys. London, Conf. Ser. 23, (1994)

[4] G. D. Watkins, J. R. Troxell and Chatterjee: *Vacancies and interstitial in silicon,* Inst. Phys. Conf. Ser. No 46 Chatter I (1978), p. 16

[5] A. Seeger and K. P. Chik: Phys. Stat. Sol. 29 (1968), p. 455

[6] H. Mehrer: *Diffusion and Ionic Transport in Borate Glasses*, Proceeding of DIMAT 2004

[7] U. Gosele, and T. Y. Tan*: The influence of point defects on diffusion and gettering in Silicon, Impurity Diffusion and Gettering in Silicon*. Ed. By R. B. Fair, B.B. Pearce, C.W.;Washburn, J. MRS. Pittsburgh, Pennsylvania (1985); p.105

[8] U. Gösele and T.Y. Tan: *Defects in Semiconductor II*, New York (1983), p. 153
[9] R. B. Fair: Diffusion and Defect Data Vol. 37 (1984), p. 1
[10] R.Fair: *Impurity Doping Processes in Silicon,* New York (1981), p. 315.
[11] S. Matsumoto, E. Arai, H. Nakamura, and T. Niimi: Japanese J. Appl. Phys.Vol.16 (1977), p. 1177
[12] S. M. Hu and Schmidt: J. Appl. Phys. Vol. 39 (1968), p. 320
[13] S. Miszuon, H. Higuchi (1985), "Investigation of point defects in Si by impurity diffusion", Impurity Diffusion and gettering in silicon, Materials Research Society Symposia Proceeding, vol. 36, Pittsburgh, Pennslvania, USA, p.125.
[14] M. Yoshida: J. Appl. Phys. Vol. 48(6) (1977), p. 2169
[15] D. Mathiot, and J.C. Pfister: Appl. Phys. Lett. 48 (1986), p. 627
[16] D. Mathiot and J.C. Pfister: *Diffusion Mechanisms and Non-equilibrium Defects in Si,* Materials Research Society Symposia, USA (1985), p. 117
[17] I.V.Belova and G.E. Murch: *An Analysis of the Effective Diffusivity in Three- Phase Composite Material Consisting of the Host and Coated Inclusions*, Proceeding of DIMAT 2004, p 32
[18] R.E Howard and A.B. Lidiard: *Matter transport in solids*, Reports on progress in Physics, 27, 160,1964
[19] Y. Mishin: *Atomistic Modelling of Diffusion in Materials*, Proceeding of DIMAT (2004)
[20] S.R.De Groot: *Thermodynamics of irreversible processes*; North – Holland Publishing Company Amsterdam, Fifth Reprint of the First Edition 1963
[21] L. Bernard: *Thermodynamics of irreversible processes*, London-Basingstoke-Mchillan (1978)
[22] Dao Khac An: *Application of the Thermodynamics of Irreversible Processes for the Simultaneous Diffusion of Boron, Arsenic and point Defects in Silicon Material*. Hungary Academy of KFKI-1990-28/E, Central Research Institute for Physics. Budapest (1990), p.1
[23] D. K. An and V. B. Dung: *Preliminary Results of Numerical Profiles for the Simultaneous Diffusion of Boron and Point Defects in Silicon using Irreversible Thermodynamic Theory*, Diffusion in Materials, Part 1, Editors Y. Limoge and J.L. Bocquet, Scitec Publication Ltd, Switzerland, (2001), pp. 647-653
[24] D.K. An, S. Barna, K. Madl, G. Battistig, J. Gyulai: Phys. Stat. Sol.(a) Vol. 118 (1989), p. 95
[25] Dao Khac An: Proceeding of the NCST of Vietnam, Vol. 9 (1997), p.135
[26] Dao Khac An, Le Hoang Mai and Pham Hoi, concentration dependence of the boron diffusion coefficient in Silicon; Phys. Stat.
[27] K. Nishi: *Process modelling and simulation*, Oki Electric Industry Co, Ltd, Proceedings of VLSI technology short course on TCAD an evolution change of the ULSI design and fabrication trend, Kyoto (1997)
[28] Dao Khac An: *Computer Calculations of Enhanced Diffusivity and Effective Activation Energy from Measured Profiles of Impurities in Silicon,* Diffusion in Material, Part 1, Editors Y. Limoge and J.L. Bocquet; Scitec Publication Ltd, Switzerland (2001), pp. 653-659.

Diffusion in Solids and Liquids, DSL-2006 I
10.4028/www.scientific.net/DDF.258-260

On the Atomistic Dynamic Modelling of Simultaneous Diffusion of Dopant and Point Defect (B, V, I) in Silicon Material
10.4028/www.scientific.net/DDF.258-260.32

DOI References
[5] A. Seeger and K. P. Chik: Phys. Stat. Sol. 29 (1968), p. 455
doi:10.1002/pssb.19680290202
[9] R. B. Fair: Diffusion and Defect Data Vol. 37 (1984), p. 1
doi:10.4028/www.scientific.net/DDF.37.1
[11] S. Matsumoto, E. Arai, H. Nakamura, and T. Niimi: Japanese J. Appl. Phys.Vol.16 (1977), p. 177
doi:10.1143/JJAP.16.1177
[12] S. M. Hu and Schmidt: J. Appl. Phys. Vol. 39 (1968), p. 320
doi:10.2118/2316-PA