COMPEL—The International Journal for Computation and Mathematics in Electrical and Electronic Engineering
Vol. 6, No. 1, 37–44 © 1987 BOOLE PRESS LIMITED

A NEW MODEL FOR THE DETERMINATION OF POINT DEFECT EQUILIBRIUM CONCENTRATIONS IN SILICON

M. BUDIL, E. GUERRERO, T. BRABEC, S. SELBERHERR and H. POETZL
Department of Physical Electronics, Institute for General Electrical Engineering and Electronics, Technical University Vienna and Ludwig Boltzmann-Institute for Solid State Physics, Vienna, Austria

ABSTRACT: In this paper the boundary conditions for point defect distributions in monocrystalline silicon are investigated. These boundary conditions are established by simple thermodynamic considerations. A circle process is used including vacancy, interstitial and Frenkel pair generation which yields a simple relationship between the vacancy and interstitial equilibrium concentrations at the surface. A new OED model is also presented which explains the $t^{-1/4}$ behaviour of the interstitial supersaturation. This model is used to simulate experiments of Mizuo and Higuchi. In this way values for the equilibrium concentrations and the diffusion coefficients of vacancies and interstitials are obtained.

1. INTRODUCTION

For a precise prediction of dopant profiles in silicon the understanding of the influence of thermal oxidation on the diffusion of dopants is of great importance. It is well established that oxidation enhanced diffusion (OED) and oxidation retarded diffusion (ORD) result from the change of the distribution of vacancies (V) and interstitials (I) by the thermal oxidation process ([1–3] and references therein). In order to clarify OED/ORD a new model is presented for the interaction between the oxidized interface and the point defects. The most essential feature of this model is the influence of oxidation on the equilibrium point defect concentrations which are not taken as constant bulk parameters but as resulting from the chemical processes at the interfaces of the semiconductor crystal. Chapter 2 introduces this basic concept which is applied to oxidizing conditions in chapter 3. In chapter 4 a process simulator [4] is applied to determine the physical parameters of the new model from experimental results available in literatur [5–8].

2. THE THERMAL EQUILIBRIUM OF POINT DEFECTS

In this chapter we shall derive a general law for the equilibrium concentration of point defects. This law ensues from a circle process using the Frenkel mechanism. First some definitions are given: A point defect is a local disorder of the crystal lattice. There exist three different ways to generate point defects.

An atom is removed from its lattice place and is brought to a surface or an interface position. Simultaneously there remains an empty site (V). This kind of point defect is called Schottky defect. The Gibbs potential to produce such a defect is ΔG_V.

—An atom from a surface or an interface is pushed into the bulk of the crystal (I). The required Gibbs potential is called ΔG_I.
—A Frenkel defect is created by pushing a lattice atom into an I site. The Gibbs potential for this process is ΔG_F.

From thermodynamics the formulae for the equilibrium concentrations of point defects can be derived. C_S is the concentration of silicon atoms in the crystal.

$$C_V^{eq} = C_S \cdot e^{-\Delta G_V/kT} \quad C_I^{eq} = C_S \cdot e^{-\Delta G_I/kT} \quad C_F = C_S \cdot e^{-\Delta G_F/2kT} \tag{1}$$

The surface of a crystal can be active or passive. Passive means that the point defects cannot react with the surface, they can only be produced in the bulk by the Frenkel pair mechanism. Many experiments show that a silicon nitride surface is nearly passive [6, 8]. An active surface reacts with the point defects generating and annihilating each kind of point defects independently. Silicon oxide surfaces are known to be active. For an infinite crystal or a crystal with a passivated surface the Frenkel mechanism is the only source of point defects. In this V and I can only be generated and annihilated as pairs and C_F is the equilibrium concentration value for V and I. However, if the surface is activated, the resulting equilibrium values will change according to the above formulas for C_V^{eq} and C_T^{eq}. The following considerations will help to clarify this.

It is possible to define three Gibbs potentials.

G_S—The surface or interface potential is defined by the process of bringing an atom from infinity outside the crystal to the crystal surface or interface.

G_I—The I potential is defined by bringing an atom from infinity outside the crystal to an I site inside the crystal.

G_V—The V potential is defined by bringing an atom from infinity outside the crystal into a vacancy site.

From the law of energy conservation the following equations are obtained:

$$\Delta G_V = G_S - G_V \quad \Delta G_I = G_I - G_S \quad \Delta G_F = G_I - G_V \tag{2}$$

There cannot be any difference between bringing an atom from a lattice site to the surface and then to an I site and bringing this atom directly from his lattice site to an I site. Hence

$$\Delta G_F = \Delta G_I + \Delta G_V \tag{3}$$

eq. (3) is inserted into eq. (1):

$$C_V^{eq} \cdot C_I^{eq} = C_F^2 \tag{4}$$

This simple relation holds for equilibrium point defect concentrations. In thermal equilibrium the generation of point defects by the Frenkel pair mechanism and the generation by the surface mechanism are in a detailed balance. The Gibbs potentials G_I and G_V are independent of the position in a crystal. Under process conditions stress in the crystal could change its values. However, we do not consider any such change. We only take into account the change of the thermal equilibrium by the surface potential. This potential does not only depend on the bulk properties of the crystal, it also depends on the environment and on any kind of chemical reaction at the surface of the crystal. We conclude that any change of the surface potential will change the thermal equilibrium concentration of V and I inversely.

$$C_I^{eq} = C_S \cdot e^{-(G_I - G_S)/kT} \quad C_V^{eq} = C_S \cdot e^{-(G_S - G_V)/kT} \tag{5}$$

We denote by C_I^{in} and C_V^{in} the thermal equilibrium concentrations for an inert ambient. Both concentrations can be evaluated from the thermodynamic potentials:

$$C_I^{in} = C_S \cdot e^{-(G_I - G_S^{in})/kT} \quad C_V^{in} = C_S \cdot e^{-(G_S^{in} - G_V)/kT} \tag{6}$$

By a suitable treatment of the surface of the crystal (e.g. by a chemical reaction) it is possible to change the surface potential.

$$C_I^{eq} = C_I^{in} \cdot e^{\Delta G_S/kT} \quad C_V^{eq} = C_V^{in} \cdot e^{-\Delta G_S/kT} \quad \Delta G_S = G_S - G_S^{in} \tag{7}$$

These formulas show that a chemical reaction at the surface can produce I and annihilate V at the same time. From many experiments it is obvious that I are produced during thermal oxidation. But most of the oxidation models use a generation term of I and constant values of the thermal equilibrium concentrations of point defects. This would keep the surface V concentration at a higher value compared with the case of pure bulk recombination. Therefore the ORD would not occur near the surface and would have a very strong dependence on the depth. Some models use an annihilation term for V to prevent this effect. In our model a bulk a bulk recombination effect is not needed because the undersaturation of V is produced directly at the surface. The difference between this model and the others is the variability of the thermal equilibrium concentrations of point defects. The Gibbs surface potential is changing in time and the concentration of point defects will follow these changes. The above considerations lead to general expressions for the boundary conditions for V and I. First of all we consider a highly active surface:

$$C_I = C_I^{eq}(t) \quad C_V = C_F^2/C_I^{eq}(t) \tag{8}$$

The concentration of point defects follows immediately the equilibrium concentration. For a lower surface activity the introduction of a reaction velocity is necessary:

$$J_I = -k_I(C_I - C_I^{eq}(t)) \quad J_V = -k_V(C_V - C_F^2/C_I^{eq}(t)) \tag{9}$$

The concentrations of point defects will follow the equilibrium concentration with a certain delay of time.

3. THE VARIATION OF THE GIBBS POTENTIAL AT THE Si–SiO$_2$ INTERFACE UNDER OXIDIZING CONDITIONS

We consider a SiO_2 layer covering a monocrystalline silicon sample in an inert ambient. Under thermal equilibrium conditions there is an exchange of silicon atoms between the Si crystal and the SiO_2 layer. The Si atoms have a certain partial pressure P at the Si–SiO$_2$ interface. From van't Hoff's law it is known that a solution with small density behaves like an ideal gas. The Gibbs potential per atom is equal to the chemical potential and can be expressed for the inert case by:

$$G_S^{in} = G_0 + kT\ln(P_{in}) \tag{10}$$

Under oxidizing conditions the partial pressure at the interface will change:

$$G_S^{\mathrm{ox}} = G_0 + kT \ln(P_{\mathrm{ox}}) \tag{11}$$

G_0 is a constant and independent of pressure. For the description of the variation of the Gibbs potential G_0 is not important.

$$\Delta G_S = G_S^{\mathrm{ox}} - G_S^{\mathrm{in}} = kT \ln(P_{\mathrm{ox}}/P_{\mathrm{in}}) \tag{12}$$

Therefore the variation of the chemical potential depends only on the partial pressure of silicon at the interface. Thus the formulas for the equilibrium concentration of I and V can be written in a simple form:

$$C_I^{\mathrm{eq}} = C_I^{\mathrm{in}} \cdot P_{\mathrm{ox}}/P_{\mathrm{in}} \qquad C_V^{\mathrm{eq}} = C_V^{\mathrm{in}} \cdot P_{\mathrm{in}}/P_{\mathrm{ox}} \tag{13}$$

The above considerations reduce the problem of determination of the I concentration to the calculation of the relation between the values of partial pressure of Si atoms in the oxide under oxidizing and inert conditions. In general the partial pressure is higher in oxidizing than in inert atmosphere. But under oxidizing conditions the oxygen is also dissolved in the oxide and tends to reduce the pressure of Si by reacting with the Si atoms. Therefore a source of Si must exist in the silicon oxide layer. This source can be found in the following chemical reaction:

$$2\mathrm{SiO} \rightleftharpoons \mathrm{Si} + \mathrm{SiO_2} \tag{14}$$

The silicon is not completely oxidized to SiO_2, because a part of the Si atoms is only oxidized to SiO. Under the assumption that this reaction occurs near the Si–SiO_2 interface, it is possible to express this silicon atom source as a current which is proportional to the oxide growth rate.

$$J_{\mathrm{Source}} = f v_{\mathrm{ox}} \tag{15}$$

f is the fraction of silicon atoms, which are oxidized to siliconmonoxide. J_{Source} is the current of produced silicon atoms. However we cannot directly use this current as a boundary condition because a part of the atoms fills up the new growing oxide layer and does not flow into the already formed silicondioxide. Therefore a correction term has to be included:

$$J_{\mathrm{Si}} = f v_{\mathrm{ox}} - C_{\mathrm{Si}} v_{\mathrm{ox}} \tag{16}$$

C_{Si} is the concentration of Si atoms at the interface and $C_{\mathrm{Si}} v_{\mathrm{ox}}$ is the amount of silicon that flows into the new oxide per unit of time. The silicon atoms diffuse into the SiO_2 and react with the oxygen. Under the assumption that the oxygen partial pressure is constant in the reaction area and the diffusion of Si atoms is faster than the oxide growth rate, we obtain

$$\frac{\partial C_{\mathrm{Si}}}{\partial t} = D_{\mathrm{Si}} \frac{\partial^2 C_{\mathrm{Si}}}{\partial x^2} - r C_{\mathrm{Si}} C_{\mathrm{O_2}} \tag{17}$$

r is a reaction constant. From the model of Deal and Grove it is known that the

oxygen partial pressure is proportional to the oxide growth rate. Thus under thermal equilibrium ($\partial C_{Si}/\partial t = 0$) the equation becomes:

$$D_{Si}\frac{\partial^2 C_{Si}}{\partial x^2} = kv_{ox}C_{Si} \tag{18}$$

Let us denote by $x = 0$ the Si–SiO_2 interface and by $x = d$ the SiO_2 surface in which d is the oxide thickness. Then the analytical solution of eq. (18) with the boundary conditions $J_{Si}(d) = 0$ and $J_{Si}(0) = J_{Si}$ as given by eq. (16) yields:

$$C_{Si} = \frac{J_{Si}}{AD_{Si}(1 - e^{-2Ad})}(e^{-Ax} + e^{A(x-2d)}) \quad A = \sqrt{\frac{kv_{ox}}{D_{Si}}} \tag{19}$$

Inserting J_{Si} from eq. (16) we obtain the Si atom concentration $G_{Si} = C_{Si}(0)$ at the Si–SiO_2 interface:

$$C_{Si} = \frac{f}{1 + \sqrt{kD_{Si}/v_{ox}} \cdot \tanh(d\sqrt{kv_{ox}/D_{Si}})} \tag{20}$$

and

$$P_{ox}/P_{in} = \frac{su_0}{1 + \sqrt{kD_{Si}/v_{ox}} \cdot \tanh(d\sqrt{kv_{ox}/D_{Si}})} \tag{21}$$

$su_0(=f/C_{Si}^{in})$ is the supersaturation for thin oxide layers ($d = 0$). The above formula combined with the formula of Deal and Grove yields a $t^{-1/4}$ law for the supersaturation as found in many OED experiments. For very slow oxidation rates ORD is observed instead of OED. The model correctly accounts also for this effect. Figs. 1 and 2 show the good agreement for short and for long oxidation time, respectively. The Model of Massoud [9] determines the oxide growth rate.

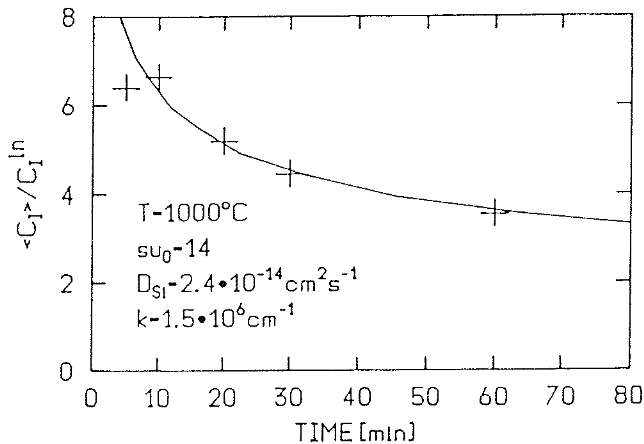

Figure 1

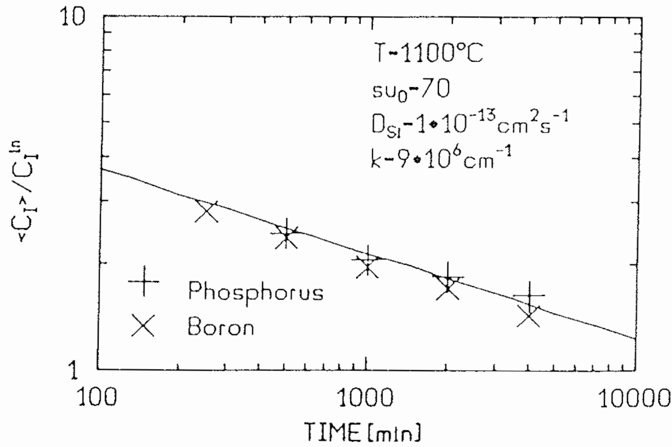

Figure 2

4. DETERMINATION OF POINT DEFECT EQUILIBRIUM CONCENTRATIONS IN SILICON

In order to determine the absolute values of the equilibrium point defect concentrations we use the general purpose one dimensional process simulator ZOMBIE [4] which solves simultaneously the diffusion equations for V and I under appropriate boundary conditions and yields the average concentration of V and I respectively. Under silicon nitride layers and inert conditions only the Frenkel pair mechanism can produce point defects. Therefore the equilibrium concentration for V and I must be equal. A comparison between diffusion of dopants under nitride and under oxide interfaces indicates that the equilibrium concentration of both point defects must also be nearly the same for oxide interfaces [6, 7]. In our calculations the products of

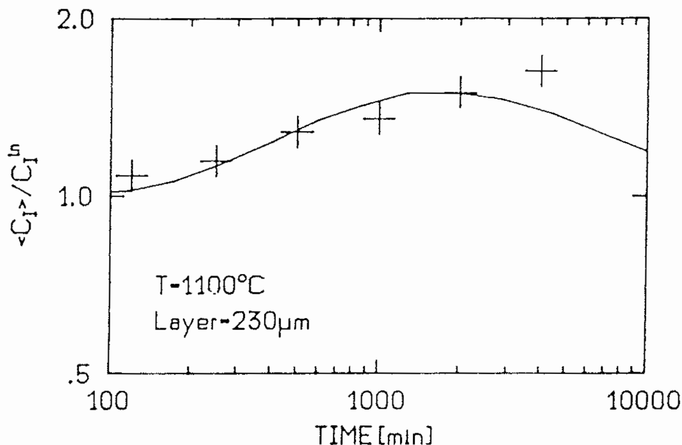

Figure 3

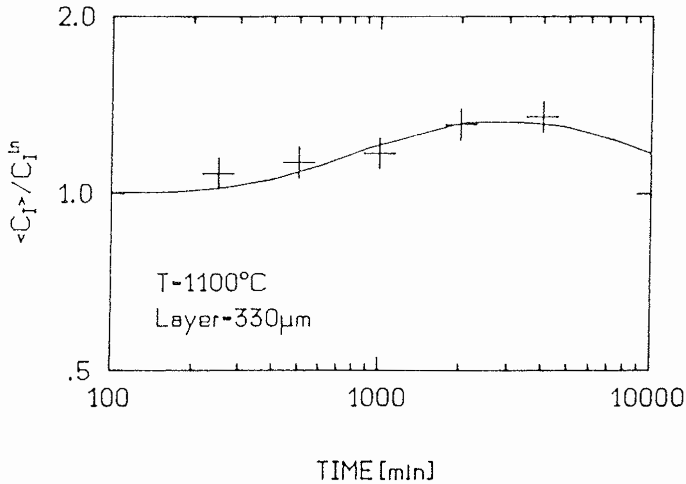

Figure 4

point defect diffusion coefficient and equilibrium concentration for both kinds of point defects were taken from the results of the gold diffusion experiments by Morehead et al. [5]. The absolute values of equilibrium point defect concentrations were now obtained by comparison of our calculations with the experiments of Mizuo and Higuchi [8] in which the average I concentration is given by the OED of phosphorus. Under the assumption of $C_I^{in} = C_V^{in} = 1.4 \times 10^{16}\,\mathrm{cm}^{-3}$, $D_I = 1.1 \times 10^{-7}\,\mathrm{cm}^2\mathrm{s}^{-1}$ and $D_V = 2.9 \times 10^{-9}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ for 1100°C we obtain a fair agreement between the results of our calculations and the experiments as shown in Fig. 3 to Fig. 4. The fairly good agreement supports our model.

5. SUMMARY AND CONCLUSIONS

This work presents a general law for boundary conditions of point defect distributions. The equilibrium concentrations of point defects is determined by the condition at the surface. This condition only can change the equilibrium concentrations inversely and is always in a detailed balance with the bulk. Additionally a model for the condition at the surface during thermal oxidation is presented that explains the observed phenomena and is useful to simulate the experiments of Mizuo and Higuchi. The simulation yields the values of the equilibrium concentrations of both kinds of point defects at 1100°C.

ACKNOWLEDGEMENTS

The authors thank Prof. Goesele for helpful encouragement. This work has been supported by the Fonds zur Foerderung der Wissenschaftlichen Forschung Projekt No. S43/10 and by the Siemens Research Laboratories, Munich, W. Germany. Thanks are also due to our Computer Center for free computer access.

REFERENCES

[1] D.A. Antoniadis and I. Moskowitz, J. Appl. Phys. 53 (1982) 6788.
[2] T.Y. Tan and U. Goesele, Appl. Phys. Lett. 40 (1982) 616.
[3] A.M. Lin, R.W. Dutton, D.A. Antoniadis and W.A. Tiller, J. Electrochem. Soc. 128 (1981) 1121.
[4] W. Juengling, P. Pichler, S. Selberherr, E. Guerrero and H. Poetzl, IEEE Trans. ED-32 (1985) 156.
[5] F. Morehead et al., Appl. Phys. 59 (1983) 690.
[6] S. Mizuo and H. Higuchi, Jpn. J. Appl. Phys. 21 (1982) 281.
[7] S. Mizuo and H. Higuchi, Jpn. J. Appl. Phys. 21 (1982) 56.
[8] S. Mizuo and H. Higuchi, J. Electrochem. Soc. 129 (1982) 2292.
[9] H.Z. Massoud, C.P. Ho and J.D. Plummer, Final Report for Period 15Feb81–31Mar82, Integrated Circuit Lab., Standford University; CA94305; pp. 194 (1982).