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INFLUENCE OF INITIAL CONDITIONS ON POINT DEFECT DIFFUSION: IMPACT ON MODELS

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SUMMARY

The commonly used partial differential equations for point defect diffusion are reviewed. Special attention is given to the initial conditions of the point defect concentrations. Our numerical simulations clearly show that the assumption of initially equidistributed point defect concentrations at process temperature is justified only for a very special choice of parameters. A more general treatment of the problem leads to an inhomogenous distribution of point defects and in consequence to strongly different concentrations beneath a silicondioxide and a siliconnitride layer even for heat treatment under inert conditions.

1. INTRODUCTION

It is generally accepted now that dopant atoms in silicon can diffuse both via silicon self interstitials and vacancies (Tan, 1983). The structure of the partial differential equations describing the migration, generation and recombination of point defects has been discussed in detail in the literature (Fahey, 1985). Most applications pay special attention to boundary conditions (Fahey, 1985; Hu, 1983), parameters (Gösele, 1985), simplifications (Hu, 1985; Law 1988) and to the applicability to describe dopant diffusion (Brabec, 1987). The initial conditions for point defect concentrations, however, have been grossly neglected. For our considerations, we use well established partial differential equations, parameters, and boundary conditions. We then show that the assumption of initially equidistributed point defect concentrations at process temperature is inconsistent with the other assumptions. We introduce a more realistic way to establish initial distributions at process temperature and examine the

system for different physically relevant boundary conditions. Our results clearly show a strong dependence of the point defect concentrations at the crystal surface on the boundary conditions.

In section 2 we review the generally accepted point defect diffusion model and the parameters used for our investigations. Section 3 shows the numerical solutions of the partial differential equations under different conditions. A discussion of the results in connection with our assumptions is presented in section 4. Finally, we propose fundamental experiments and discuss the significance of possible results.

2. MODEL FOR POINT DEFECT DIFFUSION

The diffusion of silicon self interstitials and vacancies in one dimension is generally described by the two following continuity equations:

$$\frac{\partial C_I}{\partial t} = \frac{\partial}{\partial x} D_I \frac{\partial C_I}{\partial x} - K_B (C_I C_V - C_I^{EQ} C_V^{EQ}) \tag{1}$$

$$\frac{\partial C_V}{\partial t} = \frac{\partial}{\partial x} D_V \frac{\partial C_V}{\partial x} - K_B (C_I C_V - C_I^{EQ} C_V^{EQ}) \tag{2}$$

Here and in all following equations, C denotes concentrations and D diffusion coefficients. All characters with subscripts I relate to interstitials, those with subscripts V to vacancies. K_B denotes the bulk reaction rate, superscript EQ indicates thermal equilibrium values.

These two equations have to be completed by the appropriate initial and boundary conditions. With regard to the initial conditions it has been accepted as self-evident that one can write

$$C_I = C_I^{EQ},\ C_V = C_V^{EQ} \tag{3}$$

for a given temperature.

This means that interstitial and vacancy concentrations equal initially their thermal equilibrium values at this temperature and thus are equidistributed in the crystal. The situation at the crystal boundary or at interfaces can be expressed in a quite general manner by using mixed boundary conditions.

$$J_I = -K_I (C_I - C_I^{EQ}) \tag{4}$$

(5) $$J_V = -K_V(C_V - C_V^{EQ})$$

The absolut values of the fluxes J_I and J_V are defined by

(6) $$|J_I| = D_I \frac{\partial C_I}{\partial x},\ |J_V| = D_V \frac{\partial C_V}{\partial x}$$

The fluxes are counted positive if point defects flow into the silicon. Depending on the values of the interface reaction rates K_I and K_V, the interface will act in quite a different way. Low values of these parameters characterize an inactive boundary, where, provided there are deviations from the equilibrium concentrations, the boundary will not be able to compensate for these deviations. Vanishing reaction rates lead to Neumann boundary conditions:

(7) $$J_I = J_V = 0$$

Based on the publications of Mizuo and Higuchi (1982, 1983) we consider this to be the idealization of the effects of a nitride layer on silicon. On the other hand, high values of the interface reaction rates characterize a highly active boundary. The interface will be able to compensate for deviations from the equilibrium concentrations rapidly. Infinite reaction rates lead to Dirichlet boundary conditions:

(8) $$C_I = C_I^{EQ},\ C_V = C_V^{EQ}$$

Refering to Gösele and Tan (1983), we may consider this as idealization of the effects of an oxide layer on silicon.

To perform numerical simulations for point defect diffusion, values for the parameters of the partial differential equations are needed. With regard to the parameters C_I, C_V, D_I, and D_V one is faced with the problem that there is little agreement in literature about the appropriate values for these parameters. For our simulations, the values given by Gösele and Tan (1985) have been used. It should be noted that Gösele assumes an uncertainity of a factor of about ten for these values, so that

one has to consider them as rough estimates. According to Antoniadis (1982), an activation energy of 1.4eV is assumed for the bulk reaction rate, whereas the prefactor is chosen so that at 1000C° the resulting K_B equals the value given by Budil et al. (1986). For K_I and K_V, no reliable data is available. However, the whole range of these reaction rates will be covered using Dirichlet and Neumann boundary conditions. Summming up, we use the following parameters:

$$C_I^{EQ} = 5 \cdot 10^{30} \cdot \exp(-4.4\text{eV}/kT) \quad cm^{-3}$$
$$C_V^{EQ} = 2 \cdot 10^{23} \cdot \exp(-2\text{eV}/kT) \quad cm^{-3}$$
$$D_I = 10^{-5} \cdot \exp(-0.4\text{eV}/kT) \quad cm^2/\text{s}$$
$$D_V = 0.1 \cdot \exp(-2\text{eV}/kT) \quad cm^2/\text{s}$$
$$K_B = 3.43 \cdot 10^{-12} \cdot \exp(-1.4\text{eV}/kT) \quad cm^3/\text{s}$$

3. NUMERICAL SOLUTIONS

In this section, special attention is given to the influence of initial conditions on the point defect redistribution. The general idea is that the process temperature is reached by heating up the crystal, starting at a temperature which is significantly lower. Let us consider that the wafer is already at a temperature of e.g. 800C°, and that the point defect concentrations are equal to their equilibrium values at this temperature. Now we assume that the temperature is ramped to a higher temperature (e.g. 1000C°). This time, where the end temperature is reached, is considered to be the start of the real heat treatment. If we claim for this heat treatment that the point defect concentrations equal their equilibrium values for the end temperature of the ramping step, we have to demand that possible deviations have to relax in a period which is small compared to usual diffusion times. If this is not fulfilled, the model (i.e. the differential equations, boundary- and initial conditions as well as parameters) is inconsistent. The above described procedure has been simulated numerically using the model described in section 1. The ramping rate has been 2C°/min, the end temperature is reached after 6000s. In the figures, the end of the ramping is indicated by a ↑ in the timescale. All simulations have been performed with the program package PROMIS (Pichler, 1985).

Fig. 1 and Fig. 2 show the interstitial- and vacancy concentrations for Neumann boundary conditions. Neither of the concentrations reach their equilibrium values. This is not surprising since the interface has no influence on the point defects.

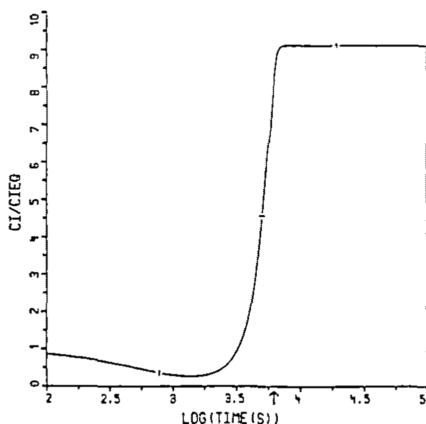

Fig. 1. Interstitial supersaturation under a Si/Si_3N_4 interface

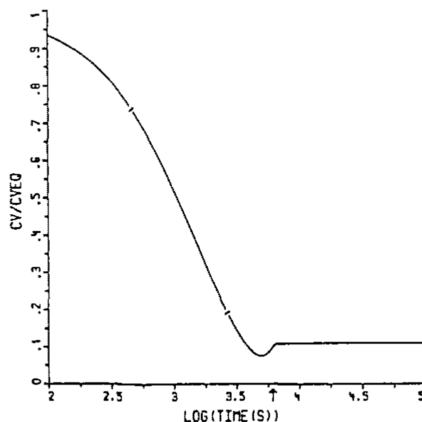

Fig. 2. Vacancy undersaturation under a Si/Si_3N_4 interface

Fig. 3 and 4 show the point defect concentrations for Dirichlet boundary conditions. In this case we would expect the deviations from thermal equilibrium to be small. This is valid for the interstitial concentration in a depth of $2\mu m$. For the concentrations of interstitials and vacancies in the middle of the wafer ($150\mu m$), however, a significant deviation from the equilibrium is shown.

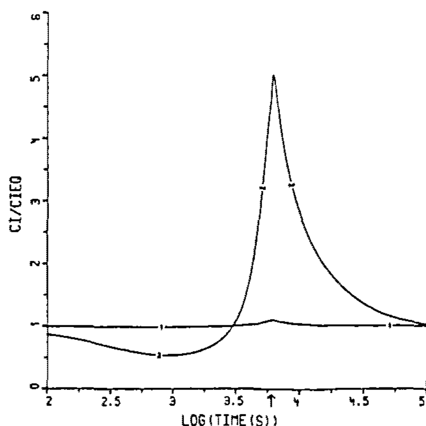

Fig. 3. Interstitial supersaturation under a Si/SiO_2 interface in a depth of $2\mu m$ (1) and $150\mu m$ (2).

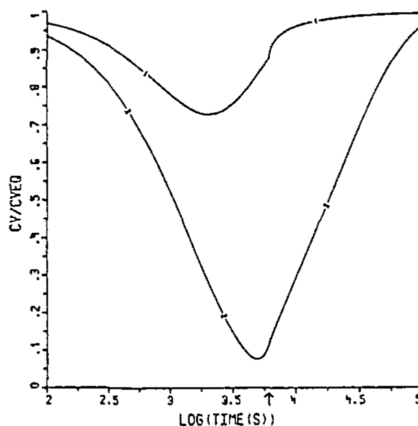

Fig. 4. Vacancy undersaturation under a Si/SiO_2 interface in a depth of $2\mu m$ (1) and $150\mu m$ (2).

At first we considered this to be the effect of a too small value for the bulk recombination rate. Fig. 5 and 6 show the point defect concentrations for $K_B \to \infty$. They are quite similar to the results obtained with the bulk recombination rate from Budil et al. (1986).

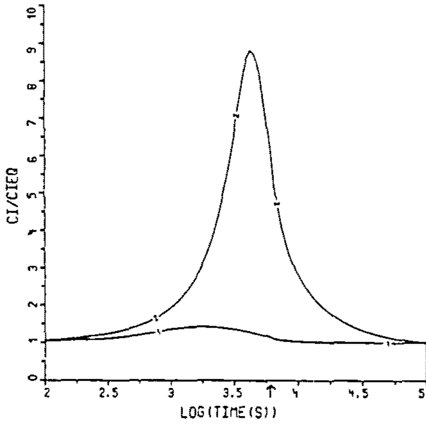

Fig. 5. Interstitial supersaturation under a Si/SiO_2 interface in a depth of $2\mu m$ (1) and $150\mu m$ (2) for $K_B \to \infty$.

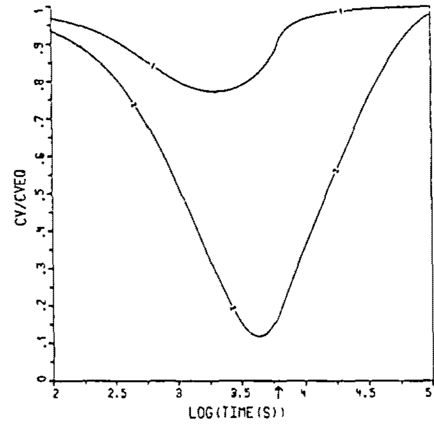

Fig. 6. Vacancy undersaturation under a Si/SiO_2 interface in a depth of $2\mu m$ (1) and $150\mu m$ (2) $K_B \to \infty$.

4. DISCUSSION

a) Influence of Initial Conditions

For the following reflections, we assume the point defect concentrations to be at least locally equidistributed. This holds certainly for silicon covered with an ideal nitride. For the center of the wafer it holds as long as the influence of the boundary is negligible. We will refer to this assumption below. It is then possible to neglect the diffusion terms in equations (1) and (2). This leads directly to

$$\frac{\partial C_I}{\partial t} = -K_B(C_I C_V - C_I^{EQ} C_V^{EQ}) \tag{9}$$

$$\frac{\partial C_V}{\partial t} = -K_B(C_I C_V - C_I^{EQ} C_V^{EQ}) \tag{10}$$

and consequently to

$$\frac{\partial C_I}{\partial t} = \frac{\partial C_V}{\partial t} \tag{11}$$

$$C_I - C_I^0 = C_V - C_V^0 \tag{12}$$

The superscript 0 refers to the initial values. Equations (9), (10) can be solved analytically. For our estimation, however, it suffices that thermal equilibrium is established for sufficiently long times in the form

$$C_I C_V = C_I^{EQ} C_V^{EQ} \tag{13}$$

If we assume that

$$C_I^0, C_V^0 \ll \sqrt{C_I^{EQ} C_V^{EQ}} \tag{14}$$

holds, an estimate for C_I and C_V can be given in the form

$$C_I \simeq C_V \simeq \sqrt{C_I^{EQ} C_V^{EQ}} \tag{15}$$

Since the only assumption needed to obtain this result is given by equation (14), this estimation is valid independently from the thermal history of the wafer. The supersaturation of interstitials is then given by

$$S_I = \frac{C_I}{C_I^{EQ}} = \sqrt{\frac{C_V^{EQ}}{C_I^{EQ}}} \tag{16}$$

For our choice of parameters the supersaturation is of the order of 9.

This is clearly shown in Fig. 1. In Fig. 3 and 5, the supersaturation has diminished due to the influence of the interface.

b) Influence of Bulk Reaction Rate

From equation (9), it is evident that the time constant needed to reach thermal equilibrium is reciprocal to K_B. If we chose $K_B \rightarrow \infty$, this means that thermal equilibrium is reached immediately. This does not mean, however, that $C_I = C_I^{EQ}$ and $C_V = C_V^{EQ}$ holds, but simply that (13) is fulfilled. This is indicated by the fact that the peak supersaturation of interstitials in Fig. 5 is larger than in Fig. 3. Therefore, the minimum value of K_B seems to be more critical. The parameter used is the smallest that we found in literature. A smaller value could lessen the maximum supersaturation under a silicondioxide interface. The supersaturation under an ideal nitride interface, however, will be unchanged as long as the value of K_B is large enough to establish thermal equilibrium.

c) Influence of Boundary Conditions

The results from section 2 clearly show that boundary conditions determine the behavior of point defects near surfaces. In the case of Neumann boundary conditions, the point defects are equidistributed in the wafer and can be computed using (9) and (10). In the case of Dirichlet boundary conditions, on the other hand, the concentrations of the point defects at the interface, and for sufficiently long times in the whole silicon crystal are determined by the interface.

d) Influence of Diffusion Coefficients

The influence of the diffusion coefficients on the point defect concentrations beneath interfaces is relatively small. Under the nitride interface, the concentrations of point defects are nearly homogenous. Therefore, the diffusion terms in the partial differential equations vanish without special regard to the exact value of the diffusion coefficients. Under the silicon dioxide interface, the point defect concentrations are determined by the boundary, again without special regard to the exact values of the diffusion coefficients.

5. CONCLUSION

Our simulations have shown that the standard model given in section 1 is incompatible to the assumption that the point defect concentrations are homogeneously distributed in the wafer. This could have severe influence on the numerical analysis of e.g. back-side oxidation experiments. We have shown that the point defect concentrations at an ideal oxide interface deviate little from the equilibrium values whereas under a nitride interface large deviations may occur. In consequence, we expect that the diffusion of e.g. phosphorus under a nitride interface is enhanced or retarded by a factor $\sqrt{C_V^{EQ}/C_I^{EQ}}$ compared to the diffusion under an oxide interface. If this effect cannot be seen experimentally, this could only be due to one of the following possibilities:

- the point defects do not only recombinate as pairs, but also as individuals. In this case, however, a change in the macroscopic defects should be observed.

- it is possible that the bulk-generation of point defects is too slow. This would mean that the value of K_B would have to be significantly smaller than our value.

- the properties of the interfaces deviate strongly from their idealizations. This is rather unlikely for the oxide interface. For the nitride interface a native oxide layer could change its characteristics. In this case, it is worthwhile to study the question whether or not Neumann boundary conditions can be attainded at all.

- as for the parameters, we have shown that their real values do not concern. There are, however, two exceptions where no effect can be seen:

  a) The equilibrium concentrations are constant with respect to the process temperature. We consider this to be unlikely.

  b) The equilibrium concentrations are equal for all temperatures. This is possible but would mean that the usual assumptions about the diffusion parameters are grossly wrong.

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