#### Universal Model for Impurity Diffusion and Oxidation of Silicon

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A new boundary condition for self-interstitials is proposed by assuming a significant fraction of the generated interstitials flowing into the oxide during thermal oxidation. The boundary condition solves several problems which can not be explained by the models reported so far:(1)stripe width dependence of nitridation enhanced diffusion of antimony, and (2)OED and ORD of boron in HCl oxidation, (3)oxidation retarded diffusion of boron and phosphorus at high temperature, (4)sublinear oxygen pressure dependence of oxidation rate constant, (5)crossover of oxidation rate between (100) and (111) orientations at low oxygen pressure.

# 1 Introduction

Thermal oxidation of silicon is one of the most fundamental processes in modern VLSI fabrication. It is widely accepted that thermal oxidation of silicon generates excess self-interstitials at the Si/SiO2 interface causing oxidation enhanced diffusion (OED) and the growth of oxidation induced stacking fault (OSF)<sup>1)</sup>. Most of the generated self-interstitials at the interface flow into the oxide and react with incoming oxygen to form new oxide adjacent to the interface<sup>2,3)</sup>. It should be noted that net oxidation rate is composed of the oxidation of the excess self-interstitials in the oxide and the direct oxidation of silicon substrate. Therefore, the new boundary condition requires to modify the well known oxidation model<sup>4)</sup> and impurity diffusion models a well. In this paper, we demonstrate that the new model well explains several phenomena on impurity diffusion and thermal oxidation whose mechanisms have not been well understood yet. Those are (1)sublinear oxygen pressure dependence of oxidation rate constant<sup>5)</sup>, (2)crossover of oxidation rate between (100) and (111) orientations at low oxygen pressure<sup>6)</sup>, (3) oxidation retarded diffusion (ORD) of boron and phosphorus at high temperature<sup>7)</sup>, (4) stripe width dependence of nitridation enhanced diffusion of antimony<sup>8)</sup>, and (5) OED and ORD of boron in HCl oxidation<sup>9)</sup>.

### 2 Physical model

Due to the volume expansion accompanied with the oxidation reaction, silicon self-interstitials are generated at the  $Si/SiO_2$  interface. The generation rate of self-interstitials is assumed to be proportional to the chemical reaction at the interface, To avoid the continuous buildup of self-interstitials at the interface, the following three annihilation mechanisms are taken into account: (1)interstitial flux into the oxide, (2)interstitial flux into the bulk silicon and (3)surface recombination at surface kinks. All mechanisms presented here are schematically illustrated in Fig. 1. The continuity equation for self-interstitials at the



Fig. 1 Schematical illustration of self-interstitial generation model.

interface results in the following formula

$$\alpha k_{\rm d} C_0 = k_{\rm n} C_0^{\frac{1}{2}} C_{\rm I} - \frac{D_{\rm I}}{m_{\rm I}} \frac{\partial C_{\rm I}}{\partial x} \bigg|_0 + K (C_{\rm I} - C_{\rm I}^*) \quad (1)$$

where  $D_{I}$  and  $m_{I}$  are the diffusion coefficient of interstitials in silicon substrate and segregation constant of interstitials at the interface, respectively.  $C_0$  denotes the oxygen concentration at the interface.  $k_{\rm d}$ and  $\alpha$  are the reaction rate constant and the number of released silicon atoms per one oxygen molecule reacting with silicon substrate. The left hand side represents the generation of interstitials. The first term of right hand side (RHS) shows annihilation of interstitials in the oxide, the second indicates the flux into the silicon and the third is recombination of interstitials at surface kinks. Note that the second term of the RHS in Eq. (1), the flux into silicon substrate, is negligibly small compared to the other terms because of the rapid reaction of silicon interstitials in the oxide<sup>3)</sup>. Large segregation coefficient of interstitials at the interface also greatly reduces the interstitial flux into the substrate. Neglecting the second term, the above equation is rewritten as

$$\frac{C_{\rm I}}{C_{\rm I}^*} = \frac{\gamma}{\beta} \frac{\alpha C_0 + \beta}{C_0^{\frac{1}{2}} + \gamma} \tag{2}$$

The LHS of Eq. (2) represents the normalized self-interstitial concentration, which is schematically shown in Fig. 2 as a function of oxygen concentration.  $C_{\rm oc}$  in Fig. 2 denotes the critical oxygen concentration at which self-interstitial concentration at

the interface becomes its equilibrium value. Note that the low oxygen concentration leads to undersaturation of self-interstitials at the interface, causing ORD of dopants<sup>7</sup>) with high interstitialcy diffusion component.



Fig. 2 Normalized self-interstitial concentration as a function of oxygen concentration at the  $Si/SiO_2$ .

### 3 Impurity diffusion

### 3.1 Stripe width dependence

According to the experimental observations reported so far, nitridation of silicon does not generate interstitials at the interface. In addition, the experiments carried out by Mizuo and Higuchi<sup>10)</sup> indicate that the Si/SiN interface acts as a reflection boundary for self-interstitial. This means that there exists no surface regrowth process at the Si/SiN interface. Under these conditions, the boundary condition for self-interstitials is rewritten in the form as

$$k_{\rm n} C_n^{\frac{1}{2}} C_{\rm I} = \frac{D_{\rm I}}{m_{\rm I}} \frac{\partial C_{\rm I}}{\partial x} \bigg|_0 \tag{3}$$

where  $C_n$  represents ammonia molecule concentration at the interface. For simplicity, we deal with one dimensional case in the following discussion. During nitridation, surface interstitial concentration is controlled by the balance between the annihilation of interstitials due to the chemical reaction in the nitride film and the outward flux of self-interstitials in the silicon substrate. The above equation is, therefore, rewritten as

$$\frac{C_{\rm I}}{C_{\rm I}^*} = \frac{1}{1 + at^{0.5}}.\tag{4}$$

where t is nitridation time and a is composed of physical parameters such as  $D_I$ ,  $m_I$ ,  $\cdots$ . According to this equation, one notices that the surface interstitial concentration is always lower than the thermal equilibrium value during nitridation which agrees with experimental observation. In the following, we use an analytical method to explain the experimental data reported by Ahn and coworkers<sup>8</sup>, stripe width dependence of Sb diffused layer. At high temperature nitridation process, the diffusion length of interstitials in bulk silicon is much larger than the stripe width. In steady state conditions, the interstitial flux in the nitride film equals to the outward flux in bulk silicon, resulting in

$$k_{\rm n} C_{\rm n}^{\frac{1}{2}} C_{\rm I} = \frac{\pi D_{\rm I} (C_{\rm I} - C_{\rm I}^*)}{\ln(2\pi\sqrt{D_{\rm I}t}/w)} \tag{5}$$

Using Eq. (5) and local equilibrium condition between vacancies and interstitials, one finds that nitridation enhanced diffusion of Sb becomes significant with increasing stripe width. This result agrees well with the experimental observations<sup>8</sup>.

# **3.2** OED and ORD in $HCl/O_2$

Nabeta et. al.<sup>9)</sup> reported that the diffusion of boron at low HCl concentration in dry oxygen is enhanced, while at high HCl concentration results in oxidation retarded diffusion. In the presence of HCl gas, generated interstitials quickly react with molecular HCl resulting in volatile SiCl compound. Therefore, annihilation rate of interstitials is proportional to the product of HCl gas pressure and interstitial concentration. The net generation rate of self-interstitials is expressed as

$$G = \alpha k_{\rm d} C_0 - k_{\rm H} [{\rm HCl}] C_{\rm I} \tag{6}$$

The second term of the LHS represents the annihilation of interstitials near the interface due to the reaction with HCl molecules. Substitution of Eq. (6) into the LHS of Eq. (1) predicts oxidation enhanced diffusion of boron at low HCl concentration, while at high HCl concentration results in ORD.

# 4 Thermal oxidation

#### 4.1 Oxygen pressure dependence

As is described above, considerable amount of interstitials generated at the interface diffuse into the oxide and react with oxygen molecules to form new oxide adjacent to the interface which is expected to significantly affect the oxidation rate. Therefore, the observed oxidation rate is composed of two components, direct oxidation of silicon substrate and oxidation of interstitials in the oxide, which is given by

$$N\frac{dx}{dt} = k_{\rm d}C_0 + k_{\rm n}C_0^{\frac{1}{2}}C_{\rm I}$$
(7)

where N is the number of silicon atoms incorporated into a unit volume of silicon oxide. The first term of the RHS represents direct oxidation of silicon and the second is the oxidation of the self-interstitials in the oxide. Substituting Eq. (2) into Eq. (7), the observed oxidation rate is expressed as a function of oxygen concentration at the Si/SiO<sub>2</sub> interface

$$\frac{dx}{dt} = \frac{k_{\rm d}}{N} \left[ C_0 + C_0^{\frac{1}{2}} \frac{\alpha C_0 + \beta}{C_0^{\frac{1}{2}} + \gamma} \right]$$
(8)

The above equation has two limiting regimes as shown in Fig. 3: at high oxygen concentration than  $C_{oc}$ , linearly dependent oxidation rate constant is obtained, while at low oxygen concentration, one-half power dependence on oxygen pressure is derived. Although at low oxygen pressure, the direct oxidation of silicon substrate is no more dominant because of the lack of oxygen molecules at the interface, the last term of in Eq. (1) in turn generates self-interstitials to maintain the interstitial concentration to its equilibrium value. The observed oxidation rate is then limited by the oxidation of the self-interstitial in the oxide which has one-half power dependence on the oxygen concentration.

# 4.2 Orientation dependence

The density of silicon atoms on the (111) oriented substrate is larger than that on (100) so that the reaction rate constant,  $k_d$ , is considered to be larger for



Fig. 3 Oxide growth rate as a function of oxygen concentration at the interface.

the (111) than (100). The recombination constant, K, is assumed to be much larger for the (111) orientation than (100) because there exist much more surface kinks on the (111) plane. Under these reasonable assumptions, the critical oxygen concentration,  $C_{\rm oc}$ , corresponding to the break point in oxidation rate versus oxygen concentration curve, becomes smaller for (111) than (100) orientation. The model described above predicts that at high oxygen partial pressure, oxidation rate is larger for (111) than (100), while at low pressure, one finds the crossover of oxidation rate between (111) and (100) oriented wafers as shown in Fig. 3. The predicted orientation dependence agrees well with the observed experimental results<sup>6</sup>.

### 5 Conclusions

A new boundary condition for self-interstitials is proposed under the assumption of a significant fraction of the generated interstitials flowing into the oxide. The comparisons between the model and the several experimental results indicate that the newly proposed model is applicable for a wide range of processing conditions, and well predicts the following phenomena, (1)stripe width dependence of nitridation enhanced diffusion of antimony, and (2)OED and ORD of boron in HCl oxidation, (3)oxidation retarded diffusion of boron and phosphorus at high temperature, (4)sublinear oxygen pressure dependence of oxidation rate constant, (5)crossover of oxidation rate between (100) and (111) orientations at low oxygen pressure.

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