A Model of {311} Defect Evolution Based on Nucleation Theory

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Abstract—A new model of $\{311\}$ defect evolution is proposed. The defects are characterized by their mean size and their concentration. The flux between free interstitials and $\{311\}$ defects is described by an expression obtained by extending the classical theory of nucleation. The model is shown to agree well with the experimental data on $\{311\}$ defect evolution of Eaglesham et al. and with the boron TED data of Chao et al.

I. INTRODUCTION

It has been well established in recent years that {311} defects are an important source of transient enhanced diffusion (TED) [1], [2]. Models to describe the evolution of {311} defects cover a wide range of complexity, from a simple solubility approximation [3], to solving rate equations or a Fokker Planck equation. Moment-based models have been developed as a compromise between efficiency and accuracy [4], [5], [6]. They describe the defect size distribution by its first few moments. In the most simple case only the first moment, i.e. the concentration of interstitials contained in the clusters, is considered. With this model [4] it is possible to explain the most apparent features of TED, including the approximately steady level of enhancement during its duration, and the dependence of its duration on implant energy and dose. However, since there is no information about the cluster size, the dependence of the interstitial binding energy on the defect size is not taken into account. This results in a somewhat too abrupt decay of the simulated number of clustered interstitials as a function of time. and in the inability of the model to predict the experimentally observed [3] gradual decrease in the diffusivity enhancement during the duration of TED. Law and Jones [5] showed that the exponential-like decay of the number of clustered interstitials may be reproduced by a two-moment model, considering the density of defects (or equivalently, the mean number of atoms per defect) in addition to the concentration of interstitials in defects. Their Ostwald ripening model seems to be empirical, though, and they identified the need for further improvement. Gencer and Dunham [6] applied a three-moment model [7] to {311} defects. Investigations of this model [8] show that the size distribution function tends to be separated into two distinct parts. One is located at the smallest cluster sizes and contains

only a small fraction of the clustered interstitials, once most free interstitials have been absorbed by clusters. The other one becomes increasingly narrow with time and moves to larger cluster sizes, reflecting the Ostwald ripening process. This suggests that it should be possible to neglect the first part and to approximate the second part by a δ -function, so that two moments are sufficient to describe the size distribution function.

In this paper we present a new two-moment model of $\{311\}$ defect evolution. The model and its motivation by the classical theory of nucleation are described in Section II.A. The formulae for Gibbs' free energy and the reaction rate constant used are presented in Sections II.B and II.C, respectively. The model predictions are compared in Section III with experimental data on the temporal evolution of the $\{311\}$ defect size and density [1], [9], and on the time variation of the B diffusivity during TED [3]. Conclusions are presented in Section IV.

II. MODEL

A. Model equations

We assume that the clusters may be described by their mean size m and their concentration $C_{\rm C}$ in clusters per cm⁻³. The model thus has to describe the flux between free interstitials (concentration $C_{\rm I}$) and clusters of size m. The two quantities determining this flux are the rate constant κ_n of the reaction between interstitial and cluster of size n, and the Gibbs' free energy ΔG_n as a function of n. Typically, the Gibbs' energy function has a maximum between n = 1 and n = m (Fig. 1), defining the critical size $n_{\rm c}$. Thus the classical theory of nucleation [10], [11] may be used to determine the rate of cluster formation. Assuming steady state conditions, the nucleation rate is proportional to the concentration $C_{\rm I}$ of interstitials, to the growth rate $\kappa_{n_c}C_{\rm I}$ of a cluster of critical size $n_{\rm c}$, and to a Boltzmann factor containing the energy barrier $\Delta G_{n_c} - \Delta G_1$ a cluster has to overcome to grow from a single interstitial (viewed as a cluster of size 1) to a stable precipitate. In order to describe also the reverse current of dissolving clusters, we propose that the dissolution rate may be written in an analogous way in terms of the concentration of clusters $C_{\rm C}$, the dissolution rate $\kappa_{n_c} C_{n_c}^{\star}$ of a critically sized cluster, and the energy barrier $\Delta G_{n_c} - \Delta G_m$ to be overcome for dissolution (cf. Fig. 1). The

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Fig. 1. Gibbs' free energy as a function of cluster size (schematic). Free interstitials have a free energy barrier of $\Delta G_{n_c} - \Delta G_1$ for nucleation. Clusters of size *m* have a free energy barrier $\Delta G_{n_c} - \Delta G_m$ for dissolution.

continuity equation for clusters therefore reads

$$\frac{\partial C_{\rm C}}{\partial t} = \kappa_{n_{\rm c}} Z \left[C_{\rm I}^2 \exp\left(-\frac{\Delta G_{n_{\rm c}} - \Delta G_{\rm I}}{kT}\right) - C_{n_{\rm c}}^{\star} C_{\rm C} \exp\left(-\frac{\Delta G_{n_{\rm c}} - \Delta G_{\rm m}}{kT}\right) \right]$$
(1)

Z is the Zeldovich factor which is given by [12]

$$Z = \left(-\frac{1}{2\pi kT} \left. \frac{\mathrm{d}^2 \Delta G_n}{\mathrm{d}n^2} \right|_{n=n_{\rm c}} \right)^{1/2} \tag{2}$$

 C_n^{\star} is the concentration of interstitials which would be in equilibrium with a cluster of size n [6]. Since for a critically sized cluster the probability for growth equals the probability for dissolution, $C_{n_c}^{\star}$ is identical to the actual interstitial concentration C_1 . Apart from nucleation and dissolution, existing clusters of size m may grow according to the growth law

$$\frac{\partial m}{\partial t} = \kappa_m (C_1 - C_m^\star) \tag{3}$$

The third equation for the three dependent variables C_{I} , C_{C} , and m is the continuity equation for interstitials

$$\frac{\partial C_{\rm I}}{\partial t} = \nabla (D_{\rm I} \nabla C_{\rm I}) - \frac{\partial (mC_{\rm C})}{\partial t} \tag{4}$$

In the final declustering phase the size m gets smaller than the critical size n_c . In this case we replace n_c in Eqs. 1 and 2 by m, thus eliminating the energy barrier for dissolution. Moreover, we damp the cluster dissolution (Eqs. 1 and 3) by an exponential function with a time constant small compared to the overall TED time to avoid time stepping problems which have also been reported in [5].

B. Gibbs' Free Energy

The Gibbs' free energy of a cluster of size n is given by

$$\Delta G_n = -nkT \ln \frac{C_{\rm I}}{C_{\rm ss}} + \Delta G_n^{\rm exc} \tag{5}$$

where C_{ss} is the interstitial concentration in equilibrium with an infinitely large {311} defect ("solid solubility"). ΔG_n^{exc} is the excess energy due to surface and strain effects. Although it must be a sublinear function of size in order for the defects to be stable, the exact form is unknown. In the absence of further information it is taken as being similar to a planar defect

$$\Delta G_n^{\text{exc}} = a_0 n^{1/2} \tag{6}$$

We therefore have three parameters to be fitted to experimental data: prefactor and activation energy of C_{ss} , and a_0 .

C. Reaction Rate Constant

The reaction rate constant κ_n is composed of a diffusion limited part κ_n^d and a reaction limited part κ_n^r according to

$$\kappa_n = \left(1/\kappa_n^{\rm d} + 1/\kappa_n^{\rm r}\right)^{-1} \tag{7}$$

The reaction limited part can be written

$$\kappa_n^{\rm r} = \nu \delta_{\rm if} A \exp\left(-\frac{\Delta G_{n \to n+1}}{kT}\right) \tag{8}$$

where $\nu = 4D_1/\delta^2$ is the diffusion jump frequency, δ_{if} the thickness of the interface between defect and matrix (taken equal to the nearest neighbor distance, $\delta = 2.35$ Å, in the matrix), and A the surface of the reaction volume. The {311} defects are assumed to have rectangular shape (length l, width w) and to grow only in length direction. The reaction volume is taken as two cylinders with capping half spheres around the short edges of the defect [6]. The radius r_0 of the cylinders and half spheres is the capture radius and is assumed to be equal to the lattice constant (5.43 Å). The Gibbs' energy $\Delta G_{n\to n+1}$ a cluster has to surmount to grow from size n to size n + 1 is neglected, since in our model we evaluate reaction rate constants only at the critical size and at the size m which is usually supercritical.

The diffusion limited reaction rate constant may be estimated for each end of the defect by approximating the reaction volume by a spherically symmetric ellipsoid. By introducing further approximations the general formula [13] may be reduced to

$$\kappa_n^{\rm d1} \approx 4\pi (w/4 + r_0) D_{\rm I} \tag{9}$$

The combined effect of the two reaction volumes is $\kappa_n^d = \kappa_n^{d1}$ in the limiting case $l \to 0$, and $\kappa_n^d = 2\kappa_n^{d1}$ for $l \to \infty$. As a smooth interpolation between these two cases we assume

$$\kappa_n^{\rm d} = 2\left\{ \left(\kappa_n^{\rm d1}\right)^{-1} + \left[\left(4\pi l D_{\rm I}\right)^2 + \left(\kappa_n^{\rm d1}\right)^2 \right]^{-1/2} \right\}^{-1}$$
(10)



Fig. 2. $\{311\}$ defect evolution after 40 keV, 5×10^{13} cm⁻² Si implantation: defect density and size during anneal at 815°C. Lines: simulation results obtained with the proposed two-moment model. Symbols: experimental data from Eaglesham et al. [1]. The error bars of the experimental data result from assuming a defect width of either 4 or 5 nm.

The width w and the length l are calculated from the areal density of interstitials in {311} defects which has been determined as 5×10^{14} cm⁻² [14], assuming a fixed width for l > w and l = w for smaller defects [6]. Although the errors introduced by the approximations in the derivation of Eqs. 9 and 10 might be as large as a factor of 2, they are unlikely to influence the final result, since it is much more sensitive to changes in the Gibbs' energy than to changes in the reaction rate constants.

III. RESULTS

The model equations presented in Section II have been implemented in PROPHET [15]. The diffusivity D_1 and the equilibrium concentration C_1^{\star} of interstitials have been chosen according to Bracht [16]. The surface recombination length has been assumed to be 10 Å. The initial conditions for the interstitial distribution after ion implantation are determined by calculating the net interstitial concentrations (i.e. interstitial minus vacancy plus dopant concentrations) using the Monte Carlo simulator IMSIL [17], [18]. It is assumed that no clusters exist after ion implantation and that the size of newly formed clusters initially is 30. The choice of the initial cluster size does not influence the final results as long as it is significantly smaller than the size calculated for the smallest anneal time and larger than some minimum value, below which clusters may not form in the model. The latter restriction is probably due to the limited applicability of nucleation theory in case of small critical sizes.

The solubility and the Gibbs prefactor were fitted to the data of Eaglesham et al. [1], [9] (Figs. 2 and 3). The values are $C_{ss} = 3.6 \times 10^{22} \text{ cm}^{-3} \times \exp(-2.22 \text{ eV}/kT)$ and $a_0 = 4 \text{ eV}$, respectively. As can be seen from Fig. 2 the model captures the Ostwald ripening effect, i.e. the increase in cluster size and the decrease in cluster density with time. A good fit of the temporal



Fig. 3. $\{311\}$ defect evolution after 40 keV, 5×10^{13} cm⁻² Si implants: interstitial density stored in $\{311\}$ defects during various anneals. Lines: simulation results obtained with the proposed two-moment model (solid and dotted lines) and with the earlier one-moment model [4] (dashed lines). Symbols: experimental data from Eaglesham et al. [1], [9]. The error bars of the 815°C data result from assuming a defect width of either 4 or 5 nm.

evolution of the defect density and size at $815^{\circ}C$ (Fig. 2), and of the number of interstitials in defects at different temperatures (Fig. 3) is obtained. For comparison, the results of the onemoment model [4] are shown in Fig. 3, assuming a {311} cluster evaporation energy of 3.57 eV. Taking the changing size and changing binding energy of the clusters into account clearly gives a better match to the overall shape of the dissolution curves.

The same model can then be applied to simulate the TED experiments of Chao et al. [3]. In these experiments the interstitial supersaturation after Si implants was monitored by TED of a boron marker layer as a function of anneal time at 750°C. In order to calculate the diffusivity enhancement $D_{\rm B}/D_{\rm B}^{\rm intr}$ from the measured profiles, an intrinsic equilibrium diffusivity $D_{\rm B}^{\rm intr}$ of 4.5×10^{-18} cm²/s at 750°C was assumed. This is a little lower than a simple extrapolation from high temperature intrinsic measurements, but still within error tolerances. The simulated diffusivity enhancement was calculated by evaluating $1/t \times \int C_{\rm I}/C_{\rm I}^{\star} dt$ at the position of the marker layer. Without changing any parameter with respect to the simulation of the Eaglesham data, the new model agrees well with the TED data (Fig. 4). The decrease in the diffusivity enhancement observed at short anneal times reflects the decrease in the interstitial supersaturation caused by the increase in the binding energy of interstitials to {311} defects during Ostwald ripening. The earlier model, which uses a fixed binding energy, cannot capture this effect. Although the evolution of the transient is well described by the present model, the final displacements are somewhat overpredicted. This does not directly affect the present model, since the final displacements are independent of the cluster model, all clusters having dissolved and given up their interstitials at the end of the transient. The deviation may



Fig. 4. Time averaged B diffusivity enhancement after various Si implants and anneals at 750°C. Lines: simulation results obtained with the proposed two-moment model (solid lines) and with the earlier one-moment model [4] (dashed lines). Symbols: experimental data from Chao et al. [3]

be due to uncertainties in the starting damage condition, or to boron clustering which has been reported at low concentrations in these layers [19].

IV. CONCLUSIONS

A model of $\{311\}$ defect evolution has been proposed which uses the classical theory of nucleation for cluster formation, an analogous approach for cluster dissolution, and a simple growth law to describe the change in cluster size. The Ostwald ripening effect is included in this model by the combination of cluster dissolution and growth. It has been shown that after calibration of the model with data on {311} defect evolution, simulations of boron TED agree well with the experimental data without change of any parameter. In contrast to a one-moment model, the new model is capable of predicting the variation of the diffusivity enhancement with time. A limitation is the inaccuracy in describing the initial nucleation and the final dissolution phase. In many cases this shortcoming will not be relevant, since these phases are short and the system behavior is determined by the long intermediate Ostwald ripening phase. Apart from this limitation, the model is general in nature, so it should be applicable also to other large defect types like dislocation loops.

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