Modeling Of Implantation Induced Transient Enhanced Diffusion Of Boron

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Boron transient enhanced diffusion (TED) is characterised by enhanced tail diffusion coupled with an electrically inactive immobile peak associated with the clustering of boron in the presence of excess interstitials. A consistent model for process simulation has to account for the formation of both interstitials clusters and dopant/interstitial clusters (e.g., $\{311\}$ defects and boron interstitial clusters). Boron interstitial clusters (BICs) can be modeled using either a finite set of clusters or using moment based models that consider a large range of cluster sizes. In this paper, we describe a model system that can successfully predict boron TED. We focus in particular on the initial stages of annealing and boron clustering models.

INTRODUCTION

Ion implantation introduces damage that on annealing leads to the phenomenon of transient enhanced diffusion (TED). Implantation introduces a large number of point defects orders of magnitude higher than the dopant concentration. These excess interstitials and vacancies recombine with each other during the initial stages of annealing. As we describe below, for low dose implants the remaining net effective interstitial excess significantly exceeds '+1' due to rapid vacancy diffusion. The remaining point defects interact with the dopants via coupled diffusion. Excess point defects also form extended defects,[1] primarily $\{311\}$ defects for interstitials and boron interstitial clusters (BICs) for boron. For $\{311\}$ defects we use a moment-based approach described in previous work.[7] Below we discuss alternatives for modeling of boron clustering, including a moment-based approach and a simplified cluster model, and compare the resulting simualtions to experimental results.

INITIAL DAMAGE

Each implanted ion creates a defect cascade, producing a large number of interstitials and vacancies. Fig. 1 shows a typical set of defect and dopant profiles from TRIM,[5] a Monte Carlo ion implantation simulator. Although the large initial interstitial and vacancy profiles are nearly equal, substracting them reveals that the surface is vacancy rich while interstitials are kicked deeper into the substrate, with the integrated net $I-V$ dose approximately equal to the implant dose. For lighter ions like boron where the displacement between interstitials and vacancies is small, a '+1' model has appeared to be a reasonable approximation,[6] and there has been considerable success in modeling TED using this simple model. However, we have found that there is considerable underestimation of diffusion using this approach for low implant doses.[7] This is because when the defect density is relatively small, the faster diffusing species can reach the surface before encountering the opposite type defect. Since based on *ab initio* calculations,[8] vacancies diffuse faster than interstitials, they are annihilated at the surface more often leading to a net 'plus' value greater than one as shown in Fig. 2. The simulations were done using a continuum diffusion simulator that used the full interstitial and vacancy distribution from TRIM as inputs. It may be noted that for moderate or high implant doses I/V recombination quickly leads to a approximately '+1' distribution, validating the effectiveness of the '+1' approach.

Experiments have shown that TED scales nonlinearly with dose.[10] This behavior cannot be satisfactorily explained using a '+1' model. We found[9] that using the '+n' factor obtained from simulations of the full I and V profiles along with fast vacancy diffusion satisfactorily explains the dose dependence of boron marker layer experiments[10] for silicon implants. As shown in Fig. 3, using this same methodology for boron TED,

we can successfully predict low dose TED, while using a '+1' model underestimates the total amount of diffusion. Note that for low doses, clustering is minimal and the model used for BICs has little or no impact.

BORON CLUSTERING

At medium to high doses, boron clustering is the predominant effect and can be simulated with a variety of models. Boron aggregation is a complicated process as there is a huge array of potential cluster compositions. Cluster models consider a subset of discrete smaller sized clusters, whereas moment-based models like KPM[11] consider a larger range of cluster sizes but make assumptions about smooth changes in properties with size and limits the system to clusters within a narrower range of B/I ratios.

Kinetic Precipitation Model (KPM)

Within KPM, the evolution of BICs is modeled by considering precipitates of different sizes as independent species (f_n) with their kinetics determined by the attachment and emission of solute atoms.[7] The aggregation process is driven by the change in free energy associated with clustering. This energy can be written as the sum of volume terms which represents the change in energy upon adding either a boron or interstitial to the B_nI_m cluster, plus the excess surface energy and strain energies associated with finite size precipitates:

$$\Delta G_{n,m} = -nkT \ln\left(\frac{C_{\mathrm{B}}}{{C_{\mathrm{B}}}^{ss}}\right) - mkT \ln\left(\frac{C_{\mathrm{I}}}{{C_{\mathrm{I}}}^{ss}}\right) + \Delta G^{\mathrm{surf}}_{n,m} + \Delta G^{\mathrm{stress}}_{n,m}. \quad (1)$$

Under the presence of an interstitial supersaturation, the optimum number of incorporated interstitials in a B_nI_m cluster can be found by minimizing the free energy $\Delta G_{n,m}$. This leads to an effective boron solid solubility that decreases with increasing interstitial supersaturation as observed experimentally.[14]

The full cluster size distribution (f_n) evolves based on the current size distribution and the boron and interstitial concentrations. However, to efficiently integrate this model into a diffusion equation solver, we use a moment-based approach[11] and keep track of only the lowest three *moments* of the distribution ($m_i = \sum_{n=2}^{\infty} n^i f_n$, where $i = 0, 1, 2$), using the closure assumption that the distribution is the one that minimizes the free energy given the moments.

Cluster Models

Cluster models use a series of kinetic reactions describing the evolution of a finite set of clusters. For example, a substitutional boron can react with a silicon self interstitial to form an immobile BI which can further react with another interstitial to form a BI_2 cluster or with an interstitial boron (B_i) to give B_2I_2. For reactions of the form A + B $\Leftrightarrow$ C, the rate of formation of C is given by,

$$R = 4\pi r_{\mathrm{cap}}(D_{\mathrm{A}} + D_{\mathrm{B}})(C_{\mathrm{A}}C_{\mathrm{B}} - \frac{C_{\mathrm{C}}}{K_{\mathrm{eq}}}) \quad (2)$$

where r_{cap} is the capture radius of the reaction and D and C represent diffusivity and concentration. In previous work, Lilak *et al.*[3] presented a boron clustering model based on the same calculations which we use in this work. Pelaz *et al.*[4] derived a similar model, but with a somewhat different parameter set. In both cases, they considered a large range of cluster sizes (8–10), with an associated large set of continuity equations and parameters.

In an effort to develop a much simpler cluster model, we analyzed a system with 10 different clusters: BI, BI_2, B_2I, B_2I_2, B_3I, B_3I_2, B_4I_2, B_4I, B_2, B_3 based on cluster energetics calculations from Zhu *et al.*[12]. We found[13] that except for B_3I and B_4I_2, all the clusters reach dynamic equilibrium with the B and I concentration within a very short time, while the two larger clusters are also in local dynamic equilibrium. At the same time, only a small subset of the clusters are ever present in significant numbers. BI_2 are the dominant cluster at very short times when the interstitial supersaturation is large. Once $\{311\}$ defects form, the interstitial concentration drops and the dominant species is B_3I.

Based on the above observations, we can simplify the system of immobile clusters from ten to just one continuity equation, that for B_3I, with the rate of formation given by

$$R_{B_3I} = k^r_{B_3I}(K_{B_3I}C_B^3C_I - C_{B_3I}) \quad (3)$$

In addition, we can also ignore the concentrations of small clusters other than BI_2, which we express in terms of the free boron and interstitial concentrations:

$$C_{BI_2} = K_{BI_2}C_BC_I^2 \quad (4)$$

We compared our simplified model to the full system and found that the results are virtually indistinguishable. It was found that both the cluster and the moment-based models can reasonably model boron TED data over a range of experimental conditions. Figs. 4 and 5 show examples of this comparison as well as to data from Intel[14] for TED at 800°C. We also found satisfactory fits for implant energies from 20–80 keV and doses of 10^{13}–2×10^{14} cm^{-2}. Similarly we found good results over a wide temperature range (700–1000 °C).

CONCLUSIONS

We have developed a set of models for predicting boron TED behavior. The focus of this work was on the initial stages of annealing and boron clustering. It was found that for low doses, the initial interstitial/vacancy recombination plays an important role, leading to a '+n' behavior. This also supports the results of atomistic calculation which conclude that vacancies diffuse faster than interstitials. For medium/high boron doses, a boron clustering model is essential. We found that consideration of either a finite set of discrete clusters or a moment-based model such as KPM can match experimental data satisfactorily for medium doses. A simple cluster model based on atomistic calculations was shown to give good results in predicting medium dose boron TED.

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[14]TED SIMS data from Intel Corporation.

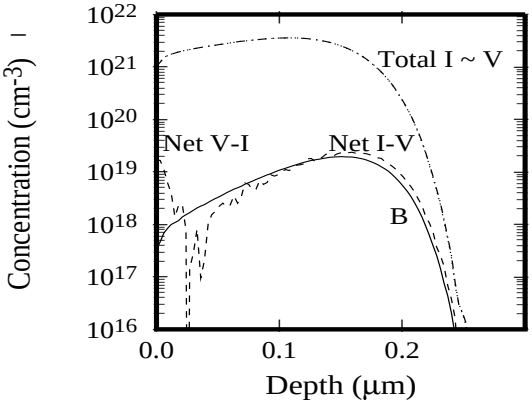


Fig. 1: Monte Carlo s imulation showing initial distributions of boron, interstitials and vacancies following a 40 keV, 2×10^{14} cm^{-2} B implant.

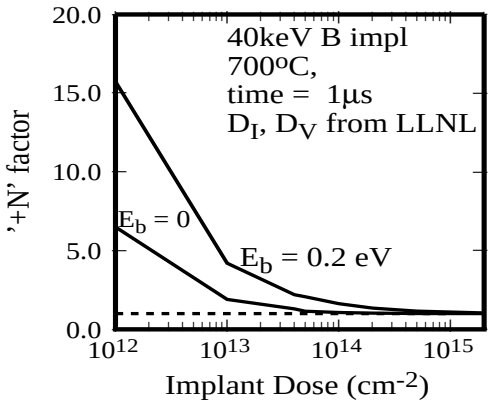


Fig. 2: Net interstitial dose remaining after the recombination process starting from the total initial defect distributions. E_b is the barrier to I/V recombination.

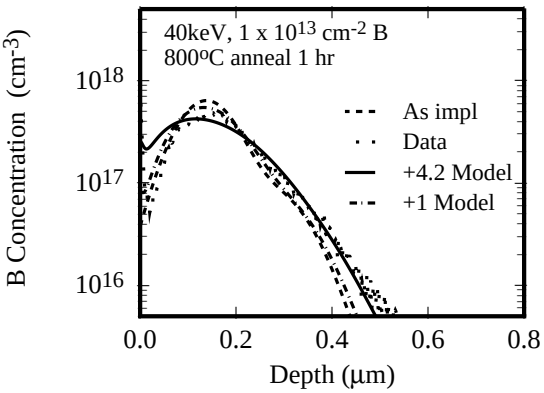


Fig. 3: Prediction of B TED f or 10^{13}cm^{-2}. A '+n' model based on the full initial defect profile is able to predict diffusion behavior seen experimentally,[14] while a '+1' model under-estimates diffusion.

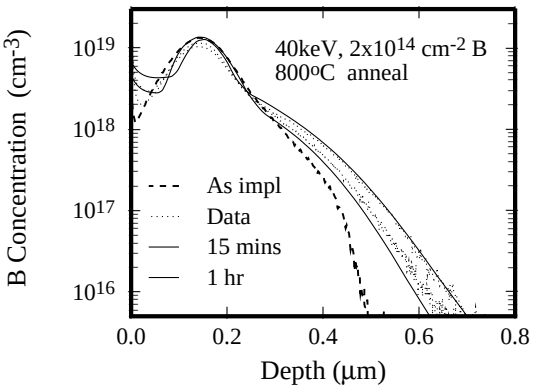
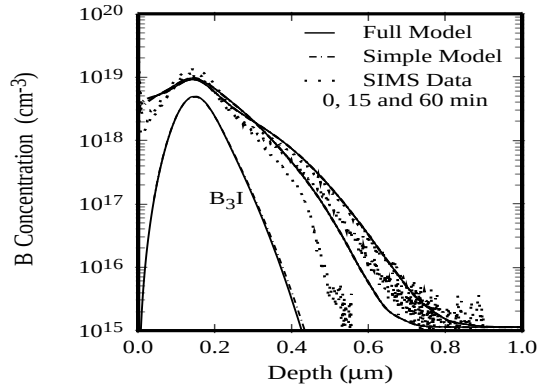


Fig. 4: Simulations results for a 2×10^{14} cm^{-2}, 40 keV B implant annealed at 800°C with KPM model compared to data from Intel.[14]



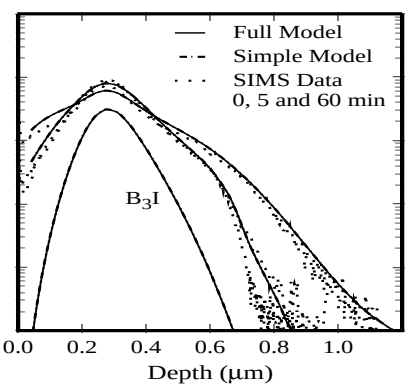


Fig. 5: Comparison of multi cluster model with the single cluster model for (b) 40keV and (c) 80keV, 2×10^{14}cm^{-2} B implants annealed at 800°C compared with SIMS data[14]. Note that the full model and simple model show indistinguishable final profiles. The B_3I concentrations for the two models (shown after a 1 h anneal) are also nearly identical.