# ATOMISTIC MODELING OF POINT AND EXTENDED DEFECTS IN CRYSTALLINE MATERIALS

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## ABSTRACT

Atomistic process modeling, a kinetic Monte Carlo simulation technique, has the interest of being both conceptually simple and extremely powerful. Instead of reaction equations it is based on the definition of the interactions between individual atoms and defects. Those interactions can be derived either directly from molecular dynamics or first principles calculations, or from experiments. The limit to its use is set by the size dimensions it can handle, but the level of performance achieved by even workstations and PC's, together with the design of efficient simulation schemes, has revealed it as a good candidate for building the next generation of process simulators, as an extension of existing continuum modeling codes into the deep submicron size regime. Over the last few years it has provided a unique insight into the atomistic mechanisms of defect formation and dopant diffusion during ion implantation and annealing in silicon. Object-oriented programming can be very helpful in cutting software development time, but care has to be taken not to degrade performance in the critical inner calculation loops. We discuss these techniques and results with the help of a fast object-oriented atomistic simulator recently developed.

### INTRODUCTION

Computer simulation is a powerful analysis and design tool, complementary to experimental techniques. It is experiencing a rapid growth which is a reflection of the unparalleled rate of increase in computing power. For example, around 1978 the typical computer available locally at British universities would take 10  $\mu$ s per floating-point operation (0.1 Mflops)<sup>1</sup> and would have about 1 Mbyte RAM. It is common nowadays to have access to machines with gigaflops and gigabytes. This combined increase in speed and memory gives many orders of magnitude increase in computing power. No experimental technique, like SIMS or RBS, has seen anything comparable to that rate of progress. In addition to that, computer costs have also been reduced by orders of magnitude, which again is not the case for experimental facilities.

The simulation of semiconductor processes, in particular, is now well established for studying new materials and new phenomena, as well as for designing new device structures. Until recently, diffusion simulators were only based on continuum type models and partial differential equation (PDE) solvers. Within this approach, to simulate the diffusion and recombination of silicon interstitials (I) with vacancies (V),

$$\mathbf{I} + \mathbf{V} \leftrightarrow \mathbf{0} \tag{1}$$

we have to solve:

$$\partial I/\partial t = D \partial^2 I/\partial x^2 - R VI$$
 (2)

The addition of a simple new mechanism, like the interaction of an I with a substitutional boron (B) to give an I-B pair  $(B_I)$ ,

$$\mathbf{I} + \mathbf{B} \leftrightarrow \mathbf{B}_{\mathbf{I}} \tag{3}$$

triggers an additional set of coupled equations like:

$$\partial I/\partial t = D \partial^{2} I/\partial x^{2} - K_{IF}BI + K_{IR} B_{I} - R VI$$
  

$$\partial B_{I}/\partial t = D \partial^{2} B_{I}/\partial x^{2} + K_{BIF}BI - K_{BIR} B_{I}$$
(4)  

$$\partial B/\partial t = - K_{BSF}BI + K_{BSR} B_{I}$$

As a consequence, computation time can increase from a few seconds or minutes for just diffusion of a single non-interacting species to several hours in the case of a complex scenario involving a variety of interacting species.

Fortunately, the shrinkage in device dimensions together with the level of performance achieved by computers, is opening the way to a new -simpler, more efficient and more accurate- type of process simulator, the atomistic diffusion simulator. The atomistic diffusion simulator simulates the movements and interactions of individual point defects. In this case the I-V recombination process (1) is implemented by simply removing both particles from the simulation box:

and similarly, the I-B interaction (3) translates into just:

PROGRAM:	annihilate(I);	
	annihilate(B);	(6)
	create(B <sub>I</sub> );	

The program can have a similar set of lines for other interactions (I-Carbon, V-Oxygen, ...). Thus, we can handle as many different interactions as we need with essentially the same computation time as for the simplest case (5). In practice we observe an increase factor of less than 2 in the computation time for the most complex simulations, compared to simple diffusion of just one single I atom.

#### Previous Approaches

Molecular dynamics (MD) has been used in many diffusion studies. It is the most accurate type of atomistic simulation. However, due to the fact that it includes all lattice atoms and involve complex force calculations, it can only simulate dimensions of several nanometers and, more importantly, just a few picoseconds or nanoseconds.

Kinetic Monte Carlo (MC) techniques have already been employed to simulate point defect diffusion in some statistical studies <sup>2, 3</sup> but limited to cascade-size regions.

Three years ago, at Bell Laboratories, we tried a step forward: Is it possible to use a kinetic Monte Carlo scheme to simulate the implants and anneals typically performed in semiconductor

device processing? To test it we developed BLAST <sup>4</sup>, an atomistic diffusion simulator, and for a typical implant (40 keV,  $5E^{13} Si^+/cm^2$ ) and anneal (815 °C, 10 min) the simulation time was about 20 hours on a typical workstation. Those simulations proved to be extremely helpful by revealing "for the first time, a complete history of the I and V populations, including the formation and ripening of defect clusters" as well as "the mechanisms leading to the success of the (empirical) '+1' model" <sup>4</sup>. The use of BLAST also led to the development of an accurate model of boron diffusion and clustering <sup>5</sup>, Fig. 1. That model provided parameters and simplified mechanisms which could be implemented in continuum process simulators, such as SUPREM or PROPHET. The conclusion, therefore, was twofold: (1) atomistic diffusion simulations were feasible, at least for research purposes if we consider the required computation time, and (2) they can provide a unique insight into the dominant mechanisms governing ion implantation and annealing.



Figure 1. Simulated and experimental profiles of two B spikes after 40 keV,  $2x10^{13}$  Si<sup>+</sup>/cm<sup>2</sup> implant and 35 min anneal at 800 °C. Thin lines represent experimental data, thick solid lines the simulated B profile, and thick dashed lines the simulated B in clusters.(from Ref.5)

### SIMULATION SCHEME

An atomistic diffusion simulator basically consists of a **simulation box**, of dimensions ranging from tens of nanometers to a few microns, containing a variety of point and extended defects. Contrary to MD, in this kinetic MC scheme lattice atoms are regarded as a background and are not included in the simulation. **Point defects** (PD's) can be in the simulation box from the beginning of the simulation -like the native carbon and oxygen impurities in silicon-, or can be incorporated through the simulation of an implant. In this case, a binary collision program like MARLOWE is used to generate one cascade, i.e., the final coordinates of an implanted ion and of all the I's and V's created by collisions. Table I shows an example of a configuration consisting of 2 V's and 5 I's. To simulate 1 s anneal with that configuration we would need to

simulate 2050 jumps. Then  $\ddot{A}t=1/2050$  s for each jump. Furthermore, we have to pick up a particle from the V's and I's with a probability proportional to 2000/2050 and 50/2050, respectively. But Table I has to be updated each time a V-I pair is recombined (as a result of a jump). The program, therefore, cycles through the following steps:

Table I. Example of a configuration.

	n	J <sub>rate</sub> (jumps/s)	Total
V	2	1000	2000
Ι	5	10	50

- 1. From the current configuration select:
  - Next event type (PD jump, emission of a PD from a cluster, ...)
  - The individual particle to be moved
- 2. Select random direction
- 3. Move particle to new position applying boundary conditions
- 4. Search for interacting neighbors at new position
- 5. Perform interaction (I-V recombination, PD capture by a cluster, ...)
- 6. Update configuration

This six-step sequence is called an **event**. When, according to the implant dose rate and box size, it is time to read in a new cascade, it is overlaid on the current configuration, which is then updated, and the simulation proceeds until the desired implant dose is reached. We can then ramp up the temperature and simulate a high temperature anneal (the event rates are temperature dependent and hence the configuration, i.e. Table I, has to be updated each time the temperature is changed).

# DEFECT TYPES

One of the most valuable features of the atomistic approach is its ability to accurately simulate any defect type. In the following we describe the properties of the defect types currently implemented in DADOS (Diffusion of Atomistic Defects, Object-oriented Simulator) recently developed at the University of Valladolid. In this implementation, PD's play a special role because they are the only defects assumed to be mobile. The interaction distance between two defects of any type is taken to be equal to the PD jump distance ( $\lambda$ =3.84 Å, second neighbors distance in silicon). The interaction can occur with or without an interaction barrier.

# Point defects

Point defects can be either **single** PD's like V, I, B, As, ... or **pair** PD's like the I-B pair, V-O pair, interstitial boron  $(B_i)$ , ... The only event type single PD's can perform is jump. Their jump rate is given by

$$J_{rate} = 6 * D_o * \exp(-E_m / kT) / \lambda^2$$
(7)

In addition to that, pair PD's can also break up like

Break up event: 
$$IB \rightarrow I + B$$
 (8)

and switch to a different configuration like

Switch event: 
$$IB \leftrightarrow B_i$$
 (9)

## **Clusters**

Clusters are agglomerates of single PD's of the same type. A cluster can perform two possible events: capture and emission of a PD. In the simulation, small clusters are allowed to grow with irregular (blob-like) shapes: a captured PD is left at the position where it just jumped. Some species, however, can grow clusters to large sizes that tend to adopt specific shapes. That is the case for V's (voids) and I's ({311} defects, dislocation loops). The current version of DADOS implements voids and {311} defects.

## Voids

Large V clusters adopt a spherical shape with the silicon atomic density,  $5 \times 10^{22}$  cm<sup>-3</sup>. When a small V cluster reaches a critical minimum size, e.g. 27 V's, it is reshaped and transformed into a void, Fig. 2.

### {311} defects

Under certain experimental conditions (implant dose, annealing time and temperature) large I clusters adopt a strip shape elongated in the <110> direction within the  $\{311\}$  planes<sup>6</sup>. In the simulation, Fig. 3, when an I jumps onto a  $\{311\}$  it is attached to the nearest end of the  $\{311\}$ . The crystallographic parameters used in the simulation are taken from Ref. 6. Emission takes place randomly from either end but with a binding energy that depends on the  $\{311\}$  size as

$$E_{bind} = 2.7 - 2.65*[N - (N - 1)]$$
 (10)

Dislocation loops could likewise be readily included in the simulation.

#### Complexes

Complexes are agglomerates of two (or more) different species. This occurs, for example, with boron and silicon interstitials  $(I_nB_m, n,m=1,2,3 ...)^5$ . Other examples are  $I_nC_m$ ,  $V_nO_m$ . Since the size is usually small, complexes are simulated with irregular shapes. Their possible events



*Figure 2. Simulated voids are spherical and have the silicon atomic density.* 



Figure 3. Simulated {311} defects. Crystallographic parameters taken from Ref. 6.

are the capture and emission of a single PD or a pair PD, like I and B<sub>i</sub>, respectively.

#### Surfaces

Surfaces are treated as extended defects in DADOS. Each surface can have any of the following features:

- Sink: for each type of PD the surface can be defined to act as a perfect sink or a perfect mirror, or an intermediate behavior through an interaction energy barrier.
- Thermal V, I generation: the surface can generate V's and I's at a rate given by their respective formation energy or can preferentially inject I's (V's) to simulate oxidation (nitridation).
- Bulk surface: when a PD is going to leave the simulation box and go into the bulk, an estimate of the random walk length is made. Based on this and on the trap concentration and binding energy, the elapsed time Δt until the PD re-enters the box is calculated. After Δt the PD is re-inserted in the box at a random position on that surface. The purpose of this simulated delay is obviously to save computation time.

DADOS has been designed as object-oriented, written in C++ (about 6000 lines of code) and simulates more than one million events per second on a 566 MHz, DEC Alpha CPU. That means it runs through the six-step sequence given above in the time it takes to calculate, for example, three simple expressions like (7). This rate can be achieved by taking advantage of the fact that, in this type of simulation, elemental arithmetic (bitwise in some cases) can be used in the innermost loops. At the same time, an object-oriented approach was adopted in order to develop a user-friendly, neat design, so that new physical models could be implemented in just a few minutes or hours. Object-oriented programming is particularly suitable for atomistic simulations, where objects are easily identifiable (PD's, voids, ...). Besides, the use of derived classes (inheritance), virtual functions, templates and other similar features available in object-oriented languages can greatly simplify the code.

### SIMULATION EXAMPLES

We have already mentioned atomistic simulations<sup>4,5</sup> that proved to be particularly useful to understand the basic mechanisms governing the behavior of V's, I's and B during ion implantation and annealing. The three simulation examples that follow are meant to further show some of the capabilities of this type of simulation.

#### Example 1: Voids Formation

Figure 4(a) shows a cross-sectional view of a 100 keV,  $10^{16}$  cm<sup>-2</sup> As<sup>+</sup> implant <sup>7</sup>. Beam heating with a high-flux ion beam was used to prevent amorphization. A 45 nm region can be identified extending from the surface which contains a high density of voids followed by a band of interstitial dislocations extending up to about 200 nm. The simulation with DADOS, shown in the bottom figure at the same scale, accurately predicts the formation of V and I clusters in the same depth ranges. The average void size, however, is smaller than in the experiment. Although in this particular experiment there is an uncertainty in the temperature, other simulations also seem to indicate that the V cluster binding energy used

$$E_{\text{bind}} = 3.65 + 4.9^* (N-1)^{2/3} - 4.9^* N^{2/3}$$
(11)



Figure 4. (a) Cross-sectional TEM of a beam-heated, 100 keV,  $10^{16}$  cm<sup>-2</sup> As<sup>+</sup> implant (from ref. 7). (b) Simulation with DADOS, drawn to the same scale (units are nm).

needs to be corrected to account for the fact that smaller clusters have a larger surface energy due to their curvature and are, therefore, less stable. The binding energy for a void of size N is the energy difference between two configurations for N vacancies: a single V plus a size N-1 void, and a void of size N. Equation (11) was derived assuming that the void energy is proportional to the number of V's at its surface, i.e. to  $N^{2/3}$ , and taking 3.65 eV as the V formation energy at the free surface (N $\rightarrow$ ). The prefactor 4.9 was chosen to fit the experimental activation energy for the divacancy, 1.2 eV. Instead of a constant, that prefactor should, therefore, decrease as N increases. Although Eq. (11) was used for all void sizes, atomistic simulations can equally well use a table of discrete values,  $E_{bind}(N)$ , specially for a range of small sizes which can be measured, like the divacancy, or calculated by molecular dynamics.

# Example 2: Interstitial {311} defects formation and dissolution

Figure 5(top) shows plan view TEM images of a 40 keV,  $5x10^{13}$  Si<sup>+</sup>/cm<sup>2</sup> implant after annealing at 800 °C for 5s and 30s, from Ref. 8. The average cluster size in the simulation is about one half the experimental value which, as in the case of voids, means that the binding energy, Eq. (10), needs to be revised. It is also possible that the capture radius used is too small. In fact, simulations of high dose, 1-5 keV Si implants which generate large {311} defects very close to the surface<sup>9</sup>, seem to suggest that capture occurs only (or preferentially) at the {311} ends. But, as stated at the beginning of this section, the aim of these simulation examples is just to illustrate some of the capabilities of this type of simulator (like those displayed in Figs. 4 and 5) and not to present definitive physical parameters.



30 s

*Figure 5. (top) Plan view TEM of a 40 keV, 5x10<sup>13</sup> Si/cm<sup>2</sup> implant after annealing at 800 °C for 5s and 30s, from Ref. 8. (bottom) Simulation with DADOS(100nm x 200nm).* 

## 0.12 im MOSFET 3 -D Process Simulation

The two preceding examples have shown the level of detail atomistic simulations can provide in the study of new materials and new phenomena. We now present an example of simulation of a 3-D device structure<sup>10</sup>. The simulation includes a 10 keV,  $5 \times 10^{14}$  cm<sup>-2</sup> As<sup>+</sup> implant to form the source/drain (S/D) extension, a 90 keV,  $6 \times 10^{12}$  cm<sup>-2</sup> BF<sub>2</sub><sup>+</sup> implant for voltage threshold adjustment, a 45 keV,  $4x10^{12}$  cm<sup>-2</sup> B<sup>+</sup> implant to prevent punchthrough, and a 1000 s anneal at 800 C. All of the implants were done through a 4 nm gate oxide. The simulation box (X<sub>max</sub>=100 nm, Y<sub>max</sub>=300 nm, Z<sub>max</sub>=150 nm) extends from the center of the channel up to 40 nm into the S/D region. Figure 6 shows the top view (a) and cross-section (b) after 10 s annealing at 800 C. In the simulation, the box surfaces X=0, X=100 nm, Z=0 and Z=150 nm are defined as mirror surfaces. Thus the gate length is 0.12 i m and the gate and S/D regions width is 0.2 im. There is an empty space from Z=100 nm to Z=150 nm to include 3-D effects at the sharp S/D corner. The front (exposed) surface, at Y=0, simulates the thermal generation of V's and I's and behaves as a perfect sink for them. The back (bulk) surface is defined as a delaying surface and located at a depth (Y=300 nm) enough to contain all the implant damage. In order to show a wider variety of the possible effects that can be revealed by atomistic simulators, it was assumed in this simulation that the As implant did not produce amorphization. The snapshots after 10 s anneal at 800 C (Fig. 6) reveal the presence, in the S/D region, of V microvoids (black) near the surface and elongated {311} defects (gray) beyond the



X (nm)

As implant range. This spatial separation is due to the heavy  $As^+$  ion mass. These {311} defects are the ones shown in Fig. 3.

Figure 7 shows a comparison between the continuum and the atomistic views of the channel region after the end of the anneal. As<sup>+</sup> <110>-channeling under the gate can be seen in the atomistic simulation due to the assumption of no amorphization. There is also boron pile up at the surface: several boron atoms have been carried to the surface by I's, in the form of mobile  $B_i$ . At the surface, the I is annihilated and leaves the immobile (substitutional) B. The boron concentration in the dashed region (containing 6 B atoms) of the atomistic simulation, Fig. 7(b), is 6 / (20nm x 20nm x 150nm) = 1x10<sup>17</sup> cm<sup>-3</sup>, which is the same as in the continuum simulation. But any microscopic spatial correlation, induced for example by the cascades or by the formation and dissolution of clusters, could be important for devices of these dimensions. And that correlation analysis can only be done with an atomistic diffusion simulator.



Figure 7.(a) Continuum simulation (from Ref. 10) and (b) atomistic simulation views of the channel region. The boron concentration in the dashed region (containing 6 B atoms) of the bottom figure is  $6/(20nm \ge 20nm \ge 10^{17} \text{ B/cm}^3)$ .

### CONCLUSIONS

Until recently, diffusion simulators were only based on continuum models and partial differential equations solvers. The performance achieved by today's computers, however, has enabled the development of a new, simpler and more accurate type, the atomistic diffusion simulator. Instead of solving equations, it directly simulates the movements and interactions of individual point and extended defects. Thus, atomistic modeling provides a simple and straightforward link between atomistic mechanisms and macroscopic behavior.

Atomistic diffusion simulators can, by their own nature, yield a level of detail such that it very closely resembles the actual experiment, not just in terms of concentration distributions (Fig. 1) but even in the microscopic representation (Figs. 4, 5 and 6). For accurate simulations of sub-0.1 im structures they can also be even more computationally efficient than their continuum counterparts.

In conclusion, atomistic diffusion simulators, as an extension of continuum simulators into the deep submicron dimensions, look like very promising tools for both helping to solve today's materials problems and for assisting in the design of state-of-the-art microelectronic devices.

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