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PREDICTING LOW ENERGY DOPANT IMPLANT PROFILES IN SEMICONDUCTORS USING MOLECULAR DYNAMICS

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Abstract

We present a highly efficient molecular dynamics scheme for calculating dopant density profiles in group-IV alloy, and III-V zinc blende structure materials. Our scheme incorporates several necessary methods for reducing computational overhead, plus a rare event algorithm to give statistical accuracy over several orders of magnitude change in the dopant concentration. The code uses a molecular dynamics (MD) model to describe ion-target interactions. Atomic interactions are described by a combination of 'many-body' and pair specific screened Coulomb potentials. Accumulative damage is accounted for using a Kinchin-Pease type model, inelastic energy loss is represented by a Firsov expression, and electronic stopping is described by a modified Brandt-Kitagawa model which contains a single adjustable ion-target dependent parameter. Thus, the program is easily extensible beyond a given validation range, and is therefore truly predictive over a wide range of implant energies and angles. The scheme is especially suited for calculating profiles due to low energy and to situations where a predictive capability is required with the minimum of experimental validation. We give examples of using our code to calculate concentration profiles and 2D 'point response' profiles of dopants in crystalline silicon and gallium-arsenide. Here we can predict the experimental profile over five orders of magnitude for <100> and <110> channeling and for non-channeling implants at energies up to hundreds of keV.

INTRODUCTION

The principal method for producing semiconductor devices requires implanting ions* into semiconductor wafers to dope regions within the substrate, and hence modify their electrical properties. The effort to realize ultra shallow junction devices

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*Within this paper, *ion* is used to refer to the implanted species, and *atom* to refer to a particle of the target material; this has no implication to the charge state of either atom type.
has resulted in current industry trends, such as the use of low energy, high mass, high
dose, and large angle implants, to create abrupt dopant profiles. The experimental
measurement of such profiles is challenging, as effects that are negligible at high
implant energies become increasingly important as the implant energy is lowered.
For example, the measurement of dopant profiles by secondary ion mass spectrometry
(SIMS) is problematic for very low energy (less than 10 keV) implants, due to limited
depth resolution of measured profiles. Also, refining SIMS protocols to obtain profiles
for new ion-target combinations, e.g. In, Sb, or N implants or Si$_{1-x}$Ge$_x$ targets is not
a trivial problem.

The use of computer simulation as an alternative method to determine dopant
profiles is well established. Binary collision approximation (BCA) codes have tradition-
ally been used, however such simulations become unreliable at low ion energies
(1,2). The BCA approach breaks down when multiple collisions or collisions between
moving atoms become significant, or when the crystal binding energy is of the same
order as the energy of the ion. Such problems are clearly evident when one attempts
to use the BCA to simulate channeling in semiconductors; here the interactions be-
tween the ion and target are neither binary nor collisional in nature, rather they occur
as many simultaneous soft interactions which steer the ion down the channel.

A more accurate, alternative to the BCA, is the use of molecular dynamics (MD)
simulation to calculate ion trajectories (3,4). However, the computational cost of tra-
ditional MD simulations precludes the calculation of the thousands of ion trajectories
necessary to construct a dopant profile. Here we present a highly efficient MD-based
scheme, that is optimized to calculate the concentration profiles of ions implanted into
semiconductors. The algorithms are incorporated into our implant modeling molecu-
lar dynamics code (5), REED-MD$^\dagger$. Our program has been demonstrated to describe
the implant of As, B, and P ions with energies in the sub MeV range into crystalline
Si in (100), (110), and non-channeling directions, and also into amorphous Si (4-6).
We have also demonstrated that the model can be extended to any ion species, and
to other diamond crystal substrates, such as C, Ge, SiC, Si$_{1-x}$Ge$_x$, and GaAs (7).

MOLECULAR DYNAMICS MODEL

The basis of the molecular dynamics model is a collection of empirical potential
functions that describe interactions between atoms and give rise to forces between
them. In addition to the classical interactions described by the potential functions,
the interaction of the ion with the electrons within the target is required for ion
implant simulations, as this is the principle way in which the ion loses energy. This
is accomplished via an empirical inelastic collision model and a phenomenological
electronic stopping-power model. The three energy loss models (nuclear collisions,
inelastic collisions, and electronic stopping) are based on a consistent description
of the electron distribution within the target. Other ingredients necessary to the
computation are a description of the target material structure, including accumulated
radiation damage and thermal vibration within the solid.

$^\dagger$Named for ‘Rare Event Enhanced Domain following Molecular Dynamics’.
Interactions between target atoms are modeled by derivatives of the many-body potential developed by Tersoff (8, 9). ZBL screened Coulomb potentials (10, 11) are used to model ion-target interactions, and to describe the close-range repulsive part of the Tersoff potentials.

We include energy loss due to inelastic collisions, and energy loss due to electronic stopping as two distinct mechanisms. It is not possible to assume that one, or other, of these processes is dominant and fit it to model all energy loss for varying energies and directions. The Firsov model (12) is used to describe the loss of kinetic energy from the ion due to inelastic collisions with target atoms. We implement this using a velocity dependent pair force, as derived by Kishinevskii (13).

A modified Brandt-Kitagawa (14) model that involves both global and local contributions to the electronic stopping is used for the electronic energy loss (4, 6). This model contains the single fitted parameter in our scheme, $r_0^*$, the 'average' one electron radius of the target material experienced by the ion. This is adjusted to account for oscillations in the $Z_1$ dependence of the electronic stopping cross-section. The parameter is fit once for each ion-target combination and is then valid for all ion energies and incident directions. By using a realistic stopping model, with the minimum of fitted parameters, we obtain excellent transferability to the modeling of implants outside the fitting set.

The target is a zinc-blende crystal semiconductor with a surface oxide or amorphous layer. The amorphous structure was obtained from a simulation of repeated radiation damage and annealing, of an initially crystalline section of material (15), and the oxide structure was obtained by annealing a periodic SiO$_2$ sample with the density constrained to that estimated for grown surface oxide (16). Thermal vibrations of atoms are modeled by displacing atoms from their lattice sites using a Debye model, with experimentally determined values of the Debye temperature. Note, we do not use the Debye temperature as a fitting parameter in our model, as is often done in BCA models (17). The thermal velocity of the atoms is unimportant as it is so small compared to the ion velocity, and is set to zero.

For high dose implants, the accumulation of damage within the target is described by a modified Kinchin-Pease (18) model:

$$\nu(E) = \begin{cases} 0 & E < E_d \\ \frac{0.2125E}{E_d} & E \geq E_d \end{cases}$$

where $E_d$ is the displacement threshold energy of the target, $E$ is energy deposited as the ion travels past one target atom, and $\nu$ is the number of Frenkel pairs generated. A profile of deposited energy against depth is recorded for each ion run. When an ion stops, the energy profile is converted to a damage profile, which is then accumulated into the total damage profile. When building target material, the total damage profile is used to generate a statistical distribution of defects. Damage saturates at a density of four Frenkel pairs per unit cell, at which point the material is assumed to be fully amorphized. Target properties are either species dependent, e.g., local electron density, or are obtained by interpolation from known values for single element materials,
e.g., lattice constant and Debye temperature.

**EFFICIENT MOLECULAR DYNAMICS ALGORITHMS**

We apply a combination of methods to increase the efficiency of this specific type of simulation. Infrequently updated neighbor lists (19, 20) are employed to minimize the time spent in force calculations. The paths of the atoms are integrated using Verlet’s algorithm (20), with a variable timestep that is dependent upon both kinetic and potential energy of atoms (19). For high energy simulations the potential energy as well as the velocity of atoms is important, as atoms may be moving slowly but have high, and rapidly changing, potential energies during impacts.

Even with the computation resources available today it is infeasible to calculate dopant profiles by full MD simulation. Although the method is $O(N)$ in the number of atoms involved, the computational requirements scale approximately as $u^4$, where $u$ is the initial ion velocity. We have developed a modified MD scheme which is capable of producing accurate dopant profiles with a much smaller computational overhead. We continually create and destroy target atoms, to follow the domain of the substrate that contains the ion. Material is built in front of the ion, and destroyed in its wake. Hence, the ion experiences the equivalent of a complete crystal, but the cost of the algorithm is only $O(u)$. The relationship between the full and restricted MD approaches is shown in Fig. 1. The ion is initially above a semi-infinite volume that is the target. As the ion approaches the surface, atoms begin to be created in front of it, and destroyed in its wake. This process is continued until the ion comes to rest at some depth in the substrate. Several thousand of such trajectories are combined to produce the depth profile of implanted ions.

![Figure 1: Schematic showing the relationship between (a) full MD, and (b) the domain following approximation.](image)

To further improve efficiency, we use three other approximations. The moving atom approximation (3) is used to reduce the number of force calculations. Atoms are divided into two sets; those that are 'on' have their positions integrated, and those that are 'off' are stationary. At the start of the simulation, only the ion is turned on. Some of the 'off' atoms will be used in the force calculations and will have
forces assigned to them. If the resultant force exceeds a certain threshold, the atom is turned on.

For high ion velocities, we do not need to use a many-body potential to maintain the stable diamond lattice; a pair potential is sufficient, as only repulsive interactions are significant. Hence, at a certain ion velocity we switch from the complete many-body potential to a pair potential approximation for the target atom interactions. We make a further approximation for still higher ion energies, where only ion-target interactions are significant in determining the ion path. This approximation, termed the recoil interaction approximation (21), brings the MD scheme close to many BCA implementations. The major difference between the two approaches is that the ion path is obtained by integration, rather than by the calculation of asymptotes, and that multiple interactions are, by the nature of the method, handled in the correct manner.

RARE EVENT ALGORITHM

A typical dopant concentration profile in a zinc-blende crystal semiconductor consists of a near-surface peak followed by an exponential type decay over several orders of magnitude in concentration. If we attempt to directly calculate a statistically significant dopant concentration at all depths of the profile we will have to run many ions that are stopped near the peak for every one ion that stops in the tail, and most of the computational effort will not enhance the accuracy of the profile.

In order to remove this redundancy, we employ an ‘atom splitting’ scheme (22) to increase the sampling in the deep component of the concentration profile. At certain splitting depths in the material, each ion is replaced by two ions, each with a statistical weighting of half that prior to splitting. Each split ion trajectory is run separately, and the weighting of the ion is recorded along with its final depth. As the split ions experience different environments (material is built in front of the ion, with random thermal displacements), the trajectories rapidly diverge from one another. Due to this scheme, we can maintain the same number of virtual ions moving at any depth, but their statistical weights decrease with depth.

1,000 real 5 keV arsenic ions implanted at normal incidence into Si {100} were split to yield a total of approximately 20,000 virtual ions. The paths taken by 27 split ions produced from the first real ion of this simulation, and the resulting distribution of the ion positions are shown in Fig. 2. The final ions are the result of between 3 and 6 splittings, depending upon the range of each trajectory. This is typical of the distribution of splittings for one real ion; the final depths of ions are not evenly distributed over the entire ion range, but are bunched around some point within this range. This reflects how the impact position of the ion and collisions during its passage through the amorphous layer affect its ability to drop into a channel once in the crystalline material. We estimate that the rare event algorithm reduces CPU time by a factor of 90 when calculating profiles over 3 orders of magnitude, and by a factor of 900 when calculating a profile over 5 orders of magnitude.
RESULTS AND DISCUSSION

The remaining figures show the calculated 1D and 2D concentration profiles for various ions into Si, SiGe, and GaAs. First, we give 2D profiles for low dose, low energy profiles to show scattering and surface effects. We then give examples of 1D profiles produced by simulations, and compare to SIMS data (23, 24). All simulations were run with a target temperature of 300 K, and a beam divergence of 1.0° was assumed. Each profile was constructed from 1,000 ions, with the splitting depths updated every 25 ions, and a domain of 3×3×3 unit cells was used. The direction of the incident ion beam is specified by the angle of tilt, θ°, from normal and the azimuthal angle φ°, as (θ, φ). In the case of the low energy (< 10 keV) implants, we assume one unit cell thickness of surface oxide; for other cases we assume three unit cells of oxide at the surface. For the low energy implants, we have calculated profiles over a change of five orders of magnitude in concentration; for the higher energy implants we calculate profiles over 3 orders of magnitude. A dose of $1 \times 10^{12}$ cm$^{-2}$ (zero damage) is used unless otherwise noted. Also shown are low dose ($< 10^{13}$ ions/cm$^2$) SIMS data; for comparison, all profiles were scaled to an effective dose of $10^{12}$ ions/cm$^2$.

2D profiles are shown projected onto the plane normal to the surface and containing the zero degree azimuth. This makes it easy to differentiate between major channeling directions; the (100) channel is vertical, and the four (110) channels appear at angles of 35° from vertical. The effect of the amount of surface disorder is shown in Fig. 3. This is an ultra-low energy implant; the <100> channel is almost closed at this energy, while the <110> channel is still wide open. The dimer reconstructed surface (minimum disorder) results in just <100> channeling, with a slight scattering into <110> channels at the end-of-range. The 1 unit cell disorder (best controlled experimental surface) gives a small amount of near-surface scattering into <110> channels. The 3 unit cell disorder (typical experimental surface) gives much more scattering.

The resulting 1D profiles are plotted along with a SIMS profile from a very clean
sample (estimated approximately 1 unit cell thickness of disorder). The tail produced by <110> channeling can clearly be seen. There is an excellent match between the 1 unit cell simulation and experiment over 2 orders of magnitude, but that is the limit of accuracy of the SIMS, while REED-MD predicts over 4 or 5 orders of magnitude.

\[ \text{Cf} \ E \sim 10^{17} \]

Figure 3: Calculated dopant profiles due to $1 \times 10^{12}$ 2 keV As (0,0) implants into Si, with varying surface oxide thickness. (a) 1D profiles and SIMS data, and 2D point response through (b) dimer reconstructed, (c) 1 unit cell surface disorder, and (d) 3 unit cells surface disorder.

Figure 4: The calculated and experimental (25) dopant profiles due to 0.5 keV B (0,0) into Si\{100\}. 
In the case of the low energy (≤ 10 keV) implants, we compare to SIMS data obtained with a thin and well controlled surface layer (25,26); here we assume one unit cell thickness of surface disorder in our simulations. For the other cases considered here (26, 27), the surface was less well characterized; we assume three unit cells of disorder at the surface, as this is typical of implanted Si. For the low energy implants, we have calculated profiles over a change of five orders of magnitude in concentration; for the higher energy implants we calculate profiles over 3 orders of magnitude. The results of the REED calculations show good agreement with the experimental data. In the case of the low energy implants, the SIMS profile is only resolved over two orders of magnitude in some cases.

There is increasing interest in the use of SiGe as a replacement for Si currently used in CMOS technology, due to its higher switching speed (28). Fig. 15 shows the effect of Ge concentration on profiles from B and As implants into Si$_{1-x}$Ge$_x$ targets.
The trend is clearly for shallower profiles with increasing Ge concentration, but this is extremely non-linear; the difference between $x = 0$ and $x = 0.2$ profiles is greater than the difference between $x = 0.2$ and $x = 0.8$ profiles. The remaining figures show the calculated concentration profiles of several ion species implanted under various conditions into GaAs substrates, and comparison with available SIMS data. The results of the REED calculations show good agreement with the experimental data, demonstrating the accuracy of our model and its transferability to many ion-target combinations and implant conditions.

Run times are dependent on the ion type and its incident direction, but are most strongly linked to the ion velocity. We obtain a runtime of approximately 10 hours per $\sqrt{\text{keV}/m_{\text{i}}}$, when calculating profiles over five orders of magnitude and running on a 200 MHz pentium pro.
Figure 9: The calculated and experimental (26) dopant profiles due to 2 keV As (0,0) into Si{100}.

Figure 10: The calculated and experimental (26) dopant profiles due to 2 keV As (7,0) into Si{100}.

CONCLUSIONS

In summary, we have developed a restricted molecular dynamics code to simulate the ion implant process and directly calculate 'as implanted' dopant profiles. This gives us the accuracy obtained by time integrating atom paths, whilst obtaining an efficiency far in excess of full MD simulation. There is very good agreement between the MD results and SIMS data for B, P, and As implants. We can calculate the dopant profile to concentrations one or two orders of magnitude below that measurable by SIMS for the channeling tail of low dose implants.

The scheme described here gives a viable alternative to the BCA approach. Although it is still more expensive computationally, it is sufficiently efficient to be used on modern desktop computer workstations. The method has two major advantages over the BCA approach: (i) Our MD model consists only of standard empirical po-
Figure 11: The calculated and experimental (26) dopant profiles due to 50 keV As (0,0) into Si{100}.

Figure 12: The calculated and experimental (26) dopant profiles due to 100 keV As (8,30) into Si{100}.

The potentials developed for bulk semiconductors and for ion-solid interactions. The only fitting is in the electronic stopping model, and this involves only one parameter per ion-target combination. This should be contrasted to the many parameters that have to be fit in BCA models. We believe that by using physically based models for all aspects of the program, with the minimum of fitting parameters, we obtain good transferability to the modeling of implants outside of our fitting set. (ii) The method does not break down at the low ion energies necessary for production of the next generation of computer technology; it gives the correct description of multiple, soft interactions that occur both in low energy implants, and high energy channeling. Hence our method remains truly predictive at these low ion energies, whilst the accuracy of the BCA is in doubt.

The program is currently being extended to include models for complex oxide surfaces, and to model cluster implants such as BF$_2$. 
Figure 13: The calculated and experimental (26) dopant profiles due to 15 keV P (0,0) into Si\{100\}.

Figure 14: The calculated and experimental (27) dopant profiles due to 100 keV P (10,15) into Si\{100\}.

Figure 15: Calculated dopant profiles for 10 keV B and As (0,0) implants into Si\(_{1-x}\)Ge\(_x\).
Figure 16: Calculated and experimental (23) dopant profiles due to Zn $3 \times 10^{13}$ cm$^{-2}$ implants into GaAs.

Figure 17: The calculated and experimental (24) dopant profiles due to 150 keV Si $3 \times 10^{13}$ cm$^{-2}$ implants into GaAs.

Figure 18: The calculated and experimental (24) dopant profiles due to 300 keV Se $3 \times 10^{13}$ cm$^{-2}$ implants into GaAs.
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Keywords:

Molecular Dynamics, Ion Implant, Binary Collision, SIMS, Semiconductors.