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Multiscale modeling of radiation damage and annealing in Si

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Abstract

The fabrication of small Si devices brings up complex physical mechanisms, whose modeling requires a multiscale approach. We illustrate the case of ion implantation and annealing in Si. Ab initio calculations and molecular dynamics simulations provide defect energetics and the physical basis for defect formation and annihilation mechanisms. Binary-collision approximation for ion implantation combined with kinetic Monte Carlo simulation for annealing is used to define the range of validity of some approximations used in continuum models.

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Keywords: Modeling; Silicon; Ion implantation; Defects

1. Introduction

The shrinking of Si device dimensions has revealed material and process limits that make the fabrication of integrated circuits very complex. The International Technology Roadmap for Semiconductors (ITRS) specifies challenges in all process technology steps for the achievement of future electronic devices with proper performance [1]. Although new materials and new concepts are being explored, Si technology is likely to remain dominant at least until 2016 [1]. Ion implantation continues as the most prevalent method of adding dopant atoms for junction formation. This process provides excellent spatial and fluence control, as well as ease of manufacture. However, as-implanted ions are usually electrically non active, and the lattice damage deteriorates the device performance. Then, a subsequent anneal of the Si substrate is necessary to permit dopant atoms to incorporate into substitutional sites and become electrically active, and to repair the lattice damage. At the same time undesirable large dopant diffusion and dopant clustering occur. These phenomena pose severe difficulties to the achievement of low-resistivity ultra-shallow junctions. Preamorphizing implants followed by low temperature regrowth offer some advantages for the realization of shallow junctions because the process provides good dopant activation with minimal diffusion [2]. However, residual damage beyond the amorphous–crystalline interface may remain if the thermal budget is too low.

Simulation tools are very helpful to optimize the fabrication process of Si devices because the realization of experimental test lots is becoming extremely expensive. Theoretical calculations, combined with dedicated experiments, have led to an improved physical understanding of complex interactions among dopants and defects responsible for dopant transient enhanced diffusion and dopant clustering [3,4]. All these interactions need to be included in process simulators to give them predictive capability of the electrically active dopant distribution resulting from ion implantation and annealing processes.

The ITRS has recognized and explicitly pointed out the need of a hierarchical modeling scheme that goes from ab initio calculations to continuum methods to develop physics-based predictive models. Detailed quantum mechanical description of the system is computationally too expensive. Ab initio methods can only handle systems

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of a few hundreds atoms and are limited to extremely short times, far from the needs of a process simulator. Nevertheless, these methods are appropriate to calculate the energies of specific atomic configurations and give excellent insight into the physics of the system. This information is used to define event rates in kinetic Monte Carlo (KMC) methods or a set of partial differential equations (PDE) in continuum methods. The description is less accurate but macroscopic time and space scales can be reached. In this paper, we present a multiscale modeling of damage evolution in Si process simulators.

2. Energetics of defects in Si

Si interstitials and vacancies are intrinsic defects in Si and are formed in large numbers during irradiation. Configurations and energetics of point defects as well as their diffusion mechanisms have been studied using first principles [5], tight binding (TB) [6] and classical potential [7] calculations. In first principles, symmetry is often enforced when searching for possible configurations and migration paths, and there is no guarantee that the minimal energy configuration is calculated. Using classical potentials full dynamical simulations of systems containing tens of thousands atoms for times on the order of nanoseconds can be performed. However, the validity of classical molecular dynamics (MD) results is given by the suitability of the parametrized potential to describe the problem under study. All these fundamental techniques provide detailed information which requires laborious analysis to extract useful parameters.

The study of the Si self-interstitial is of great interest for Si processing because it is involved in dopant diffusion affecting the junction formation in Si devices. Six different configurations (tetrahedral (T), dumbbell (D), extended (E), dumbbell-extended (DE), hexagonal and bond centered) for the *Si interstitial* have been found using ab initio, TB and classical MD simulations [5–8]. Different energetics have been obtained even for the same atomic configuration using different methods and there is no agreement about the most stable configuration. Using MD simulations with Tersoff T3 potential [9], we have found that T, D, E and DE configurations correspond to local minima and that the transition among them defines different migration paths [8]. In spite of the complexity of this microscopic description, the overall behavior can be modeled by a unique Si interstitial species with an effective formation enthalpy of 3.83 eV and a migration barrier of 0.77 eV. These particular numbers do not correspond to any of the individual interstitial configurations or diffusion mechanism, but they are the result of the averaged behavior of all of them, and can be used as input parameters in process simulators.

Another interesting defect in Si is the so-called *bond defect* or IV-pair. This defect consists of a rearrangement of bonds in the Si lattice with no excess or deficit of atoms. It introduces the five and seven member rings characteristic of the amorphous phase. MD simulations have proved that amorphization can be modeled through the accumulation of IV pairs above 25%. As it can be seen in Fig. 1, the pair distribution function of a sample obtained by quenching liquid Si and that obtained after atomic relaxation of the structure with 30% IV pairs in the Si lattice are identical and correspond to amorphous Si. The same holds for the angular distribution. Using classical MD techniques, this defect was found to be generated directly during the collision cascade as a result of a pure ballistic process [10]. Using TB calculations, Tang et al. [6] have shown that this metastable defect structure is also generated when a vacancy approaches a dumbbell interstitial instead of having immediate interstitial–vacancy recombination. They found an activation energy for recombination of ~1 eV when atoms are forced to move symmetrically. However, using MD calculations, we found a much lower energy barrier (~0.43 eV) when atoms in the defect move freely [11]. Although this defect alone is not stable enough at room temperature, its recombination rate decreases when it is surrounded by other IV pairs [12]. The recombination of amorphous pockets always starts at the interface in contact with the crystal because IV pairs at the interface are surrounded by more crystalline atoms and fewer IV pairs than those in the interior of the pocket. These results have been the basis for the development of an atomistic amorphization model implemented in a kinetic Monte Carlo code [13]. The main features of the model are: (i) the IV pair or bond defect is the building block of the amorphous phase; (ii) IV pairs are formed when a Si interstitial is within the capture radius of a vacancy and also during the collision cascade; and (iii) the activation energy for recombination increases with the number of neighboring IV pairs. This model has been able to quantitatively explain

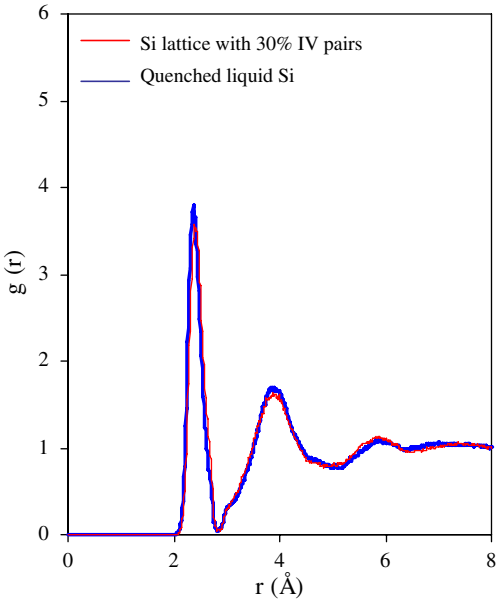

Fig. 1. Pair distribution function of amorphous Si generated from the quenching of liquid Si and after the atomic relaxation of a Si sample with 30% bond defects.

experimental results and also to provide predictive capabilities for Si processing.

3. Mechanisms of damage generation and cascade topology

The simplest method to calculate dopant and damage profiles is the analytical description based on the Pearson distribution [14]. When using these profiles in continuum process simulators, a random distribution of defects and dopants in the space is assumed following the described profile. However, each collision cascade is a dense damaged region surrounded by crystalline silicon, as schematized in Fig. 2. In some cases, it may be relevant to capture the discrete nature and local inhomogeneities of cascades. In high fluence implants, cascades overlap and there is not significant difference between the atomistic view and the "randomly distributed" view. However, for low fluence implants, a few dense damage regions along the cascade result in dilute damage when it is randomly distributed over the whole region. This difference in the damage distribution has some influence on the recombination probability of defects and damage accumulation [15]. Nevertheless, the spatial correlation associated with the *cascade topology* can be mathematically treated in continuum methods introducing a correlation factor to the standard form of the recombination rate [16].

A more detailed description of the cascade is provided by the *binary collision approximation (BCA)*. In this method all collisions between ions or recoils and Si target atoms are calculated by assuming that the energetic atom interacts only with the closest atom in its neighborhood [17]. An atom is displaced from its lattice position through a ballistic process when it receives energy larger than a threshold value of about 15 eV, starting a new recoil and leaving a vacancy behind. This method provides the atomic coordinates of the introduced ion and those of Si interstitials and vacancies generated in each collision cascade.

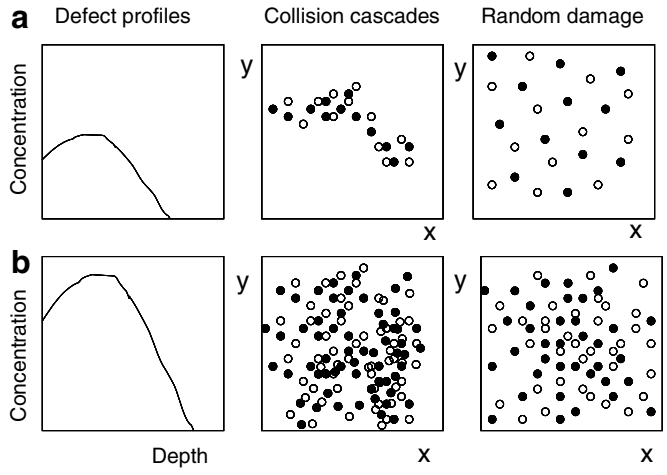

Fig. 2. Schematic that compares the damage created by collision cascades with the randomly distributed damage in the same region, for (a) low and (b) high fluences.

Thousands of cascades can easily be calculated to provide enough statistical resolution and to generate dopant and damage profiles. The description of radiation damage in terms of Frenkel pairs is acceptable in the case of light ions such as boron because they produce very dilute damage mostly consisting of isolated point defects or small Si interstitial and vacancy clusters [18]. However, BCA models do not properly describe amorphous regions formed by heavy ions.

MD simulations provide a better description of the damage generated by energetic ions, including the formation of amorphous regions [19]. Although these calculations are too expensive to be included in process simulators, they can be used to extract information about the formation mechanisms of amorphous pockets in the cascade. In addition to the ballistic process which generates damage mostly in the form of Si interstitials and vacancies, MD calculations show that amorphous pockets are formed through melting and quenching of regions where energy has been deposited. If atoms receive energy lower than ~15 eV they are not extracted from their lattice position, and energy is lost to phonons. When many neighboring atoms simultaneously receive a small amount of energy the region may melt [20]. According to the T3 potential, the minimum energy required to complete the melting process in Si is around ~1 eV/atom. However, finite regions require more energy to make up for the energy loss through diffusion to the surrounding regions. An average of about ~5–6 eV/atom is deposited in the regions that turn amorphous through the melting and quenching process. This value is significantly lower than the threshold value for the pure ballistic process. The understanding of damage generation mechanism provided by MD simulations has been used to implement improved BCA models where energy transfers below the displacement energy threshold have been considered to account for the melting process [20].

Damage generated by a melting mechanism is a disordered region with no excess or deficit of atoms. Then, upon annealing these amorphous regions rapidly regrow without leaving defects. The ballistic process for damage generation separates Si interstitials from the vacancy sites. Nevertheless, defects are still created in pairs and recombine. The excess Si interstitial generated as the implanted ion occupies a substitutional position, does not have a vacancy partner with which to recombine, and survives until it is annihilated at the surface. In process modeling, it is not always necessary to have a detailed description of the damage. For sub-amorphizing implants, excess Si interstitials resulting after damage recombination may be enough to describe the residual damage and their effects on dopant diffusion. For amorphizing implants a more accurate description of damage is required since all kind of defects account for damage accumulation that may eventually lead to complete amorphization. Simple models assume that the lattice turns amorphous when a critical defect density is reached. However, this critical value is not unique and it depends on ion mass, implant temperature and flux [21].

This dependence arises from the fact that generated damage may dynamically anneal out during the implantation process itself at different rates depending on implant parameters. Therefore, improved amorphization models based on bond defect accumulation have been developed that account for the different annealing kinetics of amorphous regions [13].

In Fig. 3 we show the residual damage for a sub-amorphizing and an amorphizing implant for two different ion fluxes we have obtained using the KMC amorphization model based on IV-pair accumulation. In both cases, the dynamic annealing during the implant is higher for the lower flux (more time between cascades) resulting in a smaller amount of damage just after the implant. For the sub-amorphizing case, damage remaining after recombination of small amorphous regions or Si interstitials and vacancies created in pairs is independent of the flux, and only the unbalanced Si interstitials survive. A slightly higher value of residual Si interstitials (1.3×10^{14} cm^{-2}) compared to the implanted fluence (10^{14} cm^{-2}) is obtained due to the net separation between Si interstitials and vacancies associated with the momentum transfer of the incoming ions. For the amorphizing implant a more effective dynamical anneal for the lower flux results in a shallower amorphous layer. During regrowth, defects contained in that layer are swept towards the surface. The residual damage beyond the amorphous–crystalline interface remains. Since a smaller amount of defects have been removed with the regrowth of the shallower amorphous layer, the amount of residual damage is significantly larger for the lower flux (5.5×10^{14} cm^{-2} compared to that for the higher flux 3.5×10^{14} cm^{-2}).

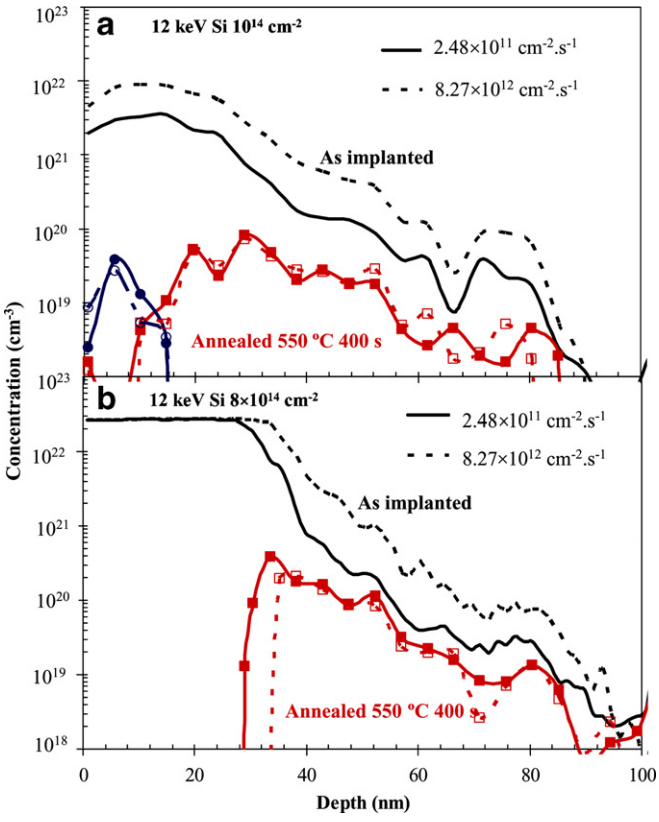

Fig. 3. Simulated damage profile (IVpairs + Si interstitials) as-implanted (lines) and residual damage (vacancy clusters -circles- and Si interstitial clusters -squares-) after anneal at 550 °C for 400 s of a 12 keV Si implant (a) 10^{14} cm^{-2} and (b) 8×10^{14} cm^{-2} at a flux of 2.48×10^{11} cm^{-2} s^{-1} (solid line) and 8.27×10^{12} cm^{-2} s^{-1} (dashed line).

4. Damage annealing

Kinetic Monte Carlo (KMC) codes handle diffusion and interaction events at the atomic level. At the same time, their results can be directly compared to experimental results. In *lattice MC* codes, atoms are located in lattice positions [22]. In *non-lattice MC codes*, only the intrinsic (Si interstitial and vacancies) and extrinsic (dopants, impurities) defects are included in the simulation cell without following any particular lattice structure [4] and larger systems can be treated. Since atoms are traced individually, a large number of them must be included in the simulation cell to reduce the statistical error. In process simulation, hundreds of Si interstitials and vacancies are typically generated by each implanted ion, which limits the number of simulated cascades. Since most of these defects readily annihilate each other (sometimes even before adding new cascades) tens of thousand of cascades can be simulated and acceptable profiles can be obtained from the discrete position of the particles. Unlike MD simulations, the vibrational movement of the Si atoms in the lattice is not simulated, and only the dynamics of the defects are followed. Each particle type and interactions (vacancy–vacancy, interstitial–interstitial interactions to form extended clusters, dopant-defect complexes, impurities that act as traps for defects, etc.) must have a well defined event rate. Parameters that define the atomic interactions, such as binding energies, capture radius, etc., are extracted from ab initio or MD calculations or from dedicated experiments. The inclusion of new defect types or interactions in the model only add new terms to the total event rate, but this hardly increases the computational load. Therefore, this technique is very powerful for complex systems where a large number of interactions need to be modeled. The main difficulty arises from the lack of well defined parameters for each interaction.

In *continuum process simulators* the physics of the system is formulated as a set of continuity equations, where each particle gain or loss is formulated in terms of its generation and recombination rates and the diffusion flux [23]. The numerical solution of these sets of nonlinear partial differential equations requires spatial and temporal discretization to reduce the derivatives into algebraic differences. The same parameters as in KMC are necessary to define the reaction rates that characterize the interactions. In continuum modeling, new species and interactions imply the inclusion of new coupled differential equations and new terms in the existing ones, adding complexity to the numerical solution. The advantages that make continuum simula-

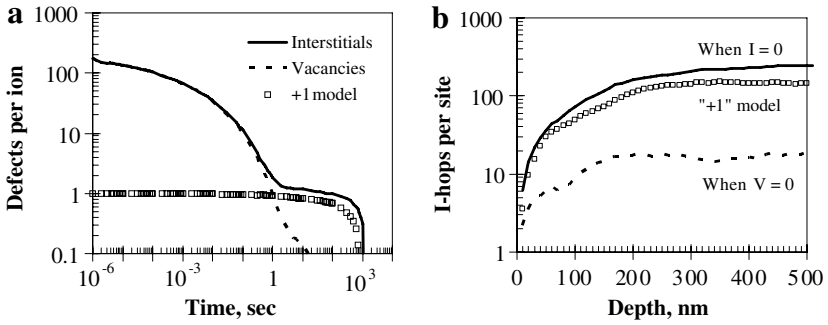

Fig. 4. (a) Time evolution of the total number of Si self-interstitials and vacancies and (b) Si interstitial hops, corresponding to a 150 keV Si implant to a fluence of 7×10^{13} cm^{-2}, annealed at 800 °C. The number of hops given until the vacancies have disappeared (when $V = 0$) is negligible compared to the number of hops given until all the interstitials have disappeared (when $I = 0$). This number is similar to the one obtained using the "+1 model".

tors the standard in industrial applications are maintained only on the basis of the simplicity of the physical models.

One of the classical simplifications used in continuum methods is the so called "*+1 model*" [24]. This approximation assumes that the Frenkel pairs generated by the implantation process recombine so quickly that very little dopant diffusion occurs prior to the Si interstitial–vacancy recombination. The excess Si interstitial generated as the implanted atom becomes substitutional, does not have a corresponding vacancy with which to recombine, and interacts with the dopants. Therefore, vacancy reactions can be skipped, and so the model simplified. In KMC, this approximation is not necessary and full damage is normally considered, giving more precise results. KMC simulations have been used to test the "+1 model" and determine its range of validity. The evolution of the total number of Si self-interstitials and vacancies, and also the number of interstitial hops during the annealing at 800 °C, for a 150 keV Si implant to a fluence of 7×10^{13} cm^{-2} is plotted in Fig. 4. Results from the "+1 model" are also plotted for comparison. The implant produces a large number of interstitials and vacancies per implanted ion. Most of them recombine quickly and vacancies disappear in a few seconds. One interstitial per implanted ion survives and agglomerates into more stable clusters. The final dissolution of those clusters takes several minutes at 800 °C. In atomistic simulations, the number of interstitial hops is a measure of the probability of an interstitial interacting with interstitially diffusing atoms and thus causing dopant diffusion. The initial concentration of Si interstitials and vacancies is so large that their average distance is small. Therefore, they recombine within a few diffusion hops. Once vacancies have disappeared, residual interstitials randomly diffuse to the surface where they are annihilated. Most diffusion hops occur during that time, giving validity to the "+1 model". KMC simulations have demonstrated that the "+1 model" is valid for light implanted ions with medium energies and fluences. For heavy ions [25] or low fluences [15], the "+1 model" underestimates the "effective" number of interstitials. In these cases, interstitial–vacancy recombination is not so efficient, and a significant number of diffusion hops occurs prior to complete vacancy annihilation. Then, a larger effective "+*n*" Si interstitials per implanted ion can be used in continuum simulators to dispense with vacancies [26].

5. Conclusions

Most process simulators used in industrial applications use continuum methods. They can be more easily coupled to other processes used in integrated circuit fabrication, such as oxidation, metal deposition, etc. They are fast and allow simulations of large sizes, by adjusting the grid size used for the spatial discretization. However, this advantage is reduced as the device size shrinks and complex physical interactions need to be modeled. Atomistic methods such as ab initio or MD can provide the mechanisms and parameters that describe the physics of the system. To reach macroscopic scales simplified models based on the physics provided by the atomistic calculations need to be performed. KMC methods can be used to define the range of validity of some approximations and also can be directly applied in process simulators of nanometer devices.

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