Effect of the Surface on Irradiation Induced Damage in Covalently Bonded Materials

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ABSTRACT

The classical molecular dynamics (MD) technique has been used to study ion beam interactions with covalently bonded materials. By using MD one can obtain detailed information on defect creation mechanisms and defect structures. The decreasing size of semiconductor devices means that the ion implantation processing step will increasingly be in the immediate vicinity of the surface of the devices. This raises the question of how much does the presence of a surface affect defect creation. This study has concentrated on studying surface or near-surface damage produced by low-energy ions.

As simulations are always only a model of reality their predictions should be tested against experimental measurements whenever possible. We have tested the validity our simulation model by comparing simulated and experimental mixing values. Mixing is one of the few experimentally measurable quantities that depends directly on the outcome of collision cascades.

We have studied the differences between defect production in the bulk material and at the surface for low-energy bombardment of Si. We have also studied the ion energy dependency of damage production in that low-energy regime. Using both simulations and experimental measurements we have also been able to study interstitial migration in Si.

We have also examined the role of chemical effects in ion implantation of materials. We investigated the differences in defect creation during low energy ion bombardment of GaAs and Ge surfaces, and carbon erosion by intensive hydrogen bombardment in fusion reactor divertors.

Finally, by using the classical MD method we have investigated the interplay between ion bombardment and strain in Ge. We found a new surface damaging mechanism.
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1 INTRODUCTION

The need for faster components in semiconductor technology leads to decreasing sizes of integrated circuit structures. There are three major reasons behind the need for decreased sizes; shorter charge carrier paths and thus higher speeds for the components, reduced power consumption and hence also heat production and increased packaging density leading to lower costs per transistor [1, 2].

Ion implantation is a routinely used method for integrated circuit processing [3, 4]. The main advantage obtained by the use of ion beam doping is that it offers good control of dopant depths and profiles [3]. The doping process is also highly reproducible. The main disadvantage of this method is that the energetic ions damage the target material. However, the amorphisation of the bulk material can in some cases be used as a means of controlling the dopant depths [3]. The processing of ever shallower junctions is expected to involve implantation of dopants into layers only a few tens of nanometers deep, and ion energies of only a few keV [5, 6]. As the structures get smaller, it is important to know to what extent the presence of surfaces and interfaces affect the outcome of ion beam induced collision cascades.

No experimental technique at the moment is able, without great difficulties, to produce a real three-dimensional (3D) picture of the damage in bulk material nor to probe the collision cascades in situ. Because of the complexity of this many-body problem, no analytical model is able to solve it, and thus one has to resort to atomic simulation methods in modelling the collision cascade. The time scales and system sizes which the classical molecular dynamics (MD) method can handle are ideally suited for collision cascades studies. The MD method involves solving individual trajectories of atoms and is thus capable of giving very detailed information.

The first MD simulations were carried out in 1959 by Alder and Wainwright using a very simple model of hard spheres [7]. This early work has laid the basis for a simulation tool that is still gaining growing popularity. The numbers of publications per year in the INSPEC database for 1967 - 1998 with the words “molecular dynamics” anywhere in the abstract, title or keywords are shown in Fig. 1. The number of publications has increased almost exponentially, showing the usefulness and importance of MD as a research method.

The MD method has been extensively applied in studies of production and annealing of ion beam induced lattice defects in bulk semiconductors (see e.g. [8–10]) and ion-beam induced amorphization of silicon (see e.g. [11–15]). There are quite a few studies of ion bombardment effects at the surface as well (see e.g. [16–20]).
2 PURPOSE AND STRUCTURE OF THIS STUDY

The purpose of this study is not to give any direct answers to problems in semiconductor technology, but rather to explore the basic physics of ion implantation. The main purpose of this study was to improve the understanding of ion beam induced damage in covalently bonded materials. We placed emphasis on to the role of the surface in defect creation. By using the classical molecular dynamics method, it has been possible to get detailed information on defect creation processes and mechanisms. The reliability of the model has also been tested by comparing experimental and simulated mixing values. An overview of ion beam induced defects in solids will be given in section 3. Section 4 will give some details of the principles of the MD method. The reliability of model potentials will be discussed in section 5. Section 6 presents the different surface related effects studied. The conclusions are given in section 7.

This thesis consist of this preface and the following six publications, published in refereed international scientific journals. The articles are referred to by the following Roman numbers in the text.

Summaries of the original papers

In this paper we studied the role of the surface on low-energy self-ion bombardment of the Si(001) surface. To deduce the role of the surface a comparison was made with collision cascade simulations in the bulk material. Emphasis was laid on getting a statistically reliable picture by simulating a large number of events. Furthermore, we also determined threshold displacement energies both in the bulk and at the surface and the melting point of silicon predicted by the Tersoff potential.


The atomic mixing in silicon was modelled in this paper. The fairly good agreement between simulated and experimental values serves as a validation of our simulation procedure. We found that the heat spike contribution to the total mixing is much lower than that of ballistic collisions.


We studied point defect creation and diffusion in the topmost layers of the $2 \times 1$ terminated Si(100) surface under 4.5 keV He atom bombardment by both experimental and simulation methods. The aim of this work was to find the threshold temperatures of vacancy and interstitial mobility. We simulated the initial defect concentration on the surface, compared the scanning tunneling results to them and found the interstitial migration threshold to be between 130 and 180 K.


The aim of this study was to determine the differences in defect creation on 50 eV ion bombardment of GaAs and Ge surfaces. Furthermore, the model potential properties of the GaAs surface was studied. It was found that, despite Ga, As and Ge having similar masses and both materials having the same lattice structure, there were considerable differences in the final defect distribution of different defect species. This illustrates the role of chemical effects in low-energy ion bombardment.


Some recent experimental measurements have shown that the erosion of carbon by intensive hydrogen bombardment decreases sharply at very high fluxes ($\sim 10^{19}$ ions/cm$^2$s). No previous
model has been able to explain this fact. The MD method is very well suited to this kind of problems and by using it we were able to show that the reason for the decreased erosion yield is the buildup of a high hydrogen content at the surface, leading to a shielding of carbon atoms by the hydrogen.


Strained SiGe is a promising future material for integrated circuit devices due to its easy bandgap altering and its high electronic speed compared to Si. We studied how the strain affects the outcome of a collision cascade. As a case study we performed simulations of ion bombardment of strained Ge. We found that large adatom islands are formed on top of the amorphous zones created by the cascades. Strain relief was also detected in the samples as the lattice atoms around the molten zone moved radially inwards.

### 3 ION BEAM INDUCED DEFECTS IN SOLIDS

As an ion\(^1\) penetrates into a medium it immediately starts to interact with it. The interactions can be divided into elastic and inelastic collisions [21]. The first one is called nuclear and the latter the electronic stopping power. Hence, the energy loss per unit length can be written as

\[
\left( \frac{dE}{dx} \right)_{\text{total}} = \left( \frac{dE}{dx} \right)_{\text{nuclear}} + \left( \frac{dE}{dx} \right)_{\text{electronic}}.
\]

Which one of the two contributions, the electronic or nuclear stopping power, is dominant depends on the velocity and the mass of the ion, and on the density of the medium. At high energies the electronic one dominates, whereas at low energies the nuclear one becomes more important (see Fig. 2). At the energies used in this study the slowing down of the projectile is governed by the nuclear stopping power.

The events caused by ion bombardment can be separated into three different phases [23, 24]. As the kinetic energy is transferred to target atoms, they can be removed from their original sites and collide with other atoms. This phase, where violent collisions take place is called the *collision phase* and depending on the ion and target atom masses and the energy of the ion, typically lasts 0.1–1 ps. The energy is deposited to the atoms close to the path of the projectile.

\(^1\)To distinguish the target and projectile atoms the incoming projectile is referred to as an ion in this study, even though there are no charge states in classical MD simulations.
The deposited energy is then transferred further into the surrounding matter by heat conductivity. This liquid-like phase, where the local temperature differences are evened, is called the \textit{thermal spike} and it lasts about 5–50 ps [25, 26].

After the thermal spike the target configuration is usually distorted, and from now on the evolution of the system is governed by temperature activated relaxation and diffusion processes, when the atoms seek the minimum energy configuration. This so called \textit{relaxation phase} can last the lifetime of a device.

### 3.1 Point Defects

There is usually an inherent concentration of point defects in semiconductor materials, because of the thermal movement of atoms. Defects produced in this way are usually uniformly distributed in the material. When an ion penetrates into the medium, it interacts with the lattice atoms and energy is transferred to them. If the transferred energy is high enough, the lattice is damaged and the damage is usually contained in a fairly small volume. Depending on the energy and mass of the projectile, either point defects or larger distortions are produced. Simple point defects can be classified as follows [27]:

1. An atom is called an interstitial if it is located somewhere else in the lattice than at the lattice
Figure 3: Simple point defects: (a) self-interstitial, (b) interstitial impurity, (c) vacancy, (d) divacancy, (e) substitutional impurity, (f) vacancy-substitutional impurity complex and (a)+(c) Frenkel pair.

1. If it is of another species than the lattice atoms, it is called an impurity interstitial, and if it is not, it is called a self-interstitial.

2. The defect is called a vacancy (also sometimes called a Schottky defect) if an atom is missing from a regular lattice site.

3. An impurity can be in a lattice site.

The lattice around point defects is always somewhat distorted, and sometimes it is impossible to tell whether an atom is a lattice or a defect atom. This is the case in the minimum energy interstitial configuration in Si. It has been found to be a so called split interstitial configuration; the interstitial and one of its neighbours form a dumbbell which is centered on the original site of this lattice atom with various configurations (see Fig. 4) [27]. The (110)-dumbbell has been found to be energetically the most favourable [28].

Naturally, there can also be defects on the surface. A vacancy is defined in the same way as in the bulk, and an extra atom on the surface is called an adatom.

### 3.2 Complex Defects and the Amorphous State

Combinations of point defects can also be formed. If the medium contains a large number of particular defects, they tend to form clusters if the temperature is high enough for defect migration. Vacancies can form divacancies, trivacancies and so on. Large clusters can arrange themselves into the shape of chains, rings or platelets [27] (see Fig. 5). In Si interstitials often form rodlike {311} defects [30]. On
Si(001) surfaces, vacancies are predominantly missing dimer vacancies (MDV) [31], i.e. two atoms missing from a reconstructed dimer site. At high temperatures the MDVs can form vacancy islands or clusters with longer axis parallel to the dimer rows [32].

A lattice can also be so strongly distorted, i.e. it has no long-range order, that it cannot anymore be considered to contain point defects, but should be considered as amorphous material. A perfect diamond crystal consists of six-membered atom rings, whereas amorphous material is thought also to contain five- and seven-membered rings [29].

Ion beam induced surface damage mechanisms (excluding chemical effects) have previously been identified to four different classes [16, 33]. The first one is sputtering, which is simply caused by kinetic energy transfer. The second mechanism is liquid flow onto the surface. Microexplosions are considered to be the third mechanism, and coherent displacement the fourth. Liquid flow can occur when the liquid produced by the collision cascade is connected to the surface so that the atoms can flow onto the surface. Microexplosions occur when a liquid is formed near the surface, and the expansion of this liquid makes the surface crack and clusters of atoms sputter. Coherent displacement happens due to the same liquid expansion; this time the pressure created inside the bulk forces atoms above it to slip along lattice planes leading to nicely formed adatom terraces on the surface. The first mechanism has been known for a long time and even simple binary collision methods model it with high accuracy [34]. The MD simulations, however, have revealed the real complexity of ion beam
induced effects at the surface, and described the last three mechanisms. As it will be shown later in
the text, there is one more mechanism for surface damage production.

3.3 Defect Analysis

3.3.1 Defect Recognition in Simulations

There are various methods to detect defects in atomistic models of solids. One way is to detect the
potential energy of the atoms and declare those atoms whose energy is far enough from crystalline
energies to be defects. The presence of the surface makes the use of the energy analysis complicat-
ed. There are two very straightforward geometrical methods to analyze the defects in the sample,
namely the Wigner-Seitz (WS) cell method and a method based on the Lindemann radius [35, 36].
Both compare the final configuration to the initial configuration and thus the surface reconstruction is
automatically taken into account.

The WS method is based on dividing the volume of the lattice into primitive cells. As the name
implies they are Wigner-Seitz cells [37]. In this method a vacancy is identified when a primitive cell
of the lattice is empty and one interstitial or more are identified when there are more than one atom in
a cell.
Another way is to use the Lindemann radius, i.e. the amplitude of lattice vibrations of atoms at the melting point. A vacancy is identified if there is no atom within the Lindemann radius from the lattice point. All the atoms outside these spheres are labelled as interstitials.

The difference between these two methods is that the Wigner-Seitz cells are space-filling, whereas Lindemann spheres are not. The WS method works well only when there are separated point defects, whereas the Lindemann radius method is very sensitive for displacements in the lattice and is therefore suited for detecting the amount of disorder in the lattice. Neither of the methods tells anything about the final lattice structure. In addition, as these methods are based on the initial configuration of atoms, they are not suited for cases where the initial lattice is under strain, and lattice atoms can move noticeably and still remain in a perfect crystalline configuration.

In cases of high ion energies which result in amorphous pockets in the medium, one needs different kinds of methods. On these occasions we have applied the structural order parameter procedure [15, 38]. In this method the angles between the neighbours of an atom are used to recognize whether the atom is in a crystalline or distorted neighbourhood.

### 3.3.2 Experimental Methods

There are many experimental methods for studying defect structures in solids, including such as Diffusive Scattering of X-rays or neutrons (DXS), Extended X-ray Absorption Fine Structure (EX-AFS), Positron Annihilation Spectroscopy (PAS), ion channeling, Transmission Electron Microscopy (TEM) and Field Ion Microscopy (FIM) [39]. These all have their own strengths and weaknesses. EXAFS gives information of the nearest neighbourhood of the defect but not of large defect structures, PAS detects only vacancies and channeling only detects interstitials in a crystalline structure. DXS, TEM and FIM can in principle give a 3D picture of different defect structures in the bulk, but there are numerous practical difficulties in their use.

As can be seen above there is no straightforward experimental way for studying ion beam induced defect structures in solids, leaving simulations as a very valuable tool for these purposes.

On the surface, the situation is somewhat better mainly because of Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM). By applying these methods one can achieve almost an atomic scale picture of the surface \(^2\). The oxidation of the surface in some cases complicates the direct observation of ion induced damage and the diffusion of defects also complicates the observation of intermediate defect structures. Nevertheless, as will be seen later in the text, these experimental and

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\(^2\)To be precise these methods do not yield an atomic, but an electronic structure.
simulation methods can be used complementarily to get a good picture of the properties of ion beam induced defects.

4 PRINCIPLES OF MOLECULAR DYNAMICS SIMULATIONS

In an MD simulation the evolution of an ensemble of atoms is followed by solving iteratively the equations of motion. Thus, we get the evolution of the system, i.e. the trajectories of this ensemble of atoms, in time. This gives very detailed information on the phenomenon studied.

In the simulations the atoms interact via a model potential. When we calculate the forces, the atoms are treated as if they were fixed in their positions and the electron configuration is the ground state configuration. This treatment can be justified by the Born-Oppenheimer approximation (adiabatic approximation) [40]. This approximation is based on the fact that the velocities of the electrons are much higher than the velocities of atoms. The typical electronic velocity is \( \sim 10^6 \) m/s [41], whereas the velocity of a Si lattice atom at 300 K is \( \sim 500 \) m/s, so it is reasonable to assume that at a particular atomic configuration all the electrons will be in their ground state. The velocity of a Si ion with an energy of, say, 100 eV is of course much higher (\( \sim 10^4 \) m/s), but with higher energies the effect of the attractive part of the potential is very small, the projectile interacts mainly via the repulsive part of the potential in which the outer electrons, which may not be in their ground state, do not contribute significantly.

Since we use full MD simulations, we cannot use too high energies for the projectiles, as the penetration ranges would become too high, requiring large boxes and thus the updating of the atom positions would become very slow. The present computer facilities limit the size of a system to a few million atoms and ion energies to about a couple of hundreds of keVs. Also, because of the small time step required (\( \sim 10^{-15} \) s) in MD simulations to get a realistic behaviour for the system, MD can be used to get information of processes taking place in the system with time scales only of the order of nanoseconds. However, as the cascades produced by the collisions of the projectile do not typically last more than a couple of picoseconds (or less), so MD is ideally suited to study these processes [42].

As only a small part of the material is used in simulations, we have to model the presence of the surrounding bulk somehow. This is done by setting periodic boundary conditions to the simulation box. In the presence of a surface, the bottom atoms of the box are usually fixed. The heat conductivity to the bulk is modelled by setting some sort of energy drains to all box sides except the surface. To
decrease the simulation time and to remove thermal deviations, the temperature of the box is also quenched down after the collision cascade has settled.

The electronic stopping of moving atoms is usually taken into account as a non-local frictional force.

The usual procedure for our collision cascade simulations is first to create a simulation box with the right surface reconstruction, and relax it. Then to gain adequate statistics, independent ions are shot into the box by varying either the starting point or angles of each ion, or both.

5 POTENTIAL RELIABILITY IN THE LOW-ENERGY COLLISION REGIME

5.1 Static Properties

A simulation is always a limited model of reality. In general there are numerous factors that affect how well the model describes the phenomenon studied. When considering collision cascades simulated by the classical MD method, the main error source is the model potential which describes the interactions between atoms. Semiempirical potentials used in the classical MD simulations are fit to some number of experimental or ab initio calculation data. The amount of fitting data is always limited, and usually only near-equilibrium properties are used. Very basic properties, such as bond lengths, binding energies, elastic constants etc. are very well defined, but data for some other properties, such as defect energies, is somewhat spread. This contributes to complicating the construction of model potentials.

There is a large number of model potentials for Si and Ge, but the most commonly ones used are the Stillinger-Weber (SW) [43] and the Tersoff [44] potentials. Balamane et al. have made a fairly comprehensive comparison of these two and other potentials for Si [45]. In conclusion, they noted that all the potentials give a good description of some properties but none of them can be considered to be superior to the others. Thus, one should always find the potential that is best suited for a particular problem. This, of course, involves testing of the potentials.

From a fundamental point of view the difference between SW and Tersoff potentials is that the SW potential is fitted only to the tetrahedral configuration and thus penalizes non-tetrahedral bonding types. On the contrast, the Tersoff potential is fitted, in addition to the diamond structure, to over- and under-coordinated configurations, and thus is expected to give a fairly good description of collision
cascades. The inability of the SW potential to describe non-tetrahedral structures can be seen from pair-correlation function of amorphous Si$_{0.5}$Ge$_{0.5}$ in Fig. 6.

### 5.2 Melting Point

So far we have only considered equilibrium properties. As ion bombardment is always a very dynamical process far from thermodynamical equilibrium, one should take dynamical properties into account as well. One dynamical property usually checked is the melting point. In paper I we determined the melting point of Si predicted with the Tersoff potential. Even though there were already some studies on this subject, we felt it was important to redo this, the reason being that in most of the previous work it was done improperly, for example by using constant volume in the simulations. Melting usually starts from surfaces and interfaces, and thus when comparing experimental and simulated melting points, one should include such discontinuities to the simulation box to avoid over- and undercooling problems. The method we used was the one discussed in detail by Morris et al. [47]; by determining the temperature where a liquid and solid co-exist in equilibrium in the same simulation cell, one should get a value that is comparable to experimental values. Our result was 2450±50 K,

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Figure 6: Experimental radial distribution function of amorphous Si$_{0.5}$Ge$_{0.5}$ compared with the ones predicted by the SW and Tersoff potentials. Experimental data is from Ref. [46]. We can see the incapability of the SW potential to reproduce the amorphous structure.
which is somewhat lower than what has been proposed in other studies [44, 45, 48, 49], but it is still considerably higher than the experimental value of 1683 K [50].

Thus the melting point of Si predicted by the Tersoff potential is not correct, whereas the SW potential has about the right melting point [45]. It has been shown that the melting point has a large effect on damage production in semiconductors [9]. Hence in cases where melting has a major influence on the outcome of the simulation, one should rather use the SW than the Tersoff potential.

5.3 Threshold Displacement Energy

One dynamical property that is quite extensively studied both by experiments and simulations is the threshold displacement energy, i.e. the energy required to remove the atom from its lattice site. We calculated the displacement energies in the (001) direction both in the bulk and at the surface [I]. It was found that even though close vacancy-interstitial pairs are formed at lower energies in the bulk, the actual replacement process which leads to a stable configuration takes place in both cases at about 16 eV. This value is within the experimentally measured range of 11–30 eV [51–54]. This indicates that the model works well on a basic level but as the experimentally measured data is so dispersed any definite conclusions of the accuracy of the potential is hard to draw.

5.4 Ion Beam Induced Mixing

There are very few experimentally measurable quantities that depend directly on the outcome of collision cascades. The ion beam induced relocation of atoms, which is called ion beam mixing, is one of those. By direct comparison of experimental and simulated values one can test the reliability of the simulation model. So far the problem preventing this comparison has been that the high energies used in the experiments have been beyond simulation capabilities.

In paper II we calculated the mixing produced by five different ion beams in amorphous silicon. The primary recoil spectrum was obtained by simulating the interactions between the ions and target atoms with an MD method which enables fast calculation of the slowing down of ions. Full MD simulations were then used to simulate the mixing at various energies, giving the total atom relocation as a function of energy. We developed a cumulative method to calculate the mixing at high energies (> 10 keV). Integration of the primary recoil spectrum weighted by the atom relocation gave simulated mixing values directly comparable with experimental data.
The simulations reproduced the experimental results to within the uncertainties, showing that the MD simulations give a reasonable description of the ballistic properties of the collision cascade. We found that the heat spike contribution to the total mixing seems to be much lower than that of ballistic collisions. This is in contrast to what has been obtained in dense fcc metals, where the mixing has been found to be derived predominantly from the heat spike [55].

### 5.5 Repulsive Part Correction

When atoms are nearby each others, neither the SW nor the Tersoff potential is valid anymore, since they have been calculated using properties in or near equilibrium. Because we are dealing with ion bombardment, there are strong collisions during the cascade, in which the configurations are far from equilibrium. To treat the strong repulsive interaction between atoms at small distances, a database calculated with the program package DMol [58], which is based on the density-functional theory [59, 60], was used.

The original potential, $V_{\text{orig}}$, and the correction part, $V_{\text{corr}}$, were smoothly joined together using a Fermi function $F(r) = (1 + e^{-bf(r-r_f)})^{-1}$

\[
V_{\text{tot}} = F(r)V_{\text{orig}} + (1 - F(r))V_{\text{corr}}. \tag{2}
\]

The values for $b_f$ and $r_f$ were chosen so that the potential remained smooth and the equilibrium part of the potential was not changed.
Table 2: Results for surface cascades. Upper part: The average number of defects per one ion after quenching. Lower part: The number of defects per eV (normalized to the 100 eV case).

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Vacancies</th>
<th>Interstitials</th>
<th>Adatoms</th>
<th>Sputtered</th>
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<td>0.92±0.05</td>
<td>0.31±0.05</td>
<td>0.019±0.013</td>
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<td>50</td>
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<td>0.007±0.007</td>
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<tr>
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## 6 SURFACE MODIFICATIONS

### 6.1 Ballistic Effects

#### 6.1.1 Low-energy Bombardment of Si(001)

As noted earlier, there are quite a few studies of low energy ion beam interactions with semiconductor surfaces. These studies, however, have usually been limited to the effects of one energy. In paper I we present simulations where the main aim was to study the role of the surface in defect production in low-energy self-ion bombardment of the Si(001)2×1 surface at several different energies below 1 keV. To deduce the role of the surface, we also simulated collision cascades in the bulk.

In order to get good statistics we calculated around 100 recoil events for most energies, both in the bulk and at the surface. The potential that we used in this study was the Tersoff potential [44]. As discussed already, it does predict the wrong melting point for Si, but as no real molten zones are produced at these low energies, this should not be a significant problem.

As a result we found that the vacancy production at the surface is a superlinear function of energy below 400 eV, i.e. the number of vacancies per incoming eV is higher at higher energies (see Table 2). The same superlinearity was found also in the bulk (see Table 3). This superlinearity extends to higher energies than could be expected on the basis of the Kinchin-Pease formula [61]. The defect production
Table 3: Damage production in bulk cascades. *Upper part*: The average number of defects per one ion after quenching. *Lower part*: The number of defects per eV (normalized to the 100 eV case, as the 50 eV case is strongly affected by the low-energy Frenkel pair production).

<table>
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<td>1.14</td>
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<tr>
<td>100</td>
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<td>200</td>
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<td>400</td>
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<tr>
<td>800</td>
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</table>

becomes linear at energies higher than 400 eV, in agreement with previously found linearity at keV energies [9].

The direct comparison of bulk and surface defects is somewhat complicated, as in the case of surface bombardment an extra atom was introduced into the lattice, whereas in the bulk case a lattice atom was used as a recoil ion. Despite the difficulties, we can see that defect production is somewhat affected by the presence of the surface at least up to an energy of 1 keV. This is due to the fact that the bond energy of a surface atom is significantly lower than that of a bulk atom and a large part of the vacancies are produced in the surface layer (see Fig. 7). The difference in the numbers is less than 20% at 100 eV and only about 5% at 800 eV.

6.1.2 Defect Migration Studies and Microexplosions

Even though silicon, due to its central role in integrated circuit technology, has been studied quite extensively, some of its very fundamental features are still unknown. One such property is the threshold temperature of defect migration. The diffusion of impurities and dopants in solids are usually governed by the properties of point defects. In paper III we utilised both experimental and simulation methods to address this problem.

A Si(001)2×1 surface was bombarded with 4.5 keV He ions. The initial defect production on the surface and also the defect distribution near the surface was obtained from MD simulations. As the
bulk defects can diffuse to the surface and change its morphology [62] the surface of a bombarded Si sample was scanned by STM measurements at various temperatures to detect the surfacing of defects. There are usually many vacancies at the surface, but adatoms are seldom observed and thus the analysis and discussions focused on adatoms. The surface protrusion found in the STM study are referred to as bright spots because it is not possible to distinguish individual adatoms. We found that the number of the bright spots at temperatures of 80 and 130 K are independent of temperature, but at 180 K the density of the spots was increased by a factor of ~3. From MD calculation we can estimate that the increase is explained by interstitials within ~2 nm of the surface which migrate to the surface.

We also found, to some surprise, that despite the low mass of helium small micro-explosions can take place on the surface. Up to 9 adatoms and 8 surface layer vacancies were produced, thus leaving craters that should be experimentally visible (see Fig. 8).
6.2 Chemical Effects

6.2.1 Comparison of GaAs and Ge Surface Bombardments

The comparison of defect production in different materials can reveal how different chemical structures and bonds affect the outcome of collision cascades. For example, it has been shown previously that the crystal structure has a large effect on many damage production processes [9].

In paper IV we studied the difference in defect production between GaAs and Ge. All the elements involved have about the same mass and both materials have the same structure, so ballistic effects should be virtually the same. As the recoil energy was low (50 eV), only point defects were expected to be produced, and thus the WS method was used for defect analysis.

The interactions were modelled with different parameter sets of the Tersoff potential [63, 64]. The importance of proper testing of the model potentials became underlined in this study. It was found that the surface reconstruction of GaAs was unstable when the original parameter set was used. Fortunately, by a small change in one parameter, the surface was made stable without changing any other equilibrium properties.

The total number of defects produced was found to be almost exactly the same in GaAs as in Ge. Thus we can say that the defect production is mainly a ballistic phenomenon. The final defect distribution among the defect species, however, was found to be very different in these two cases. The number of interstitials was considerably lower in GaAs than in Ge, whereas more adatoms and sputtered atoms...
were observed in the case of GaAs. The time dependence of defect numbers was also different. The number of interstitials reaches a constant value faster in GaAs than in Ge, whereas the other defects reach the equilibrium value later on. These facts indicate that there is a driving force in GaAs that causes the initially formed interstitials to migrate to the surface and form adatoms. Hence we can conclude that the differences between damage production in GaAs and Ge illustrate the role which chemical effects can have in low-energy ion irradiation.

### 6.2.2 Carbon Erosion

In paper V we studied carbon erosion by intensive hydrogen bombardment. A central problem in the development of a commercially viable fusion reactor is finding a suitable material for the divertor in the reactor. The divertor section of the reactor first wall is subject to the most intense erosion. Since the impurities will eventually lead to the extinction of the plasma, it is of utmost importance to find a divertor material with optimal capability to withstand radiation damage and erosion.

The most promising divertor materials found to date are all based on carbon, the reason being its low atomic mass and strong atomic bonding. Yet even the carbon-based materials erode substantially by several different and poorly understood mechanisms. Some recent experimental measurements have shown that the erosion of carbon by intensive hydrogen bombardment decreases sharply at very high fluxes ($\sim 10^{19}$ ions/cm$^2$s) [65, 66]. Previous models had not been able to explain this effect. This problem cannot be handled as a purely ballistic problem, as the entering hydrogen atoms change the chemistry of the surface. Thus the MD method is very well suited to study this problem and in fact is probably the only available method at this time. Even though the MD method is not suited for studying macroscopic erosion, it can give detailed information on the microscopic erosion mechanisms.

To mimic the conditions in the nuclear reactor, we first created an amorphous hydrogenated carbon (a-C:H) structure with an H:C ratio of about 0.4, similar to the material found in divertors after the reactor operation. We then simulated the sputtering and etching caused by 1 and 10 eV H, D and
Figure 9: The number and average depth of the hydrogen ions in a cumulative run of H bombardment of a-C:H. The figure shows a fast hydrogen buildup on the surface leading to supersaturation.

T recoils impinging on this material, and studied how the a-C:H structure changed with multiple impacts.

The results showed that during prolonged irradiation the hydrogen content in the samples saturated due to a buildup of H in the surface layers (see Fig. 9), leading to a decreased H capture cross section. This indicates that the T inventory in the first wall will decrease, and will also lead to a lower carbon etching probability, which are crucial factors for the durability of the material in the reactor.

These two studies demonstrate the role of chemical effects in ion bombardment of materials. They also show that the classical MD is very well suited for studying problems where chemical effects are present.

### 6.3 Strain Effects

SiGe is a very interesting material because of its technological applications. Heterojunctions formed with SiGe have many benefits over conventional homojunction approaches. One of the advantages is that the bandgap can be altered by changing the proportion of the Ge content and strain caused by the lattice mismatch [67]. SiGe is also faster than Si in terms of carrier mobility [2]. Development in epitaxial growth methods, such as ultra-high vacuum chemical vapour deposition (UHV/CVD),
Figure 10: A top view of one cascade event. Initial and final positions of atoms that have moved more than 0.5 Å are joined. Strain relief seems to favour the (110) direction and this results in a four-leaf clover pattern on the surface in case of symmetrical amorphous zone.

has enabled rapid production of highly uniform SiGe structures [68]. It has been found that ion implantation of strained SiGe can cause strain relaxation [69]. Equally, as the ion bombardment can change the strain in the sample, the strain can affect the outcome of a collision cascade.

We decided to approach this problem with a case study of 5 keV Xe bombardment of strained Ge [VI]. Thick strained Ge layers cannot be formed experimentally. However, sometimes a non-reality based case can be a more efficient way to start, than a study that directly reflects reality, as the effects of interest can be more distinct in them. This time the (modified) Stilliger-Weber potential [9] for Ge–Ge interactions was used, as the liquid material had a large role in this problem.

We found that large adatom islands are produced on top of amorphous zones. We also found that lattice atoms around the molten zone move radially inwards and thus cause strain relief in the sample (see Fig. 10). The strain was increased perpendicular to the surface, which has also been found experimentally [69]. The mechanism for adatom island creation is as follows: During the collision cascade, a liquid volume is first formed. As the atomic volume of the liquid atoms is somewhat smaller than the atomic volumes in the surrounding lattice, the lattice atoms relax radially inwards to the soft liquid core, causing the pressure in the liquid to rise. As the liquid cools, the transition to the amorphous phase further increases the pressure owing to its lower density, causing formation of an
adatom island on the surface. At the same time atoms below the amorphous zone are pushed deeper into the bulk and thus create strain in the z-direction.

Clearly none of the previously mentioned four surface damage mechanisms can explain the observed phenomenon. The formation of adatom islands by nucleation of single adatoms and small adatom clusters has been known for a long time, but in this case a large single adatom cluster is formed by collective movement of the atoms to the surface. Thus, this phenomenon can be classified as the fifth surface damage creation mechanism.

Preliminary tests show that the effect is also present in SiGe, although it is a lot weaker than in Ge.

7 CONCLUSIONS

It has been shown that the MD method is a very versatile tool for examining ion implantation caused effects in covalently bonded materials. The method has been used for determining energy dependences in defect production, defect migration in conjunction with experiments, mixing, chemical reactions and strain effect on collision cascades.

The results from MD simulations may not be considered, mainly because of the limitations of the potential models, to be quite correct at the quantitative level. However, the results demonstrate that the MD method can be used powerfully to look for, for example, energy dependences or damage creation mechanisms.

We have found that the vacancy production at low energies in Si is a superlinear function of energy. It has also been found that the threshold temperature for interstitial migration is Si is between 130 and 180 K. We have shown that there are definite differences in damage creation in GaAs and Ge. The decrease of carbon erosion at high hydrogen bombardment fluxes was found to originate from hydrogen buildup at the carbon surface. We have also found a new damage creation mechanism in strained Ge which cannot be attribute to ballistic effects.
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Helsinki, May 2000

Jura Tarus
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37. Since the diamond crystal structure is not a Bravais lattice, the cells centered at the lattice atoms are strictly speaking Voronoy polyhedra. See e.g. N. W. Ashcroft, N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia 1976), ch. 4.


58. DMol is a trademark of Bio Sym. Inc., San Diego, California, USA.


