Development of a ReaxFF Reactive Force Field for Si/Ge/H systems and application to atomic hydrogen bombardment of Si, Ge and SiGe (100) surfaces

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Abstract

A new reactive force-field was developed for use in molecular dynamics simulations of chemical systems composed of silicon (Si), germanium (Ge) and hydrogen (H) with the ReaxFF code. The development incorporated Ge into the ReaxFF family of reactive potentials by fitting against a diverse training set of DFT data that pertain to Si/Ge/H bonding environments. The predictive capacity of the force field was manifested in molecular dynamics simulations of the H-atom bombardment of the (100) surface of c-Si, c-Ge and c-SiGe crystalline solid slabs in order to simulate the effects of the H-plasma semiconductor cleaning process in the near-surface region. Phenomena related to surface and subsurface H adsorption, H₂ generation and surface etching were described and compared in relation to material composition and the kinetic energy of the impinging atoms.

Keywords: Reactive force field, germanium, silicon, H-plasma, semiconductor, etching

1. Introduction

Advanced electronic and photoelectric devices employ Si, Ge and Si_xGe_{1-x} and their oxides in various heterostructures. The increasing penetration of Ge in semiconductor technologies in recent years is justified by certain advantages over Si, such as increased hole and electron mobilities, smaller band gap, and lower temperature for dopant activation [1,2]. H-plasma treatment is applied to both Si and Ge-based semiconductors at various processing stages in order to passivate electrically active defects, such as dangling bonds, carbon or oxygen contaminants and clean surfaces prone to recontamination [3-6]. In other applications H-plasma is used to texture wafer surfaces by etching and re-depositing surface atoms [7]. Use of germanium-based semiconductors has increased requirements for non-disruptive surface cleaning because of persistent carbon defects, and therefore plasma treatment processes become even more crucial than for Si [6]. During H-plasma treatment of semiconductors, surface etching by hydrogenation of surface atoms to volatile species [8,9] and formation of H-induced subsurface defects [10], are crucial phenomena that may result in damage of the semiconductor near-surface region and affect subsequent treatment and deposition processes in several ways. Despite advances in surface science methods, many effects of the H-plasma treatment of semiconductor materials are not fundamentally understood, which limits the optimization of the process.

Atomic-level simulations of semiconductor materials and processes have been extensively applied for several decades. Despite much progress in first-principles quantum-mechanical methods, the computational cost of these approaches does not allow dynamic simulations for anything but very small system sizes and timescales. Empirical force fields, on the other hand, aim to describe close-to-equilibrium bonding in chemical structures and cannot handle reactive chemical events. Reactive empirical force fields aim to compromise between the chemical accuracy of QM methods and the reduced computational cost of empirical potentials. Thus, just like in many complex chemical phenomena, dynamically complex processes in Si and Ge-based semiconductor materials, surfaces and interfaces, can benefit from application of reactive force field methods. Such processes include, in the semiconductor industry, deposition, growth, surface and bulk diffusion, thermal annealing, chemical surface treatment and etching processes, material fracture dynamics etc.

The reactive force field ReaxFF [11] uses at its core description of chemical bonding and reactivity the concept of bond order and its relation to the interatomic distance between atom pairs. ReaxFF does not use fixed connectivity assignments for the chemical bonds and aims to describe bond dissociation and bond formation events within molecular dynamics (MD) simulations. Bond orders are updated at each iteration in MD simulations. The bond energies, and their angular and torsional variation, are made dependent on the bond orders. Coulomb and van der Waals interactions are calculated between all atom pairs at each simulation step. Several other energy terms are included in the force field to treat chemical effects such as lone pairs, over-coordination and under-coordination, conjugation and hydrogen bonding. More detailed descriptions have been published elsewhere [11-13]. In the process of parameterization of the force field energy terms for a specific chemical system, all parameters are optimized to minimize differences with a training set that is constructed with ab initio methods, mostly DFT. The training set typically contains structural data, reaction energies and barriers, bond-dissociation energies, equations-of-state for crystal structures, atomic charges, and other calculated chemical data derived from molecular, cluster and periodic solid-state calculations. The general principle of the force field ongoing expansion to progressively larger fractions of the periodic table, is that every effort is made not to alter optimized force field parameters in the process of adding new interactions. ReaxFF has so far found extensive applications to the diverse molecular and condensed-phase chemistries of hydrocarbons, carbon materials, silicon/silica structures, zeolites, metals, metal oxides, hydrides, biomolecules and plasma [11-22].

The ReaxFF force field for silicon and silicon oxide materials and interfaces was one of the first developed [12] and was subsequently re-parameterized to describe the interactions with water and its dissociated products H/O/OH [13]. The Si/O/H force field was used in simulations of the Si/SiO₂ interfaces [12], dynamical crack propagation in silicon [17], and the process of water dissociation and diffusion in silica [13]. In view of the increasing importance of Ge in various semiconductor applications, we initiated the task of extending the Si/O/H force field to include Ge. As a first step, the development of a Si/Ge/H ReaxFF force field is described here, and applied in MD simulations to study the atomic H bombardment process of Si, Ge and SiGe (100) surfaces, relevant to H-plasma semiconductor processing and treatment applications. The Si/Ge/O/H force field development efforts will be described elsewhere.

2. Si/Ge/H Force-field development

The force field for the Si/H system was extended in the present work to include Ge. The parameters pertaining to Si-Si and Si-H bonds were kept identical to the previous version of the force-field [13], which was in no way affected, and new parameters were fitted for Ge-Ge, Ge-Si and Ge-H interactions. Parameterization of the original Si/O/H force field, as pertaining to Si-Si and Si-H bonded systems (oxygen is not relevant in the present work) will be briefly described first as it is the basis for the Si/Ge/H force field. The parameter training set included [13] the dissociation of Si-Si bonds in the Si₂H₆ and the Si₂H₄ molecules, thus accounting for single and double silicon bonds, as well as dissociation of Si-H bonds of the SiH₄ molecule. The entire dissociation energy curves, obtained via adiabatic energy vs. bond-length DFT scans from the equilibrium distance to the dissociation limit, was taken into account in the parameterization process. The energy dependence on valence and torsion angles in the Si/O/H force field was also included in the training set. For example, for silicon bonds the angular dependence was included in the training set in the form of the adiabatic DFT energy of the Si₃H₈ molecule as a function of

the Si-Si-Si bond angle, and torsional terms were fitted by including energy differences between chair, boat and planar conformations of $c\text{-(SiH}_2)_6$ six-member rings. Several other reactions were included in the original training set, such as conversion of Si_2H_4 to $\text{H}_3\text{Si-SiH}$ and water dissociation on silicon clusters. The force field also accurately described the cohesive energy and equation-of-state DFT predictions for various silicon crystal phases, including the simple cubic Si, $\alpha\text{-Si}$ and $\beta\text{-Si}$ phases.

The incorporation of Ge into the Si/H force field and the parameterization process was facilitated by exploring the qualitative similarities among Si-Si, Si-Ge and Ge-Ge bonds and between Si-H and Ge-H bonds and was done in a systematic way. The new training set consisted of molecular and cluster DFT energy data that included formation and dissociation reactions of Ge-Ge, Si-Ge and Ge-H bonds in selected structures. The training set was selected so as to contain a sufficient number of diverse structures with Ge-Ge, Si-Ge and Ge-H bonds with different coordination environments. The same energy differences were also calculated for the analogous molecules/clusters composed entirely of Si and H using the preexisting Si/H force field. Thus, we constructed a parameter training set where the differences between Si and Ge in Si/Ge/H bonding environments was directly calculated. Afterwards, we fitted the respective Ge parameters and Ge-Ge, Si-Ge and Ge-H bonding and non-bonding interaction parameters so as to capture the difference between these bonds and the respective Si-Si and Si-H bonds. In this way, the quality of the Si/Ge/H force-field can be judged to be equivalent to the Si/H force-field and is systematically fitted to allow direct comparison between Si and Ge models, and their interaction with hydrogen. The methodology of incorporating Ge in the force field ensures its transferability to bulk and extended Ge surfaces. As the parameters were fitted to capture the differences between Si and Ge, the training set was not too extensive and was based on minimum energy structures. However, the original Si/H force field contained more extensive non-equilibrium data and complete dissociation/reaction energy curves. Thus, the bond stretch, angular and torsional dependencies, both around the equilibrium bonds and at the dissociation limit in the Si/Ge/H systems should be relatively well described as well after fitting.

Table 1 contains the majority of the energy quantities calculated with DFT for force-field fitting and the corresponding ReaxFF predictions. The DFT data were calculated with full optimizations using the Jaguar program [23], the B3LYP exchange-correlation functional [24] and LAV3P** basis sets for all atoms [25]. Selected structures for these reactions are also shown in Figure 1. The quantities in bold in Table 1 were used for force-field fitting, but all calculated reaction energies are discussed here. To illustrate the principle of adding Ge in the existing force field, note in reaction (2) of Table 1 that the Si/H force field somewhat underestimates the strength of the Si-H bond in SiH_4 (ReaxFF: 78.6 kcal/mol, DFT: 93.5 kcal/mol). The under-binding is a consequence of the compromise that is required to fit extended systems better, such as H on Si surfaces and H in bulk Si. DFT predicts that the Ge-H bond in GeH_4 is weaker than the Si-H bond by about 5.3 kcal/mol. Thus, as shown in Table 1, the Si/Ge/H force field succeeds in describing the relative strength between Ge-H and Si-H bond accurately, which means that the Ge-H bond of GeH_4 is also somewhat underestimated compared to the DFT value. Thus the parameter training set for Ge-H bonds included the difference between reactions (1) and (2), rather than reaction (1) directly. Reactions (3)-(5) in Table 1 show that the Si/Ge/H force field also succeeds in describing accurately the relative strength of Si-Si, Si-Ge and Ge-Ge bonds of small saturated molecules. The numbers reflect that the Ge-Ge single bond is weaker than the Si-Si bond, whereas the Si-Ge bond has intermediate strength. The same is true for the unsaturated double bonds of the Ge_2H_4 and Si_2H_4 molecules, as predicted in Reactions (6) and (7). Reactions (8) – (10) are slightly more complex as they

include the dissociation and full hydrogenation of larger saturated clusters of Si and Ge into SiH₄ and GeH₄ molecules. The force-field predicts the relative changes accurately.

Table 1: Energy differences for reactions in the training set of the Si/Ge/H force field, calculated with DFT (B3LYP/LAV3P**) and with the constructed ReaxFF force field. Energies included in the training set are highlighted in bold.

Reaction	ΔE , DFT (kcal/mol)	ΔE , ReaxFF (kcal/mol)
(1) Dissociation of Ge-H bond in GeH ₄ $\text{GeH}_4 \rightarrow \text{GeH}_3 + \text{H}$	88.2	72.8
(2) Dissociation of Si-H bond in SiH ₄ $\text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H}$	93.5	78.6
(1) – (2)	-5.3	-5.8
(3) Dissociation of Ge-Ge bond in H ₃ Ge-GeH ₃ $\text{Ge}_2\text{H}_6 \rightarrow 2 \text{GeH}_3$	63.8	47.9
(4) Dissociation of Si-Ge bond in H ₃ Si-GeH ₃ $\text{H}_3\text{Si-GeH}_3 \rightarrow \text{GeH}_3 + \text{SiH}_3$	66.6	51.2
(5) Dissociation of Si-Si bond in H ₃ Si-SiH ₃ $\text{Si}_2\text{H}_6 \rightarrow 2 \text{SiH}_3$	69.7	55.3
(3) – (5)	-5.9	-7.4
(4) – (5)	-3.1	-4.1
(6) Hydrogenation of H ₂ Ge=GeH ₂ to H ₃ Ge-GeH ₃ $\text{Ge}_2\text{H}_4 + 2\text{H} \rightarrow \text{Ge}_2\text{H}_6$	-151.0	-144.1
(7) Hydrogenation of H ₂ Si=SiH ₂ to H ₃ Si-SiH ₃ $\text{Si}_2\text{H}_4 + 2\text{H} \rightarrow \text{Si}_2\text{H}_6$	-158.7	-157.3
(6) – (7)	7.7	13.2
(8) Dissociation and hydrogenation of Ge-(GeH ₃) ₄ $\text{Ge-(GeH}_3)_4 + 8\text{H} \rightarrow 5 \text{GeH}_4$	-446.0	-391.6
(9) Dissociation and hydrogenation of Si-(GeH ₃) ₄ $\text{Si-(GeH}_3)_4 + 8\text{H} \rightarrow \text{SiH}_4 + 4 \text{GeH}_4$	-455.5	-403.2
(10) Dissociation and hydrogenation of Si-(GeH ₃) ₄ $\text{Si-(SiH}_3)_4 + 8\text{H} \rightarrow 5 \text{SiH}_4$	-464.5	-410.4
(8) – (10)	18.5	18.8
(9) – (10)	9.0	7.2
(11) H atom binding energy on H-terminated Ge (111) surface cluster	-25.6	-21.5
(12) H atom binding energy on H-terminated Si (111) surface cluster	-22.7	-18.1
(11) – (12)	-2.9	-3.4
(13) H atom binding energy on H-terminated Ge(100) surface cluster	-32.7	-37.6
(14) H atom binding energy on H-terminated Si (100) surface cluster	-31.1	-34.7
(13) – (14)	-1.6	-2.9
(15) Addition of 2 H atoms to internal Ge-Ge bond of Ge cluster	-67.8	-72.2
(16) Addition of 2 H atoms to internal Si-Ge bond of zincblende cluster	-65.9	-68.3

(17) Addition of 2 H atoms to internal Si-Si bond of Si cluster	-63.0	-65.6
(15) – (17)	-4.8	-6.6
(16) – (17)	-2.9	-2.7
(18) Addition of 1 H atom to internal Ge-Ge bond of Ge cluster	-12.4	-20.0
(19) Addition of 1 H atom to internal Si-Si bond of Si cluster	-7.2	-16.7
(18) – (19)	-5.2	-3.3
(20) Splitting of a Ge cluster forming two (111) surfaces and addition of 14 H atoms (energy per Ge bond)	-108.0	-97.2
(21) Splitting of a Si-Ge cluster in the (111) direction forming a Si and Ge cluster and addition of 14 H atoms (energy per Si-Ge bond)	-111.1	-100.6
(22) Splitting of a Si cluster forming two (111) surfaces and addition of 14 H atoms (7 on each surface)	-113.4	-102.9
(20) – (22)	5.4	5.7
(21) – (22)	2.3	2.3
(23) Hydrogenation of clean Ge (100) surface (energy per H atom)	-75.4	-70.3
(24) Hydrogenation of clean Si (100) surface (energy per H atom)	-84.7	-76.6
(23) – (24)	9.3	6.3
(25) Replacing a Si atom with a Ge atom in Si₃₅H₃₆ cluster	19.6	16.1
(26) Replacing a Ge atom with a Si atom in Ge₃₅H₃₆ cluster	-17.7	-11.5
(27) Replacing all Si atoms in Si₃₅H₃₆ cluster with Ge (energy per Si atom) Si₃₅H₃₆ + 35 Ge → Ge₃₅H₃₆ + 35 Si	15.0	21.0
(28) Addition of 4H atoms to Ge cluster at bulk site to form GeH ₄	-164.1	-165.1
(29) Addition of 4H atoms to Si cluster at bulk site to form SiH ₄	-159.3	-162.2
(28) – (29)	-4.8	-2.9

Figure 1: Optimized structures corresponding to some of the reactions of Table 1. Higher resolution images are provided in the Supplementary Material file. Colors: Si = Grey, Ge = Red, H = White.

Quantities related to Si and Ge surfaces are described next. Although the medium-sized clusters used here are only approximations to the extended surfaces, they are equally valid for parameterization as the same structures were optimized in the DFT and ReaxFF calculations. Reaction (11) describes the addition of one additional H to the H-saturated (111) surface of Ge and Si diamond-phase structure, as represented by the cluster shown in Figure 1. Addition of one H atom causes the destruction of one surface Ge-Ge bond. Addition of H to H-terminated Ge (111) is more exothermic than on Si (111) despite the fact that the Ge-H bond is weaker, as addition to Si (111) requires the destruction of a stronger Si-Si surface bond. Thus, the hydrogen-saturated Si (111) surface is more resistant to H addition. The effect is captured well by the force-field predictions. The same is true for the H-terminated Ge (100) surface and Si (100) surfaces shown in reactions (13) and (14). The H-terminated Si (100) surface is slightly more stable than the Ge (100), because addition of more H atoms requires the destruction of the reconstructed (100) surface dimer bonds. On the other hand, reactions (23) and (24) show that H-saturation of the clean reconstructed Si (100) surface is more exothermic than that of Ge (100). Clean Si and Ge surfaces have under-coordinated atoms and therefore H atoms are strongly bound. The higher

exothermicity of H addition to Si (100) and the bond strength to H resemble the bond strengths in SiH_4 and GeH_4 . These effects are well predicted by the ReaxFF force field. Reactions (20)-(22) describe the splitting of Si, Ge and a SiGe cluster in the (111) direction (surface formation) and the simultaneous saturation of the two surfaces with H atoms. The reaction is meant to describe two opposing effects: it takes more energy to form a Si surface, but the H-saturation of the Si surface is more exothermic. The latter effect predominates and the net process is more exothermic for Si. The case of the SiGe cluster, forming a Si and a Ge surface, shows intermediate energy change between the two. These effects and relative energies are well predicted by the force-field.

Addition of H atoms to Si and Ge interstitial bulk sites is considered next. Reactions (15)-(17) consider the addition of a pair of H atoms in bulk Ge-Ge and Si-Ge and Si-Si bonds of clusters that represent the diamond bulk structure of Ge, Si and a zincblende phase of $\text{Si}_{0.5}\text{Ge}_{0.5}$. For the Ge cluster, the addition leads to the destruction of one Ge-Ge bond and saturation of the Ge atoms with the formation of two Ge-H bonds. The addition is more exothermic for Ge because a weaker Ge-Ge bond has to be broken in the process. The energy of addition of 2 H atoms in the SiGe zincblende structure is intermediate between the pure Ge and Si cases. All energy changes for these reactions are well captured by the force field. For the addition of a single H atom in reactions (18) and (19), the interstitial H atom is inserted at the bond center position, as also predicted by periodic solid-state DFT calculations [26]. The three-center bond is relatively weak (12.4 kcal/mol for Ge and 7.2 kcal/mol for Si) as the coordination of the Si, Ge atoms involved is incomplete. Insertion of H in Ge bulk is slightly more exothermic than in Si, as it requires the destruction of a weaker Ge-Ge bond. This is captured by the force-field predictions, but the bond strength is somewhat overestimated in both cases.

Reactions (25)-(27) aim to describe the relative bond strengths of Si-Si, Ge-Ge, and Si-Ge bonds in extended diamond structures. In reaction (25) an internal Si atom in a H-saturated Si_{35} cluster is substituted by a Ge atom. The reaction is endothermic reflecting that Si-Ge bonds are weaker than Si-Si bonds. The reverse substitution in a Ge cluster is described in reactions (26) and is exothermic. Reaction (27) describes the relative cohesive energies of the Si and Ge H-saturated clusters, manifesting the greater cohesive energy of Si compared to Ge [27]. Finally, reactions (28) and (29) describe the complete hydrogenation of Ge and Si atoms in the bulk to give intercalated GeH_4 and SiH_4 molecules respectively, and the vacancy site where they reside. The latter reaction inherently contains the vacancy formation energies in these systems and the hydrogenation energy of the dissociated atoms. The force-field predicted energies for these reactions are in very good agreement with DFT.

Overall, the training set for the incorporation of Ge to the Si/H force field is a diverse set of reactions that describe Ge-Ge, Si-Ge and Ge-H bonds in small molecules and medium-sized clusters. The clusters were constructed to describe such effects as the energetics of H addition to (111) and (100) surfaces, surface formation energies, H insertion to bulk interstitial sites, cohesive energies and vacancy formation energies. Because an efficient Si/H force field was available, the emphasis was placed on predicting accurately the differences between Si, Ge and SiGe structures. Comparing DFT and ReaxFF energies for the training set after parameterization of the relevant force-field parameters, we can claim that the agreement is satisfactory and it can certainly capture the main energy effects. Furthermore, all of the comparisons between Si and Ge are in the same direction with the DFT predictions, and therefore the force field can describe differences between Si and Ge systems quite well. The observed ReaxFF / DFT deviations in absolute values can be expected for an empirical reactive force-field that attempts to be of value to both molecular and condensed-phase systems. The extensively trained and tested ReaxFF

Si/O/H force field, together with the diversity of the Ge-containing structures in the current training set, render the force field generally applicable to Si/Ge/H systems. The force field parameters are provided in the Supplementary Material file.

3. Simulations, results and discussion: Application of the Si/Ge/H force field to H-atom bombardment of Si, Ge and SiGe (100) surface

The force field developed in the previous section aims to be generally applicable to Si/Ge/H systems. Modeling of several semiconductor processes requires description of dynamic interactions between various types of Si/Ge surfaces and atomic or molecular hydrogen or SiH_x , GeH_x species. As an example application, we have chosen to apply the developed force-field to MD simulations that describe the effects of bombardment of the clean (100) surface of crystalline Si, Ge and SiGe alloys with high-energy H atoms. These simulations aim to capture the main effects of H-plasma treatment processes of the semiconductor surface and near-surface regions as a function of the kinetic energy of the impinging H atoms and the surface composition. These effects include H surface adsorption and near-surface absorption, surface recombination to form H_2 molecules, surface etching and amorphization effects. The ReaxFF code allows the introduction of additional atoms in the course of an MD run in order to follow the dynamics of a variable-mass system. It also allows the user to select the location, velocities and frequency of introduction of the additional atoms. This setup allows the effective simulation of surface bombardment processes with a constant flux of atoms or molecules.

The initial model structures in the simulations represented the (100) surface and near-surface region of crystalline Si, Ge, and a SiGe alloy. It is known that the (100) surface of c-Si and c-Ge undergo reconstruction, so that the surface consists of rows of Si or Ge dimers. In each case, an approximately cube-shaped periodic slab model was constructed. The slab was composed of 1728 Si or Ge atoms, and was periodic in the x, y directions while the z dimension of the periodic box was made very long (1000 Å) in order to introduce a large vacuum region. The force field optimized lattice constants were 5.32 Å for Si and 5.64 Å for Ge, in good agreement with experimental lattice constants (Si: 5.43 Å, Ge: 5.66 Å [28]). Thus the periodic box dimensions of the Ge model were about 6% longer than that of Si, reflecting the difference in lattice constants. Figure 2 shows one unit cell of the periodic slab of Si, from two different views, in order to show the surface dimer rows. The bottom layer was fixed to avoid translation of the slab when hit by the high-energy H atoms. The SiGe model was prepared stochastically by randomly choosing either Si or Ge for each atom with equal probability. The random result was a $\text{Si}_{855}\text{Ge}_{873}$ slab corresponding approximately to $\text{Si}_{0.5}\text{Ge}_{0.5}$ stoichiometry. The random distribution was selected to account for the fact that there is no observed atomic order in the cubic diamond crystal structure of SiGe alloys [29]. After structure optimization of the SiGe slab, the dimensions of the periodic cell were intermediate between those of Ge and Si, as expected. In particular, the x,y dimensions of cell were 31.90 x 31.90 Å for Si, 33.81 x 33.81 Å for Ge and 32.98 x 32.98 Å for SiGe.

Figure 2. The periodic slab 1728-atoms Si model used in the simulations. The upper (100) surface was subjected to H atom bombardment.

A 0.1 fs time-step was used in all molecular dynamics simulations described here. The MD simulations were performed in an NVT ensemble using a Berendsen thermostat [30] with a 50 fs damping constant. When bombarded with H atoms, only the slab atoms (Si, Ge) were thermostated, as the kinetic energy of the progressively added H atoms was selected in advance, and thus the NVT ensemble applies only to the constant-mass Si/Ge slab. In particular, the H atoms were inserted sequentially at a particular distance above the surface, one hydrogen atom being added every 100 time steps (10 fs). The H atoms were inserted at randomly selected x, y locations at a distance 50 Å above the surface with only a z-component of velocity toward the surface, corresponding to kinetic energy 1 eV or 4 eV. Thus, for each slab, two sets of simulations were performed, one for H-atoms impinging on the surface with 1 eV kinetic energy, and one with 4 eV kinetic energy. Prior to H insertion, the slab Si and Ge atoms were equilibrated at 500 K with an NVT simulation for 1 ps (10,000 time-steps). The total simulation time in the actual H-bombardment MD simulations was 7.7 ps (77,000 time-steps), thus allowing the addition of 770 H atoms during the simulation. There is a small sub-picosecond delay for the first H atom to arrive at the surface which provides more time for thermal equilibration of the slab. The temperature was monitored in each case to make sure the thermostat operated reasonably well. Figure 3 shows the temperature fluctuation during the MD simulation for the H-bombardment of the Si (100) slab. The temperature fluctuates roughly between 500-550 for 1 eV H atom bombardment and 550-600 for 4 eV H atom bombardment. Thus, the temperature is maintained reasonably close to the set temperature (500 K) at the selected H flux, but at a temperature above the set point due to exothermic H adsorption that has a heating effect. Ge and Si-Ge slabs behaved similarly. Higher H flux leads to faster heating, so that the frequency of H atom addition was chosen partly to satisfy the requirement of keeping the temperature reasonably close to the set point with a relatively weak thermostat. Furthermore, this choice was a compromise between the requirements of adding as many H atoms as possible in reasonable simulation time and allowing for sufficient time for thermal equilibration between successive hits.

Figure 3. Temperature profile of Si (100) slab during H-bombardment simulation with $T_{\text{set}} = 500$ K for 1 eV and 4 eV H atom kinetic energies.

To put these molecular dynamics simulations into experimental perspective, and comment at the outset on their limitations, it may be noted that in the simulation, the addition of 1 H atom every 100 time steps in the periodic cell corresponds to a surface flux of H about 10^{27} atoms/ cm^2 s. This flux is many orders of magnitude greater than typical experimental H-plasma conditions where a typical flux is 10^{16} atoms/ cm^2 s [9,31]. Thus, the simulation flux is 10^{11} times greater than the experimental and nothing could practically be done to avoid this difference. Thus, the surface in the simulation has much less time to relax between successive H atom hits. Events that require longer timescales, such as thermal diffusion of the H atoms in the bulk, or long-time surface etching characteristics, will necessarily remain elusive. Because of the high flux, it is necessary to use a thermostat to avoid overheating due to the impact of the exothermic adsorption process. On the other hand, a typical duration for the experiment is 2-10 minutes of H plasma bombardment [31], compared to about 10 ps of MD simulation time, which is roughly a factor 10^{13} difference. Thus, a rough estimation shows that in the course of the simulation the number of H atoms impinging onto the surface (fluence) is about the same as, roughly, 1 second of H-plasma treatment with typical experimental H-flux conditions. Thus, the simulation time is realistic to observe only the beginning steps of the process, and computationally a very high flux is required to achieve this. The results therefore can only be qualitatively compared to experimental observations. It should also be noted that H-plasma conditions result in the formation of both H atoms, as well as various charged species, which further complicates the comparison.

Six NVT runs were performed describing the bombardment of the (100) exposed clean surface of Si, Ge and SiGe slabs with H atoms of 1 eV and 4 eV kinetic energy for each slab. Snapshots of the final structures after 7.7 ps of simulation time are shown in Figure 4. ReaxFF allows for direct quantitative analysis of the fragments generated in the simulation based on a selected bond-order cutoff (0.3). Thus, under each slab shown in Figure 4, we indicate the total number of H atoms that were absorbed to the slab's bulk and surface, the number of hydrogen molecules that have formed via recombination of H atoms and the number of SiH_x and GeH_x species that were desorbed from the surface at the end of the simulation.

1 eV

H_{ads} : 151 H_2 : 186 SiH_x : 3

4 eV

H_{ads} : 237 H_2 : 103 SiH_x : 1

H_{ads} : 255 H_2 : 109 GeH_x : 0

H_{ads} : 307 H_2 : 21 GeH_x : 0

H_{ads} : 111 H_2 : 154 SiH_x : 1 GeH_x : 0

H_{ads} : 205 H_2 : 50 SiH_x : 0 GeH_x : 0

Figure 4. Snapshots of the Si (top), Ge (middle) and $\text{Si}_{0.5}\text{Ge}_{0.5}$ (bottom) slabs after 7.7 ps of bombardment with 770 H atoms at kinetic energies of 1 eV (left structures) and 4 eV (right structures) at set temperature $T = 500$ K. In each case, the number of H atoms adsorbed in the slab (H_{ads}), the number of H_2 molecules formed and the number of desorbed SiH_x and GeH_x fragments formed appear below the structures. Higher resolution images are provided in the Supplementary Material file. Colors: Si = Yellow, Ge = Red, H = Black.

Comparing the results for the Si slab, at 1 eV and 4 eV H-atom bombardment, the following observations can be made. For the lower energy H-bombardment, those H atoms that absorb reside mostly on the surface (surface adsorption), while a very small fraction of them migrate to the first sublayer (bilayer) beneath. Thus, the H-atoms do not have sufficient energy to enter deeper in the bulk. On the other hand, when H atoms impinge on the surface with 4 eV kinetic energy, they have sufficient energy to go deeper into the subsurface layer, reaching up to the 4th sublayer underneath the (100) surface. As the duration of the simulation is small and the H flux very high, the subsurface H atoms do not have sufficient time to diffuse thermally deeper in the slab, and the penetration depth represents mainly the effect of the collisions required for the H atoms to reduce their kinetic energy and bond to Si. The fragment analysis shows that many more H atoms absorb in the case of 4 eV bombardment which is justified by their higher kinetic energy that allows penetration to the subsurface. The subsurface H atoms, present at a high concentration in the first few sublayers due to the high flux, do not cause any lattice destruction as the Si bonds are preserved. On the other hand, the impingement of 1 eV H atoms results in the formation of a much larger number of H_2 molecules. Hydrogen recombination, observed in the simulations mostly by Eley-Rideal type reactions as adsorbed H atoms combine with impinging H atoms, is energetically much favored compared to the desorption of hydrogen-saturated Si and Ge molecules. The rate of H_2 generation is decreased for the higher-energy H atoms, because the higher energy collisions on the surface favors both reflection and surface penetration mechanisms. This is understood by the fact that when H atoms approach the surface with higher kinetic energies they have less time to interact with adsorbed H atoms to react.

In the case of the Si model and for both kinetic energies of the impinging H atoms, we observed the disintegration of the surface dimer rows of the (100) surface rows, and desorption of a small number of SiH_x species. All of the species SiH , SiH_2 , SiH_3 and SiH_4 were observed to form and desorb in the simulations, as well as short-lived Si_2H_x species. Several events of re-adsorption of these species were also observed. It should be expected that surface etching should proceed to the formation of volatile SiH_4 [9, 31], but the simulation timescales achievable does not allow observation of the full dynamics. Instead, we focus on the stability of the surfaces with respect to etching caused by H bombardment. These simulations show that the Si (100) surface is indeed susceptible to etching under these conditions. The number of Si atoms away from the Si surface varies throughout the simulation from 1-4 atoms (Figure 4 shows only final snapshots), and no conclusive comparison can be made on the effect of the kinetic energy of the H atoms. The higher kinetic energy of the H atoms is expected to provide more energy to break the surface Si bonds, but also results in increased penetration and reflection trajectories, which has the opposite effect.

Turning to the results for the Ge slab, it is observed in Figure 4 that the fraction of H atoms that penetrate the surface and submerge to the subsurface layer is much greater than Si. Thus, for 1 eV H-bombardment, the H atoms reach the 6th sublayer (bilayer) of the Ge slab, while for 4 eV H-bombardment many H atoms penetrate the entire slab. This is partly a consequence of the more open

lattice of Ge, leading to fewer collisions with the impinging atoms, which leads to decreased deceleration and deeper penetration of the H atoms. The decreased strength of the Ge-H interaction also contributes in the same direction. ReaxFF predicts that binding of the H atoms on the clean (100) surface of Si is stronger than on Ge by about 6.3 kcal/mol (Reactions 23-24 in Table 1). The simulations show that more H₂ molecules were generated in the case of the Si (100) surface. The snapshots show increased population of H atoms on Si compared to Ge, and enhanced formation of SiH₂ surface moieties. Formation of SiH₂ disrupts the Si-Si bonds of the surface silicon dimers and provides additional pathways for H recombination pathways via abstraction of one of the H atoms of surface SiH₂ by impinging or adsorbed H atoms. This leads to more H₂ being generated on the Si (100) surface. Consequently, the surface-to-subsurface penetration probability of H atoms hitting the Si (100) surface is lower than for Ge (100) because of enhanced H surface adsorption and recombination probability. Finally the formation of SiH_x surface species leads to increased Si desorption pathways and surface etching, as hydrogenation weakens and breaks surface Si-Si bonds.

As a consequence of greater resistance to hydrogenation of the surface atoms, especially beyond the uptake of a single H atom per Ge, the surface of Ge (100) remained mostly intact in the course of the simulation at 1 eV H bombardment as only a few surface dimers were destructed and no etching was observed. For 4 eV bombardment, the surface remained completely intact and very few H atoms were adsorbed on the surface. This behavior is very different from Si (100) that displayed extensive H surface adsorption, Si dimer destruction and etching at the same H kinetic energy. The difference for Ge (100) is justified by the combination of high H kinetic energy and greater surface resistance to hydrogenation, leading to the major fraction of H atoms penetrating to the subsurface. In summary, the simulations predict that Ge (100) is less susceptible to etching than Si (100). It is also predicted that H atoms penetrate deeper in the Ge lattice than in the Si lattice. Thus, the greater susceptibility of surface Si atoms to formation of Si-H bonds, compared to surface Ge atoms, can explain all differences observed in the simulations between Si and Ge.

The simulations pertaining to the SiGe slab bombardment showed intermediate behavior between the Si and Ge slabs in terms of depth of penetration, H₂ generation and surface etching properties. This behavior was expected in view of the intermediate lattice constant, the bond strength of Si-Ge bonds that is intermediate between Si-Si and Ge-Ge bonds and the coexistence of Si-H and Ge-H bonds. However, in the case of the SiGe slab, it was observed that H bombardment led to amorphization of the near-surface layers where H was adsorbed. This effect of structure disordering was not observed in the simulation with either pure Si or pure Ge slabs. It can be attributed to co-existence of Si and Ge atoms in the lattice and the fact that the random distribution of Si and Ge atoms in the structure causes locally different atomic environments. When H-bombarded, the formation of stronger Si-H bonds coupled with the destruction of nearby weaker Ge-Si and Ge-Ge bonds (that are weaker than Si-Si bonds), result in destruction of lattice bonds. The locally variable environment also facilitates the amorphization of the lattice. The net effect is the destruction of the ordered diamond structure in the region where H penetrates, close to the surface. This causes saturation of the surface bonds and hindered surface-to-subsurface penetration pathways and consequently the SiGe slab absorbs less H atoms than either the pure Si or Ge slabs at both 1 eV and 4 eV H-atom bombardment. It is again noted that the very high H flux in the simulation may contribute to exacerbation of this effect, as there is no time for the H atoms to diffuse thermally away from the surface, leading to very high H concentration in the near-surface region. Nevertheless, observing that all simulations were run using the same settings, it can be

concluded that the SiGe structure is more susceptible to amorphization in the near-surface region than either Si or Ge, a process that creates an increased barrier to further absorption of hydrogen.

The quantitative predictions of these simulations cannot be directly compared to experimental H-plasma irradiation of semiconductor surfaces because of the short practically achievable simulation time and the unaccounted effects of charged plasma species. Qualitative trends will be compared. Experiments [9] show that the Si (100) surface is susceptible to etching by H-plasma treatment. The (100) surface stabilizes intermediate hydride products and promotes higher etching rates in comparison to the (111) surface. In another set of H-plasma cleaning experiments on Si (100), Ge (100) and SiGe (100) surfaces [31], etching was observed on the Si (100) surface during H-plasma exposure, and was found to result in silane (SiH_4) molecules desorbing from the surface as recorded by Residual Gas Analysis. On the other hand, Ge (100) and SiGe (100) surfaces did not show any etching under the same conditions, manifesting that Ge and SiGe alloy (100) surfaces are more resistant to etching under H-plasma treatment. Angle-resolved UV photoemission spectroscopy revealed that after H-plasma treatment under the same conditions, the Si (100) surface was in the dihydride Si (100): H 2x1 state, whereas the Ge surface was clean and completely dimerized. This indicates that the Ge (100) surface is more resistant to hydrogenation and thus more resistant to etching. The observed correlation between resistance to etching and resistance to surface hydrogenation has also been used to explain the observed temperature effect on surface etching, whereby raising the surface temperature reduces surface hydrogenation and results in decreased etching [8]. Thus, these experimental observations are in agreement with the present simulation results.

4. Conclusions

- (1) A new reactive Si/Ge/H ReaxFF force-field was developed by incorporating Ge into the previously developed Si/H force field. Parameterization of the new force-field was achieved by fitting the force field parameters pertaining to Ge and its interaction with Si and H, using a diverse training set of molecular and cluster DFT calculations for the Si/Ge/H system. The force-field can capture the differences between Ge-Ge, Si-Ge and Si-Si bonds and between Ge-H and Si-H bonds in various bonding environments, as evidenced by detailed ReaxFF/DFT comparisons for surface, bulk and molecular reactions.
- (2) The capacity of the Si/Ge/H force field was manifested in NVT molecular dynamics simulations of the H atom bombardment of the (100) surface of Si, Ge and SiGe crystalline solid slabs, aiming to simulate the effects of the H-plasma semiconductor cleaning process in the near-surface region.
- (3) It was shown that the (100) surface of c-Si is more susceptible to surface hydrogenation and etching by removal of surface Si atoms while the Ge (100) surface of c-Ge is more resistant to hydrogenation and etching because of weaker Ge-H bonds.
- (4) It was shown that the impinging H atoms have higher absorption probabilities in c-Ge and penetrate deeper into the subsurface layers of c-Ge than c-Si because of the more open lattice and weaker Ge-H bonding.
- (5) It was found that SiGe alloys, compared to pure Si and Ge, show intermediate behavior in terms of surface etching and depth of penetration, but are less resistant to near-surface amorphization by H-

atom bombardment than either c-Si or c-Ge. The amorphous surface layer increases the barriers to H surface and subsurface adsorption.

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Si (100)

Ge(100)