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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, H_2 generation, and surface etching were described and compared in relation to material composition and the kinetic energy of the impinging atoms.

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]. The 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 the hydrogenation of surface atoms to volatile species [8,9] and the formation of H-induced subsurface defects [10] is a crucial phenomenon 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

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[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/SiO_2 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 Si_2H_6 and the Si_2H_4 molecules, thus accounting for single and double silicon bonds, as well as dissociation of Si-H bonds of the SiH_4 molecule. The entire dissociation energy curves, obtained via adiabatic energy vs. bond-length DFT scans from the equilibrium distance to the dissociation limit, were 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 Si_3H_8 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-$(SiH_2)_6$ six-member rings. Several other reactions were included in the original training set, such as conversion of Si_2H_4 to H_3Si-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, α-Si, and β-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 were directly calculated. Afterward, 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 and 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 the LAV3P** basis sets for all atoms [25]. Selected structures for these reactions are also shown in Fig. 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 SiH_4 and GeH_4 molecules. The force field predicts the relative changes accurately.

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 Fig. 1. The addition of one H atom causes the destruction of one surface Ge-Ge bond. The 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 the 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 the addition of more H atoms requires the destruction of the reconstructed (100) surface dimer bonds. On the