First Principles simulations of extended defects at cubic SiC surfaces and interfaces

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Keywords: Silicon Carbide; Dislocations; Point Defects; Solid Surfaces and Solid-Solid Interfaces: Structure and Energetics; Molecular Dynamics

Abstract. In this paper, we will review some recent investigations on extended defects in cubic SiC, as obtained from first-principles molecular dynamics. As an example of defects at surfaces, the formation of self-assembled nanowires, originating from coordination defects at the Carbon terminated SiC(001) surface is discussed. Furthermore, the mechanism governing the creation of a network of edge dislocations at the SiC/Si interface is presented. This system, characterized by a peculiar ~20% lattice mismatch, can be considered as a template of high lattice mismatched heterostructures, where an ab initio approach is still affordable. We will discuss differences and similarities between the (001) and (111) interfaces, and compare our results with recent experimental data.

Introduction

Silicon carbide is a group IV compound semiconductor showing unique properties, that allow to consider it as a true surface-science 'laboratory' [1]: the charge polarization of the Si-C bonds makes SiC a polar compound, midway between GaAs and ZnSe [2]; the existence of hundreds of tetrahedral SiC polytypes [3] rises fascinating fundamental problems and opens the way to many potential technological applications. From the technological point of view, SiC is an extremely promising semiconductor for high-pressure, high-temperature electronic devices, but also for biological applications. The potentialities of SiC are severely affected by the large lattice mismatch with most of the conventional substrates, that induces a poor control of growth, formation of point and extended defects (dislocation and micropipes), but also low reproducibility of doping, metallization, surface preparation and stoichiometry. Several studies have recently been devoted to the understanding, characterization and technological exploitation of SiC properties, and a number of publications and review papers appeared on the theoretical study of point defects [4,5], surface properties [2,3,6], and interface structure [7,8] in SiC. Here, without presumption of completeness, we will present the latest results of first-principles simulations on the formation mechanism, energetics and local structure of extended defects at cubic SiC surfaces and interfaces. We will focus on selected systems, where the availability of recent experimental data complete the scenario and allows to show the complementarity between the experimental and theoretical approaches.

Method

The present paper deals with first principles molecular dynamics simulations of electronic and structural properties of defects in SiC: the method [9] allows for a combined relaxation of both the ionic and electronic degrees of freedom towards the ground state configuration. Calculations are performed in the supercell approach within the Density Functional Theory (DFT), in the Local Density Approximation (LDA); the problem of coordination defects and self-assembled C-wires however requires the use of GGA [10]. An energy cutoff of at least 40 Ry is used for the plane waves expansion of the wavefunctions, depending on the pseudopotential choice [11]. The reciprocal space integration in the Brillouin Zone (BZ) is done by considering only the Γ point of the supercell. The lateral dimensions of the supercell are chosen big enough to provide a good sampling of the BZ, and non interacting defect replicas [11]; furthermore, a wide (> 8 Å) vacuum space is included to avoid spurious surface-surface interaction between supercell replicas. Calculations are always performed at the theoretical equilibrium lattice parameter, consistent with the chosen pseudopotentials. Structures are considered converged when forces acting on atoms are less than 10^{-4} a.u. (0.005 eV/Å) and energy varies by less than 10^{-5} eV/atom. Further details on the method used can be found in [5,6,12] for the SiC(001) surfaces, and in [8] for the SiC/Si interface.

Self-assembled nanowires (sp^3 coordination defects) at C-SiC(001)

Recent experiments [13] have shown that stable sp^3-like bonded carbon lines can be formed on the C-terminated SiC(001) surface [14,15], by inducing an irreversible $sp \rightarrow sp^3$ phase transition in the substrate. These sp^3 lines point at possible precursors for diamond growth on SiC surfaces, and possibly at enhancing the SiC biocompatibility.

Motivated by these recent experiments [13], we simulated the appearance of coordination defects on the C-SiC(001)-c(2x2) reconstructed surface. Starting from the ideal geometry of this reconstruction, we arbitrarily rotated some C-dimers by 90° thus inducing a local $sp \rightarrow sp^3$ transition. The calculations were performed at different defect densities, $\Theta = 1/8$, $1/4$, $1/2$. The defect formation energy, which is 1.2 eV/dimer at $\Theta = 1/8$, decreases rapidly when more defects are created at the surface, and is ~ 0.05 eV/dimer at $\Theta = 1/2$, in good agreement with the experimental findings, showing that sp^3 dimers are more probable at high defect concentrations. Our ab initio results provide further details on the structural and electronic properties of the defects, that cannot be achieved in experiment: the sp^3 defects (see Fig.1), which always lie below the sp pattern of approximately 0.4 Å, are unbuckled, with dimer bond length of 1.36-1.38 Å, depending on defect concentration. Although the sp-dimers bond length is unaffected by the presence of the sp^3 dimer, the overall sp chain geometry is modified, accordingly to the strain associated with the presence of these rotated coordination defects.

The sp^3 defect conformation which results from our calculation is in apparent disagreement with the experimental observation [13] of asymmetric sp^3 dimers lying above the sp chains, as inferred from the measured STM images. In order to make contact with experiment, we have calculated both filled and empty states STM images of the defected surface. We have found two surface states localized on the defects, and separated by a gap of 0.2 eV. These states have the same symmetry and orbital character as the HOMO and LUMO surface states found in the p(2x1) reconstruction [14]. The STM images (Fig. 1-a) computed using the Tersoff-Hamman approximation [16] are in very good agreement with the experimental ones (Fig. 1-b): the apparent buckling induced by charge distribution in the neighborhood of sp^3-like bonded carbon atoms strictly resembles its experimental counterpart.

We have furthermore evaluated the effect of the presence of other defects on the formation energy of the $sp \rightarrow sp^3$ coordination defect: to this aim, we studied a symmetric slab with a missing

sp dimer at both surfaces close to the coordination defect and optimized the atomic and electronic structures of the supercell. In this case the formation energy of the sp^3 defect is approximately seven times lower than on a clean surface with no missing dimers. These results indicate that occasional missing units on the C-SiC(001)-c(2x2) surface may represent local seeds for the *sp* to sp^3 transition observed experimentally.

The SiC/Si interface

Another example of application of first-principles calculations to complement and interpret the experimental results is provided by the large scale simulations of the SiC/Si(001) interface [8]. Thanks to the large lattice mismatch of ~ 20%, this interface may be considered as a model of high lattice mismatch heterostructure of covalent materials, where ab initio simulations are still affordable.

Notwithstanding the high mismatch, SiC can be grown on Si(001), using different techniques [7,17,18]; the microscopic description of the interface is however incomplete. Classical [7] and ab initio [19] molecular dynamics simulations indicate that pseudomorphic thin SiC films cannot be grown on Si: our investigations [19] on the stability of few (1-3) SiC bilayers on Si(001) show that SiC never grows in pseudomorphic, defect free films on this substrate, and eventually amorphous SiC layers are found to be more stable. An efficient mechanism of strain relief must be at work at the very first stages of growth to obtain an abrupt interface, and epitaxial SiC films.

A recent High-Resolution Electron Microscopy (HREM) study of this system evidenced a locally abrupt interface, with the presence of a periodic array of misfit dislocations [18]. These ones seem to be pinned at the interface, which points at a vanishing critical thickness for this heterostructure. Still it is diffcult to gain additional information from these experiments. In particular, the atomic structure and the chemical environment at the interface, which deeply affect its physical properties, remain hardly accessible.

In order to provide a thorough description of the system, we have performed a combined classical and first-principles molecular dynamics study to investigate the stoichiometry of the interface as well as its stability [8]. We first performed a structural optimization for several possible interface configurations, varying both geometry and stoichiometry, via classical molecular dynamics, in order to get the most stable structure. Slab sizes up to 60 SiC and 60 Si layers were considered. The Si-Si, Si-C, and C-C interactions were modeled by means of the empirical Tersoff potentials [20]. The relative energy of systems containing different numbers of atoms were compared in the grand canonical scheme [21]. Our classical results indicate that configurations with C atoms at the interface are always more stable. In agreement with experimental results [18], the favored core structures are those with the dislocations pinned at the interface, which corresponds to a vanishing critical thickness.

The classical MD analysis allowed us to select the core dislocation structures and slab size for the ab initio simulations. Since the relative atomic distortions are less than 2% after the 4th layer, when considering a 7/7 or a 60/60 layer slab, and the 7/7 slab reproduces correctly the asymptotic value of an infinite (60/60) system, the ab initio simulations were performed on a 7/7 layer slab. Among all the considered geometries, our first-principles simulations were performed only for the most meaningful ones: the stoichiometric interface and the one which is lowest in energy. The latter (see Fig.2, left) is obtained from the stoichiometric solution by removal of all the C atoms along the two core dislocation lines (13 atoms per supercell): this configuration is 5.69 (15.05) eV/cell lower in energy than the stoichiometric one in C-rich (C-poor) conditions respectively, in the case of a 7/7 layers slab.

The analysis of the configuration topology gives some hints for understanding this result. The set of classical calculations has indeed shown that it is preferable to have C atoms at the interface in the first SiC layer, although the stretching of carbon bonds is energetically expensive. In this

reconstructed interface, with an understoichiometric carbon layer, the first SiC layer is carbon-like, but there is only one C atom involved in the reconstructed dislocation cores. It also presents the peculiar characteristics that almost no atoms are sub- or over-coordinated, owing to the formation of a topological ring along one direction and the formation of a silicon dimer along the other. This configuration is then the best candidate to represent the atomic structure of the SiC/Si(001) interface. A qualitative indication of the residual strain distribution at the interface can be obtained by inspection of the deformation of the converged system coordinates, with respect to the ideal bulk-like positions. Fig. 2 represents the residual strain field at the interface for this geometry, evaluated in terms of atomic displacements from ideal bulk-like positions. As it is evident from simple inspection, the major deformations are localized in Si, which has smaller elastic constants than SiC. This result, along with the occurrence of a periodic dislocation network, has been recently confirmed by accurate High Resolution TEM experimental [22] and simulated [23] images. A detailed description of the structure and energetics of the several configurations studied is reported elsewhere [24].

The ab initio simulations, although providing a deeper insight and structural and electronic details that remain prohibitive in empirical calculations, validate the results obtained by classical molecular
dynamics. Based on these findings, we studied also the SiC/Si(111) interface: because of the large supercell size requested by the hexagonal lattice, we performed in this case only classical simulations [23]. The (111) surface of a zincblende crystal can be obtained either with a shuffle or a glide plane which differ for stability and number of dangling bonds; at a (111) interface the situation is furthermore complicated by the possibility of having an inversion in the layer stacking sequence. A number of different configurations have been considered thus sampling the configuration space for this interface. We first investigated the possibility of forming stoichiometric interfaces by matching a Si and a SiC layers with different terminations at the interface: two shuffle planes, two glide planes or a shuffle and a glide plane were considered. Our results indicate that interfaces between shuffle planes are always more stable. Furthermore, similarly to what was found for the SiC/Si(001) system, our calculations revealed that it is always favorable to have carbon at the interfaces. We also considered the possibility of having pseudomorphic SiC grown layers, before the dislocations start, which was found to be an unfavorable configuration. Thus, as in the β-SiC/Si(001) interface, the dislocation cores are directly pinned at the interface, in agreement with experimental evidence [18].

The dislocation core for the most stable stoichiometric interface structure is presented in Fig. 3. The structure presents under-coordinated C atoms forming three SiC bonds 1.80 Å long in a distorted sp^2 hybridisation. At variance with the SiC/Si(001) system, structures obtained eliminating the unsaturated and distorted atoms are higher in energy. We finally analysed the possibility of having a stacking inversion at the interface, which would lead to a SiC crystal structure mirrored with respect to the previous one. We found that the energy difference between the two structures lays in the error bar of our calculation, resulting than degenerate. Twins are thus likely to form directly at the Si(111) surface, as indeed revealed by recent HREM dark field micrographs [18,25].

Summary

In conclusions, the two examples of ab initio simulations of extended defects in SiC presented in this work evidence the capability of the method in complementing the experimental result, and provide a microscopic description of the defect structure. In particular, for the SiC/Si interface, which can be considered as a template of high lattice mismatched heterojunctions, the large scale calculations required to describe the dislocation network, are in very nice agreement with newest experimental results.

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