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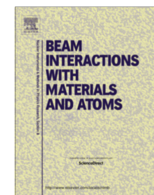

First principles defect energetics for simulations of silicon carbide under irradiation: Kinetic mechanisms of silicon di-interstitials

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ABSTRACT

Understanding the modification of the properties of silicon carbide under irradiation from the very fundamental point of view of atomic bonds and electronic structure can become possible in the next few years, thanks to the effort made in the last two decades to understand point defects from first principles calculations, but also thanks to the coupling of these results with simulation tools designed to describe larger spatial (and temporal) scales. We discuss some of the missing tiles that would allow to advance in this direction, in particular the incomplete data on defect clusters, and we present some first principles results for small silicon aggregates. We examine the stability, migration and structural evolution of Si di-interstitials in SiC. A triangular configuration is found to be the most stable in cubic SiC. Relatively small energy barriers, ranging from 0.25 to 1.2 eV, are found for the transformation of Si di-interstitials through reorientations, migration, and compact to extended transitions. We discuss the source of errors affecting our calculations as well as previous published results, which are still non-negligible.

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1. Introduction

As soon as a material is actually employed for applications of any kind, the concern for its behaviour out of thermodynamic equilibrium becomes a crucial one. Silicon carbide has diverse fields of applications. The control of defects is of utmost importance for devices based on silicon carbide as a functional material; but it is in nuclear applications that one has to face the highest defect concentrations and thus the influence of point defects is large not only on the electrical properties, but on all physical properties, including mechanical, thermal, and optical ones [1]. Although the possibility of taking into account all these properties to determine the state of the material is an advantage, the gap between theoretical understanding and measured data is clearly widened by the additional complexity. With native point defect concentrations that can reach a few percent, complex microstructures, high temperatures, and a large variety of impurities, the behaviour of silicon carbide under irradiation, as the one used for nuclear fuel cladding, or envisaged for nuclear fusion, cannot be predicted unless experiments in similar conditions have already been performed. However, the study of point defects in silicon carbide from first principles calculations, both for hexagonal and cubic polytypes, has gained precious insights into the structure and stability of the basic defects—vacancies, interstitials, antisites, divacancies, and the carbon vacancy-carbon antisite complex ($V_C C_{Si}$)—as well as into the most relevant diffusion and reaction barriers [2–6]. The relevance of the informations that can be extracted from the ab initio investigations is twofold: first, the formation, migration, and reaction energies are a necessary input for many higher scale simulations, including atomic Monte–Carlo, object/event based Monte–Carlo, and rate theory based kinetic approaches (also known as cluster dynamics); second, the structural, electronic, and vibrational properties obtained from first principles calculations can be directly or indirectly used to identify experimental features and associate them to peculiar defect species [7].

Concerning the structural and vibrational properties, the standard Density Functional Theory (DFT) approach in local or semilocal approaches is supposed to provide useful results. For some defects local vibrational modes have been calculated for comparison to experiments [8–10].

Electronic properties, conversely, are heavily affected by the well known underestimation of the band gap, so that with the LDA (Local Density Approximation) or the GGA (Generalised Gradient Approximation) also the position of defect levels in the band gap is questionable. To overcome this problem either hybrid functionals [11,12] of many perturbation theory have to be used [13,14]. However, even a reliable determination of the position of

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the electronic levels of a defect and, more directly, their spectral response, using the most advanced many body approaches, as used for the carbon vacancy [13], would not be enough to identify a defect without cross comparison to other informations extracted from a different experimental probe (here Electron Paramagnetic Resonance, or EPR).

Every possible probe is useful for cross comparison; moreover, talking of materials under or after irradiation, a further question has to be asked in advance: what are we probing? Or, in other words, what is the stationary (or frozen) state of the material that we are investigating? The reason is that we deal with a material which is certainly very far from thermodynamic equilibrium. For this reason, while a detailed investigation of any single point defect with the most advanced electronic structure methods is certainly worth the effort, it is also necessary to advance, even with the present partial lack of defect data, towards a general approach to a multi-scale simulation of the kinetics of defect populations in irradiated materials.

In a previous paper we have attempted a very simplified approach to the simulation of the kinetics leading to a stationary state in cubic silicon carbide under irradiation, starting from ab initio data for diffusion and recombination reactions [15]. Other authors have used the same approach to study the effect of the defect energy landscape and grain size on the amorphisation threshold in silicon carbide [16, 17].

In this paper we will discuss some directions to improve these models, making them more realistic, and we will present some data on one of the ingredients that are missing: the kinetics of the smallest aggregates of silicon atoms, i.e., silicon di-interstitials.

2. A bird's eye view on relevant kinetic barriers in SiC

Kinetic simulations based on rate theory describe the evolution of defect populations based on differential master equations for the average concentrations of various defect/cluster species; the key ingredient, apart from initial conditions and possible source terms to model primary damage, are the diffusion coefficients and reaction barriers for aggregation, dissociation, and transformation of species between each others. The hierarchy of energy barriers can be crucial to determine, for example, the sequence of dominant events during isocronal annealing. Many of these energy barriers have been estimated by first principles calculations. When barriers associated to different mechanisms are sufficiently far from each other, one can easily take advantage of results obtained by independent studies; conversely, when activation energies are very similar, only results obtained with exactly the same approximations can help establishing the hierarchy according to which these events take place.

As far as diffusion barriers are concerned, the fastest diffusing species are both types of interstitials, silicon and carbon ones, if we exclude the silicon tetrahedral interstitial in 4+ charge state. Entropies of diffusion have also been discussed in detail [18]. However, the precise hierarchy between the species with the lowest barriers, namely the neutral and +2 silicon interstitial and the carbon interstitials, should be investigated in more details [4,18,19]. The free energy barriers associated to the migration, but also to the rotations and some transformations of these interstitials, are expected to span an energy range between 0.1 eV to slightly more than 1 eV. Most Frenkel pair recombination barriers also fall in this energy range [15,20,21]. Other processes occurring at low temperature (i.e., again with an energy barrier of a few tenths of an eV) control the annealing of stoichiometric coordination defects (SCDs) and antisite pairs [22].

Antisite pairs recombination barriers, which also have been shown to depend on the charge state [22,23], occur in the range of 1.5–3 eV. The transformation $V_{Si} \Rightarrow V_C C_{Si}$ lies in a similar range, while the reverse ($V_C C_{Si} \Rightarrow V_{Si}$) has a barrier which, in the most favourable case (charge $Q = -1$), is close to 4 eV [14].

After these basic point defects, silicon [24] and carbon [8–10,25,26] clusters are expected to occur in a number of stable structures and sizes. Unfortunately, while the cited studies considered several stable structures and partly discussed their binding energy with respect to single interstitials species, they did not consider the kinetics for association/dissociation, i.e., the energy barriers to be overcome in order to form a cluster or to dissociate it into smaller clusters and/or single interstitial atoms. This information would be very important in order to simulate the evolution of defect populations and, eventually, of the microstructure of SiC under irradiation, also because it is clear from experiments that larger clusters nucleate in the form of dislocation loops as soon as irradiation doses and temperatures are sufficiently high [1,27,28].

In the lack of kinetic barriers one can use, as a lower limit to dissociation energies, the binding energies. We have extracted some binding energies for carbon clusters from Ref. [26] and we present them in Table 1. This table is part of a comprehensive, though still heterogeneous, compilation of relevant kinetic barriers available in the literature that we have recently produced for future use in kinetic simulations [23]. As the mentioned paper focused on neutral clusters we could only propose a couple of charged dissociations, assuming that the charge transition level reported in Ref. [26] (Section III.B) refers to the 0/+2 transition. An estimation of the dissociation barrier can be obtained by adding to the binding energy the migration barrier of the interstitial, 0.5–0.6 eV if neutral, 1.3–1.4 eV if in charge 2+ [18]. As can be seen from the table, both clusters formed by multi-carbon antisites, $(C_n)_{Si}$, and those formed by split interstitials, $(I_C)_n$, are very stable.

After irradiation or ion implantation, also silicon interstitials might coalesce into small clusters, which can, in turn, incorporate further interstitials. This phenomenon could also give rise to an extended silicon network in an amorphous structure [29]. Silicon interstitials are somewhat less mobile than carbon ones [4,18], but they are still mobiles at not so elevated temperatures (unless, maybe, in strong *p*-doping conditions). One could even expect a Bourgoin type mechanism [30] of enhanced diffusion due to electronic excitations, producing the mutual conversion from tetrahedral to split configurations ($I_{Si sp\langle 110\rangle} \leftrightharpoons I_{TC}$). For this reason aggregates of silicon interstitials should also be taken into account. However, only one work has appeared, up to date, dealing with silicon di-interstitials [24] and it was devoted to the hexagonal 4H polytype. As for carbon clusters, silicon di-interstitials are expected to have a relatively large binding energy; [24,31] they are predicted to be electrically active, but only ($0/\pm$) charge transition levels were reported, without any information on any structural change. Nothing is known on the kinetics (association, dissociation, migration) of these silicon clusters. A contribution on this aspect will be presented in the rest of the paper. We will deal here only with neutral defects, but it is clear that further understanding on the charge states of silicon interstitials and interstitial clusters is needed, both concerning their stability and their kinetics.

3. Structures and transformations of silicon di-interstitials

We report here in some detail results that have been previously described only briefly in an internal report [31]. We will discuss the limitations of the standard first principles approach and compare some easily applicable corrections that should be tested by comparison with more sophisticated approaches.

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