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First-principles simulations of Frenkel pair formation and annealing in irradiated ß-SiC

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Abstract. Using first principles molecular dynamics and Nudged Elastic Band calculations, we have investigated the effect of irradiation on cubic silicon carbide at the atomic scale, and in particular the formation of Frenkel pairs, and the crystal recovery after thermal treatment. Threshold displacement energies have been determined for C and Si sublattice, and the stability and structure of the formed Frenkel pairs are described. The activation energies for annealing these defects have then been computed and compared with experiments.

Introduction

Since it shows unique physical, chemical and mechanical properties, silicon carbide SiC has been extensively studied [1] and used in various applications, both in electronics (high-temperature, high-power, high-frequency devices, spatial environment) and in nuclear technology (fusion reactors, confinement matrices, spatial electronics). A good knowledge of the crystalline SiC behavior during and after irradiation or ion implantation is a prerequisite for all these applications. In fact during irradiation, lattice atoms are displaced, resulting in the formation of structural defects such as Frenkel pairs (FP), i.e. the stable combination of one intrinsic interstitial and one vacancy. The damage accumulates in the material, possibly leading to the deterioration of mechanical and electrical properties, and even amorphization in the case of large doses or low temperatures [2]. The accumulation of damage in SiC due to the use of ion implantation for doping has also been widely studied [3,4]. In order to recover a good crystalline quality, thermal treatments can be applied during or after irradiation. The defect concentration will change according to temperature and irradiation parameters, as a dynamic process of defect creation and recombination.

Atomistic simulations are a good complement to experiments, in order to better understand the material behavior during irradiation and its thermal recovery. In fact, while it is experimentally difficult to follow in-situ the material evolution, atomistic simulations allow the investigation of the creation and annealing of single defects. The other side of the coin is that atomistic simulations are limited to small material dimensions and short simulation times. Still, using classical interatomic potentials, one could investigate damage created by low energy cascade, and material recrystallization. First principles calculations are much more accurate, in particular for a covalent binary compound like SiC, but due to a higher computational cost, they are limited to the investigation of creation and annealing of simple defects. Recently, using first principles Molecular Dynamics (MD) simulations [5] and the Nudged Elastic Band (NEB) theory [6], we have determined the energy required to create FP in irradiated β-SiC, their structure and stability, and the activation energy for annealing the defect. The goal of this paper is to summarize all these results, and to give an overview of the creation and annealing of FP at the atomic scale in cubic silicon carbide.

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Directions	TP MD			DFT MD		
	TDE [eV]	FP	d_{FP} [a_0]	TDE [eV]	FP	d_{FP} [a_0]
C[100]	13.5	V_C+C_{TSi}	0.5	18	V_C+$CC_{<100>}$	0.87
C[110]	16.0	V_C+C_{TSi}	0.5	14	V_C+$CSi_{<0-10>}$	0.48
C[111]	37.0	V_C+C_{TSi}	0.5	38	various	
C[-1-1-1]	21.0	V_C+C_{TSi}	0.87	16	V_C+$CSi_{<010>}$	0.95
Si[100]	42.0	V_{Si}+$SiSi_{<100>}$	0.65-0.8	46	V_{Si}+Si_{TC}	1.52
Si[110]	50.0	various		45	V_C+$CSi_{<0-10>}$	1.48
Si[111]	42.0	V_{Si}+Si_{TC}	0.87	22	V_{Si}+Si_{TC}	0.87
Si[-1-1-1]	20.5	V_C+C_{TSi}	0.87	21	V_C+$CSi_{<0-10>}$	1.24

Table 1: Threshold displacement energies and associated Frenkel pairs (structure and interstitial-vacancy separation in lattice parameter a_0), for both methods. V_{Si}, V_C, Si_{TC}, C_{Tsi}, CSi, SiSi, CC are Si and C vacancies, Si and C interstitials in tetrahedral site, and dumbbells.Several possible defects are obtained in the case of Si[110] (TP) and C[111] (DFT).

Frenkel pairs creation

To investigate irradiation-induced damage, the important quantities are the Threshold Displacement Energy (TDE), i.e. the minimum energy to be transferred to a lattice atome to create a stable defect, and the structure of the resulting FP. We have performed molecular dynamics simulations with both classical interatomic Tersoff Potential (TP) [7] and first principles Density Functional Theory (DFT) [5] in order to determine these quantities. Details of the calculations are detailled in previous works [8, 9]. The table 1 reports the TDE and the formed defects for the main cristallographic directions, and for both methods.

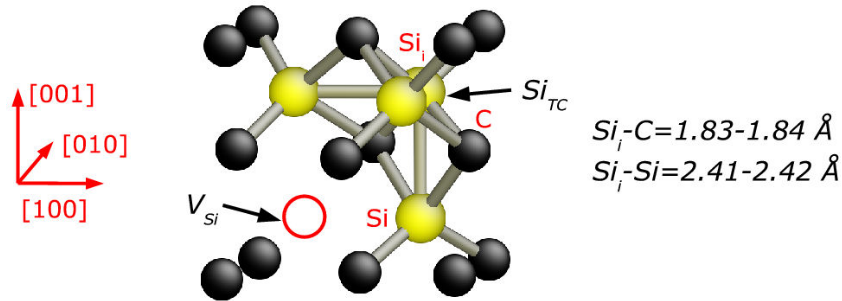

Figure 1: Structure of a FP including a Si_{TC} interstitial and a vacancy separated by 0.87 a_0. Light (dark) spheres represent the silicon (carbon) atoms.

The main difference between TP and DFT results is the structure of the formed interstitial. C_{TSi} are predominant with TP, whereas DFT lead to the formation of dumbbells, and also Si_{TC}. In fact, a C_{Tsi} interstitial is not stable in DFT computations, although it has a low formation energy as calculated with TP. A striking difference between the two sets of results is the generally larger interstitial-vacancy separation d_{FP} with DFT. Configurations with short separation are not stable if relaxed with DFT. A possible explanation is the well known tendency of classical potentials with a complex function, such as the Tersoff potential, to stabilize a large number of defect configurations. Finally, although formed defects could be very different, there is a relatively good agreement between TP and DFT regarding TDE, except for the Si[111] case. There have been several attempts to modify Tersoff-related potentials in order to improve the description of the formed interstitials in SiC. However, to our knowledge, a better description of defects, and in particular of the predominence of dumbbells and Si_{TC}, unfortunately lead to TDE 10-20 eV higher than the DFT values [8].

TDE are important quantities for determining the amount of damage created in an irradiated material. In particular, they are input data in simulation tools used for computing ion implantation

and damage profiles. Experimentally, TDE are difficult to measure, and available data in SiC span a large range of values. Theoretically, the precision of the determination is impeded by the common use of semi-empirical potentials, not always reliable for describing largely distorted atomic configurations in a covalent material like silicon carbide. Although it requires a considerable effort in computational power, the use of first principles DFT allows a better description of the elementary mechanisms of the irradiation process, and in particular for calculating TDE. Taking the weighted averages, we determined values of 19 eV for the C sub-lattice and 38 eV for the Si sub-lattice. Considering simply the threshold values, damage is readily initiated for a transferred energy of 14 eV (C) and 21 eV (Si).

FP obtained from DFT include mainly Si_{TC} and dumbbells (CC and CSi) interstitials. This was expected since these are the most stable configurations for single interstitial defects [10]. Figure 1 shows the structure of a Si_{TC} interstitial, obtained after a DFT MD determination of TDE along the Si[111] direction, and further relaxed in a large cell (216 atoms). The bonds between the extra Si and its C neighbors are sligthly shortened compared to the ideal bonds. The surrounding lattice is then weakly perturbed, which explains the relatively low formation energy of this defect.

Frenkel pairs stability and annealing

Created FP in silicon carbide are characterized by relatively short interstitial-vacancy separation d_{FP}, often lower than a lattice parameter. This short distance allows a better accommodation of the lattice distortion due to the interstitial by the vacancy. Comparing the DFT formation energy difference between FP and individual point defects (Table 2), we found that in almost all cases, there is a stabilization of FP due to the short distances.

FP	TDE [eV]	d_{FP} [a_0]	E_f [eV]	ΔE [eV]	E_a [eV]
V_C+$CC_{<100>}$	18	0.87	9.90	-0.03	1.43
V_C+$CSi_{<010>}$	14	0.48	6.69	-3.24	1.24
V_C+$CSi_{<010>}$	16	0.95	9.96	0.03	0.65
V_{Si}+Si_{TC}	46	1.52	14.08	-0.44	1.84
V_{Si}+Si_{TC}	22	0.87	13.46	-1.06	1.03

Table 2: DFT calculated data for selected FP: TDE, interstitial-vacancy separation d_{FP}, formation energy E_f, formation energy difference ΔE between FP and individual point defects, and recombination energy E_a.

In our calculations, FP remain stable at 300K over long DFT MD runs (several ps). We have investigated their stability by computing the annealing activation energies using the NEB method [11]. The results, shown in Table 2, range from 0.65 eV to 1.84 eV. These values are rather high, and explain the stability of the created FP, despite the small d_{FP}. The annealing mechanisms could be simple, with straight migration, when it is allowed by the FP geometry (e.g. Fig. 1). But we found more complex mechanisms, involving exchange or concerted motion of atoms. As an example, Figure 2 shows the minimum energy path for the annealing of the FP V_C+$CSi_{<010>}$. A concerted motion of one Si and one C atoms is required here, with an activation energy of 1.24 eV.

Experimentally, activation energies have been measured after annealing of damaged SiC. In particular, for temperatures ranging from 350K to 700K, activation energies of 1.3±0.25 eV, 1.3±0.1 eV and 1.5±0.3 eV have been obtained [12, 13]. Our calculated values are in fair agreement, so we can assume that for these temperatures, crystal recovery occurs by direct annealing of FP due to irradiation. A lower activation energy (0.3±0.25 eV) has also been reported in the temperature range 170-300K [12]. It could be associated with the annealing of FP that cannot be obtained from TDE calculations, but rather formed after migration of the mobile C interstitials.

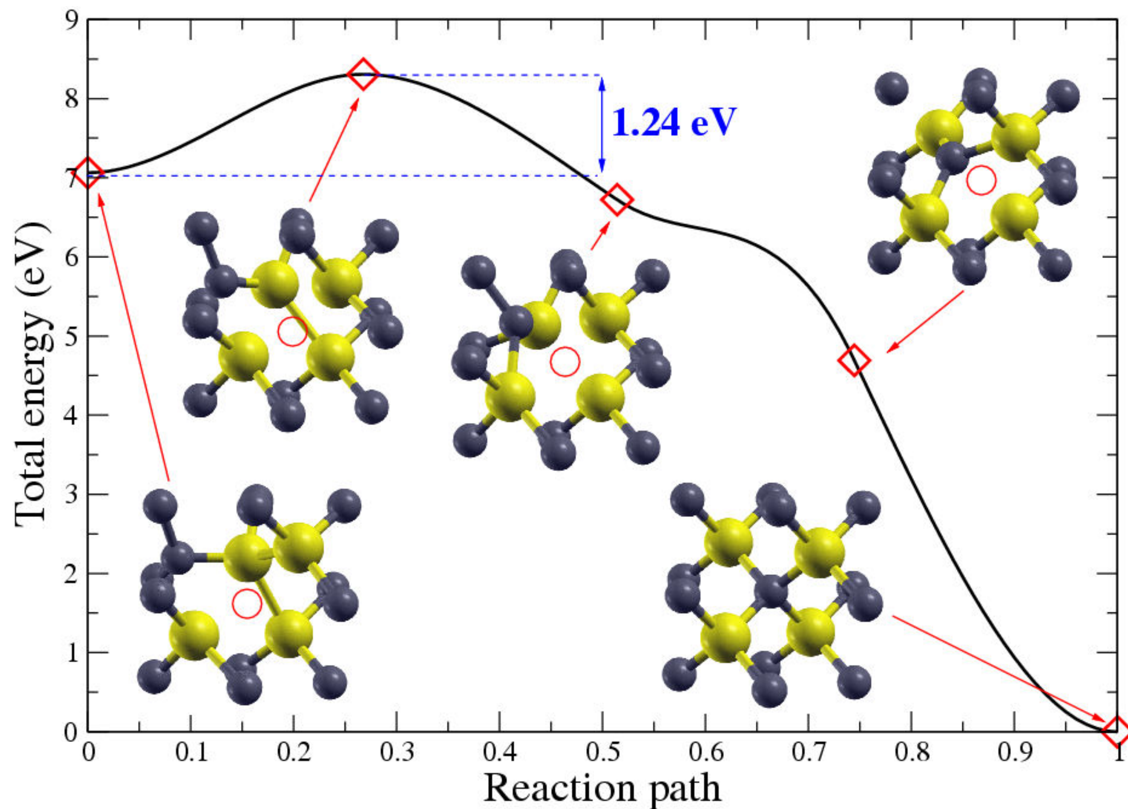

Figure 2: Minimum energy path for the recombination of the FP V_C+$CSi_{<010>}$. The insets show the different configurations encountered during the recombination. The circle marks the position of the vacancy.

Concluding discussion

In this paper, we report first principles simulations used for investigating the elementary mechanisms leading to creation of FP in irradiated β-SiC, and also crystal recovery by FP annealing. The first step, FP creation, requires the use of first principles molecular dynamics. In fact, irradiation is a complex and dynamic process, during which the material is out of equilibrium. At the atomic scale, molecular dynamics simulations are then the best tool. In few cases, it is also possible to consider the so-called sudden approximation [14], where one atom is displaced in a frozen lattice. For example, along the direction Si[111], a TDE of 22.5 eV is obtained, in very good agreement with the MD value of 22 eV. But, this approach is limited to orientations for which the displaced atom does not collide during its migration. For the cubic diamond lattice, it includes orientations Si[111], C[100], and C[-1-1-1]. But the sudden approximation yields correct results only for the Si[111] direction. For the two other cases, the computed TDE are lower than the MD result, although the sudden approximation value is expected to be an upper limit. The explanation is the formation of dumbbells at the end of both displacements, which cannot be taken into account with the sudden approximation. So, practically, this approach is not very useful. MD is then the most efficient choice for simulating the creation of FP due to irradiation, although it does not take into account electronic excitation effects.

We have used the NEB method and first principles calculations for investigating FP annealing, i.e. we have determined the static energy barrier for FP recombination in the framework of transition state theory. This approach is very well suited for SiC, since barriers are large, and characteristic times for recombination cannot be obtained within first-principles MD. Obviously, our study is then restricted to crystal recovery by post-annealing, in a thermodynamic regime.

We have shown that the approach described in this paper, although computationally demanding and restricted to small simulation systems, is valid for β-SiC. Because of the covalent character and the strength of the bonds in this material, a displaced atom forms a stable Frenkel pair at very short

distance, thus remaining in the simulation cell, without spontaneous recombination at room temperature. One can then expect similar success for other "hard" materials, such as carbides, nitrides and oxides.

Acknowledgments

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