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Ab initio study of the stability of intrinsic and extrinsic Ag point defects in 3C–SiC

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ABSTRACT

We have systematically investigated the energetics and stability of Ag atom in 3C–SiC with various charge states using first-principles calculations within large supercells. Up to 18 Ag-defect configurations have been examined, including substitutionals, interstitials, and vacancy-based complexes. A general trend is that the formation energy of Ag-defect complexes is generally lower than interstitial typed defects. With the lowest formation energy, the configuration with Ag_T_{Si}-V_C^{3+} turns out to be the most stable one. It has also been found a neutral Ag is more likely to substitute a silicon lattice site with a nearest carbon vacancy, thus forming an Ag_{Si}-V_C pair. All these data are important inputs in the next coarser-level modeling to understand the Ag migration in and release from 3C–SiC under both thermal and radiation conditions.

1. Introduction

As a promising advanced next generation fission nuclear reactor, High Temperature Gas Reactor (HTGR) stands out over conventional nuclear reactors due to its high thermal efficiency and better ability in handling safety issues. The fuel applied in this reactor is in the form of coated spherical particles, which are known as Tri-structural isotropic (TRISO) particles [1]. This type of fuel has been studied extensively in recent years as it can effectively retain and contain fission products (FPs) to reduce the risk of leakage and coolant contamination [2]. An individual TRISO fuel particle is comprised of a UO_2/UC kernel, surrounded by a carbonaceous buffer layer and subsequent isotropic layers of pyrolytic carbon, silicon carbide (SiC), and outer pyrolytic carbon. One of the main functions of these coating layers is to act as diffusion barriers for radioactive fission products (FPs), thereby keeping these FPs within the fuel particles, even under accident conditions. However, among the four layers, silicon carbide is the most important one which has advantages that provide both structural support and dimensional stability and thus act as the primary diffusion barrier to prevent FPs release [3]. Among over 200 polytypes, cubic SiC (3C–SiC, zinc-blende structure) is the most stable type below 2373 K [4] which has been widely explored in structural applications of nuclear reactors [5].

While TRISO fuel has demonstrated excellent retention of fission products and radioisotopes, release of some fission products from intact fuel can still be observed from experiments under conditions similar to accident scenarios [6,7]. It has been shown in the past few decades that ^{110m}Ag can be released in higher concentrations than other fission products [8–10] and is able to diffuse through SiC [11–13]. Multiple experiments [14–16] have also been conducted to determine the existence and formation of Ag in SiC. The first direct evidence of Ag in a neutron irradiated SiC layer was reported by Van Rooyen et al. [14] utilizing several characterization techniques, i.e. scanning transmission electron microscopy (STEM). Significant concentrations of silver were identified in both grain boundaries and triple junctions in SiC layer near the edge of IPyC. Moreover, when 6H–SiC is implanted with 360 keV Ag^+ ions to a fluence of 2×10^{16} Ag^+ cm^{-2}, voids were obtained [16] to be filled with implanted Ag following thermal annealing in the range 1250 °C -1500 °C. Similar feature to the observation in 6H–SiC is also visible in β–SiC, where Ag particles are surrounded by voids with 400 keV Ag ion implantation at room temperature to a fluence of 2×10^{16}

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Ag^+ cm^{-2} followed by annealing up to 1600 °C for 60 h [17]. However, faceted voids were not observed in as-implanted samples [17]. As suggested by the Rutherford Backscattering Spectroscopy channeling experiments [18], Xiao et al. reported that all the implanted Ag resided interstitially after implantation with 2.0 and 4.0 MeV Ag^+ ions to an average flux of 1.7×10^{12} cm^{-2} s^{-1} at 375 °C, no substitution Ag was detected even for low-fluence samples.

Despite numerous experimental investigations on Ag formation in SiC, the basic knowledge of properties of defect associated with Ag at the atomic level is sparsely understood. Only a recent study by Shrader et al. [19] has revealed Ag defects formation in bulk SiC through first-principle calculations. They have concluded Ag_{Si}-V_C^- to be the most stable defect at Si-rich limit under n-type condition. But, their result still has its limitation in accuracy, as they have used a relatively small simulation block containing 64 atoms for an undefected SiC. Therefore, in present study, we decided to provide a more comprehensive and thorough insight into the stability of defects in SiC involved with Ag impurities, together with clustering and interactions with native defects, particularly in connection with diffusion in SiC. This could have great significance to serve as both the most accurate input and primary contribution to the exploration of general behavior of Ag in SiC. While density functional theory (DFT) [20] has emerged as the most powerful approach in so many areas of solid-state physics to identify and characterize impurities and defects in a number of materials, we thus apply *ab initio* calculations to a larger model of pristine SiC containing 216 atoms. Since defects can facilitate charge transfer to their surrounding atoms, such charge transfer to and from neighboring atoms will alter potential barriers and diffusion dynamics in the formation of stable defects [21]. Thus, charge states are also included in this investigation.

2. Method

2.1. Computational approach

Calculations in this work were all performed using the density function theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP) [22]. Accurate projected augmented wave (PAW) potentials [23] were applied with valence electrons explicitly including $4d^{10}5s^1$ for Ag, $3s^23p^2$ for Si, and $2s^22p^2$for C, respectively. The generalized gradient approximation (GGA) as parameterized by Perdew-Burke-Ernzerhof (PBE) was used for exchange-correlation [24]. The model of the pristine SiC introduced was a 3C–SiC supercell with a lattice constant of 4.36 Å, which was composed of $3 \times 3 \times 3$ unit cells with 216 atoms. For all the models considered, convergence tests guided a plane wave expansion cutoff energy of 500 eV. To sample the irreducible Brillouin Zone in the structure to preserve the symmetry, a $4 \times 4 \times 4$ Monkhorst-Pack k-points mesh was carefully chosen for convergence and accuracy. Conjugated-gradient was used to fully relax all atomic positions, cell shapes, and cell volume to achieve the minimum total energy of the systems. The total energy was required to reach the convergence to a small change within 1.0×10^{-5} eV/atom between two relaxation runs, while the Hellmann-Feynman forces were minimized until the maximum force on the ion was smaller than 0.01 eV/Å. The van der Waals interactions are described by the DFT-D3 [25] throughout this study. However, despite a good structural description including atom positions and cell parameters, the usual errors intrinsic to the DFT-GGA exist. The calculated band gap for SiC was strongly underestimated amounting up to 40% of the experimental value (1.43 vs. 2.2–2.4 eV [26,27]), which is a typical issue of the DFT “band-gap problem” [28,29]. Even though there are a variety of approaches to achieve the band-gap correction, the hybrid functional has shown a great promise to alleviate the underestimation due to the moderate computational cost and robust reliability method [28,30]. Here, the correction of the band gap has been performed by Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [31,32], and the band gap has now been corrected to 2.295 eV, with this functional, which fits well with the experimental data.

2.2. Calculation of formation energy

In order to evaluate the energetic stability of these defects, we define the formation energy of the Ag-related defects in a charge state q as follow [33]:

$$E_f^q = E_{defect} - E_{perfect} - \mu_{Ag} + \sum_{X=1}^{2} n_X \mu_X + q\left(E_{VBM} + \left(E_1^{core} - E_0^{core}\right) + \mu_F\right) + E_{MP}, \tag{1}$$

$n_X = 1$, one X atom is removed;
$n_X = 0$, no change in the number of X atom;
$n_X = -1$, one X atom is added;

where E_{defect} is the total energy of a supercell containing a defect in charge state, q and $E_{perfect}$ is the total energy of a perfect 3C–SiC supercell, respectively. The integer n_X indicates the number of atoms of type X added to ($n_X < 0$) or removed from ($n_X > 0$) the supercell to form the defects. The μ_X (X = Si or C) is the corresponding atomic chemical potential describing exchange of particles with respective reservoir. The chemical potential of silver (μ_{Ag}) was calculated from a bulk crystal of silver. Electrons added or removed from the supercell are exchanged with the Fermi level, μ_F of the semiconductor host which is referenced to the valence-band maximum, E_{VBM}. The term (E_1^{core}-E_0^{core}) is electronic potential shift. The E_{MP} is a charge correction term in periodic boundary conditions due to the finite size of the supercell which is handled by Makov and Payne [34].

2.3. Charge-state transition levels

Most point defects are electrically active defects, which can exist in several different charge states, depending on the position of the Fermi level. As the Fermi level is raised, defect-induced states within the band gap become filled with electrons. A certain charge state is now realized if its formation energy $E_f^q(\mu_F)$ for a given Fermi level μ_F is lower than that of all other charge states. The commonly considered defect level corresponds to the Fermi-level positions where a transition from one charge state to another one occurs. Technically, these levels are defined as “thermodynamic transition levels,” and they correspond to the Fermi-level positions where the formation energies of two charge states of a defect are equal [35]. Then, the value of the Fermi energy μ_F where the dominating charge state changes from q to q’ is described as

$$\varepsilon(q/q') = \frac{E_f^{q'} - E_f^q}{q - q'} \tag{2}$$

where $E_f^{q'}$ and E_f^q are the formation energies of a defect in charge state q′ and q, respectively, when Fermi level is at valence band maximum (VBM). Here, we neglect the pressure- and temperature-dependent terms in the formation enthalpy of the defects. Accurate