**8.7 First-Principles Calculations of Charge States and Formation Energies of Mg Transmutant in 3C-SiC** — S. Y. Hu, W. Setyawan, W. Jiang, C. H. Henager, Jr. and R. J. Kurtz (Pacific Northwest National Laboratory)

## OBJECTIVE

To investigate the thermodynamic and kinetic properties of various transmutants in 3C-SiC using density functional theory.

## SUMMARY

We employed density functional theory to study the effect of electron potentials on charge states and the formation energies of Mg transmutant at different lattice sites in 3C-SiC. We found that $Mg_C$, $Mg_{TC}$ and $Mg_{TSi}$ most likely have charge state +2 while $Mg_{Si}$ prefers charge state -2. The results also show that the substitutional $Mg_{Si}^{-2}$ has much smaller formation energy than that of $Mg_C^{+2}$, and interstitial $Mg_{TC}^{+2}$ has lower formation energy than that of $Mg_{TSi}^{+2}$. These results imply that $Mg_{Si}^{-2}$ is the most stable substitutional defect while $Mg_{TC}^{+2}$ is the most stable interstitial defect in 3C-SiC. Since the quadrupole correction due to the spurious interactions between images of charged defects in periodic simulation cells was not taken into account, the calculated formation energies were overestimated. In future work we will examine the effect of quadrupole correction on the formation energies of defects. Additional studies on Al and Be transmutants in 3C-SiC are currently underway.

## PROGRESS AND STATUS

### Introduction

Theoretical calculations by Sawan, *et al*., [1] have predicted that at a fast neutron dose of ~100 dpa, there are ~0.5 at% Mg, ~0.15 at% Al, and ~0.2 at% Be generated in SiC through nuclear transmutation. These transmutants in SiC are expected to have potentially significant effects on phase stability, oxidation, transport properties (electrical and thermal conductivity), and elevated temperature mechanical properties. In our recent work [2], we calculated the formation and binding energies of neutral defects (intrinsic defects, Mg-related defects, and clusters) in 3C-SiC by density functional theory (DFT). The minimum energy paths and activation energies during point defect migration and small cluster evolution are studied using a generalized solid-state nudged elastic band (G-SSNEB) method with DFT energy calculations. Stable defect structures and possible defect migration mechanisms are identified. The evolution of binding energies during $Mg_2Si$ formation demonstrates that the formation of $Mg_2Si$ needs to overcome a critical nucleus size and nucleation barrier. It is also found that C vacancies promote the formation of the $Mg_2Si$ nucleus. As we know, defects in semiconductor materials such as SiC might have different charge states, which depend on the local electron potentials. In order to determine thermodynamic and kinetic properties of defects in SiC, it is necessary to identify the charge states of defects and evaluate their effect on defect properties. This progress report presents possible charge states and formation energies of Mg transmutants in 3C-SiC, calculated from DFT. Further studies of Al and be transmutants in 3C-SiC are currently underway.

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**Simulation Method**

The formation energy of a charged defect can be calculated using [3,4]

$$E^f(q) = E(q) - E_0(SiC) - \sum_{i=1}^{m} n_i\mu_i + q\left[E_{VBM} + \left(E^{core}(q) - E_0^{core}\right) + \mu_F\right] + E_{MP}(q), \quad (1)$$

where $E(q)$ is the total energy of the defected crystal, $q$ is the defect's charge, $E_0$ is the total energy of the perfect crystal, $\mu_i$ is the chemical potential of element i, $n_i$ is the difference of the number of element i (i = Si, C, Mg, Be, Al, ...) in the defected crystal with respect to that in the perfect SiC, and $E_{VBM}$ is the energy of the valence band maximum in the perfect crystal. The term $(E^{core}(q) - E_0^{core})$ is an electronic potential shift, where $E^{core}(q)$ and $E_0^{core}$ represent the corelike electronic levels in the defected and perfect crystals, respectively, and $\mu_F$ is the Fermi level measured from the valence band maximum $E_{VBM}$. The last term $E_{MP} = -\frac{q^2\alpha}{2\varepsilon L} - \frac{2\pi qQ}{3\varepsilon L^3}$ is the correction proposed by Makov and Payner [5] to correct the spurious interactions between images of charged defects in periodic simulation cells, where $\alpha$ is the Madelung constant, $\varepsilon$ the static dielectric constant, $Q$ its quadrupole moment, and $L$ the size of the simulation cell.

The charge state of defects is given by the number of electrons (or holes) associated with the defect in addition to those obtained in a neutral DFT calculation of the defected cell. These additional electrons (or holes) are associated with states in the band gap. Possible charged states of a defect can be determined by adding electrons (or holes) into the defected cell until the added charges relax into the conduction (or valence) bands, i.e., the additional charges are no longer associated with the defect. The cases where the electrons (or holes) do not relax to the conduction (or valence) band lead to charged defects. The most stable charge state for a given defect is the one that has the lowest energy for a given electron potential $\mu_e$ which is also called Fermi level $\mu_F$. The ionization level $\mu_e^{q/q'}$ of a defect, which is the position of electron potential where the most stable charge state changes from $q$ to $q'$, can be used to determine the possible charge states of a defect. If the ionization level $\mu_e^{q/q'}$ falls in the band gap ($0 < \mu_e^{q/q'} < E_{band}$), the charge states (q and q') are possible charge states of the defect. Ionization levels can be obtained by solving the following chemical potential equilibrium equation for the value of the electron chemical potential:

$$\begin{aligned} &E(q) - E_0(SiC) - \sum_{i=1}^{m} n_i\mu_i + q\left[E_{VBM} + \left(E^{core}(q) - E_0^{core}\right) + \mu_e\right] + E_{MP}(q) \\ &\quad = E(q') - E_0(SiC) - \sum_{i=1}^{m} n_i\mu_i + q'\left[E_{VBM} + \left(E^{core}(q') - E_0^{core}\right) + \mu_e\right] + E_{MP}(q') \end{aligned} \quad (2)$$

We used the Vienna Ab-initio Simulation Package (VASP) [6] with accurate projector-augmented-wave (PAW) pseudopotentials [7] and the generalized gradient approximation (GGA) of PBE96 [8] to calculate the total energy, band gap $E_{band}$, and electron potential shift

$(E^{core}(q) - E_0^{core})$ of a charged defect in 3C-SiC. Initial convergence tests guided the choice of 500 eV for the energy cutoff, $E_{cut}$. For point defects in 3C-SiC crystals, a supercell $2a_0 \times 2a_0 \times 2a_0$(about 64 atoms) is used, with a $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh [9] for Brillouin-zone sampling. All structures are relaxed with energy convergence of 1 meV and 10 meV for the electronic and ionic relaxations, respectively. Full relaxation of lattice vectors and internal atom coordinates is performed in several runs. The relaxation runs are stopped when the energy difference between runs is less than 100 meV. After the relaxation runs, a static run (one self-consistent loop) is performed to eliminate numerical error associated with the plane-wave basis set incompleteness due to the change of the lattice vectors during the relaxations. For consistency with the majority of the reference literature, we calculate defect formation energies in SiC using the Si-rich limit, with the reference states (3C-SiC, $Mg_2Si$, Si(diamond)). So the chemical potentials $\mu_i$ of C, Si and Mg can be calculated as

$$\begin{aligned} \mu_{Si} &= E_0(Si) \\ \mu_C &= E_0(SiC) - \mu_{Si} \\ \mu_{Mg} &= (E_0(Mg_2Si) - \mu_{Si})/2 \end{aligned} \tag{3}$$

For the static dielectric constant $\varepsilon$ of 3C-SiC, we take the experimental value ($\varepsilon = 9.72$). The Madelung constant used here is 3.52, which was estimated for the $2a_0 \times 2a_0 \times 2a_0$ supercell [10] [10]. In the calculations we only consider the dipole correction. The quadrupole correction usually is about one third of the dipole correction [11] which rapidly decreases with the increase of simulation cell size $(L^{-3})$.

**Preliminary Results**

The defect energies of Mg transmutant with different charges $(q = -2, -1, 0, +1, +2)$ at different lattice sites [Si, C, the tetrahedral center of Carbon atoms (TC), and the tetrahedral center of Si atoms (TSi)] in 3C-SiC have been calculated. The formation energy of a defect described by equation (1) is a linear function of electron potential $\mu_F$ for a given charge state $q$. Figure 1 plots the formation energy $E^f(q)$ of Mg with different charge states at different lattice sites as a function of electron potential $\mu_F$. Based on equation (2), the ionization level ($q/q \pm 1$) can be determined by the intersection between two linear formation energy curves with charge $q$ and $q+1$ (or $q-1$), respectively. The vertical dashed lines in Figure 1 shows the ionization levels for different defects. The segments defined by the intersections at ionization levels show the formation energy of the most stable charged defect for a given electron potential. We can see in Figure 1a that the substitutional Mg at C lattice ($Mg_C$) prefers a charge state of +2 when $\mu_F < 1.5eV$. It prefers a charge state of -2 when $\mu_F > 2.2eV$. Figure 1b shows that the substitutional Mg at Si lattice prefers a charge state of -2 for the full range of electron potential $0 < \mu_F < 2.4eV$. The charge states of interstitial Mg at TC and TSi are similar to that of $Mg_C$. It is found that $Mg_C$, $Mg_{TC}$ and $Mg_{TSi}$ most likely have charge state +2 while $Mg_{Si}$ prefers charge state -2. We notice the size difference of covalent radii of Mg, Si and C (covalent radii are 1.41Å (Mg), 1.11Å (Si) and 0.68Å (C), respectively). Mg is a little larger than Si and

much larger than C, which is consistent with the fact that C and interstitial sites (Tc and TSi) that have small space prefer positive charge states, and Si sites that have larger space prefer negative charge states. The results in Figure 1 also show that the substitutional $Mg_{Si}^{-2}$ has much smaller formation energy than that of $Mg_{C}^{+2}$, and interstitial $Mg_{TC}^{+2}$ has lower formation energy than that of $Mg_{TSi}^{+2}$. Therefore, $Mg_{Si}^{-2}$ should be the most stable substitutional defect while $Mg_{TC}^{+2}$ should be the most stable interstitial defect in 3C-SiC.

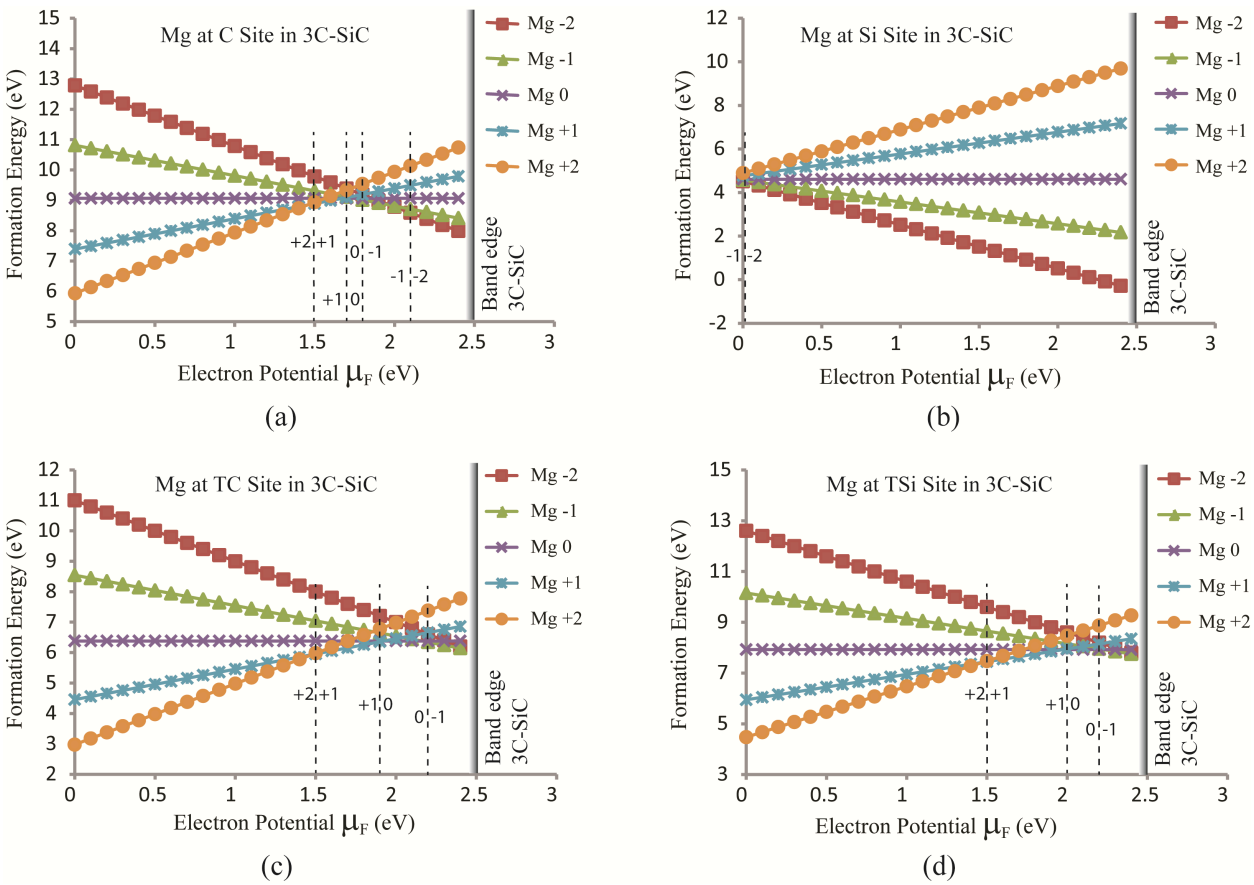


**Figure 1.** Formation energy of charged Mg at different lattice sites under different electron potential. The band gap value is taken as $E_{band} = 2.39eV$, determined from experiment [12].

## FUTURE WORK

In this report we present a part of our preliminary results that were calculated in a simulation cell $2a_0 \times 2a_0 \times 2a_0$. The results provide the thermodynamic properties including the formation energies of charged defects, possible charge states, and the most stable charged states. Since in the calculations we have not included the quadrupole correction due to the spurious

interactions between periodic images of charged defects in periodic simulation cells, the calculated formation energies are overestimated. More accurate calculations can be achieved by increasing the size of the simulation cell. In the future work, we will examine the size effect on the formation energies of charged defects, complete the formation energy calculations of other transmutants (Be and Al), and study the effect of charge states on migration mechanisms and migration energies of defects.

## ACKNOWLEDGEMENTS

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