

# Effects of carbon-related oxide defects on the reliability of 4H-SiC MOSFETs

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**Abstract**— In this work, we use density functional theory-based calculations to study the hole trapping properties of single carbon-related defects in silicon dioxide. We show that such interstitials are stable in the carboxyl configuration, where the interstitial carbon atom remains three-fold coordinated with chemical bonds to two Si atoms and an oxygen atom (Si-[C=O]-Si). Using formation energy calculations, we observed a +2 to neutral charge transition level for carboxyl defect within the 4H-SiC bandgap. This leads us to propose that carboxyl defects are likely to act as switching oxide border hole traps in the oxide and contribute to threshold voltage instabilities in a 4H-SiC MOSFET. Thus, we provide an additional candidate to the traditional oxygen vacancy hole traps in 4H-SiC MOS systems. The atomic structures of the defect in various charge states are presented. The stability-providing mechanism for the carboxyl defect in the doubly positive state is found to be the puckering of the Si atom, as in the case of positively charged oxygen vacancy hole traps.

**Keywords**— hole traps, bias-temperature instability, single-carbon interstitial, 4H-silicon carbide MOSFET

## I. INTRODUCTION

4H-Silicon Carbide (4H-SiC), owing to its superior electrical and thermal properties, is a suitable choice for future high-power, high-temperature and extreme-radiation electronic applications. However, a serious challenge that has limited this technology from attaining its full potential is its reliability. In the past, 4H-SiC MOSFETs have been observed to exhibit bias-temperature instability (BTI) of threshold voltages ( $V_{th}$ ) [1-4]. In an n-MOSFET, BTI expresses itself as a decrease (increase) in  $V_{th}$  following an applied negative (positive) gate bias making the device unreliable. For example, negative BTI aggravates subthreshold leakage current of a 4H-SiC power MOSFET and consequently, reduces its blocking voltage [1].

Switching oxide hole traps have been proposed to be a major contributor to BTI in 4H-SiC MOSFETs [1, 5]. They are believed to be physically located in the oxide side of the semiconductor/oxide interface (near-interfacial or border traps). Upon the application of a negative bias, these traps turn positively charged through hole capture. During positive gate bias cycle, they allow electrons from the semiconductor to tunnel into them and turn neutral. This switching behavior results in bias-dependent  $V_{th}$  instability in the MOS device.

Microscopically, the origin of switching oxide hole traps have been traditionally attributed to oxygen vacancies in silicon dioxide (called E' centers) [5]. Their existence and hole trapping properties have been experimentally validated using electron spin resonance (ESR) spectroscopy [6, 7]. Oxygen vacancy in SiO<sub>2</sub> has also been theoretically investigated extensively using density functional theory (DFT) [8-10]. A commonly observed phenomenon in such simulations involved puckering of the defect structure during hole capture. Here, the positively charged silicon atom moves away from the vacancy and backbonds with a lattice oxygen behind it. This structural transformation is believed to stabilize the E' center in its positively charged state and turns it into a viable hole trap [11].

In the context of 4H-SiC/SiO<sub>2</sub> interface, additional hole traps are likely to exist due to the interference of carbon and other elements (N, H etc.) in the 4H-SiC oxidation and post-oxidation annealing processes. For example, single carbon interstitials in SiO<sub>2</sub>, existing in the carboxyl configuration, has been cited as a possible hole trap in previous DFT calculations [12]. However, its structural transformation and stability have not been analyzed in detail.

In this work, we provide a comprehensive analysis of hole trapping properties of carboxyl defect present in the oxide side of 4H-SiC/SiO<sub>2</sub> interface using DFT. Firstly, the thermodynamic and kinetic feasibility of the existence of single carbon interstitial in the carboxyl configuration is studied. We then use DFT-based defect formation energy calculations to show a +2 to neutral (+2/0) charge transition level in the 4H-SiC bandgap. This suggests that the carboxyl defects are likely to act as border hole traps in the 4H-SiC/SiO<sub>2</sub> MOS system and contribute to BTI. Subsequently, we report on the stability-providing structural transformations of the defect during hole capture. Specifically, our observations include the puckering phenomenon in the carboxyl defect during hole trapping, where the Si atom moves away from the carbon atom and backbonds to an Oxygen atom on its rear side. Similar puckering transformations occur in E' centers.

## II. METHODOLOGY

### A. Computational setup

Plane-wave density functional calculations are performed using Quantum Espresso [13]. Carboxyl defects, where the interstitial carbon atom displaces a lattice oxygen and binds to

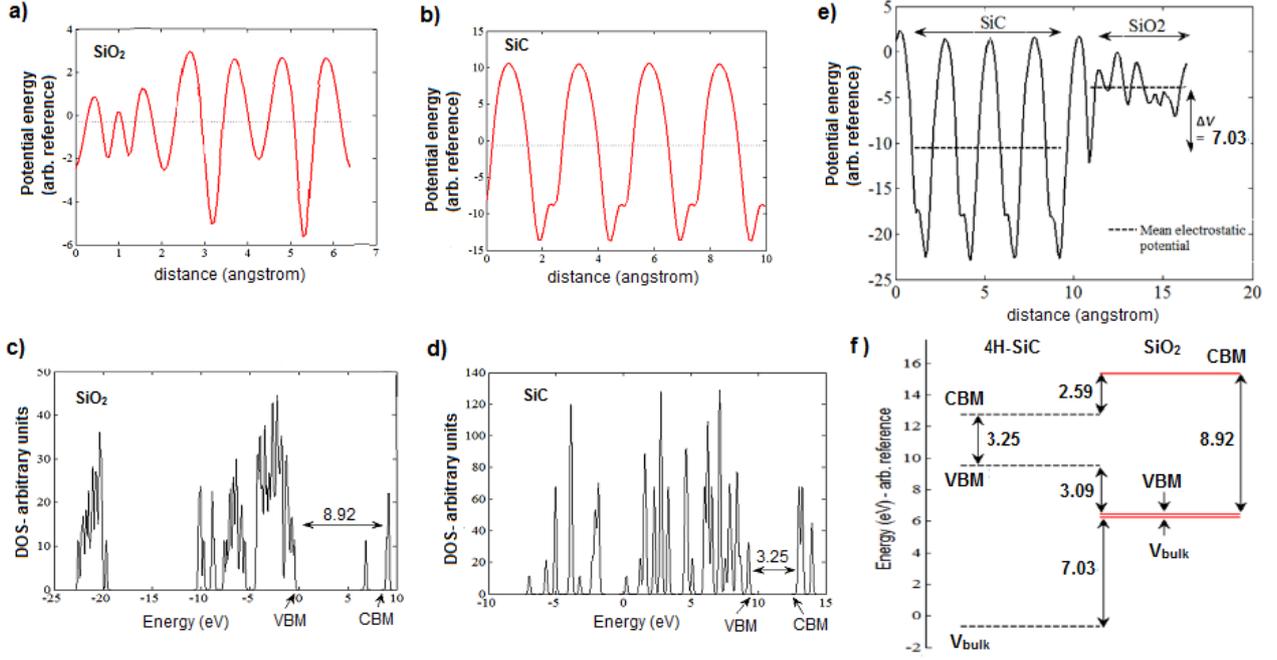


Figure 1: Details of the procedure for 4H-SiC/SiO<sub>2</sub> bandgap lineup, a) plane-averaged potential in SiO<sub>2</sub>, b) plane-averaged potential in 4H-SiC. Mean potential is shown as dotted lines. c) DOS of SiO<sub>2</sub> showing valence and conduction band extrema, d) DOS of 4H-SiC showing VBM and CBM, e) plane-averaged potential in 4H-SiC/SiO<sub>2</sub> interface. The shift in the mean potential is shown, f) Bandgap lineup between 4H-SiC and SiO<sub>2</sub>. All energies are in eV.

two Si atoms, are introduced into an amorphous SiO<sub>2</sub> supercell. The displaced oxygen remains bonded to the carbon through a double bond. Our simulations are performed with plane-wave energy cutoff set at 950 eV and Brillouin zone sampled at the Gamma point. Exchange-correlation energy is given according to the Perdew-Burke-Ernzerhof (PBE) scheme under the Generalized Gradient Approximation (GGA). Here, unscreened hybrid functionals are used where 35% of PBE exchange interaction is replaced by exact Hartree-Fock exchange. The mixing fraction was found to be adequate to reproduce the experimental bandgap of alpha-quartz (8.9 eV). Core electrons are represented using norm-conserving pseudopotentials.

### B. Formation energy calculation

The formation energy of a defect in charge state  $q$  is calculated as a function of Fermi level  $E_F$  using DFT as,

$$E_{f,q}(E_F) = E_{tot,q} - E_{tot}^{bulk} - \sum_i n_i \mu_i + q(E_v + E_F) + E_{corr,q} \quad (1)$$

Here,  $n_i$  and  $\mu_i$  represent the number of impurities and their chemical potential.  $E_{tot,q}$  and  $E_{tot}^{bulk}$  are the ground state energies calculated for relaxed supercells with the defect in charge state  $q$  and without the defect, respectively.  $E_v$  is the valence band of SiO<sub>2</sub>.  $E_{corr,q}$  stands for the correction factor used to account for the unreal electrostatic energy arising from the interactions between charged defects in nearby supercells [14].

The charge transition level (CTL) for a defect is defined as the Fermi level at which two charge states of the defect have equal energies of formation. The occurrence of an oxide defect

CTL within the bandgap of 4H-SiC is suggestive of an electron or hole trap. Thus, the alignment of 4H-SiC bandgap with respect SiO<sub>2</sub> gap is crucial.

### C. Bandgap lineup

Prior to calculating the CTL of carboxyl defect, we aligned the bandgap of 4H-SiC with respect to SiO<sub>2</sub> using the methodology described in literature [15]. Firstly, we performed hybrid functional DFT calculations independently on bulk amorphous SiO<sub>2</sub> (36 atoms) and bulk 4H-SiC (72 atoms) supercells to determine three landmarks for each component – a) the mean electrostatic potential (MEP) in the bulk (Figures 1(a) and 1(b)), b) the valence band maximum (VBM), and c) the conduction band minimum (CBM). The VBM and CBM, with MEP as reference, are identified from the respective density of states (DOS), as in Figures 1(c) and 1(d). We then constructed a realistic 4H-SiC/SiO<sub>2</sub> interface (108 atoms) using molecular dynamics and calculated the electrostatic potential in it (Figure 1(e)). The shift observed in the MEP between 4H-SiC and SiO<sub>2</sub> in the interface structure was applied to the MEPs obtained by independent supercell calculations to determine the bandgap lineup. Our result, given in Figure 1(f), is in reasonable agreement with previous *ab-initio* calculations [16] and experiment [17].

## III. RESULTS AND DISCUSSION

The thermal oxidation of 4H-SiC to form the interface is believed to be accompanied by the emission of atomic carbon [18]. Our DFT-based molecular dynamics simulation of single carbon interstitials in SiO<sub>2</sub> indicated their spontaneous incorporation into the SiO<sub>2</sub> lattice forming Si-O-C-Si linkages. However, the carboxyl configuration has been reported to be

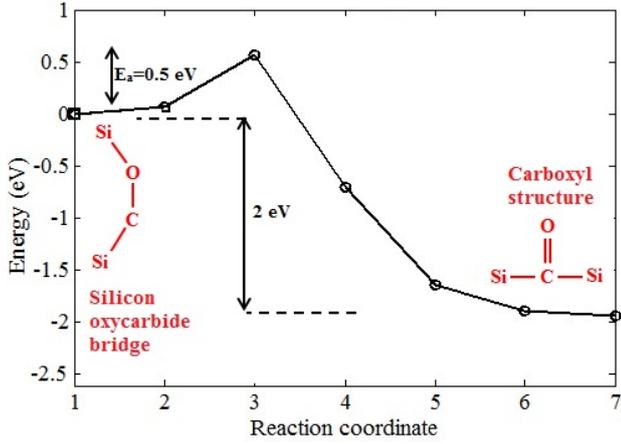


Figure 2: The minimum energy pathway showing the conversion of Si-O-C-Si structure to the carboxyl structure.

more stable [19]. We studied the conversion of Si-O-C-Si structure into the carboxyl configuration using DFT-based nudged elastic band simulations [20]. The minimum energy pathway for the process is given in Figure 2. The reaction is exothermic with an energy release of 2 eV, indicating the stability of the carboxyl configuration. Additionally, the conversion is kinetically favorable owing to relatively low activation barrier of 0.5 eV.

After establishing the thermodynamic stability of the single carbon interstitial in the carboxyl configuration, we proceed to calculate its formation energy in various charge states. We considered the neutral,  $\pm 1$  and  $\pm 2$  charge states for the defect. The formation energy was calculated as a function of Fermi level using equation (1). The stable charge states are shown in Figure 3. We noticed a +2 to neutral CTL (represented as +2/0) at 1.4 eV above the 4H-SiC VBM. This implies that for substrate Fermi levels below the (+2/0) CTL, the carboxyl defect is stable in its doubly positive state and acts as border hole traps [2]. For Fermi levels above the CTL, the holes are neutralized through electron tunneling.

The aforementioned behavior of carboxyl defects closely resembles that of  $E'$  center-related hole traps. Thus, carboxyl defects are designated as switching oxide hole traps in 4H-SiC/SiO<sub>2</sub> MOS system analogous to  $E'$  centers. We propose them to be an additional candidate defect responsible for bias-temperature threshold voltage instability in 4H-SiC MOSFETs.

We studied the structural transformations in the carboxyl defect during hole capture. They are given in Figure 4. In the neutral state (Figure 4(a)), the carbon-oxygen bond in the defect is inferred to be a double bond as its length corresponds to the bond length in ethylene. Upon the capture of the first hole, the Si atom is seen to move away from the carbon atom (Figure 4(b)). However, the structural rearrangement is not significant. The +1 charge state is an intermediate.

The capture of second hole is accompanied by remarkable structural rearrangement of the defect (Figure 4(c)). The carbon-oxygen bond length decreases and now corresponds to that of a triple bond. This suggests that the electron-rich carboxyl oxygen donates a lone pair to form an additional bond

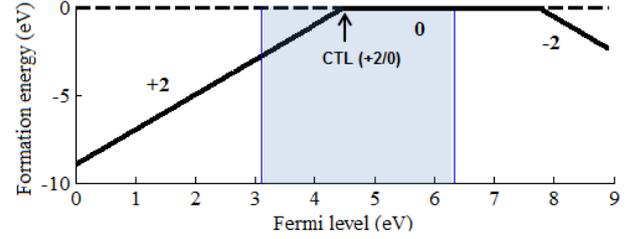


Figure 3: The formation energy of the carboxyl defect in its stable charge states (bold lines) as a function of Fermi level. The neutral defect is taken as the reference (dotted line). The shaded region represents the bandgap of 4H-SiC. A (+2/0) CTL is seen at 1.4 eV above 4H-SiC bandgap indicating the hole trapping behavior of carboxyl defect.

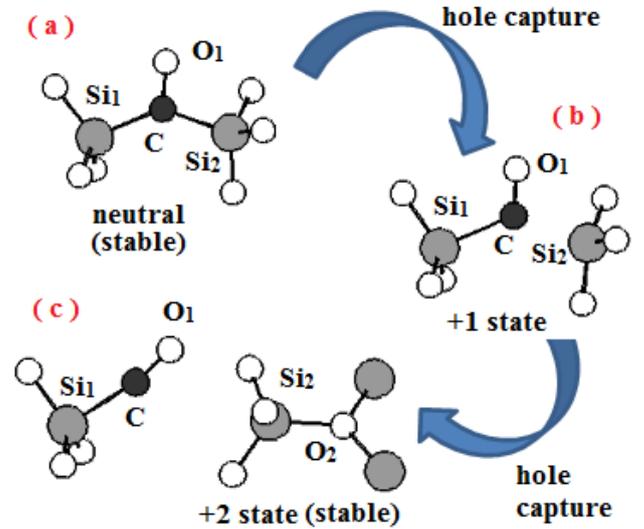


Figure 4: Structural transformation of the carboxyl defect during hole capture process. Puckering and backbonding of Si<sub>2</sub> is seen. The bond lengths are given in Table 1.

TABLE 1: Bond lengths and bond angles of the carboxyl defect in various charge states during hole capture (Figure 4).

Charge state	Bond angles (°)		Bond lengths (pm)	
0	Si <sub>1</sub> -C-O <sub>1</sub>	116	Si <sub>1</sub> -C	187
	Si <sub>1</sub> -C-Si <sub>2</sub>	135	Si <sub>2</sub> -C	186
	Si <sub>2</sub> -C-O <sub>1</sub>	109	O <sub>1</sub> -C	125
+1	Si <sub>1</sub> -C-O <sub>1</sub>	117	Si <sub>1</sub> -C	197
	--	--	O <sub>1</sub> -C	120
+2	Si <sub>1</sub> -C-O <sub>1</sub>	168	Si <sub>1</sub> -C	192
	--	--	O <sub>1</sub> -C	113
	--	--	Si <sub>2</sub> -O <sub>2</sub>	181

with the carbon upon double hole capture. Simultaneously, the silicon atom puckers and backbonds with a lattice oxygen behind it as in the case of positively charged E' center-related hole traps [8-11]. We propose that the increase in carbon-oxygen bond order and the puckering and backbonding of the Si atom provide stability for the carboxyl defect in its doubly positive charge state. In short, we identified significant resemblance in the structural and hole trapping properties of carboxyl defects and oxygen vacancies in SiO<sub>2</sub>.

#### IV. CONCLUSION

Identifying the hole trapping mechanisms on an atomic level in 4H-SiC MOSFET oxides can be vital for directing process revisions which will mitigate threshold voltage instability. Using DFT, we studied the hole trapping behavior of single carbon interstitials in their stable carboxyl defect configuration in silicon dioxide. Such defects are likely to exist in 4H-SiC MOS systems. Following the alignment of the bandgap between 4H-SiC and SiO<sub>2</sub>, we calculated the charge transition levels (CTL) of the carboxyl defect from its formation energies in different charge states. The occurrence of a +2 to neutral CTL in the bandgap of 4H-SiC suggested that the carboxyl defect is a likely candidate for border hole trap. They could be a possible contributor to bias-temperature threshold voltage instability in 4H-SiC MOSFETs. The stability-providing structural transformations in the carboxyl defect during hole capture were investigated. Phenomena like puckering and backbonding of the Si atom, as in the case of well-known E' center-related hole traps, were observed in the carboxyl defect.

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