Density Functional Theory Based Investigation of Defects and Passivation of 4H-Silicon Carbide/SiO_2 Interfaces

Shahrzad Salemi
Dept. of Reliability Engineering
UMD,
College Park, USA.
shahrzadsalemi@gmail.com

Neil Goldsman[a], Akin Akturk[a], Aivars Lelis[b]
[a] Dept. of Electrical and Computer Engineering
UMD
College Park, USA.
[b] U.S. Army Research Laboratory, 2800 Powder Mill Road,
Adelphi, USA

Abstract— **Density Functional Theory (DFT) has been used to investigate Silicon Carbide MOS structures. The energy levels of the most likely defects on both sides of the 4H-SiC(0001)/SiO2 MOS interface in the bandgap are studied. The defects are: carbon interstitials; a pair of carbons in both SiC and oxide sides of the interface; silicon vacancy in the SiC side; oxygen deficiencies in the oxide side; and dangling bonds at the interface. The effects of hydrogen, nitrogen, and phosphorus passivation have also been investigated. Density functional theory has been employed to calculate the (projected) density of states ((p)DOS), and the energy levels of the defects. The results of our calculations indicate that carbon interstitial and a pair of carbons in the SiC side, the oxygen deficiency at the interface, and silicon dangling bonds at the interface give rise to states near the conduction band. DFT calculations indicate that hydrogen, nitrogen, and phosphorus passivation can eliminate states both near the conduction, and valence bands, depending on the type, and place of the defects.**

Keywords: SiC/SiO_2 interface defects, DFT, (p)DOS, passivation

I. INTRODUCTION

Silicon Carbide based MOSFETs represent a transformational technology for power electronics. However, current power SiC MOSFETs have less than optimal performance due to the large concentration of defects at the SiC/SiO2 interface [1,2]. Although the physical origins of the high interface trap density (Dit) in SiC MOSFETs remain unclear, several defects have been identified and proposed in the literature. Deep levels of interface trap states have been attributed to carbon correlated defects [3,4], and silicon vacancy in SiC side of the interface [5]. Carbon interstitial could account for the interface defects below the conduction band [6]; carbon di-interstitial cluster $(Ci)_2$ in SiC was proposed to cause low channel mobility [7]. Oxide defects such as Si interstitial [8] and oxygen deficiency [9] have also been suggested to give rise to the near interface trap density (N_{it}).

Post oxidation annealing in different ambient environments is a technique to overcome the problem of high defect density at the interface [8-10]. The mechanism behind the passivation is not clear; nitrogen or phosphorous may passivate the dangling bonds at the interface or remove the carbon atoms (especially carbon interstitials) from the interface [12-16].

In this paper, we employed density functional theory to investigate energy levels of defects previously suggested in the literature, and the effects of passivation on them.

II. METHODOLOGY

Total and projected density of state ((p)DOS) curves are obtained using Density Functional Theory (DFT) calculations based on the Kohn-Sham Equation. The projected density of states is a way of partitioning the total density of states into respective components, such as contributions for atomic orbitals.

To perform DFT calculation, we first construct an abrupt supercell without defects, formed by putting 37-atom SiO_2 structure on a 72-atom 4H(0001)-SiC structure. The structure is called abrupt, because all silicon atoms at the interface are terminated with an oxygen atom, and there is no interlayer in between. Layers of vacuum have been placed on the top and bottom of the structure to isolate it. The dangling bonds at the top and bottom of the structures are terminated with hydrogen**.** The DFT solver Quantum Espresso [17] is used to perform relaxation, band-structure and (p)DOS calculations of the SiC/SiO_2 structures.

Determining the exact energy levels and retrieving the bandgap take place in two steps; first, the geometry optimization, and energy calculations were carried out within the normal PBE framework [18]. Next, the bandstructure is calculated, and the total and (p)DOS are then calculated and stored for further modification. Secondly, the hybrid functional [19] is used to re-calculate the energies for k points. Finally, the bandstructures are compared to that obtained with PBE, and the bandgap, and (projected) densities of states ((pDOS)) are modified, accordingly. The band gap obtained for the original abrupt structure of SiC/SiO2 is almost 3.2 eV. Once the methodology for the abrupt structure is developed, the same technique is applied to investigate the effect of defects, and their passivation. Fig. 1 shows the atomic configuration of abrupt structure.

III. THE EFFECTS OF DEFECTS AT THE INTERFACE AND SUBSEQUENT PASSIVATION

A. Silicon Vacancy in SiC Side, and its Passivation

ISBN 978-0-615-71756-2

The existence of silicon vacancy in a SiC MOSFET has been indicated experimentally by spin-dependent recombination (SDR) [5]. Our calculations show that the energy levels due to dangling bonds of four C atoms around the Si vacancy in SiC side are located at E_v+0.1, E_v+0.5, and E_v+0.7eV; each charge transfer (negative charge) shifts these energy levels by 0.2 to 0.3 eV toward the mid gap. A comparison between the DOS contributions of C atoms around the Si vacancy, and the total DOS of the whole structure shows that all levels near the valence band are caused by the carbon dangling bonds. The solid line in Fig. 2 shows the pDOS contributions of four C atoms around the silicon vacancy.

There is no evidence showing that how a Si vacancy could be passivated by the passivant atoms. First, we used H atoms to neutralize each C dangling bonds around the Si vacancy. The DOS contributions of those four C atoms together with four H atoms after H passivation are shown with dotted circle line in Fig. 2. As the result, if an H atom could passivate each C dangling bonds, then the density of states in the vicinity of the valence band will be reduced. However, due to the geometric configuration of four H passivants, passivation with H molecules may face a large energy barrier [20]. The same type of passivation is performed with one N atom located in the vicinity of the silicon vacancy. The (p)DOS after geometric relaxation shows that passivating the Si vacancy with one N atom (dotted triangle line in Fig. 2) introduces an energy level at E_v+1 eV. Here, the N atom binds with three dangling bonds of the C atoms, which results in those defect level elimination. The remaining level is the result of C dangling bond which is not paired properly.

B. Carbon Related Defects in SiC Side of the Interface and their Passivation

We investigated the electronic properties of C defects both in the form of C interstitial, and a pair of C atoms, in SiC side of the interface. For C interstitial, we performed DFT calculation in two locations of SiC substrate. While in one case, the peaks are at E_v+1eV, E_v+1.2eV, in the other occasion, the levels are at E_v+0.7, E_v+2.7, and E_v+3eV. The pDOS on the C interstitial is shown by a solid line in Fig. 3.

To study the mechanism behind C interstitial passivation, we performed several calculations with different passivants. Since the mechanism of nitridation is not clear, N passivation is studied in two ways; first we placed an N atom in the vicinity of the C interstitial. After relaxation, the DOS contributions of N together with the C atoms (dotted circle line in Fig. 3) are compared with the mere C interstitial before the passivation (the solid line in Fig. 3). As Fig. 3 illustrates, this type of N passivation eliminates all states made in the bandgap as the result of C interstitial. Here, the role of N passivation is pairing with the unsatisfied C bonds. To study the effect of N passivation via C removal from the interface, the C interstitial is replaced with an N atom, and the electronic properties are calculated after the geometric relaxation. The dotted triangle line in Fig. 3 shows the pDOS of N atom right after the replacement. As it is seen, the C removal eliminates the levels near the conduction band, while makes a peak at E_v+0.8eV. This energy level may be attributed to the lone pair of electron that nitrogen brings to the system. The same type of calculation is made with locating a P atom in the place of C interstitial. As the dotted square line in Fig.3 shows, the removal of the C interstitial with P is very similar to C removal by N. The pDOS of C interstitial together with an H atom attached to it (not shown in the figure) shows that while H passivates the states near the valence and conduction bands, it introduces new states in the midgap.

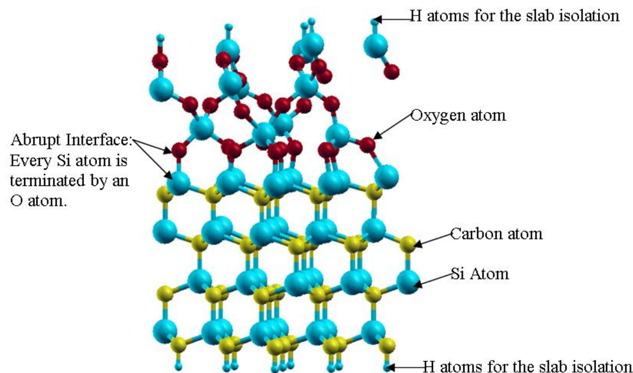

Figure 1: The atomic structure of the abrupt structure.

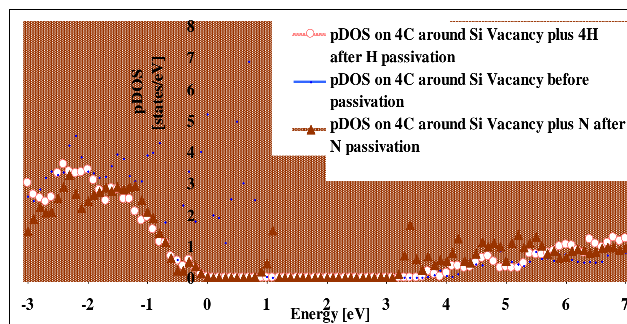

Figure 2: pDOS on 4C atoms around Si vacancy before passivation (solid line), pDOS on 4C+4H after H passivation (dotted circle line), and 4C+N after N passivation (dotted triangle line).

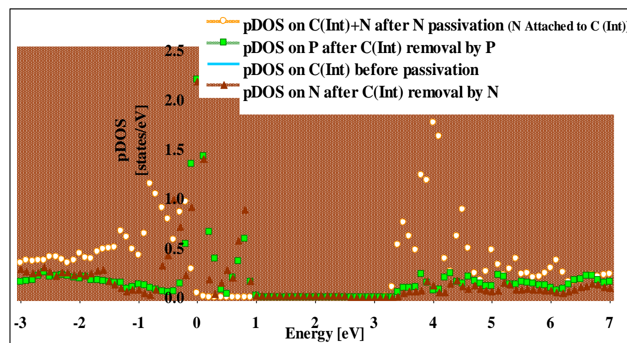

Figure 3: pDOS on C_{Int} and N after N passivation (N attached to C_{Int}, dotted circle line), pDOS on C_{Int} before passivation (solid line), pDOS on P after C_{Int} removal by P passivation (dotted square line), pDOS on N after C_{Int} removal by N (dotted triangle line) passivation.

A pair of C interstitials is another C related defect that may form during the oxidation. To investigate its possible states, they were situated in two locations in SiC near the interface. In both structures, each C of the pair bonds to one Si and one C in different neighborhoods, and result in a SiC-C-C-SiC form. The pair of carbon atoms makes sp^2 hybridizations with the average bond length of 1.39 A°. The difference between the structures comes from the relative position, and the local environment of the C pairs. While in one configuration, a pair of C atoms makes two levels in the band gap at E_v+0.4, and E_v+3.1eV, in the other configuration, it makes three levels in the band gap at E_v+0.4, E_v+1.6, and E_v+3.1eV (solid line in Fig. 4). To passivate the structure, the pair of C atoms is removed by a pair of N atoms; this replacement eliminates those levels near the conduction, and valence bands, but makes a sharp peak at E_v+1.1eV (the dotted triangle line in Fig. 4). In another attempt, an H atom is attached to each C atom of the pair. The DOS contributions of the pair of C atoms together with the H atoms attached to them (the dotted circle line in Fig. 4) show that this type of passivation introduce a sharp peak in the midgap, while it eliminates the other states.

C. Oxide Defects at the Interface and their Passivation

To study the C contamination in the oxide side of the interface, structures with both C interstitial, and a pair of C atoms have been made, and their impact on the band structure has been investigated via (p)DOS calculation. According to our calculation, C interstitial in the oxide side makes no energy level in the band gap; whereas a pair of C interstitials in the oxide makes a peak at E_v+0.1 eV.

Oxygen deficiency in the oxide is another type of defects in the oxide that suggested for degrading the mobility [9]. Here, first, the effect of O deficiency right at the interface is investigated. This type of defect leaves a Si atom with an unpaired electron perpendicular to the interface. The solid line in Fig. 5 shows the contribution of all the Si atoms at the interface together with the one that is not connected to the O. As Fig. 5 shows, this defect makes an energy level near the conduction band, at E_v+2.8 eV. Based on this DFT calculation, O deficiency located deeper of the oxide does not introduce any levels in the band gap. The N atom that is located at the vicinity of the damaged Si, binds with it after the relaxation process. As the result, the state caused by the O deficiency is eliminated from the bandgap. The dotted triangle line in Fig. 5 shows the DOS contributions of all the Si atoms at the surface after N passivation. N Passivation eliminated the O deficiency states.

To investigate the effect of three-fold-coordinated Si at the interface, a new kind of SiC/SiO_2 structure with three Si dangling bonds perpendicular to the interface is formed. Some literature gave the evidence of detecting Si-H after H passivation, which may show the creation of Si dangling bonds in the process of oxidation, and annealing [21-22]. Our calculations show that large number of Si dangling bonds at and perpendicular to the interface make broad states close to the conduction band. The process of passivation is studied by locating the passivant atoms near those three-fold coordinated Si atoms: one passivant atom for each damaged bond. The studied passivants are H, N, and P. In the case of H passivation, the Si-H bonds are not strong enough to push the states away from the gap into the conduction band (dotted circle line in Fig. 6), while N, and P passivate almost all those states. Fig. 6 shows the total DOS of the structure with dangling bonds perpendicular to the surface (solid line), and the same structure after nitrogen (dotted triangle line), and phosphorus (dotted circle line) passivation.

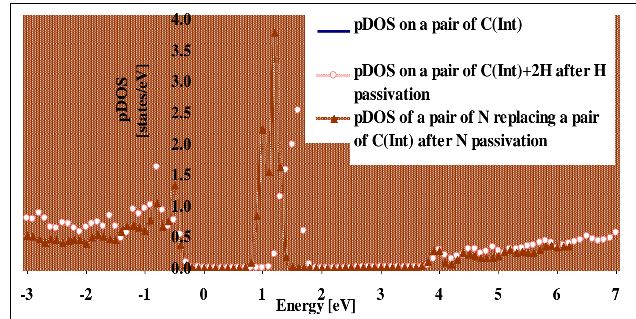

Figure 4: pDOS on a pair of C interstitial in SiC (solid line), pDOS on a pair of carbon interstitial together with two H atoms after H passivation (dotted circle line), and pDOS on a pair of N replacing a pair of C interstitial after N passivation (dotted triangle line).

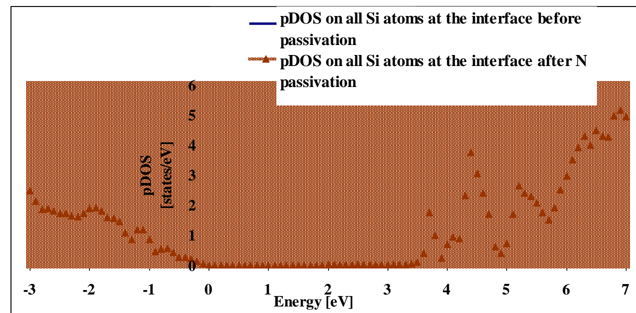

Figure 5: pDOS on all Si atoms with an oxygen deficiency at the interface (solid line), pDOS on all Si atoms after N passivation (dotted triangle line).

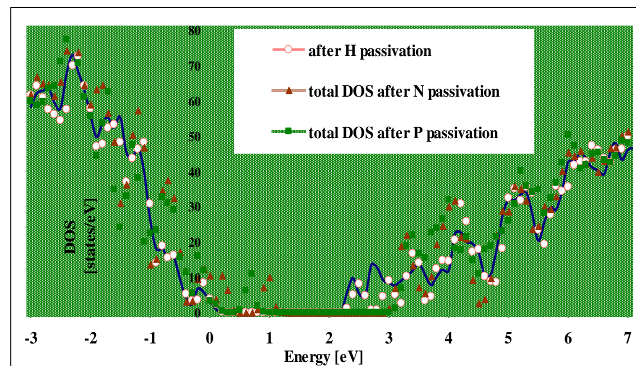

Figure 6: Total DOS of the structure with unpassivated three Si dangling bonds perpendicular to the interface (solid line), and after N Passivation (dotted triangle line), after P passivation (dotted circle line), and H passivation (open circle line).

IV. CONCLUSION

The energy levels of various defects in both sides of the SiC/SiO_2 MOS interface have been investigated by DFT-based calculations. Total and projected DOS have been used to illustrate the energy of the defects, and the effect of the defect passivation. According to our calculations, Si vacancy in SiC side of the structure gives rise to states near the valence band. Its mechanism of passivation (either by 4 H atoms, or an N atom) appears clear; the subsequent attachment of the passivant atoms forms bonding and antibonding states, located in the valence, and conduction bands, respectively. Therefore, after the passivation none of the unpaired electrons is electrically active. The calculations show that C interstitial and a pair of C atoms in SiC may introduce states in the bandgap, and near the conduction band, depending on their locations. One of the roles of passivations in this case may be the mere simple pairing, or passivating of unsatisfied bonds. Moreover, the DFT calculation shows that, even upon full geometric relaxation, both C defects increase the stress of the structure, which may introduce states in the gap. DFT simulation shows that the removal of the C atoms releases the stress, which may explain one of the mechanisms of N passivation through C removal. The resulting state near the valence band after nitridation is attributed to the lone pair of electron introduced to the system by a N atom. On the other side, O deficiency at the interface, and Si dangling bonds perpendicular to the interface give rise to levels near the conduction band. The mechanism of dangling bond passivation is the same as that explained in the case of Si vacancy. After nitridation, the structures with Si vacancy and O deficiency are compressed a little bit, which may show the formation of bonding among the dangling bonds, and passivants. In summary of the passivation, if the energy barrier allows the passivation, both H and N should passivate almost all the defects by neutralization, pairing, reconstruction and passivation of the unsatisfied bonds, on one hand, and stress removal (C removal by N), on the other hand. In some cases, the passivation introduces some levels near the valence band or in the mid gap. It should be mentioned that DFT calculation is very sensitive to the location of the defect. Moreover, the energy alignment is very critical to find the defect energy levels.

REFERENCES

[1] S. Potbhare, N. Goldsman, A. Lelis, J. McGarrity, F. B. McLean, D. Habersat, IEEE Transactions on Electron Devices, 55, 8, (2008).

[2] S. Potbhare, N. Goldsman, G. Pennington, A. Lelis, J. McGarrity; Journal of Applied Physics, 100, 044516, (2006).

[3] P. De´ak, J. M Knaup, T. Hornos, C. Thill, A. Gali, and T. Frauenheim; Phys. D: Appl. Phys. 40 6242–6253 (2007).

[4] Jan M. Knaup, P. Deak, T. Frauenheim.; Physical Review B 71, 235321 (2005).

[5] C. J. Cochrane, P. M. Lenahan, and A. J. Lelis; Appl. Phys. Lett. 100, 023509 (2012).

[6] F. Devynck, A. Pasqarello; Physica B 401–402 556–559 (2007).

[7] Xiao Shen,and Sokrates T. Pantelides; Applied Physics Letters 98, 053507 (2011).

[8] J. M. Knaup, P. Deak, T. Frauenheim, A. Gali, Z. Hajnal, W.J. Choyke; Physical Review B 72, 115323, (2005).

[9] V. V. Afanasev, M. Bassler, G. Pensl, M. Schulz; Physica. Status. solidi. (a) 162, 321 (1997).

[10] K. Fukuda, W. J. Cho, K. Arai, S. Suzuli, T. Tanaka; Appl. Phys. Lett. 77**,** 866 (2000).

[11] H. Li, S. Dimitrijev, H. B. Harrison, D. Sweatman; Appl. Phys. Lett. 70, 2028 (1997).

[12] S. Dimitrijev, H. Li, H. B. Harrison, D. Sweatman; IEEE Electron Device Letters, 18, 5, (1997).

[13] P.Jamet, S. Dimitrijev, P. Tanner; Journal of Applied Physics, 90, 5058-5063(2001).

[14] V. V. Afanas'ev, A. Stesmans, F. Ciobanu, G. Pensl, K.Y. Cheong, and S. Dimitrijev; Applied Physics Letters, 82, 4, (2003).

[15] D. Okamoto, H. Yano, K. Hirata, T. Hatayama, T. Fuyuki; IEEE Electron Device Letters, 31, 7, (2010).

[16] D. Okamoto H. Yano, K. Hirata, T. Hatayama, T. Fuyuki; Applied Physics Letters, 96, 203508, (2010).

[17] Paolo Giannozzi et al.;Condens. Matter 21, 395502 (2009).

[18] John P. Perdew, Kieron Burke, Matthias Ernzerhof; Physical Review Letters, 77, 18, 1996.

[19] A.D. Becke, Journal of chemical physics, 98, 1372, (1993).

[20] Sanwu Wang et al. al; Physical Review Letters, 98, 026101, (2007).

[21] H. Tsuchida, I. Kamata, and K. Izumi; Applied Physics Letters 70, 3072, (1997).

[22] H. Tsuchida, I. Kamata, and K. Izumi; Journal of Applied Physics, 85, 3569, (1999).