

## Atomic-Scale Mechanisms of Oxygen Precipitation and Thin-Film Oxidation of SiC

Massimiliano Di Ventra and Sokrates T. Pantelides

*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235*

(Received 5 May 1999)

We report first-principles calculations in terms of which we describe the atomic-scale mechanisms of the nucleation and growth of SiO<sub>2</sub> precipitates in cubic SiC. A three-oxygen cluster is found to be analogous to the well-known “thermal donor” in Si. Emission of a CO molecule converts it into an SiO<sub>2</sub>-like precipitate that can grow further. We propose that similar processes can account for the observed CO emission during SiC oxidation and the trapping of C atoms at the SiC-SiO<sub>2</sub> interface.

PACS numbers: 66.30.Jt, 71.55.-i, 81.65.Mq

Silicon has been the semiconductor of choice for microelectronics in part because of the excellent properties of its native oxide (SiO<sub>2</sub>) (insulating gate) and the Si-SiO<sub>2</sub> interface (low density of interface defects) that enable the fabrication of high-performance metal-oxide-semiconductor field-effect transistors (MOSFETs). In contrast, compound semiconductors, despite a host of desirable properties, do not have satisfactory native oxides. Silicon, however, falls short for applications that entail high temperatures and/or high voltages, as, for example, in switches for electrical power networks or engine sensors and controls. For such applications, a material with much larger energy gap is desirable to reduce intrinsic electron-hole generation. Many wide-gap semiconductors have all the right properties, but the lack of suitable native oxides or other dielectrics with good interface properties has so far frustrated the search.

Silicon carbide appears most promising, especially because its native oxide is none other than SiO<sub>2</sub>. The SiC-SiO<sub>2</sub> interface, however, does not have the desirable properties that characterize the Si-SiO<sub>2</sub> interface [1,2]. In particular, the electron mobility in SiC adjacent to the interface is roughly 2 orders of magnitude smaller than its bulk value [1,3–5]. The corresponding mobility reduction in Si is only a factor of 2. The reduction in mobility near the SiC-SiO<sub>2</sub> interface is clearly due to increased scattering, arising from a higher level of roughness and a higher density of interface defects, the origin and nature of which remain elusive. Understanding the atomistic origins of these effects offers the promise of controlling them in order to achieve satisfactory mobilities for SiC-based MOSFETs.

Oxygen in Si has been studied extensively both experimentally and theoretically [6–8]. It is present in Czochralski-grown material in large concentrations (10<sup>18</sup> cm<sup>-3</sup>) and is generally benign. In contrast to Si, very little is known about O in SiC. Apparently it is not incorporated in large quantities during growth. There is no experimental evidence regarding O as an isolated impurity, as clusters or precipitates. There is also very limited information regarding possible interface defects. There is indirect evidence that during thermal oxidation of SiC excess carbon in the form of clusters or graphitic

carbon precipitates remain at or near the interface [9]. The elimination of carbon complexes during thermal oxidation thus seems to be one of the limiting factors for obtaining good SiC-SiO<sub>2</sub> interfaces.

In this Letter, we report a set of first-principles calculations that explore the nucleation and growth of O precipitates in cubic SiC and then relate these results to thin-film oxidation of SiC. In particular, we study the behavior of a single O atom and subsequent clustering of O atoms. We find that, as in Si, electrically active O complexes form (thermal donors), but they are not very stable.

Instead, we find that O atoms can bind to the central C of the thermal-donor-like complex and then diffuse away as a CO molecule, leaving behind a perfectly bonded SiO<sub>2</sub> precipitate. The diffusion of CO molecules is a particularly interesting synergistic process with relatively small activation energy. CO molecules can, in fact, break up and release C in SiC. Even though the formation energy of C interstitials is very large (8–10 eV depending on the growth conditions [10]), the process of O precipitation releases C interstitials at very low energy cost (≈1.5 eV). On the basis of the above results and additional calculations of CO in SiO<sub>2</sub>, we propose a mechanism for the observed emission of CO during SiC oxidation and for the trapping of C atoms at the SiC-SiO<sub>2</sub> interface.

We performed calculations using the density functional theory and the local density approximation for exchange and correlation in the form given by Ceperley and Alder [11]. We used the ultrasoft pseudopotentials of Vanderbilt [12] for Si, C, and O. With these pseudopotentials we found a SiC lattice constant of 4.29 Å to be compared with the experimental value of 4.36 Å. We employed a plane wave basis set, an energy cutoff of 25 Ry, and supercells of 32 atoms. All structures were fully relaxed until the force on each atom was less than 0.25 eV/Å. All calculations were done with one special *k* point at (0.5, 0.5, 0.5) in the irreducible Brillouin zone [13]. Tests with a (333) Monkhorst-Pack grid [14] and supercells of 64 atoms indicate a numerical precision on the formation energies of about 0.2 eV.

*Single O atom.*—We start by describing the properties of one oxygen atom in cubic SiC for which there is

some prior work [15]. In agreement with that work, we find that an oxygen molecule is not stable in SiC because of the relatively small interstitial volume. Two distinct configurations for a single interstitial oxygen atom have essentially the same energy (within numerical error). One is shown in Fig. 1. It is similar to the bridge configuration in Si, but the bridge is now asymmetric: the Si-O distance is 1.59 Å whereas the C-O distance is only 1.42 Å. We note that the first Si-O distance is similar to the corresponding distance in bulk Si [7] while the second Si is nearer to the O in SiC than in bulk Si, thus giving a slight threefold coordination to the oxygen in this configuration. The second configuration consists of one O atom sandwiched between a Si atom and two carbons on the (110) plane (see Fig. 2). The energy necessary to bring the oxygen atom from one configuration to the other through the Si-C bond is about 0.5 eV. This energy derives essentially from the strain energy needed to stretch the Si-C distance by about 1 Å. We found higher energy configurations when the O atom displaces outside the (110) plane as is the case in bulk Si [7].

*Diffusion of single O atoms.*—The activation energy for an oxygen atom to migrate on the (110) plane from its most stable configuration between two Si atoms and one C to the equivalent position through the symmetry axis in the [001] direction (see Fig. 1) is only 0.7 eV, to be compared to the corresponding activation energy of about 2.5 eV in bulk Si [7]. When the oxygen atom moves through the symmetry axis defined by two C atoms and one Si atom the activation energy is 2.5 eV, i.e., comparable to the activation energy of O in bulk Si. The difference between the two above figures can be traced to the nearly threefold coordination of O in the configuration of Fig. 1 compared to the configuration of Fig. 2: the O atom pivoting in the (110) plane around a C (see Fig. 1) is always slightly bonded to one of the two Si atoms [16].

The two migration energies quoted above require a net activation energy for long-range diffusion of 2.5 eV. The O atom can, however, migrate with a lower activation energy from one (110) plane to another (110) plane. This

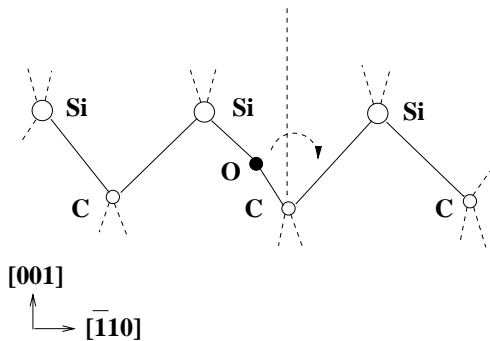


FIG. 1. Equilibrium configuration of an oxygen atom in cubic SiC between two Si atoms and one carbon atom. The atoms are all located in the (110) plane. The arrow indicates schematically the oxygen path during diffusion through the symmetry axis defined by two Si atoms and one C atom.

is done by passing from the configuration between two Si atoms and one C (Fig. 1) to the configuration between two C atoms and one Si (Fig. 2) pivoting around a Si atom by paying only 1.7 eV [17]. As in the previous case, the reason for this low activation energy is that the O along the migration path is always bound to at least two Si atoms. The single oxygen is, thus, very mobile in the SiC matrix only when it diffuses between one Si atom and two C atoms through different but adjacent (110) planes.

*Oxygen clustering.*—Two oxygen atoms bind in the (110) plane, with one of them surrounded by two Si atoms and one surrounded by two carbons (see Fig. 3). The binding energy is about 0.3 eV per oxygen atom. A lower binding of about 0.1 eV per oxygen atom has been found when both oxygen atoms are surrounded by two Si atoms, respectively. Adding a third O atom leads to the formation of a metastable complex reminiscent of the thermal donor in Si [6,7] formed by three oxygen atoms as depicted in Fig. 4. The three oxygens bind by about 0.5 eV and the defect induces a donor state in its symmetric configuration [8].

*Ejection of C as CO.*—The thermal-donor-like defect transforms to the stable defect of Fig. 5 through emission of one oxygen and the carbon atom in the middle (see Fig. 4). The remaining two oxygen atoms reside in the C split interstitial site in the [001] direction as shown in Fig. 5. The distance between the two oxygens is 2.06 Å and the structure is electrically inactive. The global process responsible for the emission of CO is exothermic with a reaction energy of about 0.7 eV. The extra energy (with respect to the thermal donor energy)  $\Delta E$  released during the process has been calculated as

$$\Delta E = E_{2O-C} + E_{CO} - 2E_{\text{bulk}}, \quad (1)$$

where  $E_{2O-C}$  is the total energy of the bulk SiC with two oxygens, one replacing a carbon (Fig. 5),  $E_{CO}$  is the total energy of the equilibrium configuration of a CO molecule in bulk SiC, and  $E_{\text{bulk}}$  is the total energy of the SiC bulk. All total energies have been calculated with supercells with the same number of Si atoms [18].

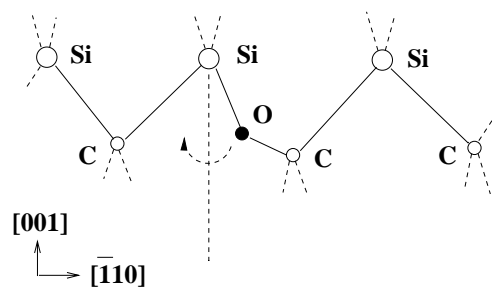


FIG. 2. Equilibrium configuration of an oxygen atom between two C atoms and one Si atom. The atoms are all located in the (110) plane. The arrow indicates schematically the oxygen path during diffusion through the symmetry axis defined by two C atoms and one Si atom. This configuration is comparable in energy (within the numerical error) to the one represented in Fig. 1.

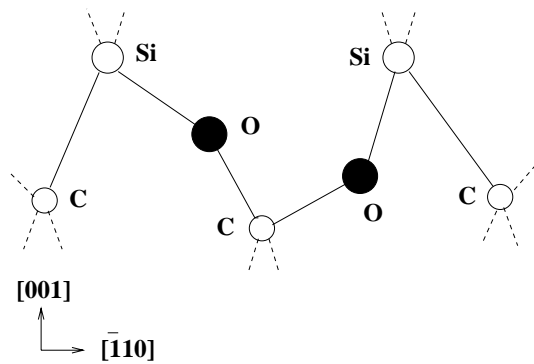


FIG. 3. Equilibrium configuration of two oxygen atoms in cubic SiC. All atoms are located in the (110) plane.

The equivalent emission of a Si atom and its replacement with two oxygen atoms has been found to be disfavored by about 8 eV per oxygen atom. The calculation proceeds in the same way as in Eq. (1) with the total energy  $E_{CO}$  replaced by the energy of the equilibrium Si split interstitial. The latter has been found to be oriented in the [001] direction as the corresponding C split interstitial.

Once formed, the CO molecule diffuses along the [110] tubular directions with the oxygen atom always moving between one Si and two C atoms in different but adjacent sites and the carbon atom “wagging” behind as a C interstitial. The barrier for the diffusion of the CO molecule has been estimated to be about  $1.6 \pm 0.3$  eV [17].

*Growth of amorphous SiO<sub>2</sub>.*—Once the small precipitate described above forms, continuation of the same process would generate a defect-free *amorphous* SiO<sub>2</sub> precipitate: a carbon atom in the (110) plane nearest neighbor of the emitted one would follow a similar path with the two oxygens replacing it in its split interstitial site oriented *perpendicular* to the [001] direction. No volumetric strain is present in this case compared to Si oxidation: the density of Si atoms in SiC is the *same* as that of SiO<sub>2</sub>, whereas in Si it is about double.

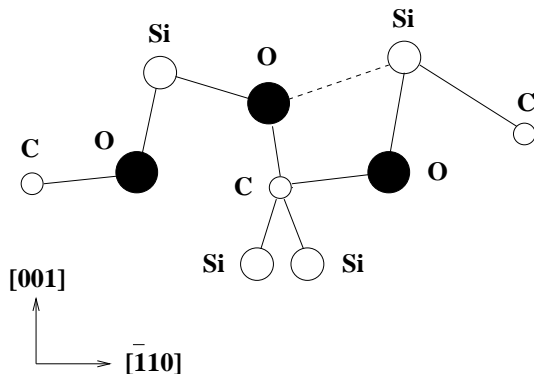


FIG. 4. Stable O<sub>3</sub> complex reminiscent of the thermal donor in Si. The central C atom bridges two Si atoms in the orthogonal plane.

*Thin-film oxidation.*—Direct calculations of the atomic-scale processes that occur at an advancing SiC-SiO<sub>2</sub> interface during thermal oxidation are not currently feasible. However, the above results are very useful to provide insight into those processes. Once a SiC-SiO<sub>2</sub> interface has formed, the interface advances by the arrival of new O atoms (typically made available by the diffusion of oxygen in SiO<sub>2</sub> [19]). Each such O atom is inserted in the next available Si-C bond at the interface. The process depicted in Figs. 4 and 5 is then a likely mechanism for the removal of C atoms in the form of CO. We computed the properties of CO in SiO<sub>2</sub> ( $\alpha$  quartz) [20] and found binding energies exceeding 4 eV at several sites. The larger binding energy (compared with CO in SiC) is due to the more open interstitial sites available in SiO<sub>2</sub>. The existence of several sites with comparable CO binding energies suggests a low migration energy. Thus, CO molecules ejected at the advancing SiC-SiO<sub>2</sub> interface during oxidation are more likely to diffuse into the SiO<sub>2</sub> and be released from the surface, as is indeed observed [1].

At a given temperature, however, a fraction of CO molecules can break either in the SiC bulk or at the advancing interface: the activation barrier for diffusion of CO in bulk SiC is comparable to the binding energy of the molecule. When a CO molecule breaks up at the interface, the oxygen binds as in Fig. 1 and contributes to further oxidation whereas the C bonds as a threefold split interstitial (see Fig. 6). Such carbon interstitials can either form further CO molecules with extra oxygen or nucleate carbon complexes. The latter complexes have been indeed observed at the interface or in the SiO<sub>2</sub> layer [9].

We conclude by examining the impact that the above insights into the oxidation process may have on the quest for a better SiC-SiO<sub>2</sub> interface. As we saw, one of the problems is the retention of C interstitials that result from the breakup of CO molecules in SiC or at the interface. Such C interstitials or C interstitial complexes can form in SiC or at the interface and may also be buried in the oxide as the interface advances. It would, therefore,

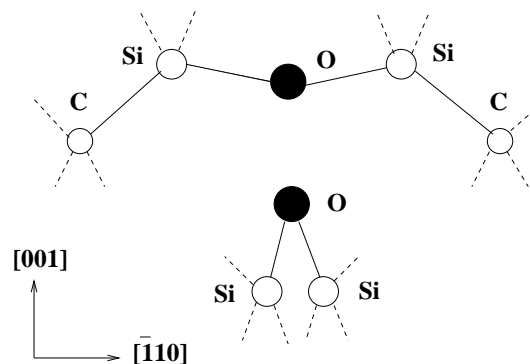


FIG. 2. The stable O<sub>2</sub> complex that is left behind after a CO molecule is emitted. The oxygens bridge two Si atoms in orthogonal planes.

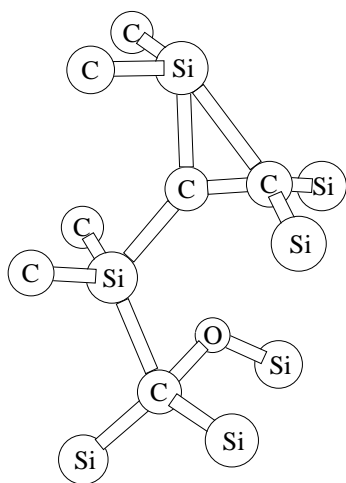


FIG. 6. Equilibrium configuration of an oxygen atom between two Si atoms and one C atom as in Fig. 1 and a nearby C split interstitial.

be desirable to have a mechanism to remove these C atoms. It has been demonstrated experimentally that pre-oxidation ultraviolet-ozone cleaning [9] or post-oxidation annealing [21] enhances the quality of the interface. It is very likely that newly supplied oxygen can combine with precipitated C atoms and diffuse out through the oxide, thus cleaning up both the interface and the oxide. We therefore propose that ozone and ultraviolet light *during* oxidation may provide the extra supply of O needed to suppress C precipitation. The C interstitials or small C precipitates in SiC, however, are likely to remain and affect carrier mobility in the MOSFET channels.

We acknowledge discussions with F. Reboredo and M. Ferconi. This work has been supported in part by a joint grant from the Defence Advanced Research Program Agency under Contract No. MDA972-98-1-0007, the Electrical Power Research Institute, under Contract No. W08069-05, by the NSF Grant No. DMR-98-03768, the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-96OR2264 with Lockheed Martin Energy Research Corporation, and by the William A. and Nancy F. McMinn Endowment at Vanderbilt University.

[1] J. Tan, M.K. Das, J.A. Cooper, Jr., and M.R. Melloch, *Appl. Phys. Lett.* **70**, 2280 (1997).

- [2] J.N. Shenoy, G.L. Chindalore, M.R. Melloch, J.A. Cooper, Jr., J.W. Palmour, and K.G. Irvine, *J. Electron. Mater.* **24**, 303 (1995).
- [3] J.W. Palmour, H.S. Kong, D.G. Waltz, J.A. Edmond, and C.H. Carter, Jr., in *Proceedings of the 1st International High Temperature Electronics Conference*, edited by P.D. King and F.V. Thome (Sandia National Laboratories, Albuquerque, New Mexico, 1991), p. 511.
- [4] S.T. Sheppard, M.R. Melloch, and J.A. Cooper, Jr., *IEEE Trans. Electron Devices* **41**, 1257 (1994).
- [5] W. Xie, J.A. Cooper, Jr., and M.R. Melloch, *IEEE Electron Device Lett.* **15**, 455 (1994).
- [6] J.W. Corbett, R.S. Mac Donald, and G.D. Watkins, *J. Phys. Chem. Solids* **25**, 873 (1964); E. Martinez, J. Plans, and F. Yndurain, *Phys. Rev. B* **36**, 8043 (1987); J.C. Mikkelsen, Jr., *Appl. Phys. Lett.* **40**, 336 (1982).
- [7] M. Ramamoorthy and S.T. Pantelides, *Phys. Rev. Lett.* **76**, 267 (1996); *Appl. Phys. Lett.* **75**, 115 (1999).
- [8] D.J. Chadi, *Phys. Rev. Lett.* **77**, 861 (1996).
- [9] V.V. Afanas'ev, A. Stesmans, M. Bassler, G. Pensl, M.J. Schulz, and C.I. Harris, *Appl. Phys. Lett.* **68**, 2141 (1996).
- [10] C. Wang, J. Bernholc, and R.F. Davis, *Phys. Rev. B* **38**, 12752 (1988).
- [11] D.M. Ceperley and B.J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- [12] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- [13] D.J. Chadi and M.L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
- [14] H.J. Monkhorst and J.P. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [15] M.A. Roberson, S.K. Estreicher, and C.H. Chu, *J. Phys. Condens. Matter* **5**, 8943 (1993); P. Deak, A. Gali, J. Miro, R. Guitierrez, A. Sieck, and T. Frauenheim, *Mater. Sci. Forum* **264-268**, 279 (1998).
- [16] Reference [15] reported larger numbers for the two activation energies. The difference is attributed primarily to the small clusters and the use of Hartree-Fock Hamiltonians.
- [17] This energy has been evaluated by constraining the O atom to move along a line that connects two (110) planes defined by the configurations of Figs. 1 and 2 pivoting around a common Si atom.
- [18] This procedure corresponds to an ideal calculation where the different defects are infinitely apart and the total number of atoms remains constant.
- [19] D.R. Hamann, *Phys. Rev. Lett.* **81**, 3447 (1998).
- [20] For the  $\alpha$ -quartz model we used a 36 atoms supercell and one  $k$ -point. The CO molecule has been placed in different configurations. The configuration in the main void along the  $c$  axis has been found to be the most stable.
- [21] L.A. Lipkin and J.W. Palmour, *J. Electron. Mater.* **25**, 909 (1996).