Atomic-Scale Dynamics of the Formation and Dissolution of Carbon Clusters in SiO_2

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Oxidation of SiC produces SiO_2 while CO is released. A "reoxidation" step at lower temperatures is, however, necessary to produce high-quality SiO_2. This step is believed to cleanse the oxide of residual C without further oxidation of the SiC substrate. We report first-principles calculations that describe the nucleation and growth of O-deficient C clusters in SiO_2 under oxidation conditions, fed by the production of CO at the advancing interface, and their gradual dissolution by the supply of O under reoxidation conditions. We predict that both CO and CO_2 are released during both steps.

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The most significant property of semiconductors is their ability to sustain heterogeneous n-type and p-type doping. This property, however, is eroded by high temperatures and high voltages that cause intrinsic excitation of electron-hole pairs across the band gap. As a result, semiconductors with significantly larger band gaps than silicon have been investigated as candidates for electronic devices suitable for high temperatures and high voltages. Silicon carbide is a particularly attractive candidate because its native oxide is SiO_2 which works so well as a dielectric in Si-based microelectronics. The presence of a third element, however, namely C, results in a wide range of phenomena that do not occur in the Si-SiO_2 system. In particular, oxidation of SiC entails the production of CO which effuses through the oxide [1,2]. Afanas'ev *et al.* have suggested that carbon clusters at and near the interface form during oxidation [3,4], but the structure and dynamics of these clusters has not been established. Lipkin and Palmour found that, after oxidation, a "reoxidation" step is necessary to produce high-quality oxides and SiC-SiO_2 interfaces [5,6]. During this step, oxygen is supplied as during oxidation, but the temperature is lowered so that no further oxidation takes place. In contrast, postoxidation heat treatment without the supply of O leads to an increase of charged defects in the oxide [7]. It is believed that the reoxidation step cleanses the interface and bulk SiO_2 of residual carbon [3]. Duscher *et al.* recently presented direct experimental evidence for the existence of carbon in as-grown samples and its removal after reoxidation [8].

The nucleation and growth of impurity clusters in semiconductors is a generic problem for which total-energy calculations are well suited to provide detailed information. In this Letter we present the results of extensive first-principles density-functional calculations that allow us to give a detailed account of the nucleation and growth of O-deficient carbon clusters in SiO_2 during oxidation conditions and their dissolution during reoxidation conditions. Basically, a CO molecule, generated at the advancing interface and diffusing through the oxide, can bind weakly to an O site in the SiO_2 network. A second CO molecule, however, can bind to the first and the new complex is very stable. Additional CO molecules can extend the cluster. *The process is helped by a passing CO that takes an O atom from the cluster and effuses as CO_2.* The net result is O-deficient clusters. During reoxidation at reduced temperatures, no further oxidation of the SiC substrate occurs so that no CO is produced. Instead, the supply of O atoms is used to "oxidize the C clusters." The process leads to the gradual dissolution of the C clusters through the formation of both CO and CO_2. These results account for the available data and lead to a prediction that can be tested, namely the effusion of CO_2 during both oxidation and reoxidation. Note in particular that, during oxidation, there is simultaneous reoxidation, accounting for the fact that the concentration of C clusters is not excessive and that substantial amounts of CO are, in fact, released. In contrast, during reoxidation, only dissolution of the clusters occurs.

The objective of the calculations was to determine one or more sequences of steps that lead to the formation of O-deficient C clusters by the aggregation of CO molecules and simultaneous release of O. Thus, sequences of stable configurations were determined. Determination of the barriers for the formation of these configurations is a laborious task because of the multitude of atoms that are involved. Test calculations were carried out in several cases by assuming specific pathways. Typical barriers were smaller than 1 eV. Since the calculations represent upper bounds and the relevant temperatures are above 1000 °C, the processes identified in this paper do, in fact, occur.

The calculations were performed within density functional theory, using the pseudopotential method and a plane wave basis set. The exchange-correlation effects were treated with local density approximation in the form of Ceperley and Alder [9]. We adopted the Vanderbilt ultrasoft pseudopotentials [10]. A plane wave energy cutoff of 40 Ry was used. All the structures were fully relaxed. Similar to earlier work [11], the calculations for the structure relaxation were conducted with one **k** point at (0.5, 0.5, 0.5), while the densities of states (DOS) were calculated with 14 inequivalent **k** points.

A supercell ($9.60811 \times 10.93795 \times 10.62372$ Å^3) containing 72 atoms, generated by Tu *et al.* [12] with a

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Monte Carlo bond-switching method [13], was used to model the amorphous SiO_2. This model corresponds to a density of 2.15 g/cm^3 for the amorphous SiO_2, close to the experimental value of 2.20 g/cm^3 at the standard pressure. The calculated DOS was found to be in good agreement with the experimental photoemission spectra [14] and previous first-principles calculations [15,16], which used different structure models to simulate the amorphous SiO_2. The SiO_2 band gap was calculated to be 5.6 eV, the same as in earlier calculations [16].

CO molecules in a perfect SiO_2 network.—We assume that the advancing interface during oxidation emits CO molecules, as found in Refs. [1] and [2], and explore the possible reactions that CO molecules can undergo in the SiO_2 matrix. A perfectly bonded network without any defects is first considered. We find that a single CO molecule can bind to a network O atom. The bound configuration (hereafter [CO]) is shown in Fig. 1(a). There is a Si-C-O-Si bridge with the extra O atom attached to the C atom so that the integrity of the CO molecule is preserved. The bond length of the CO molecule is now 1.21 Å, 0.07 Å longer than the bond length of a free CO molecule at an open interstitial site in SiO_2 (hereafter $CO^{(free)}$). While this C-O bond is more likely a double bond, another C-O bond between the carbon and the original bulk oxygen atom appears to be a single bond (with a bond length of 1.36 Å). The total energy of the [CO] configuration is 0.23 eV lower than that of the $CO^{(free)}$. This is a rather small binding energy, suggesting that both structures can exist. The energy cost for the release of a CO molecule from SiO_2 is calculated to be 0.18 eV. Hence, CO molecules at the open interstitial sites can easily escape from SiO_2, as found by experiments [1].

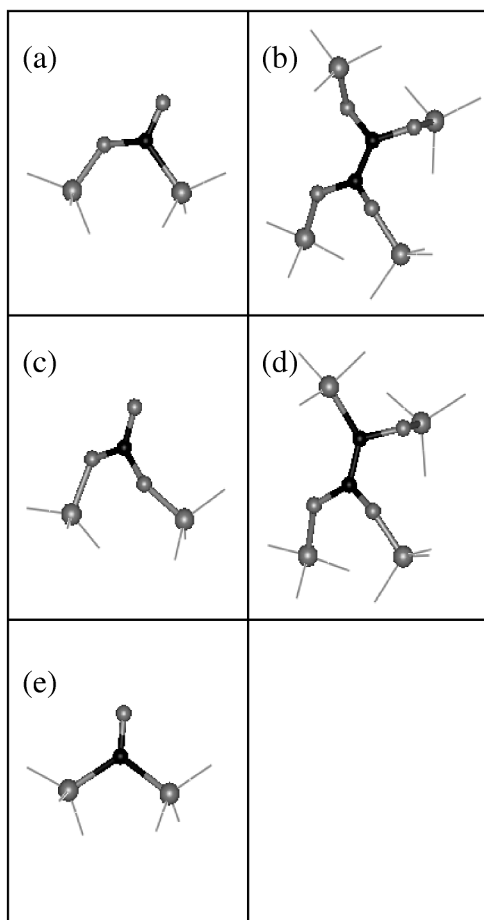


FIG. 1. Schematics of several species containing one and two C atoms: (a) [CO]; (b) $[C_2O_2]$; (c) $[CO_2]$; (d) $[C_2O]$; and (e) [C] configurations. The dark circles denote C atoms. The larger and smaller grey circles are for Si and O atoms, respectively.

The binding energy of a CO molecule in the [CO] configuration, though small, is sufficient to result in a substantial fraction of CO molecules being bound at any given time [about 9 out of 10, as estimated from $\exp(-\Delta E/kT)$ with $\Delta E = 0.23$ eV and $kT = 0.1$ eV]. When a diffusing CO molecule encounters a [CO], it can be attached to form a two-molecule complex, $[C_2O_2]$, via the reaction

$$[CO] + CO^{(free)} \rightarrow [C_2O_2]. \quad (1)$$

The energy gain is 1.6 eV, which suggests strong binding. The $[C_2O_2]$ configuration is shown in Fig. 1(b). The complex forms a bridge across a network ring with the two halves of the bridge being on different planes.

When a third CO molecule gets near the $[C_2O_2]$ structure, instead of binding, it takes one of the oxygen atoms from the cluster and forms either a CO_2 molecule at an open interstitial site ($CO_2^{(free)}$ configuration) or a CO_2-like bonded configuration ($[CO_2]$, shown in Fig. 1(c)). The $[CO_2]$ configuration has essentially the same total energy as $CO_2^{(free)}$ (only 0.04 eV lower, which is within the uncertainty of the calculations). The remaining bonded configuration ($[C_2O]$) contains two carbon and one additional oxygen atoms, as shown in Fig. 1(d). This structure is similar to the $[C_2O_2]$ configuration except for having one less oxygen atom. The above process responsible for the formation of CO_2 is exothermic with an energy gain of 0.8 eV. Such a reaction can be expressed as

$$[C_2O_2] + CO^{(free)} \rightarrow [C_2O] + CO_2^{(free)} + 0.8 \text{ eV}. \quad (2)$$

We conclude that oxidation of SiC results in the release of both CO and CO_2. There are no experimental reports about CO_2 being released. Special effort would be needed to detect it because it is probably present in the chamber already.

As more CO molecules arrive, the $[C_2O]$ complex undergoes additional reactions. First, a CO molecule binds to the $[C_2O]$ structure which results in the formation of a $[C_3O_2]$ configuration, shown in Fig. 2(a). The complex contains one C-O double bond and two C-O single bonds with bond lengths of 1.15 and 1.31 Å, respectively. The bond lengths of the two C-C bonds are 1.31 and 1.37 Å. The energy gain is again very large, 2.0 eV.

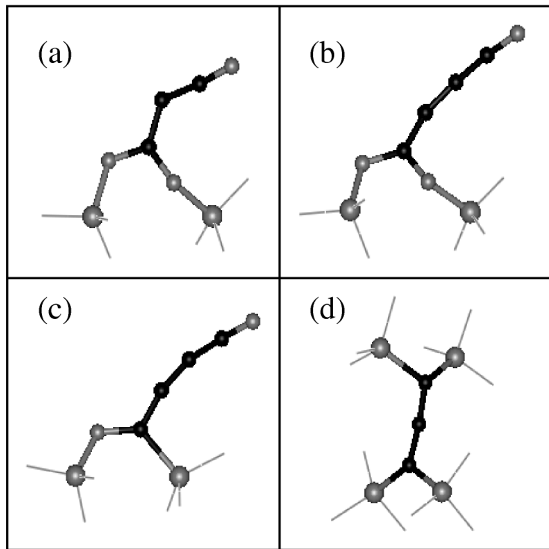
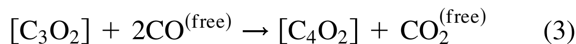


FIG. 2. The minimum-energy structures corresponding to the configurations containing clusters with three and four C atoms in SiO_2: (a) $[C_3O_2]$; (b) $[C_4O_2]$; (c) $[C_4O]$; and (d) $[C_3O_{-2}]$.

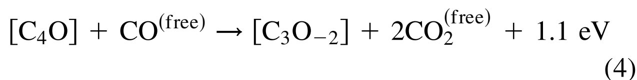
The $[C_3O_2]$ configuration is a very stable defect. The arrival of yet another CO molecule does not lead to further growth. Though another CO can be attached to $[C_3O_2]$, there is an energy cost of 0.54 eV, which makes the reaction highly unlikely. Similarly, a passing CO molecule cannot take away an O atom from $[C_3O_2]$ and become CO_2. The process again involves energy cost (0.22 eV). If, however, by coincidence, two CO molecules happen to arrive at a $[C_3O_2]$ complex at the same time (a rare event), the reaction



$$[C_3O_2] + 2CO^{(free)} \rightarrow [C_4O_2] + CO_2^{(free)} \quad (3)$$

can occur with an energy gain of 1.3 eV. The resulting $[C_4O_2]$ complex is shown in Fig. 2(b). Once it forms, this complex can again lose an O atom to a passing CO, becoming a $[C_4O]$ complex, shown in Fig. 2(c). The gain in energy is 1.4 eV.

The $[C_4O]$ is unstable, however. Upon the arrival of a CO molecule, the following reaction occurs:



$$[C_4O] + CO^{(free)} \rightarrow [C_3O_{-2}] + 2CO_2^{(free)} + 1.1 \text{ eV} \quad (4)$$

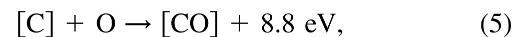
with an energy gain of 1.1 eV. Two CO_2 molecules are released and the residual defect $[C_3O_{-2}]$ consists of three C atoms in the space of two O vacancies [Fig. 2(d)]. This last defect is stable against the arrival of one or two CO molecules.

In summary, we have shown that *through a process of complex reactions CO molecules passing through SiO_2 will form oxygen-deficient carbon complexes through the emission of CO_2 molecules*. The most stable defects are $[C_3O_2]$ and $[C_3O_{-2}]$. The formation of the latter, however, necessitates an intermediate step that requires the simultaneous arrival of two CO molecules.

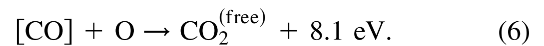
CO molecules in SiO_2 with O vacancies.—When oxygen vacancies exist in bulk SiO_2, a CO molecule fills a vacancy by forming two Si-C bonds. The resulting configuration is shown in Fig. 1(e) (thereafter as [C]). The C-O bond is a double bond with a bond length of 1.23 Å. The binding energy of the CO molecule in the [C] structure (relative to the molecule in the $CO^{(free)}$ structure) is 2.2 eV. However, this structure is not stable. When an additional CO molecule arrives, the [C] structure transforms into the $[C_2O]$ structure [Fig. 1(d)]. The energy gain is 3.0 eV.

Reoxidation.—We now examine the reactions that can occur during reoxidation when no new CO molecules are produced but oxygen is available.

First, defects containing a single carbon atom such as [C] and [CO] can be removed in the form of CO_2 molecules through the following processes:

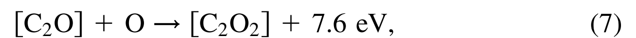


$$[C] + O \rightarrow [CO] + 8.8 \text{ eV}, \quad (5)$$

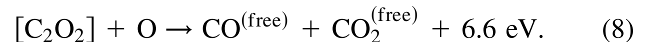


$$[CO] + O \rightarrow CO_2^{(free)} + 8.1 \text{ eV}. \quad (6)$$

Second, clusters of two carbon atoms, i.e., those in the $[C_2O]$ and $[C_2O_2]$ configurations, can be dissociated and released in the form of CO and CO_2 molecules as follows:

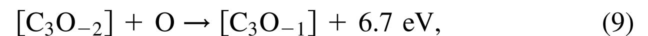


$$[C_2O] + O \rightarrow [C_2O_2] + 7.6 \text{ eV}, \quad (7)$$

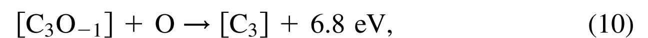


$$[C_2O_2] + O \rightarrow CO^{(free)} + CO_2^{(free)} + 6.6 \text{ eV}. \quad (8)$$

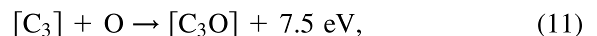
Similarly, the three-carbon clusters will be removed through the following reactions:



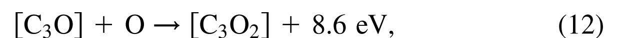
$$[C_3O_{-2}] + O \rightarrow [C_3O_{-1}] + 6.7 \text{ eV}, \quad (9)$$



$$[C_3O_{-1}] + O \rightarrow [C_3] + 6.8 \text{ eV}, \quad (10)$$



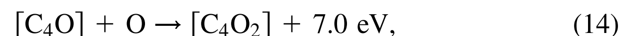
$$[C_3] + O \rightarrow [C_3O] + 7.5 \text{ eV}, \quad (11)$$



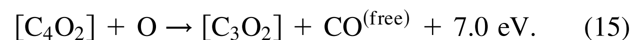
$$[C_3O] + O \rightarrow [C_3O_2] + 8.6 \text{ eV}, \quad (12)$$

$$[C_3O_2] + O \rightarrow [C_2O] + CO_2^{(free)} + 6.3 \text{ eV}. \quad (13)$$

Finally, the clusters with four carbon atoms will lose one carbon atom and reduce to three-carbon clusters as follows:



$$[C_4O] + O \rightarrow [C_4O_2] + 7.0 \text{ eV}, \quad (14)$$



$$[C_4O_2] + O \rightarrow [C_3O_2] + CO^{(free)} + 7.0 \text{ eV}. \quad (15)$$

The C_3 clusters will then be removed with further reoxidation, as shown in Eqs. (13), (7), and (8).

In summary, we have shown that the CO molecules that are generated during oxidation of SiC diffuse through the network and can form a large variety of complexes containing one, two, three, and four C atoms. One key result is that these defects are oxygen deficient, as O atoms are removed by combining with CO molecules forming CO_2 molecules. This phenomenon provides a natural explanation of the reoxidation step since we also showed that a supply of oxygen can dissolve the C clusters.

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