Energetics of nitrogen incorporation reaction in SiO$_2$

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We study using first-principles calculations the energetics, structural and electronic properties of nitrogen incorporation in SiO$_2$. We consider NO, NH, N$_2$ and atomic N as the nitriding species interacting with a Si-Si bond of an otherwise perfect SiO$_2$ network in order to simulate the nitrogen incorporation near Si/SiO$_2$ interface regions. We find that all the species react with the Si-Si bond forming bridge structures with the Si atoms without dissociating, where NH and atomic N form the most stable structures. Concerning the electronic properties, our results show that incorporated NH is the only structure which does not introduce trapping center at the interface. The structures involving NO and atomic N are acceptors, whereas that involving N$_2$ may be either a donor or an acceptor. The hydrogen passivation of the electrically active centers is also discussed.

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Oxynitride films have been extensively studied in the past years since they improve the reliability of metal-oxide-semiconductors gate insulators. The main benefits of incorporating nitrogen into ultrathin SiO$_2$ films are the reduction of gate leakage currents and the resistance to boron penetration. The growth of ultrathin oxynitride films strongly depends on the reactant species (e.g., N$_2$O, NO, NH$_3$, N$_2$) and the technique used. Nitrogen can be incorporated into SiO$_2$ using either thermal oxidation and annealing or chemical and physical deposition methods. Thermal nitridation of SiO$_2$ in NO and N$_2$O generally results in a relatively low N concentration at the near-interface (Si/SiO$_2$) region. The N incorporation is commonly associated to the reaction of NO molecule with Si-Si bonds at the interface, after diffusing through the oxide. On the other hand, N incorporation via annealing in NH$_3$ is responsible for a relatively high N concentrations into the films. This method provides both near-interface and near-surface nitridation, suggesting different nitriding species derived from NH$_3$. More recently, higher N concentrations and controlled distributions have been attained by plasma assisted methods, typically using ions and radicals derived from N$_2$ and NH$_3$ as nitrogen sources. Although the control of both the density and the distribution of nitrogen into SiO$_2$ have been achieved at few-layer level, less is known about the early stages of the N-incorporation reactions at atomic level.

In this work the energetics and structural properties of near-interface nitrogen incorporation are studied from first-principles total-energy calculations. We have considered the N$_2$, NH and NO molecules as well as atomic N as the precursor species, reacting with the Si-Si bonds in SiO$_2$ in order to simulate suboxide (Si$^{3+}$) or near-interface N incorporation. Our calculations were performed in the framework of the density functional theory, using a basis set of numerical atomic orbitals as implemented in the SIESTA code. We have used a split-valence double-$\zeta$ basis set plus the polarization functions as well as standard norm-conserving pseudopotentials.

For the exchange-correlation potential we adopt the generalized gradient approximation. We used a 72-atom $\alpha$-quartz supercell and the $\Gamma$ point for the Brillouin zone sampling. The positions of all the atoms in the supercell were relaxed until all the force components were smaller than 0.05 eV/Å. We also consider neutral and singly charged species, where the neutrality of the cell is always maintained by introducing a compensating background charge. Spin-polarization effects, which are important for the correct description of atomic and molecular reaction processes in SiO$_2$, are included throughout the calculation.

We study the chemical reactions occurring when the nitriding species NO, NH, N$_2$ and atomic N approach the Si-Si bond in the otherwise perfect SiO$_2$ network. The Si-Si bond in SiO$_2$ is formed when an O atom is removed from the network characterizing an oxygen vacancy. This local geometry is close related to those found near the Si/SiO$_2$ interface. Hereafter, the incorporated species will be called [NO], [N$_2$], [NH] and [N]. For these reactions we only consider neutral species in their ground-state spin configurations. Initially, we study the structural properties of the nitriding species inside the largest interstitial site of a perfect SiO$_2$, exploring possible reactions that they may undergo with the network. Our results show that none of the species considered in this work react with the network, remaining at the interstitial sites. This suggests that neutral species would be diffusing species in SiO$_2$. However, when we put the species close to the Si-Si bond, they are quickly incorporated into the network forming the stable structures shown in Fig. 1. We now describe in details our results for each incorporated specie.

The NO molecule shows two stable structures after reacting with the Si-Si bond. In the lowest-energy structure [NO], the N atom is threefold coordinated bonding with two Si atom, keeping the bond with the O atom, as shown in Fig. 1(a). Here, the Si-N and N-O bond lengths are 1.78 and 1.32 Å, respectively. The binding energy of NO, calculated as the difference in energy between the
interstitial and incorporated configurations, is found to be 3.8 eV. Whereas, the binding energy of the O atom in the [NO] structure is 4.2 eV. Thus, it would be easier to remove the entire NO molecules than the single O atom. Fig. 1(b) shows the second stable geometry [NO]’. Here, NO is incorporated into the Si-Si bond forming a structure similar to the peroxyl bridge of oxygens [9, 10]. This structure is 0.65 eV higher in energy than the most stable one. The Si-N, N-O, and O-Si bond lengths are 1.77, 1.40, and 1.71 Å, respectively. The energy barrier for the NO molecule to change from the metastable structure [NO]’ to the most stable one [NO] is estimated to be 0.6 eV. The lowest-energy [NO] structure is an electrically active center, exhibiting a half-occupied energy level at 1.9 eV above the density-functional valence-band maximum (VBM) of α-quartz. The [NO] dangling bond may be passivated by capturing an H atom as recently suggested [11]. We find that the reaction involving the capture of an H atom from an interstitial H2 molecule is endothermic with an energy cost of 0.78 eV. However, the [NO] passivation may occur by the capture of an interstitial H atom. In this case, the reaction is highly exothermic with an energy gain of 4.1 eV.

Figure 1(c) shows the equilibrium geometry for the NH after reacting with the Si-Si bond in SiO2. We see that the N atom binds to both Si atoms forming the Si-N-Si structure, keeping the bond with the H atom. The Si-N and N-H bond lengths are 1.72 and 1.03 Å, respectively. The binding energy of the NH molecule is found to be 6.8 eV which indicates that this radical would be one of the most stable species for interface nitridation. We also found that the H atom is strongly bound to the N atom in [NH], having a binding energy of 4.6 eV.

The equilibrium geometry for the incorporated N2 is shown in Fig. 1(d). The N2 binding energy is found to be 1.2 eV, relatively small as compared with the other nitriding species. This suggests that N2 may be easily removed from the interface escaping from the SiO2 film. Additionally, the [N2] structure introduces an empty midgap level at 2.7 eV above the VBM of α-quartz.

For the N atom we also find a very stable structure after reacting with the Si-Si bond [Fig. 1(f)]. The binding energy of the N atom is found to be 6.5 eV. [N] shows a half-occupied energy level at 0.2 eV above the VBM of α-quartz. This dangling bond may be passivated by capturing an H atom from an interstitial H2 molecule which dissociates after the contact with the [N] structure. We find that this reaction is exothermic with an energy gain of 0.82 eV, where the resulting equilibrium structure is similar to the [NH] structure [see Fig. 1(c)] plus an interstitial H atom. If the [N] passivation occurs by capturing an interstitial H atom, the reaction is highly exothermic with an energy gain of 5.0 eV.

The relative stability of incorporated nitriding species in SiO2 in thermodynamic equilibrium is obtained by comparing their formation energies. As we are simulating the nitrogen incorporation at suboxide regions, i.e., close to the Si/SiO2 interface, we consider the three most relevant charge states in order to address possible charge transfer between the incorporated species and the doped Si substrate. Therefore, the formation energies (E_f) are calculated as a function of the chemical potential of the nitriding species (µ_X) and the electron chemical potential (µ_e) as

\[ E_f([X]^q, \mu_e) = E_t([X]^q) - E_t(SiO_2) + \mu_O - \mu_X + q \mu_e, \]

where \( E_t([X]^q) \) is the total energy of the incorporated specie X in the charge state q, \( E_t(SiO_2) \) is the total energy of perfect α-quartz and \( \mu_O \) the chemical potential of oxygen. \( \mu_X \) and \( \mu_O \) are fixed at the values of their stable gas phases. Our results for the formation energies of [NO], [NH], [N2], and [N] are shown in Fig. 2. In the figure, the symbols indicate the transition states or the thermodynamics levels, whereas the slopes of the lines (positive, zero and negative) indicate the corresponding charge states. Following previous calculations [11, 12], the transition states were aligned with respect to the experimental band-gap edges of α-quartz, by matching the cal-
culated (+/−) transition state of the interstitial H atom in α-quartz with its measured value of 0.2 eV above the Si midgap[13, 14], and by using the measured valence-band offset of the Si/SiO₂ interface of 4.3 eV[12]. In Fig. 2 we also depict the experimental band gap of bulk Si where the Si midgap position is chosen to be the zero energy of μₑ.

As we are computing the energetics of the incorporated species close to the Si/SiO₂ interface, the variation of μₑ must be considered only in the energy range of bulk Si. Fig. 2 shows that negatively charged [NO] is the most stable structure at the interface. The (0/−) transition state is found at 4.3 eV above the experimental SiO₂ valence-band maximum (εᵥSiO₂). This suggests that [NO] might capture an electron from the Si substrate characterizing an acceptor center at the Si/SiO₂ interface. The same behavior is found for [N] which might be another acceptor center at the interface. For the case of [N₂] we find both donor and acceptor character, where the (+/0) and (0/−) transition states are localized at εᵥSiO₂ + 4.5 and εᵥSiO₂ + 4.8 eV, respectively. The formation energy of [N₂] is approximately 2 eV higher in energy than [NO], suggesting that [N₂] would be the less stable structure at the interface. Finally, [NH] is found to be the only electrically inactive structure at the interface, having a relatively low formation energy. This suggests that the NH molecule would be the best choice among the considered nitriding species for interface nitridation.

In summary, we find that NH would be the most stable species for interface nitridation having a binding energy as high as 6.8 eV, where the N atom is typically threefold coordinated. NO would also be a very stable species at the interface having a binding energy of 3.8 eV. Our results agree well with the finding that NO diffuses through the oxide and reacts at the near-interface region where N is bound to two Si atoms and one O atom[1]. However, NO does not dissociate spontaneously after reacting with a Si-Si bond. N₂ may also be incorporated at the interface, forming a stable structure with the Si-Si bond. However, it has a relatively low binding energy of 1.2 eV. This suggests that N₂ may be easily removed from the interface. Atomic N does not react spontaneously with the SiO₂ network as commonly believed, suggesting that it would be a diffusing species in SiO₂. The binding energy of the incorporated N is 6.5 eV, resulting in a very stable species for interface nitridation. Concerning the electrical properties, our results show that NH is the only species that does not introduce a trapping center after being incorporated at the Si-Si bond. [NO] and [N] are acceptors whereas [N₂] may be a donor or an acceptor, depending on the Fermi level position. However, [N] and [NO] may be passivated by subsequent hydrogenation processes.

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