Impact of carbon and nitrogen impurities in high-\(\kappa\) dielectrics on metal-oxide-semiconductor devices

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We investigate the electronic structure of carbon and nitrogen impurities, which are commonly incorporated during atomic-layer deposition of high-\(\kappa\) oxides such as \(\text{Al}_2\text{O}_3\) and \(\text{HfO}_2\). The impact on metal-oxide-semiconductor devices is assessed by examining formation energies, transition levels, and band alignment between the oxide and semiconductors such as \(\text{GaN}\), \(\text{Si}\), and \(\text{III-As}\). Carbon introduces charge-state transition levels near the semiconductor conduction-band edges, resulting in border traps and/or leakage current. Nitrogen acts as a source of negative fixed charge but may also be effective in alleviating the problem of carrier traps associated with native defects.

The use of high-\(\kappa\) gate oxides such as \(\text{HfO}_2\) in silicon metal-oxide-semiconductor (MOS) devices has attracted considerable attention due to requirements in device scaling. Concurrently, oxide/III-V MOS structures have been intensively investigated, with the potential of adding flexibility to device design and functionalities in MOS electronics. The oxides are typically deposited by atomic layer deposition (ALD), and promising results have been achieved with \(\text{Al}_2\text{O}_3/\text{III-V}\), exhibiting relatively low interface-state densities in MOS structures.

The carrier traps and fixed charges that are observed are commonly attributed to intrinsic point defects in the oxide dielectrics, located at or near the interface. However, there is solid evidence for the presence of significant concentrations of impurities in oxides grown by ALD, and the impact of those impurities on electronic performance has received far less attention to date. The use of metal-organic precursors and low-temperature growth conditions often results in incomplete decomposition of precursors and residual concentrations of carbon or nitrogen impurities in the oxide layer. Incorporation of up to 0.2 at. % of carbon and ~5 at. % of nitrogen has been found in \(\text{Al}_2\text{O}_3\). In \(\text{HfO}_2\), concentrations of \(\sim 10^{21}\) cm\(^{-3}\) for C and \(\sim 10^{20}\) cm\(^{-3}\) for N have been reported.

Carbon has been suggested as a cause of leakage current in \(\text{HfO}_2/\text{Si}\) MOS structures, since leakage current correlates with carbon concentration in the \(\text{HfO}_2\) layer. Nitrogen, on the other hand, has been found to lower the density of interface states and improve dielectric strength. The role of impurities in the electrical properties of \(\text{Al}_2\text{O}_3\) has not been well explored.

In this letter, we report first-principles calculations based on density functional theory for carbon and nitrogen impurities in \(\text{HfO}_2\) and \(\text{Al}_2\text{O}_3\). The few computational studies that were performed in the past were either incomplete or suffered from shortcomings in the methodology. Sankaran et al. reported \(G_0W_0\) results for electronic states of C and N in \(\gamma\)-\(\text{Al}_2\text{O}_3\) but limited their investigation to the neutral charge state. For \(\text{HfO}_2\), the prior calculations for C (Ref. 12) and for N (Refs. 17 and 18) all employed traditional density functionals such as the local density approximation (LDA) or generalized gradient approximation (GGA), which suffer from a significant underestimation of the band gap, thus rendering it difficult to derive results for defect levels.

The use of a hybrid functional within density functional theory allows for an accurate description of band gaps, thereby enabling the prediction of impurity levels with respect to the band edges. We use the screened hybrid functional of Heyd-Scuseria-Ernzerhof (HSE), implemented with the projector augmented-wave method in the \textsc{vasp} code. The HSE mixing parameter was set to 32%, resulting in band gaps of 9.2 eV for \(\text{x-Al}_2\text{O}_3\) and 5.8 eV for monoclinic \(\text{HfO}_2\). The electronic wave functions were expanded in a plane-wave basis set with an energy cutoff of 400 eV. Impurity calculations were performed using periodic boundary conditions with supercells containing 120 atoms for \(\text{x-Al}_2\text{O}_3\) and 96 atoms for monoclinic \(\text{HfO}_2\), and the integrations over the Brillouin zone were performed using a \(2 \times 2 \times 1\) and \(k\)-point grid for \(\text{Al}_2\text{O}_3\) and \(2 \times 2 \times 2\) for \(\text{HfO}_2\).

The formation energy of an impurity \(X\) in charge state \(q\) is given by:

\[
E(X^q) = E_{\text{tot}}(X^q) - E_{\text{tot}}(\text{oxide}) - \sum_i n_i (\mu_i^0 + \mu_i) + q\epsilon_F + \Delta^q,
\]

where \(E_{\text{tot}}(X^q)\) is the total energy of a supercell containing the impurity \(X\) in charge state \(q\), and \(E_{\text{tot}}(\text{oxide})\) is the total energy of the bulk oxide in the same supercell. We investigate both substitutional (\(X_{\text{Al}}, X_{\text{HF}}\), and \(X_\text{O}\) and interstitial configurations (\(X_i\)). In \(\text{HfO}_2\), two types of \(X_\text{O}\) exist: threefold-coordinated \(X_{\text{O3}}\) and fourfold coordinated \(X_{\text{O4}}\). \(n_i\) is the number of atoms of type \(i\) added to or removed from the perfect crystal, and \(\mu_i\) is the atomic chemical potential. \(\mu_{\text{Al(Hf)}}\) is referenced to the total energy per atom in bulk Al (Hf) metal \(\mu_{\text{Al(Hf)}}^0 = E_{\text{tot}}(\text{Al(Hf)})\), and \(\mu_{\text{O}}\) is referenced to the total energy per atom of an isolated \(\text{O}_2\) molecule \(\mu_{\text{O}}^0 = (1/2)E_{\text{tot}}(\text{O}_2)\). Chemical potentials for the impurities are referenced to the energy per atom of diamond for C and the \(\text{N}_2\) molecule for N. \(\epsilon_F\) is the Fermi level referenced to the valence-band maximum (VBM), and \(\Delta^q\) is the correction.

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term to align the electrostatic potentials of the bulk and defect supercells and to account for finite-cell size effects on the total energies of charged defects.\textsuperscript{23}

Figure 1 shows the calculated formation energies of C and N in Al\textsubscript{2}O\textsubscript{3} and HfO\textsubscript{2} as a function of Fermi level. For each Fermi level, only the formation energy of the charge state with lowest energy is shown. The Fermi-level positions where the charge state changes from \( q \) to \( q' \) correspond to transition levels \( (q/q') \). Formation energies depend on chemical potentials, which in turn depend on growth conditions. A reasonable choice for ALD growth conditions is to set \( \mu_{O} = -0.65 \) eV, corresponding to contact with O\textsubscript{2} gas at 270 °C and 1 Torr. Chemical potentials for Hf and Al are obtained by assuming equilibrium with HfO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. Choice of precursors, presence of other gases, and deposition temperature may all affect the precise value. Non-equilibrium deposition conditions may also allow higher temperatures in ALD oxides (as evidenced by experiment) than those that would correspond to our calculations. Activity of the impurity, are not affected by the choice of chemical potentials. The (+1/0) impurity level of C\textsubscript{Al} occurs at 4.67 eV and the (0/–1) level at 6.17 eV above the VBM in Al\textsubscript{2}O\textsubscript{3}. Hence, C\textsubscript{Al} occurs in a positive charge state for most Fermi-level positions—in spite of the high formation energy of C\textsubscript{O}. However, there is strong evidence that metal-C bonds are weakened by interactions between the metal precursor and the surface. Al–C bonds in trimethylaluminum (TMA) have been reported to be weakened by Al–Al interactions on the surface during Al\textsubscript{2}O\textsubscript{3} deposition, with a resulting activation energy for methyl-radical production of 0.56 eV.\textsuperscript{24} For ALD of HfO\textsubscript{2} using tetrakis (ethylmethylamido)hafnium (TEMAH), the surface interactions have been reported to give an energy for CH\textsubscript{4} radical production of 0.17 eV.\textsuperscript{25} Such low activation energies indicate that decomposition is not a bottleneck, and incorporation of carbon will be more likely on the site on which it has the lowest formation energy (which is the cation site, according to our calculations).

We also note that the charge-state transition levels (represented as kinks in Fig. 1), which determine the electrical activity of the impurity, are not affected by the choice of chemical potentials. The (+1/0) impurity level of C\textsubscript{Al} occurs at 4.67 eV and the (0/–1) level at 6.17 eV above the VBM in Al\textsubscript{2}O\textsubscript{3}. Hence, C\textsubscript{Al} occurs in a positive charge state for most Fermi-level positions—a conclusion that actually holds for the other configurations of N in Al\textsubscript{2}O\textsubscript{3} as well. In HfO\textsubscript{2}, all configurations of N have similar formation energies, and ultimately kinetics may determine which one is more likely to occur. But again, all these configurations will tend to be stable in the –1 charge state for the relevant Fermi-level positions.

In order to examine the impact of C and N on MOS devices, we need to align the band structure and impurity levels in the oxides with the semiconductor band edges. Figure 2 shows alignments based on band offsets taken from Refs. 5, 26, and 27. We will discuss oxides on GaN, Si, and III-arsenides separately; however, our conclusions (which will be that C acts as a carrier trap and N as a fixed-charge center) will turn out to be generally applicable.

Looking first at GaN-oxide structures, as noted above C\textsubscript{Al} is the most likely configuration for C in Al\textsubscript{2}O\textsubscript{3}. Its (+1/0) level occurs at 0.54 eV below the GaN conduction-band minimum (CBM), indicating that C in Al\textsubscript{2}O\textsubscript{3} may act as a border trap in n-GaN-based MOS structures in which the Fermi level is near the GaN CBM. Likewise, if HfO\textsubscript{2} is used as the oxide, C\textsubscript{Hf} introduces a (0/–1) level at 0.37 eV below the GaN CBM.

The nitrogen impurity levels for all N configurations in both oxides are positioned such that the impurity will be in a negative charge state for most Fermi-level positions below the midgap of GaN. Therefore, nitrogen acts as a source of negative fixed charge in the oxides. Turning now to Si-based MOS structures, the carbon impurity favors the cation sites in both Al\textsubscript{2}O\textsubscript{3} and HfO\textsubscript{2} and again introduces transition levels near the Si CBM. The C\textsubscript{Al} (+1/0) level occurs at 0.13 eV below the Si CBM, and the

**FIG. 1.** Formation energies of C and N impurities in Al\textsubscript{2}O\textsubscript{3} (left) and HfO\textsubscript{2} (right) for \( \mu_{O} = -0.65 \) eV. O3 and O4 are the threefold- and fourfold-coordinated oxygen sites.
C_{Hf} (0/–1) level at 0.04 eV above the Si CBM. These indicate that C leads to border traps and/or increased leakage current through the gate oxides, which is consistent with experimental observations on leakage-current differences between HfO$_2$ layers with different C content on top of Si.$^{11,12}$

As for nitrogen, it again leads to negative fixed charges since the transition levels occur more than ~2 eV below the Si CBM. Nitrogen may actually also have a beneficial role, in that it suppresses the formation of oxygen vacancies (which may have a tendency to form due to non-equilibrium ALD deposition conditions). Under oxygen-deficient conditions, N$_o$ has a lower formation energy than oxygen vacancies and would thus reduce the concentration of vacancy-induced carriers traps. This is consistent with experiments that report improved electrical properties when N is incorporated in HfO$_2$/Si MOS structures.$^{13-15}$

The overall features of III-As-based MOS structures are very similar to the case of oxide/Si MOS structures. The (+1/0) level of C$_{Al}$ and (0/–1) level of C$_{Hf}$ occur near the CBM of InGaAs (0.11–0.28 eV above), and hence those impurities may act as a source of border traps and/or increase leakage current. All levels for nitrogen are again well below the InGaAs VBM, indicating it will act as a negative fixed-charge center.

To summarize, we have presented hybrid functional calculations for carbon and nitrogen impurities in Al$_2$O$_3$ and HfO$_2$ and the impact of these impurities on GaN, Si, and III-As semiconductor based MOS devices. We find that carbon incorporates preferentially on the cation site and produces carrier traps with an energy level near the semiconductor CBM. Nitrogen acts as a source of negative fixed charge but may also help to reduce carrier traps due to native defects. Overall, our results call attention to the fact that incorporation of impurities (particularly carbon) is a concern in oxide dielectrics and should be more carefully controlled in order to achieve high-quality MOS devices.

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FIG. 2. Band alignment between semiconductors (III-As, Si, GaN) and oxide dielectrics (Al$_2$O$_3$, HfO$_2$). The positions of charge-state transition levels for C and N impurities in Al$_2$O$_3$ and HfO$_2$ are shown within the oxide band gaps and relative to the semiconductor band edges. The zero was set at the vacuum level, with the GaN band-edge positions taken from Ref. 28.

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