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Passivation of oxygen vacancy states in HfO$_2$ by nitrogen

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Nitrogen is known to reduce leakage currents and charge trapping in high-dielectric-constant gate oxides such as HfO$_2$. We show that this occurs because nitrogen, substituting for oxygen atoms next to oxygen vacancy sites, repels the occupied gap states due to the neutral and positively charged oxygen vacancies out of the band gap into its conduction band. The state of the negatively charge vacancy is also repelled upwards but remains as a shallow gap state. This occurs because the vacancy becomes effectively positively charged; the adjacent Hf ions relax outwards from the vacancy and shift its states upwards. We show this using *ab initio* calculation methods which do not require an empirical correction to the band gap. © *2006 American Institute of Physics*.
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INTRODUCTION

The decrease of dimensions of complementary metal oxide silicon (CMOS) transistors has led to a need to replace the SiO$_2$ gate oxide with an oxide of higher dielectric constant (K) such as HfO$_2$, in order to maintain a small gate leakage current.[1,2] The oxide must satisfy various conditions such as be stable in contact with Si and have sufficient band offsets for both electrons and holes. However, HfO$_2$-based gate stacks show some inferior properties, including atomic diffusion, growth of interfacial SiO$_2$ next to the Si, low temperature crystallization, increased boron penetration, and poorer trapping and electrical stability than those with SiO$_2$.

Incorporating nitrogen has been found to have some beneficial effects on the structural stability of high K oxide layers, particularly lower atomic diffusion rates (B, As, P, and O), reduced interfacial layer growth, raised crystallization temperatures, and lower boron penetration.[3–9] Nitrogen also has a beneficial effect on electrical properties, increasing the dielectric constant,[8] reducing the leakage currents, and improving the electrical stability.[9–14] The leakage current reduction occurs at lower fields, where the Poole-Frenkel hopping and trap-assisted tunnelling[15] are each found to be reduced. This points to a reduction in the density of gap states. Recently, experiment and theory[16,17] have shown that oxygen vacancies in HfO$_2$ give rise to defect levels in the upper gap at 0.5–1.8 eV below its conduction band edge, consistent with recent defect band models,[18] so that O vacancies are a likely origin of this conduction pathway.

It is important to understand the origin of the beneficial effects of nitrogen on the electrical properties.[19–21] An interesting model of Umezawa *et al.*[19] noted that if two nitrogen atoms substitute for oxygens next to an O vacancy, this tends to push the vacancy level up out of the gap. However, they were unable to fully confirm this idea because their calculation method uses the local density approximation (LDA).

This is well known to underestimate the band gap and can misplace the localized defect energy levels. In this paper, we carry out calculations using *ab initio* local density-based methods which give accurate band gaps to show that the neutral vacancy level is indeed moved above the conduction band edge. We also consider the states of the negative vacancy not considered by Umezawa *et al.*[19] Finally we discuss the bonding rules which explain this behavior more generally.

METHOD

The calculations are carried out on 48 atom primitive body-centered cubic supercells of cubic HfO$_2$ containing the vacancy and the two nitrogen atoms. The total energy and electronic structure were calculated using the CASTEP plane-wave code.[22] For structural relaxation the total energies were minimized using ultrasoft pseudopotentials, a plane-wave cutoff energy of 340 eV and with the Perdew, Burke, Ernzerhof (PBE) exchange-correlation functional of the generalized gradient approximation (GGA). The band energies were then calculated for this structure using the screened exchange (sX) method. The sX method is based on Hartree-Fock, but describes electron correlation by a simple screening term.[23–25] It is a well-tested method that uses norm-conserving pseudopotentials and it has been found to give good band gaps for a range of semiconductors and oxides.[24,25] It was previously used to study oxygen vacancies and interstitials in HfO$_2$.[17] A plane-wave cutoff energy of 600 eV is used for sX due to the harder norm-conserving pseudopotentials. We also calculated energy levels with the weighted density approximation (WDA),[26] a less tested method. This also gives improved band gaps,[27] and can use ultrasoft pseudopotentials, allowing much lower plane-wave cutoff energies and faster calculations. The defects are modeled as single defects within periodic supercells. The supercells should contain at least 48 atoms because of the sizable lattice relaxations around each defect. We relaxed the structure in GGA and calculated energy levels and local density of states with sX or WDA.
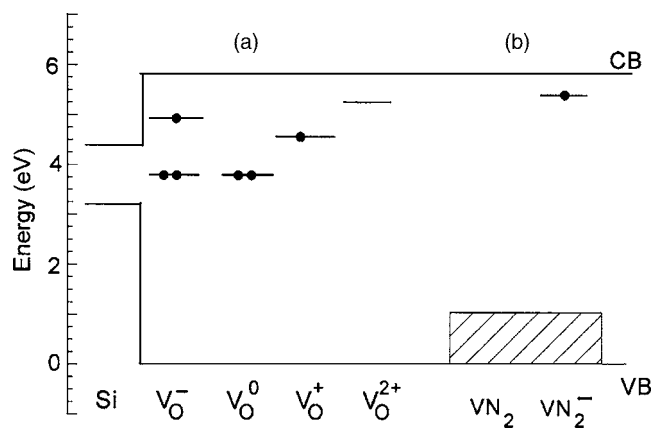
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FIG. 1. Energy levels of the (a) simple O vacancy and (b) the VN_2 center.

Relaxation within sX or WDA was not possible due to limits on computer time.

RESULTS

The band gap of cubic HfO_2 is 5.6 eV in sX, 6.1 eV in WDA, compared to 3.5 eV in GGA.[28] In pure HfO_2, the oxygen vacancy gives an energy level of A_1 symmetry deep in the gap localized on its adjacent Hf ions. It is occupied by two electrons for the neutral vacancy, V^0. Emptying this level gives the V^+ and V^{2+} charge states, Fig. 1(a). We relaxed the structure in GGA and calculated energy levels and local density of states with sX. We find that the energy levels of the unrelaxed vacancy fall in the gap, from 3.75 to 3.2 to 2.6 eV for the V^0, V^+, and V^{2+} states. This ordering is due to the repulsion of electrons when there are two electrons in the defect state. On the other hand, if the atomic positions can relax, the energy levels rise with increasing charge, from 3.8 to 4.7 to 5.2 eV for V^0, V^+, and V^{2+} states,[17] see Fig. 1(a). This is because the Hf ions adjacent to the vacancy relax outwards with increasing vacancy positive charge, which raises the levels. The Hf–Hf separation increases from 3.59 to 3.74 to 3.90 Å for V^{2+} V^0, V^+, and V^{2+} states, from the bulk value of 3.54 Å. This is summarized in Fig. 2 which plots the energy levels for each charge state against the Hf separation. Thus the effect of relaxation dominates the effect of Coulombic repulsion, and the levels rise in the gap.
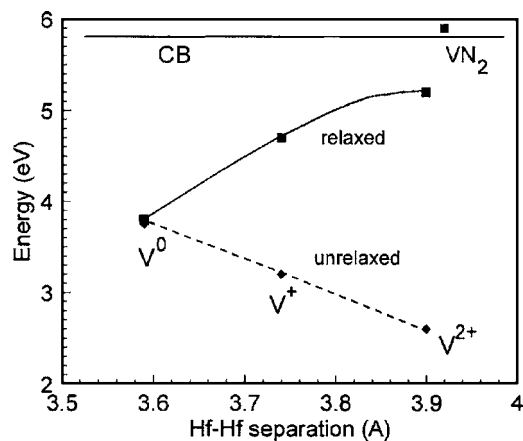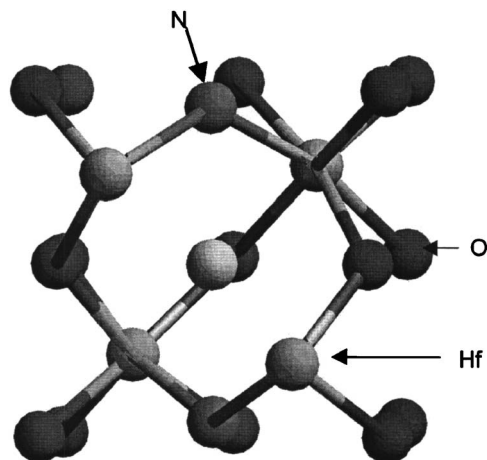

FIG. 3. View of the relaxed VN_2 center in HfO_2, Hf=brown, O=red, and N=blue. The vacancy is pale pink. Note the inward relaxations of the nitrogens towards the vacancy.

The O vacancy can also trap electrons, giving V^- and V^{2-} states. The V^0 configuration has only the A_1 gap state, with no other gap state above it. However, if an extra electron is placed on the vacancy, it undergoes an asymmetric relaxation which allows it to trap the electron in an extra state which is pulled out of the conduction band (CB). It is a singly degenerate state of B_1 symmetry. This state lies about 0.8 eV below the CB edge in sX in pure HfO_2 [Fig. 1(a)]. This is the fast electron trap seen in many trapping studies on HfO_2.[11,18,30]

We now substitute two nitrogen atoms for oxygens next to the vacancy, forming a neutral VN_2 complex, VN_2^0 (Fig. 3).[17,29] The atomic structure is relaxed in GGA, and the local density of states is calculated in GGA, sX, and WDA, for the adjacent Hf, O, and N ions to the vacancy, and on a bulk Hf ion. Figure 4 shows the density of states (DOS) in WDA. There is no gap state in either GGA, sX, or WDA, Figs. 1(b) and 4. The level previously formed by the vacancy has moved above the CB edge, due to a repulsion by the N's. The orbital character of the lower CB states is delocalized. The Hf^{4+} ions adjacent to the vacancy have relaxed away, so the separation is 3.90 and 3.94 Å, the same or greater than at the
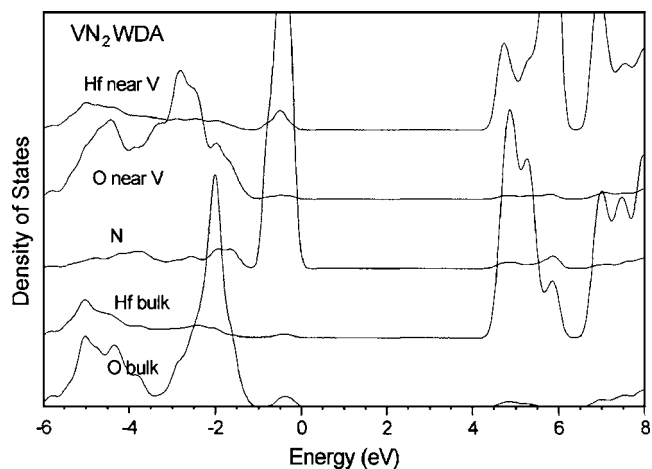

FIG. 2. Variation of the vacancy A_1 energy level with Hf–Hf ion separation.

FIG. 4. Calculated local density of states at the neutral VN_2 center. Note the absence of gap states. Extra N-related states appear above the VB.

V^{2+} in pure HfO_2. The nitrogen atoms have relaxed inwards towards the vacancy, compared to the equivalent oxygen sites.

The key point is that a nitrogen atom has one less valence electron than oxygen. Hence, when two nitrogens substitute for oxygens next to the neutral O vacancy, there would be a hole in the valence band of each N. The two electrons from the A_1 level of V^0 transfer to the N's to fill their valence states and form a closed shell. The A_1 vacancy state is now empty for the neutral VN_2 complex. Locally, the vacancy is V^{2+}. This charge causes an outward relaxation of Hf ions and increases the Hf–Hf separation to 3.90–3.94 Å as in the simple vacancy. This outward relaxation is actually slightly larger than at the V^{2+} center and it pushes the A_1 state up in the gap. Indeed, it pushes it further than in pure HfO_2, so that the A_1 state now lies above the CB edge. This is confirmed in the WDA calculation in Fig. 4, where the gap below the CB edge is clear for neutral VN_2. The same absence of gap states below the CB edge is found using sX. This confirms the result of Umezawa et al.,[19] using more robust methods. (Note that N introduces filled N $2p$ states above the oxide valence band edge, as shown by Shang et al.,[21] so the band gap of HfO_2:N is less than that of HfO_2 itself, but there are no states below the CB.)

We found that the VN_2 is still able to trap one electron. The electron can again induce an asymmetric distortion which pulls a B_1 symmetry state down from the conduction band, Fig. 1(b). The DOS was calculated by sX and WDA. However, there is now no A_1 state below it. The B_1 state has a much smaller binding energy of 0.5 eV than in simple V_O. Thus it is a shallow trap.

Now consider the experimental situation. While the HfO_2 gate oxide films are grown in an O-rich ambient, the gate electrode is subsequently deposited in the reducing conditions of metal-rich or silane chemistry. The relative ease of O diffusion in the HfO_2 film means that oxygen vacancies tend to be the dominant defect in HfO_2 films after processing the gate stack. The Fermi level would lie in the vacancy states in the oxide's upper gap.

Nitrogen can be introduced during growth or by post-deposition anneals in N_2 or NH_3. The N is attracted towards the vacancy (0.44 eV binding energy[19]). The N inhibits further O diffusion. The VN_2 center is overall neutral, so that it is no longer a charged center which could give rise to remote Coulombic scattering of carriers in the Si channel. It may give quadrupolar scattering, but this is much weaker. Reduction in the Si carrier mobility has been the another problem in devices with high K oxide dielectrics. Trap-assisted tunnelling and Poole-Frenkel hopping will be inhibited in HfO_2:N by the absence of gap states for $VN_2{}^0$ to permit any resonant tunnelling. Even in disordered cases where the levels may possibly lie below the CB edge, the smaller trap depth would reduce trap-assisted tunnelling. Electron trapping is the source of transient threshold voltage instabilities in HfO_2-based field-effect transistors (FETs).[18] The much smaller trap depth of the electron level associated with $VN_2{}^-$ in Fig. 1(b) means that any trapped electrons would soon be released back to the conduction states. This will reduce the degree of instability.

Charge transfer between V_O states and the gate electrode to create trapped holes was proposed by Shiraishi et al.[31] as a cause of the dc gate threshold voltage shifts seen in FETs due to the interaction between HfO_2 dielectric and poly-Si gates.[32] In this model, N would have a large beneficial effect of removing the vacancy gap states which drive this mechanism. It would be a way to verify this mechanism, compared to that of Fermi level pinning by Hf–Si bonds.[33]

Other configurations of N in HfO_2 are possible. Gavartin et al.[20] studied a wide range of other nitrogen configurations. However, those all produced deep gap states. It is also necessary to consider the combined effect of N and H, when NH_3 is used. Hydrogen is also a source of fixed charge. Nevertheless, the simplicity of its formation and charge compensation at VN_2 makes it an appealing model for the beneficial effect of N on trapping and leakage.

We finally consider the chemical bonding at the VN_2 complex. If excess nitrogen is added to HfO_2 containing O vacancies, the N is attracted towards the vacancy by a 0.44 eV binding energy.[19] But why does N not simply annihilate the vacancy to form a substitutional N_O site? The point is that the VN_2 center is a closed shell species. In this, although the V is a structural vacancy, in terms of valence and closed shells it is not a "chemical" vacancy. It is similar to lattice vacancies in complex oxides such as a bixbyite (In_2O_3) or a spinel (γ-Al_2O_3). There is a partial occupancy of a sublattice which can be called vacancies, O site vacancies for In_2O_3 and Al site vacancies for Al_2O_3, but these are required by valence. Despite the presence of lattice vacancies in these compounds, they do *not* give rise to gap states because they are closed shell systems. Thus in HfO_2:N, the neutral VN_2 center is a stable closed shell system and the vacancy is required. In the oxynitrides, the absence of gap states below CB was also clearly seen in the density of states of the supercell compounds $Hf_8O_{10}N_4$ and $Hf_{10}O_8N_8$ studied by Shang et al.,[21] although the importance of this was not recognized then. These compounds contain two and four VN_2 units per cell, respectively.

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