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An Unfavorable Effect of Nitrogen Incorporation on Reduction in the Oxygen Vacancy Formation Energy in Hf-based High-*k* Gate Oxides

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An effect of N incorporation into Hf-based high-*k* gate dielectrics has been studied in terms of formation of oxygen vacancies (**Vos**). The energy required to form a neutral vacancy ($\mathbf{Vo}^0$) is calculated from the first-principles total energy calculations. Our computational results clearly showed that the $\mathbf{Vo}^0$ formation energy is about 0.4 eV smaller in the vicinity of N atoms than that in pure HfO_2, indicating N incorporation accelerates $\mathbf{Vo}^0$ formation in HfO_xN_y. The additional $\mathbf{Vo}^0$s formed in HfO_xN_y, in turn, induce generation of fixed positive charge in the high-*k* bulk of MISFETs due to electron transfers from the occupied **Vo** levels to the low-lying Fermi level of the metal gate. This computational result reasonably explains a recent experimental result showing a negative shift of the flat band voltage upon N incorporation into TiN/HfO_2 MISFET. Moreover, a possible solution to this problem is suggested.

Key words: high-*k*, HfO_2, nitrogen incorporation, oxygen vacancy

1. INTRODUCTION

Oxygen vacancies (**Vos**) in Hf-based high-*k* dielectrics are a nuisance because they significantly degrade the reliability of CMOS devices. For example, the gate leakage current through HfO_2 is considered to be mediated by electron hopping through **Vo** related gap states[1,2] located about 0.4 eV above the bottom of the Si conduction band.[3] The **Vos** are also know to be electron and hole trap sites,[4,5] which induce bias temperature instability.[2]

N incorporation is known to be effective for reducing both leakage current[6-9] and electron charge tarps.[10,11] Recently, we have found that N atoms couple favorably with **Vos** in HfO_xN_y and deactivate the **Vo** related gap states by extracting electrons from them, which leads to a reduction in the gate leakage current.[12] The same effect has been observed in HfSiON.[13] Moreover, our subsequent work revealed that electron charge traps at **Vos** are also suppressed by N incorporation.[14] There are many other beneficial effects of N incorporation such as increasing the dielectric constant[6] and inhibiting crystallization.[6,7,15,16] Therefore, N incorporation into high-*k* dielectrics has become a standard technique in fabricating good quality gate insulators. Very recently, however, one adverse effect of N incorporation has been reported,[17] i.e. N incorporation into TiN/HfO_2 MISFET causes a negative shift of the flat band voltage indicating the existence of fixed positive charge in the high-*k* gate insulator. In the present study, we focused on the possibility that the positive charge is generated inside the high-*k* bulk due to N incorporation. Our suggested scenario is schematically illustrated in Fig. 1. If the energy required to form neutral $\mathbf{Vo}^0$s in the vicinity of the N atoms is relatively small, the $\mathbf{Vo}^0$s are selectively formed around the N atoms. Thus, the number of occupied **Vo** levels in HfO_xN_y is increased. This, in turn, causes the generation of positive charge because of the electron transfer from the **Vo** levels to the low-lying Fermi level of the metal gate. This scenario is based on the assumption that "the $\mathbf{Vo}^0$s are favorably formed around N atoms". Therefore, the present work is devoted to confirming this assumption in order to justify the above scenario. For this purpose, we have compared the relative stabilities of the **Vo** formation energies in HfO_2 and HfO_xN_y using the first-principles total energy calculations. Our computational results clearly show that the **Vo** formation energy is certainly reduced by 0.4 eV in the vicinity of N atoms. This indicates that N incorporation accelerates **Vo** formation, which, in turn, causes the generation of fixed positive charge. Moreover, our theoretical results suggest a possible solution to this problem .

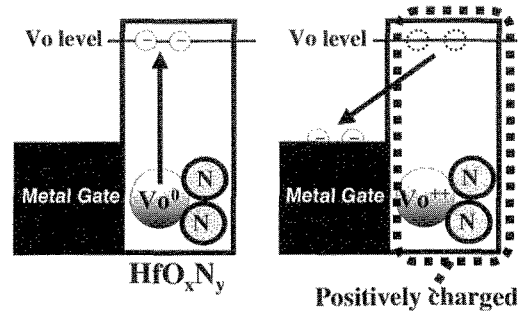

Fig. 1. Schematic illustration of suggested scenario for the generation of fixed positive charge induced by N incorporation.

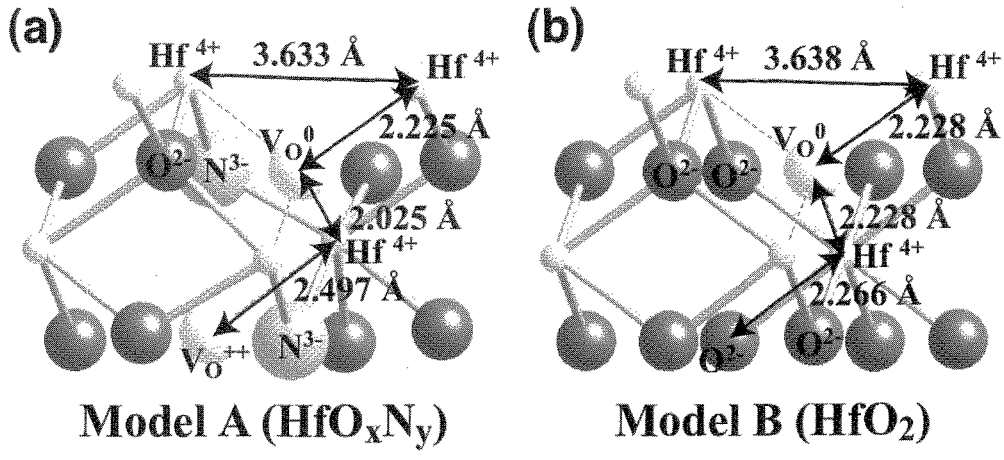

Fig. 2. Relaxed structures in the vicinity of a $\mathbf{Vo}^0$ for the models of HfO_xN_y and HfO_2. (a) In model A, two N^{3-} ions and one $\mathbf{Vo}^{++}$ are introduced into the unit cell to satisfy the charge neutrality of the system. On top of that, a $\mathbf{Vo}^0$ is also introduced to calculate the $\mathbf{Vo}^0$ formation energy. (b) In model B, one oxygen atom is removed from the unit cell of the cubic HfO_2 to model the formation of a $\mathbf{Vo}^0$ formation in HfO_2.

2. CALCULATIONS

Our theoretical calculations are based on the first-principles pseudopotential[18] approach within the framework of a generalized gradient approximation (GGA).[19,20] The models employed for HfO_xN_y and HfO_2 are based on cubic HfO_2 including 96 atoms per unit cell. The cutoff energy of the plane-wave basis set is 36 Ry. The Brillouin zone (BZ) was sampled at the Γ point. The convergence of the calculation parameters were checked by increasing the cutoff from 36 to 49 Ry, and extending the BZ sampling to eight k points beyond the Γ point. The geometries of the models employed were fully relaxed for all atoms until the residual forces were less than 4 mRy/Å. In Fig. 2, the relaxed structures around **Vos** are depicted. Here, the places of the **Vos** are represented by the locations of **Vos** in the initial structures before geometrical optimization. In model A, which represents HfO_xN_y, two O atoms are replaced by N atoms and one $\mathbf{Vo}^{++}$ and one $\mathbf{Vo}^0$ are introduced into the unit cell (Fig. 2 (a)). The composition of one $\mathbf{Vo}^{++}$ and two N^{3-} ions is convenient to retain the charge neutrality of the system. Thus, the formation energy of a neutral $\mathbf{Vo}^0$ is correctly calculated. Here, N atoms are placed at the nearest neighbor oxygen sites to the **Vos** because the N atoms couple favorably with **Vos**.[12] In model B, which represents HfO_2, one O atom is removed from the unit cell of the cubic HfO_2 to introduce a neutral $\mathbf{Vo}^0$ (Fig. 2 (b)). We found that most of the Hf–Hf and Hf–$\mathbf{Vo}^0$ distances are not very much different between models A and B except for one Hf–$\mathbf{Vo}^0$ distance; 2.025Å in HfO_xN_y, and 2.228Å in HfO_2. The difference in the Hf–$\mathbf{Vo}^0$ distances is attributed to the relaxation of Hf^{4+} ions around $\mathbf{Vo}^{++}$ in model A.[12] We consider that this slight difference between models A and B does not significantly affect the comparison of $\mathbf{Vo}^0$ formation energies between these models. We have also calculated the total energies of these models without the $\mathbf{Vo}^0$. Finally, the energies required to form a $\mathbf{Vo}^0$ per unit cell, i.e., the $\mathbf{Vo}^0$ formation energies: F(Vo) in HfO_xN_y and HfO_2 are given respectively by,

$$F_{\mathrm{HfON}}(\mathrm{Vo}) = \left[E^0_{\mathrm{HfON+2Vo}} + \frac{E_{O2}}{2}\right] - E^0_{\mathrm{HfON+Vo}}, \quad (1)$$

$$F_{\mathrm{HfO2}}(\mathrm{Vo}) = \left[E^0_{\mathrm{HfO2+Vo}} + \frac{E_{O2}}{2}\right] - E^0_{\mathrm{HfO2}}, \quad (2)$$

where $E^0_{\mathrm{HfON+2Vo}}$ is the total energy of the neutral state of the HfO_xN_y + 2**Vo** system. E_{O2} is the total energy of an oxygen molecule calculated with a unit cell the same size of as in models A and B. Our computational results obtained from Eqs. (1) and (2) clearly show that the **Vo** formation energy of model A (HfO_xN_y) is 0.4 eV smaller than that of model B (HfO_2). This indicates that $\mathbf{Vo}^0$ formation is augmented around N atoms. This result justifies the assumption used for our scenario addressed in Fig. 1.

3. PHYSICAL REASONS

A qualitative understanding of this effect due to N incorporation can be derived from the relatively strong repulsive Coulomb interaction between N^{3-} and O^{2-} ions compared with that between O^{2-} and O^{2-} ions as schematically illustrated in Fig. 3. In the case of HfO_xN_y, O^{2-} ions located near to N atoms are subject to strong repulsive Coulomb potentials from N^{3-} ions. Thus, the O^{2-} ions around N^{3-} ions are relatively unstable. The repulsive interactions are essentially reduced by the removal of a neutral O atom from around the N^{3-} ion because of the redistribution of electrons (Fig. 3 (a)). On the other hand, O^{2-} is already stable in HfO_2 and a relatively large amount of energy is required to remove a neutral O atom compared to the case in HfO_xN_y. The small redistribution of electrons in the $\mathbf{Vo}^0$ also contributes to the larger $\mathbf{Vo}^0$ formation energy in HfO_2 (Fig.3 (b)). After formation of the neutral $\mathbf{Vo}^0$, two electrons occupy the **Vo** levels that are usually located

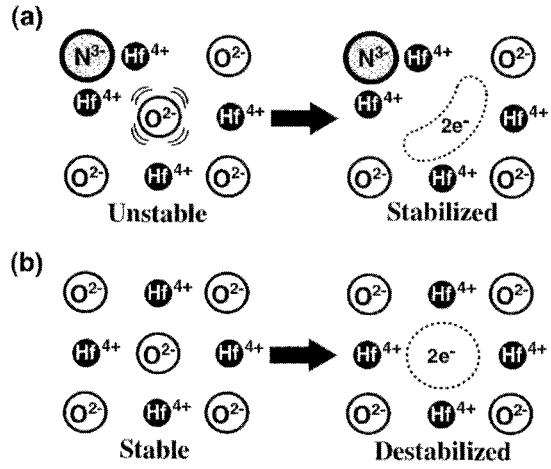

Fig. 3. Schematic illustrations of repulsive Coulomb interactions between negative ions and electrons in (a) HfO_xN_y and (b) HfO_2 before and after $\mathbf{Vo}^0$ formation.

above the metal Fermi level. Thus, these electrons can transfer to the metal gate of the MISFET. Consequently, positive charge is generated in the high-*k* dielectrics as illustrated in Fig. 1. This is a similar mechanism to the **Vo**-induced Fermi level pinning in p+poly Si gates.[21,22] This effect is undesirable because the additional $\mathbf{Vo}^0$s formation causes the generation of fixed positive charge in MISFETs that leads to negative shift of the flat band voltage and possibly degrades mobility. Therefore, adjustment of the process environment is required so that the additional $\mathbf{Vo}^0$ formation in HfO_xN_y is energetically disadvantageous. Actually, it has been reported that an increase in the ambient O_2 partial pressure after the N incorporation process is effective for this purpose.[23]

4. CONCLUSIONS

In conclusion, we have investigated the effect of N incorporation on the **Vo** formation energy in HfO_xN_y using the first-principles total energy calculations. It was found that the formation energy of $\mathbf{Vo}^0$s is essentially reduced by N incorporation, resulting in the generation of fixed positive charge in HfO_xN_y. Moreover, our theoretical analysis suggests that adjustment of the ambient O_2 partial pressure is necessary after N incorporation process to prevent the formation of additional $\mathbf{Vo}^0$s. In future, another possible location of the fixed positive charge, i.e., the high-k dielectric/Si-substrate interface should also be examined.

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