Atomic mechanism of Flat band voltage shifts by Oxide dipole Layers in High K-Metal Gate Stacks

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High dielectric constant (high K) gate oxides and metal gates are needed to continue CMOS scaling. However, control of the flat band voltage V_{fb} across the device using metal gate electrodes is a problem, especially with the temperature constraints. This has led to competition between the gate-first and gate-last approaches. An additional way to vary V_{fb} is using oxide 'capping layers' such as La_2O_3 or Al_2O_3 to shift V_{FB} in the direction for nFET or pFET, respectively [1-7]. However, its mechanism is controversial. It is also useful to understand it, to see if even better control is possible, to allow continued scaling [8].

In a critical clue to the mechanism, Toriumi et al [9,10] showed by deposition of La and Hf oxide, or Al and Hf oxide layers in different order, that the Vfb shift arose from a dipole at the lower SiO_2-oxide interface, not some 'Fermi level pinning' effect at the upper gate oxide - gate electrode interface. The nature of the dipole was variously attributed to oxygen vacancies [4], bond dipoles [11], group electro-negativity [12], changes in oxygen ion density [13], or bonding [14]. Note that if the gate stack is annealed to 1000C as in the gate-first process, the capping layer metal ions have diffused through the oxide layer [15].

The different mechanisms can be distinguished by a first principles calculation on specific atomic models of interfaces containing the different dopants. We use a 72 atom supercell to represent an epitaxial HfO_2:SiO_2 interface [16], with 9 atomic layers of HfO2 and 6 layers of beta-cristobalite, 2 interfaces and no vacuum layer. Two substitutional La, Sr, Al or Nb atoms are placed at various Hf sites. If the substitutional atom has a different valence than Hf, then an appropriate number of O vacancies (for La or Sr) or O interstitials (for Nb) are added to maintain charge balance [16].

The structure is relaxed by a total energy calculation, and the local electronic density of states (DOS) is calculated. The valence band offset (VBO) between the SiO_2 and HfO_2 layer is calculated from the local DOS, and shifts in this represent shifts in V_{FB}. Fig 1 shows some relaxed structures for various dopants (La, etc). Generally, the dopant ions segregate to the interface, and the vacancies also segregate to the interface.

Fig 2 plots the calculated VBO vs. the experimentally observed V_{FB} [4-7. We see that the VBO shift is the *same* as the V_{FB} shift *in all cases*, using experimental data from Sematech and IBM. Note that the size of the observed V_{FB} is proportional to the concentration of 'capping oxide' used, so that we are only comparing direction of shift, not magnitude.

Fig 3 plots the calculated VBO shift versus valence of the metal oxide dopant. We see that the VBO shift changes gradually from Sr to La to Nb. The calculated VBO of Al oxide is opposite to that of La oxide, although they are both trivalent. On the other hand, the calculated shift for Al oxide is in the same direction as that of Nb oxide, despite Al being trivalent and Nb being pentavalent. In view of the agreement in Fig 2, this suggests that metal valence does not determine the dipole shift. As trivalent metals introduce oxygen vacancies into HfO_2, then the oxygen vacancy model cannot be correct.

Fig 4 plots the calculated VBO shift against the work function of the metal dopant. We see that there is a monotonic variation of VBO shift and metal work function. Now, electronegativity is linearly proportional to work function. Group electronegativity is an average of metal electronegativity and oxygen electronegativity. Thus, the dopant work function scale is equivalent to group electronegativity.

These results show that calculated VBO shift does scale with metal work function. But why does this occur? The dipole is at an interface between two crystalline or amorphous phases. Within a bulk phase, the bonding consists of A–O–A–O- units. The potential shift due to a dipole at a given plane is given by [16]

$$\Delta V = \frac{Ned}{\varepsilon_0 \kappa}$$

The A-O dipole cancels the O-A dipole, on average, if κ is the same for both bonds (Fig 5a). On the other hand, if the two bonds, A-O and O-A are on different sides of a dielectric interface (Fig 5b), κ will be locally different, and there is no cancellation. A net dipole results. This is our model.

There is still a problem in obtaining sufficient pFET V_{FB} shifts. We extended the calculations to check if other oxides with high electronegativity can give a larger p shift. Of the trivalent oxides, B_2O_3 is found to give a

similar shift to Al$_2$O$_3$ (Fig 6). P$_2$O$_5$ is found to give a larger shift than Al$_2$O$_3$. However, P may be unsuitable, due to diffusion.
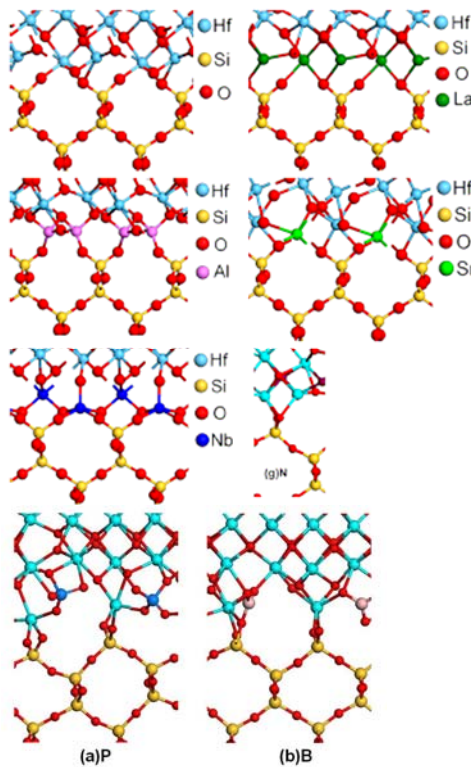

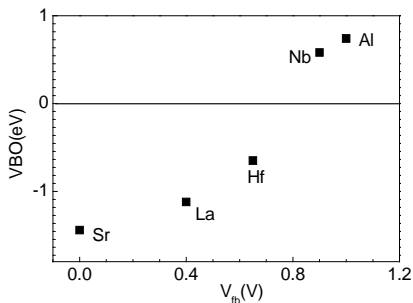Fig. 1. Bonding of metals at HfO$_2$:SiO$_2$ interfaces.

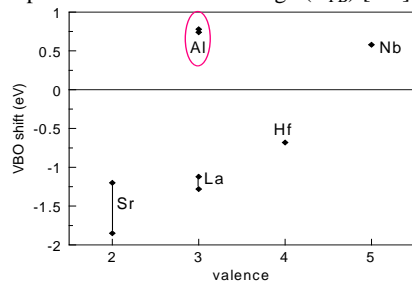Fig 2. Calculated valence band offset (VBO) vs experimental flat band voltage (V$_{FB}$) [4-7].

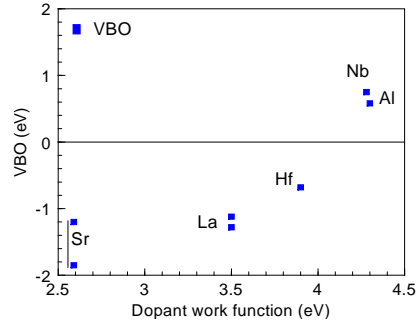Fig. 3. VBO shift vs metal valence, showing the Al anomaly.

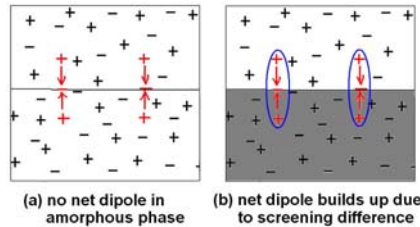Fig. 4. Calculated VBO vs dopant metal work function

Fig 5. Cancellation and non-cancellation of bond dipoles in bulk and at interfaces.
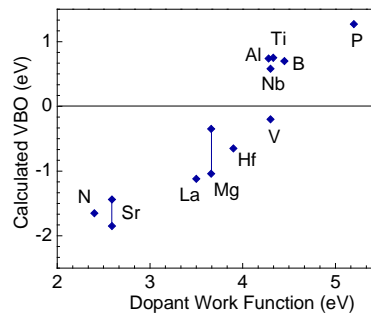

Fig 6. VBO vs dopant work function for more dopants.

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