# Interface Dipole Layers between Two Dielectrics: Considerations on Physical Origins and Opportunities to Control Their Formation

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#### Abstract

Coulomb potential barrier emerged at interfaces of different dielectric materials is understood as the result of interface dipole layer formation. The physical origins of a pair of charges should be the intrinsically induced net displacements of ions during the formation of interface. There is a room to design the interface formation process to control the dipole layer formation, which enables a selective formation of dipole layers in a laminated stack.

#### 1. Introduction

The interface dipole layer formation at high-k/SiO<sub>2</sub> interface is one of the sources of anomalous threshold voltage (V<sub>t</sub>) of high-k MOSFETs [1] in addition to the Fermi-level pinning. The first experimental evidence of the formation of interface dipole layer at high-k/SiO2 was reported based on the composition dependence of flatband voltage (V<sub>fb</sub>) shifts for HfLaOx/SiO<sub>2</sub> stacks [2]. The interface dipole layer was a new concept considering pairs of identical amount of sheet fixed charges with opposite signs emerged at the interface. When those positive and negative sheet charges locate on the different sides of an interface in a distance of atomic scale, this pair of charges induces a steep electrical potential drop in the stack, as schematically shown in Fig. 1(a). Even though such charge pair formation was an unexpected phenomenon in insulating materials, such concept of interface dipole layers at various high-k/SiO<sub>2</sub> interface is now widely accepted, after lots of experimental verifications so far, and also by theoretical modeling [3].

## 2. Possible Origins of Dipole Layer Formation

It has been generally accepted that the strength and even direction of high-k/SiO<sub>2</sub> interface dipoles depend on the employed high-k materials. As shown in **Fig. 1(b)**, experimentally observed V<sub>fb</sub> shifts can be significantly different only by changing the employed high-k dielectric materials. The effects of the interface dipole layers on V<sub>fb</sub> are clearly distinguishable from those of conventional fixed charges in dielectrics, by the fact that V<sub>fb</sub> is irrespective of the dielectric thickness. The insignificant high-k thickness dependence of V<sub>fb</sub> in Fig. 1 (b) tells that those shifts should not be attributed to conventional fixed charges.

The fact that both strength and direction sensitively change by the employed high-k material gives us some clues to consider the possible origin of the interface dipole layer formation. Since the dipole layer is formed inside insulating materials, the origin of the charge pair should be described by the accumulation of ionic charges at both sides of the interface, rather than electron/hole accumulation. In general when two different materials form an interface, one may consider a strong driving force to relax the structural strain due to the inconsistancy of atomic arrangements. In atomic scale, such strain would be partly relaxed by ionic displacements at interface. Here we should pay attention to oxygen ions which have main role to determine the structural framework of oxides in general. The interface strain relaxation is expected to be represented by the oxygen displacements, if we neglect the effects of interface reaction to form an interfacial layer. We have proposed a model to employ oxygen ionic density in oxide as an indicator of the tendency to form dipole layer when interfacing with SiO<sub>2</sub>[4]. As shown in Fig. 2, a clear correlation was found between the experimentally observed dipole-induced-V<sub>fb</sub> shift and the oxygen ion areal density calculated simply from well-known crystallographic data of typical high-k materials (Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, and La<sub>2</sub>O<sub>3</sub>) whose experimental data on dipole layer formation were reported for the interfaces with SiO<sub>2</sub> [4]. When we consider the negatively-charged oxygen ion displacements from higher to lower density side, the expected dipole direction agrees with the observed direction of V<sub>fb</sub> shift. Note that this model does not mean such oxygen density differnce results in an "ionic diffusion", but simply



Fig. 1 (a) Schematic of interface dipole layer formation at high-k/SiO<sub>2</sub> interface. (b) High-k thickness dependence of  $V_{\rm fb}$  of Au/various high-k materials/SiO<sub>2</sub>/p-Si MOS capacitors.



Fig. 2 Relationship between the calculated ratio of oxygen areal density of high-k materials ( $\sigma$ ) to SiO<sub>2</sub> ( $\sigma$ <sub>SiO2</sub>) and the experimentally reported V<sub>fb</sub> shift induced by high-k/SiO<sub>2</sub> interface dipole layers.

suggesting a "net displacement" of oxygen ion density for the structual relaxation in near-interface region. We recently found this concept would be extendable even to fluoride interfaces by considering the anion density, from the experiments on  $AlO_xF_y/Al_2O_3$  stacks [5].

This model gives a guideline to predict the interface dipole effect for new candidate high-k materials [4], but mostly limited to the cases when they are deposited on SiO<sub>2</sub>. We speculate this would be because the effects of net oxygen displacement would be emerged more clearly when the oxides with different bonding properties are froming interfaces: SiO2 with relatively covalent bonds and high-k materials with mostly ionic bonds. For example, only a very small, or negligible dipole effect has been reported for Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> [6] or Al<sub>2</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub> [7] despite the considerable difference in oxygen density. Even though data in Fig. 2 indicates the dominat role of oxygen in the formation of the interface dipole layer, the cases of materials easy-to-react with SiO<sub>2</sub> would require additional consideration, because ionic transport to form interacial layer should be the other way to relax the interface structure as mentioned above. For such material systems, for example, MgO/SiO2 and Y<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, the dipole layer formations were found to be significantly affected by annealing processes [8]. Such dipole layer formation, driven by the tendency to form interfacial layer, should not be limited to high-k/SiO2, but will be available for reactive high-k/high-k interace, for example as demonstrated for MgO/Al<sub>2</sub>O<sub>3</sub> [9].

## 3. Room for Controlling Dipole Layer Formation

To investigate the effects of SiO<sub>2</sub> formation process on the SiO<sub>2</sub>-on-Al<sub>2</sub>O<sub>3</sub> interface dipole layer formation, we fabricated the stacks with or without an insertion of ~3Å-thick metallic-Si between the top-SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> by pulsed laser deposition, followed by O<sub>2</sub> annealing for sufficient oxidation. As shown in the top-SiO<sub>2</sub> CET dependence of V<sub>fb</sub> in **Fig. 3**, the negative V<sub>fb</sub> shift due to the dipole layer formation was effectively suppressed simply by the ultrathin Si insertion, while a dipole-induced significant negative V<sub>fb</sub> shift was observed by the growth of SiO<sub>2</sub> without the insertion layer. This result indicates that the oxygen supply during the formation of SiO<sub>2</sub>-on-Al<sub>2</sub>O<sub>3</sub> interface has a crucial role in the dipole layer formation.

## 4. Large Vfb Shift Induced by Multiple Dipole Layers

Based on the above technique to suppress SiO<sub>2</sub>-on-Al<sub>2</sub>O<sub>3</sub> interface dipole layer formation, we demonstrated a selective formation of interface dipole layers in a  $(Al_2O_3/SiO_2)_2$  laminated dielectric, as shown in **Fig. 4 (a)**. After Al<sub>2</sub>O<sub>3</sub> deposition on thermally-grown SiO<sub>2</sub> on Si wafer, the second SiO<sub>2</sub> was grown by the oxidation of deposited metallic-Si at 800°C in O<sub>2</sub>, followed by the deposition of top-Al<sub>2</sub>O<sub>3</sub>. Finally Au top electrode was deposited. The increase of V<sub>fb</sub> by the formation of each interface was summarized in **Fig. 4 (b)**. From the thickness dependence of each layer we extracted the dipole layer strength formed at each interface. Note that the negative V<sub>fb</sub> shift which had been expected at SiO<sub>2</sub>-on-Al<sub>2</sub>O<sub>3</sub> interface (indicated as B)



Fig. 3 Top-SiO<sub>2</sub> CET (capacitance equivalent thickness) dependence of V<sub>fb</sub> of Au/top-SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si MOS capacitors, fabricated with or without ~3 Å-thick metallic-Si insertion between top-SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, followed by oxidation.

was effectively suppressed, probably due to the same mechanism as demonstrated in Fig. 3, while both of two Al<sub>2</sub>O<sub>3</sub>-on-SiO<sub>2</sub> interfaces (**A** and **C**) showed the dipole layer formation to induce positive V<sub>fb</sub> shift, as indicated by allows in Fig. 4 (b). Thanks to these selective formation of dipole layers, this laminated stack showed a very large V<sub>fb</sub> shift >+1.2 V by the sum of the effects of those dipole layers [10]. Since positive fixed charges were observed in the top-layer thickness dependence in our dielectrics (data not shown) such large positive shift must be dominated by the dipole layers. Such a large positive V<sub>fb</sub> shift is expected to help V<sub>t</sub> tuning of high-V<sub>t</sub> FETs, for example, power MOSFETs.

#### 4. Conclusions

At the interface between two different dielectrics the ionic displacements may induce a pair of sheet charges to result in a dipole layer formation, which is well described by the model considering net displacements of oxygen ions, or those of other ions driven by interface reactions. Based on the technique to control the dipole layer formation at  $SiO_2$ -on- $Al_2O_3$  interface by limiting oxygen supply during the  $SiO_2$  growth, we demonstrated a remakably large  $V_{\rm fb}$  shift using  $Al_2O_3/SiO_2$  laminated stack.

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Fig. 4 (a) Cross section TEM image of  $(AI_2O_3/SiO_2)_2$  on Si to demonstrate >1.2V V<sub>fb</sub> shift by dipole layers. (b) Observed V<sub>fb</sub> after the formation of each interface **A**, **B**, and **C** as indicated in (a). "Reference" represents the data for bottom-SiO<sub>2</sub>/Si stack.