

Understanding on the Impact of Interface Reactions on Dipole Strengths at MgO/SiO₂ and Y₂O₃/SiO₂ Interfaces

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Abstract

We studied the dipole-induced flat band voltage (V_{fb}) shift in MgO/SiO₂ and Y₂O₃/SiO₂ stacks annealed at various temperatures. The V_{fb} for pristine MgO/SiO₂ and Y₂O₃/SiO₂ interfaces were negatively shifted. But they shifted positively after higher temperature annealing, accompanied with silicate formation. The origin of the dipoles is discussed by paying attention to the chemical stability of the interfaces.

1. Introduction

Tuning high-k oxide composition to control the interface dipole at high-k/SiO₂ has been one of the strategies to manipulate the threshold voltage of MOSFETs[1]. Some high-k materials induce positive shift of flatband voltage (V_{fb}), but others result in negative shift. However, the impact of processing conditions on dipole strength has not been fully understood. Both MgO and Y₂O₃, which easily form silicate of certain thickness when deposited on SiO₂[2], show negative shift of V_{fb} by dipole formation[1, 3, 4]. In this paper we investigate the change in dipole strength at the MgO/SiO₂ and Y₂O₃/SiO₂ interfaces subjected to different temperature annealing and discuss the possible driving force of the dipole formation by paying attention to the chemical stability of the interfaces.

2. Experimental

After thermal growth of oxide on Si, MgO or Y₂O₃ were deposited using RF sputtering. The samples were annealed in 0.1% O₂ ambient under different temperatures (400-900°C), followed by the deposition of Au gate electrode, to form MIS capacitors. As the final step, forming gas annealing at 400°C was conducted. For MgO stacks, ~3nm-thick HfO₂ layers were deposited on MgO to avoid moisture absorption. The Y-silicate films with different compositions were also deposited by cosputtering of Y₂O₃ and SiO₂, followed by annealing at 400°C. To determine the composition of the films, x-ray photoelectron spectroscopy (XPS) was employed.

3. Results and Discussions

Dipole strength of MgO/SiO₂ stacks annealed at different temperatures were extracted by plotting CET vs $\Delta V_{fb}(\text{highk-SiO}_2)$ diagram as shown in Fig. 1(a). After excluding the fixed charge effects, ΔV_{fb} caused by dipole formation was obtained as summarized in Fig. 1(b). The dipole at MgO/SiO₂ interface shifts V_{fb} negatively for 600°C annealing, which is consistent with previous reports[3, 4], while the negative dipole disappears and even certain amount of positive dipole is formed at higher temperatures. Note that the charge effects of HfO₂ capping layers were confirmed as negligibly small. Similar trends

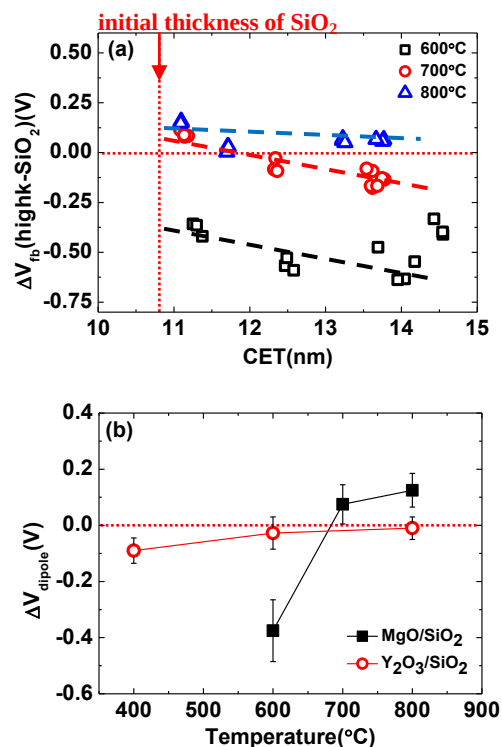


Fig. 1 (a) CET vs $V_{fb}(\text{highk-SiO}_2)$ diagram of MgO/SiO₂ annealed at different temperatures, the initial thickness of SiO₂ is 10.8nm. (b) Temperature dependence of dipole strengths of MgO/SiO₂ and Y₂O₃/SiO₂.

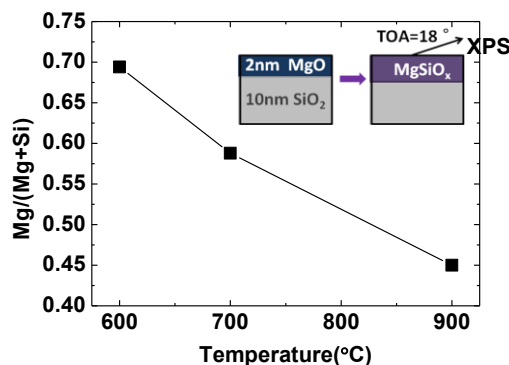


Fig. 2 Composition of ~2nm thick MgO samples annealed at different temperatures calculated from Mg2p and Si2p using XPS with a take-off angle of 18°.

were also observed for Y₂O₃/SiO₂ stacks as shown in Fig. 1(b).

To clarify the composition of silicate formed in near-interface region, thin (~2 nm) MgO on SiO₂ films annealed at different temperatures were characterized by XPS with a take-off angle of 18° to limit the detection depth around 1nm. The atomic ratio (Mg/(Si+Mg)) near the in-

terfaces for 600, 700 and 900°C samples are shown in **Fig. 2(a)**. According to the MgO-SiO₂ phase diagram, the interface is expected to be stabilized to form MgSiO₃ on SiO₂. Actually the near-interface composition is Mg-rich silicate at 600°C but approaches to MgSiO₃ by increasing the annealing temperature to 900°C. Such change of interface composition should correlate with the change of interface dipole strength. To investigate the validity of our considerations, we observed the dipole strength at the cosputtered Y-silicate/SiO₂ interfaces when we intentionally change the composition of the Y-silicate. As shown in **Fig. 3(a)** and **(b)**, the dipole-induced ΔV_{fb} for the Y₂O₃/SiO₂ interface is negative, while the negative dipole disappears for Y-silicate/SiO₂ with Y/(Si+Y)~0.5, which is corresponding to the chemically stable phase for this system (Y₂Si₂O₇). Finally it becomes positive for Si-rich silicate.

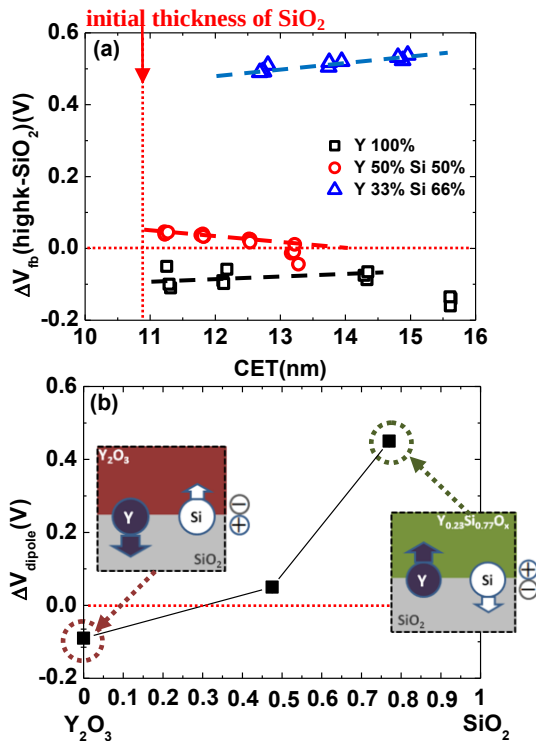


Fig. 3 (a) CET vs ΔV_{fb} (high-k-SiO₂) of Y₂O₃ and SiO₂ cosputtered samples and Y₂O₃/SiO₂ annealed at 400°C. The initial thickness of SiO₂ is 10.8nm. (b) Y/(Y+Si) atomic ratio dependence of dipole strengths. Inserts: schematics to explain how atomic migration at the interfaces leads to formation of dipole.

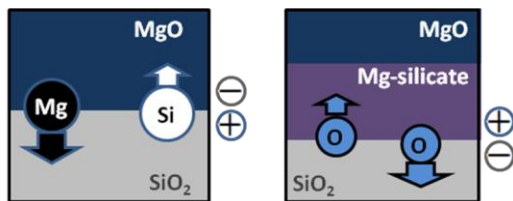


Fig. 4 Schematics of the proposed model explaining the origin of dipole-induced V_{fb} shift determined by atomic migration.

Dominant charge transfer caused by the migration of Mg at MgO/SiO₂ induces positive dipole, whereas the effects of cations are weakened and charge transfer is mainly dominated by the migration of O at silicate/SiO₂.

To explain the results so far, a possible model is discussed by paying attention to the chemical stability of the interface, which will determine the driving force of the atomic migration at the interfaces. For MgO/SiO₂ and Y₂O₃/SiO₂ interfaces, the oxides near the interfaces tend to react to form an interfacial layer with the chemically stable composition by the atomic redistribution at the interface. From molecular dynamics study of high-k/SiO₂ interfaces, redistribution of oxygen was suggested to be the origin of the interface dipole formation at Al₂O₃/SiO₂[5], but transfer of cations across the interface should have more important role in the case of Y₂O₃/SiO₂[6]. It would be also reasonable to assume that the displacement of both Mg into SiO₂ and Si into MgO at the interface will be mainly responsible for the dipole formation at MgO/SiO₂ system. As illustrated in **Fig. 4**, when the abrupt MgO/SiO₂ interface exists, we speculate that when migration of Si and Mg may have opposite effects, charge transfer across the interface would be dominated by the migration of Mg cations. Thus net positive charges appear on SiO₂ and negative charges on MgO side, resulting in the negative shift of V_{fb} . On the other hand, when silicate of certain thickness is formed, an abrupt MgO/SiO₂ interface no longer exists. The driving force to migrate Mg is weakened, and the amount of negative dipole strengths will decrease until disappearing when the silicate reaches to chemically stable composition (MgSiO₃). Considering higher oxygen density for MgO, it is not surprising that positive dipole finally appears after annealing at high temperature, since the transfer of cations are suppressed and the effect of oxygen displacement[1] may take over. The same model is applicable to the Y₂O₃/SiO₂ interface. The observed positive dipole formation for the Si-rich Y-silicate deposited on SiO₂ (shown in **Fig. 3(b)**), is consistent with our model, by assuming the driving force to separate into Y₂Si₂O₇ and SiO₂ to form stable interface. It induces upward migration of Y, which possibly result in positive charge on high-k and negative on SiO₂ side.

4. Conclusions

We have demonstrated that the abrupt MgO/SiO₂ and Y₂O₃/SiO₂ interfaces induce negative dipoles, but such negative dipole disappears by chemically stable silicate layer formation by annealing. It is considered that the chemical stability of the interface determines the driving force of negative/positive dipole formation at the interfaces.

Acknowledgements

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