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Chemical Bonding-Induced Dipole at the HfO_2/Si Interface

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1. Introduction

Formation of interface dipoles is a major issue in the V_{th} control of high-k gated MOSFETs, *e.g.,* the so-called Fermi level pinning of poly-Si/HfO_2 interfaces and large negative V_{FB} shift of direct-contact HfO_2/Si structures are most likely relevant to the interface dipoles [1,2]. Two distinct mechanisms have been proposed for the dipole formation at the HfO_2/Si interfaces, *i.e.*, chemical bonding-induced charge transfer and oxygen vacancy models [1,3-5]. For the former model, several theoretical studies suggested a critical role of interface Si-O bonds [3,4]. On the other hand, the interface Si-O bonds and vacancies have opposite thermal behavior: although the Si oxide decompose at high temperature (>600 ˚C) in inert ambient [6], the vacancies are supposedly produced under such conditions [7]. This difference provides a possibility for experimentally distinguishing these two effects. In this work, we therefore examine the impact of thermal treatment on the dipole of direct-contact HfO_2/Si interface.

2. Experimental

HfO_2 films were deposited by using an ultrahigh-vacuum (UHV) electron-beam deposition system [2,6]. We prepared two types of samples (Fig. 1). One is a HfO_2/thickness-graded SiO_2/n-type Si structure, which was used for investigating the dependence of V_{FB} on the thickness of interfacial Si oxide layer [2]. The other consists of direct-contact HfO_2/Si and HfO_2/~3-nm-SiO_2/Si structures. The contact potential difference (V_{CPD}) of this surface was measured by using an UHV Kelvin probe.

3. Results and Discussion

Figure 2 shows that the negative V_{FB} shift for the direct-contact HfO_2/Si structure is released by a monolayer thick interface Si oxide (~0.5 nm), suggesting that this phenomenon is related to an atomic-scale interface structure. The HfO_2-thickness dependence of V_{FB} shown in Fig. 3 shows that the negative V_{FB} shift is caused by interface dipoles rather than by fixed positive charges [2]. The effective work function (Φ_{eff}) of the HfO_2/SiO_2/Si stack structures is close to that of SiO_2/Si structures, suggesting that the dipoles in the HfO_2/SiO_2/Si stack structures are almost negligible. We therefore conclude that the large interface dipoles (~0.9 V) exist at the direct-contact HfO_2/Si interfaces.

It was reported that p-metal electrodes induce fixed charges in high-k materials [8]. We therefore applied the Kelvin prove to examine the intrinsic properties of the HfO_2/Si interfaces. Figure 4 shows the comparison of V_{CPD} between the direct-contact HfO_2/Si and HfO_2/SiO_2/Si stack surfaces, where $\delta V_{CPD}=V_{CPD}-V'_{CPD}$(on the HfO_2/SiO_2/Si stack surface). This result suggests that the surface of direct-contact HfO_2/Si structure is electrically charged in comparison to that of stack structure. The HfO_2-thickness dependence of δV_{CPD} shown in Fig. 5 shows that the dipoles of about 0.8 V exist in the HfO_2/Si structures even though the metal electrodes were not fabricated.

Figure 4 also shows that the dipole disappears after the UHV annealing (700˚C, 3 min), and appears again after the exposure of 8400 L O_2 at room temperature (1 L = 1×10^{-6} Torr · s). If vacancies in the HfO_2 film induce the interface dipoles, the dipole magnitude would increase after the UHV annealing. In addition, oxygen exposure likely terminates vacancies, so that the dipole should be reduced. It is obvious that our experimental results show the opposite tendency. The Si *2p* photoelectron spectra in Fig. 6 show that the as-prepared HfO_2/Si interface has a small amount of Si-O bonds (<1 ML). The interface Si-O bonds are reduced by the UHV annealing, and are slightly recovered by the O_2 exposure. From the above correlation, we consider that interface Si-O bonds contribute to the formation of interface dipoles.

The dependence of δV_{CPD} on the O_2 exposure time shown in Fig. 7 reveals that the dipole formation proceeds in a Langmuir manner. Note that the δV_{CPD} plot shows the difference of V_{CPD} between the direct-contact and stack structures, *i.e.*, the effect of HfO_2-surface reaction was subtracted. We therefore consider that the observed Langmuir manner reflects the Si oxidation reaction at the HfO_2/Si interface. Figure 7 also shows that the dipoles formed by the O_2 exposure are removed again by the UHV annealing. By using the Langmuir-type equation, we can estimate the maximum δV_{CPD} for infinite O_2 exposure time (δV^{∞}_{CPD}). The HfO_2-thikcness dependence of δV^{∞}_{CPD} shown in Fig. 5 shows that the room temperature O_2 exposure can recover about 75% of interface dipoles (Si-O bonds).

The schematic illustration in Fig. 8 summarizes the relationship between the dipole formation and interface reaction. The Si-O bonds at the HfO_2/Si interfaces are removed at 700˚C, so that the dipoles simultaneously disappear. During the O_2 exposure, oxygen can easily migrate through the HfO_2 layer [9], and reacts with Si atoms to form dipoles.

4. Conclusion

The *C-V* and Kelvin prove measurements revealed that large dipoles (>0.8 V) are induced at direct-contact HfO_2/Si interfaces. Based on the behavior during the thermal annealing and O_2 exposure, we proposed that interface Si-O bonds play an important role in the dipole formation at the HfO_2/Si interfaces.

Acknowledgments

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References

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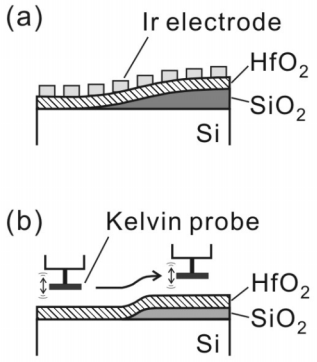

Fig. 1. Samples for the *C-V* (a) and Kelvin prove measurements (b).

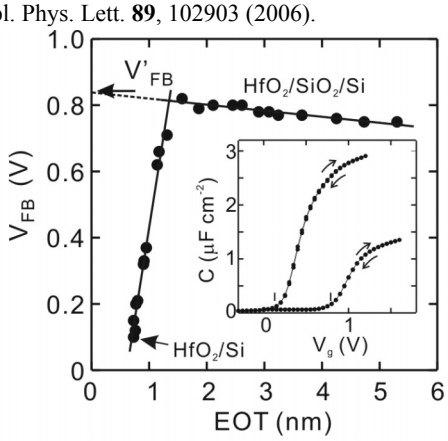

Fig. 2. V_{FB} shifts measured for the Ir/3.5-nm-HfO_2/thickness-graded SiO_2/Si structure.

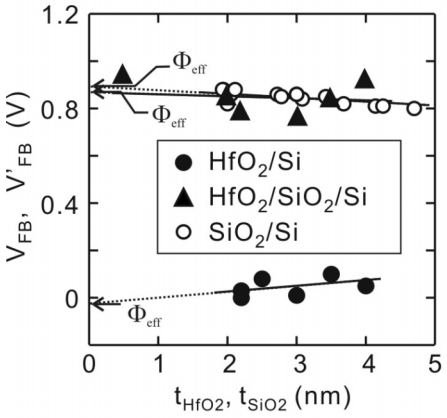

Fig. 3. Effective work functions (Φ_{eff}) of the HfO_2/Si, HfO_2/SiO_2/Si, and SiO_2/Si structures.

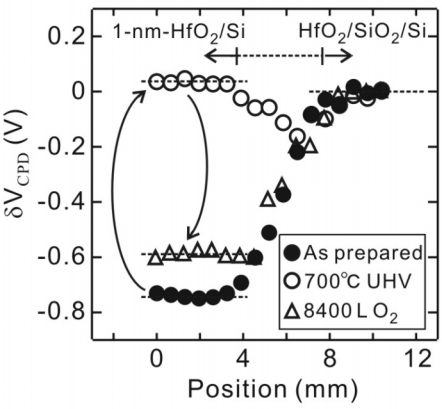

Fig. 4. Comparison of V_{CPD} between the HfO_2/Si and HfO_2/SiO_2/Si surface areas. $\delta V_{CPD}=V_{CPD}-V'_{CPD(HfO_2/SiO_2/Si)}$

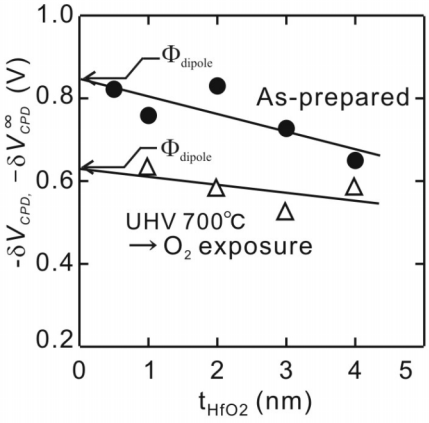

Fig. 5. Dipole magnitude (Φ_{dipole}) of the as-prepeared HfO_2/Si and O_2-exposed HfO_2/Si structures.

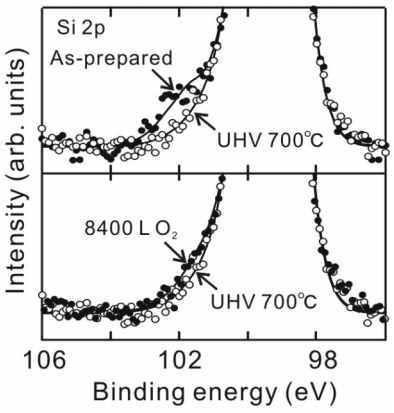

Fig. 6. Si *2p* photoelectron spectra of 1-nm-HfO_2/Si structure.

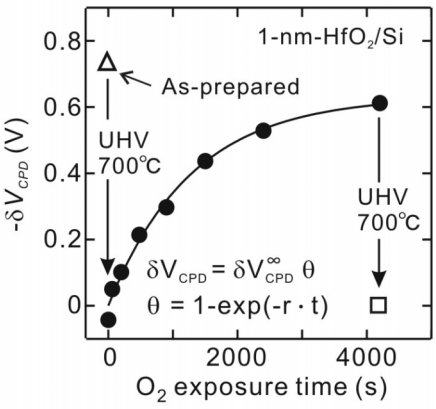

Fig. 7. Time dependent δV_{CPD} change in $2x10^{-6}$ Torr O_2.

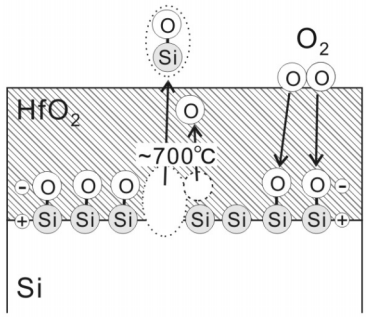

Fig. 8. Correlation between the chemical reaction and dipole formation at the HfO_2/Si interface.