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Physical Understanding of Determinant Factors for ϕeff on La-based High-k

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1. Introduction

It was reported that effective work functions (ϕeff) of p-metal elements such as Pt on Hf-based high-k depend strongly on annealing ambient: ϕeff on Hf-based high-k shows lower value than that on SiO_2 when the specimens are subjected to forming gas annealing (FGA), whereas it approaches to the value on SiO_2 when they are annealed in O_2 ambient [1,2]. Such ϕeff instability phenomenon is considered to be inherent in Hf-based materials. However, ϕeff instability of p-metals on La-based high-k materials, with which EOT is scalable to deep below 1 nm [3,4], has not been fully examined yet. On the other hand, a large Vfb shift, which is primarily determined by La-based high-k/SiO_2 interface properties, is reported [5,6]. Understanding for physical origins of the Vfb shift, however, still needs further work.

In this study, ϕeff instability at p-metal/La-based high-k is carefully examined. By taking advantage of pulsed laser deposition (PLD) method with optimized process condition, which enables direct contact of La-based high-k with Si [3,4], we address the intrinsic ϕeff of the metal/high-k without the effect of the high-k/SiO_2 interface. In addition, ϕeff change caused by the La-based high-k/SiO_2 interface is examined including the effect of annealing ambient, and its physical model is discussed.

2. Experimental

$LaAlO_3$ (LAO) and $La_2Hf_2O_7$ (LHO) were selected as La-based high-k materials. LAO and LHO films were deposited on HF-last or on 5nm thermal oxide covered 3-inch p-Si wafers by PLD, in which the film thickness was designed to increase from center to edge to change EOT values gradually for accurate estimation of ϕeff. HfSiON films and thermal oxide (SiO_2) with different thicknesses were also prepared. Metal ratios of these high-k films were as follows: La/Al=1 for LAO, La/Hf=1 for LHO and Hf/Si=0.5 for HfSiON. Pt was deposited on dielectrics by e-beam evaporation through shadow masks to define capacitor area. After the deposition of Pt, forming gas (H_2/N_2=10%) annealing was performed at 450 ^oC for 30min. Some specimens were additionally annealed in O_2 ambient at 400 ^oC for 30min after FGA. C-V measurements were performed for MIS capacitors both after FGA and FGA+O_2 annealing.

3. Results and Discussion

3.1 Difference of the ϕeff instability phenomenon between Hf-based and La-based high-k materials

Figs. 1 show Auger electron spectroscopy (AES) depth profiles for (a)LAO/Si and (b)LHO/Si. Si-oxide component was not detected and sharp interface was observed in both specimens. **Figs. 2** show EOT dependences of Vfb after FGA and FGA+O_2 annealing for (a)Pt/LAO/Si, (b)Pt/LHO/Si and (c)Pt/HfSiON/Si. Typical C-V curves are also shown in the insets. EOT and Vfb value were extracted by fitting C-V curves with ideal curves [7]. Linear relationships between EOTs and Vfb values are obtained as shown in **Figs.2**, indicating that these films contain negligible amount of extra charges and reliable ϕeff values can be extracted. **Fig. 3** shows the plots of ϕeff estimated from **Figs. 2**. In regard to the specimens after FGA, the large negative ϕeff shift that observed in the HfSiON device is not seen in the LHO and LAO devices. After the O_2 annealing, ϕeff on HfSiON approaches to the value on SiO_2, while those on LHO and LAO remain almost unchanged. The ϕeff instability of p-metals on Hf-based high-k was explained by formation and removal of oxygen vacancy at metal/high-k interface [1,2]. Based on this model, we think that ϕeff stability of p-metal on La-based high-k found in this study is owing to the strength of these materials against oxygen vacancy formation at metal/high-k interface, as is suggested for LHO [8].

It is worth noting that ϕeff on LAO and LHO were slightly higher than that on SiO_2 (**Fig. 3**). This is probably due to electron transfer from Pt to cation atoms in high-k (La and Hf), resulting in voltage drop at the Pt/high-k [9,10]. The larger positive ϕeff shift at Pt/LHO than that at Pt/LAO indicates that the larger amount of electron transfer occurs at Pt/LHO than that at Pt/LAO.

3.2 Physical origin of anomalous Vfb shift caused at La-based high-k/SiO_2 interface

The large negative ϕeff shift after FGA is clearly seen by inserting SiO_2 layer into LHO/Si, whereas such ϕeff shift is never observed without SiO_2 insertion (**Fig. 5 (a)**). The absence and existence of interfacial SiO_2 for LHO/Si and LHO/SiO_2/Si were experimentally confirmed by means of AES (**Fig.1(b)** and **Fig.4(a)**). Here we demonstrated that the voltage drop at around LHO/SiO_2 interface through FGA process is responsible for the negative ϕeff shift [5]. It is newly found that the ϕeff moves toward positive direction through O_2 annealing for Pt/LHO/SiO_2/Si (**Fig. 5 (a)**). The estimated ϕeff value for Pt/LHO/SiO_2/Si (5.5 eV) is almost identical to that for Pt/LHO/Si (5.4 eV) after the O_2 annealing, indicating that the voltage drop at LHO/SiO_2 interface disappears through the process. In contrast to ϕeff on LHO, ϕeff on LAO was found to be insensitive to both SiO_2 insertion and annealing ambient (**Fig. 5(b)**).

Based on these results, we speculate that the oxygen vacancy at La-based high-k/SiO_2 interface (Vo(i)) plays an important role in the negative ϕeff shift. There would be negative charge deviation of La_{Hf} in LHO due to different valence of La^{3+} and Hf^{4+}. La_{Hf} becomes energetically stable by adjacent Vo, because unoccupied state at the top of the valence orbital (O 2p) is filled by the electron transfer from Vo. If we assumed that such Vo would accumulate at the interface, a dipole between Vo(i) and La_{Hf} owing to the electron transfer decreases ϕeff. LAO/SiO_2 system would never suffer from the mechanism because of the same valence of La^{3+} and Al^{3+}.

4. Conclusions

The superiority of La-based high-k in ϕeff stability over Hf-based high-k is demonstrated. The ϕeff on LAO and LHO

are increased thanks to electron transfer from Pt to cation in high-k. The experiments using two stacks of LHO/SiO_2/Si and LHO/Si prove that not metal/SiO_2 interface but LHO/SiO_2 interface is responsible for the lowering of ϕeff on LHO. The change of ϕeff on LHO is due to dipole related to oxygen vacancy, which is not formed in the case of LAO.

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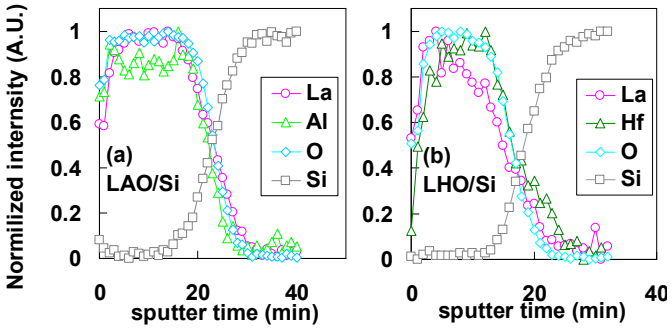
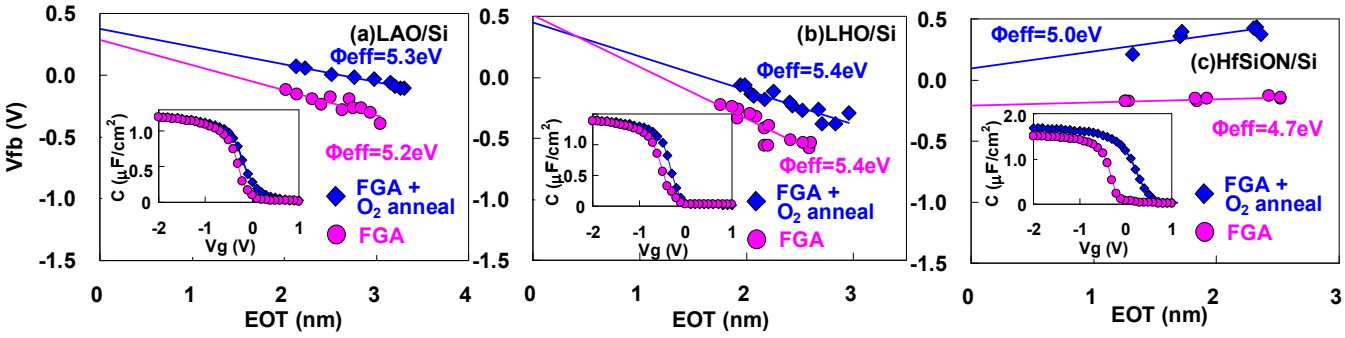


Figs. 1 AES depth profiles of LAO/Si (a) and LHO/Si (b). Si-oxide component was not detected and sharp interface was observed in both cases.



Figs. 2 EOT dependence of Vfb after FGA and FGA+O_2 annealing for Pt/LAO/Si (a), Pt/LHO/Si (b) and Pt/HfSiON/Si (c) MIS capacitors. Typical C-V curves are also shown in the insets. ϕeff was estimated from the intercept with Vfb axis (where EOT =0) of the linear extrapolation of the plot.

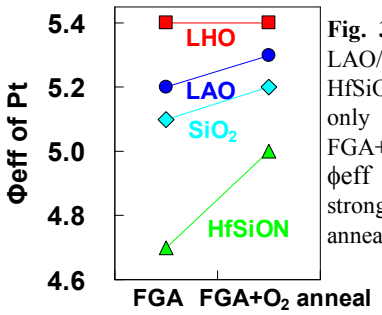
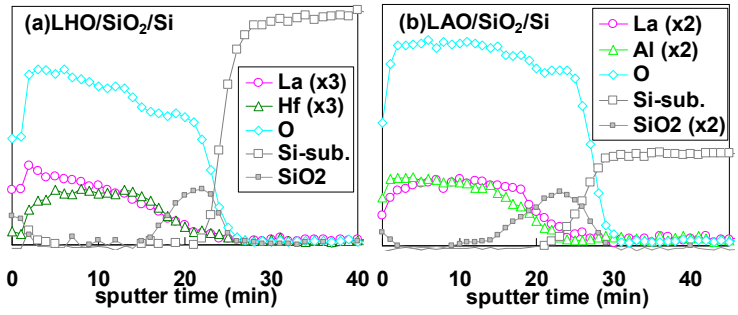
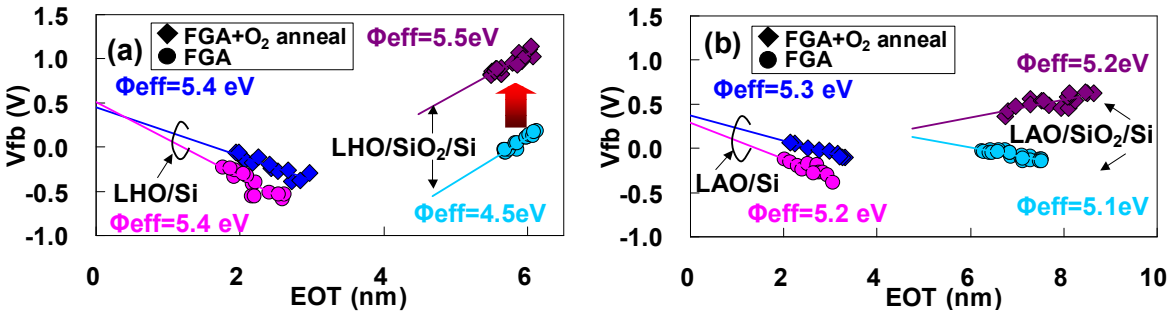


Fig. 3 ϕeff of Pt on LAO/Si, LHO/Si and HfSiON/Si-sub after only FGA and FGA+O_2 annealing. ϕeff on HfSiON strongly depends on annealing atmosphere.



Figs. 4 AES depth profiles of LAO/SiO_2/Si (a) and LHO/SiO_2/Si (b) after FGA. Target factor analysis was applied to determine chemical states..



Figs. 5 EOT dependences of Vfb after only FGA and FGA+O_2 annealing for Pt/LHO/Si, Pt/LHO/SiO_2/Si (a) and Pt/LAO/Si, Pt/LAO/SiO_2/Si (b). In the case of SiO_2-inserted capacitors, ϕeff was estimated assuming that the fixed charges responsible for the slope of EOT vs Vfb exist locally at high-k/SiO_2 interface because SiO_2 capacitor showed no EOT dependence of Vfb, indicating little charge at SiO_2/Si interface.