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Study of La Concentration Dependent V_{FB} Shift in Metal/HfLaOx/Si Capacitors

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1. Introduction

HfLaOx is a promising high-k material because it achieves both high-crystallization temperature and high permittivity [1]. In addition, it has been reported that La_2O_3 concentration increase in HfLaOx causes a negative shift of V_{FB} value [2] We think that it can be used for the V_{FB} tuning. Therefore, it is important to understand the mechanism of V_{FB} shift in this system. In this study we have investigated the origin of the La concentration dependence of V_{FB} in HfLaOx MIS capacitors.

2. Experimental

HfLaOx films were deposited on HF-last p-Si (100) by RF co-sputtering in Ar at room temperature. The post-deposition annealing in 0.1%-O_2+N_2 mixture was performed at 600°C for 30 sec. The forming gas annealing was performed at 500 °C, followed by Au or Al evaporation for gate electrode. After metal deposition, any annealing process is not performed. The film composition was determined by XPS.

3. Results and Discussion

V_{FB} values of Au/HfLaOx/Si capacitors with different La concentrations as a function of CET are shown in **Fig. 1**. The result suggests that fixed charges are relatively small. The capacitors with the larger La show the more negative V_{FB} shift, which is similar to the previously reported results [2].

Next, possible origins for the effective work function (Φ_{eff}) shift were investigated except trapped charged effect. The water absorption effect on V_{FB} was first checked, because La_2O_3 is known to be hygroscopic [3]. So, HfLaOx films with La concentrations of 20% and 40% were exposed to the air after post-deposition annealing, followed by gate electrode evaporation. **Fig. 2** shows the V_{FB} shift due to the air exposure. HfLaOx film with La concentration of 40% exhibited a larger shift than that of 20%. However the direction of V_{FB} shift is opposite (positive) in both films and it is not the origin for the V_{FB} shift.

It is likely that a dipole layer may exist in the MIS structure and cause a shift of V_{FB}. Note that the dipole layer in any position inside the film causes a given offset irrespective of the dipole position, so no HfLaOx thickness dependence should be observed as explained by Eq. (1) in the caption in **Fig.3(a)**. Four possible positions of the dipole layer were considered as shown in **Fig. 3(b)**; (1) Si/SiO_2, (b) SiO_2/HfLaOx, (3) HfLaOx/metal, and (4) HfLaOx/Si.

In order to clarify which dipole layer position in MIS structure dominantly affects V_{FB} shift, four kinds of MIS capacitors with different La concentrations in upper and lower parts were fabricated, as shown in **Fig.4**, where **t**he C-V curves corresponding to the respective capacitor structures are shown. It should be noted that V_{FB} in Cap.1 is exactly the same as that in Cap.4, while V_{FB} in Cap.2 is the same as that in Cap.3. The insensitiveness of the La concentration in the top interface clearly indicates that the Au/HfLaOx interface ((3) in **Fig. 3 (b)**) is not an origin for the V_{FB} shift with La concentration change, but a lower part (substrate side) of HfLaOx should be responsible for the V_{FB} behavior. To further confirm this result, we investigated the V_{FB} difference between Au and Al gate electrode MIS capacitors. **Fig.5 (a)** shows C-V curves using Au or Al gate electrode for three kinds of La concentration HfLaOx samples. Irrespective of La concentrations, the V_{FB} gap (ΔV_{FB}) between Au and Al gate electrode cases is about 1V, which is very similar to a value with the work function differences ($\Delta\Phi_M$) in the vacuum [4]. Φ_{eff} is plotted as a function of Φ_M in **Fig. 5 (b)**. In any La concentrations, the pinning parameter $S=\Delta\Phi_{eff}/\Delta\Phi_M \approx 1$, which implies that the top interface has very small effect, if any, on Φ_{eff} shift. The result in Fig. 5(b) also means that it was reasonable to assume no dipole layer at the La-60% and La-20% HfLaOx interface

It was reported that SiO_2 layer on high-k could suppress the V_{FB} shift of poly-Si/HfSiO/Si system [5]. So, from the viewpoint of the charge transfer between HfLaOx and Si substrate as a possible reason for V_{FB} shift, we compared HfLaOx on HF-Last Si and HfLaOx on 10nm-thick SiO_2/Si. In the case of using Hf-Last Si, the interface layer thickness was about 1nm. **Fig. 6** shows that in both cases, the difference of V_{FB} between La-66% and La-20% MIS capacitors is about 0.5V. Thus, it is concluded that 10nm-thick SiO_2 layer has very little to do with the La concentration dependence of V_{FB}, and that the charge transfer between HfLaOx and Si substrate ((4) in Fig. 3 (b)) is not the origin of the present V_{FB} shift, and furthermore that the SiO_2/Si interface possibility of the dipole layer ((1) in Fig. 3 (b)) is also ruled out.

From those considertaions, most of possible reasons have been excluded. One last and the most plausible origin is a dipole layer at HfLaOx/SiO_2 interface ((2) in Fig. 3 (b)). It is reported that high-k/SiO_2 interface can have a dipole [6]. Experimental results suggest that La introduction into HfO_2 could modulate the dipole density at high-k/SiO_2 interface, though microscopic understanding remains to clarify.

4. Conclusions

We have investigated V_{FB} characteristics of capacitors with HfLaOx dielectrics. V_{FB} value is dependent on La

concentration in HfLaOx and the increase of La concentration results in the negative shift of V_{FB}. We suggest that the most plausible origin is an existence of the dipole layer, which is dependent on the La concentration in HfLaOx, at HfLaOx/SiO_2 interface.

Acknowledgements
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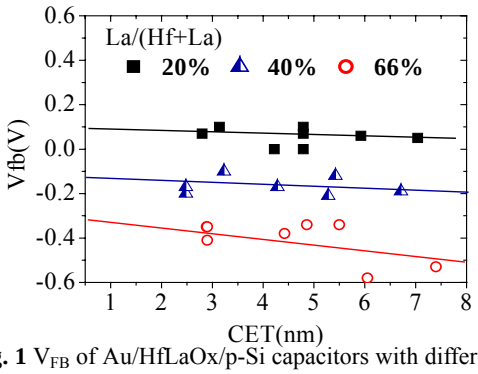

Fig. 1 V_{FB} of Au/HfLaOx/p-Si capacitors with different La concentrations as a function of CET.

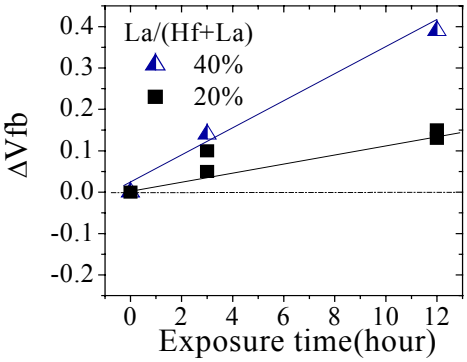

Fig. 2 V_{FB} shift as a function of the air exposure time. V_{FB} values are shifted to positive direction, which is opposite to the experimental V_{FB} shift.

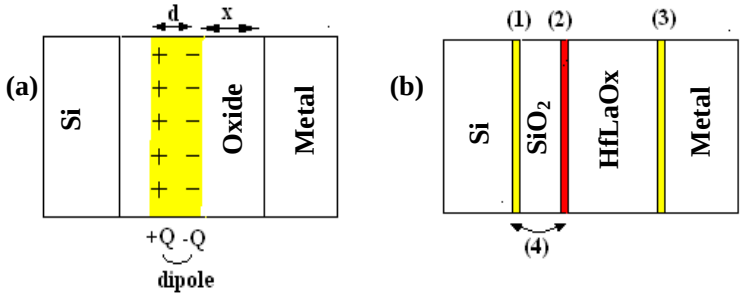

Fig. 3 (a) Simplified MOS structure with a dipole layer inside the film. The dipole layer causes a given V_{FB} shift irrespective of its position, as follows.

$$\Delta\Phi = Vfb - W_{ms} = -\frac{Q(x+d)}{\varepsilon_{ox}} + \frac{Q\cdot x}{\varepsilon_{ox}} = -\frac{Q\cdot d}{\varepsilon_{ox}} \quad \cdots\cdots \text{Eq.1}$$

(b) Possible dipole layer position; (1)Si/SiO_2 interface, (2) SiO_2/HfLaOx interface (3)HfLaOx/Metal interface, (4) interaction between HfLaOx and Si substrate [5].

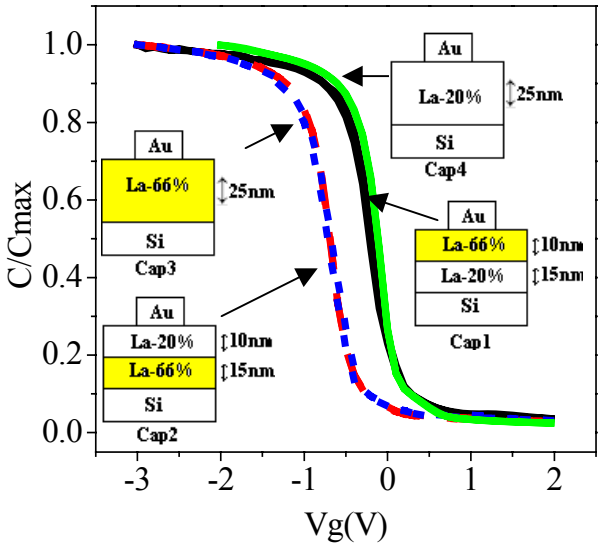

Fig. 4 C-V curves of four kinds of MIS capacitors with different La profile in the dielectrics. Cap1:Au/66%/20%/Si, Cap2:Au/20%/66%/Si. Cap3:Au/66%/Si, Cap4: Au/20%/Si. This result clearly shows that the bottom HfLaOx/SiO_2 interface determines the experimental V_{FB} shift.

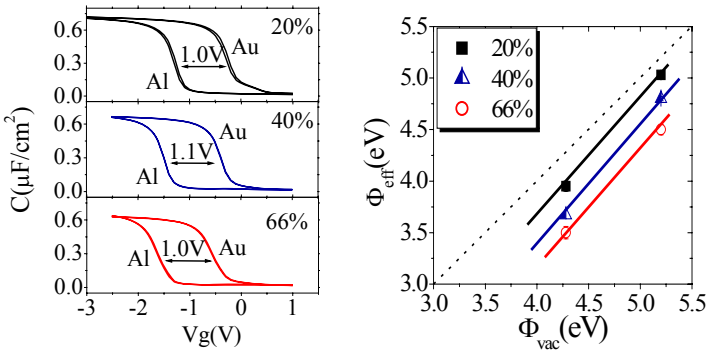

Fig. 5 (a)C-V curves for Au or Al/HfLaOx(20nm)/p-Si capacitors. $\Delta V_{FB}=V_{FB}(Au)-V_{FB}(Al) \approx 1V$ for all La composition. **(b)** Φ_{eff} as a function of vacuum work function

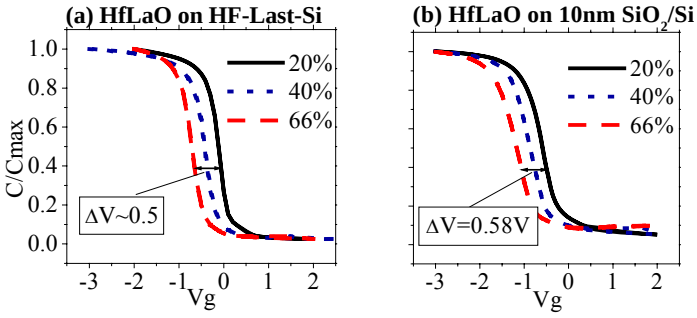

Fig. 6 Comparison of C-V curves of Au/HfLaOx(20nm)/I.L/Si and Au/HfLaOx(20nm)/ SiO_2(10nm) /Si. In both structure, the difference of V_{FB} (66% and 20%) is about 0.5~0.6V.