Effective Control of Flat-band Voltage in HfO_2 Gate Dielectric with La_2O_3 Incorporation

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Abstract**—The origin of negative flat-band shift using La_2O_3 incorporation in HfO_2 dielectrics has been extensively examined. From careful extraction of effective work function of gate electrode and fixed charges at each interface, it has been revealed that La_2O_3 at high-k/Si substrate or high-k/SiO_2 interface has either large amount of positive fixed charges or an additional dipole of 0.36 V compared to that of HfO_2/Si or HfO_2/SiO_2. Stacked MOSCAPs were fabricated and the C-V characteristics show that flat-band voltage shift is mainly determined by high-k film which is in contact to Si or SiO_2. Using HfLaO with different La concentration, the amount of shift in flat-band voltage could be well controlled, which might be due to the diffusion or pile-up of La atoms to the interface over 420 °C. This study provides further insights in controlling the threshold voltage of HfO_2 based oxides.**

I. INTRODUCTION

In complementary metal-oxide-semiconductor (CMOS) technologies, SiO_2 has been used as the gate dielectric for more than 30 years. However, large direct tunneling leakage current through thin SiO_2 film due to downsizing, alternative gate dielectrics with high permittivity (high-k) have been extensively examined [1]. HfO_2 based materials have been the promising candidates as gate dielectric thanks to its high temperature endurance with relatively high carrier mobility . One of the issues of HfO_2 based oxides is the difficulty in controlling the threshold voltage (V_{th}), as relatively high V_{th} is obtained, whatever the electrode material is. On the other hand, La_2O_3 possesses a higher permittivity compared to HfO_2 and is thermodynamically stable on Si [2]. Recently, caping or incorporation of La_2O_3 into HfO_2 has been proposed to negatively shift the V_{FB} for nMOSFET, however, the detailed mechanism is still unclear [3], [4].

In this paper, firstly we report a careful extraction method of effective work function (EWF) of gate electrode using thickness dependent flat-band voltage (V_{FB}) relation. Then, various combinations of La_2O_3 and HfO_2 stacked oxides are examined to observe the interface which is dominant for V_{FB}. Finally, HfLaO films with different La concentration were used to elucidate the effect of numbers of La atoms at the interface.

II. EXPERIMENTAL

High-k dielectrics were deposited on a 300nm-thick-SiO_2 isolated n-Si(100) wafer either with HF-last treatment or with thermally grown oxide layer with oxidation to grow 3.5nm-thick-SiO_2. HfO_2 and La_2O_3 were deposited by electron beam evaporation with O_2 supply of 0.3 sccm at a pressure of 1×10^{-4} Pa, where the base pressure was pumped down to 1×10^{-8} Pa to avoid any contamination. The substrate temperature and the deposition rate was set to 300 °C and 0.3 nm/min, respectively. HfLaO film was fabricated by depositing HfO_2 and La_2O_3 at the same time with controlled deposition rate to change the composition. The thickness of each film was designed to be 5 nm. After the high-k deposition, 60nm-thick-tungsten (W) was *in-situ* deposited by sputtering without exposing to air to avoid any moisture or carbon absorption. W was patterned by reactive ion etching (RIE) using SF_6 chemistry to form gate electrode for MOS capacitors. Wafers were then post-metallization annealed (PMA) in a rapid thermal annealing (RTA) furnace either in N_2 or in forming gas (FG)(N_2 : H_2 = 97% : 3%) ambient. N_2 annealing was carried out at 300 °C or 500 °C for 5 min, while FG annealing was done for wafers with SiO_2 interfacial oxide at 420°C for 30 min. Backside Al was deposited as a bottom electrode by thermal evaporation. Finally, capacitance-voltage (CV) characteristics of MOS capacitors were measured at 100 kHz and 1 MHz using Agilent 4284A precision LCR meter.

III. EFFECTIVE WORKFUNCTION EXTRACTION

The effective work function (EWF) of metal on a single oxide layer can be derived by the flat-band voltage shift on different oxide thickness, which can be expressed as Eq. (1),

$$V_{FB} = -EOT\left(\frac{Q_0}{\varepsilon_0\varepsilon_{ox}}\right) + \frac{\varphi_{ms}}{q} + q\Delta_{SiO2} \qquad (1),$$

where Q_0 is the fixed charge at oxide/Si interface, φ_{ms} is the work function difference of metal and Si substrate and Δ_{SiO2}

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is the dipole at metal/oxide interface. The fixed charges inside the oxide layer are neglected as the effects of these charges are small. The EWF of metal is defined as $EWF=\varphi_{ms}/q + \Delta q_{SiO2}$, which can be obtained by the y-intercept from the V_{FB}-EOT slope. When interfacial SiO_2 layer is inserted underneath high-k oxide, then the Eq.(1) can be modified to form Eq.(2).

$$V_{FB} = -EOT\left(\frac{Q_1+Q_0}{\varepsilon_0\varepsilon_{ox}}\right) + \frac{Q_1 \times EOT_{SiO2}}{\varepsilon_0\varepsilon_{ox}} + \frac{\varphi_{ms}}{q} + q\Delta_{high-k} \qquad (2).$$

Here, Q_1 is the fixed charge at high-k/SiO_2 interface and $q\Delta_{high\text{-}k}$ is the dipole presented at high-k/metal interface. Therefore, EWF of metal on high-k/SiO_2 stack can be expressed as Eq.(3).

$$EWF = \frac{Q_1 \times EOT_{SiO2}}{\varepsilon_0\varepsilon_{ox}} + \frac{\varphi_{ms}}{q} + q\Delta_{high-k} \qquad (3).$$

A schematic model of the charge locations in a Metal/high-k/SiO_2/Si stack is illustrated in figure 1 [5].

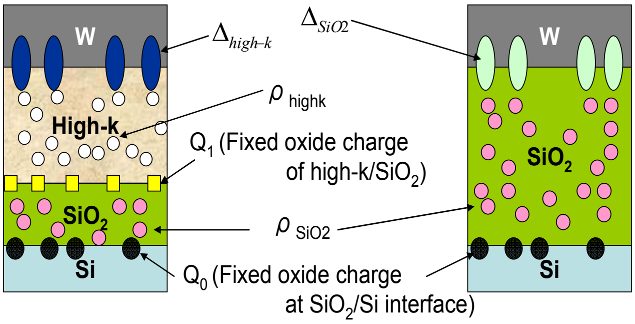

Figure 1. Schematic model of the charge locations used in the extraction of fixed charge.

Using these formulas, EWFs of W on SiO_2, La_2O_3 and HfO_2, were calculated. Figure 2(a) shows the C-V characteristics of MOS capacitors with different HfO_2 or La_2O_3 thickness on SiO_2(3.5nm) interfacial layer. Also capacitors with different SiO_2 thickness are shown. The thickness of La_2O_3 and HfO_2 vary from 5 to 10 nm. It is clear that V_{FB} of the C-V curves with HfO_2/SiO_2 was placed at positive side compare to those of SiO_2 and La_2O_3/SiO_2. Figure 2(b) shows the V_{FB}-EOT plot of the obtained CV curves, in which Q_0 of -1.7×10^{12} cm^{-2} can be obtained by SiO_2 capacitors. Q_1 on La_2O_3 and HfO_2 can be estimated to be 1.6×10^{12} cm^{-2} and -2.8×10^{12} cm^{-2}, respectively using Eq(2). In this calculation, the presence of La-silicate layer, which was revealed by TEM observation, was neglected for simplicity. Therefore, the EWF of W can be estimated as shown in table 1, where EWF on La_2O_3 shows little difference (0.06 eV) to that of SiO_2.

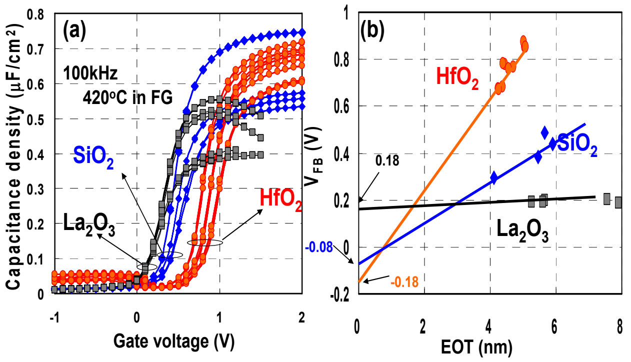

Figure 2. (a) C-V characteristics of MOS capacitors with different gate oxide. SiO_2, HfO_2/SiO_2(3.5nm) and La_2O_3/SiO_2(3.5nm) were shown. (b) V_{FB}-EOT of the obtained C-V curves

TABLE I. EFFECTIVE WORKFUNCTION OF W GATE ELECTRODE ON SiO_2, La_2O_3 AND HfO_2 ESTIMATED FROM FIGURE 2

Oxides	SiO_2	La_2O_3	HfO_2
EWF (eV)	4.26	4.20	4.56

IV. C-V CHARACTERISTICS OF HIGH-K STACKCKED MOS CAPACITORS

To elucidate the origin of V_{FB} shift of La_2O_3 and HfO_2 stacks, various combinations of double layer stacked films were examined. Figure 3 shows the schematic illustration of the fabricated MOS capacitors. The total thickness of the film was designed to have 5 nm, in which the thickness of each layer was modified from 1 to 4 nm.

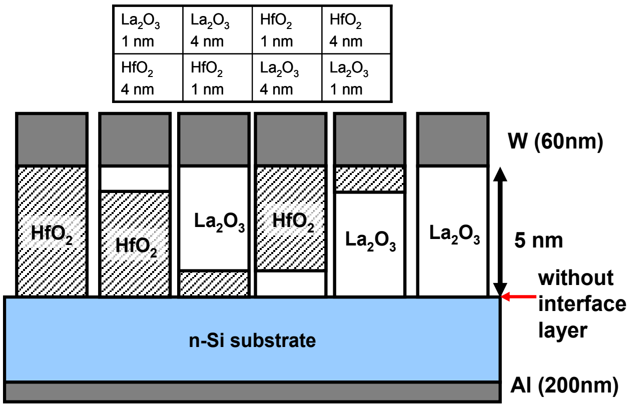

Figure 3. Schematic illustration of fabricataed La_2O_3 and HfO_2 stacked MOS capacitors. Capacitors with single La_2O_3 or HfO_2 layer are fabricated as references.

Figure 4 shows the C-V characteristics of the stacked capacitors with 300 °C PMA in N_2 ambient. The capacitors with La_2O_3 even with 1 nm insertion at high-k/Si interface showed negative V_{FB}. Almost no dependence on the insertion thickness was observed up to La_2O_3 single layer capacitor. On the contrary, the capacitors with HfO_2 at the Si interface showed positive V_{FB}, which are close to HfO_2 single layer capacitor. Therefore, it is clear from these results that the main cause for shifting the V_{FB} is determined by the high-k, which is in contact to Si substrate. As the ratio of La_2O_3 and HfO_2 has no dependence in C-V curves, the fixed charges at the interface of La_2O_3 and HfO_2 can be ignored. Thus, large amount of fixed charges or dipole at the interface can be the reason for this V_{FB} shift, in which both effects are difficult to separate. If we assume that the voltage change were all caused by the fixed charges at Si interface, the additional charge density can be estimated to be 7.2×10^{14} cm^{-2}, which seem to be too large in reality. Meanwhile, if a dipole is presented as a main origin of flat-band shift, amount of 0.36 V can be calculated at the interface.

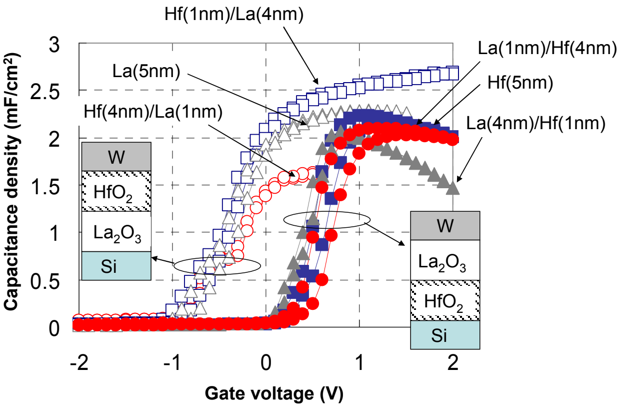

Figure 4. C-V characteristics of La_2O_3 and HfO_2 stacked MOS capacitors. The annealing was performed at (PMA 300°C).

The V_{FB} shifts of La_2O_3 and HfO_2 ratio of the stacked capacitors on annealing temperature are depicted in Figure. 5. It is clear that the high-k, which is in contact to Si substrate, determines the V_{FB} from as-deposited film up to 500 °C annealing.

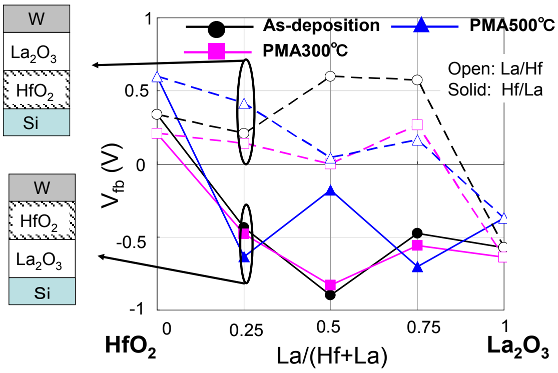

Figure 5. Flatband voltages of La_2O_3 and HfO_2 stacked capacitors with different annealing temperatures.

V. FLATBAND VOLTAGE OF HFLAO FILM

V_{FB} of HfLaO, a mixture of La_2O_3 and HfO_2 with different concentration, was examined by co-evaporation of the oxides for 1 nm. After HfLaO deposition, 4nm-thick-HfO_2 was deposited over HfLaO film. Figure 6 shows the obtained C-V curves of W/HfO_2/HfLaO stacks either on Si or on a thermally oxidized wafer. The flat-band voltage from C-V curves of HfO_2/HfLaO at 300 °C annealing showed relatively close to that of HfO_2 single layer. However, with an annealing at 500 °C, HfLaO with La_2O_3 concentration of 80% and 50% showed the same C-V curves as La_2O_3 single layer. Similar results were also observed in capacitors with SiO_2 interfacial layer, shown in figure 6(c). These results indicated that, diffusion of La_2O_3 to the substrate or SiO_2 interface occured when the samples were annealed at high temperature over 420 °C and finally La rich layers could be formed as a result of La pile-up at the bottom of HfLaO. The V_{FB} shift relative to HfO_2 single layer on annealing temperature is summarized by La_2O_3 composition in figure 7.

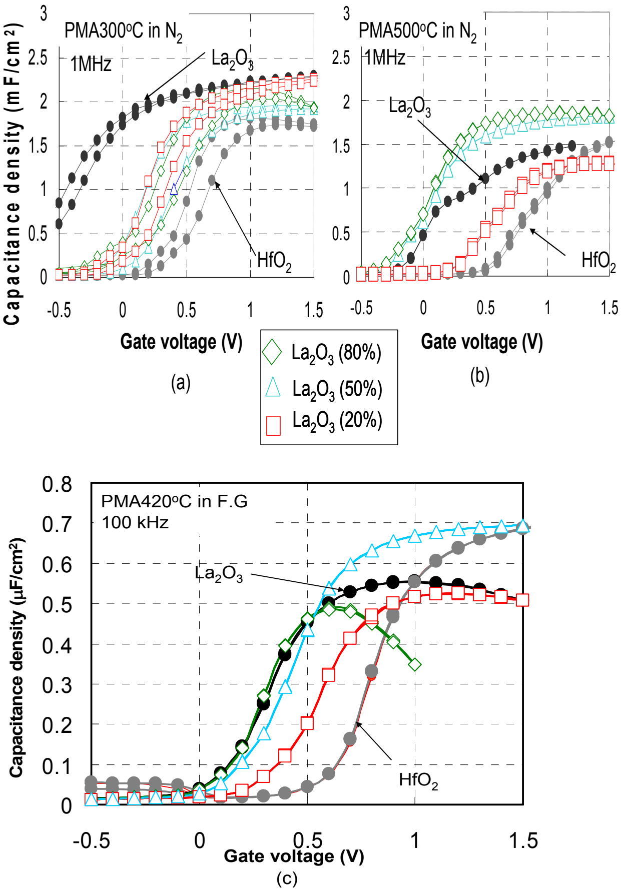

Figure 6. (a) C-V characteristics of HfO_2(5nm)/LaHfO(1 nm) on Si after PMA 300 °C , (b) 500 °C in N_2 and on (c) SiO_2(3.5nm)/Si

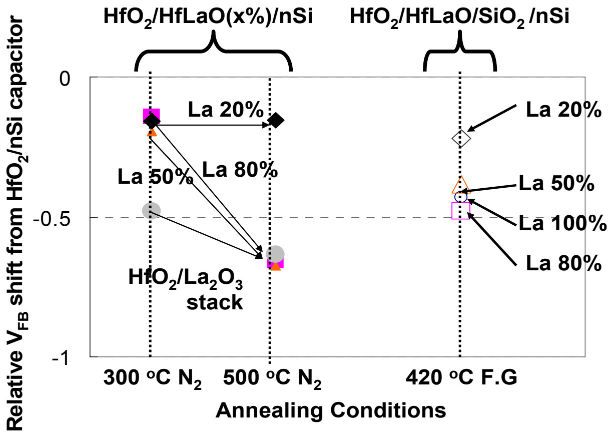

Figure 7. Relative V_{FB} difference of HfO_2/HfLaO to HfO_2 single layer.

VI. DISCUSSION

The amount of La atoms in 1 nm-thick HfLaO film with concentration of 80, 50 and 20% can be estimated to be 0.76×10^{16}, 0.48×10^{16} and 0.19×10^{16} cm^{-2}, respectively. If all of the La atoms were diffused to pile-up at HfLaO/SiO_2 interface, it can be speculated that La monolayer can be formed when HfLaO film with 80 or 50% was used. In the case of HfLaO with La concentration of 20%, the number of La atoms was not enough to cover to form a layer, therefore, some amount of Hf atoms should exist at the interface. The schematic drawing of this hypothesis is illustrated in figure 8. Figure 9 shows the V_{FB} on the amount of La at the interface of high-k/SiO_2. This relation provides further insights in controlling the threshold voltage of HfO_2 based oxides using the amount of La atoms at the interface.

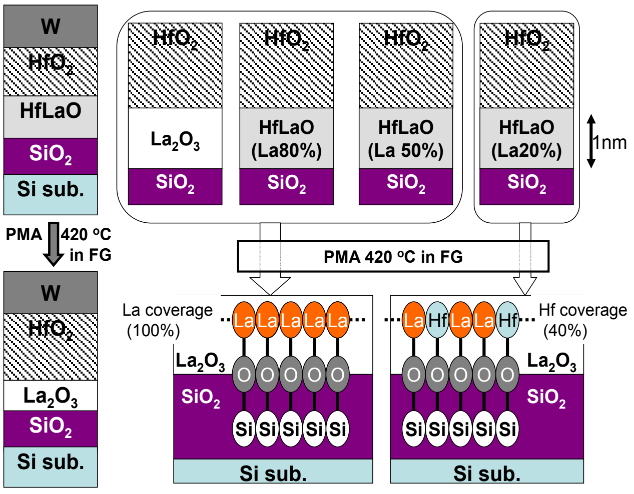

Figure 8. Model of La atoms which were separated from HfLaO layer.

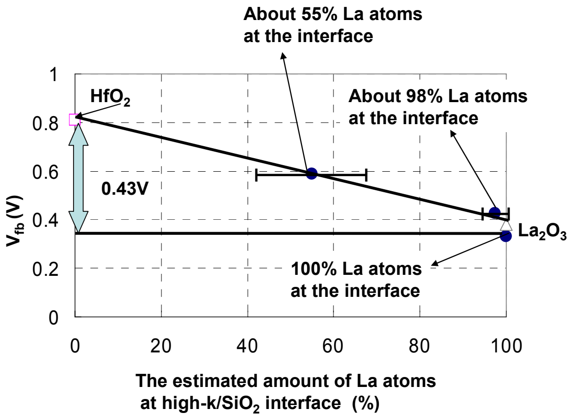

Figure 9. V_{FB} versus the amount of La atoms at high-k/SiO_2 interface

VII. CONCLUSION

The effective work function of tungsten on La_2O_3 or HfO_2 was carefully extracted by interface fixed charges and dipoles at metal/high-k interface, in which relatively large value was obtained on HfO_2. Double layer stacked structures using La_2O_3 and HfO_2 revealed that the effective way to shift the V_{FB} towards negative direction is inserting La_2O_3 at high-k/Si or high-k/SiO_2 interface. The amount of shift at the interface can be estimated to be 0.36 V. The same V_{FB} shift can be achieved with HfLaO film with high La concentration with annealing over 420 °C. On the contrary, low La concentration less than 20% showed a V_{FB} between La_2O_3 and HfO_2 single capacitors. These results strongly suggest that V_{FB} can be tuned over 0.4 V from pure La_2O_3 to pure HfO_2 stack by changing the amount of La atoms at high-k/Si interface.

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