T2R2 東京科学大学 リサーチリポジトリ
Science Tokyo Research Repository

論文 / 著書情報
Article / Book Information

Title	Control of Flat Band Voltage by Partial Incorporation of La2O3 or Sc2O3 into MfO2 in Metal/MfO2/SiO2/Si MOS Capacitors
Authors	M.Adachi, K.Okamoto, K.Kakushima, P.Ahmet, K.Tsutsui, N.Sugii, T.Hattori, H.Iwai
Citation	ECS Transactions:Physics and Technology of High-k Gate Dielectrics 5, Vol. 11, No. 4, pp. 157-167
発行日 / Pub. date	2007, 10
DOI	http://dx.doi.org/10.1149/1.2779557
権利情報 / Copyright	(c) The Electrochemical Society, Inc. 2007. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in ECS Transactions:Physics and Technology of High-k Gate Dielectrics 5, Vol. 11, No. 4, pp. 157-167

Powered by T2R2 (Science Tokyo Research Repository)

Control of Flat Band Voltage by Partial Incorporation of La_2O_3 or Sc_2O_3 into HfO_2 in Metal/HfO_2/SiO_2/Si MOS Capacitors

M. Adachi[1], K. Okamoto[1], K. Kakushima[2], P. Ahmet [1],
K. Tsutsui[2], N. Sugii[2], T. Hattori[1] and H. Iwai[1]
[1]Frontier Collaborative Research Center, Tokyo Institute of Technology,
4259-S2-20, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
[2]Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259-S2-20 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

Abstract

High-k/SiO_2 interfacial properties are most critical factors determining the high-k gate MOSFET characteristics. We fabricated MOS capacitors of metal/HfO_2/SiO_2/Si structures in which were contained in the HfO_2 layer. Flat-band voltage (V_{FB}) shifts were measured by changing composition in metal/HfO_2/$(HfO_2)_{1-x}(La_2O_3)_x$/SiO_2/Si and metal/HfO_2/$(HfO_2)_{1-x}(Sc_2O_3)_x$/SiO_2/Si structures. It was found that V_{FB} shift arises mainly from high-k/SiO_2 interface rather than metal/high-k interface. V_{FB} could be effectively controlled by incorporating La_2O_3 or Sc_2O_3 near the high-k/SiO_2 interface.

Introduction

Combination of metal and high-k dielectrics is necessary in order to achieve smaller EOT for eliminating the poly-Si gate depletion effect without excess leakage current. HfO_2 based materials have been the promising candidates for next generation gate dielectric thanks to its high temperature endurance and relatively high permittivity. One of the issues of HfO_2 based oxides is the difficulty in reducing the threshold voltage (*Vth*) as relatively high *Vth* were obtained with HfO_2 based oxides whatever the electrode material is. On the other hand, it has been reported that La_2O_3 and Sc_2O_3 produce negative shift in V_{FB} with respect to HfO_2 reference [1]. However, the detailed mechanism is not clarified yet. In this paper, first we extract the effective work function (*EWF*) of tungsten gate metal on high-k dielectrics, and then investigated the effect of La_2O_3 or Sc_2O_3 incorporation into a HfO_2 layer in a metal/HfO_2/SiO_2/Si MOS capacitor.

Experimental

Si(100) substrates with 200 nm-thick field SiO_2 in which diode holes were opened (1-10 ohm-cm) were cleaned in a mixed solution of H_2SO_4 and H_2O_2, followed by dipping in diluted HF. The substrates were then thermally oxidized to grow 3.5-nm-thick SiO_2 film. High-k dielectrics were deposited on these substrates by e-beam evaporation with O_2 partial pressure of $1x10^{-4}$ Pa. Tungsten (W) gate electrode was *in-situ* deposited by RF sputtering. The W film was lithographically patterned and etched by reactive ion etching (RIE) using SF_6 chemistry to form gate electrodes for MOS capacitors. Annealing in forming gas (3 %-H_2+97 %-N_2) was performed at 420 ^oC for 30 min. Finally, aluminum (Al) was thermally evaporated on backside of the wafers for bottom electrode. Capacitance-voltage (*C-V*) characteristics of the fabricated MOS capacitors were measured at 100 kHz using Agilent 4284A precision LCR meter, from which V_{FB} and EOT were calculated using NCSU CVC program.

The dielectrics studied here are La_2O_3, HfO_2 and Sc_2O_3. To evaluate the main reason of V_{FB} shift, laminated dielectric stacks of HfO_2/La_2O_3 were fabricated. Moreover, mixed dielectrics of HfO_2-La_2O_3 and HfO_2-Sc_2O_3 with HfO_2 atop were also fabricated by co-evaporation of the two oxides.

Results and Discussions

Effective Work Function *(EWF)* Extraction

A schematic model of the charge locations in a metal/SiO_2/Si structure and metal/high-k/SiO_2/Si structure are illustrated in Fig.1. As the thickness of the dielectric layer is small, the bulk charges of each oxide can be neglected. Indeed, the results shown in Fig. 2 revealed a linear relationship between V_{FB} and the EOT, thus, it is reasonable to assume low charge concentration inside the SiO_2 and the high-k layer. Under the assumption, the effective work function (*EWF)* of metal on a SiO_2 can be derived from the relation of V_{FB} and EOT using the following equation,

$$V_{FB} = -\left(\frac{Q_{SiO2/Si}}{\varepsilon_0 \varepsilon_{ox}}\right) \cdot EOT + \frac{\varphi_{ms}}{q} + q\Delta_{SiO2/Metal}, \quad (1)$$

where $Q_{SiO2/Si}$ is the fixed charge at the SiO_2/Si interface, φ_{ms} is the work function difference of gate metal and semiconductor and $\Delta_{SiO2/Metal}$ is the dipole at metal/oxide interface. The *EWF* of gate metal, defined as $\frac{\varphi_{ms}}{q} + q\Delta_{SiO2/Metal}$, can be extracted by the y-intercept from the V_{FB}-EOT slope. When interfacial SiO_2 layer (IL) is inserted between high-k dielectric and Si substrate, the Eq.(1) can be modified using total EOT as shown in eq.(2),

$$V_{FB} = -\left(\frac{Q_{high-k/IL} + Q_{SiO2/Si}}{\varepsilon_0 \varepsilon_{ox}}\right) \cdot EOT + \frac{Q_{SiO2/high-k}}{\varepsilon_0 \varepsilon_{ox}} \cdot EOT_{IL} + \frac{\varphi_{ms}}{q} + q\Delta_{Metal/high-k}. \quad (2)$$

Here, $Q_{high-k/IL}$, $\Delta_{high-k/Metal}$ and EOT_{IL} are the fixed charge at high-k/IL interface, the dipole at high-k/metal interface and the EOT of IL, respectively. Eventually, the *EWF* of metal on high-k/SiO_2 stack can be expressed as follows,

$$EWF_{(high-k)} = EWF_{(SiO2)} + (q\Delta_{high-k/Metal} - q\Delta_{SiO2/Metal}). \quad (3)$$

Figure 2 shows the typical *C-V* curves of La_2O_3/IL, HfO_2/IL and Sc_2O_3/IL capacitors. The difference between V_{FB}(HfO_2/IL) and V_{FB}(La_2O_3/IL) is about 0.48 V, whereas difference between V_{FB}(HfO_2/SiO_2) and V_{FB}(Sc_2O_3/SiO_2) is 0.15 V. Figure 3 shows the result of V_{FB} of La_2O_3/IL, HfO_2/IL and Sc_2O_3/IL capacitors with different high-k thicknesses. Capacitors with SiO_2 with different thickness are also shown to derive $Q_{SiO2/Si}$. Using the equations (1)-(3), *EWF* of W on SiO_2, HfO_2, La_2O_3 and Sc_2O_3 can be calculated and summarized in Table.1. The smallest *EWF* of 4.46 eV was obtained with La_2O_3, whereas relatively large value was obtained with HfO_2. These results suggest high

V_{th} in nMOSFET when HfO_2 is used as gate dielectrics. In the next subsection, the origin of V_{FB} is examined in detail.

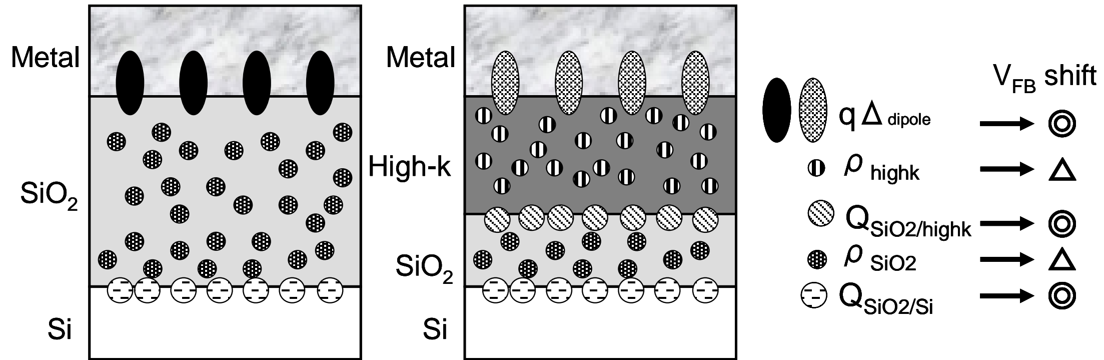

Fig.1 Schematic model of the charge locations used in the extraction of fixed charge.

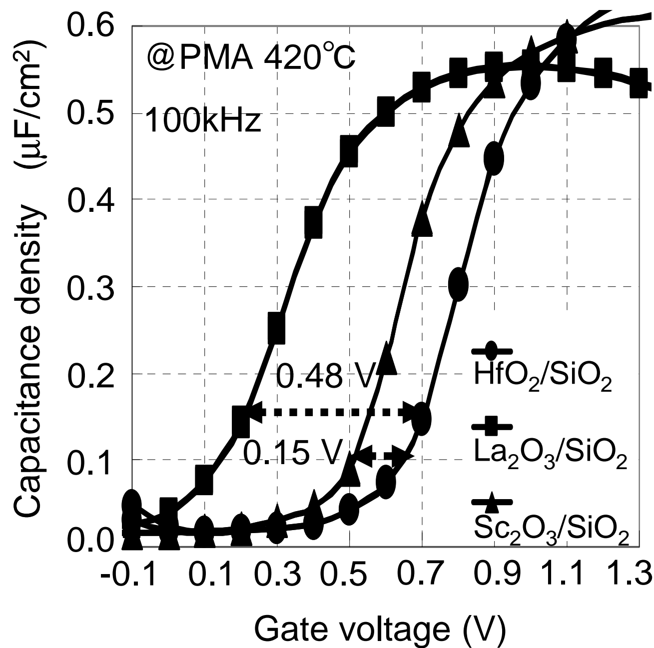

Fig.2 *C-V* characteristics of MOS capacitors with single layered high-k dielectric (HfO_2, La_2O_3, Sc_2O_3)

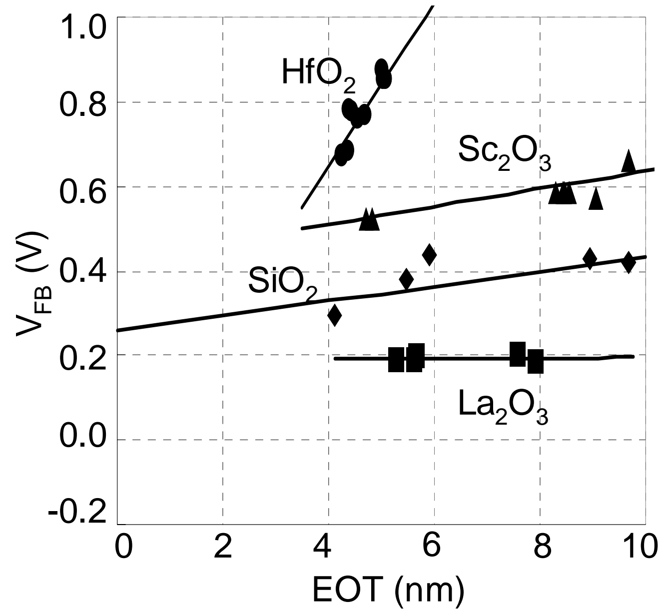

Fig.3 V_{FB}-EOT plot obtained from the analysis of *C-V* curves.

Table 1. Effective work function of W gate electrode on various gate dielectric (SiO_2, La_2O_3, HfO_2, La_2O_3)

Gate Oxide	SiO_2	La_2O_3	HfO_2	Sc_2O_3
EWF (eV)	4.59	4.46	4.80	4.75

C-V Characteristics of HfO_2/La_2O_3 Stack Structure

In order to investigate the V_{FB} shift on stacked dielectrics, double layer stacked films were fabricated, as shown in Fig. 4. Capacitors with single layer of HfO_2 or La_2O_3 are also fabricated as references. The total thickness of the high-k film was designed to have 5 nm. Figure 5 shows the *C-V* characteristics of W/HfO_2/La_2O_3/IL stacked MOS capacitors. The *C-V* curves of the stacked capacitors showed negative V_{FB}, which are close to that of the single La_2O_3 layer reference. From these results, it is clear that the V_{FB} shift is determined by the high-k material in contact to SiO_2 IL. It is known that positive charges or dipole at the interface could attribute to negative shift in V_{FB}, however, either or both effects on these results are not clarified yet. Nonetheless, it is expected that by changing the composition of high-k at the high-k/IL interface might allow precise V_{FB} control.

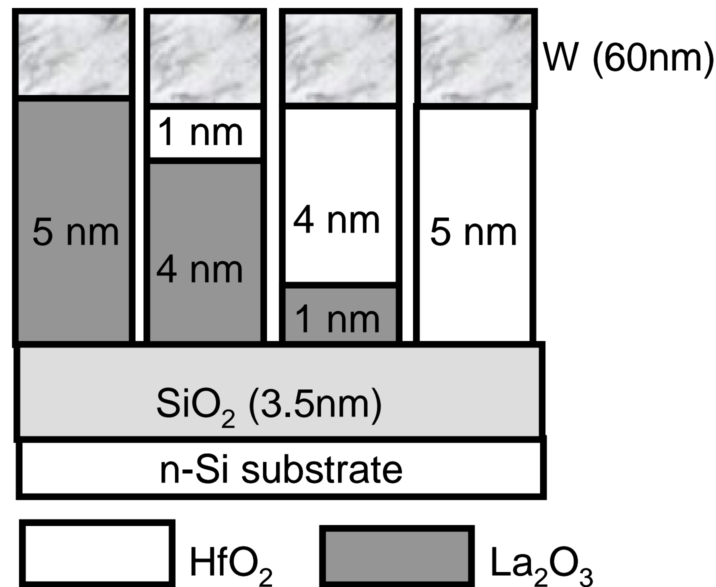

Fig.4 Schematic illustration of fabricated MOS capacitors with stack of HfO_2 and La_2O_3. Capacitors with single HfO_2 or La_2O_3 layer are fabricated as references.

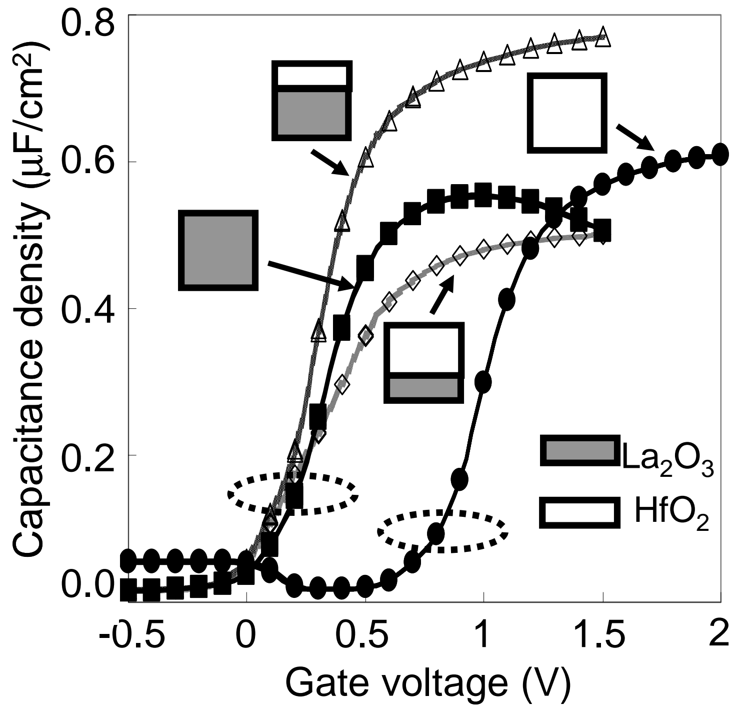

Fig.5 *C-V* curves for W/HfO_2/La_2O_3/SiO_2 stacked MOS capacitors.

V_{FB} Shift Dependence on La_2O_3 Incorporation at High-k/SiO_2 Interface

In this subsection, the V_{FB} shift depending on the amount of La_2O_3 at the high-k/SiO_2 interface is investigated. From the result that even 1 nm of La_2O_3 at high-k/SiO_2 interface can negatively shift the V_{FB}, the amount of the incorporated La_2O_3 to realize controllability of V_{FB} should be less than 1 nm. To obtain precise controllability of amount of La_2O_3 during the deposition process, we employed co-evaporation of HfO_2 and La_2O_3 with different concentration, those are 20, 50 and 80 %. The thickness of the mixed high-k layers was set to 1 nm. HfO_2 with 5 nm thickness was capped on the mixed high-k. The schematic illustrations of the fabricated capacitors are shown in Fig. 6. The *C-V* characteristics of the mixed high-k stack capacitors together with those of the references with La_2O_3 and HfO_2 capacitors are shown in Fig. 7. With the La_2O_3 concentration of 80%, the V_{FB} of *C-V* curves showed almost identical value for the La_2O_3 reference, where that of 20 % showed in between of those of HfO_2 and La_2O_3 references. With 50 % of La_2O_3 incorporation, the V_{FB} was slightly positive to the La_2O_3 reference. Also from these results, it is noted that the *EWF* of the gate metal is mainly dominated by the high-k/IL interface, not at the Metal/high-k interface. By plotting the V_{FB} on La_2O_3 concentration, as is shown in Fig. 8, we obtain a monotonic relation between concentration and V_{FB}. It can be concluded that V_{FB} can be effectively controlled by changing the concentration of the mixed high-k at the high-k/IL interface.

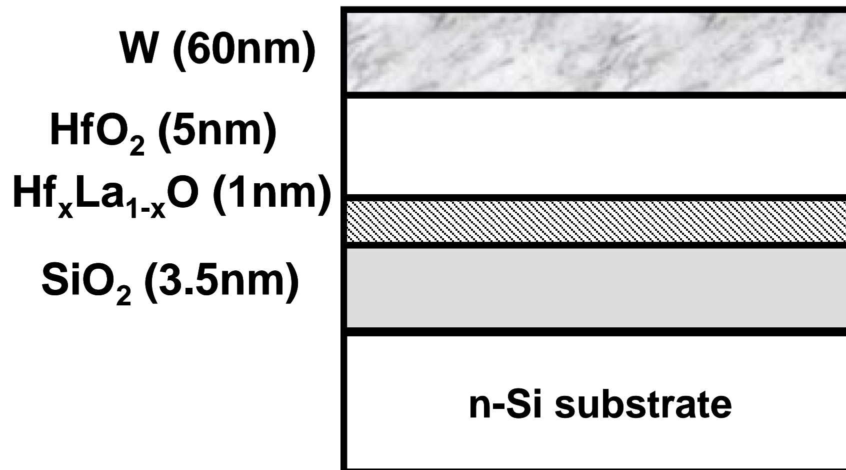

Fig.6 Schematic illustration of fabricated MOS capacitor incorporating La_2O_3 into HfO_2/SiO_2 interface

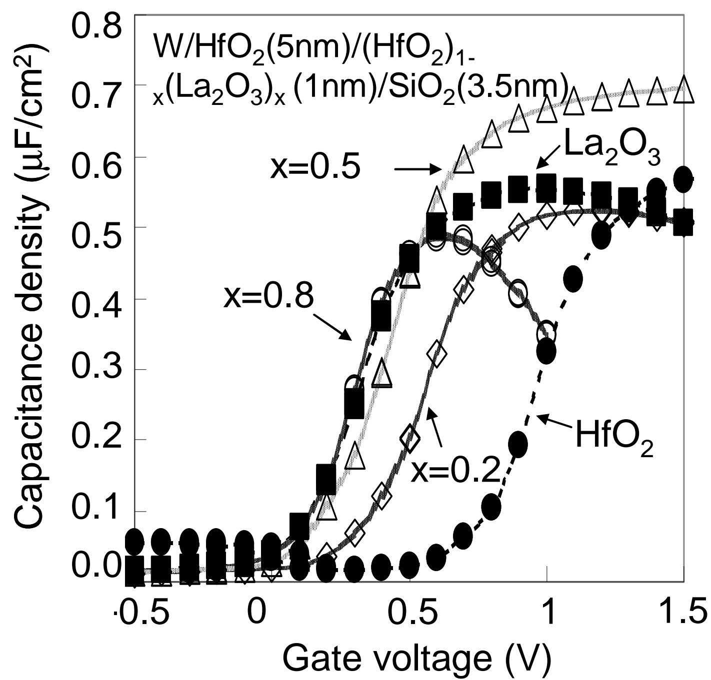

Fig.7 *C-V* curves of $W/HfO_2/(HfO_2)_{1-x}(La_2O_3)_x/SiO_2$ structure

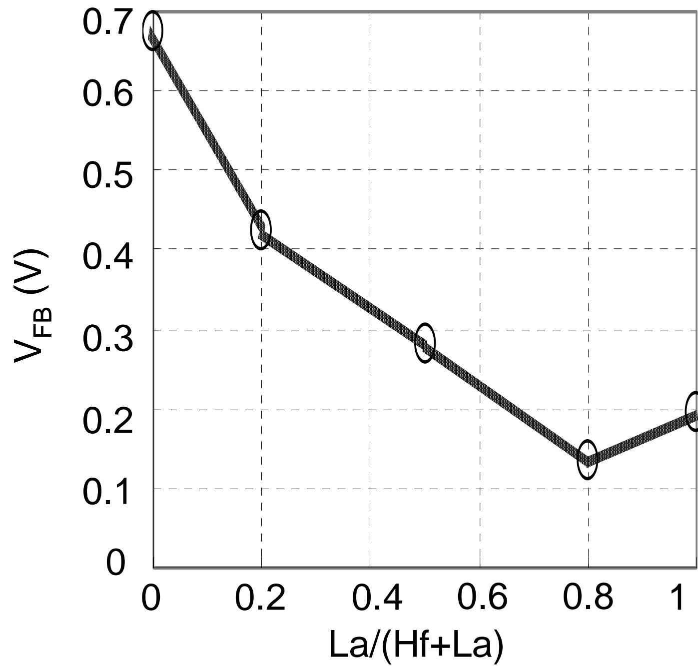

Fig.8 V_{FB} shift depending on concentration of incorporation La at HfO_2/SiO_2

<u>V_{FB} Controlled by Sc_2O_3 Incorporation into HfO_2</u>

The same experiments were carried out using Sc_2O_3 and HfO_2. In this case, the thickness of Sc_2O_3-HfO_2 mixed high-k and HfO_2 capping layer were set to 5 nm and 0.5 nm, respectively. The structure is depicted in Fig. 9. The concentrations of Sc_2O_3 were set to 33, 50 and 67%. Figure 10 shows the *C-V* curves of the Sc_2O_3 incorporated HfO_2 capacitors. Also Sc_2O_3 and HfO_2 references are shown. Negative shifts of V_{FB} with increase in the concentration of Sc_2O_3 were obtained. The relation between the concentration and V_{FB} is shown in Fig. 11. From this figure, the V_{FB} control range of 0.15 V was achieved using Sc_2O_3 incorporation into HfO_2. This value is smaller than that of La_2O_3, which can be expected from Sc_2O_3 single layer capacitor. Therefore, Sc_2O_3 and La_2O_3 incorporation technique is useful as fine and coarse tuning of V_{FB}, respectively.

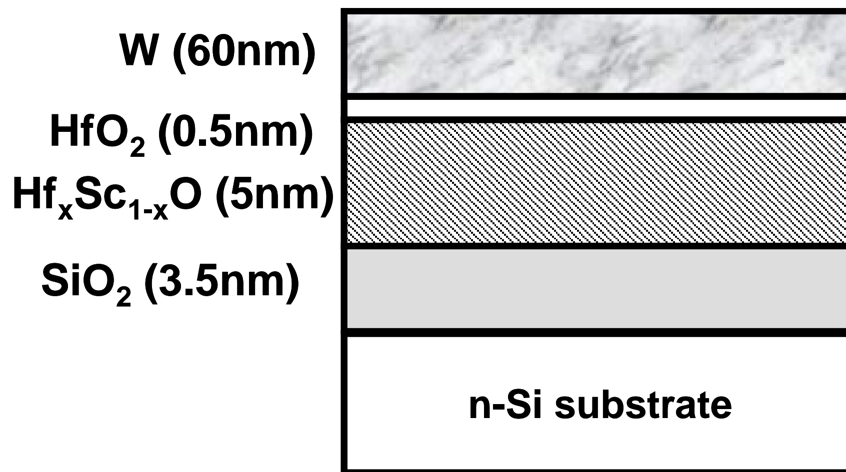

Fig.9 Schematic illustration of fabricated MOS capacitors incorporating Sc_2O_3 into HfO_2/SiO_2 interface

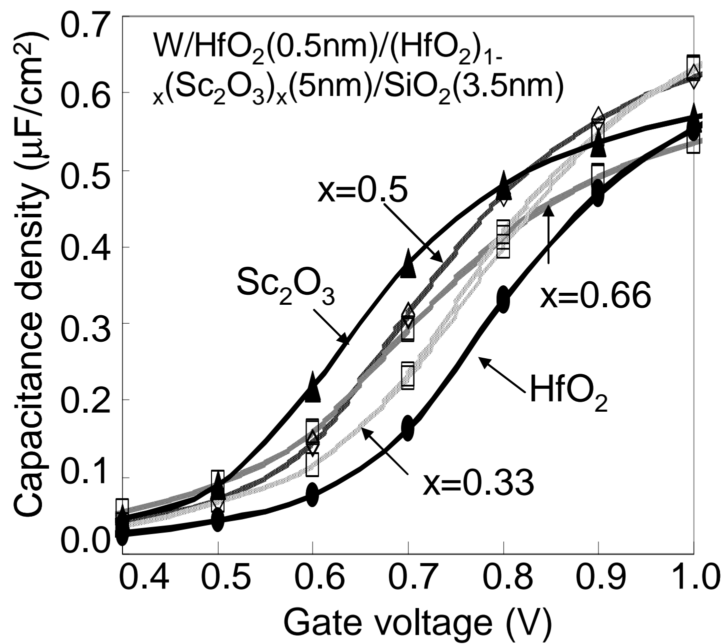

Fig.10 *C-V* curves of $W/HfO_2/(HfO_2)_{1-x}(Sc_2O_3)_x/SiO_2$ structures.

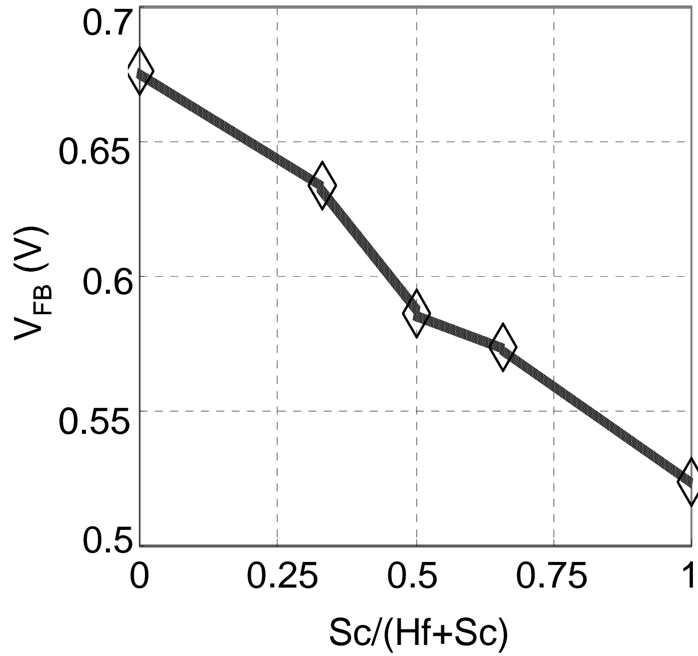

Fig.11 V_{FB} shift depending on incorporation of Sc at HfO_2/SiO_2 interface

Conclusions

The V_{FB} shift was found to be dominated by the high-k/SiO_2 interface property. The most considerable causation is an existence of the dipole at the high-k/SiO_2 interface. We observed the V_{FB} shift for the MOS capacitors using $(HfO_2)_{1-x}(La_2O_3)_x/SiO_2$ or $(HfO_2)_{1-x}(Sc_2O_3)_x/SiO_2$ as gate dielectrics. The V_{FB} is dependent on concentration of La_2O_3 or Sc_2O_3, and the large concentration results in large negative V_{FB} shift up to the V_{FB} obtained for the capacitors using La_2O_3/SiO_2 or Sc_2O_3/SiO_2. Coarse and fine tuning of V_{FB} for HfO_2 gate dielectrics were successfully observed by La_2O_3 and Sc_2O_3 incorporation, respectively. V_{FB} of MOS capacitors using high-k dielectrics could be controlled by the incorporation of La_2O_3 or Sc_2O_3 at the HfO_2/SiO_2 interface.

Acknowledgments

This work is partially supported by New Energy and Industrial Technology Develop Organization (NEDO).

References

[1] Y. Yamamoto, et al., Ext. Abst. of SSDM p.212, (2006)

[2] Vidya S. Kaushik et al., IEEE Transaction on Electron Devices Vol 53, No10, (2006)

[3] M. Kadoshima, et al., Symposium on VLSI Technology Digest of Technical Papers, p.226, (2006)

[4] Rashmi Jha et al., IEEE Electron Device Letters, Vol 25, No6, June (2004)

[5] "NCSU CVC Analysis, Version 5.0", (North Carolina State University, 2000).