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Wide Controllability of Flatband Voltage in La₂O₃ Gate Stack Structures – Remarkable Advantages of La₂O₃ over HfO₂ –

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1. Introduction

Searching for alternative materials for gate electrodes and high-k dielectrics to replace the current combination of poly-Si and SiON stacks is of intense interest for further high-performance CMOS devices. For metal gate electrodes, optimized and well-controlled work functions (WFs) are strongly required in addition to thermal stability of the stacking structures. A number of studies have been reported using HfO₂ (or HfSiON) dielectric films, and the achievement of flatband voltage (V_{fb}) control, especially for higher WF metals, has been shown to be quite formidable because of dipole formation due to oxygen vacancies (V_{OS}) formation at the metal/high-k interfaces.

In this paper, we report a systematic investigation of V_{fb} properties for HfO₂ and La₂O₃ using metal electrodes of Pt-W alloy as a means of tuning WF. We have chosen the Pt-W alloy system from the viewpoints of the thermal stability on HfO₂ and La₂O₃, and the relatively large difference in WF (ΔWF) (4.7 and 5.5 eV for W and Pt, respectively) that can be achieved by changing the number of *d*-orbital electrons from 4 (W, Group VIA) to 9 (Pt, Group VIIIA). We demonstrate that although it is difficult to maintain a difference in V_{fb} in HfO₂ capacitors, a set of La₂O₃ dielectric films and metal gate electrodes exhibits wide V_{fb} controllability and is suitable for use in CMOS devices.

2. Experimental

A combinatorial ion-sputter system was utilized to deposit a composition-spread film of the Pt-W alloy as gate electrodes. By moving a mask located between the sample and the targets (Fig. 1(a)), we control the Pt composition ratio, $R_{Pt} = N_{Pt}/(N_{Pt}+N_W)$, in a layer-by-layer fashion, where N_{Pt} and N_W are the densities of Pt and W atoms, respectively. This method enables us to fabricate about 40 variations of capacitors with R_{Pt} ranging from 0 to 1 on a single substrate.

We used two kinds of high-k dielectric films as substrates; (1) 6-nm-thick HfO₂/SiO₂/p-Si (resistivity: 0.01-0.02 Ω cm) and (2) 7-nm-thick La₂O₃/p-Si (1-2 Ω cm). The thickness of the Pt-W alloy electrodes was 60 nm, as measured by high-resolution Rutherford backscattering spectroscopy. X-ray photoelectron spectroscopy (XPS) was used to characterize the composition ratios and vacuum WFs as a function of lateral position on the specimens. Fig. 1(b) shows a schematic of the sample structure that was used for capacitance-voltage (CV) measurements in order to examine the effect of WF variation on the electrical properties. Specifically, we employed annealing in forming gas (N₂/H₂, 5% H₂) and slightly-oxidizing gas (N₂/O₂, 0.1% O₂) ambients over temperature ranges from 300-500°C and 250-400°C, respectively. We investigate, using the procedure above, the influences of V_0 formation in the dielectric films and related phenomena at the metal/high-k interfaces on controlling the values of V_{fb} .

3. Results and Discussion

A. Workfunction tuning using a binary metal alloy

The composition ratio was measured by XPS. As designed using the combinatorial system, the R_{Pt} is proportional to position (Fig. 2(a)). We evaluated vacuum WF by measuring the energies of the secondary electron offsets using XPS. By controlling the ratio R_{Pt} between 0 and 1, the vacuum WF is successfully tuned from 4.7 (W) to 5.5 eV (Pt) (Figs. 2(b)).

B. CV properties on HfO₂ and La₂O₃

Figs. 3(a) and (b) were obtained from HfO₂ and La₂O₃ capacitors with R_{Pt} ranging from 0 to 1 after forming gas annealing (FGA).

Despite the difference of 0.8 eV in WF between Pt and W, the CV curves of HfO₂ coincide, indicating Fermi-level pinning at the metal/high-k interfaces. On the other hand, as shown in Fig. 3(b), the CV curves for La₂O₃ shift toward the right as the value R_{Pt} increases, corresponding to the increase in WF. After oxidizing gas annealing (OGA) at 300°C subsequent to FGA, although the CV curves for HfO₂ show a shift, the amount of V_{fb} shift observed here is 0.32 V (Fig. 4(a)), which is much smaller than the observed vacuum ΔWF of 0.8 eV. This can be explained by a lowering of the effective WFs caused by dipole formation at the metal/high-k interface due to oxygen vacancies (V_{OS}).¹ In contrast to HfO₂, the corresponding CV curves obtained from La₂O₃ capacitors show an anomalously-large V_{fb} shift of 0.9 V, which is even slightly larger than the ΔWF between Pt and W (Fig. 4(b)).

These phenomena are clearly illustrated in Fig. 5 by plotting V_{fb} , which was extracted using the NCSU-CVC program.² In Fig. 5(a), the shift in V_{fb} after OGA subsequent to FGA for HfO₂ is shown in comparison with that after FGA only. The higher WF is, the larger the shift due to OGA becomes. Moreover, the shift can be reversed by an additional second FGA. These phenomena are consistent with the V_0 formation theory¹ and an experimental result using high WF metals such as Ru, Pt, and Re.³ This indicates that the shift in V_{fb} observed here mainly depends on the WFs of the metals rather than being due to a specific characteristic of the Pt-W system. Note that, as mentioned before, the values of V_{fb} between Pt and W (ΔV_{fb}) after OGA is only 0.32 V for HfO₂. On the other hand, the V_{fb} shift of the La₂O₃ capacitors as a function of R_{Pt} after FGA and OGA shows totally different characteristics (Fig. 5(b)). Compared to FGA, the values of V_{fb} after FGA+OGA shift upwards over the entire R_{Pt} range by ~ 0.6 V, corresponding to a reduction of fixed charges (i.e., V_{OS}) in the La₂O₃ films ($\sim 1.4 \times 10^{12}$ cm⁻²). This is because the formation of V_0 in La₂O₃ during FGA is energetically favorable compared with HfO₂. Nevertheless, we emphasize that the remarkably large difference of V_{fb} between Pt and W for La₂O₃ is achieved in both FGA and FGA+OGA processes. The values of ΔV_{fb} between Pt and W after OGA are summarized in Fig. 6. The controllable range of V_{fb} for La₂O₃ is 1.2 V after 350°C-OGA which is larger than that for HfO₂ by a factor of 3.

C. Possible mechanisms for wide V_{fb} controllability in La₂O₃

Here we focus on a mechanism for the observed wide V_{fb} controllability in the La₂O₃ capacitors. We define the slope factor $S = (\partial q V_{fb} / \partial R_{Pt}) / (\partial WF / \partial R_{Pt})$, which is the derivation of V_{fb} as a function of WF. The inset lines in Fig. 5 corresponds to the slope with $S = 1$. As shown in Fig. 7, the S factors are between 0.4-0.6 in the range of $0 < R_{Pt} < 0.6$ for both HfO₂ and La₂O₃, while the anomalous increase in $0.7 < R_{Pt} < 1$ is observed only for La₂O₃. This clearly shows that the wide controllability in La₂O₃ is due to the large S factor in the Pt-rich region.

According to a GCNL theory,⁴ the large interface hybridization between metal-occupied states and the La 5*d* orbital is desirable in achieving a high effective WF because it induces the electron transfer from Pt to La₂O₃ (Fig. 8(c)). The enthalpy of formation in Pt-La bond (-117 kJ/mole) is greater than that in Pt-O (-71 kJ/mole). This strongly suggests that Pt/La₂O₃ interface preferentially consists of Pt-La bonds, whereas at the W/La₂O₃ interface the W-O bond is preferential due to a large enthalpy of formation of -589 kJ/mole. Therefore, the large amount of electron transfer from metal to La₂O₃ is expected only in the Pt rich regions (Fig. 8), being consistent with the anomalous increase in S factors observed in $0.7 < R_{Pt} < 1$.

We have examined transmission electron microscopy (not shown) and found crystallization of La₂O₃ especially near the

Pt/La₂O₃ interface. Moreover, the interface SiO₂ layer was not observed in the Pt-W alloy/La₂O₃ structures. In addition to the bonding structures at the metal/high-k interfaces, the significant difference in ΔV_{fb} of La₂O₃ from HfO₂ may derive from the absence of SiO₂ layer at the interface and the crystal structure near the metal/La₂O₃ interfaces.

4. Conclusion

In summary, wide controllability (1.2 V) of V_{fb} has been achieved for the first time using a combination of metal alloy (Pt-W)/La₂O₃ gate stack structures. The observed controllable range is larger for La₂O₃ than for HfO₂ by a factor of 3. The wide controllability in ΔV_{fb} is stable and can be retained even after annealing processes in reducing and oxidizing ambients. We

consider that this is attributed to charge transfer at the Pt/La₂O₃ interfaces inducing increase in the effective work functions, especially at high Pt composition ratios. This study shows that La₂O₃ is one of the most promising high-k dielectric materials with metal gate electrodes for future CMOS devices in 32nm-node and beyond.

References

- [1] Shiraishi et al. 2004 VLSI Symp. Tech. Digest, p.108. [2] J.R. Hauser and K. Ahmed, Characterization and Metrology for ULSI Technology, p.235, 1998. [3] E. Cartier et al. 2005 VLSI Symp. Tech. Digest, p.230. [4] Shiraishi et al. 2005 IEDM Tech. Digest, p.43. [5] A. R. Miedema et al. J. Phys. B **12** (1979) 2255.

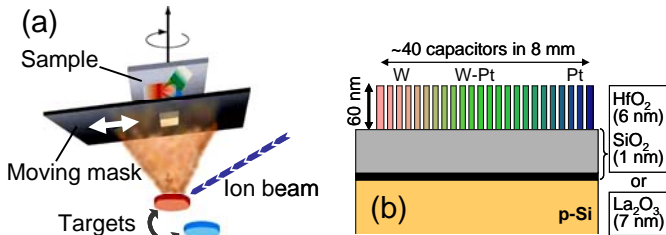


Fig. 1 (a) Schematic diagram of a combinatorial deposition system. Consists of a moving mask with a 7mm-wide square hole for controlling the composition ratio of Pt to W. (b) Capacitor structure using composition-directed Pt-W alloy electrodes deposited by the combinatorial method. The diameter of the capacitors is 100 μ m.

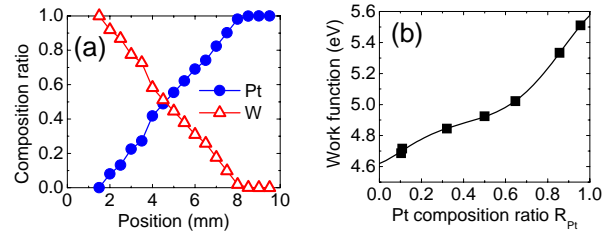


Fig. 2 (a) Composition ratio of the Pt-W alloy measured by XPS as a function of position. (b) Work function dependence on the Pt composition ratio, $R_{Pt} = N_{Pt} / (N_{Pt} + N_W)$, evaluated by the offset energies of the secondary electron.

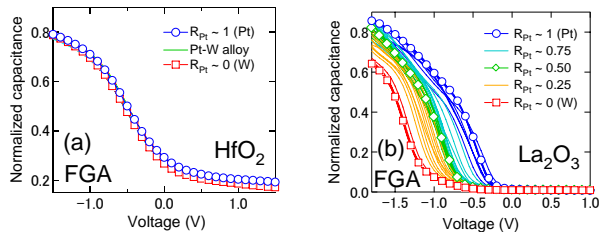


Fig. 3 CV curves after FGA obtained from (a) Pt-W/HfO₂/SiO₂/Si capacitors and (b) Pt-W/La₂O₃/Si capacitors. The CV curves from HfO₂ overlap, regardless of WF variation, while those from La₂O₃ show V_{fb} difference depending upon vacuum WFs.

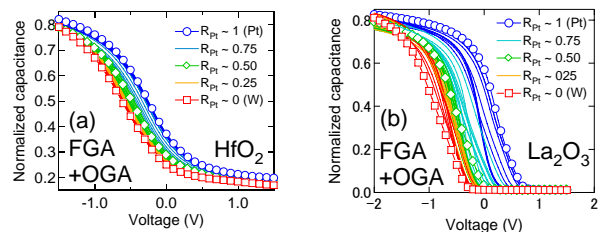


Fig. 4 CV curves after OGA at 300°C subsequent to FGA obtained from (a) Pt-W/HfO₂/SiO₂/Si capacitors and (b) Pt-W/La₂O₃/Si capacitors. In contrast to HfO₂, the La₂O₃ films show wide V_{fb} difference between Pt and W.

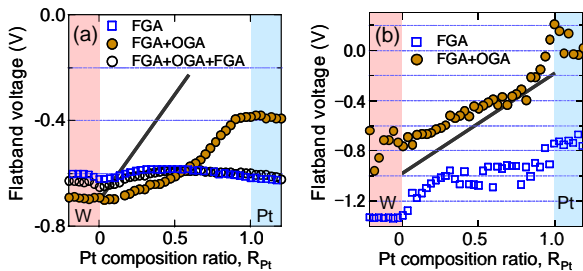


Fig. 5 V_{fb} dependence on annealing ambients as a function of the Pt composition ratio R_{Pt} of the metal electrodes. (a) HfO₂ dielectric film after FGA and OGA (300°C). (b) La₂O₃ dielectric film after FGA and OGA (300°C). The inset lines indicate the slope when $q\Delta V_{fb} = \Delta WF$. Note that in the V_{fb} of La₂O₃ after FGA+OGA, the slope is larger than the inset line at $R_{Pt} > 0.7$, indicating an anomalous phenomenon at the Pt/La₂O₃ interfaces (See Section C for detail).

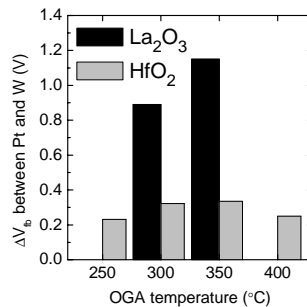


Fig. 6 V_{fb} differences between Pt and W as a function of annealing temperature in oxidizing ambient. The La₂O₃ exhibits significantly high ΔV_{fb} values compared with HfO₂.

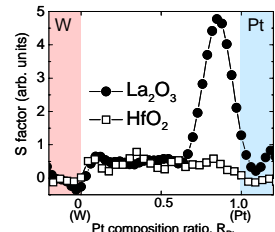


Fig. 7 Slope factor S as a function of R_{Pt} after 450°C-FGA followed by 350°C-OGA. Note that the S factor of La₂O₃ overlaps that of HfO₂ except for the anomalous increase at $0.7 < R_{Pt} < 1$, which is derived from the modulation of GCNL in the Pt/La₂O₃ system.

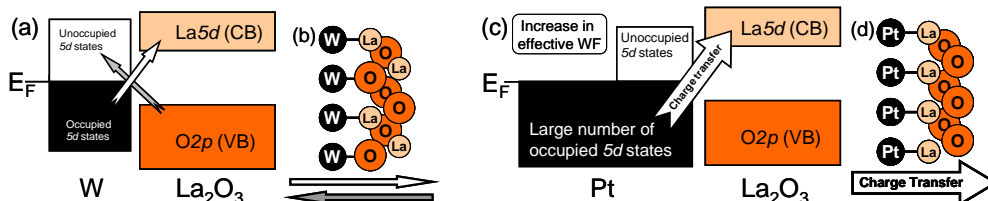


Fig. 8 Schematic illustrations of the mechanism for remarkable increase in S factors in the high Pt composition ratio regions based on the concept of generalized charge neutrality level (GCNL). Metal-O and metal-La hybridizations induce mutual interface charge transfer from La₂O₃ to metal and metal to La₂O₃, respectively. Since the interface contains both Metal-O and Metal-La bonds in the high W composition ratio region, the small amount of electron transfer is expected (a,b). However, the preferential bonding of metal-La prior to metal-O at the Pt/La₂O₃ interface results in remarkable electron transfer from metal to La₂O₃ (c,d). This can induce the anomalous increase in S factor in the high Pt composition ratio regions as observed in this experiment.