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Achieving Band Edge Effective Work Function of Gate First Metal Gate by Oxygen Anneal Processes: Low Temperature Oxygen Anneal (LTOA) and High Pressure Oxygen Anneal (HPOA) Processes

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Abstract: Novel high-pressure oxygen anneal (HPOA) process and low temperature oxygen anneal (LTOA) were developed to achieve a high effective work function (EWF, >5.2 eV) in PMOSFET with Ru metal electrode on very thin Hf silicate gate dielectric. A systematic study on the effects of Ru oxidation methods and capping metal is also presented.

Keywords: PMOSFET, metal gate, effective work function, Ru oxide, oxygen anneal, capping metal.

Introduction

For the gate electrode application, as-deposited Ru oxide exhibits high effective work function [1]. However, after the high temperature process, the EWF of RuO_2 shifts toward the midgap value. This shift has been attributed to the reduction of Ru oxide [2] during high temperature processing and forming gas anneal (FGA) [3]. Thus, maintaining a stoichiometry of Ru oxide turns out to be critically important for obtaining high EWF of the pMOS gate electrode.

In this work, both low temperature and high pressure oxygen anneals (LTOA and HPOA) were applied to supply additional oxygen into the Ru electrode, yielding >5.2eV EWF. This is the first demonstration of the band edge Ru-based electrode compatible with high temperature processing in the gate first integration scheme in a small EOT range.

Experiment

Terraced oxide PMOS capacitors [4] were fabricated on an N-type Si substrate. About 2.0 nm of Hf silicate was deposited on top of the terraced SiO_2. Thin Ru films were deposited onto the Hf silicate and oxidized using three different oxidation processes, fig. 1(a). Various thin capping layers, such as PVD or ALD TaN, followed by a thick film using either a poly Si (hybrid electrode) or metal layer with high oxygen diffusivity (full metal electrode) were used on top of the Ru oxide as illustrated in fig. 1 (b) and (c). Two integration schemes, with and without high temperature S/D activation anneal process (>1000ºC) were used to investigate the impact of the thermal budget. At the end of process flow, either a low temperature (LTOA) or high pressure oxygen anneal (HPOA) was applied.

Results and Discussion

1. Ru oxidation methods; Three oxidation processes (termed the oxidation 1, 2, and 3 in fig. 1) of a thin PVD Ru film were used to obtain a thin RuO_2 film. The oxidation 1, which results in a lower EWF than that of the oxidation 2, demonstrates lower intensity of the Ru-O bond peaks and less stoichiometric RuO_2 films as confirmed by XRD analysis. The oxidation 3, which yields both Ru-Ru and Ru-O bonds, fig. 2, resulting in a better Ru oxide electrode in terms of higher EWF and lower EOT, as seen in fig. 3.

2. Capping metal and FGA effects; The EWF of Ru oxide with the PVD TaN capping film is lower than with the ALD TaN capping, fig. 3 (a). This result can be explained by the high oxygen concentration in the ALD TaN [5] due to high carbon content. As a result, decomposition of Ru oxide is suppressed and high EWF is achieved. Fig. 3 (d) shows that the EWF of Ru oxide decreases due to FGA.

3. LTOA, HPOA effect on low temp process; Fig. 4 clearly demonstrates that LTOA boosts the EWF of Ru oxide prepared by low temperature process (i.e., without high temperature anneal process). This EWF increase is attributed to the partial elimination of O vacancies in the high-k [3] and/or the stabilization of stoichiometry of Ru oxide (i.e., RuO_2) owing to adding O to the Ru oxide and/or Ru oxide/high-k interface from LTOA process. SIMS profiles show that LTOA increases the oxygen content in TaN, Ru oxide, and Ru oxide/high-k interface (fig. 5). With HPOA, very high EWF of Ru oxide reaching up to 5.4eV can be obtained (fig. 6 (a)). Higher O pressure is known to improve O transport due to higher solubility (Henry's Law) and enhanced diffusion [6]. High O flow during HPOA enhances EWF increasing effect as shown in fig. 6 (b). Fig.7 shows the EOT vs. V_{fb} curves for various metals demonstrating the V_{fb} roll-off phenomenon [7]. V_{fb} roll-off at thin EOT is known to be a fundamental obstacle for realizing band-edge p-metals [8]. With LTOA or HPOA, however, this V_{fb} roll-off behavior is alleviated significantly presumably by eliminating O vacancies in the high-k dielectric stack (fig. 7). Fig. 8 schematically describes a possible physical mechanism responsible for this improvement. An O-poor capping electrode stack, such as PVD TaN/polySi, can provide a limited amount of O to the Ru oxide and block the transport of the external O. In the result, the Ru-O bonds, which may dissociate during high thermal processing, cannot be restored during LTOA or HPOA. On the contrary, capping layer, which is O-rich and includes only metal film, supplies additional O to the Ru oxide, Ru oxide/high-k interface, and high-k stack, resulting in higher EWFs as well as less V_{fb} roll-off.

4. LTOA, HPOA effect on high temp process; LTOA is not effective for Ru oxide/ALD TaN/poly Si gate stacks since poly-Si is believed to block the oxygen diffusion towards the metal electrode (fig. 9) [9]. On the other hand, the EWF of Ru oxide gate stacks fabricated using high temperature processing can be restored by the LTOA process when metals with high O diffusivity are used for capping Ru oxide (fig. 10). The sequence of the LTOA and FGA processes affects the final EWF of Ru oxide, suggesting that EWF is decreased during FGA due to RuO_2 decomposition, but can be reversed when followed by LTOA. HPOA more effectively increases EWF than the low temp process (fig. 10 (b)). To verify the change in EWF by LTOA (HPOA), the band offset of electrode/high-k stack was extracted using the current-voltage (J-V) method [10]. A barrier height difference of about 400meV between Ru oxide without LTOA and with LTOA is observed (fig. 11), which is consistent with the difference in their EWF values, indicating that LTOA indeed changes the work function of Ru oxide electrode. LTOA process is demonstrated to be effective in reducing threshold voltage of metal gate/high-k PMOSFETs, fig. 12.

Conclusions

A novel high pressure oxygen anneal process enables achieving a very high EWF of 5.2 ~ 5.4 eV in a standard high thermal budget PMOS fabrication process using the gate first integration scheme.

References

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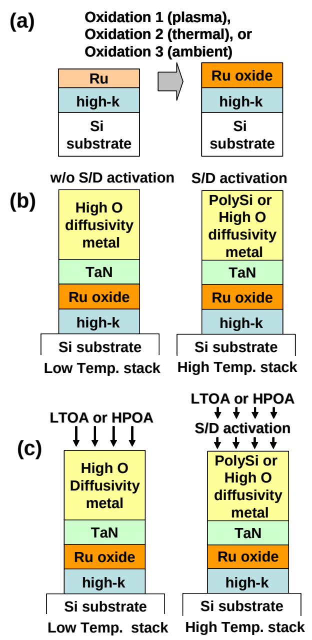

Fig. 1 Schematic of (a) Ru oxide formation by oxidation 1, 2, and 3, (b) definition of low temperature-high oxygen diffusivity metal gate stack, high temperature-polySi and high temperature-high oxygen diffusivity metal gate stack, (c) LTOA (<450°C @ 1atm) or HPOA (<450°C @ ≥10atm) process on gate stacks.

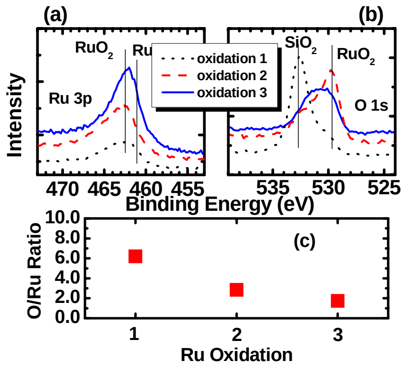

Fig. 2 XPS analysis of Ru oxide formed on Si substrate by various oxidation processes. (a) O *1s* and (b) Ru *3p* spectra, and (c) describes the composition of Ru oxides.

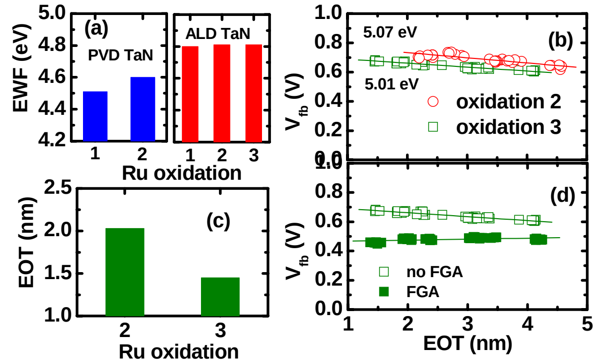

Fig. 3 (a) EWF of Ru oxide with PVD TaN and ALD TaN that got high temperature and FGA, (b) plots of EOT vs. V_{fb} and (c) EOT of as deposited Ru oxides with ALD TaN, (d) the effect of FGA on as deposited Ru oxide/ALD TaN. All MOS capacitors were fabricated on n-type Si (N_d=~1.5e15/cm^3).

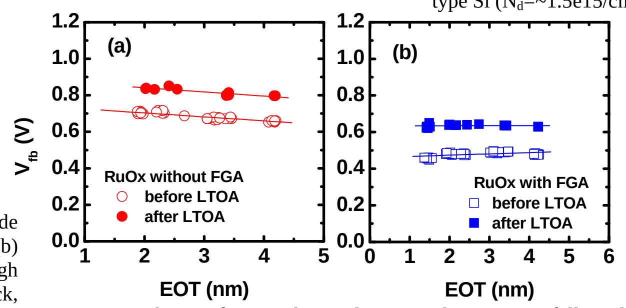

Fig. 4 EWF boost of Ru oxide metal gates with ALD TaN followed by high O diffusivity metal capping after low temperature oxygen annealing (LTOA). Observed EWF boost by LTOA of (a) before and (b) after FGA. MOS capacitors were fabricated on n-type Si (N_d=~1.5e15/cm^3).

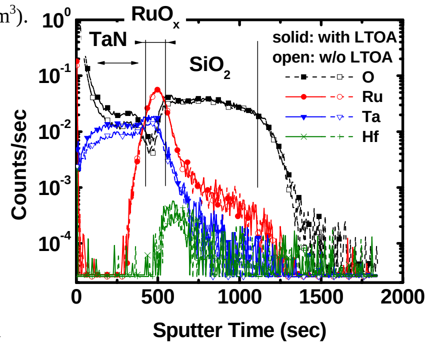

Fig. 5 SIMS profiles of RuO_x/TaN gate stack before (dot line) and after LTOA (solid line).

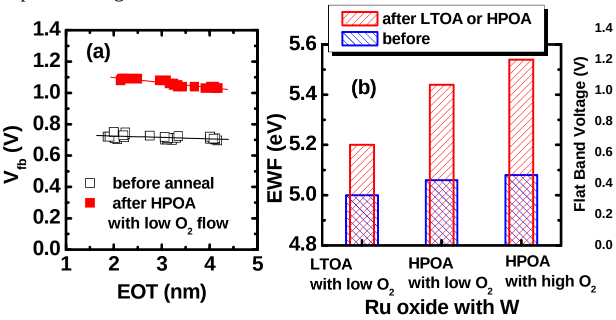

Fig. 6 (a) EWF boost of Ru oxide metal gates by high pressure oxygen anneal (HPOA), and (b) comparison of HPOA with low oxygen flow with LTOA and high oxygen flow. All capacitors were fabricated on n-type Si (N_d=~1.5e15/cm^3) with Ru oxide followed by high O diffusivity metal capping.

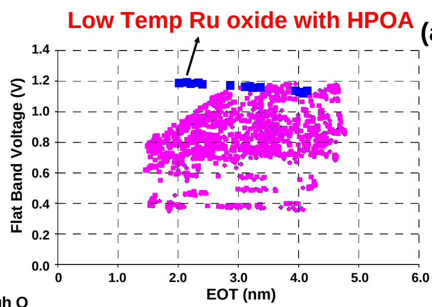

Fig. 7 Grand chart of EOT vs. V_{fb}. Ru oxide gate with HPOA exhibits a breakthrough characteristic for a PMOSFET metal.

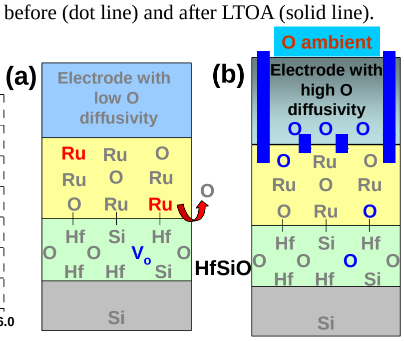

Fig. 8 (a) Decomposition of O by high thermal and hydrogen process and (b) supplying O from capping metal change EWF of Ru oxide metal.

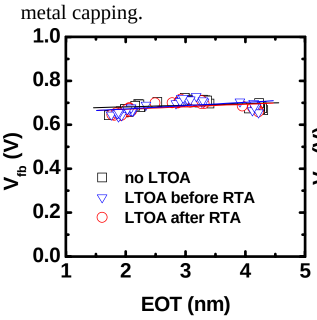

Fig. 9 EOT vs. V_{fb} plot of Ru oxide metal gates with ALD TaN/polySi capping stacks on n-type Si (N_d=~4.5e17/cm^3).

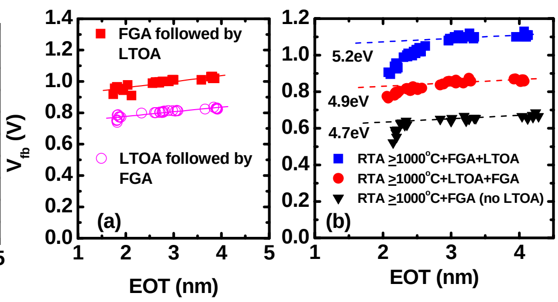

Fig. 10 EWF boost of Ru oxide metal gates by either LTOA on (a) low temperature (FGA only) and (b) high temperature (RTA ≥1000°C) processed MOS capacitors on n-type Si (N_d=~4.5e17/cm^3).

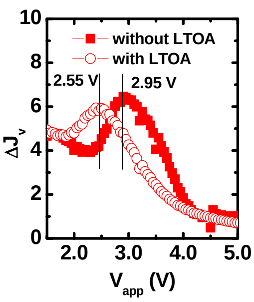

Fig. 11 Barrier height of Ru oxide/ALD TaCN without LTOA and with LTOA. Both MOS capacitors got over 1000°C annealing. LTOA was done after FGA. $\Delta J_v = d\ln(J)/dV$.

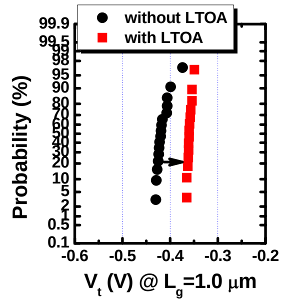

Fig. 12 The effect of LTOA on V_t of the gate first Ru-based metal gated PMOSFET.