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## PMOSFET V<sub>th</sub> Modulation Technique using Fluorine Treatment through ALD-TiN Suitable for CMOS Devices

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### Abstract

We propose that fluorine treatment (F treatment) through ALD-TiN is an excellent technique for modulating V<sub>th</sub>. Low V<sub>th</sub> with no mobility degradation is achieved with F treatment through ALD-TiN/HfO<sub>2</sub> fabricated by the gate last process. V<sub>th</sub> shift value is almost the same for each gate length. The barrier height shift attributable to F treatment corresponds closely to the V<sub>th</sub> shift. It is found that F treatment through ALD-TiN modulates an effective work function. No V<sub>th</sub> shift of nMOSFET, namely the ALD-TiN/HfSi<sub>x</sub>/HfO<sub>2</sub> stack structure, is observed with F treatment. It is confirmed that F treatment is a suitable technique for CMOS devices due to confinement of V<sub>th</sub> shift to pMOSFETs.

### Introduction

We have reported that HfSi<sub>x</sub>/HfO<sub>2</sub> using the gate last process realizes extremely high performance for nMOSFETs. Low V<sub>th</sub> is obtained in HfSi<sub>x</sub>/HfO<sub>2</sub> due to the work function near the conduction band edge [1-3]. We have also reported that ALD-TiN/HfO<sub>2</sub> realizes excellent device performance for pMOSFETs [4-5]. Therefore, ALD-TiN is considered to be an attractive material. However, an effective work function of ALD-TiN shows a quarter gap from the valence band edge [4], and a higher work function is preferable for obtaining lower V<sub>th</sub>. It has been reported, especially for p-metal/high-k stacks, that V<sub>fb</sub> shifts as a result of post process anneal conditions [6], and also that applying O<sub>2</sub> annealing directly to the metal/high-k can realize a higher work function [7]. However, the influences of these processes on device characteristics have been rarely discussed. F implantation in the channel has been reported as an effective method for modulating V<sub>th</sub> [8], but effects of fluorine on work-function-control metal have not been reported. In this study, we fabricated ALD-TiN/HfO<sub>2</sub> with F and O treatments through ALD-TiN, then evaluated the results for influences of V<sub>th</sub> modulation and device characteristics.

### Experiments

The pMOSFETs were fabricated by the gate last process as shown in Fig. 1. After dummy gate removal, HfO<sub>2</sub> was deposited by the ALD method followed by post deposition anneal (PDA). TiN gate electrodes were deposited using the ALD method, and then several gas treatments were performed through the ALD-TiN in order to control work functions. F and O treatments (with low and high O<sub>2</sub> concentrations) and N<sub>2</sub> annealing were performed at 400°C and a low O<sub>2</sub> concentration treatment at 450°C was also performed. CVD-W/TiN was deposited to fill the gate electrode. The CMP process was used for gate formation. The interlayer dielectric was formed followed by metallization, and forming gas annealing was performed at 400°C.

### Results and Discussion

Id-V<sub>g</sub> characteristics of ALD-TiN/HfO<sub>2</sub> with F and O treatment results are compared with the control (without treatment) as shown in Fig. 2. A lower V<sub>th</sub> is achieved with both F and O treatments. A larger shift is obtained with F treatment. Fig. 3 shows the V<sub>th</sub> shifts from the control with several kinds of gas treatments. The same V<sub>th</sub> as the control is obtained with N<sub>2</sub> annealing which indicates a V<sub>th</sub> shift cannot be brought about only for the thermal budget. Stronger oxidation causes a larger V<sub>th</sub> shift, and almost the same V<sub>th</sub> shift as is obtained using F treatment is achieved using a higher temperature O treatment. Fig. 4 shows hole mobility of ALD-TiN/HfO<sub>2</sub> with F treatment, O treatments at 400°C and 450°C with low O<sub>2</sub>, and the control. T<sub>inv</sub> of these samples is 1.65 nm. Hole mobility of F treatment is identical to the control while mobility degradation is observed with O treatment. In addition, further degradation is observed using the 450°C O treatment, which realizes a larger V<sub>th</sub> shift. Fig. 5 shows the interface state density of ALD-TiN/HfO<sub>2</sub> with F

and O treatments and the control evaluated by the charge pumping measurement. Interface state density resulting from F treatment is the same as the control, whereas it increases with O treatment despite lower O<sub>2</sub> concentration and lower temperature. We can conclude that F treatment through ALD-TiN is an excellent technique for realizing lower V<sub>th</sub> without mobility degradation.

In order to investigate the V<sub>th</sub> shift mechanism resulting from F treatment, ALD-TiN/HfO<sub>2</sub> stacks with and without F treatment were analyzed using backside SIMS and XPS. Backside SIMS depth profiles are compared with and without F treatment in Fig. 6. A larger F concentration is observed with F treatment, and F exists from the ALD-TiN to the HfO<sub>2</sub>/interfacial layer (IFL). Fig. 7 (a) and (b) show backside XPS spectra of F1s and Hf4f with and without F treatment. An F-Hf or Ti bond is clearly observed only in the F treatment sample. The Hf4f spectrum shape of the F treatment sample is different from that of the control. This indicates that the high binding energy ratio is further increased as a result of the F-Hf bond. The barrier heights at the ALD-TiN/HfO<sub>2</sub> interface with and without F treatment are analyzed by measuring J<sub>g</sub> versus V<sub>g</sub> curves for V<sub>g</sub> > 0V as discussed in [9-10]. The peaks in Fig. 8 show the barrier heights at the ALD-TiN/HfO<sub>2</sub> interface with a 160mV higher value obtained using F treatment. The barrier height shift of F treatment corresponds closely to the V<sub>th</sub> shift in Fig. 3, proving F treatment through ALD-TiN modulates an effective work function.

Fig. 9 shows a cross-sectional TEM image of the ALD-TiN/HfO<sub>2</sub> gate stack of a 40nm gate length pMOSFET. Fig. 10 shows J<sub>g</sub>-T<sub>inv</sub> characteristics of ALD-TiN/HfO<sub>2</sub> with and without F treatment. The T<sub>inv</sub> of ALD-TiN/HfO<sub>2</sub> is 52% thinner than that of P+poly-Si/SiO<sub>2</sub> at the same J<sub>g</sub>. The same J<sub>g</sub> characteristic is obtained with and without F treatment. V<sub>th</sub> roll-off characteristics of ALD-TiN/HfO<sub>2</sub> are shown in Fig. 11. Low V<sub>th</sub> is achieved by F treatment and the V<sub>th</sub> shift value is almost the same for each gate length. In order to evaluate F treatment effects of nMOSFET, dual metal gate structures are fabricated. The same process flow [3, 5] is used and ALD-TiN/HfSi<sub>x</sub>/HfO<sub>2</sub> (the inserted structure in Fig. 12) is formed for nMOSFET. Fig. 12 shows V<sub>th</sub> roll-off characteristics of ALD-TiN/HfSi<sub>x</sub>/HfO<sub>2</sub> nMOSFETs. No nMOSFET V<sub>th</sub> shift is observed with F treatment. We consider that the HfSi<sub>x</sub> layer under the ALD-TiN remarkably suppresses F effects. The confinement of V<sub>th</sub> shift to pMOSFETs confirms that F treatment is a suitable technique for CMOS devices.

### Conclusions

In order to achieve low V<sub>th</sub>, F and O treatments through ALD-TiN are performed and device characteristics are evaluated. O treatment modulates V<sub>th</sub> while mobility degradation is observed because of interface state density increase. F treatment also modulates V<sub>th</sub> and realizes no mobility degradation. V<sub>th</sub> shift value is almost the same for each gate length. F treatment through ALD-TiN modulates an effective work function. It is also confirmed that F treatment is a suitable technique for CMOS devices due to confinement of V<sub>th</sub> shift to pMOSFETs.

### Acknowledgements

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- CMOS device formation
- Dummy gate removal
- Pre-treatment
- ALD HfO<sub>2</sub> formation
- Post deposition anneal (PDA)
- ALD-TiN deposition
- Gas treatment
- W/TiN deposition
- Metal CMP
- NSG formation
- Metallization
- FG anneal (400°C)

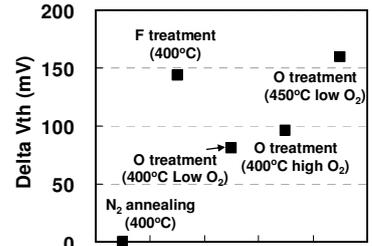
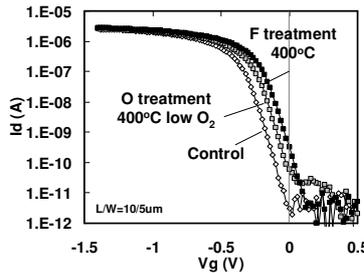
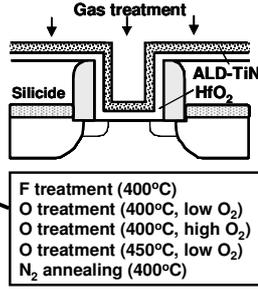


Fig. 1 Gate last process flow of ALD-TiN/HfO<sub>2</sub> gate stacks. Several kinds of gas treatments were performed through ALD-TiN film.

Fig. 2 Id-Vg characteristics of ALD-TiN/HfO<sub>2</sub> with F and O (400°C low O<sub>2</sub>) treatments and control (without treatment) at Vd = -50mV.

Fig. 3 Vth shift from the control with several kinds of gas treatments. Larger Vth shift is obtained with F and 450°C O treatments.

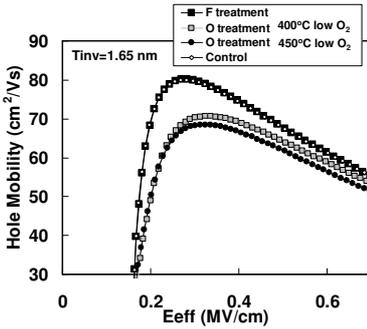


Fig. 4 Hole mobility of ALD-TiN/HfO<sub>2</sub> gate stacks with F treatment, with 400°C and 450°C with low O<sub>2</sub> treatments, and with control.

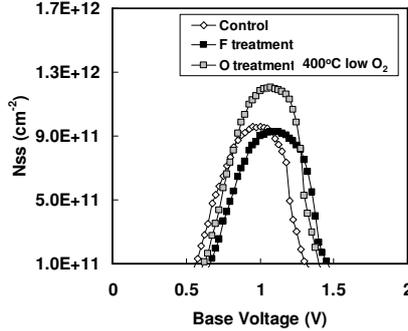


Fig. 5 Interface state density of ALD-TiN/HfO<sub>2</sub> gate stacks with F treatment, O treatment at 400°C low O<sub>2</sub> and control evaluated by charge pumping measurement.

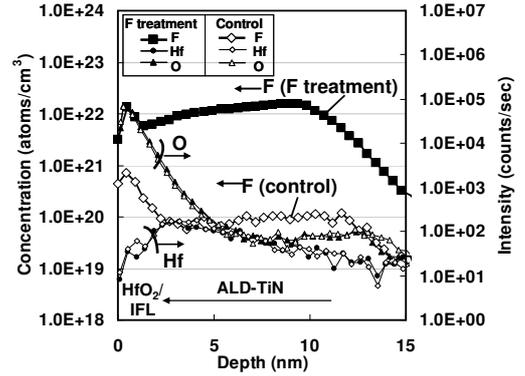


Fig. 6 Backside SIMS depth profiles were compared with and without F treatment.

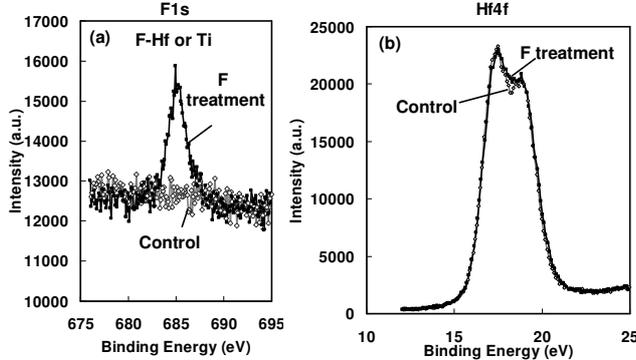


Fig. 7 Backside XPS (a) F1s and (b) Hf4f spectra of F treatment and control.

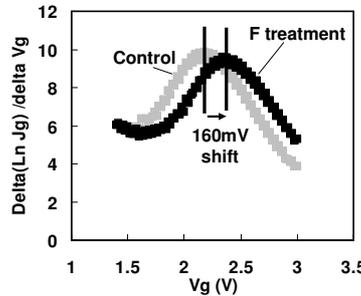


Fig. 8 Barrier heights at ALD-TiN/HfO<sub>2</sub> interface with and without F treatment.

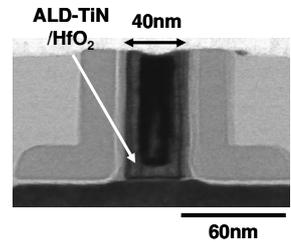


Fig. 9 Cross-sectional TEM image of ALD-TiN/HfO<sub>2</sub> gate stack of 40 nm gate length pMOSFET.

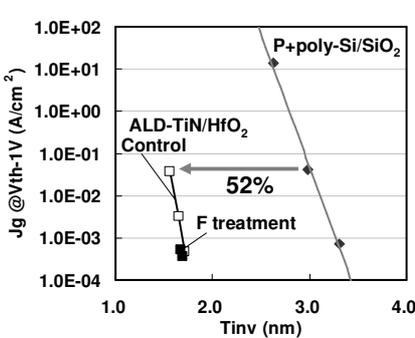


Fig. 10 Jg-Tinv of ALD-TiN/HfO<sub>2</sub> in pMOSFET. The same Jg-Tinv characteristic is obtained with and without F treatment. Tinv is reduced 52% from P+poly-Si/SiO<sub>2</sub> at the same Jg.

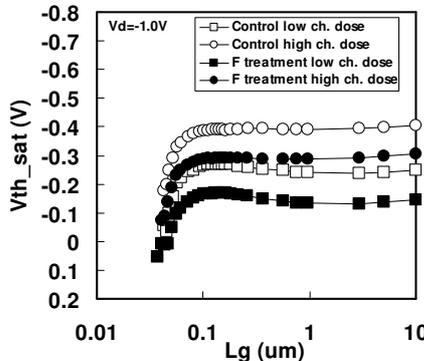


Fig. 11 Vth roll-off characteristics of ALD-TiN/HfO<sub>2</sub> gate stack with and without F treatment. Vth shift shows the same trend in each gate length.

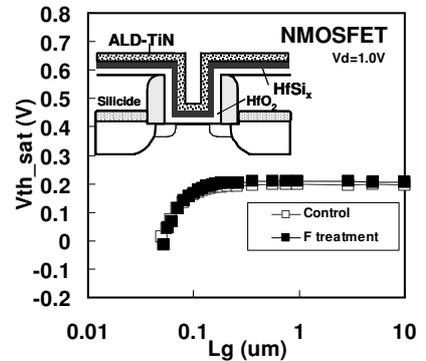


Fig. 12 Vth roll-off characteristics of ALD-TiN/HfSi<sub>x</sub>/HfO<sub>2</sub> nMOSFETs with and without F treatment. No nMOSFET Vth shift is observed with F treatment.