Extended Abstracts of the 2008 International Conference on Solid State Devices and Materials, Tsukuba, 2008, pp. 360-361

P-1-14

Optimization of the first reaction in ALD and its impact to electrical film quality of high-k/Si direct-contact gate stacks

Yukinori MORITA, Shinji MIGITA, and Hiroyuki OTA

MIRAI -Nanodevice Innovation Research Center (NIRC),
National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8569, Japan
Phone: +81-29-861-2433, E-mail: y.morita@aist.go.jp

1. Introduction

In recent aggressive scaling of the high-k gate stacks, equivalent oxide thickness (EOT) of the gate insulators reaches sub-nm regime in hp-45-nm technologies [1]. In such a situation, interlayer-less high-k/Si "direct-contact" gate stacks would be required to eliminate the EOT penalty of SiO_2 interlayer [2]. However formation of direct-contact high-k gate stack has a fatal problem with the atomic layer deposition (ALD) of high-k layers. In order to fabricate direct-contact high-k gate stacks, the oxide layer should be removed by HF-treatment followed by ALD of high-k layer. Because the HF-treated Si surfaces become "hydrophobic" with the hydrogen terminated Si bonds, it has been reported that unfavorable ALD growth features appear on hydrophobic surfaces such as island growth or incubation period of growth rate [3]. We also confirmed that serious degradation of the electronic properties based on the pinhole generation appeared on the high-k gate stacks fabricated on hydrophobic surface [4].

In order to realize direct-contact high-k gate stacks by ALD, we recently developed a novel technique of "surface hydrophilicization" for initial surface before ALD, which could turn the hydrophobic Si surface to "hydrophilic" without creating thick SiO_2 layer [4]. By using this method, we successfully fabricated sub-nm-EOT high-k gate stacks directly on Si substrate with relatively good performance. In this paper, we report the impact of the surface hydrophilicization technique to fabricate direct-contact high-k gate stacks, whose performance is verified on HfO_2/Si and HfO_2/ultra-thin Al_2O_3/Si structures.

2. Experimental

The base Si wafer was B-doped p-Si(001), which was treated by dilute HF to form H-terminated Si surface. (Fig. 1 (a)) In order to hydrophilicize this surface, the HF-treated wafers were heated up to 700˚C in N_2 to remove surface hydrogen, and exposed to H_2O vapor. (Figs. 1 (b) and (c)) On this process step (c), the H_2O molecules are expected to dissociatively chemisorb on Si dangling bonds to be Si-H and Si-OH species. The surface covered by hydroxyl functional group (-OH) shows hydrophilic nature [5], and is optimized surfaces for ALD.

On the first reaction step in ALD, the hydroxyled surface is exposed to a metalorganic source molecule (MeR_n) of high-k, which consists of a metal (Me) atom and organic functional groups (R):

$$MeR_n + \text{surface-OH} \rightarrow RH + \text{surface-O-}MeR_m \quad (1)$$

The MeR_n reacts with hydroxyled surface. The reaction produces a RH molecule and residual MeR_m, which adsorbs on the surface mediated by oxygen bonds. On the other hand, in the case on the H-terminated Si surface, the MeR_n hardly react with stable Si-H bonds. These strongly suggest that initial functional group of the surface affects deposition mode and film quality of ALD high-k.

After surface preparations, we fabricated HfO_2/Si and HfO_2/Al_2O_3/Si gate stacks with NiSi gate electrode by using gate last processes.

3. Results and discussion

Figure 2 is C-V characteristics of HfO_2 gate stacks fabricated directly on HF-last and hydrophilicized surfaces. The post deposition annealing (PDA) was performed in N_2 of 1 torr at 750˚C after ALD. The HfO_2 cycles were set at 24 cycles (~2.4nm on both surfaces). The CV of the gate stack on HF-last surface shows quite abnormal feature because of very large leakage current. On the other hand on hydrophilicized surface, the leakage current is drastically suppressed and relatively good CV is obtained.

Figures 3 show variations of (a) leakage current (Jg) and (b) EOT of the HfO_2/Si direct-contact gate stacks as functions of ALD cycles of HfO_2, which were varied from 24 to 40 cycles on HF-treated and hydrophilicized surfaces. 24 cycles of HfO_2 gate stack on HF-treated surface shows 100 times larger leakage current than that on hydrophilicized surface, making it impossible to determine EOT value. The EOT is measurable only for the gate stacks thicker than 32 cycles of ALD on HF-treated surfaces, but on hydrophilicized surfaces even 24 cycles of HfO_2 gate stack can stably be measured. Fig. 3 (b) also indicates that the EOT value on hydrophilicized surface seems thinner than those on HF-treated surface, which means the surface hydrophilicization process does not make thick oxide layer on HF-treated surface.

Figures 4 show schematic models of ALD high-k/Si direct-contact gate stacks on (a) H-terminated and (b) hydrophilicized surfaces on the basis of results in Figs. 2 and 3. On the H-terminated surface, hydrophobic surface nature initiates unfavorable ALD growth to generate pinholes in high-k layer, which remained up to 24-32 cycles of ALD growth. Such an unfavorable degradation of high-k film quality was not observed on hydrophilicized surface, because the first ALD reaction would make desirable high-k/Si connection as indicated in Eq. (1).

Figures 5 show variations of (a) Jg and (b) EOT of HfO_2/ultra-thin Al_2O_3/Si direct-contact gate stacks as functions of ALD cycles of inserted Al_2O_3 layer, which were varied from 2 to 8 cycles on HF-treated and hydrophilicized surfaces. The HfO_2 cycles were set at 20 cycles. The PDA was performed in N_2 of 1 torr at 700˚C after ALD. The HfO_2/Al_2O_3/Si gate stacks directly on the HF-treated surface show large leakage current for all 0-8 cycles of Al_2O_3 insertion layers, making them impossible to determine EOT. On the other hand on the hydrophilicized surface, the leakage current are drastically suppressed, and the EOT value of the gate stacks expectedly increases with the inserted Al_2O_3 cycles. These mean that ultra-thin Al_2O_3 layer directly deposited on hydrophilicized surface shows a quite good film quality even by their thinness. This kind of multi-layer high-k gate stack is recently very attractive from the viewpoint of modification of flatband voltage [6] or stabilization of interface. As shown in above, the surface hydrophilicization is effective to fabricate ultra-thin stacked high-k structure.

4. Summary

We presented the validity of applying a novel surface hydrophilicization method, and confirmed that serious degradation of electrical film quality of high-k/Si direct-contact gate stacks on HF-treated surface was improved by only changing chemical property of the initial surface before ALD. By using this method, good quality of direct-contact HfO_2/Si and multi-layer HfO_2/ultra-thin Al_2O_3/Si structures are realized.

Acknowledgements

Part of this study was carried out in the MIRAI Project, supported by NEDO. We would like to express our thanks to Dr. A. Toriumi of The University of Tokyo and Dr. T. Nabatame of Selete for their encouragement in the MIRAI Project.

References

[1] ITRS 2007, technology roadmap.

[2] N. Miyata, Appl. Phys. Lett. **89** (2006) 102903.

[3] D. H. Triyoso et. al., JVST. **B 22** (2007) 2121.

[4] Y. Morita et. al. , in preparation.

[5] H. Ibach et. al., Solid State Commun. **42** (1982) 57 .

[6] K. Iwamoto et. al. Appl. Phys. Lett. **92** (2008) 132907.

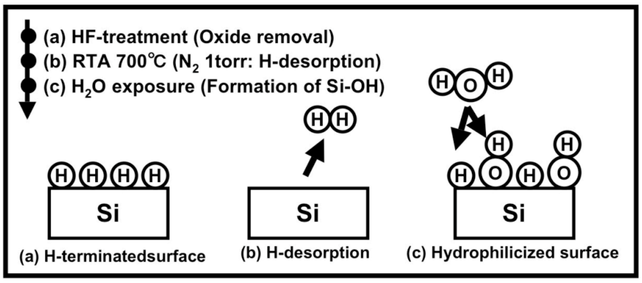

Fig. 1 Process flow and schematic models of surface hydrophilicization.

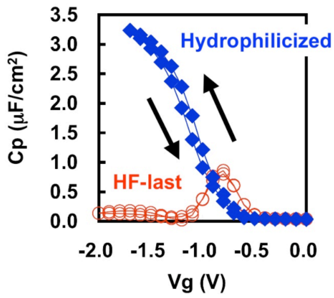

Fig. 2 Typical C-V characteristics of HfO_2/Si direct-contact gate stacks fabricated on HF-last (open circle) and hydrophilicized surfaces (diamond). The HfO_2 cycles were set at 24 cycles.

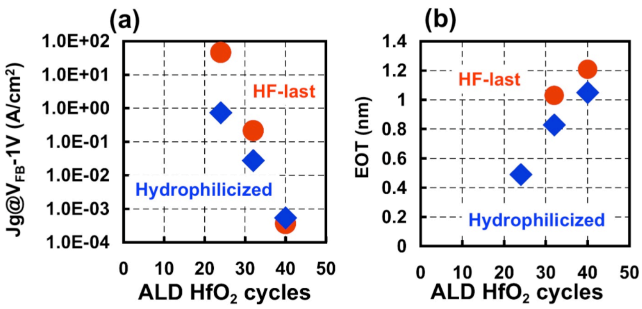

Fig. 3 Plots of (a) Jg vs ALD cycles and (b) EOT vs ALD cycles of HfO_2/Si direct-contact gate stacks fabricated on HF-treated (circle) and hydrophilicized (diamond) surfaces.

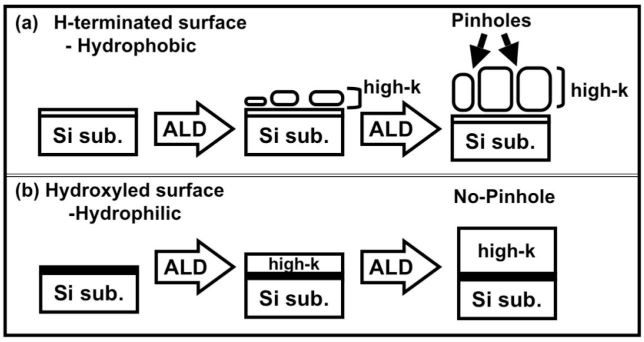

Fig. 4 Schematic models of ALD high-k/Si direct-contact gate stacks on (a) H-terminated and (b) hydrophilicized surfaces.

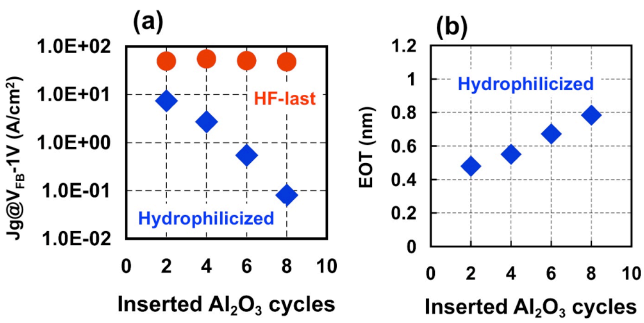

Fig. 5 Plots of (a) Jg vs ALD cycles and (b) EOT vs ALD cycles of ultra-thin Al_2O_3 insertion layer for HfO_2/Al_2O_3/Si direct-contact gate stacks fabricated on HF-treated (circle) and hydrophilicized (diamond) surfaces. HfO_2 cycles were set at 20 cycles.