Atomic-layer deposition of ZrO_2 gate dielectrics with a Si nitride barrier layer

Hiroyuki Ishii and Anri Nakajima

Research Center for Nanodevices and Systems, Hiroshima University
1-4-2 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

Phone: +81-824-24-6274, Fax: +81-824-22-7185, E-mail: nakajima@sxsys.hiroshima-u.ac.jp

1. Introduction

Recently, the substitution of conventional SiO_2 with a high-dielectric-constant thin film as the gate dielectrics for sub-0.1 μ m MOSFETs has received extensive attention from the viewpoint of gate leakage current. One of the most promising candidates for the replacement of SiO_2 is ZrO_2 [1].

Recently, in view of film uniformity, thickness control capability and low thermal budget, the application of self-limiting atomic-layer deposition (ALD) is accelerating in the fabrication of various gate dielectrics [2]. For the ALD of ZrO_2 gate dielectrics, the alternating exposure of $ZrCl_4$ and H_2O gases has most commonly been applied to date [3]. However, in the ALD using the source gases, ZrO_2 shows island-like growth when deposited directly on Si [3] and has a risk of Cl contamination and particle adhesion to the substrate surface. Zirconium tertiary-butoxide [$Zr(t\text{-}OC_4H_9)_4$, ZTB] is one of the alternative Zr precursors with the highest vapor pressure, allowing evaporation at low temperatures. Although the ALD of ZrO_2 using ZTB was reported in the thick region ($\geq$250nm) [4], in the ultrathin region no report has been published.

On the other hand, it is well known that a chemical reaction between ZrO_2 and the Si substrate occurs during film deposition in oxygen ambient or oxygen-containing source gas ambient [3,5]. The growth of the interfacial oxide layer increases equivalent oxide thickness (EOT). To prevent this growth, it is efficient to form a thin barrier layer for oxygen indiffusion. In this study, we have formed an ultrathin ZrO_2 layer by ALD using ZTB and H_2O as source gases. We have also formed an ultrathin Si nitride layer by ALD between ZrO_2 and the Si substrate and found that it acts as an effective barrier against oxygen indiffusion.

2. Experiments

The ALD of ZrO_2 layers was carried out by alternately supplying ZTB and H_2O gases on p-type Si (100) wafers (~10 $\Omega\cdot$cm). The Si surfaces were terminated with hydrogen in a 0.5 % HF solution to suppress native oxidation before the ALD. ZTB exposure followed by H_2O exposure was cyclically repeated 2-15 times at the substrate temperature of 200 °C. The H_2O exposure time was 60 s. The vapor pressures of ZTB and H_2O during the deposition were controlled to 0.04 and 0.13-1.05 kPa, respectively. Just after the ALD, *in situ* N_2 annealing was carried out for 5 min at 400 °C. In the ALD-ZrO_2/ALD-Si-nitride stack structure, about 0.5-nm-thick Si nitride was deposited by the ALD process using $SiCl_4$ and NH_3 gases [2].

3. Results

Self-limiting properties of the film growth was confirmed with ZTB exposure time (Fig.1).

A saturated film thickness of about 2.5 nm was achieved at 5 deposition cycles with vapor pressure of H_2O from around 0.1 to 1.05 kPa (Fig.2), which is consistent with the result for ZTB exposure time of 60 s shown in Fig.1.

The deposited thickness is in linear relation with the number of deposition cycles though some offset thickness occurred (Fig.3). This offset thickness is about 1.5 nm and is considered to be due to the presence of the interfacial oxidized Si layer. From the slope of the linear line in the figure, the growth rate is estimated to be about 0.1-0.3 nm/cycle. One monolayer of amorphous ZrO_2 is estimated to be ~0.2 nm thick since the layer. From the slope of the linear line in the figure, the growth rate is estimated to be about 0.1-0.3 nm/cycle. One monolayer of amorphous ZrO_2 is estimated to be ~0.2 nm thick since the Zr-O distance is obtained to be 0.22 nm from the ionic radius [6]. Therefore, it is likely that the layer-by-layer growth of ZrO_2 takes place in our experiment.

XPS spectra [Fig.4(a)] shows a strong signature of typical ZrO_2 bonding. Zr peak energies(182.3 and 184.7eV) coincide with those of Zr-O bond [7]. The Si2p peak at 102.4 eV indicates the existence of Si-O bonds in the interfacial layer. The separation between oxidized and unoxidized Si signals is 2.9 eV [Fig.4(b)], which is lower than the ~4 eV measured for SiO_2 on Si [5]. This indicates that the interfacial Si oxide is substoichiometric.

A high-resolution cross-sectional TEM micrograph shows [Fig.5(a)] that ALD ZrO_2 has an amorphous structure even after annealing at 400 °C. Uniform thickness of ALD ZrO_2 is observed. The thickness of the interfacial layer is observed to be ~1.2 nm by TEM. Figure 5(b) shows the ALD-ZrO_2/ALD-Si-nitride stack structure. In this sample, annealing at 850 °C for 3 min in N_2 ambient was added to 400 °C annealing. A noteworthy feature is that a smooth interface was observed between the ZrO_2 and Si nitride layers. The growth of the interfacial Si oxide layer is observed to be suppressed. This is understood from the fact that the thickness of the interfacial amorphous layer (~0.5 nm) coincides with that of the initially deposited ALD Si nitride.

Figure 6 shows the C-V curve of an Al/ALD-ZrO_2/ALD-Si-nitride capacitor measured at 20 kHz. The EOT of the stack dielectrics is obtained to be 1.8 nm from the accumulation capacitance (at -2.0 V) and the physical thickness observed from TEM (T_{phy} =4.7 nm) of the stack film. T_{phy} consists of the ZrO_2 layer (T_{phy} =4.2 nm) and the underlying Si nitride layer (T_{phy} =0.5 nm). Taking these T_{phy} values into account, the ε_r value of the ALD ZrO_2 layer is obtained to be 11.

4. Conclusions

In summary, ultrathin ZrO_2 films were successfully formed by alternately supplying ZTB and H_2O gases for the first time. Self-limiting properties of film growth with ZTB exposure time and H_2O vapor pressure were achieved at the growth temperature of 200 °C. TEM observation showed that the Si nitride barrier layer successfully suppressed the formation of the Si oxide interfacial layer.

References

[1] Y.-Z. Hu and S.-P. Tay, J. Vac. Sci. & Technol. B 19, 1706 (2001).
[2] A. Nakajima, Q.D.M. Khosru, T. Yoshimoto, T. Kidera, and S. Yokoyama, IEDM Technical Digest, 133 (2001).
[3] M. Copel, M. Gribelyuk, and E. Gusev, Appl. Phys. Lett. 76, 436 (2000).
[4] K. Kukli, M. Ritala, and M. Leskela, Chem. Vap. Deposition 6, 297 (2000).
[5] T.S. Jeon, J.M. White, and D.L. Kwong, Appl. Phys. Lett. 78, 368 (2001).
[6] C. Kittel, Introduction to Solid State Physics , 7th ed. (Wiley, New York, 1996).
[7] C.M. Perkins, B.B. Triplett, P.C. McIntyre, K.C. Saraswat, S. Haukka, and M. Tuominen, Appl. Phys. Lett. 78, 2357 (2001).

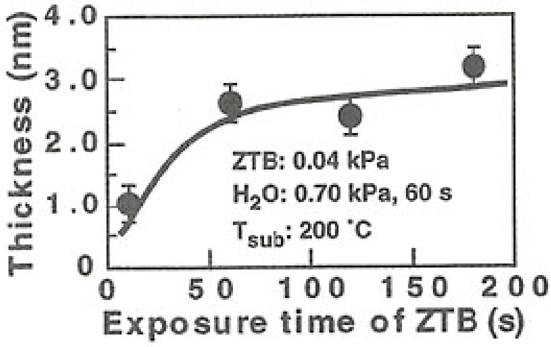


Figure 1 Dependence of the ALD ZrO_2 film thickness on the ZTB exposure times after 5 deposition cycles. Vapor pressure of H_2O was 0.70 kPa. The film thickness was measured by ellipsometry, under the assumption that the refractive index of ZrO_2 was 2.05.

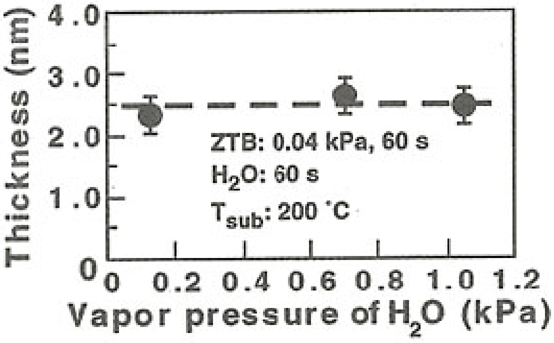


Figure 2 Dependence of the ALD ZrO_2 film thickness on the H_2O vapor pressure after 5 deposition cycles. ZTB exposure time was 60 s.

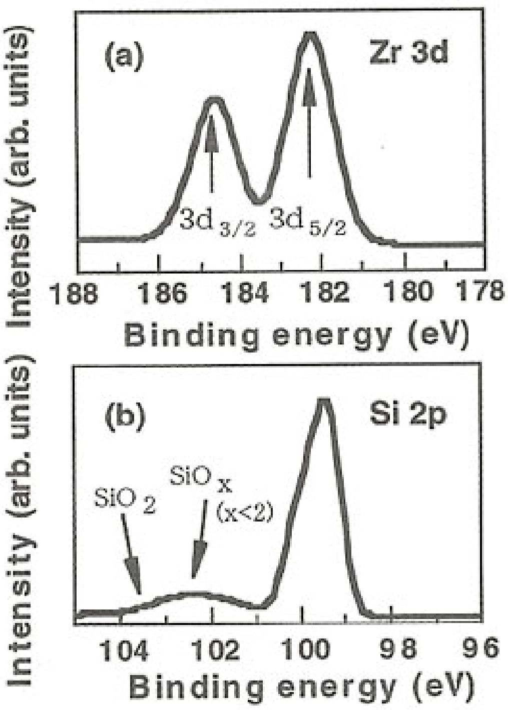


Figure 4 X-ray photoelectron spectroscopy (XPS) spectra of the (a) Zr3d and (b) Si2p core levels for the ALD ZrO_2. Number of deposition cycles was 5. ZTB exposure time was 60 s. H_2O vapor pressure was 0.70 kPa. Take-off angle was 90°.

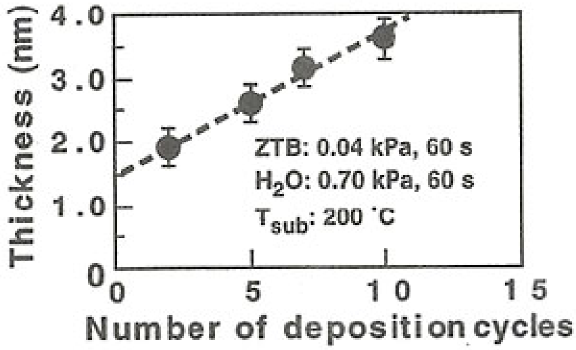


Figure 3 Thickness of ALD ZrO_2 versus number of deposition cycles. The thickness of ZrO_2 was measured by ellipsometry. ZTB exposure time was 60 s. H_2O vapor pressure was 0.70 kPa.

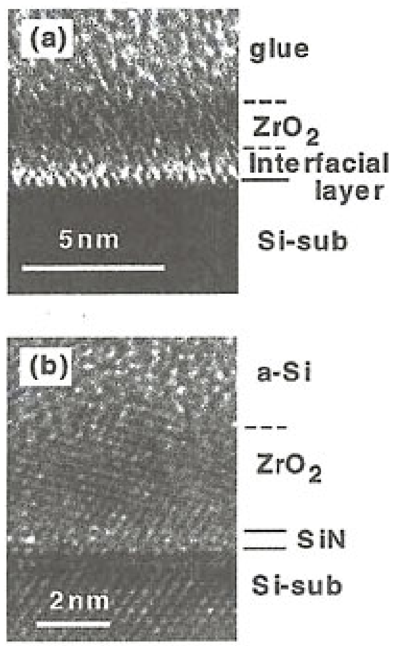


Figure 5 High-resolution cross-sectional TEM micrograph of (a) ALD-ZrO_2 and (b) ALD-ZrO_2/ALD-Si-nitride stack films. ZTB exposure time was 60 s. H_2O vapor pressure was 0.70 kPa. For the stack film, 850 °C annealing was added for 3 min after the ALD and the annealing (400 °C for 5 min) of ZrO_2. Number of deposition cycles of underlying ALD Si nitride was 2 (T_{phy} =~0.5 nm).

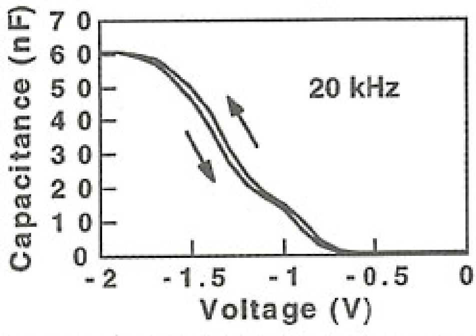


Figure 6 Capacitance-voltage (C-V) characteristics at 20 kHz for ALD-ZrO_2/ALD-Si-nitride capacitor. Number of deposition cycles was 15 and 2 for ZrO_2 and Si nitride, respectively. ZTB exposure time was 60 s. H_2O vapor pressure was 0.70 kPa. The observed hysteresis (ΔV_{FB} =50 mV) is considered to be due to charge trapping in ZrO_2 and/or the ZrO_2/Si-nitride interface and the damage which occurred during Al sputtering for electrode formation.

Background (3)-Why ALDZrO_2 by using ZTB?

ALD of ZrO_2

commonly used ---- $ZrCl_4$ and H_2O

- particle adhesion due to solid source
- Cl contamination

$Zr(t\text{-}OC_4H_9)_4$, ZTB

(liquid source at room temperature under 1atm)

ALD using ZTB and H_2O

ALD in thick region ---- Kukli *et al.* (2000)

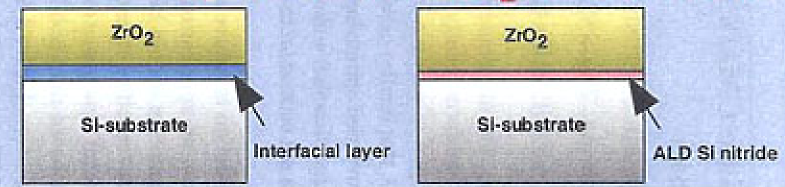
Research Center for Nanodevices and Systems, Hiroshima University

Purpose

Formation of an ultra thin ZrO_2 by ALD using ZTB and H_2O

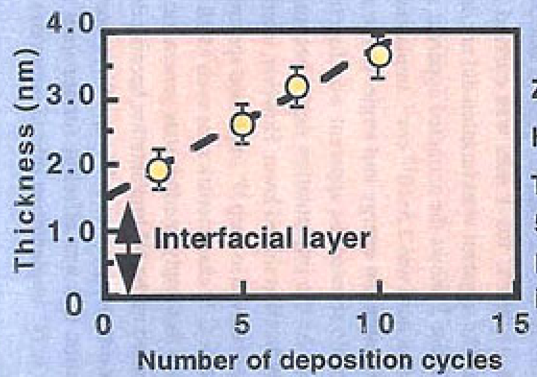
Growth of interfacial layer (SiO_x)

Suppression of interfacial layer by forming an ultra thin Si nitride layer by ALD between ZrO_2 and Si substrate



Research Center for Nanodevices and Systems, Hiroshima University

Dependence of ZrO_2 thickness on deposition cycles



Conditions

ZTB: 0.04kPa, 60s

H_2O: 0.7kPa, 60s

Tsub: 200°C

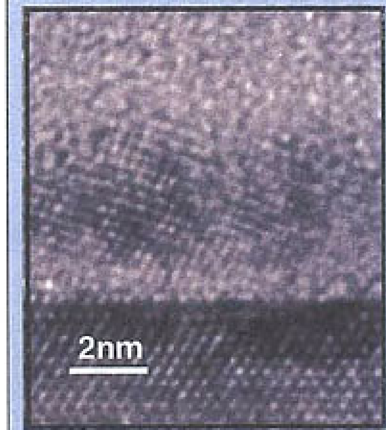
5cycles

Post annealing 400°C in N_2 for 5 minutes

Deposition rate = 0.22 nm / cycle

Research Center for Nanodevices and Systems, Hiroshima University

TEM cross section of stack structure



a-Si

ZrO_2

Si nitride

Si-sub

Conditions

ZTB: 0.04kPa, 60s

H_2O: 0.7kPa, 60s

Tsub: 200°C

5cycles

Post annealing 400°C in N_2 for 5 minutes

Annealing 850°C after ALDZrO_2 Si nitride thickness is about 0.5 nm

Research Center for Nanodevices and Systems, Hiroshima University