Suppressed crystallization of Hf-based gate dielectrics by controlled addition of Al_2O_3 using atomic layer deposition

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We demonstrate significantly improved thermal stability of the amorphous phase for hafnium-based gate dielectrics through the controlled addition of Al_2O_3. The $(HfO_2)_x(Al_2O_3)_{1-x}$ films, deposited using atomic layer deposition, exhibit excellent control over a wide range of composition by a suitable choice of the ratio between the Al and Hf precursor pulses. By this method, extremely predictable hafnium aluminate compositions are obtained, with Hf cation fractions ranging from 20% up to 100%, as measured by medium energy ion scattering. Using x-ray diffraction, we show that $(HfO_2)_x(Al_2O_3)_{1-x}$ films with Hf:Al$\sim$3:1 (25% Al) remain amorphous up to 900 °C, while films with Hf:Al$\sim$1:3 (75% Al) remain amorphous after a 1050 °C spike anneal. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1522826]

Industry roadmaps indicate that sub-15-Å oxides will be required for sub-0.1-μm complementary metal–oxide–semiconductor (CMOS) technology.[1,2] In the search for suitable candidates to replace conventional SiO_2 as the gate oxide, thermodynamic stability on Si is one of the essential properties to be considered.[2,3] Among these few thermally stable candidates, Hf-based dielectrics such as HfO_2,[2,4–8] $((Hf,Zr)O_2)_x(SiO_2)_{1-x}$[9–12] and $(HfO_2)_x(Al_2O_3)_{1-x}$[13] are the most promising materials for their superior chemical and electrical properties. Although it has recently been shown that polycrystalline HfO_2 can achieve very low leakage current,[4] it is desirable that the gate oxide films remain amorphous throughout CMOS processing to eliminate electrical and mass transport along the grain boundaries. As-deposited HfO_2 films grown using atomic layer deposition (ALD) technique are crystalline,[14] however, alloying HfO_2 with Al_2O_3 is a practical approach for improving the thermal stability of amorphous $(HfO_2)_x(Al_2O_3)_{1-x}$, while maintaining a relatively high dielectric constant of $\kappa\sim15$.[7] Previous studies on Zr-silicate[11,12] and Hf-silicate[11] films show that for ~50% Zr or Hf cation fraction, crystallization begins at 800–900 °C. It has also been reported that sputtered $(ZrO_2)_x(Al_2O_3)_{1-x}$ films[15,16] and jet-vapor-deposited $(HfO_2)_x(Al_2O_3)_{1-x}$ films[13] show increased stability of the amorphous phase. In the study by Zhu *et al.*,[13] 1000 Å jet-vapor-deposited films (~31% Al) begin to crystallize at 900 °C. In this study, we demonstrate excellent control over a wide range of Hf-aluminate compositions (20–100% Hf fraction) using ALD. Films with up to 75% Hf cation fraction exhibit significantly improved thermal stability of the amorphous phase under standard CMOS thermal budgets of 900 °C for 30 s.

Hafnium aluminate films were grown on *p*-Si (100) wafers ($\rho = 5-10\ \Omega$ cm) with a 5–10 Å SiO_2 interfacial layer grown by rapid thermal oxidation. This SiO_2 underlayer was used to provide active surface sites and to ensure well-behaved subsequent $(HfO_2)_x(Al_2O_3)_{1-x}$ ALD film growth.[17,18] The films were deposited in an ASM Pulsar2000™ module at a substrate temperature of 300 °C. By using nitrogen (flow rate ~800 sccm) as both the carrier and purging gas, gas phase reactions between precursors are prevented. The two pairs of precursors pulsed in each deposition cycle were $H_2O/HfCl_4$ (hafnium tetrachloride) and H_2O/TMA (trimethylaluminum), for depositing HfO_2 and Al_2O_3, respectively. The composition and thickness of the Hf-aluminate films were controlled by varying two parameters: (1) the ratio of cycles between the HfO_2 and Al_2O_3 reactants being pulsed and (2) the total number of cycle repetitions.

Samples A to E were inspected *ex situ* using medium energy ion scattering (MEIS).[19] To determine the stoichiometry of the films, MEIS results were acquired using a 100 keV H^+ ion beam channeled along a ⟨112⟩ axis to reduce the

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TABLE I. Summary of the precursor pulses ratio and total number of cycle repetitions to obtain the desired thickness and composition for samples used for XRD analysis. The notation *x*-*y*-*z* refers to the value listed in the columns labeled *x*, *y*, and *z*.

Samples	Number of cycles pulsed in 1 *bilayer*		Number of *bilayers*
(*x*-*y*-*z*)	H_2O/TMA (*x*)	$H_2O/HfCl_4$ (*y*)	(*z*)
1-3-80 (F)	1	3	80
2-3-60 (G)	2	3	60
2-1-92 (H)	2	1	92

Si substrate contribution to the signal of the film containing light elements such as O and Al. Thicker ~200 Å films (samples F, G, and H) were used for x-ray diffraction (XRD) analysis. To investigate the thermal stability of the amorphous $(HfO_2)_x(Al_2O_3)_{1-x}$, samples were either rapid thermal annealed (RTA, for annealing times$\leq$10 min) or furnace annealed (for annealing times$>$10 min), both in an N_2 ambient. XRD patterns were taken with a Brücker-AXS system incorporated with a 2D detector.[20] All signals were collected with the samples continuously rotated through the range of $10° < 2\omega < 40°$.

Table I summarizes the deposition procedure for samples F to H. The *x*-*y*-*z* notation is explained as follows: one *bilayer* consists of *x* H_2O/TMA cycles, followed by *y* $H_2O/HfCl_4$ cycles. The total number of *bilayers* is represented by *z*. Figure 1 shows the MEIS spectra for samples A through E. The area under the Hf peak increases with the total number (i.e., the product of *y* and *z*) of $H_2O/HfCl_4$ cycles, as expected, corresponding to an increasing amount of Hf in the film. It is worthwhile to note that both samples D and E have 60 $H_2O/HfCl_4$ cycles, yet integration under the respective Hf peak areas in Fig. 1 shows that sample D contains approximately 8% more Hf than sample E. The sample and detector alignments during MEIS analysis were arranged to ensure that no significant channeling in the oxide films occurred. This suggests that there is an increased incorporation of Hf per cycle when Al_2O_3 is present in the film. This observation is further supported by the fact that for a fixed number of Hf cycles (36), there is a continuous decrease in Hf coverage for samples A (1-1-36), B (4-4-9), a sample with 6-6-6 cycles and pure HfO_2 with 36 Hf cycles (latter two samples not shown). All of the aluminate samples containing 36 Hf cycles consistently have 8% to 13% more Hf than the pure HfO_2 sample with 0-1-36 cycles.

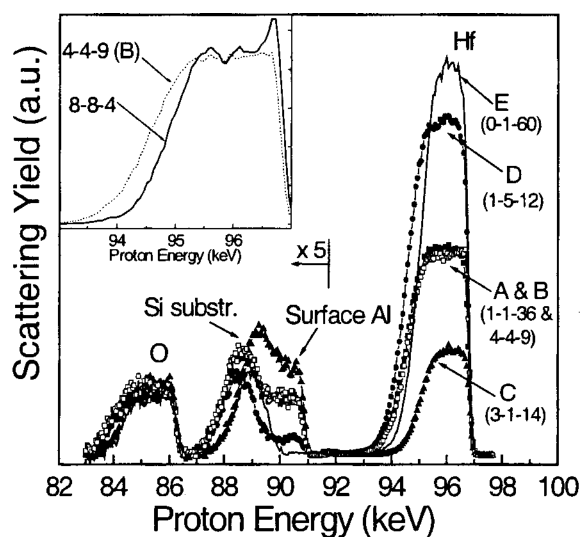

FIG. 1. MEIS proton backscattering spectra obtained from as-deposited Hf-aluminate films (samples A to E). The inset shows the Hf peak for sample A and a sample with 8-8-4 cycles. Oscillations in the Hf peak are only clearly observed on sample 8-8-4, indicating that full bilayer intermixing persists for samples with bilayers at least up to 4 cycles of each oxide.

TABLE II. Percentage of Al in the films (calculated from separate HfO_2 and Al_2O_3 growth rates and densities) agrees well with the experimental data obtained from MEIS. The ability to obtain a reasonably accurate film thickness by using an ellipsometer (manufacturable tool) fulfills one of the practical requirements in integrating Hf-aluminate films into a CMOS process.

Samples (*x*-*y*-*z*)	Calculated Al fraction (%)	Measured Al fraction[a] (%)	Simulated thickness (Å)	Ellipsometric thickness[b] (Å)
1-1-36 (A)	62.7	59.5	45	45
4-4-9 (B)	62.7	60.3	45	46
3-1-14 (C)	83.5	81.2	38	35
1-5-12 (D)	25.2	21.4	43	46
0-1-60 (E)	0	0	32	37

[a]Results from MEIS.
[b]Measured using a refractive index $n=2.08$.

To illustrate the intermixing effect in the ALD process, the Fig. 1 inset shows clearly that full bilayer intermixing continues to occur for samples with bilayers up to four cycles of each oxide (since sample B has a smooth Hf peak, and shows no signs of alternating composition with depth), whereas the sample with 8-8-4 cycles clearly exhibits oscillations in the Hf peak, indicating distinct HfO_2 and Al_2O_3 regions. Note that intermixing of Hf and Al still does occur on a scale of ~5 Å, even for the sample with 8-8-4 cycles (based on MEIS simulations). It can therefore be concluded that intermixing does occur in both samples A and B, but that the relative enhancement of Hf incorporation per cycle decreases as the number of cycles in each HfO_2 layer is increased (i.e., as subsequent Hf cycles become further removed from the underlying Al_2O_3 layer). All of these observations support the previously-mentioned suggestion that the presence of Al_2O_3 facilitates increased Hf incorporation.

These results may be explained by "backfilling" of precursors for several cycles in the ALD process. For any given metal precursor pulse, such as $Al(CH_3)_3$, steric hindrance from the ligands (e.g., CH_3) of each precursor molecule prevent neighboring surface sites from reacting. The subsequent H_2O pulse then reacts with these ligands, replacing them with smaller OH ligands, thus making the neighboring surface sites available for reaction. The next metal precursor pulse therefore backfills or intermixes with the previous metal pulse by reacting with sites on the same monolayer plane in the film. For the case of sample B, all four consecutive $HfCl_4$ pulses react (backfill) with the same underlying Al_2O_3 layer. Although it is not fully understood why the backfilling mechanism with Al_2O_3 is more effective at incorporating Hf, one possibility is that the methyl (CH_3) ligands on Al are much larger than the chlorine (Cl) ligands on Hf, such that the CH_3 ligands initially block out more neighboring bond sites in a given Al layer compared to a corresponding Hf layer. This would cause a more significant backfilling

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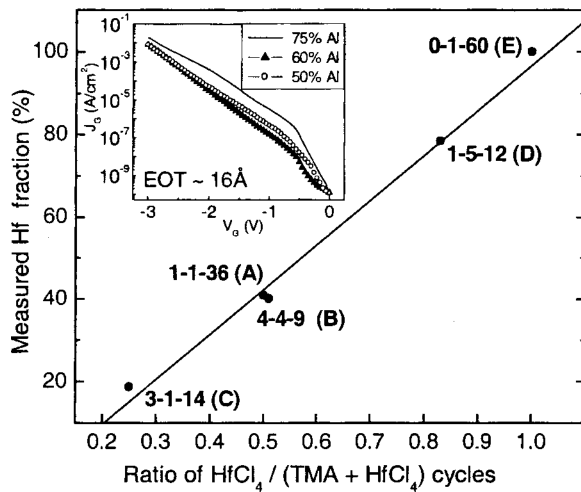

FIG. 2. A linear relationship exists between the Hf fraction in the film and the ratio of $HfCl_4/(TMA+HfCl_4)$ cycles, providing a useful guideline for attaining desired compositions of the Hf-aluminate films. The inset shows 16 Å EOT films (annealed at 900 °C for 10 sec in N_2) with 75%, 60%, and 50% Al, which exhibit a reduction in J_G of 10^2 to $10^4\times$ as compared to SiO_2 for the same EOT and bias conditions.

effect for Al, where many subsequent metal precursor pulses [either $Al(CH_3)_3$ or $HfCl_4$] could continue to react with the underlying Al_2O_3 layer, once the CH_3 ligands are replaced by OH.

The calculated fraction of Al in the films shown in Table II was estimated based on the measured growth rate of Al_2O_3 (0.86 Å per cycle) and HfO_2 (0.59 Å per cycle), and the measured density of Al_2O_3 (74% of fully dense Al_2O_3).[21] The density of HfO_2 was assumed to be equal to the bulk value (10.01 g/cm^3).[21] Considering this extremely predictable growth behavior, shown in Fig. 2, the composition of $(HfO_2)_x(Al_2O_3)_{1-x}$ ALD films can clearly be tailored to the desired stoichiometry using a manufacturable deposition technique. The $I-V$ characteristics (Fig. 2 inset) of several Hf-aluminate compositions with n^+ poly-Si gates show a significant reduction in leakage current density, J_G, by a factor of 10^2 to $10^4\times$, compared to SiO_2 of the same equivalent oxide thickness (16 Å) and bias conditions.[6]

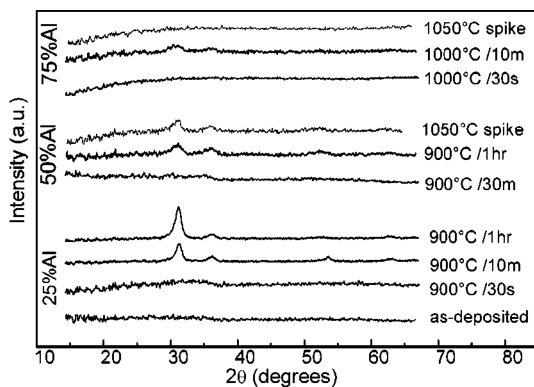

FIG. 3. XRD scans obtained from annealed films (F, G, and H) show significant improvement in stability of the amorphous phase as the percentage of Al increases. Note that the composition with 75% Al remains amorphous after a 1050 °C spike anneal.

Figure 3 shows the improved thermal stability of the amorphous phase by alloying HfO_2 with Al_2O_3. It can be seen that the as-deposited film for all three compositions remains amorphous, and the onset of crystallization increases from 900 °C (10 min) for the sample with 25% Al to 900 °C (1 h) for the sample with 50% Al. The sample with 75% Al remains amorphous up to a spike anneal at 1050 °C (soak time <1 s).

Hafnium aluminate films deposited by ALD have been obtained over a wide range of composition with excellent control of both film stoichiometry and thickness. Since the anticipated thermal budget in CMOS integration is in the range of 900 to 1000 °C, the thermal stability of the amorphous $(HfO_2)_x(Al_2O_3)_{1-x}$ films shown in this study indicate that this material is a very promising candidate for future gate dielectric applications.

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[1] *International Technology Roadmap for Semiconductors* (Semiconductor Industry Association, San Jose, CA, 2001) [http://public.itrs.net/].
[2] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).
[3] K. J. Hubbard and D. G. Schlom, J. Mater. Res. **11**, 2757 (1996).
[4] J. M. Hergenrother, G. D. Wilk, T. Nigam, F. P. Klemens, D. Monroe, P. J. Silverman, T. W. Sorsch, B. Busch, M. L. Green, M. R. Baker, T. Boone, M. K. Bude, N. A. Ciampa, E. J. Ferry, A. T. Fiory, S. J. Hillenius, D. C. Jacobson, R. W. Johnson, P. Kalavade, C. A. King, A. Kornblit, J. T.-C. Lee, W. M. Mansfield, J. F. Miner, M. D. Morris, S.-H. Oh, J. M. Rosamilia, K. Steiner, D. A. Muller, P. M. Voyles, J. L. Grazul, E. J. Shero, M. E. Givens, C. Pomarede, M. Mazanec, and C. Werkhoven, Tech. Dig. Int. Electron Devices Meet., 51 (2001).
[5] S. J. Lee, H. F. Luan, C. H. Lee, T. S. Jeon, W. P. Bai, Y. Senzaki, D. Roberts, and D. L. Kwong, Tech. Dig. VLSI Symp., 133 (2001).
[6] E. P. Gusev, D. A. Buchanan, E. Cartier, A. Kuman, D. DiMaria, S. Guha, A. Callegari, S. Zafar, D. A. Neumayer, M. Copel, M. A. Gribelyuk, H. Okorn-Schmidt, C. D'Emic, P. Kozlowski, K. Chan, N. Bojarczuk, L.-Å. Ragnarsson, P. Ronsheim, K. Rim, R. J. Fleming, A. Mocuta, and A. Ajmera, Tech. Dig. Int. Electron Devices Meet., 451 (2001).
[7] G. D. Wilk, M. L. Green, M.-Y. Ho, B. W. Busch, T. W. Sorsch, F. P. Klemens, B. Brijs, R. B. van Dover, A. Kornblit, T. Gustafsson, E. Garfunkel, S. Hillenius, D. Monroe, P. Kalavade, and J. M. Hergenrother, Tech. Dig. VLSI Symp., 88 (2002).
[8] K. Onishi, Chang Seok Kang, R. Choi, Hag-Ju Cho, S. Gopalan, R. Nieh, E. Dharmarajan, and J. C. Lee, Tech. Dig. Int. Electron Devices Meet., 659 (2001).
[9] A. Callegari, E. Cartier, M. Gribelyuk, H. F. Okorn-Schmidt, and T. Zabel, J. Appl. Phys. **90**, 6466 (2001).
[10] G. Lucovsky and G. B. Rayner, Jr., Appl. Phys. Lett. **77**, 2912 (2000).
[11] D. A. Neumayer and E. Cartier, J. Appl. Phys. **90**, 1801 (2001).
[12] G. Rayner, Jr., R. Therrien, and G. Lucovsky, Mater. Res. Soc. Symp. Proc. **611**, C1 (2000).
[13] W. Zhu, T. P. Ma, T. Tamagawa, Y. Di, J. Kim, R. Carruthers, M. Gibson, and T. Furukawa, Tech. Dig. Int. Electron Devices Meet., 464 (2001).
[14] M.-Y. Ho, H. Gong, G. D. Wilk, B. W. Busch, M. L. Green, P. M. Voyles, D. A. Muller, M. Bude, W. H. Lin, A. See, M. E. Loomans, S. K. Lahiri, and P. I. Räisänen, J. Appl. Phys. (to be published).
[15] R. B. van Dover, D. V. Lang, M. L. Green, and L. Manchanda, J. Vac. Sci. Technol. A **19**, 2779 (2001).
[16] Y. Ma, Y. Ono, L. Stecker, D. R. Evans, and S. T. Hsu, Tech. Dig. Int. Electron Devices Meet., 149 (1999).
[17] S. Haukka and T. Suntola, Interface Sci. **5**, 119 (1997).
[18] M. Copel, M. Gribelyuk, and E. Gusev, Appl. Phys. Lett. **76**, 436 (2000).
[19] J. F. van der Veen, Surf. Sci. Rep. **5**, 199 (1985).
[20] Brücker-AXS GmbH, Karlsruhe, Germany [http://www.bruker-axs.com].
[21] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 80th ed. (CRC, Boca Raton, FL, 1999–2000), p. 38ff.

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