

Electrical properties of HfO₂ deposited via atomic layer deposition using Hf(NO₃)₄ and H₂O

J. F. Conley, Jr.^{a)} and Y. Ono
Sharp Labs of America, Camas, Washington 98607

R. Solanki
Oregon Graduate Institute, Department of Electrical and Computer Engineering, Beaverton, Oregon 97006

G. Stecker and W. Zhuang
Sharp Labs of America, Camas, Washington 98607

(Received 28 October 2002; accepted 19 March 2003)

We report on the electrical properties of HfO₂ deposited via atomic layer deposition using Hf(NO₃)₄ precursor for metal/oxide/semiconductor gate dielectric applications. Thin films, with less than 1% variation in accumulation capacitance over a 150 mm wafer, have been deposited directly on hydrogen-terminated Si wafers. The effective dielectric constant of thin (<10 nm) films was in the range of $\kappa_{\text{eff}}=10-12$, the breakdown voltage was about 6–9 MV/cm, and the leakage current was between 3–6 orders of magnitude lower than that of SiO₂. The relative benefit of lower leakage current of HfO₂ over SiO₂ decreased with decreasing effective thickness. Electron trapping was observed under constant voltage stressing. © 2003 American Institute of Physics.
[DOI: 10.1063/1.1575934]

A critical component of a metal/oxide/semiconductor (MOS) field-effect transistor is the SiO₂ gate oxide. Due primarily to excessive leakage and reliability concerns caused by continued scaling of MOS technology, the thin SiO₂ gate oxide must eventually be replaced by a high dielectric constant material.¹ Among the many potential high- κ replacement materials currently under investigation, HfO₂ has recently emerged as one of the leaders.^{2–21} One of the most promising deposition techniques for high- κ materials is atomic layer deposition (ALD).^{2,5,6,10,20–24} In ALD, materials are deposited layer by layer in a self-limiting fashion, allowing for atomic scale control. The most widely used ALD precursors for metal oxides are metal-chlorides such as HfCl₄ and ZrCl₄.^{10,19,21–23} Unfortunately, ALD of metal oxides using metal chloride precursors exhibits poor initial deposition on H-terminated Si, necessitating the use of a thin interfacial silicon oxide or silicon nitride layer to achieve uniform growth.^{19,21–23} Since an effective oxide thickness (EOT) of less than 1 nm will be required within the next 5 years,² the need for an initial few monolayers of a lower dielectric constant material would be a serious drawback. An alternate precursor that has been used for chemical vapor deposition (CVD) of HfO₂ is Hf(NO₃)₄.^{2,12} Recently, the use of Hf(NO₃)₄ as a precursor for ALD has been shown to produce smooth and uniform initial deposition directly on H-terminated Si,^{5,6,20} potentially eliminating the need for an initial interfacial layer of SiO₂. In this work, we report on the electrical properties of HfO₂ deposited via ALD using Hf(NO₃)₄ precursor.

HfO₂ films were deposited using alternating surface saturating reactions of Hf(NO₃)₄ and H₂O vapor on a custom built ALD chamber for 150 mm wafers. Hf(NO₃)₄ precursor was synthesized in house¹⁸ and was held at 88 °C

during deposition. Immediately prior to deposition, wafers were dipped in dilute HF to remove any native oxide. The temperature of the wafer during deposition was approximately 170 °C. After deposition, all films received an *in situ* anneal for 30 s in N₂ at approximately 420 °C (anneals at temperatures greater than 400 °C were previously found to result in densification of the films and the removal of residual nitrogen).^{5,6,20} Film thickness and refractive index (1.97) were determined using spectroscopic ellipsometry. X-ray diffraction, atomic force microscopy (AFM), and x-ray photoelectron spectroscopy (XPS) characterization of similar films appears elsewhere.^{5,6,20} TiN gate capacitors of area 100 $\mu\text{m} \times 100 \mu\text{m}$ were formed using a photolithographic process. Patterning of the ~190-nm-thick TiN gate was followed by a 30 min, 450 °C anneal in N₂/H₂. Capacitance measurements were made using an HP 4284 LCR meter. Leakage and breakdown measurements were made using an Agilent 4156A semiconductor parameter analyzer.

Figure 1 shows a plot of optical thickness versus the number of deposition cycles for HfO₂ films deposited via

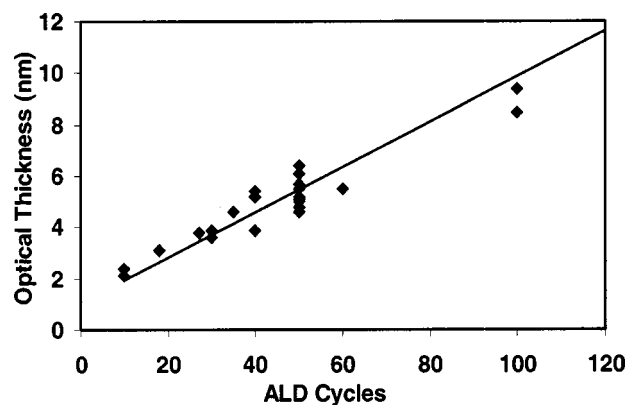
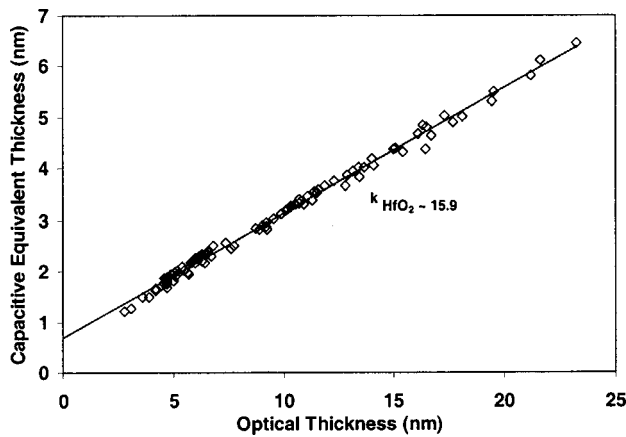


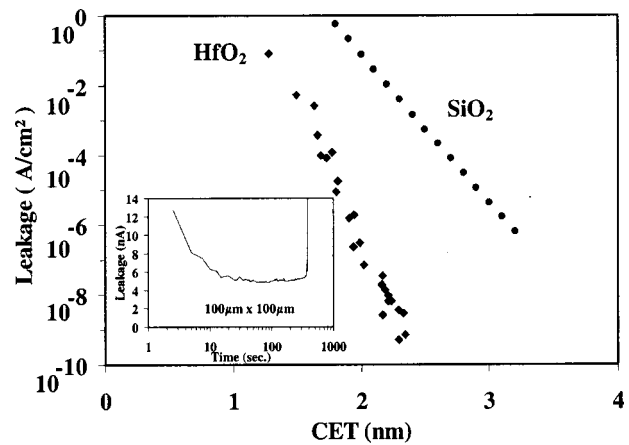
FIG. 1. Optical thickness vs number of ALD cycles.

^{a)}Electronic mail: jconley@sharplabs.com

FIG. 2. CET vs optical thickness for a series of HfO₂ films.

ALD using Hf(NO₃)₄ precursor. A deposition rate of ≈ 0.08 – 0.14 nm/cycle was observed over the range of deposition cycles and several different “batches” of Hf(NO₃)₄. The linear dependence of thickness on the number of cycles is an indication of the ALD regime. Incubation cycles are not required indicating the absence of a nucleation barrier as seen for HfCl₄ ALD on H-terminated Si.^{19,21–23} Previous AFM images of one and two cycle depositions²⁰ indicated that the initiation and growth does not appear to roughen the Si surface. Variation of less than 1% in both film thickness and accumulation capacitance (C_{\max}) was measured across the 150 mm wafers. The deposition rate was found to be sensitive to both the substrate and precursor temperature. A much higher deposition rate of 0.36 nm/cycle from a preliminary report⁵ has been traced to cleanliness of the deposition chamber that was used.²⁰ More careful control of the deposition conditions in the custom tool has since resulted in lower and better controlled deposition rates, more consistent with those typically reported for ALD.^{21–24}

Shown in Fig. 2 is a plot of capacitive equivalent thickness (CET) versus optical thickness for a series of HfO₂ films. CET was determined from C_{\max} with Si surface in accumulation. Slight distortion of capacitance–voltage (CV) traces was observed at 10 kHz (not shown) due to interface trapping and distortion in accumulation was observed at frequencies below 1 kHz due to leakage. CV hysteresis ranged from 0 to ≈ 40 mV and can likely be controlled through process optimization. The final film likely consists of a HfO₂ layer on top of an interfacial layer. In order to extract the dielectric constant of only the HfO₂ layer and the thickness of the interfacial layer, we assumed that the structure of the interfacial layer was independent of film thickness. From the slope of the plot in Fig. 2, we extracted a “bulk” HfO₂ dielectric constant of approximately $\kappa_{\text{HfO}_2} \approx 15.9$. For thin HfO₂ films less than 10 nm thick, an effective dielectric constant (including both the HfO₂ layer and the interfacial layer) of $\kappa_{\text{eff}} \approx 10$ – 12 was obtained. For example, we found a CET of 1.5 nm and an effective dielectric constant of 10.5 for a 4-nm-thick film. The κ that we obtain for the HfO₂ layer (≈ 15.9) is lower than the reported bulk value (25–30) and for films deposited via dc magnetron sputtering (≈ 28),⁷ CVD using Hf-*t*-butoxide (≈ 26),⁸ or Hf β -diketonate (22–25).⁹ However, both k_{eff} and k_{HfO_2} are consistent with other results for HfO₂ films deposited via CVD using Hf-

FIG. 3. Absolute leakage current density vs CET for a series HfO₂ films (SiO₂ from Ref. 25). The inset shows absolute leakage vs time for constant voltage stressing.

nitrate ($\kappa_{\text{HfO}_2} \approx 17$),¹² metalorganic CVD ($\kappa_{\text{stack}} \approx 6.6$),³ ALD ($\kappa_{\text{stack}} \approx 10.6$),⁴ and ALD using HfCl₄ ($\kappa_{\text{HfO}_2} \approx 17$ – 18).¹⁹ Note that because the CET does not account for quantum effects, our estimates of electrical thickness and k_{eff} may be considered conservative. Excess oxygen was detected by XPS raising the possibility that it may play a role in reducing the bulk κ of the HfO₂ layer.⁵ Our thin HfO₂ films also have a slightly lower density (8.5 g/cm³) and refractive index (1.97) than that of bulk material (9.68 g/cm³, ~ 2.01),²⁰ consistent with films deposited using HfCl₄.²¹ This suggests that reduced film density may in part explain the reduced dielectric constant. Finally, the y intercept of the plot indicates the presence of an interfacial layer. If we assume that this layer is SiO₂ (dielectric constant $\kappa_{\text{IL}} = 3.9$), then its thickness would be approximately 0.7 nm. As quantum effects are not accounted for, the actual thickness would be somewhat thinner. The exact chemical makeup and thickness of the interfacial layer are unknown. Recent electron spin resonance work¹¹ suggests that the interfacial layer is not pure SiO₂ but rather a medium- κ material such as HfSiO_{*x*}. It is not known whether this interfacial layer is inherent to the use of Hf(NO₃)₄ precursor which is known to be strongly oxidizing. Optimization of deposition parameters and post-deposition annealing may allow for a reduction in the thickness of this layer. Further investigation is underway.

Figure 3 shows a comparison of leakage (at an accumulation bias of $V_g = -1$ V) versus CET for HfO₂ and SiO₂ (SiO₂ leakage adapted from Ref. 25). Leakage for the HfO₂ films is at least three orders of magnitude lower than SiO₂ of equivalent CET. For a 1.14 nm EOT film (including quantum effects), a leakage current density of 5.4×10^{-3} A/cm² was obtained. It is seen in Fig. 3 that the HfO₂ curve has a steeper slope than the SiO₂ curve. Previous reports comparing leakage in HfO₂ to SiO₂ have been mixed. Data reported by Kang *et al.*¹⁶ shows that the slope of HfO₂ is less than SiO₂, suggesting a relative improvement of the HfO₂ leakage benefit as thickness is decreased. In Gusev *et al.*,¹⁴ it appears that the slope of the HfO₂ leakage current density versus thickness is roughly parallel to that of SiO₂, while in Hergenrother *et al.*¹⁵ the slope of the HfO₂ leakage appears to increase around 1.5 nm. A report by Ma *et al.*¹² shows results consistent with ours. A recent modeling letter by Yeo *et al.*²⁶

concludes that, due to reduced barrier height and electron effective mass, the slope of log (leakage current density) versus thickness will be steeper for high- κ dielectrics than for SiO₂. Our results, as well as those of Ma *et al.* and Yeo *et al.*, indicate that the leakage benefit of using HfO₂ will decrease with decreasing effective thickness. Extrapolation of a straight line fit to both the SiO₂ and HfO₂ data in Fig. 3 indicates that they will intersect at a finite thickness which will be the tunneling thickness of the interfacial layer.¹² At this point, since all of the high- κ material has been removed and only the interfacial layer remains, the slope will decrease. Note that the intersection point in our plot (the interfacial layer thickness) will be affected by the fact that we have not accounted for quantum effects, which would reduce the intersection point by 0.2–0.3 nm.

A typical plot of leakage current versus time for -5.2 V constant voltage stress is shown as an inset in Fig. 3 for an approximately 3.1 nm CET HfO₂ film on *p*-type Si. Initial electron trapping is followed by eventual hard breakdown. Ramped voltage testing (not shown) indicates that in the optical thickness range of 1.5–5.0 nm, breakdown occurs at a field of 6–9 MV/cm, corresponding to an effective oxide field of 21–24 MV/cm. The breakdown voltage tends to increase slightly with decreasing thickness. (These results may have been affected by probe pressure effects.) Although electron trapping is evident in these films deposited via ALD using Hf(NO₃)₄ precursor, it is likely that the charge trapping properties of HfO₂ in general will be, as for SiO₂, deposition method dependent. Electron trapping has also been observed in gamma irradiated ALD HfO₂ deposited using Hf(NO₃)₄ precursor¹⁷ as well as for electrically stressed HfO₂.¹⁴ The electron mobility of HfO₂ gate *n*-type MOS devices (not shown) was found to be approximately equivalent to that for HfO₂ gates deposited via ALD using HfCl₄ precursor, but only approximately half that of SiO₂, consistent with recent results.^{4,13,14} The electron trapping may play a role in mobility reduction as well as in HfO₂ film reliability.

ALD HfO₂ films deposited using Hf(NO₃)₄ precursor were found to have good electrical characteristics including low leakage and high equivalent breakdown strength. For a 4.0-nm-thick HfO₂/TiN gate capacitor, a capacitive equivalent thickness of 1.5 nm, corresponding to $k_{\text{eff}}=10.5$, and a leakage current density more than three orders of magnitude lower than SiO₂ was obtained. Although leakage was found to be much lower than SiO₂, leakage in HfO₂ was found to increase much more rapidly with decreasing thickness, indicating that the leakage benefit of HfO₂ over SiO₂ will decrease with decreasing effective thickness. Our results indicate that ALD using Hf(NO₃)₄ precursor is a promising

method for depositing high quality HfO₂ films. The capability of initiating deposition directly on H-terminated Si may be an advantage over the more commonly used HfCl₄ precursor. Before HfO₂ can replace SiO₂, however, improvement of carrier mobility near the interface will be necessary.

- ¹G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.* **89**, 5243 (2001).
- ²R. C. Smith, T. Ma, N. Hoilien, L. Y. Tsung, M. J. Bevan, L. Colombo, J. Roberts, S. A. Campbell, and W. L. Gladfelter, *Adv. Mater. Opt. Electron.* **10**, 105 (2000).
- ³C. Hobbs, H. Tseng, K. Reid, B. Taylor, L. Dip, L. Hebert, and R. Garcia, *Tech. Dig. - Int. Electron Devices Meet.*, 651 (2001).
- ⁴Y. Kim, G. Gebara, M. Freiler, J. Barnett, D. Riley, J. Chen, and K. Torres, *Tech. Dig. - Int. Electron Devices Meet.*, 455 (2001).
- ⁵J. F. Conley, Jr., Y. Ono, W. Zhuang, D. J. Tweet, W. Gao, S. K. Mohammed, and R. Solanki, *Electrochem. Solid-State Lett.* **5**, C57 (2002).
- ⁶J. F. Conley, Jr., Y. Ono, D. J. Tweet, W. Zhuang, and R. Solanki, *Mater. Res. Soc. Symp. Proc.* **716**, 73 (2002).
- ⁷B. H. Lee, L. Kang, W. J. Qi, R. Nieh, Y. Jeon, K. Onishi, and J. C. Lee, *Tech. Dig. - Int. Electron Devices Meet.* **1999**, 133 (1999).
- ⁸S. Sayan, E. Garfunkel, and S. Zuzer, *Appl. Phys. Lett.* **80**, 2135 (2002).
- ⁹M. Balog, M. Schieber, M. Michman, and S. Patai, *Thin Solid Films* **47**, 247 (1977).
- ¹⁰M. Cho, J. Park, H. B. Park, C. S. Hwang, J. Jeong, and K. S. Hyun, *Appl. Phys. Lett.* **81**, 334 (2002).
- ¹¹A. Y. Kang, P. M. Lenahan, J. F. Conley, Jr., and R. Solanki, *Appl. Phys. Lett.* **81**, 1128 (2002).
- ¹²T. Ma, S. A. Campbell, R. Smith, N. Hoilien, H. Boyong, W. L. Gladfelter, C. Hobbs, D. Buchanan, C. Taylor, M. Gribelyuk, M. Tiner, M. Copel, and J. J. Lee, *IEEE Trans. Electron Devices* **48**, 2348 (2001).
- ¹³D. Barlage, R. Arghavani, G. Dewey, M. Doczy, B. Doyle, J. Kavalieros, A. Murthy, B. Roberds, P. Stokley, and R. Chau, *Tech. Dig. - Int. Electron Devices Meet.* **2001**, 231 (2001).
- ¹⁴E. P. Gusev, D. A. Buchanan, E. Cartier, A. Kumar, D. DiMaria, S. Guha, and A. Callegari, *Tech. Dig. - Int. Electron Devices Meet.* **2001**, 451 (2001).
- ¹⁵J. M. Hergenrother, G. D. Wilk, T. Nigam, F. P. Klemens, D. Monroe, and P. J. Silverman, *Tech. Dig. - Int. Electron Devices Meet.* **2001**, 51 (2001).
- ¹⁶L. Kang, K. Onishi, Y. Jeon, B. H. Lee, C. Kang, W. J. Qi, R. Nieh, S. Gopalan, R. Choi, and J. C. Lee, *Tech. Dig. - Int. Electron Devices Meet.* **2001**, (2001).
- ¹⁷A. Y. Kang, P. M. Lenahan, and J. F. Conley, Jr., *IEEE Trans. Nucl. Sci.* **49**, 2636 (2002).
- ¹⁸W. Zhuang, J. F. Conley, Jr., Y. Ono, D. R. Evans, and R. Solanki, *Integr. Ferroelectr.* **48**, 3 (2002).
- ¹⁹G. D. Wilk, M. L. Green, M.-Y. Ho, B. W. Busch, T. W. Sorsch, F. P. Klemens, B. Brijs, R. B. van Dover, and A. Kornblit, *IEEE 2002 Symp. on VLSI Tech. Dig.*, 2002, p. 89.
- ²⁰J. F. Conley, Jr., Y. Ono, D. J. Tweet, W. Zhuang, and R. Solanki, *J. Appl. Phys.* **93**, 712 (2003).
- ²¹M. L. Green, M. Y. Ho, B. Busch, G. D. Wilk, T. Sorsch, T. Conrad, B. Brijs, W. Vandervorst, P. I. Raisanen, D. Muller, M. Bude, and J. Grazul, *J. Appl. Phys.* **92**, 7168 (2002).
- ²²M. Copel, M. Gribelyuk, and E. Gusev, *Appl. Phys. Lett.* **76**, 436 (2000).
- ²³M. Tuominen, T. Kannianen, and S. Haukka, in *Electrochemical Society Proceedings*, 2000, Vol. 2000-9, pp. 271–282.
- ²⁴T. Suntola, *Mater. Sci. Rep.* **4**, 261 (1989).
- ²⁵B. Brar, G. D. Wilk, and A. C. Seabaugh, *Appl. Phys. Lett.* **69**, 2728 (1996).
- ²⁶Y. C. Yeo, T. J. King, and C. Hu, *Appl. Phys. Lett.* **81**, 2091 (2002).