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

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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 5.10–12, 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. Among the many potential high-κ replacement materials currently under investigation, HfO2 has recently emerged as one of the leaders. One of the most promising deposition techniques for high-κ materials is atomic layer deposition (ALD). 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. 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. An alternate precursor that has been used for chemical vapor deposition (CVD) of HfO2 is Hf(NO3)4. 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, 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 house 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). TiN gate capacitors of area 100 μm×100 μm 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
ALD using Hf(NO$_3$)$_4$ precursor. A deposition rate of $\approx 0.08-0.14$ nm/cycle was observed over the range of deposition cycles and several different “batches” of Hf(NO$_3$)$_4$. 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 HfCl$_4$ ALD on H-terminated Si.\textsuperscript{19,21–23} Previous AFM images of one and two cycle depositions\textsuperscript{20} 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 ($C_{\text{max}}$) 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 report\textsuperscript{7} has been traced to cleanliness of the deposition chamber that was used.\textsuperscript{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.\textsuperscript{21–24}

Shown in Fig. 2 is a plot of capacitive equivalent thickness (CET) versus optical thickness for a series of HfO$_2$ films. CET was determined from $C_{\text{max}}$ 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 $\approx 40$ mV and can likely be controlled through process optimization. The final film likely consists of a HfO$_2$ layer on top of an interfacial layer. In order to extract the dielectric constant of only the HfO$_2$ 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” HfO$_2$ dielectric constant of approximately $\kappa_{\text{HfO}_2} \approx 15.9$. For thin HfO$_2$ films less than 10 nm thick, an effective dielectric constant (including both the HfO$_2$ 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 $\kappa$ that we obtain for the HfO$_2$ layer ($\approx 15.9$) is lower than the reported bulk value (25–30) and for films deposited via dc magnetron sputtering ($\approx 28$).\textsuperscript{7} CVD using Hf-t-butoxide ($\approx 26$),\textsuperscript{8} or Hf $\beta$-diketonate (22–25).\textsuperscript{9} However, both $k_{\text{eff}}$ and $k_{\text{HfO}_2}$ are consistent with other results for HfO$_2$ films deposited via CVD using Hf–

FIG. 2. CET vs optical thickness for a series of HfO$_2$ films.

nitrile ($\kappa_{\text{HfO}_2} \approx 17$),\textsuperscript{12} metalorganic CVD ($\kappa_{\text{stack}} \approx 6.6$),\textsuperscript{3} ALD ($\kappa_{\text{stack}} \approx 10.6$),\textsuperscript{14} and ALD using HfCl$_4$ ($\kappa_{\text{HfO}_2} \approx 17–18$).\textsuperscript{19} Note that because the CET does not account for quantum effects, our estimates of electrical thickness and $k_{\text{eff}}$ may be considered conservative. Excess oxygen was detected by XPS raising the possibility that it may play a role in reducing the bulk $\kappa$ of the HfO$_2$ layer.\textsuperscript{3} Our thin HfO$_2$ films also have a slightly lower density (8.5 g/cm$^3$) and refractive index (1.97) than that of bulk material (9.68 g/cm$^3$, $\approx 2.01$),\textsuperscript{20} consistent with films deposited using HfCl$_4$.\textsuperscript{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 SiO$_2$ (dielectric constant $\kappa_{\text{SiO}_2} \approx 3.9$), 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 work\textsuperscript{11} suggests that the interfacial layer is not pure SiO$_2$ but rather a medium-$\kappa$ material such as HfSiO$_3$. It is not known whether this interfacial layer is inherent to the use of Hf(NO$_3$)$_4$ 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 HfO$_2$ and SiO$_2$ (SiO$_2$ leakage adapted from Ref. 25). Leakage for the HfO$_2$ films is at least three orders of magnitude lower than SiO$_2$ of equivalent CET. For a 1.14 nm EOT film (including quantum effects), a leakage current density of $5.4 \times 10^{-3}$ A/cm$^2$ was obtained. It is seen in Fig. 3 that the HfO$_2$ curve has a steeper slope than the SiO$_2$ curve. Previous reports comparing leakage in HfO$_2$ to SiO$_2$ have been mixed. Data reported by Kang et al.\textsuperscript{16} shows that the slope of HfO$_2$ is less than SiO$_2$, suggesting a relative improvement of the HfO$_2$ leakage benefit as thickness is decreased. In Gusev et al.\textsuperscript{14} it appears that the slope of the HfO$_2$ leakage current density versus thickness is roughly parallel to that of SiO$_2$, while in Hergerother et al.\textsuperscript{15} the slope of the HfO$_2$ leakage appears to increase around 1.5 nm. A report by Ma et al.\textsuperscript{12} shows results consistent with ours. A recent modeling letter by Yeo et al.\textsuperscript{26} suggests the interfacial layer is not pure SiO$_2$ but rather a medium-$\kappa$ material such as HfSiO$_3$. It is not known whether this interfacial layer is inherent to the use of Hf(NO$_3$)$_4$ 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.

FIG. 3. Absolute leakage current density vs CET for a series HfO$_2$ films (SiO$_2$ from Ref. 25). The inset shows absolute leakage vs time for constant voltage stressing.

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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. 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 precursor as well as for electrically stressed HfO₂. 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. The electron trapping may play a role in mobility reduction as well as in HfO₂ films deposited using Hf(NO₃)₄ precursor are 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_{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.