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# Densification and improved electrical properties of pulse-deposited films via *in situ* modulated temperature annealing

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We find that the modulated temperature annealing of pulse-deposited high dielectric constant films, in which brief *in situ* elevated temperature anneals are performed after every deposition cycle, results in film densification, a reduction in interfacial layer thickness, and a strong improvement in electrical properties. The densification and improvement of electrical properties could not be achieved solely by postdeposition annealing at temperatures up to 850 °C. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1667619]

Identification of a suitable high dielectric constant replacement material for $SiO_2$ as the gate oxide in metal/oxide/semiconductor field effect transistors poses a potential barrier to continued scaling of these devices. A leading candidate replacement material is $HfO_2$.[1–8] The most promising technique for deposition of $HfO_2$ and other high-*k* films is atomic layer deposition (ALD).[2–9] Currently, the leading ALD precursor combination for deposition of $HfO_2$ is $HfCl_4$ with $H_2O$ vapor as the oxidant.[2,4,7] However, the use of $HfCl_4$ requires an initial thin layer of silicon oxide or nitride for smooth initiation of deposition on H-terminated Si—a serious drawback.[2,4] Another precursor combination, $Hf(NO_3)_4$ and $H_2O$, was shown to allow ALD of high-quality $HfO_2$ directly on H-terminated Si.[3,5,6] Recently, a dual metal precursor (DMP) method was reported in which metal chlorides, such as $HfCl_4$, were alternated with $Hf(NO_3)_4$ to deposit $HfO_2$ and other high-*k* films.[8] The $Hf(NO_3)_4$ acted as both a metal and oxygen source and enabled initiation directly on H-terminated Si. The use of dual metal containing precursors resulted in a greater than 1 monolayer (ML) per cycle deposition rate. The DMP technique is promising in that it avoids the use of a separate oxidizing agent such as $H_2O$,[8] which has been linked to charge trapping and can lead to additional unwanted oxidation of the interface.[7] These DMP films were found to exhibit a leakage current density two to three orders lower than $SiO_2$ of equivalent electrical thickness. However, the film density was lower and the leakage current density was greater than that of $HfO_2$ films deposited using other precursor combinations.[8]

In this letter, we describe an *in situ* modulated temperature annealing (MTA) technique in which rapid thermal anneals are performed after each DMP deposition cycle. We find that these additional low-temperature anneals result in densification, a reduction of interfacial layer thickness, and an improvement of electrical properties.

$HfO_2$ films were deposited on 150 mm prime grade (100) Si substrates using alternating pulses of $Hf(NO_3)_4$ and $HfCl_4$ in a custom-built ALD chamber either in turbo- or rough-vacuum mode. $HfAlO_x$ films were deposited by substituting $HfCl_4$ with $AlCl_3$. The wafer temperature during deposition was targeted at 170 °C. A brief *in situ* rapid thermal anneal at ~420 °C was performed after each deposition cycle—referred to here as MTA. Other films (non-MTA) received only a single postdeposition anneal (PDA) at ~420 °C. A temperature of ⩾400 °C was chosen because it has been shown that a PDA at 400 °C is sufficient to induce densification.[3] A deposition cycle consisted of the sequence: 5 s $Hf(NO_3)_4$ pulse/10 s $N_2$ purge/15 s $HfCl_4$ (or $AlCl_3$) pulse/10 s $N_2$ purge/30 s 420 °C $N_2$ anneal (+~5 min for cooling and stabilization at 170 °C). Note that neither pulse nor anneal times have been optimized for production. Prior to all depositions, wafers were dipped in dilute HF to remove any native oxide and produce a H-terminated Si surface. In order to immediately initiate deposition on hydrogen-terminated Si, the $Hf(NO_3)_4$ pulse must start the sequence. $Hf(NO_3)_4$ served as the oxidant; no $H_2O$ or other oxidizing agent was used. $Hf(NO_3)_4$ was synthesized in house[10] and was held at 88 °C during deposition. $HfCl_4$ and $AlCl_3$ were obtained commercially and held at 160 °C and 88 °C, respectively. Film thickness and refractive index were determined using spectroscopic ellipsometry (SE), crystalline phase using x-ray diffraction (XRD), density using x-ray reflectivity (XRR), and interfacial layer thickness using transmission electron microscopy (TEM). Electrical measurements were performed with an LCR meter and a semiconductor parameter analyzer on photolithographically defined 100 $\mu$m×100 $\mu$m capacitors. Gate patterning was followed by a 30 min 400 °C anneal in $N_2/H_2$. The capacitive equivalent thickness (CET) of the films was estimated from $C_{max}$ at 1 MHz, neglecting quantum effects.

$HfO_2$ films were grown using various numbers of deposition cycles. The as-deposited films were visually uniform with a thickness variation of less than ±5% over a 6 in. wafer. Figure 1 is a plot of ellipsometric thickness at the center of the wafer versus the number of deposition cycles for DMP films with and without[8] MTA. In both cases, the thickness was linearly dependent on the number of deposition cycles. For the films that did not receive MTA, the deposition rate was reported to be ~0.7 nm/cycle.[8] For the MTA films, the deposition rate is reduced by over a factor of 2; an average deposition rate of 0.31 nm/cycle is extracted from a linear fit. Also shown in Fig. 1 are $HfAlO_x$ films deposited

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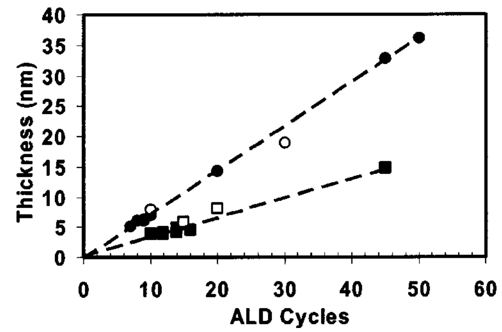

FIG. 1. Plot of thickness vs deposition cycles for DMP HfO$_2$ (solid) and HfAlO$_x$ (open) films deposited with (squares) and without MTA (circles, adapted from Ref. 8).

with and without MTA. The deposition rate for the MTA HfAlO$_x$ films is reduced by roughly the same amount. The reduction in the deposition rate with the incorporation of the MTA is attributed to the desorption of incompletely reacted ligands and/or Hf- [ligand] at the higher temperature. Although the deposition rate is lower for DMP films that received MTA, it is about 1 ML per cycle, much higher ($\sim 2\times - 8\times$) than what is typically observed for conventional ALD of HfO$_2$.[2–6] Other groups have reported high deposition rate/cycle ALD based on catalytic reactions.[11,12] The deposition rate is enhanced here because metal is deposited twice per cycle.[8,13]

Using SE, the MTA HfO$_2$ films were modeled as transparent, with $n = 2.15$ at $\lambda = 632.8$ nm. By comparison, the refractive index of the films deposited without MTA was $n = 1.97$.[8] Figure 2 shows XRR data for DMP HfO$_2$ films deposited using 45 deposition cycles [Fig. 2(a)] with and [Fig. 2(b)] without MTA. Modeling indicates that the use of MTA decreases the thickness by more than 50%, while increasing the density to 9.8–10 g/cm$^3$. This density is close to the bulk value of 10.1 g/cm$^3$ and approximately 20% higher than that of the non-MTA DMP HfO$_2$ films (7.8–8.2 g/cm$^3$).[7] As shown in Table I, the density of the MTA films is also higher than that of ALD HfO$_2$ films using HfCl$_4$/H$_2$O (8.7 g/cm$^3$),[4] Hf(NO$_3$)$_4$/H$_2$O (8.5 g/cm$^3$),[3] Hf amide/H$_2$O (9.23 g/cm$^3$),[14] and chemical vapor deposition (CVD) HfO$_2$ films using Hf *t*-butoxide at 330 °C (8.7 /cm$^3$).[15] XRD data (not shown) reveal a mixed phase when MTA films are crystallized, consisting of a tentatively identified orthorhombic phase in addition to the widely observed monoclinic phase.

TABLE I. Summary of refractive index and density for HfO$_2$.

| HfO$_2$ precursors | Refractive index ($n$) | Density (g/cm$^3$) |
|---|---|---|
| Hf(NO$_3$)$_4$/H$_2$O+PDA | ~1.96 | 8.5[d] |
| HfCl$_4$/H$_2$O | 2.08[a] | 8.7[a] |
| Hf(NO$_3$)$_4$/HfCl$_4$+PDA | ~1.96[b] | 7.8–8.2[b] |
| Hf(NO$_3$)$_4$/HfCl$_4$+MTA | ~2.15 | 9.8–10.0 |
| Hf—amide/H$_2$O | 2.05[c] | 9.23[c] |
| CVD HfO$_2$ | ⋯ | 8.7[e] |
| Bulk HfO$_2$—monoclinic | ~2.0 | 10.1[f] |
| Bulk HfO$_2$—orthorhombic | ⋯ | 10.6[g] |

[a] From Ref. 4.
[b] From Ref. 8.
[c] From Ref. 14.
[d] From Refs. 3 and 5.
[e] From Ref. 15.
[f] From Ref. 16.
[g] From Ref. 17.

Without MTA, it was found that this level of densification could not be achieved by postdeposition annealing at temperatures up to 850 °C. For example, for the films shown in Fig. 2, the as-deposited thickness (including a ~420 °C *in situ* PDA) for the film deposited without MTA was ~31.8 nm, while the thickness of the MTA film was ~14.7 nm, a 54% decrease. Subsequent 10 min isochronal annealing at temperatures up to 650 °C of the non-MTA film resulted in a final thickness of 30.4 nm, a decrease of ~4%. For another set of films, the non-MTA sample received a PDA approximately equal to the thermal budget of the MTA films (15 min@450 °C), resulting in a thickness decrease of ~5%. A subsequent 2 min anneal at 850 °C decreased thickness by only an additional 9%.

Shown in Fig. 3(a), a TEM of a DMP MTA HfO$_2$ film revealed that the thickness of the interfacial layer between the HfO$_2$ and the Si substrate was only 0.5–0.6 nm thick.[18] For comparison, shown in Fig. 3(b), an ALD HfO$_2$ film [deposited using Hf(NO$_3$)$_4$ and H$_2$O] that did not receive MTA had an interfacial thickness of ~1.0–1.2 nm.

Figure 4(a) is a plot of CET versus ellipsometric thickness for DMP HfO$_2$ films deposited with and without MTA, and variously deposited Hf(NO$_3$)$_4$/H$_2$O baseline films. It is seen that, concomitant with the density increase, the MTA films exhibit an up to 20% improvement in $k_{\mathrm{eff}}$ over the baseline Hf(NO$_3$)$_4$/H$_2$O films and DMP films without MTA. For a physical thickness of 4.0 nm, an MTA film was found to have a CET of 1.4 nm, corresponding to $k_{\mathrm{eff}} = 11.3$, and leakage (at 1 V) in the range of $3\times 10^{-4}$ A/cm$^2$. Current–voltage curves (not shown) indicated a nonoptimized hyster-

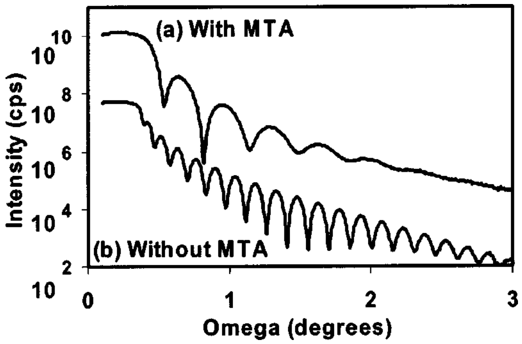

FIG. 2. XRR measurements of DMP HfO$_2$ films deposited (a) with and (b) without MTA.

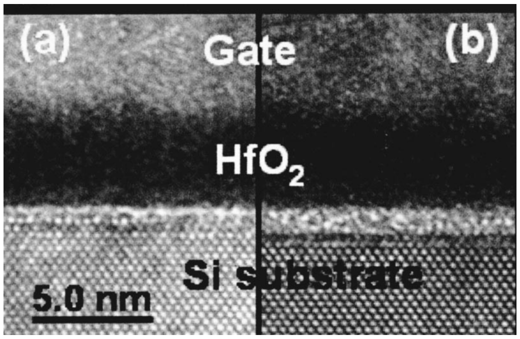

FIG. 3. TEM image of (a) DMP HfO$_2$ film with MTA and (b) ALD HfO$_2$ film without MTA.

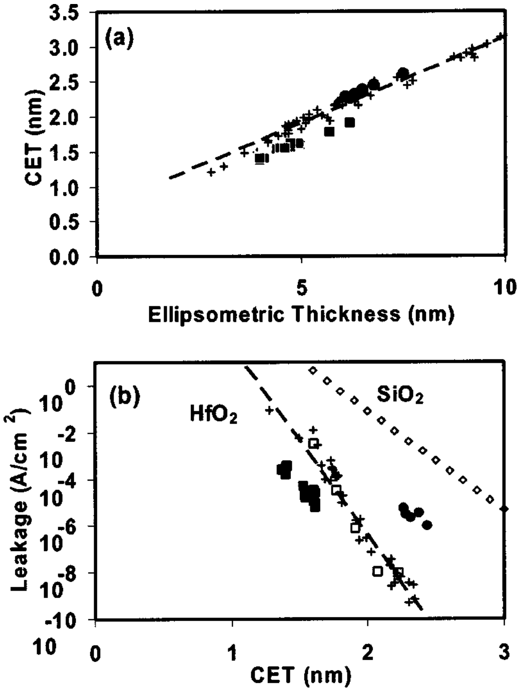

FIG. 4. Plot of (a) CET vs ellipsometric thickness and (b) leakage vs CET for DMP $HfO_2$ films with (squares: Open—roughing pump, closed—turbo pump) and without MTA (circles, adapted from Ref. 8), ALD $HfO_2$ films using $Hf(NO_3)_4/H_2O$ (crosses, adapted from Ref. 6), and $SiO_2$ films (diamonds, adapted from Ref. 19).

esis as low as 30 mV. Limited ramped voltage results indicated hard breakdown at an effective field of approximately 22 MV/cm, roughly equivalent to that observed for $Hf(NO_3)_4/H_2O$ films.

Shown in Fig. 4(b) is a plot of leakage current density at an applied accumulation bias of 1 V versus CET for DMP $HfO_2$ films deposited with and without MTA, variously deposited baseline ALD $Hf(NO_3)_4/H_2O$ films, and $SiO_2$ films.[19] The leakage current density of the MTA $HfO_2$ films deposited using the high-vacuum condition is approximately two orders less than that for ALD $HfO_2$ films deposited using various other techniques and much less than the non-MTA DMP films.

We have found that the density, interfacial layer thickness, and electrical properties of dual metal precursor pulse deposited films can be improved by a "MTA" technique in which a brief *in situ* anneal is performed after every deposition cycle. $HfO_2$ and $HfAlO_x$ films were deposited using this method. $HfO_2$ films deposited directly on H-terminated Si exhibited leakage four to six orders less than $SiO_2$ of equivalent electrical thickness, a 10%–20% improvement in dielectric constant, and approximately two orders lower leakage than $HfO_2$ deposited via ALD of $Hf(NO_3)_4/H_2O$. A density of 9.8–10 g/cm$^3$ was achieved for thin film $HfO_2$. This densification and improvement of electrical properties could not be achieved after deposition was complete, even after annealing at temperatures up to 850 °C. The MTA technique thus offers a relatively low-temperature method of film densification. Gusev *et al.*[20] suggested that Cl contamination in ALD $HfO_2$ (deposited using $HfCl_4/H_2O$) was due to incompletely reacted precursor ligands. We propose that the *in situ* anneals drive off residual precursor ligands, purifying and densifying the film. The advantage of performing the anneal step after each cycle is to remove the excess ligands before the buildup is so great that they cannot be removed by a single postdeposition anneal. This technique may be necessary to produce optimal ALD films, particularly in films where low density or precursor impurity incorporation is a problem.

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