

## Pulsed deposition of metal–oxide thin films using dual metal precursors

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A technique for depositing high-dielectric-constant metal–oxide thin films is demonstrated that consists of alternating pulses of metal–chloride precursors and  $\text{Hf}(\text{NO}_3)_4$  in which  $\text{Hf}(\text{NO}_3)_4$  is used as an oxidizing agent as well as a metal source. The use of  $\text{Hf}(\text{NO}_3)_4$ , rather than a separate oxidizing agent such as  $\text{H}_2\text{O}$ , minimizes the potential for oxidation of the Si interface. Unlike  $\text{HfCl}_4$ , a widely used precursor, the high reactivity of  $\text{Hf}(\text{NO}_3)_4$  initiates uniform deposition on H-terminated Si beginning with the first pulse. Effective dielectric constants obtained for  $\text{HfO}_2$  films produced by this method were comparable to  $\text{HfO}_2$  films deposited using other methods and the leakage current densities were three orders of magnitude less than  $\text{SiO}_2$  of the same equivalent thickness. Deposition of  $\text{HfAlO}_x$  and  $\text{HfZrO}_x$  ternary oxide films was also examined. The deposition rate for films produced using this method is greater than one monolayer per cycle, indicating a mechanism that is different from standard atomic-layer deposition. © 2004 American Institute of Physics. [DOI: 10.1063/1.1643545]

Control of the leakage current through the thin  $\text{SiO}_2$  gate oxide is currently one of the key technical challenges that must be overcome to continue scaling of metal/oxide/semiconductor field-effect transistors (MOSFETs). A potential solution to this problem lies in finding a high-dielectric constant replacement for  $\text{SiO}_2$ .<sup>1</sup> Metal–oxide thin films such as  $\text{HfO}_2$ ,  $\text{ZrO}_2$ ,  $\text{La}_2\text{O}_3$ , and  $\text{HfAlO}_x$  are currently under intense investigation as potential replacements. One of the most promising techniques for deposition of these films is atomic-layer deposition (ALD) in which alternating, purge separated, saturating pulses of reactants are used to deposit films one atomic layer at a time.<sup>2</sup> Currently, the most widely used ALD precursors are the metal chlorides ( $\text{MCl}_x$ , where  $x$ =the valence of metal). The use of these precursors with  $\text{H}_2\text{O}$  as an oxidizing agent allows ALD of high quality films with good electrical characteristics.<sup>3</sup> However, metal chlorides do not allow smooth initial deposition on hydrogen terminated Si surfaces.<sup>3,4</sup> Recently, it has been demonstrated that a thin ( $\sim 0.7$  nm) initial layer of chemically grown  $\text{SiO}_2$  is necessary for metal chlorides to initiate a smooth deposition.<sup>4</sup> Since an equivalent oxide electrical thickness of less than 1 nm will be required of a high- $k$  gate oxide stack, this requirement of a few initial monolayers of  $\text{SiO}_2$  may limit the scaling potential of ALD films deposited using metal–chloride precursors.

Another class of precursors known as metal nitrates [ $\text{M}(\text{NO}_3)_x$ ] has been used for chemical vapor deposition (CVD)<sup>5,6</sup> and, when alternated with  $\text{H}_2\text{O}$ , has been shown to allow ALD<sup>7–9</sup> directly on H-terminated Si. High quality films with good electrical characteristics have been achieved using metal nitrates.<sup>5–9</sup> However, ALD  $\text{HfO}_2$  films deposited using Hf nitrate and  $\text{H}_2\text{O}$  may contain excess oxygen,<sup>7–9</sup> which would suggest that the electrical properties might be

further improved by reducing oxygen content.

In this letter, a deposition technique is introduced that utilizes only metal precursors, one of which provides the oxidizing species. Deposition of high quality  $\text{HfO}_2$  films is achieved using alternating pulses of  $\text{Hf}(\text{NO}_3)_4$  and  $\text{HfCl}_4$ . In addition,  $\text{HfAlO}_x$  and  $\text{HfZrO}_x$  ternary oxide films were deposited using  $\text{AlCl}_3$  and  $\text{ZrCl}_4$ , respectively. In this deposition method,  $\text{Hf}(\text{NO}_3)_4$  plays the role of oxidizing agent as well as that of a metal source. The use of a separate oxidizing agent (such as  $\text{H}_2\text{O}$ ,  $\text{O}_3$ , etc.), which can result in enhanced oxidation of the Si interface,<sup>10</sup> is avoided. Ritala *et al.*<sup>11</sup> have recently used metal alkoxides as oxygen sources for deposition of metal–oxide thin films. The use of  $\text{Hf}(\text{NO}_3)_4$  reduces the potential for carbon contamination. This method is promising in that it allows the use of the widely available metal chlorides to deposit films directly on H-terminated Si. The deposition rates per cycle are found to be much higher than for standard ALD.

$\text{HfO}_2$  films were deposited on 150 mm prime grade (100) Si substrates using alternating pulses of  $\text{Hf}(\text{NO}_3)_4$  and  $\text{HfCl}_4$  precursors in a custombuilt ALD chamber.  $\text{HfAlO}_x$  and  $\text{HfZrO}_x$  films were deposited using alternating pulses of  $\text{Hf}(\text{NO}_3)_4$  and either  $\text{AlCl}_3$  or  $\text{ZrCl}_4$ . All precursor pulses were separated by  $\text{N}_2$  purges.  $\text{Hf}(\text{NO}_3)_4$  served as the oxidant;  $\text{H}_2\text{O}$  or other oxidizing agents were not used. For comparison,  $\text{HfO}_2$  films were also deposited via ALD using  $\text{Hf}(\text{NO}_3)_4$  and  $\text{H}_2\text{O}$ .  $\text{Hf}(\text{NO}_3)_4$  was synthesized inhouse<sup>12</sup> and was held at 88 °C during deposition, whereas  $\text{HfCl}_4$  was obtained commercially and held at 160 °C. The wafer temperature during deposition was set between 150 and 190 °C. Immediately prior to all depositions, wafers were dipped in diluted HF to remove any native oxide and produce a H-terminated Si surface. The film thickness and refractive index were determined using a spectroscopic ellipsometer (SE). The film phase and density were determined using

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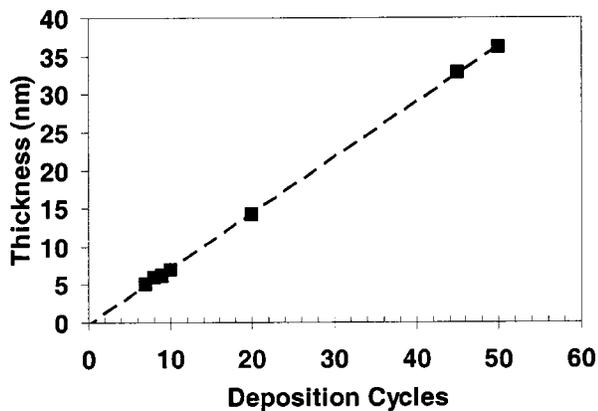


FIG. 1. Plot of the thickness vs the number of deposition cycles for films deposited via alternating pulses of  $\text{Hf}(\text{NO}_3)_4$  and  $\text{HfCl}_4$ .

x-ray diffraction (XRD) and x-ray reflectivity (XRR).

Electrical measurements were performed on photolithographically defined  $100\ \mu\text{m} \times 100\ \mu\text{m}$  capacitors. Gate patterning was followed by a 30 min,  $450\ ^\circ\text{C}$  anneal in  $\text{N}_2/\text{H}_2$ . Capacitance versus voltage (*CV*) measurements were made using an HP 4284. Leakage current density and ramped breakdown measurements were made using an Agilent 4156 A. The capacitive equivalent thickness (CET) of the films was conservatively estimated from  $C_{\text{max}}$ , neglecting quantum effects.

Figure 1 shows a plot of the average film thickness versus the number of deposition cycles for  $\text{HfO}_2$  films deposited at  $170\ ^\circ\text{C}$ . Each “dual precursor” cycle consists of  $\text{Hf}(\text{NO}_3)_4/\text{N}_2/\text{HfCl}_4/\text{N}_2$ . A postdeposition *in situ* anneal (PDA) for 60 s at approximately  $400\ ^\circ\text{C}$  was performed. Films were visually uniform. SE measurements indicated that the  $\text{HfO}_2$  films could be modeled as transparent with  $n=1.96$  at  $\lambda=632.8\ \text{nm}$ , roughly equivalent to  $\text{HfO}_2$  films deposited using ALD of  $\text{Hf}(\text{NO}_3)_4$  and  $\text{H}_2\text{O}$ .<sup>7,8</sup> Less than  $\pm 6\%$  variation in thickness and  $C_{\text{max}}$  was measured across a 150 mm wafer. The thickness was observed to be linearly dependent on the number of cycles, with an average deposition rate of approximately 0.7 nm/cycle (extracted from the slope of a linear fit to the data in Fig. 1). The linear fit intersects very close to the origin, indicating that “incubation” cycles were not required, i.e., initiation occurred directly on H-terminated Si. At a given temperature, the deposited thickness/cycle appeared to approach saturation at long pulse times, similar to ALD growth. The deposition rate was approximately 5–15 times greater than what has been reported for ALD of  $\text{HfO}_2$  using either  $\text{Hf}(\text{NO}_3)_4$  and  $\text{H}_2\text{O}$  or  $\text{HfCl}_4$  and  $\text{H}_2\text{O}$ .<sup>4–7</sup> Thus, this method may allow more efficient deposition of  $\text{HfO}_2$  films in quasi-ALD mode. Deposition rates of greater than one monolayer per cycle were also reported by Hausmann *et al.*,<sup>13</sup> and were explained as a catalytic reaction. Possible explanations for multimonomer deposition per cycle in this work are that (1) both precursors are metal sources, (2) the availability of excess oxygen atoms from the reactive nitrate ligands to oxidize several chloride molecules, and (3) incorporation of excess ligands due to the low deposition temperature (ALD using  $\text{HfCl}_4$  is typically performed at  $300\ ^\circ\text{C}$ ). The deposition conditions are sensitive to a number of parameters and have not been optimized.

XRR analysis of several films deposited with and without PDA (not shown) indicated that the dual precursor films were smooth [0.3–0.4 nm root mean square (rms) roughness] and that the  $400\ ^\circ\text{C}$  PDA resulted in densification, with the density increasing from  $\sim 6.2$  to  $7.8\text{--}8.2\ \text{g}/\text{cm}^3$ , about 5% less than that reported for other deposition methods. Densification is likely due to the removal of excess precursor ligands. XRD analysis was employed to confirm that the as-deposited films remained amorphous after the initial  $400\ ^\circ\text{C}$  *in situ* PDA. A  $600\ ^\circ\text{C}$  anneal was sufficient to render the films polycrystalline monoclinic.

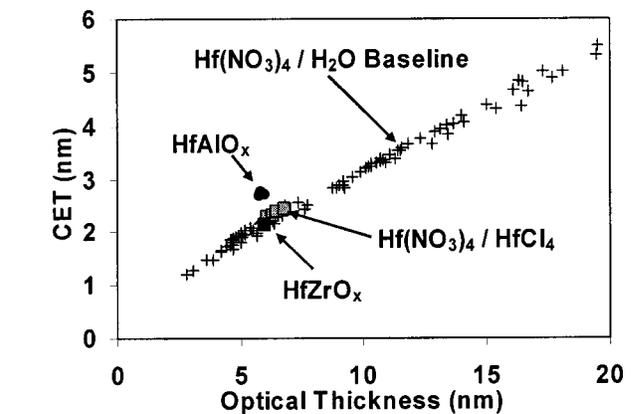


FIG. 2. Comparison of the CET vs the ellipsometric thickness for dual precursor  $\text{HfO}_2$  films (closed squares), ALD  $\text{HfO}_2$  films using  $\text{Hf}(\text{NO}_3)_4/\text{H}_2\text{O}$  (crosses, replotted from Ref. 9),  $\text{HfAlO}_x$  films (closed circles), and a  $\text{HfZrO}_x$  film (gray square).

Current-voltage (*CV*) and *IV* measurements were made on a variety of  $\text{TiN}/\text{HfO}_2/\text{Si}$  capacitors. Figure 2 shows a plot of the electrical versus ellipsometric thickness for  $\text{HfO}_2$  films deposited via the dual precursor method (closed symbols) and, as a comparison, the films deposited via ALD using  $\text{Hf}(\text{NO}_3)_4/\text{H}_2\text{O}$  (crosses). For films of ellipsometric thickness less than 20 nm, the dielectric constant of the  $\text{Hf}(\text{NO}_3)_4/\text{HfCl}_4$  films is about equal to the baseline  $\text{Hf}(\text{NO}_3)_4/\text{H}_2\text{O}$  films. For thicker dual precursor  $\text{HfO}_2$  films (not shown), the dielectric constant is not quite as good as the baseline. Figure 3 is a plot of the leakage current density versus the CET. Leakage of the dual precursor film is approximately three orders of magnitude less than that of  $\text{SiO}_2$  (Ref. 14) of similar CET, but greater than that of  $\text{HfO}_2$

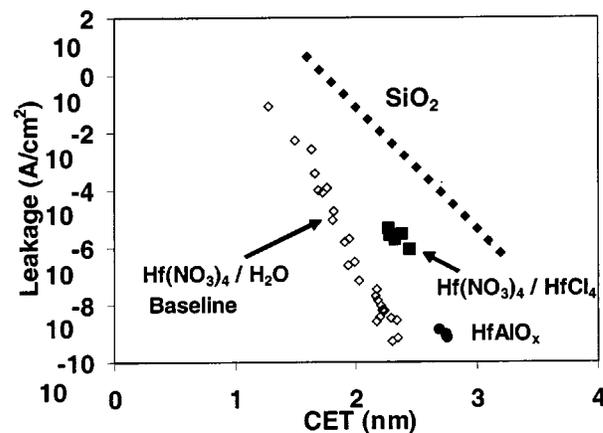


FIG. 3. Comparison of the leakage vs the CET for dual precursor  $\text{HfO}_2$  films (closed squares),  $\text{SiO}_2$  films (closed diamonds, adapted from Ref. 14), ALD  $\text{HfO}_2$  films using  $\text{Hf}(\text{NO}_3)_4/\text{H}_2\text{O}$  (open diamonds, adapted from Ref. 9), and  $\text{HfAlO}_x$  films (closed circles).

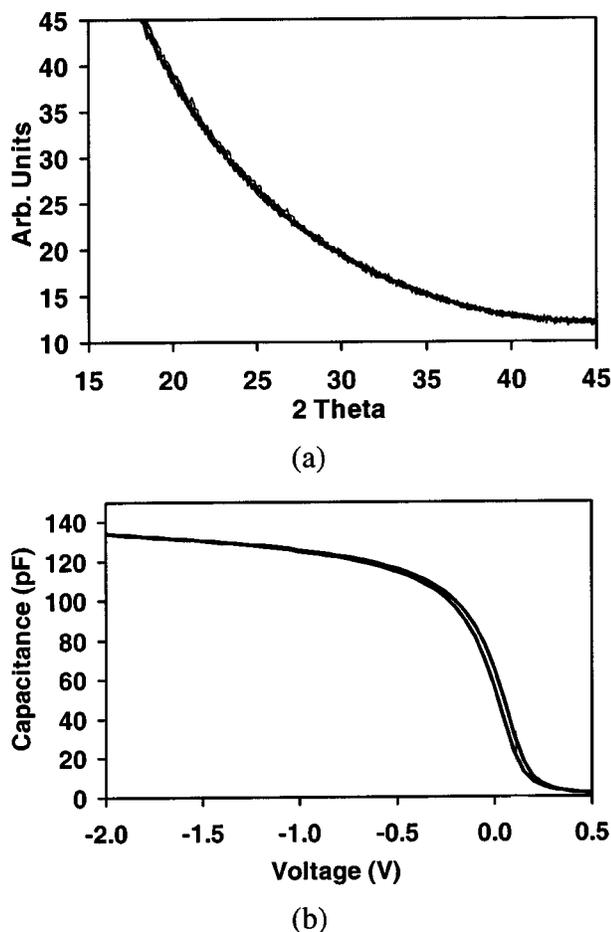


FIG. 4.  $\text{HfAlO}_x$  films deposited using  $\text{Hf}(\text{NO}_3)_4$  and  $\text{AlCl}_3$ . (a) XRD spectrum of 3 nm thick film isochronal annealed at temperatures up to 900 °C. (b) CV curves for 5.9 nm thick film.

posited via  $\text{Hf}(\text{NO}_3)_4/\text{H}_2\text{O}$ . The hysteresis was generally less than 50 mV. Although the absolute capacitor breakdown fields ( $E_{\text{bd}}$ ) are  $\sim 6$  MV/cm, typically much lower than  $\text{SiO}_2$  ( $>15$  MV/cm), effective breakdown fields (using the CET) are  $>15$  MV/cm, comparable to what is typically reported for  $\text{HfO}_2$  films.

Finally, it was demonstrated that  $\text{Hf}(\text{NO}_3)_4$  can be used as an oxidizing agent for other metal halides. Shown in Fig. 4(a) is a series of XRD scans of an  $\sim 3$  nm thick  $\text{HfAlO}_x$  film deposited using alternating pulses of  $\text{Hf}(\text{NO}_3)_4$  and  $\text{AlCl}_3$  that were exposed to a 400 °C postdeposition  $\text{N}_2$  anneal. The film was subsequently exposed to a series of 10 s isochronal  $\text{N}_2$  anneals from 500 to 950 °C. No peaks in the range of  $2\theta=15^\circ\text{--}45^\circ$  appeared at temperatures up to 900 °C. An additional trace at 950 °C (not shown) also showed no signs of crystallization. The crystallization temperature of the  $\text{HfAlO}_x$  film was higher than that for  $\text{HfO}_2$  films, consistent with reports for other Al-doped films.<sup>15</sup> Shown in Fig. 4(b) is a CV trace of a 5.9 nm  $\text{HfAlO}_x$  film with hysteresis of  $\sim 30$  mV, an effective dielectric constant of approximately 8.5, between  $\text{SiO}_2$  and  $\text{HfO}_2$  of equivalent thickness (see Fig. 2), and leakage more than four orders of magnitude less than  $\text{SiO}_2$  (see Fig. 3).  $\text{HfZrO}_x$  films deposited using alternating pulses of  $\text{Hf}(\text{NO}_3)_4$  and  $\text{ZrCl}_4$  also exhibited reasonable

electrical characteristics. For a 6 nm film deposited using 10 cycles,  $k_{\text{eff}}\sim 11$  was obtained (see Fig. 2) with hysteresis of  $\sim 50$  mV.

The use of  $\text{Hf}(\text{NO}_3)_4$  as an oxidizing agent for metal chlorides was found to be a promising method for depositing high- $k$  metal oxides directly onto H-terminated Si. This method avoids the use of  $\text{H}_2\text{O}$  or other separate oxidizing agents which can lead to enhanced oxidation of the Si interface. In addition to  $\text{HfO}_2$  using  $\text{HfCl}_4$ , it was shown that  $\text{Hf}(\text{NO}_3)_4$  can also be used as an oxidizing agent for other precursors such as  $\text{AlCl}_3$  and  $\text{ZrCl}_4$  to produce ternary metal-oxide films such as  $\text{HfAlO}_x$  and  $\text{HfZrO}_x$ . The deposition rate was found to be much higher than for conventional ALD,<sup>11,13</sup> likely due to the incorporation of metal during both precursor cycles. The density of  $\text{HfO}_2$  deposited from dual precursors was about 5% lower than monolayer deposition, even after a 400 °C PDA. Postdeposition annealing plays a critical role in determining the film properties, especially when multimonolayers are deposited per cycle. For a given material, to first order, higher density results in a higher refractive index and a higher dielectric constant. Additional annealing or other processes to improve film density may thus result in an improvement in dielectric properties. Work is ongoing to deposit films using  $\text{Hf}(\text{NO}_3)_4$  and other nitrates as an oxygen source for other classes of precursors (e.g., TMA), to optimize electrical properties, and to determine how these films impact channel electron mobility.

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