Chem. Mater. **2004,** *16,* 3497−3501

Atomic Layer Deposition of Insulating Hafnium and Zirconium Nitrides

Jill S. Becker, Esther Kim, and Roy G. Gordon*

Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

Received March 21, 2004. Revised Manuscript Received June 15, 2004

Highly uniform, smooth, and conformal coatings of higher nitrides of hafnium and zirconium were produced by atomic layer deposition from homoleptic tetrakis(dialkylamido)-metal(IV) complexes and ammonia at low substrate temperatures (150−250 °C). The precursor vapors were alternately pulsed into a heated reactor, yielding 1.15−1.20 Å of metal nitride film for every cycle. Successful depositions were carried out on silicon, glass, quartz, and glassy carbon. All of the films showed good adhesion to the substrates, were chemically resistant, and did not oxidize over time. The films were characterized by Rutherford backscattering spectrometry and ellipsometry. These films were amorphous as deposited, as shown by X-ray diffraction and transmission electron microscopy. Step coverage is 100% in vias with an aspect ratio of 40:1, as determined by scanning electron microscopy. Evidence is given for the existence of nitrogen-rich phases with compositions Hf_3N_4 and Zr_3N_4. These two materials are insulating, transparent, and colored, in contrast to the well-known mononitrides, which are shiny, gold-colored, and highly conducting.

I. Introduction

The mononitrides of hafnium and zirconium of stoichiometry MN (M = Hf, Zr) are all metallic conductors.[1] On the other hand, the higher nitrides of hafnium and zirconium, M_3N_4, are reported to be transparent insulators or semiconductors.[2−11] In general, the properties of group IV nitrides are well-understood for nitrogen-poor materials,[1] but the nitrogen-rich compositions remain an active area of research.

Thin films of M_3N_4 have been prepared by chemical vapor deposition (CVD)[5−12] and by some physical vapor deposition (PVD) techniques,[6−11] such as ion beam deposition, triode ion plating, reactive sputtering, and ion implanting.

In atomic layer deposition (ALD), gaseous precursors are dosed alternately onto a surface on which they undergo self-limiting reactions with each other. Films grown by ALD have very uniform thickness and excellent conformality. Because ALD has several advantages over CVD or PVD, including better step coverage, denser films, and better control of morphology, microstructure, and stoichiometry, there is a clear need to develop ALD routes to the M_3N_4 phases so that a wider variety of applications can be realized.

In this paper, we report the atomic layer deposition of thin films of Hf_3N_4 and Zr_3N_4 using homoleptic tetrakis(dialkylamido)metal(IV) complexes and ammonia at low substrate temperatures (150−250 °C).

Table 1. Metal Dialkylamides

precursor		mp (°C)
tetrakis(dimethylamido)hafnium	$Hf(NMe_2)_4$	30
tetrakis(ethylmethylamido)hafnium	$Hf(NEtMe)_4$	liquid
tetrakis(diethylamido)hafnium	$Hf(NEt_2)_4$	liquid
tetrakis(dimethylamido)zirconium	$Zr(NMe_2)_4$	58
tetrakis(ethylmethylamido)zirconium	$Zr(NEtMe)_4$	liquid
tetrakis(diethylamido)zirconium	$Zr(NEt_2)_4$	liquid

II. Experimental Section

Precursors. The compounds $Hf(NMe_2)_4$, $Hf(NEtMe)_4$, $Hf(NEt_2)_4$, $Zr(NMe_2)_4$, $Zr(NEtMe)_4$, and $Zr(NEt_2)_4$ (listed in Table 1) were synthesized from the metal chlorides and the lithium salts of the corresponding amines, on the basis of the synthetic preparations published by Bradley and co-workers.[13,14] Once all of the precursors became commercially available, they were obtained from Strem and Aldrich Chemical Co. The purity of all precursors was checked by ^1H NMR before use.

ALD Reactor. The ALD experimental setup, illustrated in Figure 1, consisted of an inert carrier/purge gas delivery assembly, an ammonia delivery line, an organometallic pre-

* Corresponding author. E-mail: gordon@chemistry.harvard.edu.

(1) Toth, L. E. *Transition Metal Carbides and Nitrides*; Margrave, J. L., Ed.; Refractory Materials Vol. 7; Academic Press: New York, 1971.
(2) Straboni, A.; Pichon, L.; Girardeau, T. *Surf. Coatings Technol.* **2000**, *125*, 100.
(3) Sanz, J. M.; Soriano, L.; Prieto, P.; Tyuliev, G.; Morant, C.; Elizalde, E. *Thin Solid Films* **1998**, *332*, 209.
(4) Prieto, P.; Galán; Sanz, J. M. *Phys. Rev. B.* **1993**, *47*(3), 1613.
(5) Fix, R.; Gordon, R. G.; Hoffmann, D. M. *Chem. Mater.* **1991**, *3*, 1138.
(6) Solynshko, L. N.; Chistyi, I. L.; Drobot, A. D.; Yampol'skii, V. I. Egorov, V. N. *Sov. J. Opt. Technol. (Engl. Transl.)* **1981**, *48*, 562.
(7) Yee, D. S.; Cuomo, J. J.; Frisch, M. A.; Smith D. P. E. *J. Vac. Sci. Technol. A* **1986**, *4*, 381.
(8) Salmenoja, K.; Korhonene, A. S.; Erola, E.; Molarius, J. M. *Appl. Phys. Lett.* **1986**, *49*, 505.
(9) Johansson, B. O.; Hentzell, H. T. G.; Harper, J. M. E.; Cuomo, J. J. *J. Mater. Res.* **1986**, *1*, 442.
(10) Ristolainen, E. O.; Molarius, J. M.; Korhonen, A. S.; Lindroos, V. K. *J. Vac. Sci. Technol. A* **1987**, *5*, 2184.
(11) Netterfield, R. P.; Martin, P. J.; McKenzie, D. R. *J. Mater. Sci. Lett.* **1990**, *9*, 972.
(12) Atagi, L. M.; Samuels, J. A.; Smith, D. C.; Hoffman, D. M. *Matomic Res. Soc. Symp. Proc.* **1996**, *40*, 289.
(13) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857.
(14) Bradley, D. C.; Gitlitz, M. H. *J. Chem. Soc. (A)* **1969**, 980.

10.1021/cm049516y CCC: $27.50 © 2004 American Chemical Society
Published on Web 08/06/2004

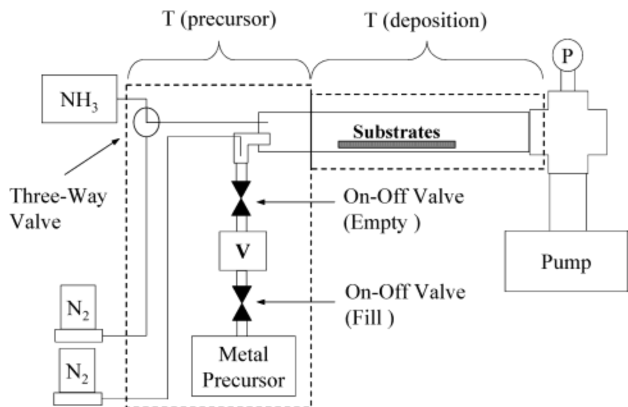

Figure 1. Schematic drawing of the experimental ALD apparatus.

Table 2. Rotary Vane Pumps Used

Edwards model	reported pumping speed, L/min	effective pumping speed, L/min	total pressure in reactor, Torr (with N_2)
RV3	75	43	0.35
RV8	195	61	0.25
RV12	283	76	0.20

cursor handling system, and an ALD flow reactor. The parts are described below.

Depositions were carried out in a flow ALD reactor that consisted of a stainless steel tube (40 cm in length and 2.2 cm in inner diameter) heated in a tube furnace attached to a rotary vane oil pump (Figure 1). The precursors are introduced alternatingly from one end of the tube into the heated reaction/deposition zone that is 25 cm long. Within this zone the substrates sit on an aluminum or stainless steel substrate holder (25.5 cm long, 2.15 cm wide, 0.9 cm deep), which is introduced from the other end of the reactor via a removable flange. The substrate holder takes up the lower half of the stainless steel tube. The surface area of the reactor wall in this region is 180 cm^2 and of the substrate holder is 111 cm^2. The total surface area in the deposition zone is 291 cm^2. Under ideal deposition conditions, film was deposited on all surfaces in this region.

Depositions were carried out at temperatures ranging from 150 to 300 °C.

Inert Gas and Ammonia Delivery Systems. The inert-gas delivery system supplied the carrier gas, nitrogen, for the metal-containing precursor and the ammonia. Nitrogen (impurities < 1 ppm) was purified by passing it first through a drying column of P_2O_5 and then a Mykrolis inert gas purifier (Model WPMV200SI). The purifier was rated by the manufacturer to produce an outflow containing less than 1 ppb of oxygen and 1 ppb of water. This nitrogen was also used as the purge gas between doses of precursors. The length of purging between doses affected the film growth (see below). Each precursor had its own nitrogen line fed through separate 1.0 mm inner diameter stainless steel tubing and introduced into the reactor through a bored-through flange at one end of the tube. Mass flow controllers were set at 10 sccm for each precursor, giving a total constant nitrogen gas flow of 20 sccm at all times. Depending on which size of pump was used to remove the excess unreacted precursors, byproducts, and nitrogen from the other end of the reactor, the total pressure in the reactor was constant and lower than any of the vapor pressures of the precursors (see Table 2). The pressure difference introduces the precursors into the deposition zone. Using a pump with a lower pumping speed increases the exposure of the precursors, giving them more time to react. This was especially important in depositing conformally down into high-aspect-ratio trenches.

Electronic-grade ammonia, obtained from Matheson, was sent through a Mykrolis gas purifier (Model WPMV200SM) before entering a two-position gas chromatography (GC) valve

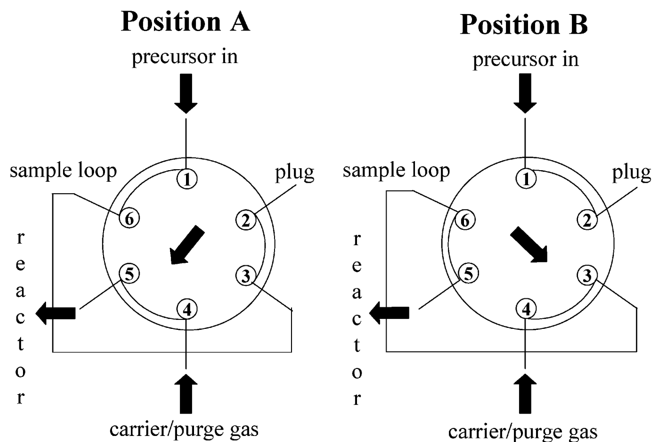

Figure 2. A schematic diagram illustrating the filling of a sample loop with ammonia in position A and emptying it in position B.

Table 3. Precursor Temperature

precursor	precursor temp (°C)	precursor	precursor temp (°C)
$Hf(NMe_2)_4$	75	$Zr(NMe_2)_4$	75
$Hf(NEtMe)_4$	100	$Zr(NEtMe)_4$	95
$Hf(NEt_2)_4$	130	$Zr(NEt_2)_4$	120

purchased from Valco Instruments (Model DC6WE). The GC valve was connected to the reactor via 1.0 mm inner diameter stainless steel tubing and controlled electronically by two-position microelectronic actuators to be either in position A, where only nitrogen gas enters the reactor and ammonia fills the GC sample loop, or position B, where the sample loop is emptied within 1 s and ammonia is dosed into the reactor (Figure 2). The ammonia dose was controlled by changing the size of the sample loops from 10 μL to 1 mL (all at 20 psig). Under normal deposition conditions (using the RV12), the ammonia was dosed for 1.0 s, at a pressure of 20 psig, using a 50 μL sample loop. This corresponds to an ammonia dose of 14.1 nmol/cm^2 and an exposure of 5.6×10^4 langmuir/cycle.

Precursor Handling System. The precursors were each placed in a 40 mL stainless steel container. The container was kept at a certain temperature depending on which precursor was used to provide enough vapor pressure to allow for a saturating vapor dose (Table 3). For $Hf(NMe_2)_4$, for example, this corresponds to a hafnium precursor dose of 1.5 nmol/cm^2 and an exposure of 5.8×10^3 langmuir/cycle. This vapor was introduced into a closed-off vapor space of 26.8 mL via an electronically controlled air actuated diaphragm valve that was opened for 1.0 s. This valve was known as the “fill valve”. The vapor space was then nearly emptied through a second air actuated valve known as the “empty valve”. This valve too was opened only for a second while the fill valve was closed. All of the valves, GC and air actuated, as well as the precursor reservoir, were kept in an oven to regulate the temperature. The amount of metal precursor was varied by doing from 1 to 10 multiple doses before an ammonia vapor dose was introduced, to test the self-limiting behavior of the surface reactions. At least 5 s of purging was allowed between the introductions of precursors. One ALD reaction cycle is defined as one dose of the metal precursor, followed by a minimum of 5 s purging, and then one dose of ammonia, followed by a minimum of 5 s purging. At all times during the deposition, nitrogen flow was kept constant. During a purge, no precursors were introduced into the reactor.

Depositions. The ALD system, loaded with substrates, was purged for at least 3 h before each deposition to displace air and moisture. This was the minimum time experimentally determined to keep the oxygen content of all the films as low as possible. It was also the time needed to get the rate of rise in the system, when isolated from the pump, to be reduced to 1 mTorr/min. Silicon substrates were prepared by removing

the native oxide with dilute hydrofluoric acid solution and rinsing with distilled water, creating a hydrophobic surface. Next, the substrates were irradiated by ultraviolet light from a mercury lamp in air (forming ozone) until the surface became hydrophilic (normally 3 min). Then the substrate was placed in the chamber on the substrate holder via a removable flange near the connection between the deposition chamber and the vacuum pump. Another silicon substrate with elliptical narrow holes (0.17 μm × 0.30 μm × 7.3 μm deep) was also cleaned and placed in the chamber onto the substrate holder.

Film Characterization. Film thickness and refractive index were determined by ellipsometry (Rudolph Auto-El II fixed wavelength 632.8 nm). Composition and number of atoms per unit area were determined by Rutherford backscattering spectroscopy (RBS) using a beam of 2.0 MeV He^+ (General Ionics Model 4117, 1.7 MeV Tandetron) for samples grown on glassy carbon and on silicon. Surfaces were examined by scanning electron microscopy (Leo 982 high-resolution emission SEM). Roughness measurements were made by atomic force microscopy (AFM) (Nanoscope III and IV, Digital Instruments). X-ray diffraction (XRD) (Scintag Model XDS2000) and electron diffraction by transmission electron microscopy (TEM) (Philips EM420T) was used to determine that the films were amorphous. Conformality (step coverage) was evaluated using a SEM to image cleaved cross sections of holes with aspect ratios greater than 40:1. For dielectric measurements, the films were deposited onto platinum electrodes evaporated onto silicon substrates and were covered by evaporated platinum electrode pads.

III. Results and Discussion

New processes for ALD of Hf_3N_4 and Zr_3N_4 are reported. Pure films of these phases were obtained by ALD reactions of homoleptic tetrakis(dialkylamido)-metal(IV) complexes with ammonia. Control experiments using only these metal dialkylamide precursors and no ammonia showed no deposition on substrates previously deposited with nitride or on bare substrates at temperatures from 150 to 300 °C (depending on the precursor used). Similar low-temperature reactions utilizing metal alkylamide precursors were found to be suitable for ALD of other nitrides, including the metallic conductors VN and Nb_3N_4 and the insulators AlN and Ta_3N_5.[16]

After the desired number of cycles was completed, the substrates were removed from the reactor. The substrates were examined by ellipsometry and found to have a film with uniform thickness along the 25 cm length of the deposition zone (see Figure 3). The thickness was linear in relation to the number of cycles (see Figure 4). The film growth started right within the first few cycles and no "initiation" period was observed. Successful depositions were carried out on all substrates tested, including silicon, glass, quartz, glassy carbon, stainless steel, aluminum, and platinum.

In all cases, the refractive indexes were not dependent on the temperature at which the films were deposited. The refractive indexes for the zirconium nitride films were in the range of 2.8−3.2. These values are in good agreement with those reported in the literature.[5] The refractive indexes of hafnium nitride films were in the range of 2.4−2.5. The refractive indexes were strongly dependent on oxygen content (from residual oxygen or water in the carrier gas); for example, the indexes were

(15) Zerr, A.; Miehe, G.; Riedel, R. *Nature Mater.* **2003**, *2*(3), 185−189.
(16) Becker, J. S.; Gordon, R. G. Unpublished work.

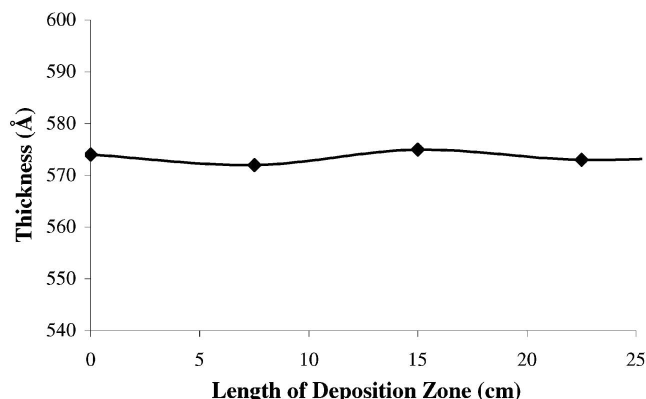

Figure 3. Uniformity of thickness for a Hf_3N_4 film along a 25 cm deposition zone at 200 °C for 500 cycles.

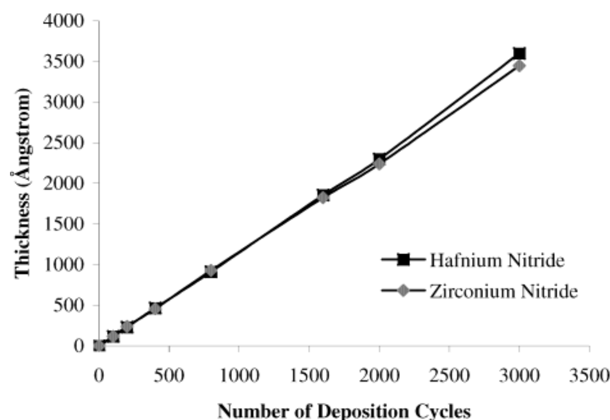

Figure 4. The linear relationship between film thickness and the number of deposition cycles at 200 °C for Hf_3N_4 and Zr_3N_4 is shown.

2.1−2.2 for zirconium nitride films containing greater than 8 atom % of oxygen. The same was true for hafnium nitride films contaminated with more than 5 atom % oxygen. The reactivity of ammonia with $Hf(NMe_2)_4$ and $Zr(NMe_2)_4$ was much greater than with $Hf(NEtMe)_4$, $Hf(NEt_2)_4$, $Zr(NEtMe)_4$, and $Zr(NEt_2)_4$. We infer this conclusion because only the films grown with $Hf(NMe_2)_4$ and $Zr(NMe_2)_4$ were without any appreciable oxygen contamination. For this reason, the rest of this paper deals with films grown only from the tetrakis(dimethylamido)metal(IV) complexes.

The ALD saturated growth rates for Hf_3N_4 and Zr_3N_4 was 1.1−1.2 Å per cycle in the ALD window of 200−250 °C (Figure 5). The increase in thickness per cycle at higher temperatures is due to thermal decomposition of the precursor. The slightly higher film growth at lower temperatures may be due to some physisorption of the precursor(s) adding to the thickness. One can use a higher nitrogen flow and/or a larger pump to avoid physisorption of excess material, by moving the excess precursor out of the deposition zone more quickly. Physisorption can also be reduced by increasing the purge time between precursors, but this lengthens the overall deposition process as well. In addition, extra long purge times can allow the precursor to decompose on the surface of the substrate before it can react with the next dose of ammonia. Such self-decomposition of the precursor on the surface can lead to incorporation of impurities, such as carbon, into the films.

Films obtained from tetrakis(dimethylamido)zirconium(IV) and ammonia in the temperature range of

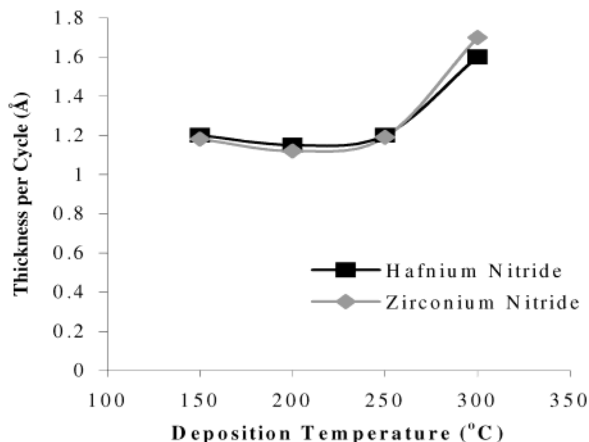

Figure 5. ALD saturated growth rates of Hf_3N_4 and Zr_3N_4, as a function of substrate temperature.

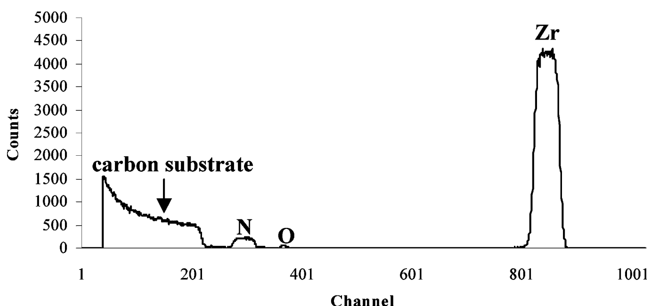

Figure 6. Rutherford backscattering spectra of zirconium nitride deposited from $Zr(NMe_2)_4$ and ammonia at 175 °C on a carbon substrate.

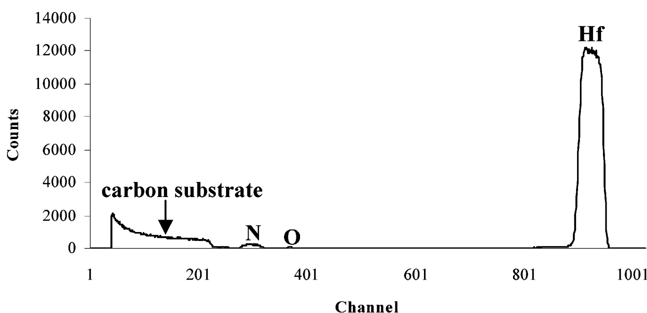

Figure 7. Rutherford backscattering spectra of hafnium nitride deposited from $Hf(NMe_2)_4$ and ammonia at 200 °C on a carbon substrate.

150−200 °C had a metal-to-nitrogen ratio of 1:1.3 as determined by RBS (Figure 6). This ratio is consistent with the nitrogen-rich phase Zr_3N_4. The hafnium nitride films, obtained from tetrakis(dimethylamido)hafnium(IV) complexes and ammonia in the temperature range of 150−250 °C, also had a metal-to-nitrogen ratio of 1:1.3 (Figure 7). For both the zirconium and hafnium nitride films, the stoichiometries were independent of the deposition temperature. No carbon or oxygen was detected in the films by RBS. Evidence of a slight surface oxidation can be seen in the spectra, but this did not increase over time. The carbon content in the zirconium and hafnium nitrogen-rich films was always below 0.5 atom %. The density of Hf_3N_4 and Zr_3N_4 was found by combining RBS and ellipsometry data to be 9.4 g/cm^3 (bulk value = 13.058 g/cm^3)[15] and 6.3 g/cm^3 (bulk value = 6.34 g/cm^3),[15] respectively. TEM and XRD revealed that the films as deposited were amorphous.

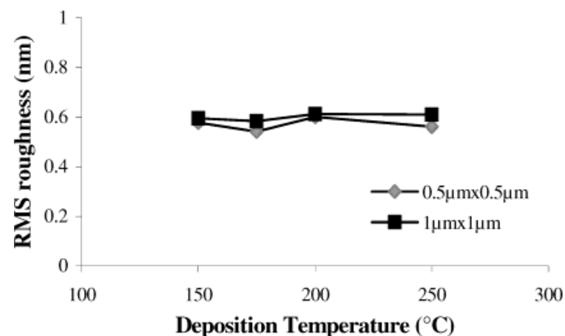

Figure 8. The effect of ALD deposition temperature on the rms film roughness of Hf_3N_4 (500 cycles).

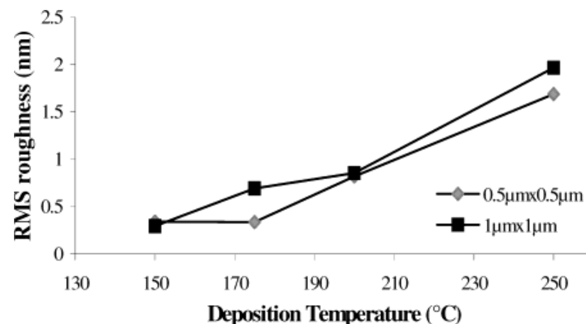

Figure 9. The effect of ALD deposition temperature on the rms film roughness of Zr_3N_4 (500 cycles).

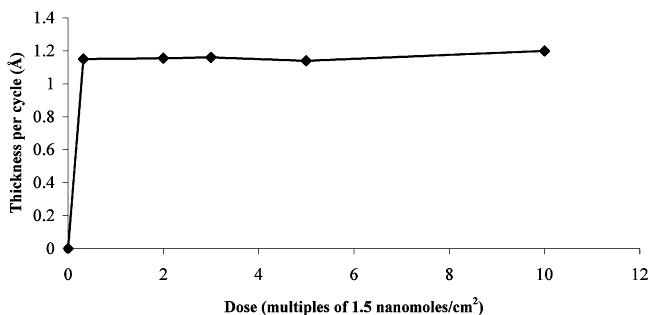

Figure 10. Self-saturating growth of Hf_3N_4 for 1−10 multiple doses of the hafnium precursor.

The nitride films have very smooth surfaces. Atomic force microscopy confirmed that the surface roughness of the deposited layer for Hf_3N_4 was minimal [root-mean-square (rms) roughness = 0.5−0.6 nm]. The bare substrate itself has a rms roughness = 0.2−0.3 nm. The rms roughness was independent of film thickness and consistent over the ALD temperature range (Figure 8). This was not the case for Zr_3N_4 (Figure 9). The surface roughness increased with increasing temperature due to an increasing contribution from CVD growth. Starting at temperatures above 200 °C, the $Zr(NMe_2)_4$ precursor starts to decompose. Typical values for Zr_3N_4 rms roughness are 0.8 nm at 200 °C and 0.5 nm at 175 °C. These values are similar to those of amorphous hafnium and zirconium oxides and lower than those of the polycrystalline oxides.[17]

Repeated nitride films were grown under identical conditions, except that the number of the metal doses per cycle was increased from 1 to 10. The film thickness and its properties were unchanged. These results show

(17) Hausmann, D. M.; Kim, E.; Becker, J.; Gordon, R. G. *Chem. Mater.* **2002**, *14*(10), 4350.

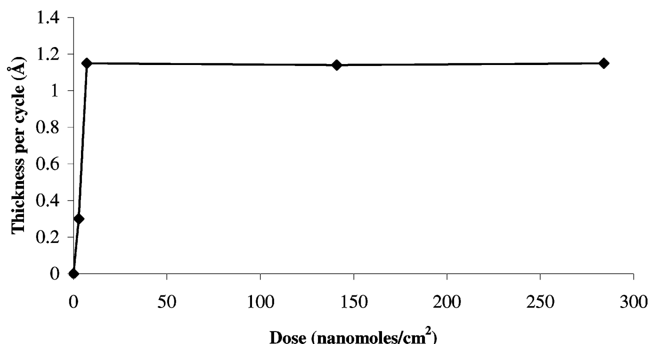

Figure 11. Self-saturating growth of Hf_3N_4 for varying doses of ammonia.

that the surface reactions of the metal precursor(s) are self-limiting. Figure 10 is a demonstration of the self-limiting reaction of the hafnium precursor. Similar results were obtained for the zirconium precursor.

Similarly, the ammonia dose required for saturation was tested using different sized sample loops for the two-position GC valve. Figure 2 shows how the sample loop is filled in position A and emptied in position B. Figure 11 is a demonstration of the self-limiting reaction of ammonia. The sizes of the doses here correspond to up to 284 nmol/cm^2 using a 10, 50, and 500 μL and 1 mL sample loop at 20 psi. Saturation occurs for doses above 7 nmol/cm^2. The film thickness and its properties were unchanged by the ammonia dose. These results show that the surface reactions of the ammonia are self-limiting.

Conformality of coatings in high-aspect ratio holes is another sensitive test of whether a pair of ALD reactions saturate by a self-limiting mechanism. A scanning electron micrograph (SEM) was taken of a wafer with narrow holes having an aspect ratio greater than 40:1 coated with Hf_3N_4 and then cleaved to show a cross-section of the coated holes. The SEM in Figure 12 shows that the walls of the narrow hole are covered with a perfectly conformal coating. Similar results were obtained for Zr_3N_4. This result demonstrates the excellent step coverage achieved by ALD utilizing these precursors.

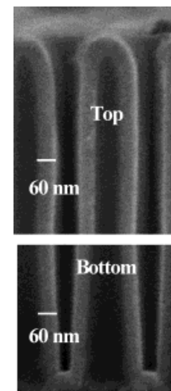

Figure 12. A cross-sectional scanning electron micrograph of holes 0.17 μm × 0.3 μm × 7.3 μm deep in a silicon wafer uniformly coated with a 60 nm thick hafnium nitride film as deposited at 200 °C (500 cycles). An exposure of approximately 3.0×10^4 langmuir/cycle was used for the hafnium precursor and 5.6×10^4 langmuir/cycle for ammonia.

In preliminary experiments, the dielectric constants of Hf_3N_4 and Zr_3N_4 were found to be 30 and 36, respectively.

IV. Conclusion

Hafnium and zirconium nitride films were deposited by ALD from metal alkylamides and ammonia under mild deposition conditions (150−250 °C) in a nonoxidizing and noncorrosive atmosphere. The films produced were pure, smooth, and amorphous with well-controlled, uniform thicknesses and stoichiometries.

Acknowledgment. We would like to thank Infineon for providing the etched wafer shown in Figure 12. This work was supported in part by the National Science Foundation. We also thank Philippe de Rouffignac for taking the electrical measurements.

CM049516Y