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ALD of Hafnium Oxide Thin Films from Tetrakis(ethylmethylamino)hafnium and Ozone

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Hafnium oxide (HfO_2) thin films were deposited from tetrakis(ethylmethylamino)hafnium (TEMAH) and ozone (O_3) by atomic layer deposition (ALD) on 200 mm silicon wafers. The O_3 half-reaction shows good saturation behavior. However, gradual surface saturation is observed for the TEMAH half-reaction. Within wafer non-uniformity of less than 1% and step coverage of about 100% were achieved for trenches with aspect ratio of around 40:1. The film thickness increased linearly as the number of cycles increased. From susceptor temperatures of 160-420°C, the lowest deposition rate (Å/cycle) and the highest refractive index is observed at 320°C. The atomic ratio of hafnium to oxygen determined by Rutherford backscattering is 1:2.04 for the films deposited at 320°C. The carbon and hydrogen content determined by secondary ion mass spectroscopy (SIMS) decreased as the susceptor temperature increased from 200 to 320°C. Lower carbon and hydrogen levels were obtained in the control films made with H_2O than the films made with O_3. A reaction mechanism of the TEMAH + O_3 ALD process is discussed. The results show that an O_3-based ALD HfO_2 deposition is promising for microelectronic applications.
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Hafnium oxide (HfO_2) has been extensively studied as a potential alternative to silicon dioxide due to its high dielectric constant and relatively high thermal stability with respect to a silicon surface.[1,2] Among numerous techniques that have been used to deposit HfO_2 thin films, atomic layer deposition (ALD) showed great advantages in depositing conformal films on high-aspect-ratio structures.[3-6] The most established ALD HfO_2 deposition processes used water (H_2O) as the oxygen source.[5,6] 100% step coverage and excellent electrical properties have been achieved for the H_2O-based reactions using hafnium alkylamides as the hafnium precursors.[2,7] Because H_2O tends to physisorb on surfaces strongly, the purge time needed to sufficiently remove the physisorbed H_2O from the reactor surface could be long, especially at low temperature.[6] For practical applications, long purge time means low throughput (wafers per hour), which in turn means high cost. Generally speaking, in order to reduce the purge time, precursors (and their by-products) that can be easily removed from the reactor surface are desirable. Ozone (O_3) is a strong oxidizing agent and is highly volatile, which makes it one of the most promising alternative oxygen sources in ALD processes. Actually, O_3-based ALD was studied for cerium oxide thin-film deposition by Mölsä and Niinistö some years ago.[8] However, O_3-based ALD HfO_2 deposition has not been widely reported and the reaction mechanism has not been well understood. This paper addresses whether O_3 is a good ALD reactant for HfO_2 deposition and evaluates the advantages and disadvantages of the O_3-based ALD processes compared to the H_2O-based ALD processes, as well as discussing the possible mechanism for the O_3-based processes.

Experimental

The ALD reactor used in our experiment was a Genus StrataGem ALD system which was designed to process 200 mm silicon wafers (Fig. 1). Precursor vapor was delivered into the reactor chamber vertically with a Genus precursor delivery system. The O_3 generator was an Ebara prototype ozonizer. The carrier oxygen gas flow rate was 0.5 slpm, and the catalytic N_2 gas flow rate was 0.5 sccm. The ozone concentration was 150-200 g/m^3 (7.5-10 mol %). A stainless steel gas line for delivering O_3 was heated to 115°C at the reactor end. Because the half life of O_3 at 120°C is 1.5 h[9] and O_3 stayed in the gas line for less than 1 min during the process, more than 99% O_3 should have survived from thermal decomposition at 115°C if there were no chemical reactions with the inner surface of the gas line. Argon was used as the hafnium precursor carrier gas and purge gas. The process chamber pressure was in the range 100-500 mTorr. The susceptor (Si substrate holder) temperature was in the range 160-420°C. The substrate temperature was 20-30°C lower than the susceptor temperature. The substrates were 200 mm Si(100) wafers for most of the characterizations. For step coverage tests, patterned wafers with elliptical holes 0.17 × 0.22 × 7.5 μm deep etched in silicon were used. For the composition measurements, a polished glassy carbon substrate was used. After a wafer was transferred into the reactor, it was heated for 30 s before the deposition started. The reactor was a warm wall reactor with wall temperature of 110-140°C. Liquid tetrakis(ethylmethylamino)hafnium (TEMAH) of 99 + % chemical purity purchased from Sigma-Aldrich Fine Chemicals was used as the hafnium precursor. The Hf precursor container was heated in the range from 75 to 95°C, corresponding to a vapor pressure of 0.05 to 0.27 Torr.[6] When H_2O was used as an oxidant, the container was at room temperature, corresponding to a vapor pressure of 20 Torr. An Inficon Transpector CIS2 gas analysis system was attached to the process chamber for collecting residual gas analysis (RGA) data of the by-products of the ALD reaction.

Characterization Methods

The film thickness was measured with a spectroscopic ellipsometer made by J. A. Woollam Co., Inc. 16 points along the radius from 0 to 97 mm from the center to the edge of the wafer were measured. The thickness uniformity, index of refraction, deposition rate linearity, and temperature dependence of the deposition rate were evaluated based on the ellipsometer measurements. Within wafer nonuniformity (WIWNU) was defined as the standard deviation divided by the average film thickness. The step coverage was measured by scanning electron microscopy (SEM). About 1000 Å HfO_2 film was deposited on a polished glassy carbon substrate for composition analysis by Rutherford backscattering spectroscopy (RBS). Integration of the area of the hafnium and oxygen peaks was used to determine the atomic ratio of hafnium to oxygen. The carbon and hydrogen content was measured by secondary ion mass spectroscopy (SIMS) and RBS by the Evans Analytical Group in Sunnyvale, California. A Materials Development Corporation three-function mercury probe with an electrode area of 0.525 mm^2 was used to

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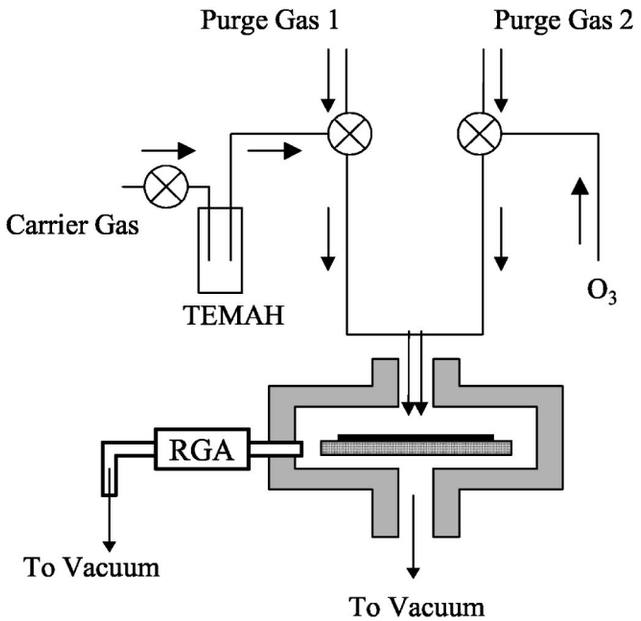

Figure 1. Schematic of the Genus StrataGem ALD system.

measure the capacitance of the HfO_2 films on low-resistivity Si wafers. The dielectric constant values were calculated from the measured capacitance, the ellipsometric thickness of the HfO_2 film, and an estimated measured thickness of 10.5 Å of native SiO_2.

Results

Deposition rate—saturation behavior.—Different amounts of the Hf precursor (TEMAH) were delivered into the ALD reactor by adjusting the TEMAH pulse time at a susceptor temperature of 250°C. The deposition rate increased sharply as the TEMAH pulse time increased from 200 to 500 ms (Fig. 2). Further increase of the TEMAH pulse time above 500 ms caused the deposition rate to increase slightly, showing that the Hf precursor half-reaction was reaching a self-limited state for Hf pulse times longer that 500 ms. The slow increase of the deposition rate indicates a gradual saturation behavior of TEMAH. Similar TEMAH saturation experiments

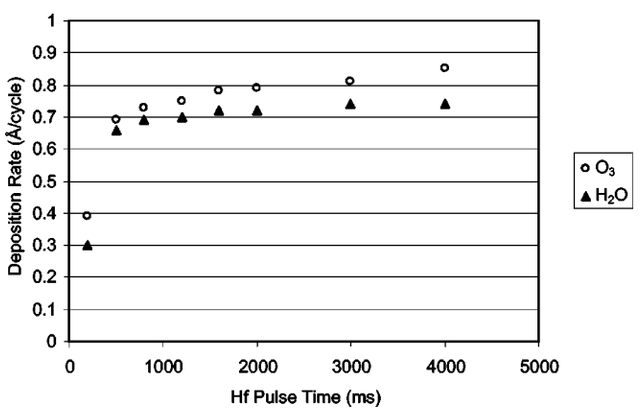

Figure 2. The saturation curves of TEMAH for both O_3- and H_2O-based HfO_2 ALD at 250°C susceptor temperature. The pulse time was fixed at 400 ms for both O_3 and H_2O. Low deposition rate at 200 ms showed that the surface was not saturated. A slow increase of the deposition rate after the 500 ms pulse time showed that TEMAH was a good ALD reactant, though the saturation curve was not perfectly flat.

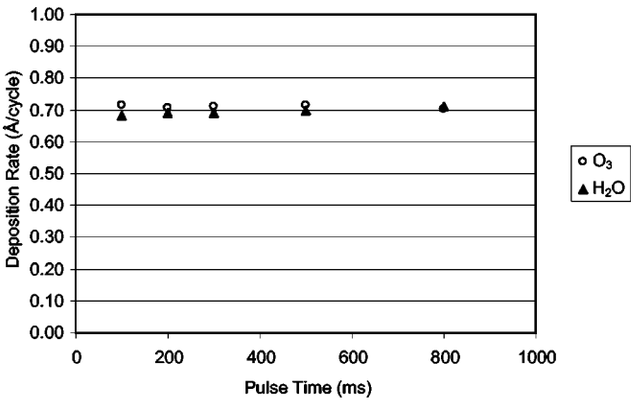

Figure 3. The saturation curves of oxidants O_3 and H_2O at 250°C susceptor temperature. TEMAH pulse time was fixed at 800 ms. Both O_3 and H_2O had good self-limiting characteristics and were indicative of being good ALD reactants with TEMAH.

were also done by using H_2O as the oxygen source. TEMAH showed a somewhat flatter saturation characteristic for the H_2O-based processes. The variation of the deposition rate with respect to the exposure time above 500 ms is about 3×10^{-5} (Å/cycle)/ms.

Different O_3 pulse times from 100 to 800 ms gave a very similar deposition rate, showing that O_3 is a useful reactant for ALD. Within the range studied, H_2O also showed good saturation (Fig. 3). Both the H_2O-based process and the O_3-based process exhibit self-limiting reactions in their ALD half-reaction with TEMAH.

Deposition rate—control experiment (O_2 *vs.* O_3).—A control experiment was carried out at a susceptor temperature of 200°C to examine whether O_2 could react with TEMAH to deposit a film. Two 60-cycle depositions were conducted at exactly the same experimental conditions except that one was deposited with O_2, and the other was deposited with O_3. The ellipsometer measurements showed that the measured average thickness of the O_2-made film was 24 Å, and the average refractive index was 1.4. Because there was a layer of native SiO_2 with 10.5 Å thickness, the 24 Å measured thickness probably reflected the native SiO_2 layer and the Hf precursor adsorbed or decomposed on the SiO_2 layer. The average thickness of the film made with O_3 was 58 Å, and the average refractive index was 2.01. The results indicate that O_3 was substantially more reactive than O_2 for deposition of HfO_2 film at 200°C. This result is consistent with the chemical vapor deposition (CVD) experiments reported by other researchers.[3]

Deposition rate—WIWNU.—By carefully adjusting the pulse time, purge time, and other experimental conditions, WIWNU of less than 1% was achieved. A group of typical thickness profiles for the O_3 process are shown in Fig. 4. The films were deposited at 250°C susceptor temperature with different hafnium pulse times. Longer pulse times give higher deposition rates, which is consistent with the gradual increase in deposition rates shown in Fig. 2. It was observed that shorter purge time usually resulted in higher nonuniformity. The necessary purge time to deposit uniform films depends on many experimental parameters such as deposition temperature, the amount of precursor that was delivered into the reactor, and the process pressure of the reactor, etc.

Deposition rate—linearity.—By changing the number of cycles of deposition in the experiment, the thickness of ALD film changed linearly (Fig. 5). This showed a good digital control of film thickness. Again, the deposition rates with O_3 are higher than with H_2O, as shown in Fig. 2. The intercept of the fitting line at the thickness axis was due to the (~10.5 Å) native oxide on the silicon wafers.

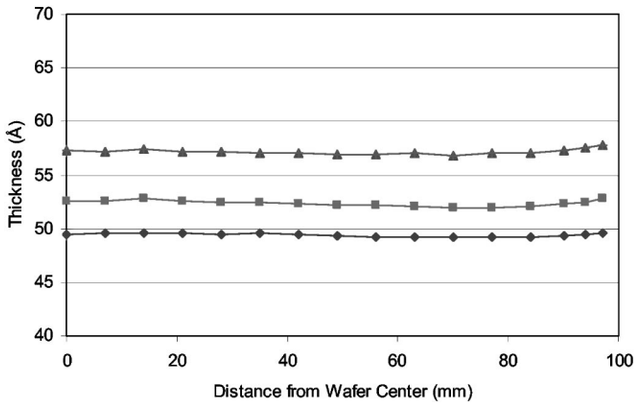

Figure 4. Typical profiles of O_3-based ALD HfO_2 films deposited on 200 mm wafers. The WIWNU is less than 1%. From the bottom to the top, the Hf pulse time was 0.8, 1.2, and 2.0 s.

The slope of the fitting line was deposition rate in Angstroms per cycle. The data was taken at 250°C susceptor temperature.

Temperature dependence of deposition rate and refractive index.—As the susceptor temperature increased from 160 to 320°C, the film deposition rate decreased slightly. As the susceptor temperature increased to 370°C, the deposition rate started to increase, indicating the onset of thermal decomposition of TEMAH. As the susceptor temperature increased further to 420°C, the deposition rate increased sharply, indicating that much more thermal decomposition took place in film deposition (Fig. 6a). Therefore, in the current apparatus, to have a good ALD process for TEMAH, it is necessary to deposit films at a susceptor temperature lower than 370°C.

The temperature dependence of refractive index was plotted in Fig. 6b. As the susceptor temperature increased from 160 to 320°C, the refractive index of films made with O_3 increased significantly. The increase of refractive index of films made with H_2O was much less than that of films made with O_3, though it showed similar trend. At lower temperatures ($T < 320$°C), the films made with O_3 had lower refractive index than the films made with H_2O. As the susceptor temperature is increased, the difference of the refractive index between the films made with O_3 and the films made with H_2O decreased. As the susceptor temperature further increased to 420°C, the refractive index dropped sharply for both O_3 and H_2O made films, also coinciding with precursor thermal decomposition.

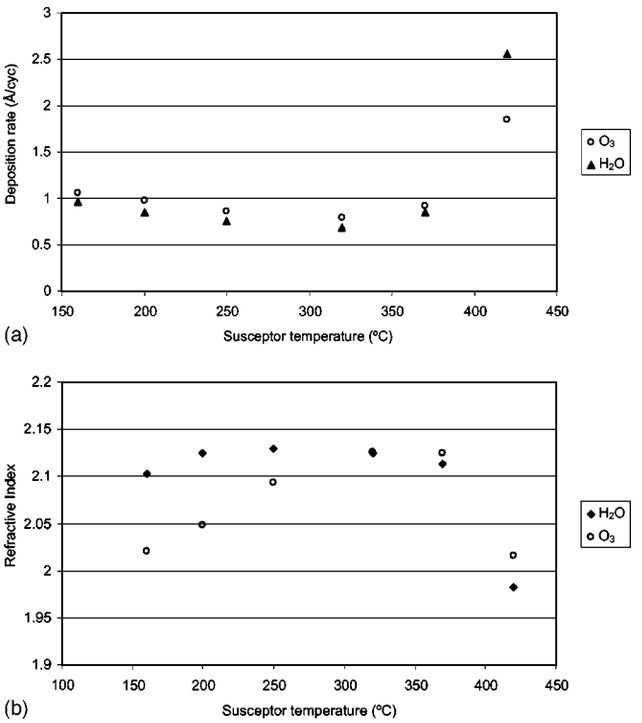

Figure 6. (a, top) Temperature dependence of the deposition rate of TEMAH + O_3 /H_2O ALD reaction. The sharp increase of the deposition rate at 420°C indicates a major thermal decomposition of TEMAH. (b, bottom) Temperature dependence of the refractive index of the HfO_2 films. The refractive index increases as the susceptor temperature increases to 320°C, suggesting film quality improved as the susceptor temperature increased. A decrease of the refractive index after 370°C suggests poor film quality associated with CVD decomposition of TEMAH.

Step coverage.—A step coverage of 100% was achieved on patterned 200 mm wafers with aspect ratios of about 40. The SEM images also showed that the film was very smooth (Fig. 7), indicating that an amorphous film was formed at 200°C. Using a 5 times lower O_3 dose gave lower step coverage (Fig. 8). It was also observed that the step coverage decreased as the deposition temperature increased for the same exposure dose and purge conditions.

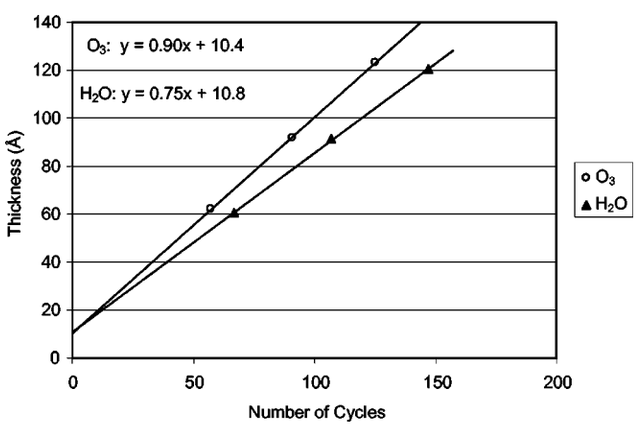

Figure 5. The film thickness changed linearly as the number of cycles increased in the deposition. The slope in the fitting equation is the deposition rate, and the intercept is the thickness of the native oxide of the Si wafer.

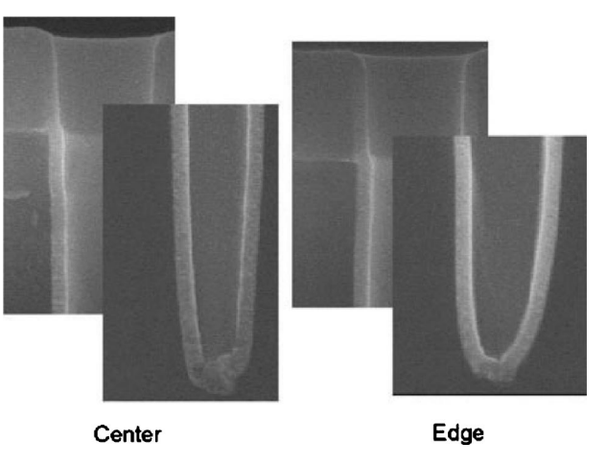

Figure 7. 100% step coverage of the ALD HfO_2 film made at 200°C on the deep trenches located at both the center and the edge of a 200 mm wafer with an initial aspect ratio of 40.

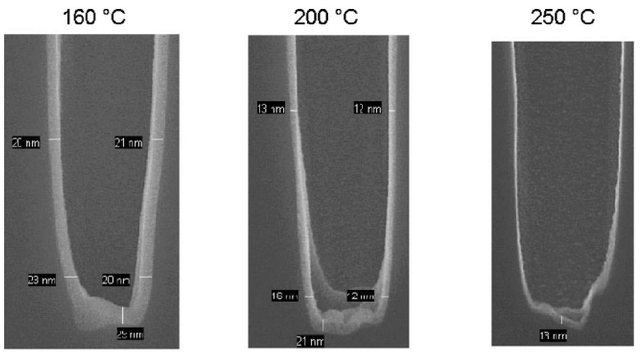

Figure 8. Step coverage of ALD HfO_2 film deposited at different temperatures using the same process conditions. Films made at higher deposition temperatures had lower step coverage.

This effect maybe due to thermal decomposition of the O_3 molecules as they travel down to the bottom of the hole, which is more rapid at higher temperatures.

Composition and impurities.—The RBS spectrum of a HfO_2 film deposited at 320°C was shown in Fig. 9. Because a glassy carbon substrate was used in the RBS sample preparation, the oxygen peak was not overlapped with the Si substrate background spectrum. Integration of the area of the oxygen and the hafnium peak gave atomic area density of oxygen and hafnium in the film. The integration of the oxygen peak gave 4.82×10^{17} atom/cm^2 and integration of the hafnium peak gave 2.36×10^{17} atom/cm^2. The atomic ratio was Hf:O = 1:2.04. Considering the experimental accuracy of RBS, the film composition is considered stoichiometric.

The carbon and hydrogen (H) content was measured with SIMS. Because there was no good reference for SIMS calibration, only the relative content was obtained from SIMS. It was found that the C and H content decreased as the susceptor temperature increased. The change of the impurity level due to the substrate temperature change for the H_2O-based films was very small; for the O_3-based films, as the susceptor temperature increased from 200 to 320°C, the impurity level decreased by more than an order of magnitude. At a susceptor temperature of 200°C, the impurity level of O_3-based films was much higher than that of H_2O-based films. As the susceptor temperature increased to 320°C, the impurity levels of O_3-based and H_2O-based films were low and comparable.

To estimate the upper limit of C and H content, an RBS measurement for the sample with highest carbon content was conducted.

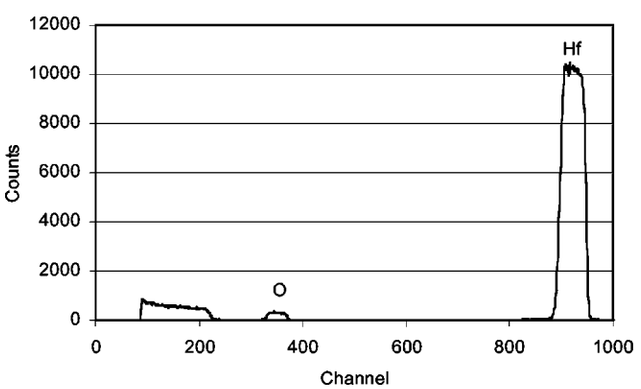

Figure 9. RBS spectrum of the HfO_2 film deposited on a glassy carbon substrate at 320°C susceptor temperature. The atomic ratio of hafnium to oxygen in the film given by integration of the area of the oxygen and the hafnium peaks was Hf:O = 1:2.04.

Table I. SIMS data.

T (°C)	C-O_3	H-O_3	C-H_2O	H-H_2O
200	26.2	14.1	1.98	2.85
250	14.9	5.98	0.882	1.35
320	1.94	0.598	0.588	1.15

The simulation of the RBS result showed that the carbon content was about 7%. It was therefore estimated that the C content of the measured film was safely less than 10%. By using the RBS measured atomic percentage of C as the scale, the upper limit of C and H content in other samples was obtained (Tables I and II, Fig. 10).

An interesting observation was that in the O_3-based ALD HfO_2 films, the H content was lower than the C content. Conversely, in the H_2O-based HfO_2 films, the H content was higher than the C content, which is not surprising because the atomic ratio of C to H is 3:8 in the hafnium precursor. The unusual higher C content in the O_3-based films provides some insight for the reaction mechanism (see the discussion part below).

The trends in the C residue for HfO_2 films using O_3 *vs.* H_2O was carried out using a stacked film approach. Al_2O_3 layers were deposited between each HfO_2 layer. Each HfO_2 layer was deposited with different temperatures or oxidants. The experimental configuration is shown in Fig. 11. The stack of films was then analyzed by SIMS, and these data are shown in Fig. 12. The carbon contamination in the O_3-grown films decreased as the susceptor temperature increased. The carbon contamination in the H_2O-grown films did not change significantly as the susceptor temperature increased. Clearly at the lower temperatures, the O_3-grown films have more C than the H_2O-grown films. At higher temperature, the difference of the carbon contamination between the O_3-grown films and the H_2O-grown films is negligible. Our observation is consistent with a latest publication.[10]

Dielectric constant.—Low-resistivity Si wafers were used in dielectric constant measurement. The films for capacitance-voltage (C-V) measurement were made at three different temperatures, 200, 250, and 320°C. For each temperature, two samples of different thickness, around 140 and 190 Å, were prepared. For each wafer, at least six locations at about half the radius were measured. It was found that the variation of measured capacitance was less than 10% of the average capacitance. The average capacitance was used to calculate the dielectric constant. The thickness of the native SiO_2 (10.5 Å) was considered in calculation. Dielectric constant of the films made at 200, 250, and 320°C was about 16, 18, and 20, respectively (Fig. 13). The thickness dependence of the dielectric constant could not be determined in our experiment.

Throughput.—A recipe with 2.8 s cycle time, where Hf pulse = 500 ms, Hf purge = 1000 ms, O_3 pulse = 300 ms, O_3 purge = 1000 ms, was used to deposit blanket films of HfO_2 on a 200 mm Si wafer. 70 cycles was needed to deposit 50 Å HfO_2 based on the deposition rate obtained at 320°C and 200 mTorr process pressure. Considering 60 s overhead time that is needed for transferring and heating up a wafer, each wafer needs 256 s to be processed. Therefore the throughput of the O_3-based process was 3600/256 = 14 wafers/h.

Table II. Estimated upper limit of atomic percentage.

T (°C)	C-O_3	H-O_3	C-H_2O	H-H_2O
200	10.00	5.38	0.76	1.09
250	5.69	2.28	0.34	0.52
320	0.74	0.23	0.22	0.44

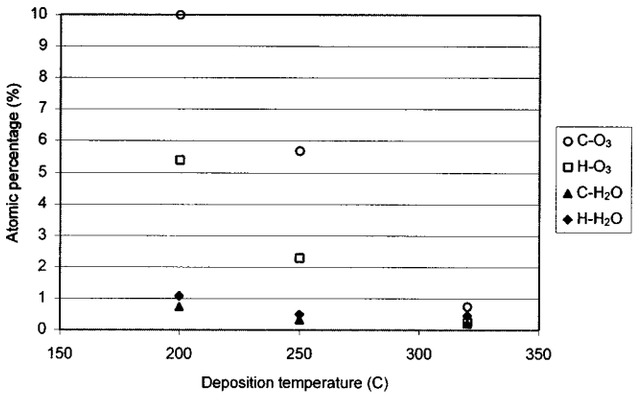

Figure 10. The carbon and hydrogen impurities measured by SIMS. At 200°C, the H_2O-based ALD HfO_2 films showed much lower impurity level than the O_3-based ALD HfO_2 films. The difference between the O_3- and H_2O-based ALD films became small as the susceptor temperature increased to 320°C.

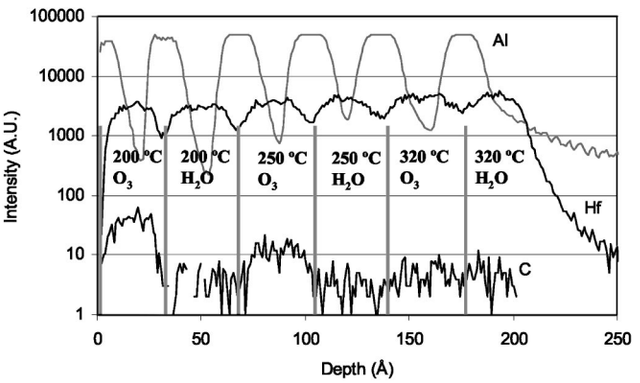

Figure 12. SIMS data of the 12-layer HfO_2 / Al_2O_3 stack, showing higher carbon content for the O_3-grown films deposited at lower temperatures.

Discussion

Saturation.—Saturation behavior of an ALD reactant depends on many factors such as dosage, purge time, purge gas flow rate, and deposition temperature, etc. For example, if two precursor dosages are different, the amount of precursor left in the reactor after the same purge time is not the same, especially for very retention-prone precursors such as H_2O and NH_3. Insufficient purge time leaves more overdosed precursor in the reactor to react with the second precursor in the gas phase. Gas phase reactions from the remnant reactants lead to CVD components of the film. Shorter purge time results in more CVD components in the film. To have true ALD saturation data for evaluation purposes, the purge time has to be sufficiently long to keep the amount of CVD components in the film very low.[11] Uniformity is a good indictor of whether the purge time is sufficient for chemically self-limiting ALD reactions. As the simplest one-dimensional example, ALD films deposited in a horizontal flow reactor can have thicker leading edge or thicker trailing edge when the purge time is insufficient. A thicker leading edge may be caused by circulations (which can trap more precursor) at the input to the reactor. A thicker trailing edge could be related to back streaming. A longer purge time should improve the thickness uniformity in both cases.

However, longer purge time is not always better. The most significant drawback of a long purge time is that it results in a low productivity, which is the major barrier for process commercialization. An additional problem is that some precursors decompose appreciably at process temperatures within a few seconds. In this case, a longer purge time may result in more thermal decomposition of the precursor and leave more impurities in the film. If the precursor decomposes fast enough on the substrate surface, the reaction may be no longer self-limiting. A fast increasing deposition rate can be a good indication of this kind of thermal decomposition. The deposition rate shown in Fig. 6a indicates that the exposure conditions used in these experiments do not result in significant thermal decomposition of TEMAH below 300°C. However, if exposure times longer than those used in these experiments are used, then thermal decomposition may appear at lower temperatures.

Temperature dependence.—The temperature dependence of the refractive index showed good consistency with the temperature dependence of the impurity levels over the temperature range studied. First, for the O_3-based films, the refractive index of the films increased significantly as the susceptor temperature increased from 200 to 320°C, which was consistent with the significant decrease of their impurity level. For the H_2O-based films, the refractive index increased slightly as the susceptor temperature increased from 200 to 320°C, which was consistent with the minor decrease of their impurity level. Second, at a lower susceptor temperature (200°C), the O_3-based films had a much lower refractive index than the H_2O-based films, which was consistent with the fact that the O_3-based film had much higher impurity level than the H_2O-based films at 200°C. As the susceptor temperature increased, the difference in refractive index between the O_3-based films and the

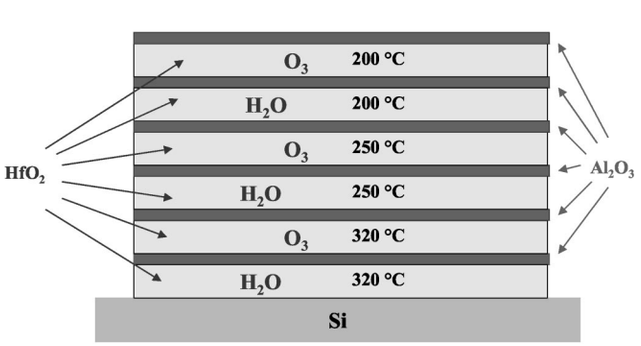

Figure 11. A 12-layer stack of HfO_2 and Al_2O_3 films grown at different conditions. The six layers of Al_2O_3 films were used as markers.

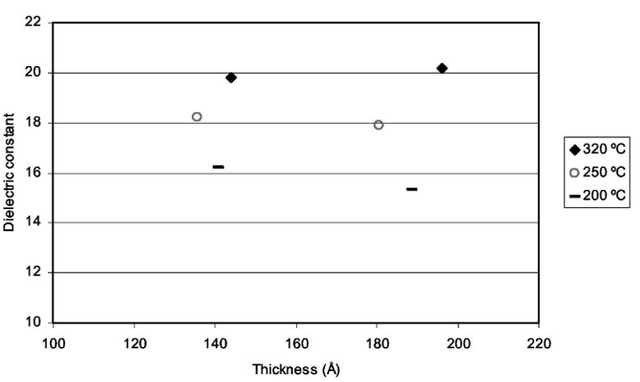

Figure 13. Dielectric constant of the HfO_2 films measured with a mercury probe. As the susceptor temperature increased from 200 to 320°C, the dielectric constant of the HfO_2 films increased from 16 to 20.

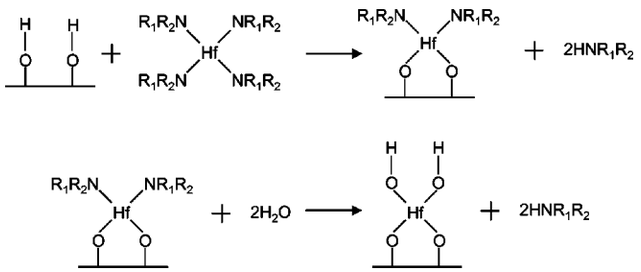

Figure 14. A possible HfAA + H_2O reaction mechanism. A hydroxylated surface is necessary to initiate the reaction. A HfAA molecule reacts with chemisorbed OHs and produces two alkylamine molecules as by-products. In the second half-reaction, H_2O removed the other two alkylamine ligands to form a hydroxylated surface for the next cycle of reaction.

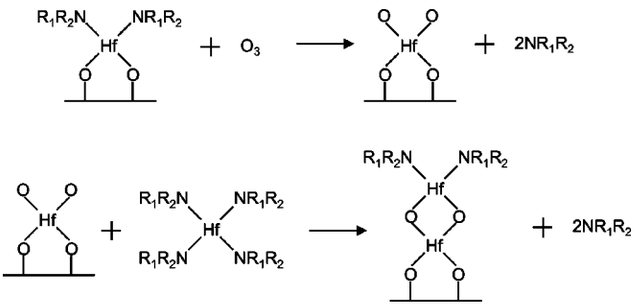

Figure 15. A possible HfAA + O_3 reaction mechanism. O_3 molecules react with a chemisorbed HfAA and produces two alkylamine radicals as by-products. In the second half-reaction, HfAA reacts with oxidized surface to produce another 2 alkylamine radicals.

H_2O-based films decreased, which was consistent with the fact that the difference of impurity level between the O_3-based films and the H_2O-based films decreased. As the susceptor temperature increased to 320°C, the refractive index of the O_3-based films and the H_2O-based films became very close, which was consistent with the similar impurity levels of the O_3-based films and the H_2O-based films.

The temperature dependence of the refractive index was also consistent with the temperature dependence of the dielectric constant data. The implication of this consistency is that the impurities incorporated in the films have a negative effect on electrical properties. The higher the impurity level, the lower the refractive index. We were not able to distinguish the change of the dielectric constant caused by different impurities such as C, N, or H separately, because none of them can be singly incorporated into the film without having others at the same time.

Possible mechanism of TEMAH + O_3 ALD reaction.—A two-step mechanism for the ALD reaction[6] of hafnium alkylamide (HfAA) and H_2O is as follows: HfAA first reacts with a hydroxylated surface to eliminate two alkylamine ligands; then H_2O reacts with chemisorbed HfAA to remove the other two alkylamine ligands and regenerates a new hydroxylated surface (Fig. 14). The Hf-N bonds in the HfAA molecule are selectively cleaved by H_2O molecules. The by-product of this reaction is ethylmethyl amine (HNEtMe). Based on this mechanism, the impurity of the film should mostly be due to the unremoved NEtMe ligands or by-product HNEtMe molecules that were trapped in the film. The ratio of the impurities should be N:C:H = 1:3:8 for incompletely reacted Hf-(NEtMe) or N:C:H = 1:3:9 for a trapped by-product HNEtMe. In both cases, the H content is higher than the C content.

The saturation characteristics of the half-reactions for the oxidants are nominally the same within our experimental determination for O_3 and for H_2O. The half-reactions for the TEMAH are also similar, but with the O_3-based TEMAH half-reaction being somewhat less ideally saturating. Thus the final reaction state for the saturating reactions for both O_3 and H_2O are indicative of self-limiting behavior. However, the saturating characteristics do not necessarily give insight to the reaction pathways.

RGA data shows that there are a complex set of by-products of the O_3 reaction. There are strong signals with intensity ordering at amu = 44, 18, 29, and 30, suggesting that CO_2 or N_2O (44), H_2O (18), and CH_2O (29,30) are major products. The signals at amu 58 and 59 are negligible, suggesting that HNEtMe is not a final product. Because both NO and NO_2 have strong signals at 30 (but not at 29), we cannot eliminate NO or NO_2 as possible final products. The final information that would be important in considering a reaction mechanism would be the relatively high C residue in the O_3 reaction film.

For the O_3-based reaction, we speculate that most $Hf(NEtMe)_4$ molecules are cleaved at the Hf-N bonds by O_3. The major ''intermediate'' by-product is*NEtMe. The* indicates that it is not a stable molecule. The*NEtMe then is oxidized by O_3 into final by-products CO_2, H_2O, CH_2O, and NO_2/NO, etc. The by-product H_2O can be the source of hydroxyls and thus can partially rehydroxylate the surface. It is also possible that part of the surface is terminated with Hf-O instead of Hf-O-H. Because a Hf-O bond has an unpaired electron, it may cleave an incoming $Hf(NEtMe)_4$ molecule at the Hf-N bond in the next Hf half-reaction (Fig. 15). However, O_3 is so reactive that it may also cleave the N-C bonds and C-H bonds of either by-products or ligands that are still attached to Hf to produce H_2O, CO_2, N_2O/NO, and other by-products. Use of O_3 does not totally eliminate the presence of H_2O from the reactor environment but significantly reduces it.

Our SIMS data showed that the C content was higher than the H content in the O_3-based ALD HfO_2 films. This suggests that H has been removed from C-H bond of either by-products or the ligands that are still attached to the Hf to produce H_2O or OH. The species with their H atoms removed may have more than one unpaired electron so that they can bind strongly on the surface and cannot be easily removed from the surface or be further oxidized by O_3. This explains why the C content is higher than the H content in the O_3-based films. As the deposition temperature increases, the kinetic energy of the C-containing species is closer to the activation energy of desorption or the activation energy of oxidation by O_3, which means more C-containing species can be removed from the surface or be oxidized by O_3. Because a H_2O molecule or a Hf-OH can only cleave a Hf-N bond, the major by-product is HNEtMe, and there are no H-removed C-containing species that can bind on the surface strongly. This is why the C content in the O_3-based films is higher than that of the H_2O-based films.

Comparison to H_2O.—The advantage of O_3-based ALD processes is that the O_3 purge time is much shorter than H_2O purge time, which suggests that H_2O generated in O_3-based processes is much less than H_2O that is delivered into the reactor in H_2O-based processes. To have better step coverage, a lower deposition temperature is desired. However, at lower temperature, *e.g.*, 200°C, the impurity levels of the O_3-based HfO_2 films are much higher than that of the H_2O-based ALD HfO_2 films. If the impurity levels are proved to have unacceptable negative effect on film properties, another way to improve the electrical properties of O_3-based films has to be found. The trade-off of good conformality against higher residual C at lower deposition temperatures remains a challenge for the TEMAH/O_3 chemistry. The reduction of C using combinations of

O_3 and H_2O or the use of plasma[12] exposures for leaching C impurities may be pathways, but this is beyond the scope of this work.

Conclusions

ALD HfO_2 thin films deposited from TEMAH and O_3 are stoichiometric. A gradual saturation was observed for the TEMAH half-reaction. However, the O_3 or H_2O half-reactions showed a good saturation behavior within the range of the exposure times that studied, suggesting that O_3 and H_2O are good ALD reactants with TEMAH. The film thickness increased linearly as the number of cycles increased. A WIWNU of less than 1% was achieved. The lowest deposition rate and the highest refractive index was observed at 320°C susceptor temperature. Evidence of TEMAH thermal decomposition was observed at and above 370°C. A nominal 100% step coverage was achieved for trenches with aspect ratio of ~40:1. The carbon and hydrogen content decreased as the susceptor temperature increased from 200 to 320°C by an order of magnitude for the O_3-based ALD films. The difference in the impurity levels between the O_3-made films and the H_2O-made films decreased as the susceptor temperature increased and became trivial at 320°C. Hence, TEMAH + O_3 may be used while making consideration of various trade-offs. Throughput of 14 wafers per hour was achieved on planar wafers using O_3 at 320°C. Our results show that TEMAH + O_3 ALD is promising for mass production.

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