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Atomic Layer Deposition of Hafnium Oxide Using Anhydrous Hafnium Nitrate

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Atomic layer deposition of uniform thin hafnium oxide films has been demonstrated directly on H-terminated silicon surfaces using anhydrous hafnium nitrate ($Hf(NO_3)_4$) precursor and H_2O vapor. Atomic layer deposition was initiated on hydrogen terminated silicon surfaces and occurred at substrate temperatures as low as 160°C. X-ray diffraction analysis indicated that as-deposited films were smooth, uniform, and amorphous, and that film morphology can be altered by a post-deposition anneal. X-ray photoelectron spectroscopy analysis indicated that films are oxygen rich, contain silicate, and that residual NO_3 and NO_2 from the precursor can be eliminated by a post-deposition anneal. For a ~57 Å HfO_2 film, a dielectric constant of $\kappa \cong 10.5$ and a capacitive equivalent thickness of ~21 Å were obtained.
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A suitable replacement to silicon dioxide as a gate dielectric for future semiconductor devices must fulfill a number of stringent requirements.[1] Among these are the precise control of the deposition thickness and uniformity over the wafer surface area. A deposition technique that may be able to meet this requirement without damaging the crystal silicon structure is atomic layer deposition (ALD), in which individual monolayers of a given material are laid down in a self-limiting fashion.[2-6] Two promising replacement candidates for SiO_2 are HfO_2 and ZrO_2,[1,3-11] due to their high bulk dielectric constants, thermal stability on Si,[7] wide bandgaps and large band offsets.[8] The ALD of HfO_2 and ZrO_2 has recently been demonstrated by alternately exposing substrate surfaces to vapors of hafnium- or zirconium-tetrachloride precursor and water vapor.[3-6] Although excellent uniformity and initiation of the deposition have been reported on SiO_2 and Si_3N_4 surfaces, a number of ALD cycles are required to produce total coverage of a hydrogen terminated Si surface since displacement of Si-H bonds with the tetrachloride species is not easily achieved. This difficulty of initiation of deposition on H-terminated silicon can lead to high surface roughness and deposition inconsistencies. (The motivation for direct deposition on H-terminated or HF etched Si is to avoid the presence of a low κ interfacial layer.) Moreover, metal tetrachlorides also have a tendency to incorporate trace amounts of chlorine in the film, which can lead to stability and reliability problems. Use of a precursor that allows for better control of the initiation of deposition on H-terminated Si might aid in optimization of the interface properties and improvement of the carrier mobility in transistors.

A set of precursors that has generated much interest recently are the anhydrous nitrates of hafnium or zirconium, $Hf(NO_3)_4$ or $Zr(NO_3)_4$.[11,12] These precursors would not leave hydrocarbon or halogen impurities and the nitrogen oxide byproducts should be easily removed. They have been used in chemical vapor deposition (CVD) mode at temperatures from 300 to 500°C to generate metal oxide films.[12]

We report here the initial results of our investigation on the use of anhydrous hafnium nitrate, $Hf(NO_3)_4$, as a precursor for atomic layer deposition of HfO_2 on H-terminated Si substrates. HfO_2 films were characterized using spectroscopic ellipsometry, X-ray diffraction and reflectivity, X-ray photoelectron spectroscopy (XPS), and capacitance *vs*. voltage measurements.

Experimental

Anhydrous hafnium nitrate precursor was synthesized by refluxing hafnium tetrachloride over dinitrogen pentoxide at 30°C and then purified by sublimation at 110°C and 0.1 mm Hg to yield white crystals.[13] Unlike previous methods,[13] dinitrogen pentoxide was generated by the reaction between solid P_2O_5 and fuming nitric acid. Vapors were trapped at liquid N_2 temperature into a reaction flask containing $HfCl_4$.[14]

A Microchemistry F-120 ALD reactor was used to deposit thin HfO_2 films on silicon substrates. Both p- and n-type 150 mm prime grade (100) wafers of resistivities 4 to 30 Ω cm or 4 to 10 Ω cm, respectively, were cleaned with standard SC-1 and SC-2 solutions and then cleaved into square pieces 5 cm on a side. Immediately prior to film deposition, the substrates were dipped into dilute HF solution to produce a H-terminated surface. For deposition, the precursor temperature was set between 80 and 85°C (chosen based on measured thermal gravimetric analysis properties of the precursor). Because these metal nitrate precursors easily decompose thermally, determination of the substrate temperature for ALD growth required optimization. To determine the highest temperature at which no CVD was observed (which was about 180°C), a set of dummy runs was performed to grow thick films over a wide range of temperatures using only hafnium nitrate. The occurrence of CVD from thermal decomposition was detected by the obvious thickness nonuniformities in the resulting films that reflected the flow pattern of precursor from the source to the pump. Based on these results, at the appropriate substrate temperature, the introduction of water pulses resulted in the deposition of uniform films, an indication of the ALD regime. ALD was observed at temperatures as low as 160°C. The films in this study were deposited at 180°C. A typical ALD pulse sequence cycle was as follows: the first pulse is of metal nitrate (0.6 s), then a N_2 pulse of 0.6 s, followed by a pulse of H_2O vapor (0.6 s), and finally a 0.6 s N_2 pulse. This reaction sequence was repeated until the desired thickness was reached.

Spectroscopic ellipsometry (SE) analysis of the films was performed on a Sentech SE-800, while X-ray diffraction (XRD) and reflectivity measurements were made using a Philips X'Pert system. Electrical measurements were performed on dot capacitors made by evaporating platinum through a shadow mask. An HP4284A LCR meter was used for capacitance-voltage measurements. XPS measurements were performed at a commercial laboratory[15] using a Physical Electronics Quantum 2000 with a monochromated Al Kα (1486.6 eV) X-ray source.

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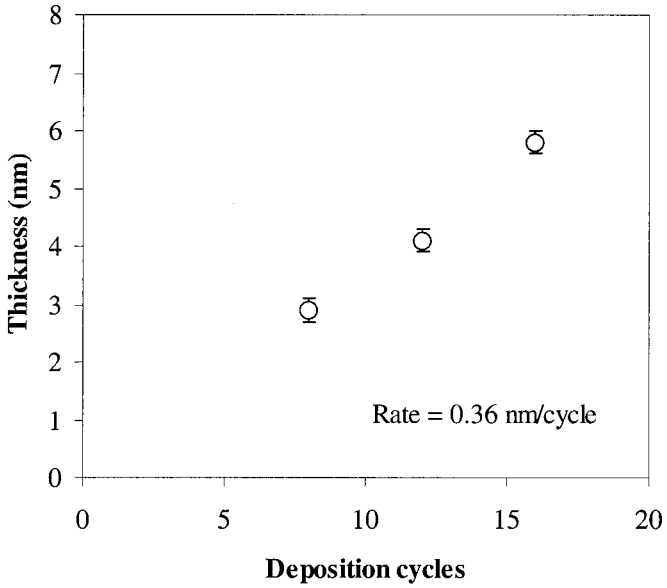

Figure 1. Thickness measured by spectroscopic ellipsometry as a function of the number of deposition cycles.

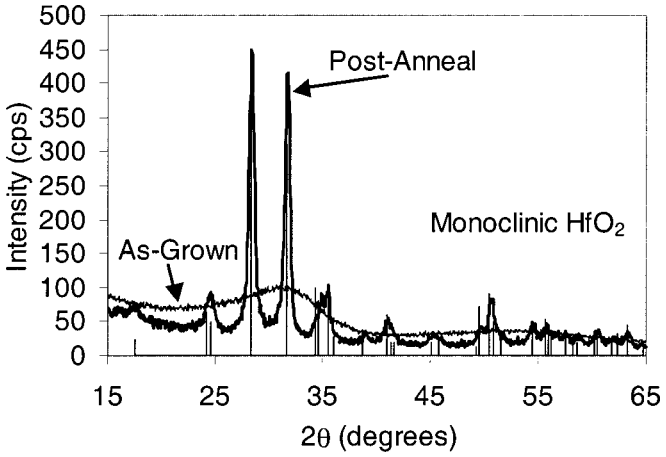

Figure 2. XRD phase scans of a 400 cycle deposition of HfO_2 as-deposited and after 850°C anneal in N_2 for 5 min. The peaks indicate monoclinic crystallites.

Results and Discussion

Figure 1 shows a plot of thickness *vs*. the total number of deposition cycles. A deposition rate of ~0.36 nm/cycle is observed over a range of deposition cycles. For thicker films (~400 cycles) the deposition rate was calculated to be ~0.29 nm/cycle. The deposition rate is highly sensitive to factors such as the condition of the deposition chamber, the history of the quartz ware, and precursor purity. For a single cycle deposition, a thin film covering the entire surface was detected, demonstrating the advantage of this nitrate precursor over the chloride sources.

The refractive index of a thick film of HfO_2 (deposited via 400 cycles of ALD) was determined by spectroscopic ellipsometry (SE). Modeling the film to the measured Delta-Psi spectrum resulted in a thickness of ~115.2 nm. The real component of the refractive index, *n*, at 632.8 nm was 1.847 ± 0.005. The imaginary component, *k*, was zero, interpreted to indicate that the as-deposited film was transparent. It has been reported that as-deposited metal-rich sputtered thin HfO_2 films have a strong *k* component which can be reduced to zero by an oxygen anneal.[10] A Cauchy film model was used to fit the data, giving coefficients of $n_0 = 1.801$, $n_1 = 2.09 \times 10^4$, and $n_2 = -1.03 \times 10^9$ where $n(\lambda) = n_0 + n_1\lambda^{-2} + n_2\lambda^{-4}$ with λ in nm.

Shown in Fig. 2 and Fig. 3 are XRD and reflectivity measurements made on the same thick HfO_2 sample used for SE measurements. Shown in Fig. 2, the XRD phase scan of the as-deposited film revealed no sharp peaks, indicating that it is amorphous or only weakly crystallized. Films deposited via CVD at 400°C have been reported to be monoclinic.[11] The HfO_2 film was crystallized by a 300 s 850°C rapid thermal anneal in N_2. The post-anneal XRD phase scan (Fig. 2) indicates a monoclinic phase,[16] with ~300-400 Å crystallites.

The excellent uniformity of the as-deposited film is indicated by the high number of oscillations seen in the X-ray reflectivity scan in Fig. 3 (see inset). Theoretical modeling of X-ray reflectivity spectra (Fig. 3, lower spectrum) indicated a thickness of 1275 Å, a density of 6.7 g/cm^3, a surface roughness of 8 Å rms, and a Si substrate roughness of 3 Å rms. Analysis of the post-anneal reflectivity data (Fig. 3, upper spectrum) indicated a 985 Å thick film with a density of 8.5 g/cm^{-3}, a roughness of 12 Å rms, and a Si substrate roughness of 4.5 Å rms, suggesting that, in addition to crystallization, the anneal also densified, thinned, and roughened the film. Post-anneal SE measurements indicate a decrease in thickness from 115.2 to 100.3 nm and an increase in *n* from 1.847 ± 0.005 to 1.899 ± 0.005, consistent with thinning and densification. The thickness reduction is not surprising as anneals are routinely used to densify oxides deposited at lower temperatures (these films were deposited at 180°C). Note that the density of the annealed films approaches that of the value reported for bulk HfO_2 (9.68 g/cm^3).[17]

X-ray refraction and reflectivity analysis of a ~51 Å film (not shown) revealed an as-deposited amorphous structure which also crystallizes, densifies, and thins when annealed for 300 s at 850°C in N_2. The postanneal trace revealed a single broad peak at $2\theta = \sim 30°$ (centered approximately between the two largest monoclinic phase peaks). We are as yet unable to make a positive identification of the thin film phase. Thin (~51 Å) HfO_2 films did not show signs of crystallization until annealed at temperatures greater than ~700°C, consistent with Lee *et al.*[18] This indicates that this deposition technique for HfO_2 is compatible with the anticipated post-deposition thermal budget of replacement gate technology. The amorphous phase of the as-deposited films is desirable since one might expect less leakage current due to lack of grain boundaries.

XPS was performed on a twelve-cycle ALD HfO_2 sample before and after a forming gas anneal at 450°C for 30 s. The analysis

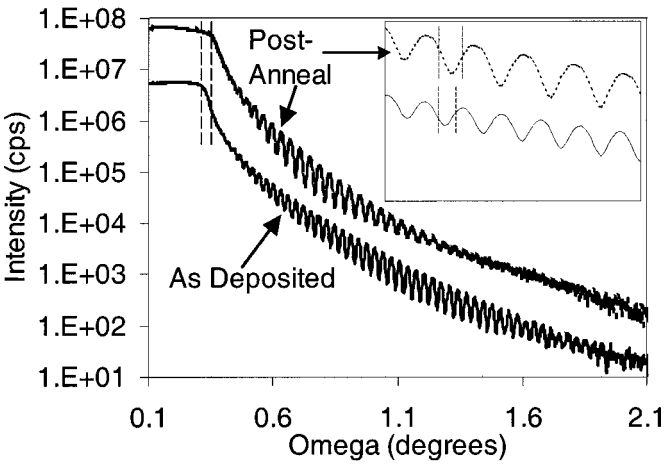

Figure 3. X-ray reflectivity spectra of a 400 cycle deposition of HfO_2 (solid) as-deposited and (dashed) after 850°C anneal in N_2 for 5 min. Inset shows uniformity of oscillations.

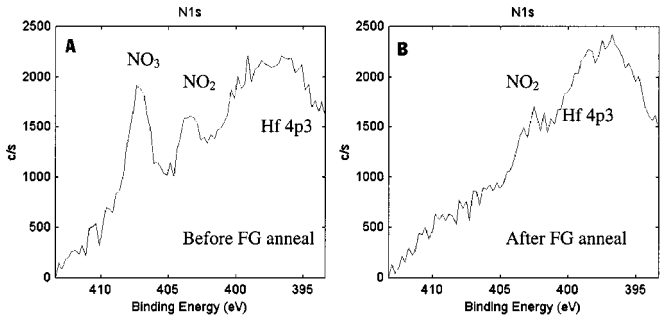

Figure 4. XPS spectra of nitrogen related peaks (A) before and (B) after a 30 s anneal at 450°C in forming gas.

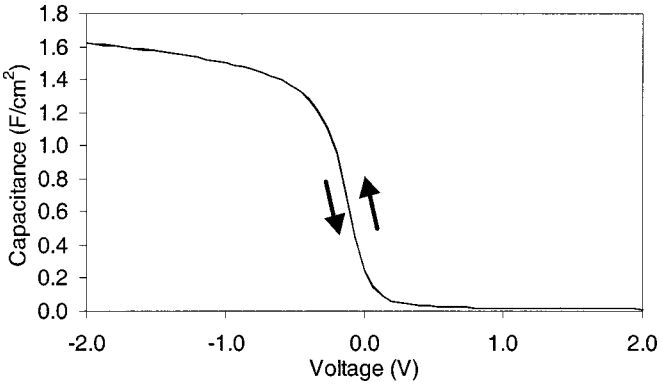

Figure 5. Capacitance *vs*. voltage curve of a p-type, ~57 Å HfO_2 capacitor.

determined that the main constituents of the as-deposited film were oxygen (62.3%) and hafnium (16.1%), indicating an oxygen rich film. Other elements detected were carbon (13.8%) which was surface contamination, silicon (5%) presumably from the substrate, fluorine (0.7%) from the HF last clean, zirconium (0.9%) which is inherently contained in the hafnium source, and nitrogen (1.2%), in the form of NO_3 and NO_2, from the nitrate precursor. After the forming gas anneal, the main difference was the reduction in nitrogen content to 0.2% and a small reduction in oxygen to hafnium ratio to 2.76 as measured in the film after a light sputter etch to remove surface contamination. The presence of a thin interfacial silicate layer is also suggested which is unchanged by the post-deposition anneal. Shown in Fig. 4, a high resolution XPS scan of the nitrogen bonding indicates that some residual NO_3 from the precursor remains in the as-deposited film (Fig. 4a) but is eliminated after anneal (Fig. 4b). This loss of nitrogen and oxygen may account for the film shrinkage that was observed via spectroscopic ellipsometry and X-ray reflectivity.

Dot capacitors were formed by evaporating a Pt film through a shadow mask. A post-metalization anneal was performed in 5% H_2 in N_2 at 400°C for 60 s. The thin HfO_2 films remained amorphous after this anneal. A capacitance *vs.* voltage trace of ~200 μm diam, ~57 Å thick HfO_2 capacitor on p-type Si is shown in Fig. 5. The capacitive equivalent thickness (CET) of the HfO_2 was determined from the maximum accumulation capacitance ($V_g = -2.0$ V) and estimated to be CET ~21 Å, corresponding to a dielectric constant, $\kappa_{HfO2\text{-}stack} \sim 10.5$. This value for κ is consistent with that recently reported by Kim *et al.* for an HfO_2 gate stack,[19] but lower than that reported for bulk HfO_2 ($\kappa = 25$).[1] There are several likely reasons why the thin film dielectric constant might be expected to be lower than the bulk value. (Note that the reduced κ is probably not due to the decrease of dielectric constant that is theoretically predicted in ultrathin, ultrahigh-κ films.[20]) First, the CET estimate we report is conservative and neglects substrate quantum effects which, if taken into account, could reduce the thickness by 2-3 Å and correspondingly increase κ. Second, it should be emphasized that the overall κ value reported here is for the entire dielectric stack and not just the HfO_2 layer. It is likely that a thin interfacial layer is present which effectively reduces the overall κ value. Possible interfacial layers include silicate (detected by XPS) and SiO_2. Since Hf-silicate has a reported κ range of 15-25, it is very likely that SiO_2 is also present. Finally, the excess oxygen (detected by XPS) could reduce the "bulk" κ of the HfO_2 layer. It should be noted that this work is preliminary and it is anticipated that process optimization will result in substantially thinner CET films. Further details of the electrical properties of these films will be reported.[21]

Conclusions

Hafnium nitrate, $Hf(NO_3)_4$, was found to be a viable precursor for the ALD formation of carbon and halogen free HfO_2. Atomic layer deposition was initiated on hydrogen terminated silicon surfaces and occurred at substrate temperatures as low as 160°C. A single cycle deposition resulted in a uniform film covering the entire surface of the wafer, demonstrating a clear advantage of $Hf(NO_3)_4$ over chloride precursors. XRD analysis indicated that as-deposited films were smooth, uniform, and amorphous, and that film morphology can be altered by a post-deposition anneal. XPS analysis indicated that films are oxygen rich and that residual NO_3 and NO_2 from the precursor can be eliminated by a post-deposition anneal. For a ~57 Å HfO_2 film, a dielectric constant of $\kappa \cong 10.5$ and a CET $\cong 21$ Å (neglecting quantum effects) were obtained. This work demonstrates that very thin films of HfO_2 can be deposited directly on silicon without the need for an initial low κ interfacial layer of SiO_2 and may be optimized for gate dielectric purposes.

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