On the Application of a Thin Ozone based Wet Chemical Oxide as an Interface for ALD high-k deposition

B. Onsia[1, 2, a], M. Caymax[1], T. Conard[1], S. De Gendt[1, 2], F. De Smedt[2], A. Delabie[1], C. Gottschalk[3], M. Green[4], M. Heyns[1], S. Lin[4], P. Mertens[1], W. Tsai[4] and C. Vinckier[2]

[1] Imec, kapeldreef 75, B-3001 Heverlee, Belgium

[2] K.U.Leuven, Afd. Fysische en Anal. Chemie, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

[3] Astex GmbH, Wattstraße 11-13, D-13355 Berlin, Germany

[4] Former Int. Sematech assignees at imec, ISMT, 2706 Montopolis Drive, Austin, Texas, USA

[a] Bart.Onsia@imec.be

Keywords: high-k, Atomic Layer Deposition (ALD), ozone, oxide, interface

Introduction

In order to keep pace with CMOS scaling trends, alternative gate oxide materials, with a high dielectric constant, were proposed. To have a low interface trap density, good mobility [1], and good Atomic Layer Deposition (ALD) growth characteristics [2], the presence of an interfacial oxide layer is still prerequisite. Hydroxyl groups are the key players for the initiation of the ALD reaction [3].

In this work the application of downscaled ozone based wet chemical oxide as a surface pre-treatment for ALD high-k deposition is examined.

Oxide thickness scaling

From all the different methods to render a surface hydroxyl covered, a wet chemical oxide surface seems to be the perfect candidate, from a growth perspective. Deposition on a wet chemical oxide underlayer shows almost no barrier to film nucleation, enables linear and predictable growth at constant film density [4]. Of course the interfacial oxide contributes to the EOT, therefore the thickness should be minimized. Ideally the silicon surface would be completely covered by hydroxyl groups, without having an underlying oxide. This combines the highest surface hydroxyl density with the lowest oxygen content. Clearly, scaling down the thickness of wet chemical oxides is necessary. The thickness of an ozone based wet chemical oxide can be tuned by controlling dip time, ozone concentration, temperature, … The next sections summarize the development of a concept to an industry ready process.

Experimental

P type monitor wafers were used, which received an imec®-clean and a 30 second 2% HF dip. The resulting hydrophobic and oxide free, hydrogen terminated Silicon wafer is then subjected to the various wet chemical ozone treatments at 20ºC and without pH adjustment unless otherwise specified. The resulting oxide thickness is subsequently measured on a Plasmos SD2000 @ 633 nm or an ASET F5 from KLA-Tencor, both tools making use of the ellipsometry technique. Ozone was generated using a Sorbios SEMOZON 90.2HP ozone generator, at a flow of 2 l/min, except for the experiments as described in the flow through mode, where a MKS LIQUOZON® Single system is used. Ozone concentration was monitored using an electrochemical ozone cell from Orbisphere Model 31330.15, or the UV based ozone sensor delivered with the LIQUOZON® tool.

Hardware

Static mode experiments are done by bringing ozone in a DI-water filled beaker through a quartz frit. Ozone flow is stopped during the dip of the wafers. Figure 1 shows that varying the time is not a good approach, because the initial oxidation rate is very fast making time control rather tedious. Lowering the ozone concentration, however, is clearly yielding thinner oxides, which proves the concept that the thickness of the wet chemical ozone oxide can be scaled down. Unfortunately, the resulting oxide, as measured by ellipsometry, shows a non-uniformity in thickness of more than 20%, the main part of this non-uniformity being a vertical gradient. A lower oxide thickness is observed at the top of the wafer. This is inherent to the set-up, because during the dip, ozone outgasses at the liquid air interface. In addition ozone concentration is reducing during the dip because the supply is stopped. This non-uniformity does not show up in the data of Figure 1, because oxide thickness was measured using the molybdenum blue method [6], which yields a wafer surface averaged oxide thickness.
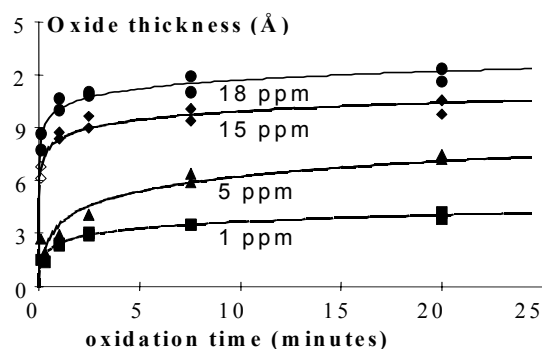

Figure 1: Time dependency of the final oxide thickness, with ozone concentration as parameter, static mode.

Re-circulation mode. Water is re-circulated over a process tank in which a diffuser is bubbling ozone. During the dip, ozone supply is shut down. Static boundary layer thickness is reduced by the continuous flow, hence facilitating the ozone transport to the wafer surface. Figure 2 (solid markers and lines) shows the influence of ozone concentration and dip-time on the final oxide thickness. Oxide thickness increases with dip-time, but unfortunately non-uniformity does as well. A higher ozone concentration, 3 ppm instead of 1 ppm, yields a higher oxide thickness without a non-uniformity increase. Therefore it is better to control the ozone concentration to scale the oxide thickness, while keeping the dip-time short.
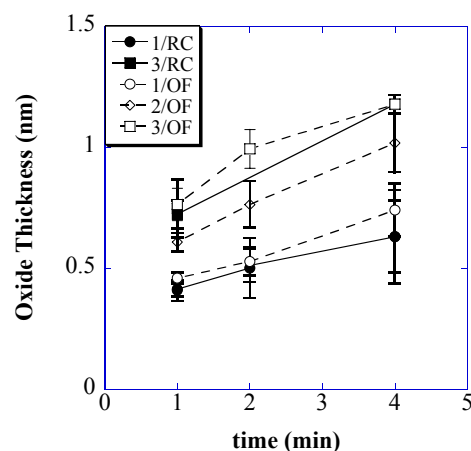

Figure 2: Oxide thickness versus dip time for different ozone concentrations and hardware modes ($[O_3]_{aq}$ in ppm / RC: re-circulation; OF: overflow).

Flow through mode. For this mode a LIQUOZON® Single is used. The tool delivered ozonized water at a flow of about 15 l/min. Figure 2 (open markers and dashed lines) shows oxide thickness

as a function of ozone concentration and dip time. The data are comparable with the re-circulation mode, but show a reduced non-uniformity. This is probably due to the continuous supply of ozonized water. The LIQUOZON® Single hence provides an industry ready solution for the ultra-thin wet chemical ozone oxide surface preparation for ALD high-k deposition.

Process

In the re-circulation set-up the effect of some process parameters was examined.

Influence of temperature (kinetic effect) Upon cooling down the O_3/DIW, reaction rate goes down as well as diffusion of reactants through the boundary layer. This makes the process less time critical. Figure 3 shows that, indeed, the slope of the oxide thickness versus dip-time curve is lowered, which is due to a reduced oxidation rate. Uniformity stays quite constant over the examined time window, which can be explained by a reduced O_3 decay at lower temperature.
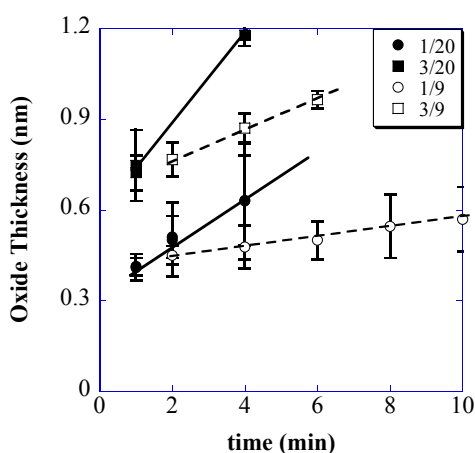

Figure 3: Oxide thickness versus dip-time for different ozone concentrations and temperatures ($[O_3]_{aq}$ in ppm / T in ºC). The lines are drawn to guide the eye and do not imply a model.

Table I: The influence of additives on the ozone concentration and the oxide thickness for a 1-minute dip at room temperature in a re-circulation set-up.

additive	pH	$[O_3]_{aq}$ sp (ppm)	$[O_3]_{aq}$ meas. (ppm)	thickness (nm)	stdev (nm)	uniformity (%)
none	neutral	1	1.1-1.0	0.33	0.04	10.85
HCl	2	gen. sp.	1.2-1.1	0.49	0.05	10.08
	2	1	1.1-1.0	0.47	0.05	9.78
HAc	2.5	gen. sp.	1.8-1.8	0.57	0.05	8.33
	2.5	1	1.1-1.1	0.50	0.04	8.35

Influence of additives (equilibrium effect) Another way to slow down the O_3 decay reaction is by adding a radical scavenger (e.g. HAc: acetic acid). On the other hand changing the pH can affect the ozone solubility. Moreover, changing the pH can also affect the final oxide thickness. These factors playing simultaneously make it difficult to predict the overall effect. Table I shows the results of these experiments. The first line of the table shows the result for the neutral dip. In the first line for either HCl or HAc addition the same ozone generator setting was kept as for the neutral dip (gen. sp.). For HAc, a higher ozone concentration is obtained, which can be attributed to a lower decay during build-up and an increased solubility. Next, the ozone concentration is again brought to the same value as for the neutral dip. Here the effect on the final oxide thickness can be observed. It is clear that adding HCl or HAc increases the final oxide thickness, which is a pure pH effect [5]. For both additives also an improved uniformity is observed, compared to the neutral dip. A reduced ozone decay, see measured ozone concentration data in the third column, leads to an improved bath stability and hence a better uniformity. This effect is very pronounced for HAc.

Electrical results

Gate last NMOS capacitors were fabricated with a scaled chemical oxide. About 2 to 4 nm HfO_2 without a post-deposition anneal was used as the dielectric. The gate material was either in-situ Phosphorus doped furnace polycrystalline Silicon or sputtered TiN. The gate stacks were activated with a 1000 ºC anneal in oxygen. The EOT *vs.* gate leakage scaling of the poly-HfO_2 stacks is as shown in Figure 4. Using an initial chemical oxide interface of approximately 0.4 nm, a favorable leakage reduction is obtained (~2-5 order of magnitude) with a minimum EOT achieved of around 1.2 nm. For the TiN gates EOT could be scaled even further down to 0.8 nm
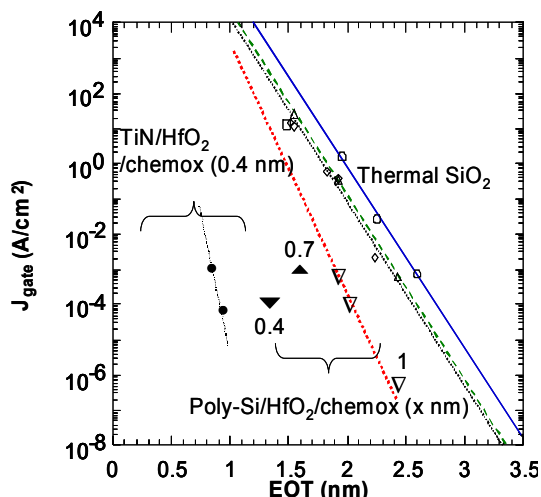

Figure 4:EOT-leakage scaling of poly – ALD HFO_2 on chemical oxide as compared to SiO_2.

Conclusions

Lowering the ozone concentration has proven to be the best way to control the thickness of a wet chemical ozone oxide. The process can be made less time critical and more robust using low temperature DI-water. Adding a scavenger prevents ozone decay, yielding a better uniformity of the oxide thickness. Lowering the pH of the solution enhances ozone stability, but yields a thicker oxide, so set-points should be adapted accordingly. Electrically the chemical oxide interface was demonstrated to enable a downscaling of EOT to 1.2 nm, with a HfO_2/poly-Si gate stack and even further down to 0.8 nm EOT with a HfO_2/TiN gate stack integration.

The wet chemical ozone oxide treatment has been proven to be a viable solution for ALD surface preparation. This work has also shown that the idea has successfully been implemented in a commercially available tool.

References

[1] C. Kizilyaili, P.K. Roy, F. Baumann, R.Y. Huang, D. Hwang, C. Chacon, R. Irwin, Y. Ma and G. Alers, in Symposium on VLSI Technology Digest of Technical Papers, IEEE, p. 216 (1998).
[2] Y.B. Kim, M. Tuominen, I. Raaijmakers, R. de Blank, R. Wilhelm and S. Haukka, Electrochemical and solid state letters 3(7), p. 346 (2000).
[3] K. Kukli, J. Aarik, A. Aidla, H. Siimon, M. Ritala and M. Leskela, Appl. Surf. Sci. 112, p. 236 (1997).
[4] M.L. Green, M.Y. Ho, B. Busch, G.D. Wilk, T. Sorch, T. Conard, B. Brijs, W. Vandervorst, P.I. Raisanen, D. Muller, M. Bude, J. Grazul, J. Appl. Phys. 92(12), p. 7168-7174 (2002).
[5] F. De Smedt, C. Vinckier, I. Cornelissen, S. De Gendt and M. Heyns, J. Electrochem. Soc. 147(3), p. 1124 (2000).
[6] F. De Smedt, G. Stevens, S. De Gendt, I. Cornelissen, S. Arnauts, M. Meuris, M. Heyns and C. Vinckier, J. Electrochem. Soc. 146(5), p. 1873 (1999).