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Uniform Ultrathin Oxide Growth for High-k Preclean

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Introduction

The continuous scaling of integrated circuits has driven the thickness of the gate dielectric in MOS devices to levels at which standard silicon oxide realizes excessive leakage. New materials with higher dielectric constant (high-k) than silicon oxide are being developed which can give sufficient capacitance and larger physical thickness resulting in acceptable leakage [1]. While silicon oxide gate dielectrics have been easily grown by oxidizing the silicon substrate, high-k materials must be deposited onto the silicon substrate. Surface termination prior to deposition of high-k materials has a critical impact on the performance of these films. Depositing high-k materials directly on bare silicon has been problematic leading to silicide formation and decreased electron mobility [2]. A solution to this problem is to leave the surface oxide-terminated prior to high-k deposition. However, an oxide termination layer that is too thick will defeat the purpose of depositing a high-k material, so it is important to produce a very thin oxide termination layer. This is illustrated for the case of a 12Å equivalent oxide thickness (EOT) target. Figure 1 illustrates that as the interfacial SiO_2 layer becomes thinner, a thicker high-k film can be deposited while still achieving the 12Å EOT target, resulting in much lower leakage.

Silicon oxidation by standard cleaning solutions and ozonated water has been utilized and studied for many years [3-9]. Ozonated water at room temperature can be used to grow a uniform oxide at saturated thicknesses of 8-10Å [5-8]. However, if is difficult to produce a uniform oxide at lesser thicknesses with ozonated water at room temperature.

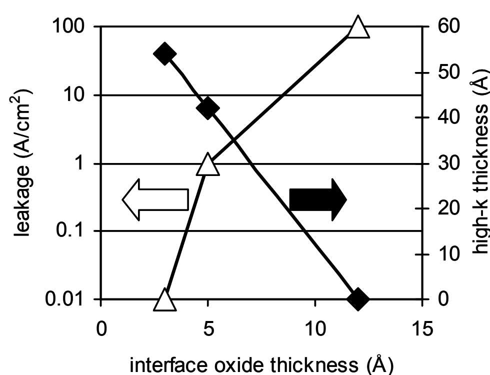

Figure 1. Relationship between leakage and interface oxide thickness for a 12Å EOT gate dielectric formed using a high-k material with a dieletric constant of 24. Thinner interface oxide allows a thicker high-k material (◆) resulting in lower leakage (△).

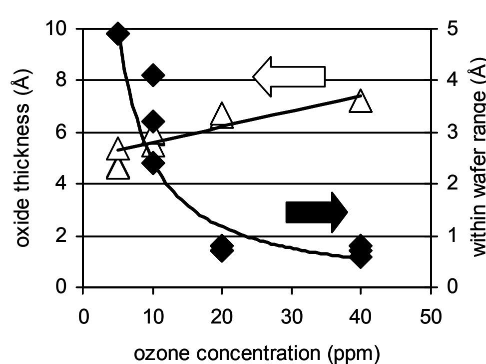

Figure 2. Oxide growth with room temperature, 40ppm ozonated water for 60 seconds produces uniform saturated oxide films at about 8Å thickness. Attempts to grow thinner oxide films (△), by lowering the ozone concentration produce much higher non-uniformity (◆).

Oxide Growth with Room Temperature Ozonated Water

Silicon oxide growth in ozonated water is a well-known technique for creating a passivated, hydrophilic surface as a part of surface preparation processes [4-9]. The growth of an oxide layer in room temperature ozonated water is widely believed to be governed by the field-enhanced diffusion of O^- species, which form from the decomposition of O_3, from the liquid-oxide interface to the

oxide-silicon interface [6,8] where they react with Si to form SiO_2. When the oxide layer reaches a thickness at which the field is too weak to support field-enhanced diffusion, the layer stops growing.

Ellipsometric measurement of oxide films grown at these thicknesses is open to some interpretation, and, as we will see below, may not correlate directly with other types of measurements. However, these measurements provide a good indication of the relative thickness and uniformity of a film within a given set of experiments. In these studies, oxide thickness was measured with a Rudolph Caliber 300 spectroscopic ellipsometer using a single wavelength 633nm laser at multiple angles. To eliminate the effects of atmospheric organic contamination, wafers were baked on a hot plate for 3 minutes at 250C immediately prior to measurement.

Uniform oxide films are easily obtained by exposing the silicon substrate to the ozonated water long enough for the saturated thickness to be grown. Exposure to water with an ozone concentration of 40ppm for 60 seconds is sufficient to produce a uniform oxide 8Å thick. Attempts to grow thinner oxide films by using less concentrated ozone are shown in Figure 2. The level of non-uniformity in these "sub-saturated" films is further illustrated for a nominal 6Å film on the left side of Figure 3.

It is not clear what causes non-uniformity in the sub-saturated oxide film. It is postulated that initial oxide growth under these conditions proceeds in islands rather than by strict layer-by-layer growth. Previous studies on the mechanisms on oxide growth [6,8] under these conditions have not addressed uniformity. Other studies of the mechanisms for thin oxide growth under gas phase conditions with O_2 or O_3 [10,11] generally indicate layer-by-layer growth. It seems likely that the initial propagation of oxide growth (layer-by-layer or island) will be different in the aqueous environment. The uniformity of thin oxide films grown with ozonated water is significantly improved with a controlled sequence of saturated oxide growth, followed by uniform etching.

Uniform Oxide Etching

Uniform etching of silicon oxide with dilute HF is achieved in an optimized single tank configuration that has been described previously [12]. Highly uniform oxide etching can be achieved on wafers that are already immersed in a non-etching solution by injecting dilute HF into the rapidly and well-mixed tank. Good mixing and rapid transition from non-etching to etching and back to non-etching solutions is achieved with engineered design and placement of injection nozzles in the immersion tank and with optimized flow rates.

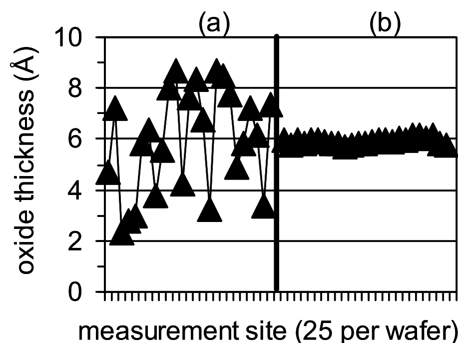

Figure 3. (a) Oxide growth with room temperature, 10ppm ozonated water for 60 seconds produces a non-uniform oxide film at about 6Å thickness. (b) Using the 2-step process of saturated growth followed by controlled, uniform etching produces a very uniform oxide film at about 6Å thickness.

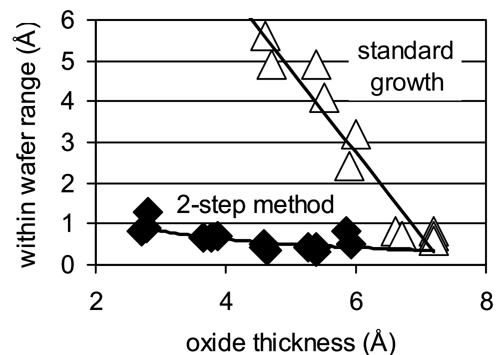

Figure 4. Oxide thickness range as a function of final oxide thickness for a standard growth method by varying ozone concentration (△) and for the new 2-step growth method by growing to sautration and uniformly etching back (◆).

Two-Step Process for Uniform Ultrathin Oxide

The concept to achieve a uniform, yet ultrathin oxide layer on the silicon surface involves combining highly uniform saturated oxide growth using ozonated water with highly uniform oxide etching using in-situ dilute HF injection. After removing native oxide in 200:1 dilute HF, the wafers are rinsed and then exposed to 40ppm ozonated water at room temperature. Exposure to ozonated water is held for 10 minutes to insure optimal uniformity of the saturated oxide film. After rinsing, the wafers are exposed to dilute HF (400:1 to 800:1) using the well-mixed chemical injection system for the required length of time to reach the desired final oxide thickness. The right side of Figure 3 shows the results of this two step method for a 6Å oxide film. Figure 4 further illustrates the much improved uniformity for various oxide thicknesses down to 3Å.

The ultrathin oxide films are also stable enough to enable standard manufacturing procedures allowing the pre-cleaned wafers to be stored for a reasonable length of time prior to high-k film deposition. Figure 5 shows that a 3Å thick oxide film adds less than 0.5Å to total thickness after 24 hours of exposure to ambient conditions (~20ºC, ~40% relative humidity).

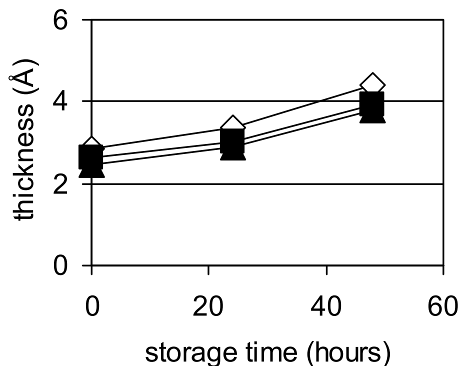

Figure 5. Oxide thickness for three different wafers as a function of storage time at ~20C, 40% relative humidity. The thickness grew by less than 0.5Å over a 24-hour period

Table I. SiO_2 layer thickness measured before Al_2O_3 deposition and extrapolated from post-deposition film measurements.

Nominal Pre-Clean Measurement (Å)	Extrapolated from Al_2O_3 Measurement (Å)
1.0	11.4
3.3	13.8
4.6	14.6

Pre-Clean for Al_2O_3 ALD

To test this pre-clean process, ALD alumina was deposited on prepared surfaces. Wafers were cleaned and prepared in one facility, packaged, sealed and shipped to another facility, and then deposited with ALD alumina within 12 hours. Nominal ozone oxide thicknesses of 1Å, 3.3Å, and 4.6Å were used. A series of wafers in each group were exposed to either 24, 44, 58, or 116 ALD cycles. The final dielectric thickness was then measured by ellipsometry and a plot of thickness vs. ALD cycles was created. Extrapolating back to 0 cycles gives an indication of the interfacial oxide thickness. Table I shows a comparison of the post-ALD extrapolated SiO_2 thickness with the nominal pre-clean measurement. The order of the extrapolated interfacial oxide thickness agrees with the pre-clean measured oxide thickness, however the values are much higher.

The increase in interfacial oxide thickness can be explained either by growth of native oxide during the transfer from facilities 1 to facilities 2 or by surface dependent growth of ALD films. ALD processes are known to exhibit surface-selective growth [13]. The growth mode, i.e. how the material is arranged on the surface during the growth, is of critical importance. On an H-terminated surface, island growth seems to occur in the Al_2O_3 ALD growth, whereas on a chemical oxide

deposited surface, like those used in this study, continuous ALD growth occurs yielding a thicker film. The reason for the apparent thicker interfacial layer can not be explained from these experiments. Further studies, as reported by Moon and Cho [14], of initial ALD growth on H-terminated and chemical oxides are needed to understand the interfacial film thickness.

Summary

Highly uniform, ultrathin oxide growth has been achieved with a novel combination of saturated oxide growth and uniform oxide etch. Use of this oxide growth method as the final step of a pre-clean process for high-k gate dielectrics will enable thicker high-k films while maintaining equivalent oxide thickness enabling higher performance, lower leakage high-k gate stacks. Initial work on integrating the ultrathin oxide as a pre-clean for high-k film deposition is promising and needs to be studied in much more detail.

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