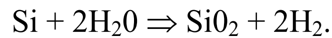
OP-B WET OXIDATION

filename: WETOX

The growth of $Si0_2$ on Si can be carried out in an atmosphere that is either dry (see) or wet. In the presence of H_20, the oxidation of silicon proceeds via the reaction



$$Si + 2H_20 \Rightarrow Si0_2 + 2H_2.$$

There are two major differences between wet- and dry-grown oxides: 1) oxide growth rate; and 2) dielectric breakdown strength of the oxide. The growth rate in wet ambients is much faster than in dry (the parabolic rate constant for wet oxidation is about 25 times larger than that for dry oxidation at 1050˚C). This is primarily due to a much higher solid solubility of H_20 in $Si0_2$ than 0_2 in $Si0_2$, thus providing a much larger supply of oxidizing species to the Si surface. We supply the H_20 vapor to our furnace using a simple bubbler. A flask containing high purity water is heated to approximately 95˚C to achieve an appreciable vapor pressure of H_20 (approximately 640 Torr), and then a carrier gas (in our system, 0_2) is bubbled through the water. The H_20-saturated gas then passes into the furnace.

The second difference between wet and dry oxides is the lower dielectric breakdown strength of wet-grown oxides. This is largely due to the slightly more porous nature of a wet oxide compared to a dry oxide. Typical values for our wet-grown oxides are in the neighborhood of 8 MV/cm.

REFERENCES

VLSI Fabrication Principles, S. K. Ghandi, Wiley-Interscience, 1983, ch 7.

VLSI Technology, ed. S. M. Sze, McGraw-Hill, 1983, ch 4.

WET OXIDATION PROCEDURE

1. Check H20 bubbler to make sure it is full. Turn heater controller ON; set point should be 94.0˚C.

2. Set furnace temperature controller to 100/260/100 on the 900 scale (check for updates!). This will achieve a temperature of 1050˚C in the flat zone. Allow 30 min. for furnace and bubbler to stabilize.

Steps 1 and 2 should normally be performed by the lab TA before you arrive.

3. Five (5) minutes before loading wafers turn 0_2 gas supply to bubbler ON, set for 150 with steel ball. This is to pre-fill the furnace tube with steam.

4. Remove furnace tube end cap and place it behind the furnace load tray. Carefully remove the pull-rod from its storage tube, and pull the wafer boat out onto the load tray. Replace pull-rod and allow 1 min. for the boat to cool.

NOTE: NEVER USE ANY PULL-ROD OTHER THAN THE ONE SPECIFICALLY FOR THE FURNACE YOU ARE USING!

5. LOAD WAFERS: Place clean Si chips in the wafer boat slots. DO NOT TOUCH THE BOAT WITH YOUR TWEEZERS.

6. Using the pull-rod, perform a slow push of the boat into the furnace flat zone. This should take approximately 1 min. The flat zone is reached when the end of the pull-rod reaches the mark on the furnace tray. Replace pull-rod in its storage tube, and loosely replace furnace end cap.

THE PULL-ROD WILL BE VERY HOT: DO NOT TOUCH ANY PORTION WHICH HAS BEEN INSIDE THE FURNACE.

7. Allow boat to remain in the flat zone for the desired wet-ox time with the bubbler 0_{22} supply on.

8. At the end of the wet-ox time, turn the bubbler 0_2 supply OFF, and turn the DRY 0_2 supply ON, set for 100 with the steel ball. Continue this DRY oxidation for 10 min.

9. At the end of the 10 min dry-ox remove the furnace end cap and pull the wafer boat out onto the furance tray. ALLOW BOAT TO COOL FOR 2 MIN. Remove samples.

10. Store boat in furnace neck, replace cap and pull-rod, turn OFF ALL GAS SUPPLIES.

Stand-by (end of lab shut-down)

-Boat should be in the furnace neck.

-All gas supplies OFF.

-BUBBLER HEATER MUST BE OFF.

-Furnace controller: 100/100/100 on the 500 scale.

Color Chart for SiO_2 (from Ghandhi, p 413)

Intensity enhancement occurs at the wavelength $\lambda_k = \frac{2nd}{k}$, where k = 1, 2, 3,..., d = film thickness, and n = index of refraction of film (1.46 for SiO_2). Also note cyclical reappearance of the colors as the thickness increases. The repeat wavelengths λ_k are related by $\lambda_k = \frac{4nd}{2k+1}$ with k, n, and d defined as above.

Table 12: Color Chart for Thermally Grown $S10_2$ Films Observed perpendicularly Under Daylight Fluorescent Lighting (adapted from Ghandhi)

Thickness (µm)	Color and Comments
0.05	Tan
0.07	Brown
0.10	Dark violet to red violet
0.12	Royal blue
0.15	Light blue to metallic blue
0.17	Metallic to very light yellow green
0.20	Light gold or yellow-slightly metallic
0.22	Gold with slight yellow orange
0.25	Orange to melon
0.27	Red violet
0.30	Blue to violet blue
0.31	Blue
0.32	Blue to blue green
0.34	Light green
0.35	Green to yellow green
0.36	Yellow green
0.37	Green yellow
0.39	Yellow
0.41	Light orange
0.42	Camation pink
0.44	Violet red
0.46	Red violet
0.47	Violet
0.48	Blue violet
0.49	Blue
0.50	Blue green
0.52	Green (broad)
0.54	Yellow green
0.56	Green yellow
0.57	Yellow to "yellowish" (not yellow; light creamy gray or metallic)
0.58	Light orange or yellow to pink borderline
0.60	Carnation pink

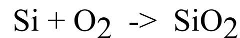
(µm)	Color and Comments
0.63	Violet red
0.68	"Bluish" (Not blue; borderline between violet and blue green; looks grayish)
0.72	Blue green to green (quite broad)
0.77	"Yellowish"
0.80	Orange (rather broad for orange)
0.82	Salmon
0.85	Dull, light red violet
0.86	Violet
0.87	Blue violet
0.89	Blue
0.92	Blue green
0.95	Dull yellow green
0.97	Yellow to "yellowish"
0.99	Orange
1.00	Carnation pink
1.02	Violet red
1.05	Red violet
1.06	Violet
1.07	Blue violet
1.10	Green
1.11	Yellow green
1.12	Green
1.18	Violet
1.19	Red violet
1.21	Violet red.
1.24	Carnation pink to Salmon
1.25	Orange
1.28	"Yellowish"
1.32	Sky blue to green blue
1.40	Orange.
1.45	Violet
l.46	Blue violet
1.50	Blue

Thickness	

OP-C: Dry Oxidation and Chlorine Oxidation of Silicon

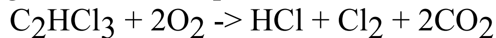
filename: DRYOX

In order to make MOS devices we must grow a very clean, high quality oxide on our silicon. Such devices depend for their operation on the physics of the interface between the silicon and the SiO_2, and the growth of this interface must be very carefully performed. The oxidation of silicon in dry O_2 is straight forward, proceeding via the reaction

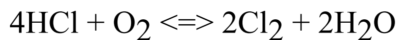


$$Si + O_2 \rightarrow SiO_2$$

We can grow our oxides in such an environment, but for gate oxidations we introduce a small amount of gaseous trichloroethylene (TCE). In the high temperature furnace the following reactions take place



$$C_2HCl_3 + 2O_2 \rightarrow HCl + Cl_2 + 2CO_2$$



$$4HCl + O_2 \Leftrightarrow 2Cl_2 + 2H_2O$$

The presence of all these species affects the oxidation process; for this particular process the equilibrium concentrations are such that CO_2, Cl_2, and HCl are the dominant species present. We can observe one change in the oxide growth quite easily: both the linear and parabolic rate constants increase when TCE is added to the gas stream.

We introduce chlorine during our gate oxidations because it has been found to greatly improve the quality of the grown SiO_2. Such oxides have a greater dielectric breakdown strength. The incorporation of chlorine into the oxide also tends to immobilize sodium, normally a highly mobile ionized species that can cause very unstable threshold shifts in MOSFETs. In addition to improving oxide properties, the chlorine improves the quality of the underlying silicon as well. The chlorine interacts with and removes deep lying impurities in the silicon; this can cause a significant increase in minority carrier lifetimes. Another very important effect is the reduction in oxidation induced stacking faults (OSF's) during halogenic oxidation. When chlorine is present, it is believed to cause an increase in silicon vacancy concentration near the silicon surface. Since OSFs are the result of excess interstitial silicon, an excess of vacancies can combine with the interstitials, thus reducing the number of OSFs.

References:

"Role of Chlorine in Silicon Oxidation," J. Monkowski, Solid State Technology, Part I, July 1979; Part II, August 1979.

"Some Effects of `Trichloroethylene Oxidation' on the Characteristics of MOS Devices," G.J. Declerck et al., J. Electrochem Soc. 122, 1975, 436-439.

"Trichloroethylene Oxidation of Silicon," J.R. Flynn, M.S. Thesis, University of Illinois of Urbana-Champaign, 1980.

Operating Procedure

1. Check TCE bubbler and make sure it is full. The thermometer attached to the bubbler should read between 23°C and 25°C.

2. Set furnace temperature controller to 100/445/100 on the 900 scale. This will give a temperature of 1100°C in the furnace flat zone. Allow 30 min. for furnace and bubbler to stabilize.

Steps 1 and 2 should normally be performed by the lab TA before you arrive.

3. Starting with all gases off, turn the O_2 supply ON, flow meter set at 150 with the steel ball. Allow the furnace tube to flush with O_2 for two (2) minutes.

4. Remove furnace tube end cap and place it behind the furnace load tray. Carefully remove the pull-rod from its storage tube, and pull the wafer boat out onto the load tray. Replace pull-rod and allow 1 min. for the boat to cool.

NOTE: NEVER USE ANY PULL-ROD OTHER THAN THE ONE SPECIFICALLY FOR THE FURNACE YOU ARE USING!

5. LOAD WAFERS: Place clean Si chips in the wafer boat slots. DO NOT TOUCH THE BOAT WITH YOUR TWEEZERS.

6. Using the pull-rod, perform a slow push of the boat into the furnace flat zone. This should take approximately 1 min. The flat zone is reached when the end of the pull-rod reaches the mark on the furnace tray. Replace pull-rod in its storage tube, and loosely replace furnace end cap.

THE PULL-ROD WILL BE VERY HOT: DO NOT TOUCH ANY PORTION WHICH HAS BEEN INSIDE THE FURNACE.

7. Start the oxidation timing. Reduce O_2 flow to 66 with the glass ball.

OPTIONAL 7a.: FOR CHLORINE INJECTION ONLY
After oxidation in pure O_2 has proceeded for five minutes, turn the TCE bubbler gas supply (marked CHLORINE on the gas panel) ON, set to 116 with the glass ball.

8. After the desired oxidation time has elapsed, turn the CHLORINE gas OFF (if used), wait 30 seconds, and then turn the O_2 supply OFF. Immediately turn the N_2

supply ON, set to 100 with the steel ball. Allow samples to soak in N_2 for 5 minutes.

9. At the end of the 5 minute N_2 soak, remove the furnace end cap and perform a slow pull of the boat from the furnace: this should take approximately one minute. Allow samples to cool for one minute, then remove them.

10. Store boat in furnace neck, replace cap and pull-rod, turn OFF N_2 supply, and turn O_2 supply back ON, but set for about 5 with the glass float.

Standby:

-Boat should be in the furnace neck.

-TCE (CHLORINE) gas supply OFF, N_2 OFF, O_2 ON, set for 5.

-TCE Bubbler glass stopcocks CLOSED

-Furnace controller: 100/100/100 on the 500 scale.