Silicon Oxidation Studies Using Ellipsometry

Table of Contents

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1 Introduction/Learning Outcomes

An important step in silicon microelectronics processing is the formation of an oxide layer to act variously as a diffusion barrier, an insulator, or an interface to a metallization [Refs. 1, 2]. Oxide layers can also be used as the dielectric for on-chip capacitors.

Thermal oxidation of silicon in dry or wet oxygen is a widely used process in VLSI. The purpose of this experiment is to evaluate the growth kinetics of the oxidation process as a function of processing parameters such as temperature or atmosphere [Refs.3, 4]. You will also be exposed to ellipsometry, an important optical instrument in thin film technology [Ref. 5]. Some background reading [e.g. Refs. 3,4,7] is strongly recommended.

By completing this experiment, you should gain the following:

- An understanding of the theory behind growth kinetics of silicon oxide layers
- Experience fabricating silicon oxide layers in a controlled production environment
- Experience with ellipsometry, an import measurement technology in thin film studies

2 Theory

The formation of the oxide of silicon (SiO_2) on a silicon surface is termed *oxidation*. The ability to form this oxide (SiO_2) is the cornerstone of the planar (in a plane, i.e. two dimensional) processing of silicon integrated circuits. Although there are many different ways in which to form this oxide, the process most often employed is thermal oxidation [Refs. 6, 7]. It is this method that will be explored in this experiment.

The method of thermal oxidation enables the user to produce SiO_2 films of desired thickness and beneficial Si/SiO_2 interface properties. It is due to this control that thermal oxidation is the most common growth technique found in silicon processing. Thermally grown SiO_2 is used in layers or in thicknesses ranging from 6 nm to 10^3 nm typically. Some of the functions of these films include: a) masking against ion implantation and diffusion; b) passivation of the silicon surface; c) isolation of individual devices (e.g. local oxidation of silicon, LOCOS); d) use as a gate oxide and capacitor dielectric in MOS devices; and e) use as a tunneling oxide in electrically alterable ROMs.

Freshly cleaved silicon rapidly forms a very thin native oxide layer when exposed to an oxidizing ambient (e.g. oxygen, water, water vapour) at room temperature. The oxidation is self-limiting as surface silicon is covered by the native oxide of about 1 to 2 nm thickness. At elevated temperatures more rapid growth and thicker oxides result.

The reactions governing the formation of SiO_2 are given as:

$$Si(solid) + O_2(vapor) \rightarrow SiO_2(solid) \qquad \textit{Dry Oxidation} \qquad (1)$$

$$Si(solid) + 2H_2O(vapor) \rightarrow SiO_2(solid) + 2H_2 \qquad \textit{Wet Oxidation} \qquad (2)$$

The oxidation reaction occurs initially at the ambient-silicon interface. As the oxide grows, the reaction continues at the SiO_2/Si interface while consuming fresh substrate silicon there. Based on the relative densities and molecular weights of Si and SiO_2, it is found that the amount of silicon consumed is 44% of the final oxide thickness, as shown in Figure 1. This relationship is technologically important for controlling step heights that form at the SiO_2/Si interface between areas subjected to varying degrees or duration of exposure to oxidizing ambients as a result of masking (patterning) processes [Ref. 2]. Such step heights govern the topographical evolution of the silicon device structure.

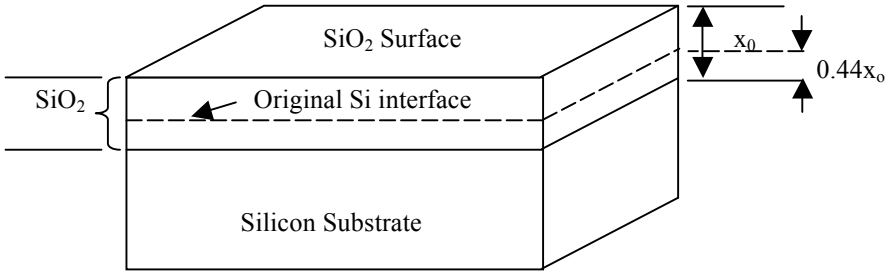

Figure 1 - Thermal oxidation of silicon

The Linear-Parabolic model proposed by Deal and Grove assumes that the oxidation of SiO_2 on Si occurs as a result of two fluxes that sequentially transport the oxidizing species from the gas to the Si/SiO_2 interface, where a third flux is involved in the consumption of the oxidant by the reaction with silicon [Refs. 6, 7]. This model accurately represents the growth kinetics of silicon oxidation for certain conditions, and further reading on this model is highly recommended.

3 Facility/Equipment (Please request a demonstration before operation.)

3.1 Oxidation Facilities (See facility/equipment care instructions and follow carefully.)

Figure 2 shows a (quartz) tube furnace in which a crucible carrying multiple silicon chips is centrally positioned. Ambient gas flows through either a dry channel (99.999% pure nitrogen, <1ppm water, <1ppm oxygen) or a wet channel (99.999% oxygen humidified by bubblers) with appropriate pneumatics. A spouted, 300ml tall-form Pyrex beaker serves as endcap to limit back-diffusion of air at the tube exit and minimize the steady state flowrate of process gases.

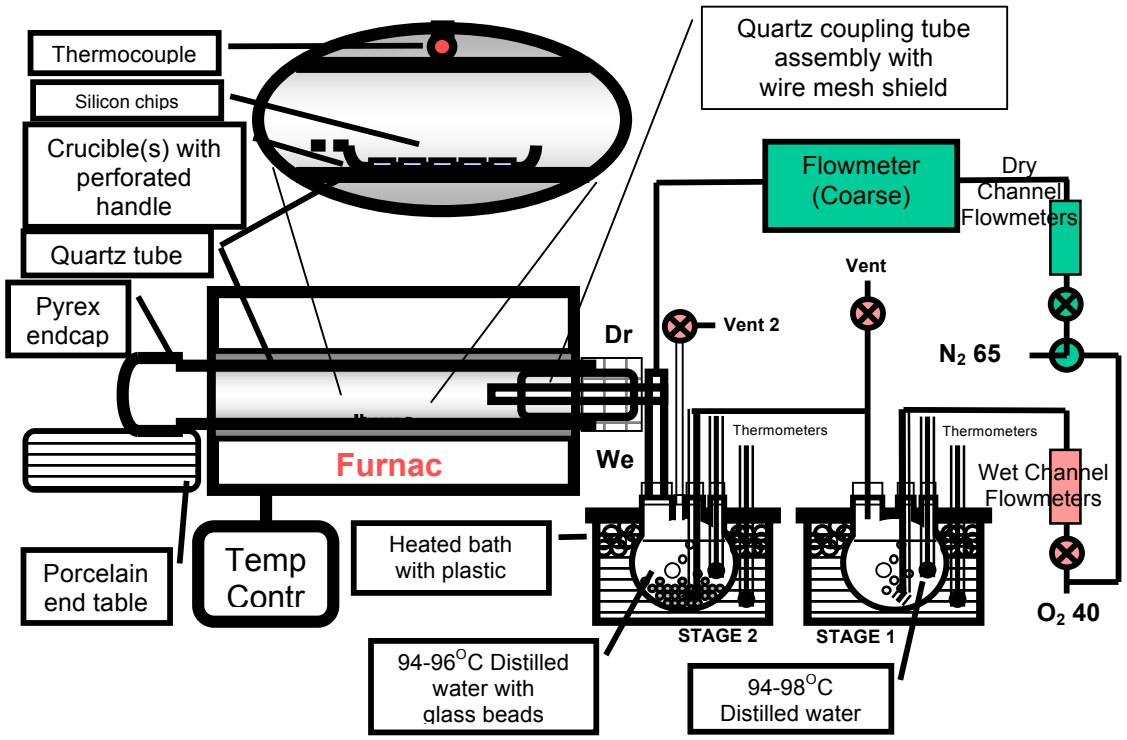

Figure 2 – Oxidation apparatus

For wet oxidation, high purity oxygen controlled by needle valves at two flowmeters in series (Matheson tubes 602, 604) is fed through a wet channel comprising a 2-stage bubbler. Each stage is a 500 mL flask of distilled water to be heated to the 94 - 98°C range by immersion in a water bath in turn temperature-controlled by a digital dial for repeatable setting. The stage 2 bath should be set to a temperature of 98 ± 1°C. This is the highest possible setting short of vigorous boiling in this bath, and correspondingly sets a quiescent flask temperature of 96 ± 1°C without carrier gas bubbling. The stage 1 bath should be maintained at 94 - 98°C. Thermometers monitor both flask and bath temperatures. Distilled water is used to fill both flasks and baths. The stage 1 flask should be filled with 500ml of water, and the stage 2 flask with 400ml for proper operation. The stage 2 flask has a glass diffuser and glass beads to stabilize temperature. Stage 1 has a perforated Teflon tubing as diffuser. Plastic beads limits evaporation and stabilize temperature at both baths. Water from both the flask and bath of each stage can be removed by thoroughly siphoning each with the corresponding squeeze bottle-tubing kit provided. For access, use the glass thermocouple (TC2) adaptor on Stage 2 and the adaptor with a glass rod handle on Stage 1. Temperature drop in Stage 2 water is limited to 2 degrees C during bubbling cycles. The water vapour pressure in the wet oxygen stream is thus maximized by a high flowrate without boiling or causing liquid injection into the furnace. The incoming water vapour pressure at the furnace tube would be close to atmospheric as the above-mentioned endcap effectively vents the flask to atmosphere through the furnace tube.

The following table summarizes the proper SHUTDOWN and IDLE conditions for the pneumatic plumbing:

Vent 1 (Needle valve on post): Default is Full CCW (maximum vent)
N2/O2 (wall-mounted valve): Default is O2 (wet channel carrier gas)

CONDITION	N2 Bottle Valve [Regulator]	O2 Bottle Valve [Regulator]	DRY N2/O2 Select	N2 PURGE ON/OFF	DRY Channel Flowmeter Valve	WET Channel Flowmeter Valve
SHUTDOWN	Closed [CCW]	Closed [CCW]	DRY N2	OFF	Closed	Closed
IDLE	Open [65 psi]	Open [40 psi]	DRY N2	ON	6 LPM air equivalent	Closed

Vent 1 relieves pressure in Stage 1 and should never be completely closed. Vent 2 is under pneumatic control, opening during dry N2 purge to keep moisture from the furnace tube and closed otherwise.

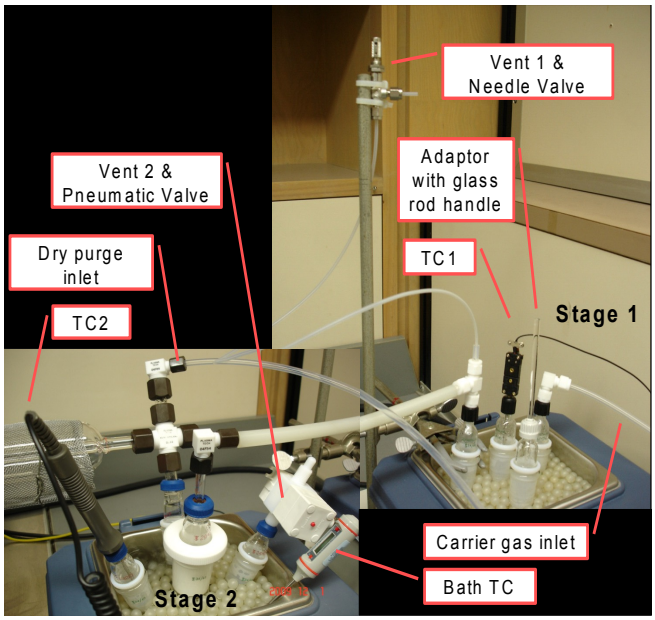

Fig.3 Picture of water source

When selected for nitrogen purge, the dry channel allows to chemically arrest wet oxidation of samples while in the furnace and in transit at the tube exit where the endcap is necessarily off. Given an appropriate N2 flowrate, as controlled by fine (Matheson tube 601) and coarse (10 LPM air equivalent) flowmeters in series, N2 purge on/off controls the oxidation time. The following summarizes the operation of both modes:

CONDITION	N2 and O2 Bottle Valve	DRY N2/O2 Select	N2 PURGE ON/OFF	DRY Channel Flowmeter Valve	DRY Coarse Flowmeter	Wet Channel Flowmeter Valve Tube 602 (mm)
DRY N2 PURGE	Open	DRY N2	ON	Open	6 LPM (Air Equiv.)	Closed
WET O2		DRY N2	OFF	Closed	NA	Open 110mm max. (S.S. bead)

Following the pneumatic settings appropriate to each condition as shown in the above table, a wet oxidation cycle follows starts from the DRY N2 PURGE condition, then to the WET O2 condition (default: max. wet channel setting) then back to the DRY N2 PURGE condition upon completion.

In (dry) N2 purge mode:

- The 4-way valve supplies N2 to the dry channel flowmeters as well as pneumatic pressure to keep Vent 2 open so moisture from the Stage 2 flask would escape there.
- The manual valve at the dry channel flowmeter can be pre-adjusted and left manually open.
- The manual valve at the wet channel flowmeter must be manually closed.
- Vent 1 continues to relieve Stage 1 hot water vapour pressure.

In (wet) oxidation mode:

- The 4-way valve cuts off N2 supply to the dry N2 purge and allows the pneumatic pressure to collapse through the valve at Vent 2, which is then normally closed. The moisture carrier gas (wet O2) then flows only to the furnace tube.
- The manual valve at the wet channel flowmeter must be manually open and adjusted slowly to the desired flowrate in order to avoid injecting liquid water into the furnace – a very important aspect for safety and cleanliness.
- The steady state oxygen flowrate, affects the degree of cooling in both Stage 1 and 2 flasks, the water temperature of the latter being most important to sustain. Typical temperature drop in both flasks due to bubbling is only two degrees C.
- While maximizing the steady state oxygen flowrate operating range, Stage 1 can be over pressured (against the flow impedance of the Stage 2 bubbler) from both inlet gas pressure and the vapour pressure of near-boiling water such that Vent 1 is required at least for safety. Vent 1 has a needle valve that can be adjusted for optimum pressure maintenance and relief. Stage 1 being a heat exchanger itself, the adjustment of flowrate and Vent 1, while having an effect on Stage 1 water temperature, should not impact Stage 2 temperature excessively. The possibility of adjusting Vent 1 also means the oxygen flowmeter reading (Tube 602, glass or stainless steel bead) does not uniquely determine carrier gas throughput in the Stage 2.
- However, the apparatus has proved satisfactory with the Vent 1 needle valve wide open – hence a default setting. Under this condition, a maximum carrier gas flow rate (as measured by the 150mm 602 flow tube) of 110 mm by the S.S. float is recommended empirically.

The ceramic (Alundum, i.e. vitrified aluminum oxide) crucible has a perforated handle to facilitate manipulation by a hooked (quartz) push-rod. Another jig constructed from a pair of quartz tubes provides a protective rest for the tip of the push-rod when idle but hot. Tongs are provided to handle hot crucibles and the endcap during sample loading/unloading cycles. A porcelain crucible (not shown in Fig.2, carries silicon chips and sits in the Alundum crucible as a secondary vessel. A porcelain end table provides support for the endcap as well as a working surface when transferring silicon samples from a hot porcelain

crucible to a cooling surface before their further transfer to a plastic "waffle pack" (also called bare die tray).

The push-rod is never handled by bare hands to eliminate finger grease contamination. Although it can be safely handled in Nitrile gloves up to 1/3 of the cool end, thermal mitts are recommended instead for those prone to forget this and at the expense of dexterity. The very end of the push-rod is at room temperature where contact or proximity of hand/face should be avoided as burns can result from infrared strongly guided through the rod.

The furnace temperature is controlled by an Omega CN2100 Controller. The temperature sensor is a thermocouple mounted on the heating jacket at approximately the geometric centre of the furnace but outside the quartz tube. Silicon sample or crucible temperature is therefore not directly measured but the thermocouple temperature is assumed to be representative. To set the process sequence, use the following steps:

a. Check power connections (230 VAC and 115VAC).
b. On the Controller Keypad, press TUNE, LAST, YES in sequence
c. Repeatedly press PARAMETER to cycle through the parameter values
d. Set Ramp and Soak: YES gives a linear warm up and a subsequent hold; NO allows you to set a continuous temperature
e. Press END OF TUNE
f. To start the process press MANUAL/AUTO
g. Monitor warm-up to ensure proper operation and no excessive temperature transients
h. To shut down, set to room temperature under MANUAL mode.

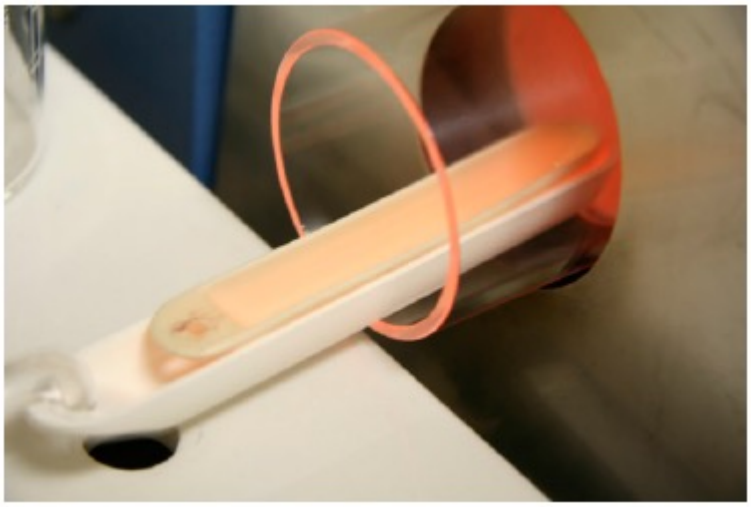

Fig.4 Crucibles assembly being inserted (chips not shown)

3.2 Thickness Measurement by Ellipsometer

There is a Gaertner Rotating Analyzer Ellipsometer available to measure oxide thicknesses ranging potentially from a few tens to about 1000 nanometers, depending on experimental details and variations. (Model LS104SA with LS104B controller, S/N 1533-AK.. Software: NI-DAQ Driver and GEMP v.1.2, 1998. PCI interface card. Gaertner Scientific Corp., Skokie, Illinois. 1-847-673-5006. See manuals at the workstation). Data can be downloaded in a text file for exporting to spreadsheets. NIST traceable calibration samples at 100∐ and 900∐ (nominal) thicknesses, SiO2 on 100mm Si Wafers are provided.

4 Designing Your Lab

Theoretical Considerations

1. What is the Deal-Grove Model? What variables do you know ahead of time, and what could you measure?
2. Under what conditions is the Deal-Grove model accurate?
3. What advantages might wet oxidation have over dry oxidation (or vice versa)?

Predictions

1. Referring to the theory section and other sources, use parameter values from literature to estimate the growth rate as a function of time and plot it

Experimental Considerations

1. Plan a sequence of measurements to establish the wet oxidation rate
2. How will you accurately measure oxidation time?
3. What is an ellipsometer and how is it used in this experiment?

Design Considerations

1. Make a flow chart/procedure of a typical wet (and dry) oxidation fabrication process from start to finish. Make sure you write down and understand what each component of the plumbing is for and its function
2. Devise strategies to ensure consistent fabrication conditions from batch to batch, and lab period to lab period

5 Lab Safety and Upkeep

5.1 Health and Safety

1. Compressed gases – As long as regulators are properly attached and operated at low pressures (=<20 psi), there should be minimal direct hazard. See Ref. 8 for safety instructions.

2. High temperatures – The furnace is operable up to 1100^{o}C such that all precaution must be taken to avoid burns. Do not open the furnace casing while it is heated. Note the following hot items (and proper handling tools): endcap (tongs for beakers), crucible (tongs), push-rod (padded mitts, quartz tube stand), silicon chips (metal tweezers, porcelain cooling dish). Avoid burn from guided infrared at the tip of the push-rod when handling it there (see Section 3).

3. Steam – Water near boiling point has a vapour pressure close to 1 atmosphere. When the wet channel is selected, the much increased steam pressure is relieved through the furnace tube to atmosphere. Boiling in the water flask is to be avoided to preclude uncontrolled moisture content and pressure hazard. When moist oxygen is further heated in the furnace, it behaves as a rapidly expanding gas with unsaturated steam. The effluent steam is bled into the lab. through the beak of the endcap and should be kept in mind as a burn hazard.

4. Hot water – up to 2 litres of boiled distilled water will be handled in each lab. session.

5. Vacuum – The coupling tube assembly has a vacuum jacket over which a wire mesh implosion shield is always applied.

6. Lasers – The ellipsometer laser beam, although low power (about 1 mW), can be reflected off silicon samples and shiny tools. Wear safety eyewear when aligning beam.
7. Glass/Quartzware – Handle gently and report any breakage and chipping for proactive replacement.

5.2 Equipment/Facility Care

1. Generic care (daily):

1.1 Observe all cleanliness protocols and leave no litter.

1.2 Keep all items (including documentation) at original workstation.

1.3 Return all mobile items to toolboxes and storage facility provided.

1.4 Exit all programs to idle at operating system level.

1.5 Promptly report all malfunction, damages, losses, and material depletion to the faculty member in charge of the experiment.

2. Experiment-specific care:

2.1 Follow proper compressed gas turn-on and shut-down procedure to avoid a sudden high pressure surge. Release regulator pressure (handle fully CCW) before opening and closing the shut-off valve on the cylinder. Upon shut-down, always bleed off the regulator pressure by temporarily operating the control valves of the pneumatic system.

2.2 Always wear clean Nitrile gloves when handling cold furnace parts (crucibles and quartz tube) to avoid figure grease contamination and its subsequent burning.

2.3 Always wear clean Nitrile gloves when handling glassware. Clean glassware regularly by rinsing in distill water and then IPA. Invert over cleanroom cloth or paper for storage.

2.4 Move crucible at about 1 cm/sec inside the furnace to avoid thermal shock of crucibles.

2.5 Alundum crucibles suffer thermal shock upon entering or exiting the furnace especially without a buffer period (e.g. 1 min.) sitting at the mouth of the furnace. A hot Alundum crucible also suffers thermal shock when unloaded from the furnace tube directly to the cold porcelain end station.

2.6 The manual valve at the wet channel flowmeter must be manually open and adjusted slowly to the desired flowrate in order to avoid injecting liquid water into the furnace – a very important aspect for safety and cleanliness.

2.7 Teflon coated seals on bubblers should be sealed with a very gentle twisting action to start seal, but not made too tight to avoid damage when heated.

2.8 A reference sample (silicon and silicon dioxide) is available to check ellipsometry basic function.

6 References

* Indicates availability of photocopy at experiment station.

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8. *Safety Infogram, Canadian Centre for Occupational Health and Safety, Laboratories; I09, Compressed Gas Regulator Use.

9. Flowmeter Calibration Data for Matheson tubes 601 (air), 602 (oxygen), BOC (formerly Matheson Gas Products Canada, Inc., 530 Watson Street East, Box 89, Whitby, Ontario L1N 5R9 1(905) 668-3397, 1(800) 263-2620.)

10. *Certification of Measurement (Traceable to NIST), Standard 100Å and 900Å SiO2 on 100mm Si Wafers, Gaertner Scientific Corporation Models L118SW-100 and L118SW-900.