Revision History

Chapter 1.9

VLSI Etchants

Notes on Etch Rate Tests

NanoLab Manual Chapter 1.9 is based upon Etch Rates for Micromachining Processing (©1996 IEEE) by Kirt R. Williams and Richard S. Muller, IEEE Journal of Microelectromechanical Systems, Vol. 5, No. 4, December 1996. The complete article is available at the link above. All prepared samples prepared and etch tests for this report were performed in the Berkeley NanoLab. Sample preparation and etchants are discussed on the following pages. Measurement techniques and other notes are given below.

The original etch report has been expanded and updated. The new etch report is available at Etch Rates for Micromachining Processing – Part II (©2003 IEEE) by Kirt Williams, Kishan Gupta, and Matt Wasilik, IEEE Journal of Microelectromechanical Systems, Vol. 12, No. 6, December 2003. The updated report includes substrates, thin films and etchants from several laboratories and not addressed in the original report. Some highlights of the updated report are quartz, pyrex, and sapphire substrates; silicon-germanium, gold, and tungsten thin films; Cu aqueous etchants, and SF6/C4F8 and XeF2 gas etches.

Transparent Films (poly, oxides, nitrides, photoresists) were coated over the entire wafer and etched unpatterned. Their thicknesses were measured on the Nanospec using refractive indices determined by ellipsometry and verified with the Nanospec. These RIs are listed in the samples section of this report. (The RI of my low-stress nitride films was significantly different using the Nanospec than the ellipsometer. I used the ellipsometer RI, which agreed with published data.)

Five points were measured before each etch, the films were etched, then the same five points (to within a few millimeters) were measured again. The average of the differences of these five points, divided by the etch time, determined the etch rates.

Opaque Films (single-crystal silicon, metals) were patterned with photoresist. In some cases, the photoresist was left on the wafers for the etch. In others, as appropriate, the material was patterned and the PR was removed before the etch test. The SCS was covered with patterned nitride for the hot KOH etch.

A step height near the center of the wafer was measured with the Alphastep, the film was etched, and then the same step (to within a few tenths of a millimeter) was measured again. The step height difference and the etch rate of the photoresist or substrate then determined the etch rate of the film.

Plasma Etching

Plasma etching was done for one-half or one minute with one wafer in the etch chamber. Care was taken to avoid plasma-hardening effects with the photoresist samples.

Plasma etch rates on patterned wafers can be quite different from those listed here for two reasons:

1. Some plasma etch rates tend to increase when there is less surface area to be etched, due to higher etch gas concentrations.
2. Usually be etched under those conditions (e.g., oxide in the poly etcher, LAM 1). These wafers were etched alone so that no etch gas was consumed by the normally etched material.

Wet Etching

Faster wet etches were done for one minute (even less for a few very rapid etches). All slower wet etches were done for at least 10 minutes to get a more accurate measurement.

Accuracy

For etches in which the computed standard deviation was smaller than the average rate, that etch rate is listed. In cases where the standard deviation was larger than the average (or the surfaces were very rough when Alphastep measurements were used), an upper limit is given (i.e. < 50). Etch rates of zero are given where the films were thicker after the etch, as often happened with photoresist in wet etches. In a few cases, the entire film was etched off in a short time; a lower limit is listed for these etch rates. My measurements are rounded to two significant figures. I estimate my results to be good to within ± 10% ± 5 A/min.

Final Notes

Because etch rates will vary with surface area exposed, cleanliness of chamber, other materials present, age and previous use of solution, temperature of solution, temperature of chamber, other variables, and seemingly, phase of the moon, do not expect your results to be the same as those listed here! I have therefore included etch rates that other lab users and I have observed for many of the etchant/material combinations to give an idea of how much etch rates can vary. Note that the top rows (all my own observations) are with fresh solutions and recently cleaned chambers, while the "Observed Range" high and low can be for older solutions, etc.

Sample Preparation

Most of the materials listed here are commonly used in the NanoLab; others have been included for comparison. Three different popular KTI photoresist hardbake times were used to determine the effect of longer bake times.

SC Si <100>

Single Crystal Silicon with <100> orientation.

Poly n+

In-situ heavily n-doped polycrystalline silicon. RI = 3.97.
Deposited on a wafer with thermal oxide already on it to enable thickness measurements.
Deposited in Tylan 11 using recipe SDOPOLYG: SiH_4 = 120 sccm, PH_3 = 1 sccm, 650ºC.
No anneal.

Wet Ox

Silicon dioxide grown in water vapor. RI = 1.46.
Grown in Tylan 2 using program SWETOXB: grown at 1100ºC, p = 1 atm, with a 20 minute N_2 anneal at 1100ºC.

Dry Ox

Silicon dioxide grown in dry oxygen. RI = 1.46.
Grown in Tylan 2 using program SDRYOXB: grown at 1100ºC, p = 1 atm, with a 30 minute N_2 anneal at 1100ºC.

LTO Undop

Undoped, annealed low temperature oxide. RI = 1.46.
Deposited in Tylan 12 using recipe VDOLTOC: SiH_4 = 60 sccm, O_2 = 90 sccm, PH_3 = 0 sccm (no doping), 450ºC, p = 300 mT.
Annealed in N_2 in Tylan 2 using program N2 ANNEAL at 1000ºC for 60 minutes.

PSG Unanl

High-doped phosphosilicate glass with no anneal. RI = 1.47.
Deposited in Tylan 12 using recipe VDOLTOC: SiH_4 = 60 sccm, Od = 90 sccm, PH_3 = 10.3 sccm (high doping), T = 450ºC, p =300 mT.

PSG Hidop

High-doped, annealed phosphosilicate glass. RI = 1.48.
Deposited in Tylan 12 using recipe VDOLTOC: SiH_4 = 60 sccm, O_2 = 90 sccm, PH_3 = 10.3 sccm (high doping), T = 450ºC, p = 300 mT.
Annealed in N_2 in Tylan 2 using program N2ANNEAL at 1000ºC for 60 minutes.

Stoch Nitrid

Stochiometric silicon nitride (Si3N4). RI = 1.99.
Deposited in Tylan 9 using program SNITD: NH3 = 75 sccm, SiH_2Cl_2 = 25 sccm, p = 200 mT, T = 800ºC.

Low-σnitrid

Low-stress silicon nitride (silicon-rich Si_xN_y).RI = 2.18.
Deposited in Tylan 9 using program SNITD.V : NH_3 =16 sccm, SiH_2Cl_2 = 64 sccm, p = 300 mT, T = 835ºC.

Al/2% Si

Sputtered aluminum with 2% silicon in the target.
Deposited in the CPA at P = 4.5 kW, track speed = 20 cm/min, p = 6 mT.

Sput Tung

Sputtered tungsten.
Deposited in the CPA at P = 4.5 kW, track speed = 10 cm/min, p = 6 mT.
(Most of my tungsten peeled off my wafers due to residual stress. P = 2.9 - 3.1 kW should reduce this problem.)

Sput Ti

Sputtered titanium.
Deposited in the CPA at P = 4.5 kW, track speed = 10 cm/min, p = 6 mT.

Sput Ti/W

Sputtered 90% titanium/10% tungsten alloy.
Deposited at Stanford; conditions unknown.
Used as an adhesion layer for tungsten.

KTI 20 mn

OCG 825 (G-line) photoresist hardbaked 20 minutes at 120ºC. RI = 1.63.
Deposited using svgcoat program 2.

KTI 1 hr

OCG 825 (G-line) photoresist hardbaked 1 hour at 120ºC. RI = 1.65.
Deposited using svgcoat program 2.

KTI 1 dy

OCG 825 (G-line) photoresist hardbaked 1 day at 120ºC. RI = 1.67.
Deposited using svgcoat program 2.

OGG

OGG 700-10 (I-line) photoresist hardbaked 30 minutes. RI = 1.63.
Deposited using svgcoat program 1.

Etchants and Tips on their Use

All etches were done at room temperature (about 20ºC) unless otherwise indicated.
All wet etches were done with fresh solutions, agitating occasionally.
All plasma etches were done with recently cleaned chambers.

Conc. HF (49%)
10:1 HF
25:1 HF
5:1 BHF
Silicon Etchant – Polycrystalline Silicon (Bell Labs)
Phos. Acid 160ºC
KOH 80ºC
TMAH 90ºC
Al Etchant
Ti Etchant #2
H_2O_2 30%
Piranha 120ºC
Acetone
Tech-c O_2 50 W
Tech-c O_2 400 W
Tech-c SF_6+He 100 W
Tech-c Freons+He 200 W
LAM 1 300 W
LAM 2 850 W
LAM 2 450 W

LAM 3 Al Recipe
LAM 3 W Recipe
Tegal

Conc. HF (49%)

Concentrated hydrofluoric acid (49% by weight).
From bottle.
Etches oxides very rapidly. Often used to remove sacrificial PSG when micromachining.

10:1 HF

1 : 10 HF : H_2O (HF from bottle).
Typically used for stripping oxide and HF dips.

25:1 HF

1:25 HF: H_2O (HF from bottle).
Used for HF dips to strip native oxide without removing much of other oxides on the wafer.

5:1 BHF

5 : 1 buffered hydrofluoric acid (a.k.a. buffered oxide etch, BOE).
From bottle.
Pattern with photoresist.
Because this solution is buffered, its etch rate does not vary much with use. Best for controlled etching of oxides.

Silicon Etchant – Polycrystalline Silicon (Bell Labs)

This solution is mixed and bottled by NanoLab staff. Bottles are stored in the tall blue etchant cabinet in 582A.
Etch rate ~ 100 Å/sec
33% DI water / 3% NH_4F / 64% HNO_3
Bottle content:
960 ml DI water
75 ml NH_4F
1890 ml HNO_3

Phos. Acid 160ºC

Phosphoric acid (85% by weight) at 160ºC.
From bottle.
Heated at designated bath in msink7.
Used for wet etching of nitride. The nitride is typically patterned with densified low-doped PSG (densifying at 1000ºC for an hour will not affect low-stress nitride).
If the PSG mask is not densified, it will be removed faster and may also have microcracks through which the acid can seep.
The nitride can also be patterned with poly.
Etch rate varies significantly with temperature.
The rate (in A/min, T in ºC (!)) fits the equation 0.0872exp[0.0386T].

KOH 80ºC

Potassium hydroxide solution at 80ºC.
Mixed from 1000 g KOH pellets : 2 liters H_2O.
Heated at left side of msink4.
Solution is self heating. Let it sit a few hours before using.
Pattern with nitride.
Used for anisotropic etching of single-crystal silicon.
Attacks (100) and (110) planes much faster than (111) planes.
Etch rates listed here are down in the <100> direction.

TMAH 90ºC

3:2 25% TMAH : H_2O (25% TMAH from bottle)
90ºC
Etch rate ~ 50 micrometers/hour
Occasional addition of water to the bath during long etches is required.

Additional information about this etch is located in the msink4 manual and the pocket wafer process module.

Al Etchant

Aluminum Etchant - Transene Type A dispensed direct from bottle. Used at 50ºC
This solution is sold commercially by Transene Company, Inc.
Composition: 80% H3PO4, 5% HNO3, 5% CH3COOH, 10% DI
Etch rate at 50ºC = 6000 A / min
Etch rate decreases with use.

Ti Etchant #2

Second titanium etch solution listed in the lab manual.
Mixed from 20 : 1 : 1 H_2O : HF : H_2O_2.
Titanium wet etch. Due to HF content, it also etches oxides.
Pattern with photoresist.

H_2O_2 30%

Concentrated hydrogen peroxide (30% by weight).
From bottle.
Used to wet etch tungsten and its alloys, which can be patterned O_2 with photoresist.

Piranha 120ºC

Piranha solution at msink8.
This consists of about 3.5 gallons of H_2SO_4 held at 120ºC to which 250 ml of H_2O_2 is added immediately before use.
Used to clean wafers. Strips photoresist and metals, while not affecting silicon, oxides, and nitrides.

Acetone

Used to strip photoresist.
While acetone readily stripped all the photoresists listed in this table, its effectiveness depends on the processing the PR has gone through. Heating the PR by a few tens of degrees above 120ºC, either while hardbaking or during a process step, will make it significantly harder. Some plasma processing will have a similar effect (known as "plasma hardening"). In such cases, an oxygen plasma can be used to remove the PR.

Tech-c O_2 50 W

Technics-c plasma, O_2 = 51.1 sccm, 50 W.
One wafer.
Used for "descumming" freshly developed photoresist (typically for one minute).
Unbaked OCG 825 PR was removed at 330 A/min during a descum test.

Tech-c O_2 400 W

Technics-c plasma, O_2 = 51.1 sccm, 400 W.
One wafer.
This oxygen plasma is used to ash (strip) photoresist for 5 - 10 minutes. A power of 300 W for 7 min is also often used. It has been argued that the lower power is better because less plasma hardening occurs stripping. The Technics-c can hold up to four 4-inch wafers. A loading effect, in which the etch rate decreases when there is more to etch, is seen. In a 400 W PR stripping test, ashing four wafers at the same time was 23% slower than one alone.

Tech-c SF_6+He 100 W

Technics-c plasma, SF_6 = 12.9 sccm, He = 21.0 sccm, 100 W.
One wafer.
Used to plasma etch nitride. Unfortunately, it removes poly isotropically at about the same rate.
Pattern with photoresist.
This etch exhibits a severe loading effect. It is not only affected by the number of wafers in the chamber, but also by the fraction of surface area of nitride exposed. Furthermore, the etch rate varies with position in the chamber, so wafers should be rotated 3-4 times during an etch (some users also move their wafers among the four positions in a "planetary" motion).

Plasma etching, especially at higher power, heats the chamber, which may affect etch rates and thus selectivity. During all Technics-c tests, the plate temperature varied from 20 to 30ºC.

Tech-c Freons+He 200 W

Technics-c plasma, CF_4 (Freon 14) = 10.0 sccm, CHF_3 (Freon 23) = 5.0 sccm, He = 10.0 sccm, 200 W. One wafer.
Another nitride plasma etch. Same gases as LAM 2 uses.

LAM 1 300 W

LAM 1 plasma, standard recipe: CCl4 = 130 sccm, O_2 = 15 sccm, He = 130 sccm, gap = 1.5 cm, p = 280 mT, P = 300 W.
Poly plasma etch.
Pattern with photoresist. If total etch times longer than about 2 minutes are required, break the etch up into several shorter times, giving the PR a chance to cool and thus erode less.

LAM 2 850 W

LAM 2 plasma, standard recipe: CF_4 = 90 sccm, CHF_3 = 30 sccm, He = 120 sccm, gap = 0.38 cm, p = 2.8 T, P = 850 W.
Oxide plasma etch.
Also etches nitride well, but such use is allowed by special permission only.
Pattern with photoresist.
If total etch times longer than about 2 minutes are required, break the etch up into several shorter times, giving the PR a chance to cool and thus erode less.

LAM 2 450 W

LAM 2 plasma, standard recipe, but lower power: CF_4 = 90 sccm, CHF_3 = 30 sccm, He = 120 sccm, gap = 0.38 cm, p = 2.8 T, P = 450 W.
Some users have had better results using this lower power.

LAM 3 Al Recipe

LAM 3 plasma, standard recipe: BCl_3 = 50 sccm,
N_2 = 50 sccm, Cl_2 = 30 sccm, $CHCl_3$ = 20 sccm, p = 250 mT, P = 250 W.
All etches followed by airlock processing: CF_4 = 90 sccm, O_2 = 10 sccm, P = 400 W, for 1 minute.
Aluminum plasma etch. For thick layers of Al, either thicker photoresist or especially hardened PR must be used (use the hardening process known as "PRIST"). The airlock recipe, necessary to remove chorine from the wafers, is not supposed to do any etching.

LAM 3 W Recipe

LAM 3 plasma, tungsten recipe: SF6 = 20 sccm, p = 100 mT, P = 125 W. No airlock processing.
Tungsten plasma etch.
Attacks poly isotropically.
By special permission only.
This process may be replaced a tungsten etch in the Tegal etcher.

Tegal

Tegal plasma etcher is not ready for use at this date.
It will be used for etching both nitride and tungsten.