Etch Rates for Micromachining Processing

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Abstract— **The etch rates for 317 combinations of 16 materials (single-crystal silicon, doped, and undoped polysilicon, several types of silicon dioxide, stoichiometric and silicon-rich silicon nitride, aluminum, tungsten, titanium, Ti/W alloy, and two brands of positive photoresist) used in the fabrication of microelectromechanical systems and integrated circuits in 28 wet, plasma, and plasmaless-gas-phase etches (several HF solutions, H_3PO_4, $HNO_3 + H_2O + NH_4F$, KOH, Type A aluminum etchant, $H_2O + H_2O_2 + HF$, H_2O_2, piranha, acetone, HF vapor, XeF_2, and various combinations of SF_6, CF_4, CHF_3, Cl_2, O_2, N_2, and He in plasmas) were measured and are tabulated. Etch preparation, use, and chemical reactions (from the technical literature) are given. Sample preparation and MEMS applications are described for the materials. [193]**

I. INTRODUCTION

When designing a new process to fabricate micromachined devices, the etch rate of each layer that is to be patterned must be known. While the etch rates of many etchants that target specific materials (e.g., thermally grown silicon dioxide in 5:1 buffered hydrofluoric acid) are commonly known, the etch rates of the masking and underlying films are frequently not quoted in the literature. This paper provides this information for 317 different combinations of 16 materials and 28 etches used in the micromachining of microelectromechanical systems (MEMS) and in integrated-circuit processing. These etch-rate data, based on tests performed in the U. C. Berkeley Microfabrication Laboratory (Berkeley Microlab), are tabulated in Tables I and II.

The first sections of this paper describe the preparation and use of the wet and dry etches in Tables I and II, listing chemical reactions and variation of etch rate with such factors as temperature and concentration, based on literature on the subject. Recognizing that there are many sources of etch-rate variation, brief lists of these sources are given at the end of these wet- and dry-etch sections. The succeeding sections describe the sample preparation and MEMS applications for each of the materials, the measurement techniques used, and finally discuss the data in the tables.

II. THE WET ETCHES

A. Comparison of Wet and Dry Etches

The etches in the tables are divided into wet and plasma and plasmaless-gas-phase ("dry") etches. The advantages and disadvantages of wet and dry etching are well known [1], [2]; the most important for micromachining are as follows. Wet etching is usually isotropic (desirable in some cases), can have a selectivity that depends on crystallographic direction, and can be very selective over masking and underlying layers. Plasma etching uses fresh chemicals for each etch (resulting in less chemical-related etch-rate variability) and can be vertically anisotropic (as well as isotropic), allowing the patterning of narrow lines. When removing a sacrificial layer in micromachining, wet etching has the disadvantage of capillary-force pulldown of free-standing structures [3]. This can be avoided by using a supercritical-liquid drying process [4] or by switching to a dry-etched sacrificial layer [5], [6].

B. Wet-Etch Chemicals

All of the chemical mixtures made in the Berkeley Microlab and discussed in the next section are by volume, with one noted exception. Conversely, those prepared and bottled by chemical-supply companies are by weight.

Many of the chemicals used in wet etching are not supplied in pure form. Acetic acid is supplied pure and sulfuric acid nearly pure (96%), while other acids normally come in lower concentrations for various reasons. Phosphoric acid is a deliquescent solid at room temperature [7]. Above the 85% concentration at which it is supplied, it is very viscous and tends to oligomerize into polyphosphoric acids. Pure hydrofluoric acid has a boiling point of 19.5°C [7]. As supplied at 49% concentration, it has a greatly reduced vapor pressure, increasing personal safety and allowing room-temperature storage in unpressurized containers. Nitric acid is a liquid in the range near room temperature, but tends to decompose above the supplied concentration of 70%. Sulfuric [8] and acetic [9] acids are liquids that are completely miscible in water at room temperature at all concentrations to 100%. Hydrofluoric acid [10] is also a completely soluble liquid below its boiling point.

An extensive list of other wet etchants for a variety of semiconductors, metals, insulators, and other compounds has been compiled by Vossen and Kern [11].

C. Information about Individual Wet Etches

In this section, each etchant is listed by its name from Table I in italics, followed by its complete name, target material, notes on use, information on the reaction(s) that occur, if known from the technical literature, and major sources of etch-rate variation. For brevity, etchants with the same reactions (e.g., all HF solutions) are discussed together. The etchants are grouped by target material. Unless otherwise noted, all of the wet etchants are isotropic.

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TABLE I

Wet-Etch Rates for Micromachining and IC Processing (Å/min)

The top etch rate was measured by the authors with fresh solutions, etc. The center and bottom values are the low and high etch rates observed by the authors and others in our lab under less carefully controlled conditions.

ETCHANT EQUIPMENT CONDITIONS	TARGET MATERIAL	MATERIAL																
		SC Si <100>	Poly n^+	Poly undop	Wet Ox	Dry Ox	LTO undop	PSG unanl	PSG annld	Stoic Nitrid	Low-σ Nitrid	Al/ 2% Si	Sput Tung	Sput Ti	Sput Ti/W	OCG 820PR	Olin HntPR
Concentrated HF (49%) Wet Sink Room Temperature	Silicon oxides	-	0	-	23k 18k 23k	F	>14k	F	36k	140	52 30 52	42 0 42	<50	F	-	P 0	P 0
10:1 HF Wet Sink Room Temperature	Silicon oxides	-	7	0	230	230	340	15k	4700	11	3	2500 2500 12k	0	11k	<70	0	0
25:1 HF Wet Sink Room Temperature	Silicon oxides	-	0	0	97	95	150	W	1500	6	1	W	0	-	-	0	0
5:1 BHF Wet Sink Room Temperature	Silicon oxides	-	9	2	1000 900 1080	1000	1200	6800	4400 3500 4400	9	4 3 4	1400	<20 0.25 20	F	1000	0	0
Phosphoric Acid (85%) Heated Bath with Reflux 160°C	Silicon nitrides	-	7	-	0.7	0.8	<1	37	24 9 24	28 28 42	19 19 42	9800	-	-	-	550	390
Silicon Etchant (126 HNO_3 : 60 H_2O : 5 NH_4F) Wet Sink Room Temperature	Silicon	1500	3100 1200 6000	1000	87	W	110	4000	1700	2	3	4000	130	3000	-	0	0
KOH (1 KOH : 2 H_2O by weight) Heated Stirred Bath 80°C	<100> Silicon	14k	>10k	F	77 41 77	-	94	W	380	0	0	F	0	-	-	F	F
Aluminum Etchant Type A (16 H_3PO_4 : 1 HNO_3 : 1 HAc : 2 H_2O) Heated Bath 50°C	Alumnium	-	<10	<9	0	0	0	-	<10	0	2	6600 2600 6600	-	0	-	0	0
Titanium Etchant (20 H_2O : 1 H_2O_2 : 1 HF) Wet Sink Room Temperature	Titanium	-	12	-	120	W	W	W	2100	8	4	W	0 0 <10	8800	-	0	0
H_2O_2 (30%) Wet Sink Room Temperature	Tungsten	-	0	0	0	0	0	0	0	0	0	<20	190 190 1000	0	60 60 150	<2	0
Piranha (~50 H_2SO_4 : 1 H_2O_2) Heated Bath 120°C	Cleaning off metals and organics	-	0	0	0	0	0	-	0	0	0	1800	-	2400	-	F	F
Acetone Wet Sink Room Temperature	Photoresist	-	0	0	0	0	0	-	0	0	0	0	-	0	-	>44k	>39k

Notation: - =test not performed; W=not performed, but known to *W*ork (≥ 100 Å/min); F=not performed, but known to be *F*ast (≥ 10 kÅ/min); P=some of film *P*eeled during etch or when rinsed; A=film was visibly *A*ttacked and roughened.
Etch areas are all of a 4-inch wafer for the transparent films and half of the wafer for single-crystal silicon and the metals.
Etch rates will vary with temperature and prior use of solution, area of exposure of film, other materials present (e.g., photoresist), film impurities and microstructure, etc. *Some variation should be expected.*

All wet etching was done at room temperature (about 20°C in the temperature-controlled Berkeley Microlab), unless otherwise indicated. All wet etching was done with fresh solutions, agitating occasionally. To remove the vapors created by the etchants, all wet etching was done under fume hoods.

1) Silicon Dioxide Wet Etchants: Notes: All of the silicon dioxide etchants given here are based on hydrofluoric acid. HF-based etchants are used mainly for etching silicon dioxide, although they can also be used to remove silicon nitride. In our tests, they were observed to etch polysilicon very slowly, but other researchers have noted that various solutions attack polysilicon at the grain boundaries, resulting in noticeable surface roughness [12], [13]. Recent research indicates that HF can diffuse *through* thin (<0.2-μm) polysilicon to etch underlying low-temperature oxide (LTO) [13], [14].

HF-based solutions should be handled with polypropylene, high-density polyethylene (HDPE), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), or similar-material containers and tools (not glass containers, which will be attacked). In the Berkeley Microlab, molded PVDF has replaced welded polypropylene in most room-temperature chemical tanks in an effort to reduce particle counts and contamination from chemicals that have leaked into cracks in the welds. PTFE cassettes are used.

Reaction: Several similar reactions for the HF-based etching of silicon dioxide are given in the literature. For pure HF etching, the overall reaction is [2], [15]

$$\mathrm{SiO_2 + 6HF \rightarrow H_2SiF_{6(aq)} + 2H_2O}.$$

Kikuyama *et al.* [16] give the reaction in BHF solutions as

$$\mathrm{SiO_2 + 4HF + 2NH_4F \rightarrow (NH_4)_2SiF_6 + 2H_2O}$$

and the reaction involving the $\mathrm{HF_2^-}$ ion (discussed below) as

$$\mathrm{SiO_2 + 3HF_2^- + H^+ \rightarrow SiF_6^{2-} + 2H_2O}.$$

HF is a weak acid; except when present in very small concentrations, it does not completely dissociate into $\mathrm{H^+}$ and $\mathrm{F^-}$ ions in water [16]. Judge [17] and Deckert [18] have found the etch rate of both silicon dioxide and silicon nitride to increase linearly with the concentrations of both HF and $\mathrm{HF_2^-}$ for concentrations lower than 10 M, while being independent of the concentration of $\mathrm{F^-}$ ions alone. The $\mathrm{HF_2^-}$ complex attacks oxide about 4.5 times faster than HF. Higher-order complexes, such as $\mathrm{H_2F_3^-}$, appear to occur at higher HF concentrations (e.g., in 49% HF) and attack oxide even faster than $\mathrm{HF_2^-}$ [17]. Thus, the etch rate increases faster than linearly with HF concentration.

In buffered 15 M HF solutions, for pH values above about 1, the concentration of $\mathrm{HF_2^-}$ is greater than that of HF [17]. For more acidic solutions, there is sufficient hydrogen to combine with the fluoride to make HF the dominant species. As HF and $\mathrm{HF_2^-}$ are consumed, the etch rate decreases. Buffering with $\mathrm{NH_4F}$ helps keep the pH and thus the concentrations of HF and $\mathrm{HF_2^-}$ constant, stabilizing the etch rate [16].

The etch rate of silicon dioxide increases with temperature. Judge gives an apparent activation energy of 0.29 eV over the temperature range 30 to 60 °C for concentrated HF and higher activation energies as the ratio of $\mathrm{NH_4F}$ to HF increases [17]. By contrast, Parisi *et al.* found the apparent activation energy to be independent of buffer ratio at 0.43 eV over the range 25 to 55°C [19].

Tenny and Ghezzo found the etch rates of annealed phosphorus-doped LTO to increase monotonically with both $\mathrm{P_2O_5}$ content and concentration of HF in BHF solutions [20], the same result found by Monk for HF solutions [13]. Tenny and Ghezzo concluded that the $\mathrm{P_2O_5}$ in the glass etches more rapidly than the $\mathrm{SiO_2}$. They also found that for annealed borosilicate glasses, the etch rate in strong solutions of HF decreases for small concentrations of $\mathrm{B_2O_3}$, before rising for concentrations above 17 molar percent.

Monk [13] has done a thorough characterization on the transport of HF and $\mathrm{H_2SiF_6}$ during the undercutting of oxide sacrificial layers. He found that for deep micromachined undercuts, the etch rate is controlled by diffusion (i.e., slower for longer undercutting) and is not affected by agitation of the bath.

Concentrated HF (49%): Concentrated hydrofluoric acid (49% by weight, remainder water). Produced commercially.

Notes: Etches oxides very rapidly. Often used to remove sacrificial oxide when micromachining. Concentrated HF tends to peel off photoresist, while lower concentrations (less than 3:1) do not [21].

10:1 HF: 10:1 $\mathrm{HF{:}H_2O}$: concentrated HF (49% HF).

Notes: Typically used for stripping oxide and for HF dips, diluted HF is cheaper than buffered HF.

25:1 HF: 25:1 $\mathrm{HF{:}H_2O}$: concentrated HF (49% HF).

Notes: This slow etch is used for HF dips to strip native oxide without removing much of the other oxides that may be on a wafer.

5:1 BHF: 5:1 buffered hydrofluoric acid (also known as buffered oxide etch, or BOE). "5:1" refers to five parts by weight of 40-weight-percent ammonium fluoride (the buffer) to one part by weight 49-weight-percent hydrofluoric acid, which results in a total of about 33% $\mathrm{NH_4F}$ and 8.3% HF by weight [22]. Produced commercially, the pH is about 3.

Notes: This etchant can be masked with photoresist (the adhesion is much better than in concentrated HF). Because it is buffered, its etch rate does not vary as much with use. It is the often best choice for controlled etching of oxides. Some researchers have, however, observed a slight attack of 5:1 BHF on polysilicon, causing surface roughening [12].

2) Silicon Nitride Wet Etchant:

Phosphoric acid (85%): Phosphoric acid (85% by weight, remainder water) at 160°C. Produced commercially. In the Berkeley Microlab, this etchant is heated in a PFA tank with a Pyrex reflux system to return condensed water vapor to the solution.

Notes: Phosphoric acid is used for the wet etching of silicon nitride. Our nitride is typically masked with densified PSG (densifying at 1000°C for an hour does not affect low-stress nitride). If the PSG mask is not densified it is removed faster and may also have pores through which the acid can seep. The nitride can also be patterned with polysilicon.

At 160 °C, the vapor pressure over 85% phosphoric acid is slightly more than one atmosphere, with the vapor being virtually pure water [23].

Reaction: The literature does not list a chemical reaction for the etching of silicon nitride. Gelder and Hauser propose that the water in the solution hydrolizes the nitride to some form of hydrous silica and ammonia [23].

Gelder and Hauser [23] report the "real" activation energy for the etching of silicon nitride in a constant concentration of 94.5% phosphoric acid as 0.99 eV. The "apparent" activation energies, taken with the etch temperature and boiling point being the same (i.e., for varying concentrations of H_3PO_4) are 0.55 eV for silicon nitride, 1.20 eV for silicon dioxide, and 1.15 eV for silicon. These apparent activation energies take into account the effects of temperature on both concentration of H_3PO_4 in the solution and the etch reactions themselves.

As the water content in the etch bath decreases (e.g., due to evaporation), the etch rate of silicon nitride decreases, while the etch rate of silicon dioxide increases [23], so the use of a reflux system is important in maintaining a constant etch rate and mask selectivity.

3) Isotropic Silicon Wet Etchant:

Silicon etchant: Wet silicon etchant. This solution is mixed and bottled in the Berkeley Microlab from 126:60:5 HNO_3 (70%) : H_2O : NH_4F (40%).

Notes: This etch, similar to the $HNO_3 + H_2O + HF$ etches discussed in a series of papers by Robbins and Schwartz [2], [24], is used mainly for polysilicon wet etching. The slight change in chemistry was used earlier at Trilogy [25]. It can be masked by photoresist.

Reaction: A simplified description of the reaction is that the nitric acid in the solution oxidizes the silicon, then the hydrofluoric acid (formed from the fluoride ions in this acidic solution) etches the oxidized compound. Many metal etches not discussed in this paper also remove material in this two-step manner. The overall reaction is [2], [26]

$$18HF + 4HNO_3 + 3Si \rightarrow 3H_2SiF_{6(aq)} + 4NO_{(g)} + 8H_2O.$$

Turner has found the peak etch rate of silicon to occur at an HF:HNO_3 ratio of 4.5, the same ratio as in the balanced reaction given above [26]. The rate-limiting step for the etch solution in this table, which has a low HF concentration, is the supply of HF to the reaction site [26]. The etch rate of a given bath decreases with use as the HF is depleted. The use of NH_4F rather than HF results in a buffer action, keeping the HF and HF_2^- (both responsible for etching the oxidized silicon) concentrations from changing as rapidly with use [25]. Used solutions turn yellow due to dissolved NO gas.

4) Orientation-Dependent Silicon Wet Etchants:

KOH 80 °C: Potassium hydroxide solution at 80 °C. Mixed from 1 kg KOH pellets : 2 liters H_2O. This solution is about 29% KOH by weight because the KOH pellets normally contain 10 to 15% water [27]. It is heated in a perfluoroalkoxy polytetrafluoroethylene (PFA) tank with recirculating pump.

Notes: This solution is self heating. It should be allowed to equilibrate before using for a controlled temperature. When etching single-crystal silicon, the silicon can be masked with silicon nitride. To reduce undercutting of the nitride mask, a HF dip should be carried out immediately before the nitride deposition to remove any native oxide.

We have found that the KOH in unagitated solutions tends to stratify, resulting in etch-rate variation from the top to the bottom of the solution. This problem was solved by the use of a recirculation pump.

KOH is used for orientation-dependent etching (ODE) of single-crystal silicon. ODE's attack {111}-type planes, which have a high bond density, much more slowly than other planes [2], [28]. (Unfortunately, this high-bond-density reasoning for slow-etch-rate planes cannot be extended to explain the etch-rate ratio between {100} and {110} planes [28].) The etch rate listed in Table I is the one perpendicular to the surface of the (100) wafers used for this etch-rate test. KOH stops etching on very heavily doped p-type material [29].

Isopropyl alcohol is sometimes added to KOH solutions. This decreases the etch rate, but improves uniformity, reducing the requirement for stirring [30]. It also slows {110}-plane and accelerates {111}-plane etching (not affecting {100} planes much) and lessens the severity of the etching of convex corners [28].

(Other inorganic hydroxides [29], [30], organic hydroxides such as tetramethyl ammonium hydroxide (TMAH) [31], [33], and ethylenediamine pyrocatechol (EDP) [29], [30], an organic base, are orientation-dependent etchants similar to KOH. In the Berkeley Microlab and others, EDP has been found to be better than KOH at stopping abruptly at heavily boron-doped regions [29], [32]. TMAH has the advantages of not being a source of sodium (which contaminates the gate oxide in MOS circuitry) and not attacking aluminum when it has been "doped" with a small amount of silicon [33].)

Reaction: Several different reactions for KOH etching of silicon are listed in the literature [2], [30]. Seidel *et al.* list the gross reaction as [30]

$$Si + 2\ OH^- + 2\ H_2O \rightarrow SiO_2(OH)_2^{2-} + 2H_{2(g)}.$$

Glembocki *et al.* list a very similar reaction [34]. This chemical reaction is independent of the source of the hydroxide ion, whether LiOH, NaOH, or KOH, in agreement with experiment.

The dependence of the reaction on p-type doping is explained by Seidel *et al.* [30] and also by Raley *et al.* [32]: At intermediate steps in the etch, four free electrons are generated that reside near the surface before being exchanged. P-type doping reduces this surface supply of electrons. The etch rate decreases as the fourth power of the concentration for p-type doping beyond degeneracy, which occurs at about 2×10^{19} cm^{-3} active boron atoms.

Seidel found the etch-rate ratio for {110} to {100} to {111} planes to be about 160:100:1 at 20 °C, decreasing to 50:30:1 at 100 °C [30]. In contrast, Kendall measured even higher ratios of 400:200:1 at 85 °C and discussed the extreme difficulty in making these measurements [28].

The etch rate in KOH increases with temperature. Seidel *et al.* give activation energies for the concentration of KOH in Table I (29% by weight) of 0.59 eV for (100) silicon and 0.84 eV for silicon dioxide [30]. They also found that, at 80 °C, the etch rates of (100) silicon and silicon dioxide peak at concentrations of about 18 and 34 weight %, respectively. Lower concentrations of either H_2O or OH^-, both used in the reaction, result in lower etch rates. The surfaces, however, appear rough and insoluble white residues form for KOH concentrations below 20% [35]. The temperature and KOH concentration effects on the etch rate (ER) of (100) silicon were empirically found to fit well to the equation [30]

$$ER_{\mathrm{Si\ in\ KOH}} = k_0[\mathrm{H_2O}]^4[\mathrm{KOH}]^{1.4}e^{-E_A/kT}$$

where the etch rate is in μm/h, the concentrations are in mol/liter, $k_0 = 2480\ \mu\mathrm{m/hr}\cdot(\mathrm{mol/liter})^{-4.25}$, and $E_A = 0.595$ eV.

5) Metal Wet Etchants:

Aluminum Etchant Type A: Aluminum etchant Type A at 50 °C. This solution, sold commercially, is composed of 80% phosphoric acid, 5% nitric acid, 5% acetic acid, and 10% water [36]. Some formulations may include a surfactant. According to the manufacturer, this etchant is designed to etch aluminum at 6000 Å/min at 50 °C. It is heated in a PFA tank.

Notes: This etch is used for wet etching of aluminum. It can be masked with photoresist.

Reaction: In this multistep etch [37], the aluminum is first oxidized by the nitric acid. The phosphoric acid and water simultaneously etch the resulting oxide. With the concentrations given, these two processes occur at roughly the same rate, so that either could be the rate-limiting step [37]. Because the phosphoric acid also removes the native aluminum oxide, no additional component is needed for this purpose.

The etch rate increases with temperature and decreases significantly with use due to depletion of the active chemicals.

Similar solutions with a reduced fraction of water etch more rapidly [37]. Agitating aids etch-rate uniformity across a wafer, as well as helping to remove the hydrogen bubbles that evolve. If not removed, these bubbles can block the flow of reactant to the surface, resulting in localized etch nonuniformity.

Titanium Etchant: Mixed from 20:1:1 H_2O : HF (49%) : H_2O_2 (30%).

Notes: HF is the active ingredient is this etchant, so it also etches oxides. Raising the fraction of HF in the solution increases the etch rate. Titanium etched in this solution can be masked with photoresist.

Reaction: No reaction is given in the literature. Titanium is known to be readily oxidized, so it likely forms an oxide from the water and peroxide, which is readily etched by the HF in this solution.

H_2O_2 (30%): Hydrogen peroxide (30% by weight). Produced commercially.

Notes: This etchant is used to wet-etch tungsten and its alloys, which can be masked with photoresist. We have observed that H_2O_2-etching of tungsten sometimes leaves a residue.

Reaction: In this etch, a film of tungsten oxide is formed that is dissolved in the hydrogen peroxide [38]. This etchant also etches tungsten/titanium alloys, but not pure titanium.

The etch rate rises with temperature, but any significant increase may cause a photoresist mask to be eroded or to peel. CVD silicon-based masking layers, successful for other films, cannot be used with tungsten, as the silicon reacts to form tungsten silicides during the high-temperature deposition. Sputtered aluminum is a suitable mask layer, although when used, it becomes difficult to observe the end of the aluminum etch either optically or electrically.

(Another tungsten etch, which has been found in our lab not to leave the residue mentioned above, contains 1 liter H_2O, 34 g $K_3Fe(CN)_6$, 13.4 g KOH, and 33 g KH_2PO_4. It can be patterned with photoresist, does not attack oxide or nitride at an appreciable rate, and etches tungsten at 340 Å/min).

6) Wet Wafer Cleaning:

Piranha 120 °C: Piranha in 120 °C heated bath. In the Berkeley Microlab, piranha consists of about 5.6 liters of 96% H_2SO_4 heated to 120 °C in a PFA tank, to which 100 ml of 30% H_2O_2 is added immediately before each use.

Notes: Piranha has been in use for wafer cleaning for decades [1], [39], [40]. The term refers to a hot solution of H_2SO_4 and H_2O_2 mixed in any ratio [39], [40]. In lower ratios of H_2SO_4 to H_2O_2 (e.g., 5:1), the solution is noticeably self-heating (no external heat source is needed).

Piranha is used in the Berkeley Microlab for 10 min to clean organic and metallic contaminants from wafers before furnace steps. Kern and Puotinen [41] have observed that the desorption of 90% of monatomic metal films from silicon into similar acidic peroxide solutions can take several minutes.

Reaction: Like other acidic hydrogen peroxide solutions, piranha strips photoresist and other organics by oxidizing them, and removes metals by forming complexes that stay in the solution [41], [42]. It does not affect silicon dioxide and silicon nitride and has the minor effect on bare silicon of forming a thin layer of hydrous silicon oxide [41]. This oxide film is typically removed with a short (10-s) 10:1 or 25:1 HF dip after the piranha clean and rinse.

Acetone: Acetone spray from a photoresist developing machine.

Notes: Acetone is used to strip photoresist (PR) and for lift-off patterning of films [1], [2]. The machine used in the Berkeley Microlab gives a stream of fresh acetone for PR stripping.

An acetone bath would be used for liftoff processes [1], [2]. Lift-off processes can be sped up by heating the acetone (with a loose lid to slow evaporative loss) or by placing it in an ultrasonic tank.

While acetone readily stripped 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 120 °C, either while hardbaking or during a process step, will make it significantly harder to dissolve [1]. Some plasma processing gives rise to a similar effect (known as "plasma hardening"). In such cases, an oxygen plasma, a commercial PR stripper (such as Baker PRS-2000), or piranha can usually be used to remove the PR.

Reaction: Acetone breaks down the structure of the photoresist, making it soluble [1].

D. Wet-Etch-Rate Variation

The wet-etch rates given in Table I can vary for reasons that are usefully divided into three groups: the etch setup, the material being etched, and the layout and structure on the substrate. The most significant effects on the wet-etch rate in each of these categories are as follows (due to space constraints, the reader is referred to the references for detailed information on these sources of etch-rate variation).

Etch-rate variation due to the etch setup is a function of 1) temperature [43]; 2) loss of reactive species [43]; 3) loss of liquids to evaporation [30], [44]; 4) mixing; 5) stratification of the solution; 6) etch-product blocking of chemical flow [2]; 7) elapsed time from the start of the etch; 8) applied potential [2], [4], [5]; 9) illumination [45]; and 10) contamination. Etch-rate variation due to the material being etched is affected by 11) impurities in or on the material being etched [20], [46]; 12) microstructure [15], [47], [48]; and 13) film stress [49], [50]. Etch-rate variation due the layout and structure on the substrate is affected by 14) the distribution and fraction of surface area of the exposed target layer (loading) [2], [15], and 15) the structure geometry [13].

III. THE PLASMA AND PLASMALESS-GAS-PHASE ETCHES

A. Purposes of the Etch Gases

Because many gases are used in more than one of the etches in Table II, each gas (in italics) and its purpose are presented here.

1) Oxygen (O_2): dissociates into O radicals, which are more reactive. Oxygen has several purposes. Pure O_2 plasmas are used to etch photoresist. In plasmas involving CF_4, O atoms displace F in the CF_4 molecule, generating more free F [51]. This can both increase the etch rate and cause enough F to be present to allow the formation of C-F sidewall polymer films.

2) Sulfur Hexafluoride (SF_6): SF_6 is one source of very reactive F atoms that etch all of the materials in Table II except for aluminum. Fluorine atoms are not very selective, etching most of these materials at rates varying by less than a factor of 5. Molecular fluorine (F_2) is not used for silicon etching because it is hazardous, and, for reasons not understood, it leaves rough surfaces [11], [52].

3) Tetrafluoromethane (CF_4, carbon tetrafluoride, Freon 14): CF_4 is a source of F and also a source of C, both of which are required for C-F sidewall-polymer formation.

4) Trifluoromethane (CHF_3, Freon 23): CHF_3 is another source of F and C, but with a lower ratio of F to C.

5) Chlorine (Cl_2): Cl_2 dissociates into Cl atoms, which are quite reactive. Like F, Cl etches most materials, including aluminum.

6) Trichloromethane ($CHCl_3$, chloroform): $CHCl_3$ supplies chlorine for etching and carbon and chlorine for sidewall polymer formation [52].

7) Boron Trichloride (BCl_3): BCl_3 etches the native aluminum oxide film on aluminum. It also scavenges O_2 and H_2O in the vacuum system, preventing oxide growth [53].

8) Helium (He): He can be used in plasma etching as a diluent and a plasma stabilizer [51]. Diluents give the user another process control variable. For example, an inert gas can be added to increase the total pressure while keeping the partial pressures of the other gases constant. In addition, some gas species can improve energy transfer from the "hot" electrons to reactive gas molecules (e.g., He enhances the dissociation of BCl_3 [51]).

9) Nitrogen (N_2): N_2 is also used as a diluent.

10) Hydrogen fluoride vapor (HF): HF vapor evaporates rapidly from concentrated HF solutions. Like its liquid counterpart, it can be used for etching silicon oxides.

11) Xenon Difluoride (XeF_2): XeF_2 is supplied as granular crystals. At room temperature, it has an equilibrium vapor pressure of about 4.5 Torr [54]. XeF_2 supplies fluorine atoms in the plasmaless-gas-phase etching of silicon and some other materials.

12) Other Gases: Many other gases in various combinations have been used for plasma etching, as discussed in several of the references [1], [2], [51]–[53].

B. Information About Individual Plasma and Plasmaless Gas-Phase Etches

All of the plasma etches in Table II were done with recently cleaned chambers. The plasma etches are fairly anisotropic unless otherwise noted. The anisotropic plasma etches presented in this section have recipes that are based on the manufacturers' general recommendations for each machine, adapted to yield a useful compromise among a reasonably fast etch rate for the target material, fairly straight sidewalls, and selectivity over a photoresist mask layer.

In this section, the etches are grouped by reactive plasma species and target material. The reactions listed are summaries; the occurrence of a complicated series of subreactions, adsorptions, and possibly energetic ion involvement should be considered typical. Details of some of the reactions are given in the references.

Each etch is listed by its name from Table II in italics, which includes the gases, their flow rates, equipment brand and model number, power, pressure, electrode gap, and operating frequency.

The plasmaless-gas-phase etchants, HF vapor and XeF_2, are listed with the plasma etches because they are more similar to chemical–plasma etching than to wet etching: reactant and product flow occurs in the gas phase and there is a fresh flow of reactants to the etch surface.

1) Fluorocarbon-Plasma Silicon-Dioxide Etches: Reaction: It appears that CF_x ($x \leq 3$) radicals chemisorb on the SiO_2 and dissociate. The radicals supply carbon to form CO, CO_2, and COF_2 gases from the oxygen in the film. They also supply fluorine to form SiF_4 gas [55]. Overall reactions such as the following occur [2]:

$$3SiO_2 + 4CF_3 \rightarrow 2CO + 2CO_2 + 3SiF_4$$
$$SiO_2 + 2CHF_2 \rightarrow 2CO + H_2 + SiF_4.$$

CF_4+ CHF_3+ He (90:30:130 sccm), Lam 590, 450 W, 2.8 T, gap = 0.38 cm, 13.56 MHz: Parallel-plate configuration, graphite electrode (others are aluminum), driven electrode area $\approx$ 350 cm^2.

Notes: This etch targets silicon dioxide, but also etches silicon nitride well. It can be patterned with photoresist (PR). This etch is anisotropic (fairly vertical sidewalls).

If total etch times longer than about 2 min are required, the etch is often broken up into several shorter times, giving the photoresist a chance to cool and thus erode less.

TABLE II

Plasma- and Plasmaless-Gas-Phase-Etch Rates for Micromachining and IC Processing (Å/min)

The top etch rate was measured by the authors and others in our lab with clean chambers, etc. The center and bottom values are the low and high etch rates observed by the authors and others under less carefully controlled conditions.

ETCHANT EQUIPMENT CONDITIONS	TARGET MATERIAL	MATERIAL															
		SC Si <100>	Poly n+	Poly undop	Wet Ox	Dry Ox	LTO undop	PSG unanl	PSG annld	Stoic Nitrid	Low-σ Nitrid	Al/ 2% Si	Sput Tung	Sput Ti	Sput Ti/W	OCG 820PR	Olin HntPR
CF$_4$+CHF$_3$+He (90:30:120 sccm)	Silicon	W	1900	2100	4700	W	4500	7300	6200	1800	1900	-	W	W	W	2200	2000
Lam 590 Plasma	oxides		1400	1500	2400			3000	2500								
450W, 2.8T, gap=0.38cm, 13.56MHz			1900	2100	4800			7300	7200								
CF$_4$+CHF$_3$+He (90:30:120 sccm)	Silicon	W	2200	1700	6000	W	6400	7400	6700	4200	3800	-	W	W	W	2600	2900
Lam 590 Plasma	oxides		2200	1700	2500		6000	5500	5000	4000						2600	2900
850W, 2.8T, gap=0.38cm, 13.56MHz			2700	2100	7600		6400	7400	6700	6800						6700	7200
SF$_6$+He (13:21 sccm)	Silicon	300	730	670	310	350	370	610	480	820	620	-	W	W	W	690	630
Technics PE II-A Plasma	nitrides	300	730	670					230		550					690	
100W, 250mT, gap=2.6cm, 50kHz sq. wave		1000	800	760					480		800					830	
CF$_4$+CHF$_3$+He (10:5:10 sccm)	Silicon	1100	1900	W	730	710	730	W	900	1300	1100	-	W	W	W	690	600
Technics PE II-A Plasma	nitrides																
200W, 250mT, gap=2.6cm, 50kHz sq. wave																	
SF$_6$+He (175:50 sccm)	Thin	W	6400	7000	300	W	280	530	540	1300	870	-	W	W	W	1500	1400
Lam 480 Plasma	silicon			2000	220					830						1300	
150W, 375mT, gap=1.35cm, 13.56MHz	nitrides			7000	400					2300						1500	
SF$_6$+He (175:50 sccm)	Thick	W	8400	9200	800	W	770	1500	1200	2800	2100	-	W	W	W	3400	3100
Lam 480 Plasma	silicon									2100						3100	
250W, 375mT, gap=1.35cm, 13.56MHz	nitrides									4200						3400	
SF$_6$ (25 sccm)	Thin	W	1700	2800	1100	W	1100	1400	1400	2800	2300	-	W	W	W	3400	3100
Tegal Inline Plasma 701	silicon				1100					2800						2900	
125W, 200mT, 40°C	nitrides				1600					2800						3400	
CF$_4$+CHF$_3$+He (45:15:60 sccm)	Si-rich	W	350	360	320	W	320	530	450	760	600	-	W	W	W	400	360
Tegal Inline Plasma 701	silicon																
100W, 300mT, 13.56MHz	nitrides																
Cl$_2$+He (180:400 sccm)	Silicon	W	5700	3200	8	-	60	230	140	560	530	W	W	-	-	3000	2700
Lam Rainbow 4420 Plasma		5000	3400	3200	8											2400	
275W, 425mT, 40°C, gap=0.80cm, 13.56MHz		5000	6300	3700	380											3000	
HBr+Cl$_2$ (70:70 sccm)	Silicon	W	450	460	4	-	0	0	0	870	26	W	W	-	-	350	300
Lam Rainbow 4420 Plasma			450		4											350	
200W, 300mT, 40°C, gap=0.80cm, 13.56MHz			740		10											500	
Cl$_2$+BCl$_3$+CHCl$_3$+N$_2$ (30:50:20:50 sccm)	Aluminum	W	4500	W	680	670	750	W	740	930	860	6000	W	-	-	6300	6300
Lam 690 RIE												1900				3700	3300
250W, 250mT, 60°C, 13.56MHz												6400				6300	6100
SF$_6$ (80 sccm)	Tungsten	W	5800	5400	1200	W	1200	1800	1500	2600	2300	-	2800	W	W	2400	2400
Tegal Inline Plasma 701					2000						1900		2800			2400	
200W, 150mT, 40°C, 13.56MHz					2000						2300		4000			4000	
O$_2$ (51 sccm)	Descumming	-	0	0	0	0	0	0	0	0	0	0	0	0	-	350	300
Technics PE II-A Plasma	photoresist																
50W, 300mT, gap=2.6cm, 50kHz sq. wave																	
O$_2$ (51 sccm)	Ashing	-	0	0	0	0	0	0	0	0	0	0	0	0	-	3400	3600
Technics PE II-A Plasma	Photoresist																
400W, 300mT, gap=2.6cm, 50kHz sq. wave																	
HF Vapor	Silicon	-	0	0	660	W	780	2100	1500	10	19	A	0	A	-	P 0	P 0
1 cm over plastic dish	oxides																
Room temperature and pressure																	
XeF$_2$	Silicon	4600	1900	1800	0	-	0	0	0	120	2	0	800	290	-	0	0
Simple custom vacuum chamber		2900	1100	1100						120	0		440	50			
Room temperature, 2.6 Torr		100k	2500	2300						180	2		1000	380			

Notation: - =test not performed; W=not performed, but known to *Work* (≥ 100 Å/min); F=not performed, but known to be *Fast* (≥ 10 kÅ/min); P=some of film *Peeled* during etch or when rinsed; A=film was visibly *Attacked* and roughened.

Etch areas are all of a 4-inch wafer for the transparent films and half of the wafer for single-crystal silicon and the metals.

Etch rates will vary with temperature and prior use plasma chamber, area of exposure of film, other materials present (e.g., photoresist), film impurities and microstructure, etc. *Some variation should be expected.*

CF_4+ CHF_3+ He (90:30:130 sccm), Lam 590, 850 W, 2.8 T, gap = 0.38 cm, 13.56 MHz: Parallel-plate configuration, graphite electrode (others are aluminum), driven electrode area $\approx$ 350 cm^2.

Notes: This is a faster oxide etch than the lower-power etch above, but with lower selectivity to photoresist.

2) Fluorine-Atom-Plasma Silicon-Nitride Etches: Reaction: Fluorine atoms are adsorbed onto the surface one at a time. In a surface reaction, volatile products are formed. The overall reaction is [2]

$$\mathrm{Si_3N_4 + 12F \rightarrow 3SiF_4 + 2N_2}.$$

The apparent activation energy for F-atom etching of Si_3N_4 is about 0.17 eV [53].

SF_6+ He (13:21 sccm), Technics PE II-A, 100 W, 250 mT, 50 kHz sq. wave: Parallel-plate configuration, fixed gap $\approx$ 2.6 cm, driven electrode area $\approx$ 600 cm^2. The chamber holds four wafers; the test was performed with one wafer.

Notes: This etch is used to plasma-etch silicon nitride. It can be masked 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 nitride surface area that is exposed. Furthermore, the etch rate varies with position in the chamber, so wafers should be rotated three or four times during an etch for uniformity.

Plasma etching, especially at higher power, heats the chamber, which can affect etch rates and thus selectivity. During all Technics PE II-A tests, the plate temperature varied from 20 to 30°C.

CF_4+ CHF_3+ He (10:5:10 sccm), Technics PE II-A, 200 W, 250 mT, 50 kHz sq. wave: Parallel-plate configuration, fixed gap $\approx$ 2.6 cm, driven electrode area $\approx$ 600 cm^2. The chamber holds four wafers; the test was performed with one wafer.

Notes: This silicon nitride plasma etch uses fluorocarbons rather than SF_6 as the source of F atoms.

SF_6+ He (175:50 sccm), Lam 480, 150 W, 375 mT, gap = 1.35 cm, 13.56 MHz: Parallel-plate configuration, driven electrode area $\approx$ 350 cm^2.

This silicon nitride plasma etch is in a single-wafer system. The slower etch rate than the etch listed below is intended for thin nitride films. It can be patterned with photoresist. The etch is anisotropic (fairly vertical sidewalls).

SF_6+ He (175:50 sccm), Lam 480, 250 W, 375 mT, gap = 1.35 cm, 13.56 MHz: Parallel-plate configuration, driven electrode area $\approx$ 350 cm^2.

Notes: This silicon nitride plasma etch is faster and therefore useful for thicker nitride films. It can be patterned with photoresist.

If total etch times longer than about 2 min are required, the etch is often broken up into several shorter times, giving the PR a chance to cool and thus erode less.

SF_6 (25 sccm), Tegal Inline Plasma 701, 125 W, 200 mT, 13.56 MHz: Parallel-plate configuration, fixed gap $\approx$ 3.8 cm, driven electrode area $\approx$ 250 cm^2.

Notes: This slower etch is intended for thinner, stoichiometric silicon nitride films.

CF_4+ CHF_3+ He (45:15:60 sccm), Tegal Inline Plasma 701, 100 W, 300 mT, 13.56 MHz: Parallel-plate configuration, fixed gap $\approx$ 3.8 cm, driven electrode area $\approx$ 250 cm^2.

Notes: This etch has a different gas chemistry than the previous etch, aimed at thicker, silicon-rich nitride films.

3) Plasma Silicon Etches:

Cl_2+ He (180:400 sccm), Lam Rainbow 4420, 275 W, 425 mT, 40 °C, gap = 0.80 cm, 13.56 MHz: Parallel-plate configuration, driven electrode area $\approx$ 390 cm^2.

Notes: This is an anisotropic silicon plasma etch. An SF_6 step prior to this one is typically used to break through the native oxide.

This etch has been used to micromachine 80-μm-deep trenches with fairly vertical sidewalls [56].

Reaction: Chlorine atoms are chemisorbed one at a time on the silicon surface, eventually forming volatile $SiCl_4$ [53]. The overall reaction is

$$\mathrm{4Cl + Si \rightarrow SiCl_4}.$$

Chlorine etching of undoped silicon occurs very slowly in the absence of ion bombardment [53]. Unlike F-atom silicon etches, Cl- and Br-based etches tend to be vertical [51].

As the Fermi level rises, the energy barrier for charge transfer of chemisorbed Cl, a step in the etch process, falls [53]. Thus, p-type doping slows etching while n-type doping accelerates it.

Chlorine-based plasma etch rates of single-crystal silicon can also depend on crystallographic orientation. Kinoshita and Jinno found that, with CCl_4 + He plasmas, the $\{100\}$ and $\{110\}$ planes could be etched faster than the $\{111\}$ planes [57]. The selectivity was not, however, as great as with KOH- or EDP-based etches.

HBr + Cl_2 (70:70 sccm), Lam Rainbow 4420, 200 W, 300 mT, 40 °C, gap = 0.80 cm, 13.56 MHz: Parallel-plate configuration, driven electrode area $\approx$ 390 cm^2.

Notes: This is another anisotropic silicon plasma etch, with better selectivity of silicon over oxide.

Reaction: Bromine atoms probably react with silicon in a manner similar to chlorine as described above.

4) Plasma Metal Etches:

Cl_2+ BCl_3+ $CHCl_3$+ N_2 (30:50:20:50 sccm), Lam 690, 250 W, 250 mT, 60 °C, 13.56 MHz: Parallel-plate grounded-chuck configuration, fixed gap $\approx$ 2.5 cm, driven electrode area $\approx$ 350 cm^2.

Notes: This is an anisotropic aluminum plasma etch due to the sidewall inhibitor formed from the $CHCl_3$ [52].

Due to poor selectivity, for thick layers of Al, thicker photoresist, plasma-hardened PR, or a more-durable masking layer must be used. The higher temperature is used to keep the etch product volatile so that it leaves the wafer [2] and does not coat the chamber or exhaust plumbing.

Reaction: The dominant overall reaction below 200 °C [52] is

$$\mathrm{2Al + 3Cl_2 \rightarrow Al_2Cl_6}.$$

Cl_2 rather than Cl appears to be the main etchant [52]. The etch product becomes $AlCl_3$ at higher temperatures [11], [52].

All aluminum etches in the Berkeley Microlab are followed by airlock plasma processing: $CF_4 = 90$ sccm, $O_2 = 10$ sccm, $P = 400$ W, for 1 min. The airlock recipe is not intended to do any etching. It replaces the chlorine in the residual Al_2Cl_6 with fluorine. If this step were not performed, the chlorine would form hydrochloric acid upon exposure to atmospheric moisture, causing later corrosion of the aluminum.

SF_6 (80 sccm), Tegal Inline Plasma 701, 200 W, 150 mT, 40 °C, 13.56 MHz: Parallel-plate configuration, fixed gap ≈ 3.8 cm, driven electrode area ≈ 250 cm^2. Grounded chuck.

Notes: This tungsten plasma etch is fairly isotropic. CF_4 added to the feed gas increases anisotropy as sidewall polymers form, but slows the etch rate.

The chuck is heated to enhance the etch rate.

Reaction: The overall reaction is

$$W + 6F \rightarrow WF_6.$$

5) Oxygen-Plasma Photoresist Etches: Reaction: Oxygen atoms "burn" or "ash" (a misnomer) the organic photoresist, forming mostly H_2O, CO_2, and CO [53]. Activation energies for O-atom etching of photoresist have been measured in the range of 0.22 to 0.65 eV [53]. Below 60 °C, PMMA has an activation energy of about 0.2 eV [52].

O_2 (51 sccm), Technics PE II-A, 50 W, 300 mT, 50 kHz sq. wave: Parallel-plate configuration, gap ≈ 2.6 cm, driven electrode area ≈ 600 cm^2. The chamber holds four wafers; the test was performed with one wafer.

Notes: This plasma-processing step is used for "descumming" (removing undesired thin layers) of freshly developed photoresist, typically for one minute. Unbaked OCG 820 PR was removed 6% faster than hardbaked PR during a descum test.

O_2 (51 sccm), Technics PE II-A, 400 W, 300 mT, 50 kHz sq. wave: Parallel-plate configuration, fixed gap ≈ 2.6 cm, driven electrode area ≈ 600 cm^2. The chamber holds four wafers; the test was performed with one wafer.

Notes: This oxygen plasma is used to ash (strip) photoresist for 5–10 min. A power of 300 W is also often used. It has been argued that lower power is better because there is less possibility of plasma hardening during stripping and of damage to MOS devices.

A loading effect, in which the etch rate decreases when there is more photoresist surface area, has been observed. In a 400 W PR stripping test, ashing four wafers at the same time was 23% slower than ashing one alone.

6) Plasmless HF-Vapor Silicon-Dioxide Etch:

HF Vapor, 1 cm over plastic dish, Room temperature and pressure: Notes: Like liquid-based HF etches, HF vapor etches silicon dioxide. It has been used to remove native oxide from silicon before the growth of epitaxial silicon [58] and other processes such as the XeF_2 etching of silicon.

In these tests, the HF/H_2O vapor condensed into droplets on the surfaces of the oxide samples during the 1-min etch, causing faster etching where these droplets had formed. This nonuniform etching can be greatly reduced by etching in "pulses," removing the wafer from the vapor before droplets form and allowing it to evaporate.

HF vapor may also be suitable for vapor-phase removal of a sacrificial oxide layer for micromechanical fabrication; however, caution should be used with photoresist masks, which may peel (in these tests, the photoresist peeled when the wafers were rinsed).

In these tests, thermal oxide was etched at one third the rate of unannealed PSG. Other researchers have found that this selectivity goes up by two orders of magnitude when the wafers are heated to 50 °C [59].

Reaction: The overall reaction is [58]

$$SiO_2 + 4HF \rightarrow SiF_4 + H_2O.$$

Water is assumed to catalyze the reaction [58], so a pure HF vapor may have a much slower etch rate than that over the 49% HF/51% H_2O used here. There is a brief incubation time at the beginning of the etch during which water molecules condense on the surface to be etched [58].

7) Plasmaless XeF_2 Silicon Etch

XeF_2, Simple custom vacuum chamber, room temperature, 2.6 Torr: Notes: XeF_2 was first synthesized in 1962 [60] and has been the subject of several papers on silicon etching [54], [61], but was only recently "rediscovered" for its suitability for micromachining [62].

XeF_2 gas has the unusual capability to etch silicon at a significant rate without requiring a plasma to generate reactive species. As with chemical-plasma etching [52], etching is isotropic. The etched surface in deeply etched bulk silicon has been reported to have a roughness of several micrometers [62].

XeF_2 has been used to micromachine free-standing structures made of aluminum and polysilicon protected by a layer of oxide [62]. XeF_2 has the advantage over wet silicon etchants of gently etching without applying capillary forces, and the advantage over plasma etches of being extremely selective over almost all of the traditional masking layers, such as silicon dioxide, some silicon nitrides, and photoresist.

Because the native oxide on silicon surfaces completely stops etching, the silicon etch samples in these etch-rate tests were dipped in 10:1 HF, rinsed, and spun dry a few minutes before the etch rate tests. A period of 18 h in a wafer box in room air was found to be sufficient to grow enough native oxide on doped polysilicon to stop etching completely.

The etch rate has been reported to be extremely load-dependent [62], and measured values in our lab are as low as 11 nm/min (for some regions of the wafer) when an entire 4-in. wafer is exposed to the XeF_2, up to 10 μm/min for small chips of silicon.

The etching apparatus used for these etch-rate measurements allowed exposure of a 4-in. wafer to a 3.5-liter volume of XeF_2 at its room-temperature equilibrium pressure for 30 s, after which the etch chamber was pumped down for 30 s. For etches of total time longer than 30 s (all data here are for one minute of etch time), this "pulsed-etching" cycle was repeated.

Reaction: XeF_2 molecules are physisorbed on the silicon surface [61] and dissociate to release volatile xenon atoms, while the fluorine atoms (not F_2 [54]) remain to react with the silicon to form volatile SiF_4. The overall reaction is

$$2XeF_2 + Si \rightarrow 2Xe + SiF_4.$$

The limiting step in the etching process appears to be the supply of fluorine atoms to the reaction site. Different steps in the supply processes dominate at different temperatures, causing a minimum in the etch rate of silicon as a function of temperature at around 410 K [61]. Ibotson *et al.* hypothesize that the etch rate increases below 410 K because the surface coverage of physisorbed XeF_2 is greater (the XeF_2 is less volatile), and this is the etch-rate-limiting step. When the etch-rate data at these lower temperatures were fitted to an Arrhenius equation multiplied by the density of XeF_2, the effective activation energy was found to be negative at -0.14 eV (which corresponds to a positive activation energy for desorption). Above 410K the surface coverage is lower, but direct impact dissociation greatly increases the supply of fluorine atoms for the reaction. The effective activation energy for these higher temperatures was found to be 0.26 eV.

The etch rate of silicon has been observed to be proportional to the density of XeF_2 molecules for pressures below 0.5 Torr, rising less than linearly at higher pressures [61]. The etch rate has been found to be proportional to the incident flux of XeF_2 under flow that is force-blown perpendicular to the surface.

While according to several references, XeF_2 alone does not etch silicon dioxide and nitride (to the contrary, stoichiometric silicon nitride was etched slowly in our tests), it does etch these dielectrics in the presence of ion or electron bombardment and under UV radiation [54]. This may help to explain why fluorine atoms are nonselective in plasma etches.

C. Plasma-Etch-Rate Variation

Assuming that an etch chemistry (reactive gases and additives), reactor configuration (grounded or driven wafer holder), and RF-power supply (which sets the frequency and power range) have been selected, we have identified a number of factors that can affect plasma-etch rates. These sources of etch-rate variation can be divided into three categories: the etch setup, the material being etched, and the layout and structure on the substrate. The most significant effects on plasma-etch rate in each category are as follows (due to space constraints, the reader is referred to the references for detailed information on these sources of etch-rate variation).

Etch-rate variation due to the etch setup is a function of 1) power [52]; 2) pressure [52], [63]; 3) gas-flow rates [53]; 4) temperature [52], [53]; 5) film blocking of chemical flow [1], [64]; 6) elapsed time from the start of the etch; 7) materials present in the plasma chamber [2]; 8) changes in the etch chamber (e.g., wear of the electrode); and 9) contamination. Etch-rate variation due to the material being etched is affected by 10) impurities in or on the material being etched [53]; 11) microstructure; and 12) film stress. Etch rates also vary as a consequence of the layout and structure due to the 13) distribution and fraction of surface area of the target layer exposed (loading effect) [15]; and 14) specimen structure geometry.

IV. SAMPLE PREPARATION/MEMS APPLICATIONS

Most of the materials listed in the etch-rate tables are frequently used in the U. C. Berkeley Microfabrication Laboratory for micromachining and IC fabrication. The materials are discussed in the following list, which shows the abbreviated material names from Tables I and II in italics. The refractive index (RI) of each transparent film, used in thickness measurements, is listed. Preparation methods for the films are given, along with some MEMS applications and comments.

SC Si $\langle 100 \rangle$*:* Single-crystal silicon, lightly doped with boron, with $\langle 100 \rangle$ orientation.

Single-crystal silicon, in the form of wafers, is the standard starting material for bulk micromachining [65].

Poly n^+*:* In-situ heavily n-doped polycrystalline silicon. RI $= 3.97$.

Deposited on a wafer with thermal oxide already on it to enable interferometric thickness measurements. Deposited in a Tylan LPCVD furnace with the recipe $SiH_4 = 120$ sccm, $PH_3 = 1$ sccm, 605 °C, $p = 300$ mT. No anneal.

This deposition temperature and pressure were chosen to yield a low, tensile residual stress [47] suitable for micromachined beams and shells.

Poly, both doped and undoped, is a common MEMS structural material.

Poly undop: Undoped polycrystalline silicon. RI $= 3.97$.

Deposited on a wafer with thermal oxide already on it to enable interferometric thickness measurements. Deposited in a Tylan LPCVD furnace with the recipe $SiH_4 = 100$ sccm, 605 °C, $p = 300$ mT. No anneal.

Wet Ox: Silicon dioxide thermally grown in water vapor. RI $= 1.46$.

Grown in a Tylan atmospheric-pressure furnace with the recipe 1100 °C, O_2 carrier gas at 200 sccm, H_2O vapor at a pressure just below 1 atm (the water source is at 98 °C), and a total pressure of 1 atm, followed by a 20-min N_2 anneal at 1100 °C.

Thermal oxide has been used for thin sacrificial layers and for sealing cavities [66].

Dry Ox: Silicon dioxide thermally grown in dry oxygen. RI $= 1.46$.

Grown in a Tylan atmospheric-pressure furnace with the recipe 1100 °C, $N_2 = 200$ sccm, $O_2 = 4000$ sccm, $p = 1$ atm, followed by a 30-minute N_2 anneal at 1100 °C.

Dry oxidation, with its slow growth rate, can be used for very thin oxide layers of controlled thickness.

LTO undop: Undoped, annealed low-temperature oxide. RI $= 1.46$.

Deposited in a Tylan LPCVD furnace with the recipe $SiH_4 = 60$ sccm, $O_2 = 90$ sccm, $PH_3 = 0$ sccm (no doping), 450 °C, $p = 300$ mT. Annealed in N_2 in a Tylan atmospheric-pressure furnace at 1000 °C for 60 min.

LTO is used as a sacrificial layer, but it has a much slower etch rate than that of PSG in HF-based etches. It is only etched slightly faster than thermal oxides.

PSG unanl: Doped phosphosilicate glass with no anneal. RI $= 1.47$.

Deposited in a Tylan LPCVD furnace with the recipe $SiH_4 = 60$ sccm, $O_2 = 90$ sccm, $PH_3 = 10.3$ sccm (considered a high doping level), $T = 450\,^\circ$C, $p = 300$ mT.

Unannealed PSG has a much higher etch rate than annealed PSG. It has, however, been observed in the Berkeley Microlab to outgas during subsequent high-temperature steps, causing bubbling in overlying films, so it is not used as frequently as annealed PSG.

PSG annld: Doped, annealed phosphosilicate glass. RI = 1.48.

Deposited in a Tylan LPCVD furnace under the same conditions as the unannealed PSG above, then annealed in N_2 in a Tylan atmospheric-pressure furnace at 1000 °C for 60 min. This PSG has about 5.5 molar percent P_2O_5 in SiO_2.

Oxides, usually chemical-vapor-deposited rather than thermally grown, are common sacrificial materials in micromachining. PSG (a doped LTO) etches much faster than undoped LTO in HF solutions, and is therefore preferred in structures requiring significant undercut.

Stoic Nitrid: Stoichiometric silicon nitride (Si_3N_4). RI = 1.99.

Deposited in a Tylan LPCVD furnace with the recipe $NH_3 = 75$ sccm, $SiH_2Cl_2 = 25$ sccm, $p = 200$ mT, $T = 800\,°C$.

Stoichiometric silicon nitride is used in masking and for layers that are not free-standing. High tensile residual stress precludes its use in free-standing structures.

Low-σ Nitrid: Low-stress silicon nitride (silicon-rich Si_xN_y). RI = 2.18.

Deposited in a Tylan LPCVD furnace with the recipe $NH_3 = 16$ sccm, $SiH_2Cl_2 = 64$ sccm, $p = 300$ mT, $T = 835\,°C$.

Low-stress silicon nitride is used for optically transparent membranes and shells [67], [68]. The refractive index rises with silicon content.

Al/2% Si: Sputtered aluminum with 2% silicon in the target.

Deposited in a CPA 9900 Sputtering System with the recipe $p = 4.5$ kW, track speed = 20 cm/min, $p = 6$ mT. The substrate temperature was not controlled during sputtering and rose above room temperature.

Aluminum is used for interconnects and as a structural material in conjunction with organic sacrificial layers such as polyimide [5], [6].

Sput Tung: Sputtered tungsten.

Deposited in a CPA 9900 Sputtering System with the recipe $P = 4.5$ kW, track speed = 10 cm/min, $p = 6$ mT. The substrate temperature was not controlled during sputtering and rose above room temperature.

Tungsten, both sputtered (with thermal anneal for stress control) and CVD, is used for interconnects that can withstand high-temperature processing [69] as well as for a structural material [70].

Sput Ti: Sputtered titanium.

Deposited in a CPA 9900 Sputtering System with the recipe $P = 4.5$ kW, track speed = 10 cm/min, $p = 6$ mT. The substrate temperature was not controlled during sputtering and rose above room temperature.

Titanium, being very reactive, is one of the few metals with good adhesion to oxide and nitride (aluminum and chromium are others). It is used as an adhesion layer for other, less-adhesive films, such as tungsten and gold.

Sput Ti/W: Sputtered 90% titanium/10% tungsten alloy.

Deposited in a Balzers 450 Sputtering System.

Ti/W is used as an adhesion layer for sputtered and CVD tungsten.

OCG 820PR: OCG 820 (G-line sensitive) positive photoresist. RI = 1.65.

Spun on using an SVG photoresist coater at 6000 rpm for 30 s. Hardbaked 30 min at 120°C (experiments showed that baking for over 1 day had little difference on etch rate from 30 min of hardbaking).

For situations requiring a more durable resist, hardbaking at a higher temperature (up to 180°C), plasma hardening, or deep UV hardening can be done [1].

Photoresist hardening can also occur unintentionally during plasma etching. Difficult-to-remove PR can usually be removed in an oxygen plasma, piranha etch, or a commercial photoresist stripper (e.g., J. T. Baker PRS-2000 at 90°C).

In addition to masking, various photoresists [71] and other polymers [5], [6] have been used as sacrificial layers in micromachining and as liftoff layers in patterning [1]. Photoresist has been etched with acetone, but oxygen plasmas are most common for micromachining removal of polymers, largely because no liquid is involved (liquid capillary forces cause free-standing structures to be pulled down as the liquid dries [3]).

Olin HntPR: Olin Hunt 6512 (I-line-sensitive) positive photoresist.

Spun on using an SVG photoresist coater. Hardbaked 30 min at 120 °C. RI = 1.63.

V. ETCH-RATE MEASUREMENT TECHNIQUES

Transparent films (polysilicon, oxides, nitrides, photoresists) were each coated over an entire 100-mm (4-in.) wafer and etched without patterning. While 100% wafer area is rarely etched at once in MEMS and IC processing, a full-wafer etch was carried out to avoid effects caused by the presence of different materials in the etch. The film thicknesses were measured interferometrically with a NanoSpec AFT interferometric film-thickness-measurement system, which was found to give very repeatable measurements. Refractive indexes (RI's) were determined by ellipsometry and verified with the NanoSpec. These RI's are listed in the samples section of this report. (The apparent RI of the low-stress nitride films was significantly different when measured using the NanoSpec than by using the ellipsometer. We give the ellipsometer RI, which most often agrees with published data.)

Five locations on each wafer were measured before each etch, the films were etched, and then the same five locations (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 rate.

Opaque films (single-crystal silicon, metals) were etched several different ways to allow for measurement. Most of the metal etches were done with a photoresist masking layer covering about 50% of the wafer. Previously patterned tungsten on a film of silicon nitride was used for tungsten in KOH and in the oxygen plasmas. Single-crystal silicon (SCS) with a nitride mask was used for SCS in KOH.

Five step heights distributed around the wafer were measured with a Tencor Alphastep 200 step profiler, the film was etched, then the same steps (to within a few tenths of a millimeter) were measured again. The average step-height difference (and the etch rate of the masking layer, if nonzero) were used to determine the etch rate of the film.

Wet etches having moderately fast rates (>1000 Å/min) were done for one minute (even less for a few very rapid etches). Slower wet etches were done for at least 10 min to get a more accurate measurement. Materials with reported etch rates slower than 10 Å/min were etched for at least 30 min.

Plasma and plasmaless-gas-phase etching were done for 1 min (or, for a few very rapid etches, for 30 s), with one wafer in the etch chamber. Care was taken to avoid plasma-hardening effects with the photoresist samples (fresh samples were used for each etch test).

Accuracy of measurements: An etch rate is listed if the computed standard deviation was smaller than the average rate. In cases where the standard deviation was larger than the average (or the surfaces were very rough when Alphastep measurements were used) indicating significant variation across the wafer, an upper limit equal to the average plus one standard deviation is given (e.g., <50 Å/min). Etch rates of zero are recorded if the films were *thicker* after the etch, as often happened with photoresist in wet etches (the photoresist absorbed water). In a few cases, such as PR in acetone, the entire film was removed in a very short time; a lower limit is listed for these etch rates (e.g., >44 kÅ/min). The measurements are rounded to two significant figures. The results are estimated to be accurate to within ±5% or ±5 Å/min, whichever is smaller.

VI. ETCH-RATE RESULTS

A. Etch-Rate Tables

The etch-rate data is divided into two tables. Table I covers wet etches; Table II deals with plasma and plasmaless-gas-phase etches. Etches are grouped by target material. Etch rates are reported in the commonly used units of angstroms per minute.

For each combination of material and etchant (e.g., n^+ poly and silicon etchant), up to three values are listed. For 317 of the combinations, the top value is the etch rate measured by the authors using fresh solutions, clean chambers, controlled temperatures, etc. (e.g., 3100 Å/min for n^+ poly in wet silicon etchant).

Recognizing that etch rates vary due to many process factors (e.g., previous use of solution or plasma chamber, temperature, area of wafer exposed), we have included further data in the tables on the observed range of etch rates to provide an idea of the range of etch rates that might be expected. When available, the middle and bottom numbers are the slowest and fastest etch rates, respectively, observed by the authors and others in our laboratory during the past five years, using fresh and used solutions, "clean" and "dirty" plasma chambers, and looser temperature control (e.g., 1200 and 6000 Å/min for n^+ poly in silicon etchant). These observed variation ranges for etch rates are quite wide in a number of cases. Wider ranges usually occur for etches performed by many lab users. In some instances, the observed variation is small. This may either indicate that the etch is particularly repeatable or, perhaps, that only a few results were reported by other lab users. Therefore, an etch with a narrow range of reported rates in the tables should not be interpreted as being particularly repeatable.

In some cases, an etch rate was not measured but something else significant happened. For cases in which the film (usually photoresist) peeled, a "P" is entered in the tables. When the material was not etched significantly but was attacked forming a rough surface, an "A" is listed.

Etch-rate tests for many of the combinations of materials and etches in the tables were not performed, often due to cross-contamination concerns in the plasma-etching equipment. When known, based on both published reports and local experience with the chemicals and materials involved, we have included in Tables I and II whether 70 of these combinations support an etch rate of at least 100 Å/min (denoted by a "W" for "works" in the tables), and whether the etch is very fast (at least 10 kÅ/min, denoted by an "F").

Because of their strong dependencies on many factors, *etch rates should not be expected to exactly match those listed in Tables I and II.* The tabulated etch rates are to be understood as being order-of-magnitude repeatable and valid when considering relative etch rates for different materials.

B. Discussion of Etch-Rate Data

Several conclusions can be drawn from the data in the etch-rate tables. Some are considered common knowledge among those familiar with micromachining and semiconductor processing or are expected from the literature on the subject.

Wet etches tend to be more selective than plasma etches. Plasma etches using SF_6, CF_4, or CHF_3, which supply fluorine radicals, are particularly nonselective.

For hydrofluoric-acid-based etching of various types of silicon dioxide, we find that for weaker concentrations of HF (going from 25:1 to 10:1), the etch rate increases almost linearly with concentration, but rises much faster going to concentrated HF. No difference in the etch rates of wet and dry thermally grown silicon dioxide is observed.

Annealing PSG greatly slows its etch rate in most wet etches, but does not affect the plasma-etch rate significantly. Annealed, undoped LTO etches much more slowly in all of the wet etches, and slightly more slowly in the plasma etches than the annealed PSG (doped LTO), approaching the slow etch rate of the thermal oxides.

N^+ polysilicon etches faster than undoped poly in the silicon wet etchant and in the chlorine-based plasma, but the two etch at roughly the same rate in the fluorine-based plasmas.

Stoichiometric silicon nitride etches at the same rate or faster than the silicon-rich low-stress nitride in all of the etches except HF vapor.

Tungsten is removed slowly or not at all in all of the wet etches tested, including HF and KOH solutions, making it a candidate for a structural material in micromachined devices.

Titanium is etched so much faster than most silicon oxides in HF solutions that it is possible to stop a titanium etch on oxide.

The etch rates of the two brands of positive photoresist studied are within 15% of each other in most of the etches, with neither photoresist always being removed more slowly or rapidly. In results not reported in the table, we varied the hardbake time of the OCG 820 from its standard 30 min to 1 h and 1 day. Surprisingly, this had a negligible effect on the removal rate.

The oxygen plasmas, intended for descumming and stripping photoresist, attack only photoresist.

Piranha, intended for cleaning metals and organics from wafers, attacks only the metals and photoresists in these tests.

Xenon difluoride selectively etches silicon, as well as titanium and tungsten. It unexpectedly (but repeatedly) also etches stoichiometric silicon nitride, but not silicon-rich nitride.

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Etch Rates for Micromachining Processing—Part II

Kirt R. Williams, *Senior Member, IEEE*, Kishan Gupta, *Student Member, IEEE*, and Matthew Wasilik

***Abstract*—Samples of 53 materials that are used or potentially can be used or in the fabrication of microelectromechanical systems and integrated circuits were prepared: single-crystal silicon with two doping levels, polycrystalline silicon with two doping levels, polycrystalline germanium, polycrystalline SiGe, graphite, fused quartz, Pyrex 7740, nine other preparations of silicon dioxide, four preparations of silicon nitride, sapphire, two preparations of aluminum oxide, aluminum, Al/2%Si, titanium, vanadium, niobium, two preparations of tantalum, two preparations of chromium, Cr on Au, molybdenum, tungsten, nickel, palladium, platinum, copper, silver, gold, 10 Ti/90 W, 80 Ni/20 Cr, TiN, four types of photoresist, resist pen, Parylene-C, and spin-on polyimide. Selected samples were etched in 35 different etches: isotropic silicon etchant, potassium hydroxide, 10:1 HF, 5:1 BHF, Pad Etch 4, hot phosphoric acid, Aluminum Etchant Type A, titanium wet etchant, CR-7 chromium etchant, CR-14 chromium etchant, molybdenum etchant, warm hydrogen peroxide, Copper Etchant Type CE-200, Copper Etchant APS 100, dilute aqua regia, AU-5 gold etchant, Nichrome Etchant TFN, hot sulfuric+phosphoric acids, Piranha, Microstrip 2001, acetone, methanol, isopropanol, xenon difluoride, $HF+H_2O$ vapor, oxygen plasma, two deep reactive ion etch recipes with two different types of wafer clamping, SF_6 plasma, SF_6+O_2 plasma, CF_4 plasma, CF_4+O_2 plasma, and argon ion milling. The etch rates of 620 combinations of these were measured. The etch rates of thermal oxide in different dilutions of HF and BHF are also reported. Sample preparation and information about the etches is given. [1070]**

***Index Terms*—Chemical vapor deposition (CVD), etching, evaporation, fabrication, materials processing, micromachining.**

I. INTRODUCTION

WHEN designing a microfabrication process, the etch rate of each material to be etched must be known. Knowing the etch rates of other materials that will be exposed to the etch, such as masking films and underlying layers, enables an etch process to be chosen for good selectivity (high ratio of etch rate of the target material to etch rate of the other material)—if one exists. While several large literature-review compilations of etches that target specific materials have been made [1], [2], these only report etch rates in some cases, and rarely have corresponding selectivity information. This paper provides such information, expanding on an earlier paper [3] to give 620 etch rates of 53 materials in 35 etches that have been used or may be used in future fabrication of microelectromechanical systems (MEMS) and integrated circuits (ICs) (approximately 50 etch rates measured in the earlier paper have been included in this one). These data allow the selection of new combinations of structural material, underlying material, and etchant for micromachining.

Table I summarizes the etches tested, abbreviated names for the etches, and the target materials for each. Table II lists etch rates of Si,Ge, SiGe, and C in the SI units of nm/min (not Å/min as in the earlier tables) [3]. Table III covers films and wafers that are primarily silicon dioxide, produced under many different conditions. Table IV is on silicon nitride and aluminum oxide. Table V covers the metals Al, Ti, V, Nb, Ta, and Cr. Table VI continues with the metals Mo, W, Ni, Pd, Pt, Cu, Ag, Au, alloys 10 Ti/90 W, 80 Ni/20 Cr, and compound TiN. Finally, Table VII gives etch rates of organics: photoresists, a resist pen, and a spin-on polyimide.

Section II of this paper lists the materials etched, their preparation, and some uses or potential uses in MEMS and ICs. Section III describes the preparation and applications of the wet and dry etches that were studied, as well as some key experimental results. Section IV describes etch-rate measurement techniques, and Section V discusses the results.

II. SAMPLE PREPARATION

The preparation of the samples in the etch-rate tables is described below, listed by the labels (in italics) used across the tops of the tables. All coated materials were deposited on 100-mm-diameter silicon wafers. For the isotropic silicon etchant, potassium hydroxide, and a few other etches, the wafers were first coated with LPCVD silicon nitride so that etches would not penetrate into the silicon or attack the back side of the wafer.

In several cases, similar materials were prepared using different methods (e.g., wafer form, PECVD, LPCVD, and ion-milled silicon dioxide; annealed and unannealed films) to study and emphasize the effect on their etching characteristics.

Existing or potential MEMS applications are given for the materials. Many of the materials were discussed in more detail previously [3].

A. Silicon, Germanium, SiGe, and Carbon

(100) Si Low-Doped Wafer: Single-crystal silicon, (100) orientation, phosphorus-doped n-type, resistivity of 3–40 Ω-cm, grown with the Czochralski (CZ method). Single-crystal silicon is the standard starting material for bulk micromachining.

Float-Zone Si Wafer: Single-crystal silicon, (100) orientation, undoped, grown with the float-zone (FZ) method for a high resistivity of $>$10 000 Ω-cm. Float-zone wafers have been used as substrates in RF MEMS application to reduce eddy-current loss.

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TABLE I
ETCH DESCRIPTIONS, ABBREVIATIONS, AND TARGET MATERIALS

Etchant	Etchant Abbrev.	Target Material
Isotropic Silicon Etchant "Trilogy Etch" (126 HNO_3 : 60 H_2O : 5 NH_4F), ~20ºC	Si Iso Etch	Silicon
KOH (30% by weight), 80ºC	KOH	Silicon ODE
10:1 HF (10 H_2O : 1 49% HF), ~20ºC	10:1 HF	Silicon Dioxide
5:1 BHF (5 40% NH_4F : 1 49% HF), ~20ºC	5:1 BHF	Silicon Dioxide
Pad Etch 4 from Ashland (13% NH_4F + 32% HAc + 49% H_2O + 6% propylene glycol + surfactant), ~20ºC	Pad Etch 4	SiO_2, not Al
Phosphoric Acid (85% by weight), 160ºC	Phosphoric	Silicon nitride
Al Etchant Type A from Transene (80% H_3PO_4 + 5% HNO_3 + 5% HAc +10%H_2O), 50ºC	Al Etch A	Aluminum
Titanium wet etchant (20 H_2O : 1 H_2O_2 : 1 HF), ~20ºC	Ti Etch	Titanium
Chromium etchant CR-7 from Cyantek (9% $(NH_4)_2Ce(NO_3)_6$) + 6% $HClO_4$ + H_2O), ~20ºC	CR-7	Chromium
Chromium etchant CR-14 from Cyantek (22% $(NH4)_2Ce(NO3)_6$) + 8% HAc+ H2O), ~20ºC	CR-14	Chromium
Molybdenum etchant (180 H_3PO_4 : 11 HAc : 11 HNO_3 : 150 H_2O), ~20ºC	Moly Etch	Molybdenum
Hydrogen peroxide (30wt% H_2O_2, 70wt% H_2O), 50ºC	H_2O_2 50ºC	Tungsten
Copper etchant type CE-200 from Transene (30% $FeCl_3$ + 3-4% HCl + H_2O), ~20ºC	Cu $FeCl_3$ 200	Copper
Copper etchant APS 100 from Transene (15-20% $(NH_4)_2S_2O_8$ + H_2O), 30ºC	Cu APS 100	Copper
Dilute aqua regia (3 HCl : 1 HNO_3 : 2 H_2O), ~30ºC	Dil. Aqua regia	Noble metals
Gold etchant AU-5 from Cyantek (5% I_2 +10% KI + 85% H_2O), ~20ºC	AU-5	Gold
Nichrome etchant TFN from Transene (10-20% $(NH_4)_2Ce(NO_3)_6$) + 5-6% HNO_3 + H_2O), ~20ºC	NiCr TFN	NiCr
1 H_2SO_4 : 1 H_3PO_4, 160ºC	Phos+Sulf	Sapphire
Piranha (~50 H_2SO4 : 1 H_2O_2), 120ºC	Piranha	Cleaning
Microstrip 2001 photoresist stripper, 85ºC	Microstrip	Photoresist
Acetone, ~20ºC	Acetone	Photoresist
Methanol, ~20ºC	Methanol	Cleaning
Isopropanol, ~20ºC	IPA	Cleaning
XeF_2, 2.6 mTorr, homemade chamber	XeF_2	Silicon
HF + H_2O vapor, 1 cm over dish with 49% HF	HF vapor	Silicon dioxide
Technics plasma, O_2, 400 W @ 30 kHz, 300 mTorr	Technics O_2	Photoresist
STS ASE DRIE, mechanical chuck, high frequency, typical recipe	DRIE HF mech.	Silicon
STS ASE DRIE, electrostatic chuck, high frequency, typical recipe	DRIE HF ES	Silicon
STS ASE DRIE, mechanical chuck, stop-on-oxide (low-frequency platen), typical recipe	DRIE LF mech.	Silicon
STS ASE DRIE, electrostatic chuck, stop-on-oxide (low-frequency platen), typical recipe	DRIE LF ES	Silicon
STS 320 RIE, SF_6, 100 W @13.56 MHz, 20 mTorr	STS 320 SF_6	Si, SiN, metals
STS 320 RIE, SF_6 + O_2, 100 W @13.56 MHz, 20 mTorr	STS SF_6+O_2	Si, SiN, metals
STS 320 RIE, CF_4, 100 W @13.56 MHz, 60 mTorr	STS 320 CF_4	Si, SiO, SiN
STS 320 RIE, CF_4 + O_2, 100 W @13.56 MHz, 60 mTorr	STS CF_4+O_2	Si, SiO, SiN
Ion milling with argon ions at 500 V, ~1 mA/cm^2, normal incidence (Commonwealth data)	Ion Mill	Everything

Notation:
BHF = buffered hydrofluoric acid
DRIE = deep reactive ion etch
RIE = reactive ion etch
STS ASE = Surface Technology Systems Advanced Silicon Etch

Polysilicon LPCVD Undoped: Undoped polycrystalline silicon deposited in a Tylan low-pressure chemical-vapor deposition (LPCVD) furnace with recipe SiH_4 flow rate $= 100$ sccm, temperature (T) $= 605$ °C, pressure (p) $= 300$ mtorr. Deposited on a wafer with 100 nm of thermal oxide on it to enable interferometric thickness measurements. Refractive index (RI) $= 3.97$. Undoped poly, which has a high sheet resistance as deposited, is the most common structural material for surface micromachining. It can be doped with ion implantation or by diffusing in dopant atoms from an adjacent film (e.g., PSG, below) at high temperature.

Polysilicon LPCVD In-Situ n^+*:* An n-type, phosphorus-doped polycrystalline silicon deposited in a Tylan LPCVD furnace with recipe $SiH_4 = 100$ sccm, 1.6% PH_3/balance $SiH_4 = 2$ sccm, $T = 610$ °C, $p = 300$ mtorr. Deposited on a wafer with thermal oxide on it to enable interferometric thickness measurements. $RI = 3.97$. *In situ* doping gives a conducting film, useful for thicker films and in cases in which other considerations limit the temperature. The deposition rate is about $1/3$ that of undoped polysilicon under similar conditions.

Poly Ge LPCVD Undoped: Undoped polycrystalline germanium deposited in Tystar LPCVD furnace with recipe $GeH_4 =$

TABLE II
ETCH RATES OF Si, Ge, SiGe, AND C (nm/min)

Etch	Si (100) Wafer	Float-Zone Si Wafer	Poly Si LPCVD Undoped	Poly Si LPCVD In-situ n^+	Poly Ge LPCVD Undoped	Poly SiGe LPCVD *P*-type	Graphite Ion-Milled
Si Iso Etch	150	W	100	310	890	550	60
KOH	1100	F	670	>1000	-	-	-
10:1 HF	S	S	0	0.7	0	0.42	-
5:1 BHF	0	S	0.2	0.9	R 1.8	0.45	R 17
Pad Etch 4	S	S	S	S	-	-	-
Phosphoric	0.17	S	S	0.7	0.13	0.40	
Al Etch A	S	S	<0.9	<1	13	0.11	-
Ti Etch	S	S	S	1.2	-	-	-
CR-7	0	S	0	S	260	0.35	< 0.5
CR-14	S	S	0	S	-	-	-
Moly Etch	-	-	-	-	-	-	-
H_2O_2 50ºC	S	S	S	S	460	0.13	-
Cu $FeCl_3$ 200	-	-	-	-	-	-	-
Cu APS 100	-	-	-	-	-	-	-
Dil. Aqua regia	0	0	0	0	-	-	-
AU-5	S	S	0	S	-	-	-
NiCr TFN	0	S	S	S	-	-	-
Phos+Sulf	0.86	S	S	S	-	-	-
Piranha	0	S	0	0	soft	0	-
Microstrip	S	S	S	S	-	-	0
Acetone	S	S	0	0	-	-	-
Methanol	S	S	0	S	-	-	S
IPA	S	S	S	S	-	-	S
XeF_2	460	W	180	190	-	-	-
HF vapor	S	S	0	0	-	-	-
Technics O_2	S	S	0	0	-	-	0
DRIE HF mech.	1500	1600	W	W	-	-	-
DRIE HF ES	2400	W	W	W	400	1400	-
DRIE LF mech.	2400	W	W	W	-	-	-
DRIE LF ES	2000	W	W	W	170	1040	-
STS 320 SF_6	W	W	W	W	-	-	-
STS SF_6+O_2	1500	W	W	W	-	-	-
STS 320 CF_4	W	W	W	W	-	-	-
STS CF_4+O_2	95	-	-	-	-	-	-
Ion Mill	38	38	38	38	-	-	4.4

Notation:
W = Etch known to work, but etch rate not measured
F = Etch known to be fast, but etch rate not measured
S = Etch rate known to be slow or zero, but etch rate not measured
R = Film was visibly roughened or attacked
T = Thicker after etch (due to swelling or compound formation)
P = Some of film peeled during etch or when rinsed
I = Incubation time before etching fully starts
C = Film congealed
soft = a soft material remained after etching

Ion-Milled = Ion-mill deposited
LPCVD = low-pressure chemical-vapor deposition
poly Ge = polycrystalline germanium
poly SiGe = polycrystalline SiGe
poly Si = polycrystalline silicon

100 sccm, T = 400 °C, p = 300 mtorr. The polygermanium deposition was preceded by the deposition of silicon seed layer approximately 6 nm thick using the recipe $Si_2H_6 = 100$ sccm, T = 400 °C, p = 300 mtorr.

Germanium forms an oxide that is soluble in water. Thus, water with a high concentration of dissolved oxygen etches germanium. Hydrogen peroxide is a useful etchant for Ge, etching faster at higher temperature.

Polygermanium has been used in surface micromachining as a sacrificial layer in conjunction with a polycrystalline SiGe structural layer, using warm hydrogen peroxide as the etchant [4]. The relatively low deposition temperatures are compatible with CMOS circuitry with aluminum interconnections.

Poly SiGe LPCVD p-*Type:* A p-type polycrystalline silicon-germanium deposited in a Tystar LPCVD furnace with recipe $SiH_4 = 100$ sccm, $GeH_4 = 58$ sccm, $B_2H_6 = 60$ sccm, T =

TABLE III
ETCH RATES OF SILICON DIOXIDE (nm/min)

Etch	Fused Quartz Wafer	Pyrex 7740 Wafer	Thermal Oxide Wet-Grn	Ann. LTO LPCVD Calogic	Unan. LTO LPCVD Tylan	Ann. LTO LPCVD Tylan	Unan. PSG LPCVD Tylan	Ann. PSG LPCVD Tylan	Oxide PECVD Unannealed	Oxide PECVD Annealed	Oxide Ion-Mill
Si Iso Etch	12	R 140	8.7	15	-	11	400	170	100	25	43
KOH	6.7	11	7.7	8.1	-	9.4	-	38	15	7.8	8.0
10:1 HF	26	W	23	W	W	34	1500	470	W	W	W
5:1 BHF	130	43	100	150	W	120	680	440	490	240	82
Pad Etch 4	29	17	31	W	38	W	200	W	160	W	W
Phosphoric	0.23	3.7	0.18	S	0.21	0.21	2.7	1.8	-	-	S
Al Etch A	S	-	0	S	S	0	S	< 1	0	S	S
Ti Etch	-	-	12	W	W	W	W	210	W	W	-
CR-7	R < 0.4	R 0	0.02	0	S	S	S	S	0	0	0
CR-14	S	-	0.01	S	S	S	S	S	S	S	S
Moly Etch	-	-	-	-	-	-	-	-	-	-	-
H_2O_2 50ºC	S	S	0	S	S	S	S	S	S	S	S
Cu $FeCl_3$ 200	-	-	-	-	-	-	-	-	-	-	-
Cu APS 100	-	-	-	-	-	-	-	-	-	-	-
Dil. Aqua regia	0	-	0	0	0	0	0	0	0.7	S	S
AU-5	S	-	S	S	S	S	S	S	0	S	S
NiCr TFN	S	-	S	S	S	S	S	S	S	S	S
Phos+Sulf	S	-	0.057	S	S	S	S	S	S	S	S
Piranha	R 0	R 0	0	0	S	0	S	0	0	0	0
Microstrip	S	S	S	S	S	S	S	S	S	S	S
Acetone	S	S	0	S	S	0	S	0	S	S	S
Methanol	S	S	S	S	S	S	S	S	S	S	S
IPA	S	S	S	S	S	S	S	S	S	S	S
XeF_2	S	-	0	S	S	0	0	0	S	S	S
HF vapor	W	W	66	W	W	78	210	150	W	W	W
Technics O_2	S	S	0	S	S	0	0	0	S	S	S
DRIE HF mech.	S	-	S	7.5	6.2	6.9	9.5	11	9.5	S	S
DRIE HF ES	S	-	24	W	W	W	W	W	W	W	W
DRIE LF mech.	S	-	S	3.6	9.8	9.4	15	15	4.0	S	S
DRIE LF ES	S	-	24	W	W	W	W	W	W	W	W
STS 320 SF_6	W	-	W	W	W	W	W	W	W	W	W
STS SF_6+O_2	35	10	29	38	55	48	73	60	55	32	30
STS 320 CF_4	W	W	W	33	W	W	W	W	W	W	W
STS CF_4+O_2	41	31	44	42	51	46	69	62	51	43	21
Ion Mill	W	W	39	W	W	W	W	W	W	W	W

Notation:
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F = Etch known to be fast, but etch rate not measured
S = Etch rate known to be slow or zero, but etch rate not measured
R = Film was visibly roughened or attacked
T = Thicker after etch (due to swelling or compound formation)
P = Some of film peeled during etch or when rinsed
I = Incubation time before etching fully starts
C = Film congealed
soft = a soft material remained after etching

Ann. LTO = annealed low-temperature oxide
Ann. PSG = annealed phosphosilicate glass
LPCVD = low-pressure chemical vapor deposition
PECVD = plasma-enhance chemical-vapor deposition
Unan. LTO = unannealed low-temperature oxide
Unan. PSG = unannealed phosphosilicate glass

400 °C, p = 300 mtorr. This film is approximately 48 atomic % Ge.

Graphite Ion-Milled: Graphite ion-mill-deposited (also known as ion-beam-deposited) in a Commonwealth Scientific system from a graphite target with argon ions at 1250 V, current density of about 2 mA/cm^2 (~200 mA over most of a 5-inch-diameter target), chamber p = 3×10^{-4} torr. Graphite has had little or no use in MEMS to date. In this work, it was found to be easily deposited and etched in silicon isotropic etchant. It may find use as a hard mask for plasma etching due to its low etch rate, and as a dry lubricant in MEMS.

B. Silicon Dioxide

Fused Quartz Wafer: Wafers of General Electric 124 or NSG N fused quartz source material, >99.99% silicon dioxide, with amorphous structure (as opposed to true crystalline quartz). This material is commonly referred to simply as "quartz." It is compatible with silicon-wafer processing steps, and may find application as a substrate in RF MEMS as it is not conductive, eliminating eddy-current losses.

Pyrex 7740 Wafer: Corning Pyrex 7740 glass, 81% SiO_2, 13% B_2O_3, 4% Na_2O, 2% Al_2O_3. Pyrex 7740 (and the very

TABLE IV
ETCH RATES OF SILICON NITRIDE AND ALUMINUM OXIDE (nm/min)

Etch	Stoich Si Nit. LPCVD	Si-Rich Si Nit. LPCVD	PECVD Silicon Nit. Low RI	PECVD Silicon Nit. High RI	Sapphire Wafer	Aluminum Oxide Ion-Mill	Aluminum Oxide Evap
Si Iso Etch	-	0.23	> 66	12	R < 0.7	99	12
KOH	0	0	0.67	0	R 0	> 2500	> 800
10:1 HF	1.1	S	-	-	S	-	-
5:1 BHF	S	1.3	60	8.2	0	-	160
Pad Etch 4	0.41	S	-	1.6	S	-	-
Phosphoric	4.5	2.7	W	20	< 0.1	-	> 5
Al Etch A	S	< 0.05	-	-	R < 2	65	5.7
Ti Etch	0.99	S	-	-	S	-	-
CR-7	S	0	< 0.14	0	R 0	0.34	0.075
CR-14	S	S	-	-	S	-	-
Moly Etch	-	-	-	-	-	-	-
H_2O_2 50ºC	0	S	S	S	S	-	-
Cu $FeCl_3$ 200	-	0	-	-	-	-	-
Cu APS 100	-	0	-	-	-	-	-
Dil. Aqua regia	0	0	-	-	S	-	1.1
AU-5	S	0	-	-	-	-	-
NiCr TFN	S	S	-	-	-	-	-
Phos+Sulf	2.9	S	W	10	< 0.3	-	-
Piranha	0	0	< 0.04	0	R 0	97	19
Microstrip	S	S	S	S	S	-	-
Acetone	0	0	S	S	S	0	S
Methanol	S	0	S	S	S	0	S
IPA	S	0	S	S	S	0	S
XeF_2	12	-	-	-	-	-	-
HF vapor	1.0	1.9	-	-	S	-	-
Technics O_2	0	S	S	S	S	S	S
DRIE HF mech.	W	21	W	W	S	S	S
DRIE HF ES	W	W	W	W	S	S	S
DRIE LF mech.	W	26	W	W	S	S	S
DRIE LF ES	W	W	W	W	S	S	S
STS 320 SF_6	W	W	W	W	S	S	S
STS SF_6+O_2	150	150	200	190	2.2	0.55	0.41
STS 320 CF_4	34	W	W	W	S	S	S
STS CF_4+O_2	120	> 130	240	110	0	< 2	< 0.2
Ion Mill	13	9.4	W	W	W	10	10

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T = Thicker after etch (due to swelling or compound formation)
P = Some of film peeled during etch or when rinsed
I = Incubation time before etching fully starts
C = Film congealed
soft = a soft material remained after etching

Evap = evaporated
Ion-Mill = ion-mill deposition
PECVD = plasma-enhanced chemical-vapor deposition
Si-Rich Si Nit. = silicon-rich silicon nitride
Stoich Si Nit. = stoichiometric silicon nitride

similar Borofloat glass) are used in anodic bonding to silicon due to the high content of mobile sodium ions and to the good match of thermal expansion rates. The large amounts of non-silicon-dioxide "impurities" give it noticeably different etching characteristics, etching slower in 5:1 BHF, but faster in silicon isotropic etchant.

Thermal Oxide Wet-Grown: Silicon dioxide grown in a Tylan atmospheric-pressure furnace with the recipe O_2 carrier gas at 200 sccm, H_2O vapor at a pressure just below 1 atm (the water source is at 98 °C) at 1100 °C, and a total pressure of 1 atm, followed by a 20-min N_2 anneal at 1100 °C. RI = 1.46. Thermal oxide forms a conformal coating on silicon. It is denser and etches more slowly than chemical-vapor-deposited oxides.

Ann. LTO LPCVD Calogic: Low-temperature silicon dioxide (LTO) deposited in a Calogic low-temperature

TABLE V
ETCH RATES OF AL, Ti, V, Nb, Ta, AND Cr (nm/min)

Etch	Aluminum Evap	Al + 2% Si Sputtered	Titanium Sputtered	Vanadium Evap	Niobium Ion-Mill	Tantalum Evap	Tantalum Ion-Mill	Chromium Evap	Chromium Ion-Mill	Patterned Cr on Au Evap
Si Iso Etch	60	400	300	9600	79	5.8	5.3	R 8.8	-	< 2.3
KOH	12,900	F	soft	< 12	3.2	S	2.8	4.2	-	0
10:1 HF	W	250	1100	S	S	S	S	S	S	-
5:1 BHF	11	140	W	< 2	0	S	R 0	0	< 0.3	P
Pad Etch 4	1.9	R < 15	< 2	S	S	S	S	S	S	-
Phosphoric	> 500	980	-	-	0	-	0	100	-	-
Al Etch A	530	660	0	-	-	-	-	T 0	-	1.0
Ti Etch	150	240	1100	-	-	-	-	0	S	-
CR-7	3.8	S	< 2	60	R 0	S	< 0.7	170	150	110
CR-14	0	0.8	< 2	15	-	-	-	93	W	120
Moly Etch	> 20	-	-	-	-	-	-	R 0	-	-
H_2O_2 50ºC	T 0	0.25	-	-	-	-	-	110	W	-
Cu $FeCl_3$ 200	35	W	-	-	-	-	-	0.053	S	-
Cu APS 100	< 0.3	-	-	-	-	-	-	0	S	-
Dil. Aqua regia	600	W	< 0.5	-	0	S	< 2	0	S	-
AU-5	-	-	-	-	-	-	-	0	S	-
NiCr TFN	> 46	-	-	-	-	-		> 170	W	W
Phos+Sulf	W	W	-	-	-	-		I > 500		
Piranha	> 5200	W	240	-	6.3	S	T 0	> 16	5.7	R 0
Microstrip	-	-	-	-	-	-	-	-	-	-
Acetone	S	0	0	S	S	S	S	S	S	S
Methanol	S	S	S	S	S	S	S	S	S	S
IPA	S	S	S	S	S	S	S	S	S	S
XeF_2	S	0	29	W	W	W	W	-	-	-
HF vapor	R	R	R	-	-	-	-	S	S	-
Technics O_2	S	0	0	S	S	S	S	S	S	S
DRIE HF mech.	-	-	4.9	-	-	-	-	-	-	-
DRIE HF ES	-	-	-	-	-	-	-	-	-	-
DRIE LF mech.	-	-	-	-	-	-	-	-	-	-
DRIE LF ES	-	-	-	-	-	-	-	-	-	-
STS 320 SF_6	-	-	-	-	W	W	W	< 1	< 0.7	S
STS SF_6+O_2	< 2.8	-	-	-	26	W	37	< 1	< 0.9	S
STS 320 CF_4	S	S	-	-	-	-	-	< 1	< 3	-
STS CF_4+O_2	0.87	1.5	-	-	14	-	21	< 1.3	< 1.2	-
Ion Mill	73	W	38	W	W	42	42	58	58	W

Notation:
W = Etch known to work, but etch rate not measured
F = Etch known to be fast, but etch rate not measured
S = Etch rate known to be slow or zero, but etch rate not measured
R = Film was visibly roughened or attacked
T = Thicker after etch (due to swelling or compound formation)
P = Some of film peeled during etch or when rinsed
I = Incubation time before etching fully starts
C = Film congealed
soft = a soft material remained after etching

Evap = evaporated
Ion-Mill = Ion-mill deposited

chemical-vapor-deposition (LPCVD) furnace with the recipe $SiH_4 = 74$ sccm, $O_2 = 105$ sccm, p = 500 mtorr, T = 495 °C. RI = 1.46, then annealed in N_2 at 1000 °C for 60 min. LTO is used instead of thermal oxide in many applications due to its relatively low deposition temperature and the ability to deposit thick films on surfaces other than silicon. LTO should be annealed prior to the deposition of another film at higher temperature (e.g., polysilicon) because it will outgas hydrogen, which can cause the overlying film to bubble.

Unan. LTO LPCVD Tylan: LTO deposited in a Tylan LPCVD furnace with the recipe $SiH_4 = 60$ sccm, $O_2 = 90$ sccm, p = 300 mtorr, T = 450 °C, no anneal.

Ann. LTO LPCVD Tylan: LTO deposited as above, then annealed in N_2 at 1000 °C for 60 min. RI = 1.46.

TABLE VI
ETCH RATES OF Mo, W, Ni, Pd, Pt, Cu, Ag, Au, TiW, NiCr, AND TiN (nm/min)

Etch	Molybdenum Evap	Tungsten Sputtered	Nickel Evap	Palladium Evap	Platinum Evap	Copper Evap	Silver Evap	Gold Evap	10Ti/90W Ion-Mill	80Ni/20Cr Evap	TiN Sputtered
Si Iso Etch	11,000	13	21	0	0	37	49	0	23	-	soft
KOH	0	0	0	0	0	T 0	T 0	0	> 300	-	-
10:1 HF	S	0	S	S	S	S	S	S	S	S	S
5:1 BHF	< 0.3	<2	< 1.1	0	0	R < 5	R < 5	0	R < 0.2	R < 1.5	2.5
Pad Etch 4	S	S	-	-	-	-	-	-	-	-	-
Phosphoric	-	-	-	-	-	-	-	0	2.5	-	-
Al Etch A	-	-	29	-	-	> 2900	-	-	-	-	-
Ti Etch	-	11	-	-	-	-	-	-	0	-	-
CR-7	3.3	3.2	1.7	0	0	280	450	0	0.62	11.2	-
CR-14	soft	0	< 2	0	< 3	19	-	-	-	0.22	< 2
Moly Etch	690	-	-	-	-	-	-	-	0	-	-
H_2O_2 50°C	-	150	-	-	-	-	-	-	W	-	-
Cu $FeCl_3$ 200	-	-	21	-	-	3900	T 0	-	-	-	-
Cu APS 100	-	-	0	-	-	2500	-	-	-	-	-
Dil. Aqua regia	650	5.2	100	390	3.6	600	W	680	3.7	-	-
AU-5	-	-	0	T 0	< 2	T 0	T 0	660	-	-	-
NiCr TFN	680	-	13			690	-	-	-	83	-
Phos+Sulf	-	-	-	-	-	-	-	-	-	-	-
Piranha	18	-	380	3.0	< 3	88	600	0	0.78	92	-
Microstrip	-	-	-	-	-	-	-	-	-	-	-
Acetone	S	S	S	S	S	S	S	S	S	S	S
Methanol	S	S	S	S	S	S	S	S	S	S	S
IPA	S	S	S	S	S	S	S	S	S	S	S
XeF_2	W	80	-	-	-	-	-	-	W	-	-
HF vapor	-	0	S	-	S	R	-	S	-	-	-
Technics O_2	S	0	S	S	S	S	S	S	S	S	S
DRIE HF mech.	5.7	4.9	S	S	S	S	S	S	4.6	S	-
DRIE HF ES	-	-	-	-	-	-	-	-	-	-	-
DRIE LF mech.	-	-	-	-	-	-	-	-	-	-	-
DRIE LF ES	-	-	-	-	-	-	-	-	-	-	-
STS 320 SF_6	73	W	S	S	S	S	-	S	W	S	-
STS SF_6+O_2	130	W	0.71	3.1	7.4	S	-	S	550	3.7	-
STS 320 CF_4	W	-	-	-	-	-	-	S	-	-	-
STS CF_4+O_2	150	-	-	1.0	1.4	-	-	8.3	49	0	-
Ion Mill	54	38	66	130	88	110	220	170	W	18	W

Notation:
W = Etch known to work, but etch rate not measured
F = Etch known to be fast, but etch rate not measured
S = Etch rate known to be slow or zero, but etch rate not measured
R = Film was visibly roughened or attacked
T = Thicker after etch (due to swelling or compound formation)
P = Some of film peeled during etch or when rinsed
I = Incubation time before etching fully starts
C = Film congealed
soft = a soft material remained after etching

Evap = evaporated
Ion-Mill = Ion-mill deposited

Unan. PSG LPCVD Tylan: Phosphosilicate glass (PSG) deposited in a Tylan LPCVD furnace with the recipe $SiH_4 = 60$ sccm, $O_2 = 90$ sccm, $PH_3 = 10.3$ sccm, $p = 300$ mtorr, $T = 450$ °C, no anneal. RI = 1.47. PSG is LTO doped with P_2O_5, typically in the 5–10% range. It is used as a sacrificial layer in micromachining because it etches much faster than undoped LTO in HF solutions.

Ann. PSG LPCVD Tylan: PSG deposited as above, then annealed in N_2 at 1000 °C for 60 min. RI = 1.48. Like pure LTO, PSG should be annealed prior to the deposition of another film at high temperature (e.g., polysilicon) because it will outgas hydrogen, which can cause the overlying film to bubble. Annealing results in a lower etch rate in HF solutions.

Oxide PECVD Unannealed: Silicon dioxide deposited in an STS 310 plasma-enhanced chemical-vapor-deposition (PECVD) system with the recipe $2\%SiH_4/Ar = 500$ sccm, $N_2O = 1410$ sccm, $P = 10$ W at 13.56 MHz, $p = 800$ mtorr, $T = 300$ °C. RI = 1.46. PECVD silicon dioxide usually contains 2–9 atomic % hydrogen [5]. PECVD oxide can be deposited at an even lower temperature than LPCVD films.

TABLE VII
ETCH RATES OF RESISTS, PARYLENE, AND POLYIMIDE (nm/min)

Etch	S1822 Positive Photoresist	OCG 820 Positive Photoresist	Futurrex Positive Photoresist	Futurrex Negative Photoresist	Act. Mrk. Resist Pen	Parylene Type C	Spin-On PI 2556 Polymide
Si Iso Etch	P 0	0	P 21	290	-	0.019	0
KOH	> 17,900	F	> 13,000	> 18,000	F	0.42	T 0
10:1 HF	S	0	-	-	S	4.4	S
5:1 BHF	0	0	21	5.0	< 3	0.16	5.5
Pad Etch 4	T 0	-	-	-	-	-	-
Phosphoric	P 120	55	P 77	> 400	-	0.55	-
Al Etch A	0	0	-	-	-	-	-
Ti Etch	< 0.5	0	-	-	-	-	-
CR-7	0	S	0	< 0.5	3.8	-	0
CR-14	0.24	S	S	S	S	-	S
Moly Etch	230	-	-	-	-	-	-
H_2O_2 50ºC	R T 0	S	S	S	S	T 0	S
Cu $FeCl_3$ 200	0.48	S	S	S	S	-	S
Cu APS 100	0	S	S	S	S	-	S
Dil. Aqua regia	0	S	T 0	T 0	T 0	-	T 0
AU-5	P 0	S	S	S	S	-	S
NiCr TFN	0.57	S	S	S	S	-	S
Phos+Sulf	F	F	F	F	F	-	-
Piranha	> 92,000	F	> 59,000	> 59,000	>15,000	2.6	>17,000
Microstrip	> 94,000	F	> 85,000	> 60,000	>11,000	-	520
Acetone	> 176,000	F	> 120,000	> 87,000	>26,000	0.77	0
Methanol	> 36,000	-	P C >16,000	> 27,000	P	0.093	0
IPA	> 1000	-	480	910	-	T 0	0
XeF_2	S	0	S	S	S	-	S
HF vapor	-	P 0	S	S	S	-	S
Technics O_2	300	340	200	470	370	220	370
DRIE HF mech.	30	W	W	W	54	-	-
DRIE HF ES	W	W	W	W	W	27	-
DRIE LF mech.	35	W	34	W	W	-	-
DRIE LF ES	W	W	W	W	W	15	-
STS 320 SF_6	120	W	I 64	140	W	-	140
STS SF_6+O_2	180	-	I 130	320	170	-	200
STS 320 CF_4	42	W	W	72	W	-	-
STS CF_4+O_2	130	-	I 100	190	52	-	160
Ion Mill	R < 100	W	W	W	W	W	W

Notation:
W = Etch known to work, but etch rate not measured
F = Etch known to be fast, but etch rate not measured
S = Etch rate known to be slow or zero, but etch rate not measured
R = Film was visibly roughened or attacked
T = Thicker after etch (due to swelling or compound formation)
P = Some of film peeled during etch or when rinsed
I = Incubation time before etching fully starts
C = Film congealed
soft = a soft material remained after etching

Act. Mrk. = Action Marker

Oxide PECVD Annealed: Silicon dioxide deposited as above, then annealed in N_2 at 1000 °C for 60 min. RI $= 1.46$. Annealing densifies the film, resulting in a lower etch in HF solutions.

Oxide Ion-Milled: Silicon dioxide ion-mill-deposited from a silicon-dioxide target in a Commonwealth Scientific system with argon ions at 1250 V, current density of about 2 mA/cm^2, $p = 3 \times 10^{-4}$ torr. RI $= 1.57$. Ion milling is the lowest temperature deposition method studied here, with the wafer remaining near room temperature.

C. Silicon Nitride

Stoich. Si Nit. LPCVD: Stoichiometric silicon nitride (Si_3N_4) deposited in a Tylan LPCVD furnace with the recipe $SiCl_2H_2 = 25$ sccm, $NH_3 = 75$ sccm, $p = 200$ mtorr, $T = 800$ °C. RI $= 1.99$. Silicon nitride is used as an etch mask, thermal-oxidation mask, and wafer-capping material due to its low permeability to moisture. It typically has a high tensile residual stress.

Si-Rich Si Nit. LPCVD: Silicon-rich, low-stress silicon nitride deposited in a Calogic LPCVD furnace with the recipe $\mathrm{SiCl_2H_2} = 159$ sccm, $\mathrm{NH_3} = 40.5$ sccm, $\mathrm{p} = 280$ mtorr, $\mathrm{T} = 850\ ^\circ\mathrm{C}$. $\mathrm{RI} = 2.24$. Low-stress silicon nitride typically has a tensile residual stress below 50 MPa, allowing its use in micromachining as a freestanding film.

PECVD Silicon Nit. Low RI: Silicon nitride deposited in an STS 310 PECVD system with a relatively low ratio of silicon to nitrogen with the recipe 2%$\mathrm{SiH_4/Ar} = 100$ sccm, $\mathrm{N_2} = 2000$ sccm, power alternating between $\mathrm{P} = 60$ W at 13.56 MHz for 6 s and 25 W at 187 kHz for 3 s, $\mathrm{p} = 750$ mtorr, $\mathrm{T} = 350\ ^\circ\mathrm{C}$. $\mathrm{RI} = 1.88$. PECVD silicon nitride is deposited at a much lower temperature than LPCVD and can contain well over 10 atomic percent hydrogen [5], and is therefore frequently written as $\mathrm{Si_xN_yH_z}$ or SiN:H. High frequency typically yields tensile silicon nitride films; low frequency typically gives compressive films. “Mixed-frequency” nitride such as this has a lower absolute value of stress.

PECVD Silicon Nit. High RI: Silicon nitride deposited as above, but with a relatively high ratio of silicon to nitrogen by increasing the flow of 2%$\mathrm{SiH_4}$/Ar to 500 sccm. $\mathrm{RI} = 2.53$. This PECVD silicon nitride has a significantly lower etch rate in HF solutions than its low-index counterpart above, but still etches much faster than LPCVD nitride.

D. Aluminum Oxide

Sapphire Wafer: Clear, colorless, pure crystalline aluminum oxide wafer. (Aluminum oxide is also known as alumina or corundum.) These wafers are referred to as sapphire in the electronics industry, although true sapphire has a small amount of titanium, giving it a blue color. Sapphire has been used as substrate for silicon-on-insulator (SOI) wafers. Sapphire was the most chemically inert material tested for this paper.

Aluminum Oxide Ion-Milled: Aluminum oxide ion-mill-deposited in a Commonwealth Scientific system from a sapphire target with argon ions at 1250 V, current density of about 2 mA/cm^2. The sapphire was held to a copper backing plate with copper-loaded vacuum grease. A small area of this grease was exposed during deposition. Adhesion of the film to the wafer was good. Like silicon dioxide, aluminum oxide is relatively inert. Aluminum oxide films have been used as dielectrics and protective coatings.

Aluminum Oxide Evaporated: Aluminum oxide electron-beam evaporated from an alumina source. Wafer temperature was not controlled and was near room temperature during deposition. $\mathrm{RI} = 1.66$.

E. Aluminum

Aluminum Evaporated: Aluminum evaporated from a tungsten wire in a Veeco evaporator. Aluminum is commonly used for electrical interconnections due to its ease of use and good conductivity. It is well known to have good adhesion to silicon and silicon dioxide.

Al + 2% Si Sputtered: Aluminum sputtered using argon in a CPA 9900 sputtering system with the recipe $\mathrm{p} = 6$ mtorr, $\mathrm{P} = 4.5$ kW, $\mathrm{track\ speed} = 10$ cm/min. Aluminum with a small percentage of silicon, added to prevent “spiking” of metal into the substrate, is a common material for IC interconnects.

F. Transition Metals

Titanium Sputtered: Titanium sputtered using argon in a CPA 9900 sputtering system with the recipe $\mathrm{p} = 6$ mtorr, $\mathrm{P} = 4.5$ kW, track $\mathrm{speed} = 10$ cm/min. Titanium is well known to have good adhesion to silicon and silicon dioxide, and is frequently used as an adhesion layer for less-adhesive metals such as gold.

Vanadium Evaporated: Vanadium electron-beam evaporated in a CHA evaporator at a rate of 0.1 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. Vanadium was found to have good adhesion to silicon and silicon dioxide, as evaluated by firmly pressing 3M Scotch Tape onto the film, then peeling the tape off without removing the metal. Vanadium thus has potential as an alternative adhesion layer.

Niobium Ion Milled: Niobium ion-mill-deposited in a Commonwealth Scientific system with argon ions at 1250 V, current density of about 2 mA/cm^2, $\mathrm{p} = 3 \times 10^{-4}$ torr. Niobium was found to have good adhesion to silicon, so it has potential as an alternative adhesion layer.

Tantalum Evaporated: Tantalum electron-beam evaporated in a CHA evaporator at a rate of 0.1 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. Tantalum was found to have good adhesion to silicon and silicon dioxide, so it has potential as an alternative adhesion layer. As one of the high-melting-temperature metals, tantalum has been used as a hot filament in inert atmospheres.

Tantalum Ion-Milled: Tantalum ion-mill-deposited in a Commonwealth Scientific system with argon ions at 1250 V, current density of about 2 mA/cm^2, $\mathrm{p} = 3 \times 10^{-4}$ torr. Tantalum deposited using this method also was found to have good adhesion to silicon and silicon dioxide.

Chromium Evaporated: Chromium evaporated from a tungsten strip in a CHA evaporator at a rate of 0.1 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. Chromium is well known to have good adhesion to silicon and silicon dioxide, and is frequently used as an adhesion layer for less-adhesive metals such as gold.

Chromium Ion Milled: Chromium ion-mill-deposited in a Commonwealth Scientific system with argon ions at 1250 V, current density of about 2 mA/cm^2, $\mathrm{p} = 3 \times 10^{-4}$ torr.

Patterned Cr on Au Evaporated: Evaporated chromium previously lithographically patterned and etched, sitting on a continuous layer of gold (which itself has a chromium adhesion layer). This was done to study the potential electrochemical effect of this commonly used system of two metals in contact.

Moly Evaporated: Molybdenum electron-beam evaporated in a CHA evaporator at a rate of 0.5 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. The evaporated molybdenum used in these tests had good adhesion to silicon, but was found to have only fair adhesion to oxide: it did not peel when Scotch tape was lightly pressed, but did when firmly pressed and removed. We have found it to have good adhesion when sputtered. Molybdenum has a relatively low thermal coefficient of expansion and has been used as a heat sink attached to silicon. It has been used in MEMS as the electrode material for film-bulk acoustic resonators [6].

Tungsten Sputtered: Tungsten sputtered using argon in a CPA 9900 sputtering system with the recipe $\mathrm{p} = 6$ mtorr, $\mathrm{P} = 4.5$ kW, $\text{track speed} = 10$ cm/min. An adhesion layer of titanium was used under the tungsten. Tungsten also has a relatively low thermal coefficient of expansion and has been used as a heat sink attached to silicon. Tungsten has been used in MEMS as a hot filament in vacuum [7] and as an interconnect material compatible with high-temperature processing.

Nickel Evaporated: Nickel electron-beam evaporated in a CHA evaporator at a rate of 0.3 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. A 10-nm adhesion layer of chromium was used under the nickel. Nickel has been used as a diffusion-barrier layer in contacts, a seed layer for electroplating (immediately after removing its native oxide), and as the metal to which solder adheres.

Palladium Evaporated: Palladium electron-beam evaporated in a CHA evaporator at a rate of 0.15 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. A 10-nm adhesion layer of chromium was used under the palladium. Like platinum, palladium has been used as catalyst, for example in the hydrogenation of carbon compounds [2]. In these tests, it was etched more easily than platinum.

Platinum Evaporated: Platinum electron-beam evaporated in a CHA evaporator at a rate of 0.15 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. A 10-nm adhesion layer of chromium was used under the platinum. Platinum has been used in thin-film heaters, resistive temperature sensors, and as a diffusion-barrier layer in contacts due to its inertness and stability. It is also well-known as a catalyst and has been used in fine-grain form (for large surface area) in microscale fuel cells. Platinum is often used as the electrode layer on which lead zirconate titanate (PZT) is grown for good crystal orientation. In this work it was the most difficult metal to etch.

Copper Evaporated: Copper evaporated from a tungsten boat in a CHA evaporator at a rate of 0.17 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. A 10-nm adhesion layer of chromium was used under the copper. Copper is second to only to silver in its electrical conductivity, and is presently used in high-speed integrated circuits. Plated copper has been employed in MEMS for high-Q inductors.

Silver Evaporated: Silver electron-beam evaporated in a CHA evaporator at a rate of 0.5 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. A 10-nm adhesion layer of chromium was used under the silver. Silver was found to form a dark tarnish (due to sulfide formation, not oxidation [8]) within days of deposition.

Gold Evaporated: Gold electron-beam evaporated in a CHA evaporator at a rate of 0.5 nm/s. The pressure was below 9×10^{-7} torr at the start of the evaporation. A 10-nm adhesion layer of chromium was used under the gold. Gold, which is an excellent electrical conductor, has many applications in electronics: Because it does not corrode like copper and aluminum, it has been used in mechanical contacts and bond pads. Micromachined switches have employed gold or its alloys. Gold surfaces are wetted well by many solders, but are also rapidly dissolved, so an underlying metal layer (e.g., Ni or Pt) must be used.

G. Metal Alloys and Compound

10 Ti/90 W Ion-Milled: 10% titanium/90% tungsten alloy ion-mill-deposited in a Commonwealth Scientific system with argon ions at 1250 V, current density of about 2 mA/cm^2, $\mathrm{p} = 3 \times 10^{-4}$ torr. This alloy is commonly used as a combination adhesion/diffusion-barrier layer.

80 Ni/20 Cr Evaporated: 80% nickel/20% chromium (at the source) alloy evaporated from a tungsten wire in a Veeco evaporator. Due to their inertness at higher temperature and relatively low thermal conductivity, nickel-chromium alloys have been used for heaters.

TiN Sputtered: Titanium nitride sputtered using in a Varian/Novellus MI2 sputtering system with the recipe $\text{argon} = 55$ sccm, $\text{nitrogen} = 65$ sccm, $\mathrm{P} = 7.2$ kW, $\mathrm{T} = 375\ ^\circ\mathrm{C}$. TiN is used as an adhesion layer.

H. Resists

S1822 Positive Photoresist: Shipley Microposit S1822 positive photoresist, dispensed, and spun at 4600 rpm for 30 s for a thickness of 2.2 μm, soft baked on a hot plate at 115 °C for 60 s, then hard baked in an oven at 110 °C for 30 min $\mathrm{RI} = 1.65$.

OCG Positive 820 Photoresist: OCG (formerly KTI) 820 photoresist, dispensed, and spun at 6000 rpm for 30 s for a thickness of 1.1 μm, soft baked on a hot plate, then hard baked in an oven at 120 °C for 30 min $\mathrm{RI} = 1.65$.

Futurrex Positive Photoresist: Futurrex PR1-4000A photoresist, dispensed, and spun at 2000 rpm for 45 s for a thickness of 4 μm, and soft baked at 120 °C for 90 s on a hot plate (no hard bake was done per the manufacturer's instructions). $\mathrm{RI} = 1.65$. This photoresist is formulated for a slow plasma-etch rate. In SF_6- and CF_4-based plasmas, it was found to barely etch for about 10 min (an "incubation time"), after which it started to etch more rapidly.

Futurrex Negative Photoresist: Futurrex NR5-8000 photoresist, dispensed, and spun at 5000 rpm for 45 s for a thickness of 6 μm, and soft baked at 145 °C for 60 s on a hot plate (no hard bake was done per the manufacturer's instructions). Unlike most photoresists, Futurrex positive and negative photoresists use the same developer.

Action Marker Resist Pen: ITW Dymon Action Marker Fine Line 33 PC-901 Blue resist pen, written onto a wafer and allowed to dry (no bake). This resist pen is convenient for rapidly masking an area or touching up photoresist before a wet or dry etch. It is rapidly stripped in acetone or photoresist stripper. Thicknesses were measured using profilometry.

I. Parylene and Polyimide

Parylene Type C: Parylene Type C deposited using a Specialty Coating Systems Model PDS 2010 Labcoter 2 system by heating the solid source material, the dimer di-para-xylylene, to 175 °C to sublimate it, then heating the dimer vapor to 690 °C to cleave the molecules into the monomer para-xylylene, finally depositing it on the substrate at room temperature and $\mathrm{p} = 25$ mtorr to form a film of the polymer poly-(para-xylylene). Parylene is the trade name of the polymer, given by Union Carbide. $\mathrm{RI} = 1.65$.

There are several types of Parylene: Parylene-N can be envisioned as a polymer of benzene rings with CH_2 groups on opposite ends. Parylene-C has a chlorine atom substituted for one of the hydrogen atoms in the benzene rings, while Parylene-D has two such substitutions. Parylenes are very inert chemically: of the etches tested, Parylene-C only had a significant etch rate in the oxygen plasma and ion mill (it also etched in a separate test in an SF_6 plasma). Deposition is conformal and pinhole-free. Parylenes are also biocompatible and have a relatively low gas permeability. The flexibility of Parylene films has allowed their use in such MEMS applications as miniature valves and wings [9].

Spin-On PI 2556 Polyimide: DuPont PI2556 spin-on polyimide, dispensed, and spun at 4000 rpm for 60 s for a thickness of 1.1 μm, held at 20 °C for 30 min, then baked at 100 °C for 30 min, and finally at 250 °C for 120 min (the manufacturer's instructions call for the last bake to be 300 °C for complete crosslinking). $\mathrm{RI} = 1.82$.

III. ETCH DESCRIPTIONS AND INFORMATION

The wet and dry etches are described below, listed by the abbreviation labels (in italics) in the etch-rate tables. Information about the etch properties is included. Further documentation, including many chemical reactions, was presented previously [3].

A. Wet Etches

Si Iso Etch: Isotropic Silicon Etchant "Trilogy Etch," mixed from 126 parts HNO_3 : 60 parts H_2O : 5 parts NH_4 F). $T \approx 20$ °C (room temperature). This solution should be mixed several hours before use to yield a stable etch rate. Similar commercial preparations are also available. During use, agitation increases uniformity. The solution gets weaker with use. Silicon etching in hydrofluoric acid-nitric acid-water (HF-nitric) and hydrofluoric acid-nitric acid-acetic acid (HNA) etch systems has been well characterized by Schwartz and Robbins [10].

This etchant is intended for isotropically etching silicon, both polycrystalline and single-crystal. It can be used to round off sharp corners formed during orientation-dependent etching and scallops and ridges formed during deep-reactive ion etching (DRIE) to lower the stress concentration of mechanical components. Silicon iso etch was also found to etch graphite, vanadium, niobium, and molybdenum at moderate to very high rates. Due to the small amount of HF formed upon mixing, it also slowly etches silicon dioxide. Photoresist can be normally be used as a mask with this etchant, although two of the resists used in these tests peeled.

Silicon and many metals are etched by the same sequence of steps in HNA etchants: Nitric acid is a powerful oxidizing agent. In nitric acid alone, the silicon or metal is oxidized to form a tough oxide film. The addition of hydrofluoric acid to the solution causes some of these metal oxides to be etched. A representative overall reaction is that for niobium [11]:

$$\mathrm{Nb} + 5\,\mathrm{HNO}_{3(\mathrm{aq})} + 6\,\mathrm{HF}_{(\mathrm{aq})} \rightarrow \mathrm{H}^{+} + \mathrm{NbF}_6^{-} + 5\,\mathrm{NO}_{2(\mathrm{g})} + 6\,\mathrm{H_2O}_{(\mathrm{l})}.$$

KOH: 30% potassium hydroxide (by weight) in water. $T = 80$ °C. This solution can be mixed from solid pellets and water, or from a diluted commercially prepared aqueous solution. It is used for crystal-orientation-dependent etching (ODE) of silicon, for etching n-type silicon to a heavily-doped p-type etch stop, and for electrochemically etching p-type silicon to an n-type etch stop. Data on etch rates at different KOH concentrations and temperatures and different silicon doping levels, as well as etch-stop mechanisms, have been documented by Seidel *et al.* [12], [13]. KOH and other orientation-dependent etches have been summarized by Williams [14].

TABLE VIII
ETCH RATES OF THERMAL OXIDE IN VARIOUS DILUTIONS OF HF AND BHF (nm/min)

Etchant	Thermal Oxide Etch Rate
Conc. HF (49%)	2300
10:1 HF	23
25:1 HF	9.7
100:1 HF	2.3
5:1 BHF	100
10:1 BHF	50

Notation:
BHF = buffered hydrofluoric acid
conc. = concentrated

While KOH is most often used for ODE of single-crystal silicon (SCS), it can also be used for rapid etching of shallow cavities of any shape, if the exact shape at the perimeter is not of concern. KOH has a high etch rate for both polycrystalline silicon and germanium, as well as for heavily ion-implanted SCS that has not been annealed.

KOH was found to etch silicon dioxides, LPCVD silicon nitride, and most of the transition metals tested slowly. High-refractive index PECVD nitride etched sufficiently slowly to be useful as a mask. Aluminum and photoresist were very rapidly etched. KOH is commonly masked with LPCVD silicon nitride, a sandwich of PECVD oxide and nitride (to reduce pinholes), or gold with a chromium adhesion layer.

10:1 HF: Mixed from 10 parts H_2O:1 part 49% HF, by volume. $T \approx 20$ °C (room temperature). HF etches silicon dioxide. Such diluted HF solutions are used to strip thin layers of oxide and native oxide. The solution gets weaker with use. The etch rates of thermal oxide in various dilutions of HF are given in Table VIII. The etch rate is linear with concentration for dilutions in the 10:1 to 100:1 range.

5:1 BHF: Mixed from 5 parts 40% NH_4F:1 part 49% HF, by volume. $T \approx 20$ °C (room temperature). After mixing, buffered hydrofluoric acid (BHF) solutions should sit for several hours to stabilize, as the etch rate will initially be much higher than in equilibrium. Commercial mixes are also available. BHF, also known as buffered oxide etch (BOE), is used for its stable etch rate with use. The etch rates of thermal oxide in 5:1 and 10:1 BHF are also given in Table VIII. The etch rate in 10:1 BHF is exactly half that in 5:1 BHF.

Pad Etch 4: Pad Etch 4 from Ashland is a commercial mix of 11–15%NH_4F + 30–34%CH_3COOH + 47–51%H_2O + 4–8% propylene glycol + surfactant [15]. $T \approx 20$ °C (room temperature). This etchant is formulated to etch through a silicon dioxide dielectric layer, with the etch slowing greatly on aluminum pads or contacts. In these tests pure Al etched only slowly, but a long exposure was found to roughen the surface of Al/2%Si, making it impossible to report an etch rate. Photoresist can be used as an etch mask for Pad Etch.

Phosphoric: Phosphoric Acid (85% by weight), 160 °C. It is one of the few wet etches for silicon nitride. Because it etches photoresist, another masking material, such as oxide, must be used. The etch rates reported here for stoichiometric and silicon-rich LPCVD silicon nitrides are faster than reported earlier [3]. The etch rate is very sensitive to temperature, and this bath was likely a few degrees hotter. Hot phosphoric acid was also found to rapidly etch aluminum.

Al Etch A: Aluminum Etchant Type A from Transene is a commercial mix of 80% H_3PO_4+5% HNO_3+5% CH_3COOH+ 10% H_2O [16]. $T \approx 50$ °C. It is formulated to selectively etch aluminum. It was also found to rapidly etch copper. Photoresist can be used as an etch mask for this etchant.

Ti Etch: Titanium wet etchant is mixed from 20 parts H_2O:1 part 30% H_2O_2:1 part 49% HF, by volume. $T \approx 20$ °C (room temperature). Being a dilute HF solution, this etches oxides relatively slowly. Photoresist can be used as an etch mask for this etchant.

CR-7: Chromium etchant CR-7 from Cyantek is a commercial mix of 9% $(NH_4)_2Ce(NO_3)_6$ + 6% $HClO_4$+H_2O [17]. $T \approx 20$ °C (room temperature). This etchant is formulated to selectively etch chromium, and was also found to etch copper and silver at useful rates. The manufacturer lists its shelf life as 12 months. Photoresist can be used as an etch mask for this etchant.

The chemical reaction for etching Cr is [18]

$$3\mathrm{Ce(IV)(NH_4)_2(NO_3)_{6(aq)}} + \mathrm{Cr_{(s)}} \underset{\mathrm{H^+}}{\rightarrow} \mathrm{Cr(III)(NO_3)_{3(aq)}} + 3\mathrm{Ce(III)(NH_4)_2(NO_3)_{5(aq)}}$$

where the H^+ on the arrow indicates an acidic solution. The Ce^{4+} ions are reduced to Ce^{3+}, while the Cr metal is oxidized to Cr^{3+}. The etch products are soluble, and further reactions may occur in solution [18]. The perchloric acid is a stabilizer for the ceric ammonium nitrate.

CR-14: Chromium etchant CR-14 from Cyantek is a commercial mix of 22% $(NH_4)_2$ $Ce(NO_3)_6$+8% CH_3COOH+H_2O [19]. $T \approx 20$ °C (room temperature). This etchant is also formulated to selectively etch chromium. It was also found to slowly etch vanadium and copper. When molybdenum was etched, it left behind a soft compound. The manufacturer lists its shelf life as 3 months. It etches chromium a little slower than CR-7, but over several years of use we found it to have more a consistent etch rate, as well as much less undercut of photoresist. The etch reaction is the same as for CR-7. The stabilizer is instead acetic acid.

Moly Etch: Molybdenum wet etchant is mixed from 180 parts H_3PO_4:11 parts CH_3COOH:11 parts 70% HNO_3:150 parts H_2O, by volume. $T \approx 20$ °C (room temperature). It can be masked with photoresist, which is etched at a moderate rate.

$H_2O_2$50 °C: Hydrogen peroxide (30% by weight). $T = 50$°C. Hydrogen peroxide targets tungsten, but etches it slowly. Heating increases the etch rate. Ultrasonic agitation (not done here) aids in etch uniformity by helping to remove bubbles. Warm H_2O_2 was also found to slowly etch chromium.

Cu $FeCl_3$ 200: Copper etchant type CE-200 from Transene is a commercial mix of 30% $FeCl_3$ + 3–4% HCl + H_2O [20]. $T \approx 20$ °C (room temperature). When silver was placed in the solution, the film became thicker. CE-200 can be patterned with photoresist.

$FeCl_3$ dissociates in water to generate Fe^{3+} and Cl^- ions. One of the reactions for etching of copper with ferric chloride is [21]

$$\mathrm{Cu_{(s)}} + 2\mathrm{Fe^{3+}} + 3\mathrm{Cl^-} \rightarrow \mathrm{CuCl_3^-} + 2\mathrm{Fe^{2+}}.$$

Other chloride complexes are also formed. The Fe^{3+} ions are reduced to Fe^{2+}, which remain in solution, while the copper metal is oxidized to Cu^{2+}. HCl assists in the dissolution of the ferric chloride, and also etches copper itself [21]. The manufacturer recommends rinsing in a 5–10% HCl solution after etching (not done here) before a final water rinse.

Cu APS 100: Copper etchant APS 100 from Transene is a commercial mix of 15–20% $(NH_4)_2$ S_2O_8 + H_2O [22]. $T = 30$ °C. Photoresist can be used as an etch mask for this etchant. The overall reaction for ammonium persulfate etching of copper is [21]

$$\mathrm{Cu_{(s)}} + \mathrm{(NH_4)_2S_2O_{8(aq)}} \rightarrow \mathrm{CuSO_{4(aq)}} + \mathrm{(NH_4)_2SO_{4(aq)}}.$$

Dil. Aqua Regia: A diluted solution of aqua regia mixed from 3 parts 37% HCl:1 part 70% HNO_3:2 parts H_2O (standard aqua regia does not have the additional water). The solution is self heating to about 30 °C for tens of minutes for the shallow dish used in these tests. The water was added to the standard aqua regia solution to reduce the attack of photoresist. Aqua regia targets noble metals. In these tests, it was found to etch gold and palladium, but only slowly etch platinum (heating is require for a useful etch rate of Pt). It was also found to etch nickel, copper, molybdenum, and aluminum. Because the HCl evaporates off when left open, it should be mixed just before use.

Gold reacts with chlorine, bromine, and iodine at elevated temperatures to form the corresponding halides, but reacts only slowly with fluorine [23]. At room temperature, the nitric acid in aqua regia is an oxidizing agent, while the addition of hydrochloric acid provides nascent chlorine to form a soluble etch product. Similar overall reactions are given in the literature [8] and [23], including [24]

$$\mathrm{Au_{(s)}} + 4\mathrm{H^+} + \mathrm{NO_3^-} + 4\mathrm{Cl^-} \rightarrow \mathrm{AuCl_4^-} + \mathrm{NO_{(g)}} + 2\mathrm{H_2O_{(l)}}.$$

The HCl in aqua regia can be replaced with HBr or HI [23], but not HF [8], as gold does not form a soluble fluoride [25]. Thus, HF-nitric solutions such as the silicon isotropic etch do not etch gold.

AU-5: Gold etchant AU-5 from Cyantek is a commercial mix of 5% I_2 + 10% KI+85% H_2O [26]. $T \approx 20$ °C (room temperature). It is formulated to selectively etch gold. Such iodine solutions are the color of dark coffee, making it impossible to observe a submerged sample. Rinsing with running water must be done to remove the solution from the surface. Isopropanol or methanol can be used for a faster rinse [18]. AU-5 can be patterned with photoresist. Rather than etching palladium, silver, and copper, it formed a compound that increased the film thickness above that of the original metal.

The overall reaction for etching gold is [18]

$$2\mathrm{Au}_{(\mathrm{s})} + \mathrm{I}_{2\,(\mathrm{aq})} \rightarrow 2\mathrm{AuI}_{(\mathrm{aq})}.$$

The potassium iodide increases the solubility of both the iodine and gold(I) iodide in water [18], [27], allowing a greater concentration of reactant in the solution and the etch product to be removed so that the etch can proceed.

NiCr TFN: Nichrome etchant TFN from Transene is a commercial mix of 10–20% $(NH_4)_2$ $Ce(NO_3)_6$)+5–6% HNO_3+H_2O) [28]. $\mathrm{T} \approx 20\ ^\circ\mathrm{C}$ (room temperature). It is formulated to etch nickel-chromium alloy. It etched pure nickel slowly, but etched chromium, copper, and molybdenum faster than the NiCr alloy. Photoresist can be used as an etch mask for this etch.

Phos + Sulf: A mix of 1 part 96% H_2 SO_4:1 part 85% H_3 PO_4. $\mathrm{T} = 160\ ^\circ\mathrm{C}$. This solution is listed as an etchant for sapphire [1], [2], but did not etch it even at this high temperature.

Piranha: The Piranha (also known as sulfuric-peroxide) used here is a mix of ~50 parts 96% H_2SO_4:1 part 30% H_2O_2. $\mathrm{T} = 120\ ^\circ\mathrm{C}$. The hydrogen peroxide is added just before use. It is used as a cleaning solution that strips organics and some metals. In these tests, it was indeed found to etch photoresist, the resist pen, and polyimide very rapidly, but only slowly attacked the Parylene C. It also etched aluminum, nickel, and silver rapidly. Chromium was etched slowly, which allows it to be used for the cleaning of photomasks.

Microstrip: Arch Microstrip 2001 is a commercial photoresist stripper mixed from 45–55% n-methyl pyrrolidone and 40–55% 2-(2-aminoethoxy)ethanol [29]. $\mathrm{T} = 85\ ^\circ\mathrm{C}$. It is formulated to strip resists without affecting structural materials. In these tests, it very rapidly removed the photoresists and the resist pen, while etching the polyimide at a moderate rate and not etching graphite.

Acetone: Pure acetone, also known as dimethyl ketone. It is used to strip photoresist and for cleaning off organics. It removed photoresists rapidly, as expected, but did not etch polyimide.

Methanol: Pure methanol. It is used for cleaning and in supercritical drying. Like acetone, methanol removed photoresist, but did not etch polyimide.

Isopropanol: Pure isopropanol, also known as isopropyl alcohol (IPA) and 2-propanol. It is used for cleaning off organics. In contrast to methanol, isopropanol was found to remove photoresist at a moderate rate.

B. Dry Etches

Most dry etches employ a plasma to generate reactive species, but several plasmaless-vapor-phase etches have been used in the fabrication of MEMS.

XeF_2, 2.6 mtorr, Homemade Chamber: Xenon difluoride gas (no plasma) from a solid source at its full vapor pressure at room temperature. It targets silicon, as well as metals that form volatile fluorides such as Ti, W, Mo, and Ta [30]. It does not etch silicon dioxide, aluminum, or photoresist, and only slowly etches silicon nitride. Commercial XeF_2 etchers are now available. Other noble-gas fluorides have also been used to etch silicon [14].

HF Vapor Over Dish: HF+H_2O vapor evaporated at room temperature from liquid 49% HF/H_2O, with wafer continuously exposed ~1 cm over the dish. Like liquid HF, HF vapor targets silicon dioxides. Continuous exposure to the vapor results in droplet condensation on the wafer after about 25 s at room temperature, with the underlying areas having higher oxide etch rate. "Pulsed" etching, in which the wafer is alternately held over the liquid for 15 s, then removed and optionally heated for 15 s, eliminates droplet formation. Simply heating the wafer while over the HF/H_2O also inhibits condensation, while still allowing etching to occur. In these tests, photoresist survived etching, but peeled when rinsed.

Manual vapor etching of oxide is particularly useful in cases where fragile structures cannot tolerate loading into a plasma etcher and where high selectivity is needed. Other users of this etch have found a nonvolatile residue left behind when doped oxides such as PSG [31] or silicon oxynitride [32] are exposed to HF vapor. Titanium and copper have been found to form nonvolatile fluoride layers [31]. While we found aluminum to be attacked, it has also been found to form a thick fluoride film when anhydrous HF + H_2O was used under more controlled conditions [31]. Commercial HF-vapor etchers are now available.

Technics O_2: Technics West PE II-A plasma etcher using the recipe O_2 $\mathrm{flow\ rate} \approx 51$ sccm, power $(\mathrm{P}) = 400$ W at 30 kHz, pressure $(\mathrm{p}) \approx 300$ mtorr. Oxygen plasmas are used for stripping and descumming photoresist, as well as cleaning off other organics. In these tests, the photoresists, Parylene, and polyimide etched at about the same rate, but the graphite was not etched.

DRIE HF Mech: Surface Technology Systems (STS) Advanced Silicon Etch (ASE) inductively coupled plasma DRIE tool, using a typical Bosch-process recipe for nearly vertical trenches with high platen frequency [33], [34]: etch for 6 s with $\mathrm{SF_6} = 80$ sccm, coil $\mathrm{P} = 600$ W at 13.56 MHz, platen $\mathrm{P} = 12$ W at 13.56 MHz, $\mathrm{p} \approx 12$ mtorr; then passivate for 5 s with $\mathrm{C_4F_8} = 80$ sccm, coil $\mathrm{P} = 600$ W at 13.56 MHz, platen $\mathrm{P} = 0$ W, $\mathrm{p} \approx 8$ mtorr. The etching and passivation steps are alternated. The platen structure has 20 °C coolant flowing through it, while the wafer heats to about 65 °C during an etch. The wafer clamping in this particular etcher, required due to backside helium pressure for improved heat transfer, is mechanical.

This etcher and recipe are designed for deep, near-vertical etching of silicon. The etch rate of silicon is a strong function of the area of silicon exposed and the trench aspect ratio (depth/width) for deep etches, slowing with increases in each. The etch rate also tends to be noticeably slower at the center of the wafer. In these tests, a higher-than-typical area of ~50% was exposed. Due to a relatively short etch time, only shallow trenches were formed. Experience with several such etchers and chucks (with either mechanical or electrostatic wafer clamping) shows that the etch rate and profile are highly variable with equipment. Recipes are usually not transferable from one machine to another and can be affected by seemingly small changes in the setup of an etcher.

Photoresist and oxide have been used as masks for DRIE. These tests confirmed very high selectivity of etching silicon over photoresist and silicon dioxide, and also found high selectivity over silicon nitride. The manufacturer recommends not using metal masks. Several metals with volatile fluorides were tested and found to etch slowly with this recipe.

DRIE HF ES: Surface Technology Systems ASE inductively coupled plasma DRIE tool, using a typical Bosch-process recipe for nearly vertical trenches with high platen frequency: etch for 9 s with $\mathrm{SF_6} = 130$ sccm, $\mathrm{O_2} = 13$ sccm, coil $\mathrm{P} = 600$ W at 13.56 MHz, platen $\mathrm{P} = 12$ W at 13.56 MHz; then passivate for 7 s with $\mathrm{C_4F_8} = 85$ sccm, coil $\mathrm{P} = 600$ W at 13.56 MHz, platen $\mathrm{P} = 0$ W; $\mathrm{APC} = 66\%$; with electrostatic wafer clamping.

DRIE LF Mech: Surface Technology Systems ASE inductively coupled plasma DRIE tool, using a typical low-platen frequency, stop-on-oxide recipe for nearly vertical trenches [35]: etch for 5 s with $\mathrm{SF_6} = 125$ sccm, coil $\mathrm{P} = 600$ W at 13.56 MHz, platen $\mathrm{P} = 30$ W at 380 kHz pulsed on and off on the order of 10 milliseconds (the exact timing is proprietary), $\mathrm{p} \approx 28$ mtorr; then passivate for 6.7 s with $\mathrm{C_4F_8} = 150$ sccm, coil $\mathrm{P} = 600$ W at 13.56 MHz, platen $\mathrm{P} = 0$ W, $\mathrm{p} \approx 28$ mtorr; with mechanical wafer clamping.

DRIE LF ES: Surface Technology Systems ASE inductively coupled plasma DRIE tool, using a typical low-platen frequency, stop-on-oxide recipe to greatly reduce notching, for nearly vertical trenches: etch for 8 s with $\mathrm{SF_6} = 80$ sccm, coil $\mathrm{P} = 600$ W at 13.56 MHz, platen $\mathrm{P} = 30$ W at 380 kHz pulsed on and off on the order of milliseconds (the exact timing is proprietary), $\mathrm{p} \approx 12$ mtorr; then passivate for 5 s with $\mathrm{C_4F_8} = 80$ sccm, coil $\mathrm{P} = 600$ W at 13.56 MHz, platen $\mathrm{P} = 0$ W, $\mathrm{p} \approx 8$ mtorr; with electrostatic wafer clamping.

STS 320 SF_6: Surface Technology Systems 320 parallel-plate RIE tool, using the recipe $\mathrm{SF_6} = 25$ sccm, $\mathrm{P} = 100$ W at 13.56 MHz, $\mathrm{p} = 20$ mtorr. The driven electrode area is about 900 cm^2. This etch targets silicon, silicon nitride, and transition metals with volatile fluorides. Photoresist can be used as an etch mask for this etch.

STS SF_6+O_2: Surface Technology Systems 320 parallel-plate RIE tool, using the recipe $\mathrm{SF_6} = 25$ sccm, $\mathrm{O_2} = 10$ sccm, $\mathrm{P} = 100$ W at 13.56 MHz, $\mathrm{p} = 20$ mtorr. The driven electrode area is about 900 cm^2. This etch targets silicon, silicon nitride, and transition metals with volatile fluorides. The addition of oxygen increases the etch rate of the target materials, but also increases the etch rate of the photoresist, which can reduce the selectivity.

STS 320 CF_4: Surface Technology Systems 320 parallel-plate RIE tool, using the recipe $\mathrm{CF_4} = 25$ sccm, $\mathrm{P} = 100$ W at 13.56 MHz, $\mathrm{p} = 60$ mtorr. The driven electrode area is about 900 cm^2. This etch targets silicon dioxide, which can be patterned with photoresist or a nonvolatile metal such as chromium. This recipe results in fluorocarbon polymer buildup on the chamber walls and a reduced etch rate over time. A small amount of fluorocarbon residue left on the wafer can affect the later formation of electrical contacts if it is not removed.

TABLE IX
ETCH RATES OF GOLD DEPOSITED BY THREE METHODSIN TWO ETCHANTS (nm/min)

Etchant	Ion-Milled Gold (at 1000 V)	Evaporated Gold (at 0.5 nm/s)	Electroplated Gold ($\mathrm{NaAuSO_3}$, 40 mA/cm2)
Cyantek AU-5	490	660	560
Dilute aqua regia	530	680	1000

STS CF_4+O_2: Surface Technology Systems 320 parallel-plate RIE tool, using the recipe $\mathrm{CF_4} = 25$ sccm, $\mathrm{O_2} = 5$ sccm, $\mathrm{P} = 100$ W at 13.56 MHz, $\mathrm{p} = 60$ mtorr. The driven electrode area is about 900 cm^2. $\mathrm{CF_4}$-based etches typically target silicon dioxide, but this etch was found to etch silicon nitride and silicon even faster than oxide. The addition of oxygen in this recipe increases the oxide etch rate but also increases the photoresist etch rate, significantly reducing the selectivitiy. The oxygen also reduces fluorocarbon polymer buildup on the chamber walls, yielding a more stable etch rate over time.

Ion Mill: Commonwealth Scientific ion mill, ion milling with argon ions at 500 V, current density of ~ 1 $\mathrm{mA/cm^2}$, chamber $\mathrm{p} = 2 \times 10^{-4}$ torr, at an angle normal to the wafer. Ion milling with an inert gas such as argon is a purely physical process, so any material can be etched by this method. The surface of unpatterned S1822 photoresist became wavy after a 10-min etch but retained most of its thickness, so this photoresist may not be a useable masking material.

C. Etch-Rate Variation

Many reasons for etch-rate variation were enumerated earlier [3], [14]. One of the most significant is the properties of the material, which are a result of the production method and subsequent processing (e.g., annealing). This is apparent by inspection of Table III: materials that are primarily silicon dioxide have widely varying etch rates in 5:1 BHF and other etchants.

As another demonstration of the effect of deposition conditions, gold was deposited using three different methods: ion milling and evaporation, as described in Section II, and by electroplating from a sodium gold sulfite bath at current density of 40 $\mathrm{mA/cm^2}$. The etch rates in the AU-5 and dilute aqua regia solutions are given in Table IX. Ion-milled gold, which is the densest, has the lowest etch rate in both etchants. Electroplated gold, known for having a lower density than the bulk metal, has a significantly higher etch rate in dilute aqua regia.

Another example of etch-rate variation with material deposition method is given in Table X. PECVD silicon nitride was deposited using the recipe described in Section II, but with varying flow rates of 2% $\mathrm{SiH_4}$/Ar. For the lowest silane flow rates, the silicon content is probably lowest, which agrees with the low index of refraction. These films have the highest etch rates in 10:1 BHF. Higher silane flow rates yield increasingly higher indexes of refraction and lower etch rates. The lowest etch rate, 2.5 nm/min, is still much faster than for LPCVD silicon nitride (which has much less hydrogen).

TABLE X
PECVD SILICON NITRIDE INDEXES OF REFRACTION AND ETCH RATES IN 10:1 BHF (nm/min)

2% Si in Ar (sccm)	Index of Refraction	Etch Rate in 10:1 BHF (nm/min)
70	1.83	11
100	1.88	7.3
200	2.03	4.3
500	2.53	2.7
750	2.57	2.8
1000	2.67	2.5

IV. ETCH-RATE MEASUREMENT TECHNIQUES

All films were coated onto 100-mm silicon wafers. The transparent films, opaque films, and wafer substrates required different measurement techniques.

Most of the data presented here has not been reported before. In the cases in the tables for which new data was not taken, etch rates were transferred from our earlier paper [3]. In case of discrepancies, the newer data is reported. Most of the ion-mill data for the elements is from Commonwealth Scientific [36] and agrees with our few measurements. This outside data is included due to the usefulness of this tool.

Measured etch rates are rounded to two significant figures.

A. Transparent Films

The transparent films in these tests are polycrystalline silicon, silicon dioxide, silicon nitride, alumina, photoresist, parylene, and polyimide. Refractive indexes (RIs) were measured with a Gaertner Scientific ellipsometer at 632.8 nm for most films (the RI of polysilicon is already known). These RIs were used in interferometric thickness measurements using a NanoSpec AFT tool. Polycrystalline silicon was deposited on a wafer that already had 100 nm of thermal oxide to give reflections that could be detected by the NanoSpec.

To reduce the number of samples to be prepared, some wafers were divided into quarters. For wet etches and dry etches with manual wafer loading, the quarter wafers were used. At least three thickness measurements were made before and after etching. Etching was done without masking. For dry etches with automatic wafer loading, a whole wafer was used and five points were measured. The average thickness difference, divided by the time, gives the etch rate.

B. Opaque Films and Wafers

The opaque films used in these tests are graphite, the metals, titanium nitride, and the resist pen. Ge and SiGe films, while not opaque, were measured with this group. The wafers are single-crystal silicon, fused quartz, Pyrex 7740, and sapphire. These samples could not be measured by the simpler interferometric method, and a calibrated Dektak II profilometer was used. In most cases, the wafer had photoresist applied and patterned, with about 50% of the wafer area exposed. In a few cases, the resist pen was used to make a mask. For testing the photoresists and resist pen themselves, the photoresist was patterned and ink was simply drawn onto a wafer known not to etch. For cases in which the etchant is known to rapidly etch photoresist (e.g., in KOH and Piranha), a mask of evaporated Cr/Au was used. For cases in which a silicon wafer is known to etch rapidly (e.g., in silicon isotropic etchant and KOH), the wafers were first coated with LPCVD silicon nitride to protect both sides.

Etches were performed, the photoresist (or Cr/Au) was stripped off, and at least three step heights were measured. The average step height divided by the time gives the etch rate.

For very rapid etches, step heights were measured where the removal of Kapton tape after deposition had left a blank spot on the wafer. The materials were etched until visibly gone and the time recorded. The initial thickness divided by the time gives the etch rate.

C. Etch Times

Etching times were selected to give a thickness change typically in the range of 0.1 to 1 μm to give good confidence to the results.

As expected, however, many samples etched very slowly. In these cases, the etches were performed for at least 20 min to give a reasonable step height or interferometric thickness change, if any. For the samples measured by profilometer, when it was impossible to see a clear step amidst the roughness, an upper limit of etch rate (e.g., <2 nm/min) is given. This is calculated by dividing the roughness by the etch time.

In some other cases, the etch was so rapid (e.g., photoresist in Piranha and acetone) that it was impossible to tell exactly when the film was gone due to clouds or bubbles blocking view of the film. For these cases, a lower limit of the etch rate is reported (e.g., $>92\,000$ nm/min). This is calculated by dividing the initial thickness by the time at which the clouds or bubbles had dissipated enough to view the cleared wafer.

V. ETCH-RATE RESULTS AND DISCUSSION

Etch rates were reported in Tables II–VII. Selectivities can readily be calculated from these data.

Not all materials were etched in all etchants due to time limitations and contamination concerns with the plasma etchers. Certain materials commonly used in micromachining were considered key materials (undoped polysilicon, thermal silicon dioxide, stoichiometric LPCVD silicon nitride, Al/2%Si, chromium, and S1822 photoresist) and were etched in most etchants in order to determine their compatibility. Similarly, certain etches (isotropic silicon etchant, potassium hydroxide, 5:1 BHF, CR-7 chromium etchant, Piranha, ion milling, and SF_6+O_2, and CF_4+O_2 plasmas) were considered to be key etchants and most materials were etched in them.

One of the realities of putting materials in etchants intended to etch a different material is that a clear result is not attained. In many cases materials were roughened, but little etching apparently occurred. The degree of roughening probably depends on the microstructure (i.e., grain size and dislocation density) and thus varies with the method of material preparation.

At the bottom of Table I is a summary of the letter notations used in the tables. In cases where etch rates were not measured by the authors, but the etches are known from experience with similar materials or from the literature to *work*, be relatively *fast* (faster than ~500 nm/min), or be *slow* (slower than ~10 nm/min) or have zero etch rate, the notations W, F, or S, respectively, are used. If the film was *roughened* or attacked, the notation is R. This may include an upper limit of etch rate (e.g., <1 nm/min) if an exact value could not be determined. If the film was *thicker* after being exposed to the etch, the notation is T. This occurred with the photoresists absorbing some of the liquid and swelling, and in other cases in which an insoluble compound formed. If the film *peeled* during the etch or rinsing, the notation is P. Some etches initially had a very slow etch rate during an "*incubation time*," and are so noted by I. Films that *congealed* are noted with C. Films that remained after exposure to the etch, but were *soft* have a notation of *soft*.

A. Discussion of the Etches

Intended uses of the etches and specific information about the materials were given in Sections II and III. More general observations are given here.

KOH did not appreciably etch most of the transition metals and the silicon nitrides, and had a zero etch rate for Mo, W, Ni, Pd, Pt, and Au. These might be used in micromachining as structural materials, with the underlying silicon substrate being removed in KOH.

The HF solutions, 5:1 BHF and 10:1 HF, did not appreciably etch most of the transition metals, and had a zero etch rate for Nb, Cr, Ta, Pd, Pt, and Au. The exception is Ti, which etches even faster than the silicon dioxides in 10:1 HF. Thus, Cr, 10 Ti/90 W, or TiN should be used rather than Ti as an adhesion layer in the presence of HF. The metals with a slow HF etch rate might be used in surface micromachining as structural materials, with silicon dioxide being the sacrificial layer.

Piranha removed most metals at moderate to fast rates. Nb, Ta, Cr, Mo, Pd, Au, and 10 Ti/90 W were etched only slowly (Au not at all), allowing the use of Piranha for cleaning with these metals present.

Microstrip 2001 and acetone dissolved the resists tested rapidly. Methanol removed some resists and made a mess of others, causing them to peel or congeal. Isopropanol had much less effect, with the slow removal of resist.

The oxygen plasma only etched the organics, but did not measurably etch graphite.

The STS DRIE's etched silicon and germanium much faster than the oxides, nitrides, and photoresists, making the latter useful as masking layers. The transition metals tested, all of which have volatile fluorides, etched only slowly.

The SF_6+O_2 plasma etch etched silicon the fastest, the silicon nitrides at a moderate rate, and the silicon dioxides slowly. Moderate etch rates were also measured for Mo and 10 Ti/90 W. Other metals, which do not have volatile etch products, were removed slowly due to sputtering.

The CF_4+O_2 plasma etched the silicon nitrides faster than silicon or oxide, but at only a moderate rate. For the metals tested, molybdenum had a moderate etch rate, and other metals again were removed slowly due to sputtering.

Ion milling can remove any material due to its purely physical nature, and is thus thought often of as having roughly the same etch rate for different materials. The data, however, show that there actually is a wide range of etch rates such that some materials can be used as etch masks for others. Graphite is etched very slowly. The metals Ag, Au, Pd, Cu, and Pt are all etched more than 20 times faster.

B. Discussion of the Materials

Changes in the deposition method of pure materials, as well as the addition of small amounts of impurities, tend to produce much greater differences in etch rate for wet etchants than for plasma etching. Comparing the etch rates of the various silicon nitrides in the 5:1 BHF and SF_6+O_2 plasma illustrates this point, with the ratio of fastest- to slowest-etching nitride in BHF being 46, but only 1.3 for the plasma etch. Comparing the etch rates of the many silicon dioxide samples in 5:1 BHF and in $CF1_4+O_2$ plasma gives similar results.

PECVD oxides and nitride etch faster in most etchants than their LPCVD counterparts. Annealing both PECVD and LPCVD oxides reduces the etch rate in HF solutions. Annealed LTO has similar etching properties to thermal oxide.

Unlike sapphire, the aluminum oxide films were etched in most of the wet etchants tested.

Samples of patterned Cr on top of Au were produced to study a possible electrochemical effect. This Cr etched slower in CR-7, but faster in CR-14, as compared to evaporated Cr on Si. In this particular test, Cr on Au peeled off in 5:1 BHF, but we have successfully used Cr as an adhesion layer for Au in surface-micromachined devices in which the Cr was exposed.

Silver grew thicker in AU-5 and in Cu $FeCl_3$ 200 etchant, perhaps due to the formation of insoluble compounds such as AgI.

Metals deposited by evaporation, in which the atoms forming the film arrive with low energy, tend to etch faster than the denser films deposited by sputtering and by ion milling, with high-incident-energy atoms.

TiN became soft in silicon isotropic etchant. Titanium became soft in KOH. Molybdenum became soft in CR-14. The etch rates reported are based on the difference between the initial thickness and the thickness of the remaining material.

Polyimide stands up to wet etchants better than the resists, but has similar etch rates in the plasma etches. Parylene-C did not etch appreciably in the wet etchants.

VI. CONCLUSION

The data in the tables show useful etchants for most materials, as well as indicating in which etchants the materials will survive. They can also be used to calculate selectivities to choose masking layers should photoresist not be sufficient.

For surface micromachining, the traditional system of materials and etchant is a structural material of polysilicon, an underlying layer of polysilicon, a sacrificial layer based on silicon dioxide, silicon nitride, or silicon wafer, and an HF-based etchant. These data show that a number of other materials might be substituted as the structural layer: LPCVD silicon nitride, V, Nb, Ta, Cr, Mo, W, Pd, Pt, Cu, Ag, Au, 90 Ti/10 W, 80 Ni/20 Cr, or polyimide. For bulk micromachining of a silicon wafer with KOH to leave a freestanding film, many of the same materials might be used: silicon nitride, Nb, Ta, Cr, Mo, W, Ni, Pd, Pt, and Au. Other systems might be used, such as a sacrificial layer of Al etched with Aluminum Etchant Type A, and a structural layer of PECVD silicon dioxide, Ti, or Cr. Another possibility is a sacrificial layer of polysilicon or single-crystal silicon etched with XeF_2, and a structural layer of SiO_2, Au, or Pt. Many more systems can be deduced from the data.

Alternative materials systems for MEMS will be of interest in the future for many reasons: A previously unused structural material will be desired, for example, for its chemical inertness, for its high or low Young's modulus, for its high or low thermal conductivity, for its low deposition temperature, or for its biological compatibility. These data will aid in selecting appropriate etchants, substrates, and coexisting materials.

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