Wet-Chemical Etching and Cleaning of Silicon

January 2003

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A Introduction

Research and manufacturing related to silicon devices, circuits, and systems often relies on the wet-chemical etching of silicon wafers. The dissolution of silicon using liquid solutions is needed for deep etching and micromachining, shaping, and cleaning. Also, wet-chemistries are often used for defect delineation in single crystal silicon materials. In this paper, a review of the typical wet-chemical recipes used by engineers is given. As many sources as possible have been used to present a concise listing of etchants and processes.

B Wafer Cleaning

A sequence of chemistries is typically used to clean silicon wafers. This sequence was first developed at the RCA laboratories, and is therefore often referred to as the RCA process. This chemical sequence does not attack the silicon material, but selectively removes the organic and inorganic contamination that resides on the wafer surface. The following is a typical RCA process; many variations to the ordering of the sequence and chemical ratios are used throughout the industry.

- General Clean: A general cleaning is accomplished by using a mixture of Sulfuric Acid and Hydrogen Peroxide. Mixing these chemicals is dangerous and generates extreme heat. This industry standard clean removes organic and inorganic contamination from the wafer. 2-10 minute clean is recommended. Strong rinse in DI water is required after this cleaning step.
- Particle Removal: A Megasonic clean (at about 70 C) in a 5:1:1 ratio mixture of DI water: Ammonium Hydroxide : Hydrogen Peroxide will remove silica and silicon particles from the wafer, as well as remove certain organic and metal surface contamination. 2-10 minute clean is recommended. Strong rinse in DI water is required after this cleaning step.
- Oxide Removal: A 15-60 second dip in 1:20 HF:DI water will remove the native oxide layer and any contamination in the oxide from the wafer surface. HF is extremely dangerous and must be handled with great care. Strong rinse in DI water is required after this cleaning step.
- Metal Contamination Removal: A Megasonic clean (at about 70 C) in a 6:1:1 ratio mixture of DI water: HCL : Hydrogen Peroxide will remove certain ionic and metal surface contamination. 2-10 minute clean is recommended. Strong rinse in DI water is required after this cleaning step.
- Spin Rinse Dry: Wafers should be rinsed and dried in a standard spin-rinse dryer.

Megasonic agitation is commonly used with the chemical bath and most commonly with the particle removal step. Also, heavy DI rinse steps are used between each chemical treatment. DI rinsing may use dump-baths, over-flow baths, and spray-dump baths, as well as combinations. Proper removal of all cleaning chemistry with 18MegaOhm DI water is critical and needed after each chemical bath. Any text book on the topic of semiconductor or silicon processing is an excellent resource for further information regarding the RCA cleaning process (for example see S.Wolf and R. Tauber, "Silicon Processing:Vol.1", Lattice Press, CA, 1986).
There are commercially available premixed cleaning solutions that can be used directly to clean wafers and serve the same purpose of the RCA cleaning process. These chemicals typically achieve the function of several cleaning steps with one solution (see for example JT Baker, Baker Clean Solution).

C Anisotropic KOH Etching

KOH is one the most commonly used silicon etch chemistry for micromachining silicon wafers.

1. Anisotropic KOH Etching Rates vs. Orientation

The KOH etch rate is strongly effected by the crystallographic orientation of the silicon (anisotropic). Table 1 relates silicon orientation-dependent etch rates (µm min^{-1}) of KOH to crystal orientation with an etching temperature of 70°C. Table 1 is taken directly from [1]. In parentheses are normalized values relative to (110).

Crystallographic Orientation	Rates at different KOH Concentration		
	30%	40%	50%
(100)	0.797 (0.548)	0.599 (0.463)	0.539 (0.619)
(110)	1.455 (1.000)	1.294 (1.000)	0.870 (1.000)
(210)	1.561 (1.072)	1.233 (0.953)	0.959 (1.103)
(211)	1.319 (0.906)	0.950 (0.734)	0.621 (0.714)
(221)	0.714 (0.491)	0.544 (0.420)	0.322 (0.371)
(310)	1.456 (1.000)	1.088 (0.841)	0.757 (0.871)
(311)	1.436 (0.987)	1.067 (0.824)	0.746 (0.858)
(320)	1.543 (1.060)	1.287 (0.995)	1.013 (1.165)
(331)	1.160 (0.797)	0.800 (0.619)	0.489 (0.563)
(530)	1.556 (1.069)	1.280 (0.989)	1.033 (1.188)
(540)	1.512 (1.039)	1.287 (0.994)	0.914 (1.051)
(111)	0.005 (0.004)	0.009 (0.007)	0.009 (0.010)

The (110) plane is the fastest etching primary surface. The ideal (110) surface has a more corrugated atomic structure than the (100) and (111) primary surfaces. The (111) plane is an extremely slow etching plane that is tightly packed, has a single dangling-bond per atom, and is overall atomically flat. As shown above, the strongly stepped and vicinal surfaces to the primary planes are typically fast etching surfaces.

2. KOH Etching Rates vs. Composition and Temperature

Table 2 relates silicon orientation-dependent etch rates of KOH to percent composition, temperature, and orientation. Table 2 is taken directly from [2]. As with all wet-chemical etching solutions, the dissolution rate is a strong function of temperature. Significantly faster etch rates at higher temperatures are typical, but less ideal etch behavior is also common with more aggressive etch rates. Also, heavy boron doping can significantly harden the silicon and sharply reduce the etch rate.

Etchant	Temperature (°C)	Direction (plane)	Etch rate (µm min^{-1})	Remarks	Reference
20% KOH: 80% H_2O	20	(100)	0.025	Near Peak etch rate at the conc. across temperature	[3]
	40	(100)	0.188		
	60	(100)	0.45		
	80	(100)	1.4		
	100	(100)	4.1		
30% KOH: 70% H_2O	20	(100)	0.024	Smoother surfaces than at lower concentration	[3]
	40	(100)	0.108		
	60	(100)	0.41		
	80	(100)	1.3		
	100	(100)	3.8		
	20	(110)	0.035		
	40	(110)	0.16		
	60	(110)	0.62		
	80	(110)	2.0		
	100	(110)	5.8		
				Faster etch rate for (110) than for (100)	
40% KOH: 60% H_2O	20	(100)	0.020		[3]
	40	(100)	0.088		
	60	(100)	0.33		
	80	(100)	1.1		
	100	(100)	3.1		
20% KOH: 80% 4 H_2O: 1 IPA)	20	(100)	0.015	Lower etch rate Smoother Less undercutting Lower (100) : (111) etch-rate ration	[3]
	40	(100)	0.071		
	60	(100)	0.28		
	80	(100)	0.96		
	100	(100)	2.9		
44% KOH: 56% H_2O	120	(100)	5.8	High Temperature	[4]
		(110)	11.7		
		(111)	0.02		

23.4% KOH: 63.3% H_2O: 13.3% IPA	80	(100) (110)	1.0 0.06	Sensitive to boron concentration	[5]

D Anisotropic TMAH (tetramethylammonium hydroxide) Etching

Similar to KOH etching, TMAH is commonly used for fast removal and silicon micromachining.

1. TMAH Etching Rates vs. Orientation

The orientation dependence of the TMAH etch rate is similar to KOH and varies similarly in accordance to the atomic organization of the crystallographic plane. Table 3 relates silicon orientation-dependent etch rates of TMAH (20.0wt%, 79.8°C) to orientation. Table 3 is taken directly from [6].

Orientation	Etching rate (μm min^{-1})	Etching rate ratio	
		(i j k)/(100)	(i j k)/(111)
100	0.603	1.000	37
110	1.114	1.847	68
210	1.154	1.914	70
211	1.132	1.877	69
221	1.142	1.894	69
310	1.184	1.964	72
311	1.223	2.028	74
320	1.211	2.008	73
331	1.099	1.823	67
530	1.097	1.819	66
540	1.135	1.882	69
111	0.017	0.027	1

2. TMAH Etching Rates vs. Composition and Temperature

Similar to KOH, the TMAH etch rate varies exponentially with temperature. Table 4 relates silicon orientation-dependent etch rates of TMAH to percent composition, temperature, and orientation. Table 4 is taken directly from [2].

Etchant	Temperature (°C)	Direction (plane)	Etch rate (µm min^{-1})	Remarks	Resources
5% TMAH: 95% H_20	60	(100)	0.33		[7]
	70		0.48		
	80		0.87		
	90		1.4		
	60	(110)	0.64		
	70		0.74		
	80		1.4		
	90		1.8		
	60	(111)	0.026		
	90		0.034		
10% TMAH: 90% H_20	60	(100)	0.28		[7]
	70		0.41		
	80		0.72		
	90		1.2		
2% TMAH: 98% H_20	80	(100)	0.65		[8]
		(111)	0.41		
5% TMAH: 95% H_20	80	(100)	0.63		[8]
		(111)	0.013		
10% TMAH: 90% H_20	80	(100)	0.57		[8]
		(111)	0.014		
22% TMAH in H_20	90	(100)	0.9	(110) is fastest without surfactant	[9]
		(110)	1.8		
		(111)	0.018		
22% TMAH in H_20 + 0.5% surfactant	90	(100)	0.6	(100) is fastest with surfactant	[9]
		(110)	0.12		
		(111)	0.01		
22% TMAH in H_20 + 1% surfactant	90	(100)	0.6	Surfactants effect saturates	[9]
		(110)	0.1		
		(111)	0.009		

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E EDP

Similar to KOH, EDP is often used for fast removal and silicon micromachining. Table 5 relates silicon orientation-dependent etch rates in EDP solutions to Temperature and Orientation.

Etchant	Temperature (°C)	Direction (plane)	Etch rate	Remarks	Reference

			(µm min^{-1})		
500 ml $NH_2(CH_2)_2NH_2$: 88g $C_6H_4(OH)_2$: 234 ml H_20	110	(100) (110) (111)	0.47 0.28 0.028	EDP ‘T’ etch Oldest EDP formula ER rises to > 0.83 µm/min after exposure to oxygen	[10]
500 ml $NH_2(CH_2)_2NH_2$: 160g $C_6H_4(OH)_2$: 160 ml H_20	115	(100)	0.45	EDP ‘F’ etch Fast etch rate Must be used at high T to avoid residue	[11]
F etch above w/1.0g $C_6H_4N_2$	115	(100)		Faster w/ pyrazine Less sensitive to oxygen Smoother	[11]
F etch above w/3.0g $C_6H_4N_2$	115	(100)	1.35		[11]
500 ml $NH_2(CH_2)_2NH_2$: 80g $C_6H_4(OH)_2$: 3.6 $C_6H_4N_2$: 66ml H_20	50 75 95 105 110	(100) (100) (100) (100) (100)	0.075 0.22 0.43 0.57 0.75	EDP ‘S’ etch Slower etch rate Suitable for lower temperature use without residue	[11]
46.4 mol% $NH_2(CH_2)_2NH_2$: 4 mol% $C_6H_4(OH)_2$: 49.4 mol% H_20	118	(100) (110) (111)		Stops on p^{++}	[12]
250 ml $NH_2(CH_2)_2NH_2$: 45g $C_6H_4(OH)_2$: 120ml H_20	110	(100) (111)			[13]

F Isotropic Silicon Etches

Often, isotropic etchants having dissolution rates independant of orientation are needed. These chemical mixtures tend to uniformly remove material, and are limited by the mass transport of chemical species to the crystal surface. The actual surface reaction rates are so great that variations to atomic structure do not alter the reaction speed relative to chemical transport.
Table 6 lists several common recipes and is taken directly from [14].

Formula	Comments	Reference
HF, HNO_3	See [14] p73	

HF, HNO_3, H_20 or CH_3COOH	Various combinations give different etch rates	[15]
900ml HNO_3, 95 ml HF, 5ml CH_3COOH, 14g $NaClO_2$	15 μm/min	[16]
745 ml HNO_3, 105 ml HF, 75 ml CH_3COOH, 75 ml $HClO_4$	170 A/sec	[17]
50 ml HF, 50 ml CH_3COOH, 200 mg $KMnO_4$ (fresh)	Epi Etching 0.2 μm/min	[18]
108 ml HF, 350g NH_4F per L H_20	Epi Etching n type 0.2-0.6 ohm-cm; 0.43 A/min p type 0.4 ohm-cm; 0.45 A/min p type 15 ohm-cm; 0.23 A/min	[19]

G Silicon Defect Delineation Etches

Certain chemical etchants are strongly dependent on defects, and defect structures in the single crystal silicon. These etchants are commonly used to high-light or delineate defects in the material.
Table 7 lists the most common defect delineation mixtures, and is taken directly from [14]

	Formula	Name	Application	Shelf Life	Ref
1	1 ml HF, 1 ml C_2O_3 (5M)	Sirtl	111 Silicon Approx 5min etch	5 min	[20]
2	1 ml HF, 3 ml HNO_3, 1 ml CH_3COOH	Dash	111 oe 100 n or p (works best on p) Approx 15 hr etch	8 h	[21]
3	2 ml HF, 1 ml $K2Cr_2O_7$ (0.15M) 2 ml HF, 1 ml Cr_2O_3 (0.15M)	Secco Secco	100 or 111 silicon 100 or 111 silicon	5 min 5 min	[21] [21][20]
4	200 ml HF, 1 HNO_3		P-N delineation		[20]
5	60 ml HF, 30 ml HNO_3 60 ml H_20 60 ml CH_3COOH, 30 ml (1g CrO_3 to 2 ml H_20)	Jenkins Wright	general use does not roughen defect free regions Approx 30 min etch	6 wks	[21][20] [22]
6	2 ml HF, 1 ml HNO_3, 2 ml $AgNO_3$ (0.65M in H20)	Silver	epitaxial layer faults		[20]
7	5 gm H_5IO_6, 5 mg Kl in 50 ml H_2O, 2 ml HF	Sponheimer Mills	Etch 5-20 seconds junction delineation		[22]

8	Shipley 112°				[23]
9	6 ml HF, 19 ml HNO				[23]
10	(150g/l (1.5M) CrO_3 to H_20) to HF 1:1	Yang			[24]
11	600 ml HF, 300 ml HNO_3 28g $Cu(NO_3)_2$, 3 ml H_20	Copper Etch			[25]
12	1000 ml H_2O, 1 drop (1.0N) KOH 3.54g kBr, .708g $KbrO_3$				[25]
13	55g $CuSO_4$, SH20, 950 ml H_20, 50 ml Hf	Copper Displacement			[25]
14	1 ml HF, 3 ml HNO_3	White	15 secs. PN Junction etch with stron light		
15	3 ml HF, 5 ml HNO_3, 3 ml CH_3COOH	CP-4	10 sec – 3 min P-N Junctions		[26]
16a	25 ml HF, 18 ml HNO_3, 5 ml CH_3COOH/.1Br2 10 ml H_20, 1g $Cu(NO_3)_2$	SD1	2-4 min reveals edge and mixed dislocations		[26]
16b	100 ml HF; .1 to .5 ml HNO3		P stain		[26]
16c	50 ml dilute $Cu(NO_3)_2$ 1 to 2 drops HF		N stain		[26]
16d	4% NaOH add 40 NaClO until no H_2 evolution from Si		80ºC specimen thinning (float specimen on surface of etch)		[26]
17	300 ml HNO_3, 600 ml HF 2 ml Br_2, 24g $Cu(NO_3)_2$ dilute 10:1 wtih H_2O	Sailer	Etch 4 hr Epi Stacking Faults		[27]
18	a) 1) 75g CrO_3 in 1000 ml H_2O mix 1 part 1) to 2 parts 48% HF b) mix part 1) to 2 parts 48% HF to 1.5 parts H_2O	Schimmel	Resistivity greater than .2 ohm-cm (111) oe (100) approx 5 min Resistivity less than .2 ohm-cm		
19	5g H_5IO_6, 50 ml H_2O, 2 ml HF, 5mg Kl	Periodic HF	Junction Deliniation		

H Conclusion

There are many wet-chemical etch recipes known for etching silicon. These processes are used for a variety of applications including micromachining, cleaning, and defect delineation. The detailed behaviour and rate of the etchant will vary between laboratory enviroments and exact processes. However, the data and phenomena recorded above have been reported by many researchers and manufactures.
For further details the reader is encourage to fully explore the direct and indirect references sited.

I References

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