UNIVERSITY OF CAMBRIDGE
Department of Engineering

IB Paper 8
Electrical Engineering

Lecture 12
Fabricating Devices: Etching

https://www.vle.cam.ac.uk/course/view.php?id=69961

Introduction

- We have seen that, using photolithography, it is possible to form a patterned polymer layer on the surface of a sample
  - However, we require some means by which this pattern can be transferred to the sample itself
  - This usually requires the removal of surface layers of material – known as ***surface micromachining*** – or of large amounts of the substrate itself – known as ***bulk micromachining***
  - Material must therefore be etched away in a controlled fashion to create the desired structures
- Etching divides very neatly into two well defined categories:
  1. ***Wet etching***
     - Immersion of the substrate in a liquid
  2. ***Dry etching***
     - Exposure to reactive species in the gas phase

Wet Etching

- The wet etching of microstructures by immersion in a reactive chemical mixture involves three main steps
  1. Transportation of reactants to the surface to be etched
  2. Chemical reaction between the reactants and the surface
  3. Transportation of reactant products away from the surface
- If step 1 is the rate limiting step in the process then the reaction is said to be ***mass transfer limited***, whist if step 2 is the rate limiting step, then the process is said to be ***reaction rate limited***
- Etching is characterised by:
  - Etching rate
  - Etch selectivity
  - Etch uniformity

- Isotropic Etching
- Most wet chemical etches are ***isotropic*** in nature
  - In other word, they etch all crystal planes of a material at the same rate, and so a single etch rate can be used to describe the process
  - Therefore, assuming that the masking material is completely resistant to the etch (we will return to this assumption shortly), isotropic wet etching tends to produce a very characteristic undercut profile

- Isotropic etching is widely used for
    - Removal of work damaged surfaces
    - Rounding of sharp, anisotropically etched corners which can be a source of stress concentrations
    - Removal of roughness created by dry or anisotropic etches
    - Simple pattering
    - Creation of free standing structures by undercutting
- It is of particular importance in the last two cases that only desired regions are actually etched
    - For this reason, it is important that the etching rate of the masking material is much slower than that of the material to be etched
    - A high degree of ***selectivity*** is therefore required
- A large number of wet etches have been characterised for a range of MEMS materials, allowing a sensible choice of etchant for a particular system

Etch Rates for Micromachining and IC Processing (Å/min) v. 4.4 29 July 1996

U.C. Berkeley Microfabrication Laboratory / Berkeley Sensor & Actuator Center / Kirt R. Williams

The top etch rate was measured by the author with fresh solutions, clean chambers, etc.

The center and bottom values are the low and high etch rates observed by the author and others in the UCB Microlab using fresh and used solutions, clean and "dirty" chambers, etc.

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
CF_4+CHF_3+He (90:30:120 sccm) Lam 590 Plasma 450W, 2.8T, gap=0.38cm, 13.56MHz	Silicon oxides	W	1900 1400 1900	2100 1500 2100	4700 2400 4800	W	4500	7300 3000 7300	6200 2500 7200	1800	1900	-	W	W	W	2200	2000
CF_4+CHF_3+He (90:30:120 sccm) Lam 590 Plasma 850W, 2.8T, gap=0.38cm, 13.56MHz	Silicon oxides	W	2200 2200 2700	1700 1700 2100	6000 2500 7600	W	6400 6000 6400	7400 5500 7400	6700 5000 6700	4200 4000 6800	3800	-	W	W	W	2600 2600 6700	2900 2900 7200
SF_6+He (13:21 sccm) Technics PE II-A Plasma 100W, 250mT, gap≈2.6cm, 50kHz sq. wave	Silicon nitrides	300 300 1000	730 730 800	670 670 760	310	350	370	610	480 230 480	820	620 550 800	-	W	W	W	690 690 830	630
CF_4+CHF_3+He (10:5:10 sccm) Technics PE II-A Plasma 200W, 250mT, gap≈2.6cm, 50kHz sq. wave	Silicon nitrides	1100	1900	W	730	710	730	W	900	1300	1100	-	W	W	W	690	600
SF_6+He (175:50 sccm) Lam 480 Plasma 150W, 375mT, gap=1.35cm, 13.56MHz	Thin silicon nitrides	W	6400	7000 2000 7000	300 220 400	W	280	530	540	1300 830 2300	870	-	W	W	W	1500 1300 1500	1400
SF_6+He (175:50 sccm) Lam 480 Plasma 250W, 375mT, gap=1.35cm, 13.56MHz	Thick silicon nitrides	W	8400	9200	800	W	770	1500	1200	2800 2100 4200	2100	-	W	W	W	3400 3100 3400	3100
SF_6 (25 sccm) Tegal Inline Plasma 701 125W, 200mT, 40°C	Thin silicon nitrides	W	1700	2800	1100 1100 1600	W	1100	1400	1400	2800 2800 2800	2300	-	W	W	W	3400 2900 3400	3100
CF_4+CHF_3+He (45:15:60 sccm) Tegal Inline Plasma 701 100W, 300mT, 13.56MHz	Si-rich silicon nitrides	W	350	360	320	W	320	530	450	760	600	-	W	W	W	400	360
Cl_2+He (180:400 sccm) Lam Rainbow 4420 Plasma 275W, 425mT, 40°C, gap=0.80cm, 13.56MHz	Silicon	W 5000 5000	5700 3400 6300	3200 3200 3700	8 8 380	-	60	230	140	560	530	W	W	-	-	3000 2400 3000	2700
HBr+Cl_2 (70:70 sccm) Lam Rainbow 4420 Plasma 200W, 300mT, 40°C, gap=0.80cm, 13.56MHz	Silicon	W	450 450 740	460	4 4 10	-	0	0	0	870	26	W	W	-	-	350 350 500	300
Cl_2+BCl_3+$CHCl_3$+N_2 (30:50:20:50 sccm) Lam 690 RIE 250W, 250mT, 60°C, 13.56MHz	Aluminum	W	4500	W	680	670	750	W	740	930	860	6000 1900 6400	W	-	-	6300 3700 6300	6300 3300 6100
SF_6 (80 sccm) Tegal Inline Plasma 701 200W, 150mT, 40°C, 13.56MHz	Tungsten	W	5800	5400	1200 2000 2000	W	1200	1800	1500	2600	2300 1900 2300	-	2800 2800 4000	W	W	2400 2400 4000	2400
O_2 (51 sccm) Technics PE II-A Plasma 50W, 300mT, gap≈2.6cm, 50kHz sq. wave	Descumming photoresist	-	0	0	0	0	0	0	0	0	0	0	0	0	-	350	300
O_2 (51 sccm) Technics PE II-A Plasma 400W, 300mT, gap≈2.6cm, 50kHz sq. wave	Ashing Photoresist	-	0	0	0	0	0	0	0	0	0	0	0	0	-	3400	3600
HF Vapor 1 cm over plastic dish Room temperature and pressure	Silicon oxides	-	0	0	660	W	780	2100	1500	10	19	A	0	A	-	P 0	P 0
XeF_2 Simple custom vacuum chamber Room temperature, 2.6 Torr	Silicon	4600 2900 100k	1900 1100 2500	1800 1100 2300	0	-	0	0	0	120 120 180	2 0 2	0	800 440 1000	290 50 380	-	0	0

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.
Rates measured are rounded to two significant figures.
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 or plasma chamber, area of exposure of film, other materials present (e.g., photoresist), film impurities and microstructure, etc. *Some variation should be expected.*

- By way of an example, let us consider how we might create a freestanding silicon cantilever using only wet chemistry
  - We will need to find a sacrificial material that can be removed from underneath the cantilever without attacking the Si
  - A good candidate is silicon oxide that is readily attacked by buffered hydrofluoric acid (bHF)
  - SiO_2 dissolves in HF according to the reaction

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

  - H_2SiF_6 is soluble in water, and so may be transported away from the reaction surface
  - bHF does not significantly etch Si, so we will be able to undercut a cantilever structure, however, we require some means of patterning a continuous layer of Si

- The most common etchants for silicon are mixtures of HF with an oxidising agent, such as nitric acid (HNO_3) and either water or acetic acid (CH_3COOH)
- Initially silicon is oxidised in the presence of holes by

$$Si + 2H^{+} \rightarrow Si^{2+} + H_2$$

- Water is dissociated in the solution,

$$H_2O \rightarrow (OH)^{-} + H^{+}$$

- and the hydroxyl ions combine with the positively charged silicon ions to form silicon oxide,

$$Si^{2+} + 2(OH)^{-} \rightarrow Si(OH)_2$$

$$Si(OH)_2 \rightarrow SiO_2 + H_{2(gas)}$$

- The surface layer of SiO_2 formed on the silicon is then etched by the HF through reaction 10.1
- We can then construct the full fabrication process

Step 1
Start with a 'silicon-on-insulator' (SOI) wafer consisting of a 10 μm thick layer of silicon oxide on a silicon with a 0.5 μm layer of Si on top. A 2 μm thick layer of photoresist is added.

Step 2
The photoresist is patterned to protect the cantilever, and a HNO_3:HF:CH_3COOH etch used to remove the unwanted poly-Si.

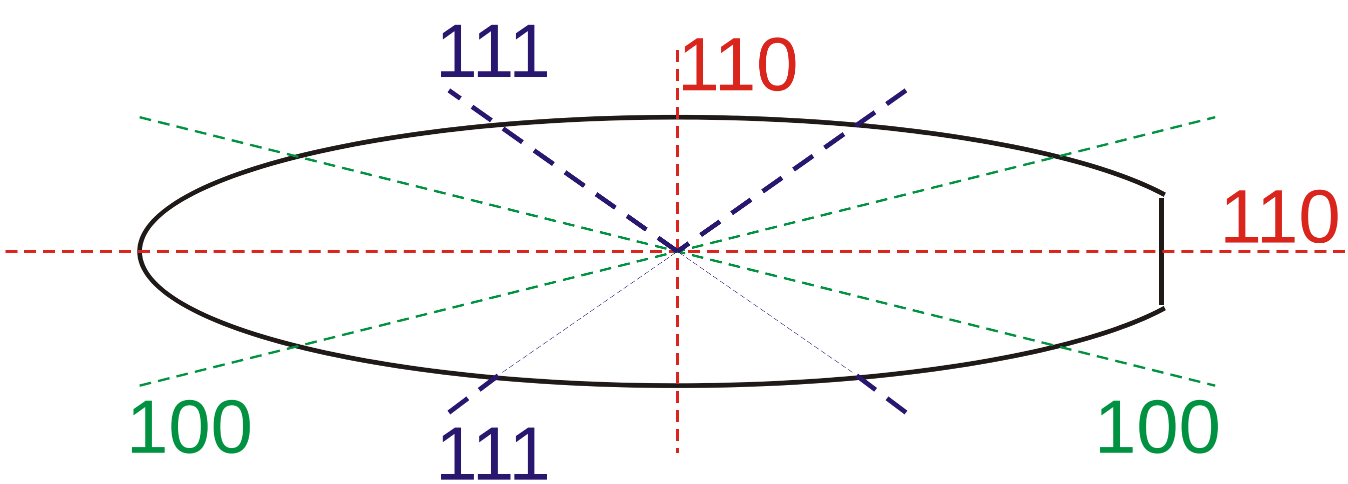
Step 3
A bHF etch is then used to undercut the cantilever.

Step 4
Finally, the remaining photoresist is removed by acetone. Acetone has a low surface tension, and so in drying does not cause the cantilever to collapse.

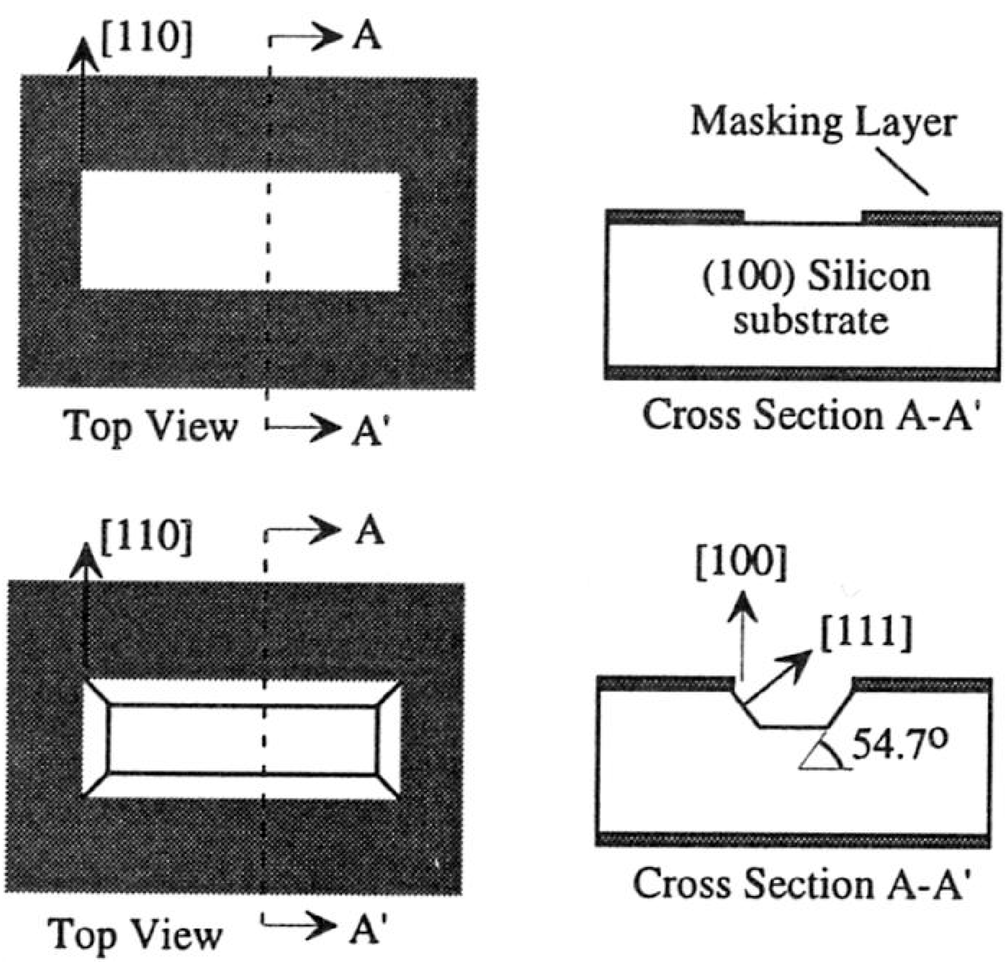
- # Anisotropic Etching
- Whilst most wet etches are isotropic, in some cases the wet chemical etch rate varies with crystallographic orientation, resulting in anisotropy
  - In the case of silicon, the most common anisotropic etchants are strong bases
    1. Aqueous potassium hydroxide (KOH) (sometimes with isopropyl alcohol, IPA)
    2. Tetramethylammoniumhydroxide (TmAH)
    3. Ethylene diamine pyrochatecol (EDP)

			Etch Rate [μm hr^{-1}]	
Etchant	Temper-ature [°C]	Si(100)	Si(110)	Si(111)
KOH: H_2O	80	84	126	0.21
KOH	75	25-42	39-66	0.5
EDP	110	51	57	1.25
N_2H_4 H_2O	118	176	99	11
NH_4OH	75	24	8	1

- Orientation dependence is a consequence of the fact that different crystalline surfaces will have varying structures
  - The (111) surface of c-Si is particularly stable as a silicon atom on the surface will only have one of its four bonds pointing out of the surface with the other three pointing back into the bulk of the material
  - This results in a stable surface with a high surface density of atoms
  - As KOH etching, for example, proceeds by the insertion of an OH group into a Si—Si bond, the etch rate of the Si(111) surface is suppressed



- The result of this is that if a masking pattern is produced on the surface of a Si(100) wafer with sides in the <110> directions, then a groove will be etched with sides at an angle of 54.7° with respect to the surface plane
  - For short etching times, rectangular features will yield U-shaped grooves with (111) oriented sidewalls and a (100) oriented base



- The etch will proceed with time until only stable (111) surfaces remain
  - Rectangular features will produce v-grooves, whilst square patterns will produce inverted pyramids

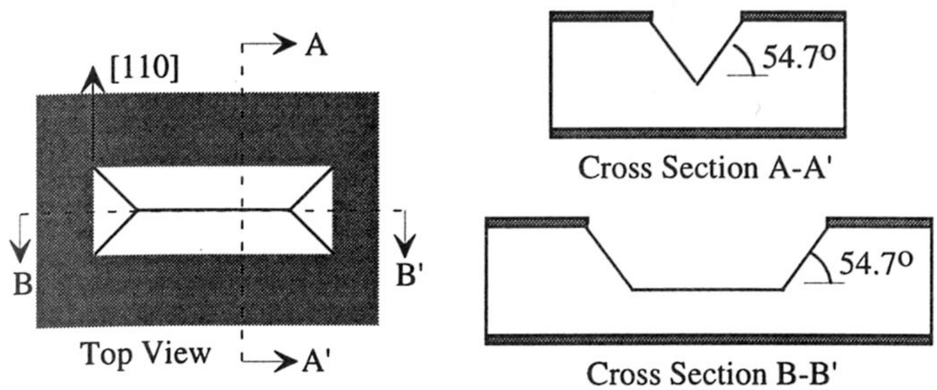


Figure 3.21. If the structure of Fig. 3.20 is allowed to continue, a self-terminating V-groove is formed, with all surfaces bounded by {111} planes.

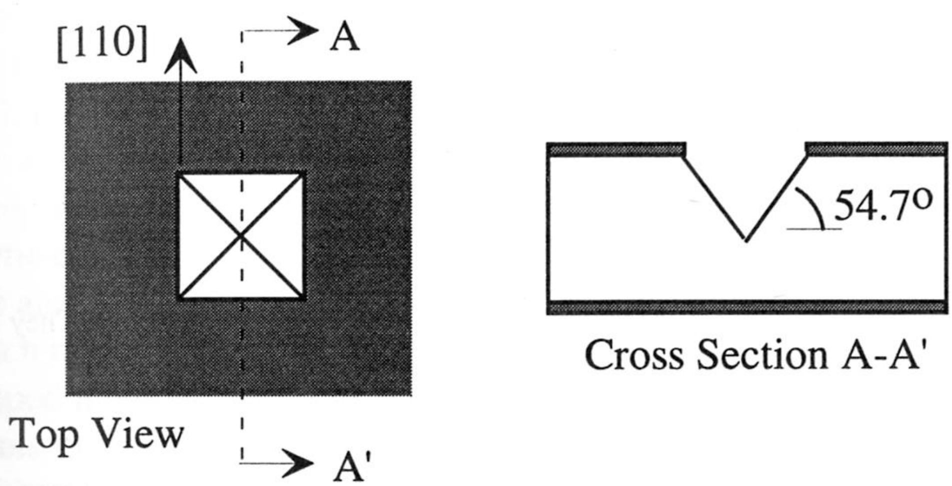
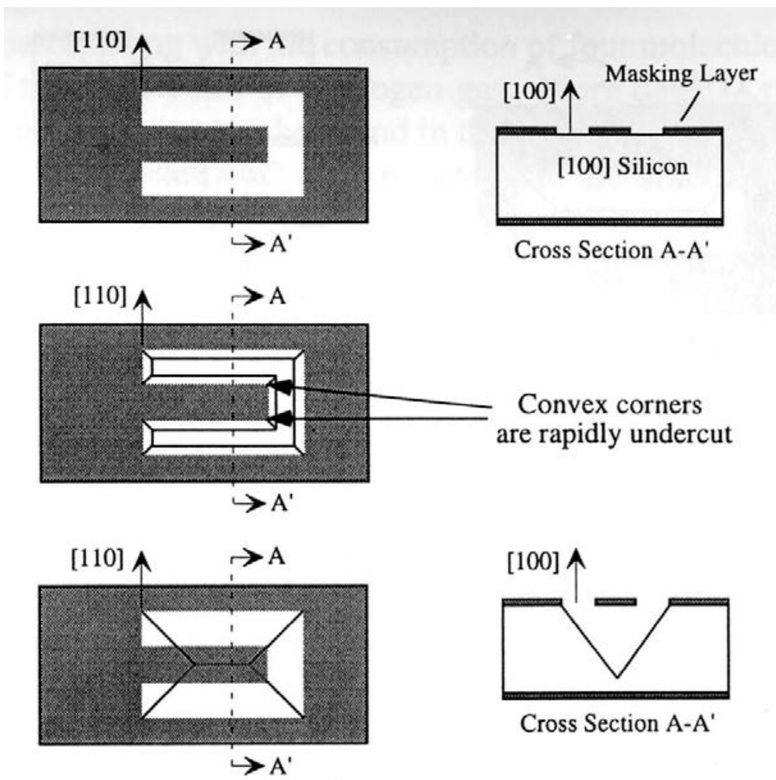
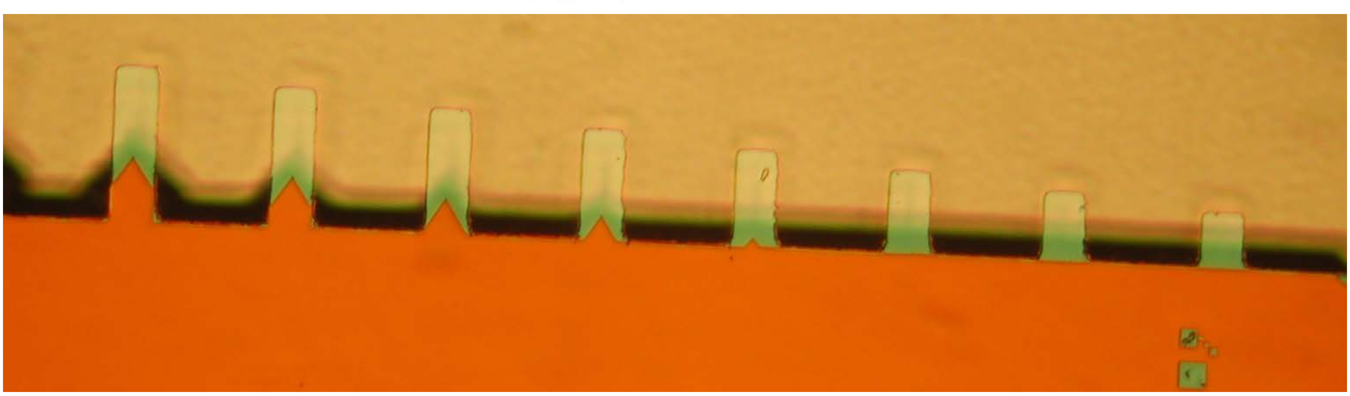


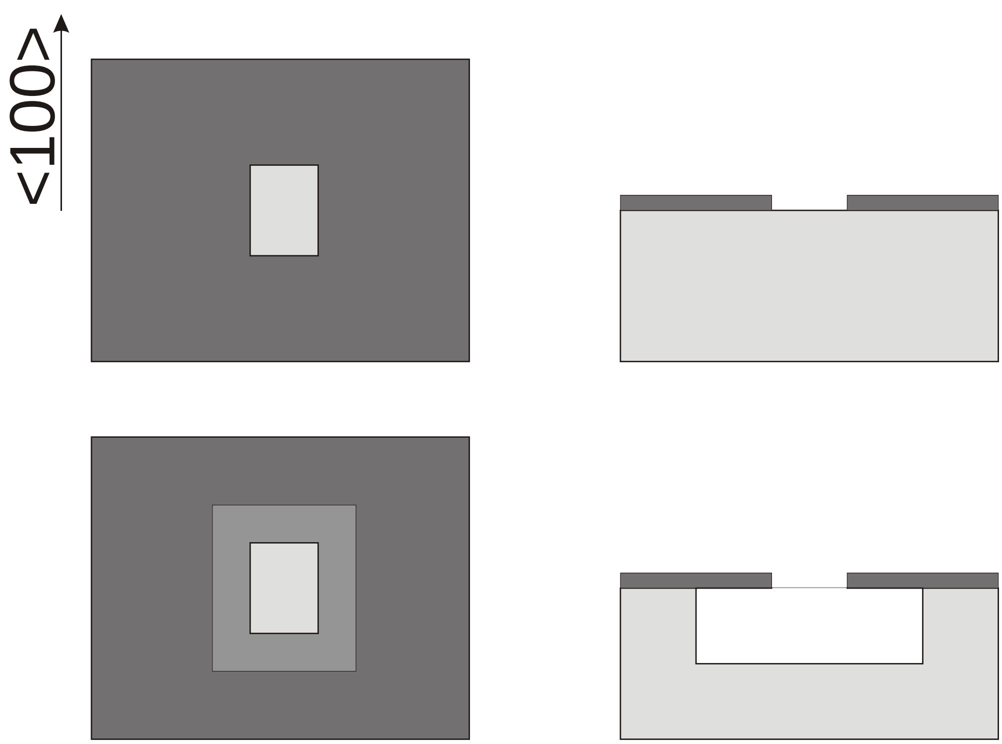
Figure 3.22. A square <110>-oriented mask feature results in a pyramidal pit.

- So far, all the edges between (111) planes have been concave, and these edges are essentially stable in the KOH etch
- However, convex edges are not stable and are efficiently undercut
- The allows the fabrication of free standing structures without the need for a sacrificial layer between the superstructure and the substrate





- Alternatively, structures with vertical sidewalls may be produced by orienting rectangular sides with the <100> directions
  - In this case, the initial etching into the silicon bulk will reveal (100) sidewalls as well as the (100) base
  - All surfaces will be etched at the same rate
  - Therefore, the surface mask will be undercut on all four sides, with the undercut distance being the same as the etch depth to a good first approximation
  - Unlike the previous example, so stable (111) facets are exposed, so this process is not self-limiting



- The following points should be noted regarding anisotropic etching using KOH
    1. The highest etch rate is achieved for a 20% solution at ~85° C
    2. KOH will efficiently remove most photoresists, and so it is necessary to use a 'hard mask'
        - This involves using a material on the surface of the silicon, such as silicon nitride or silicon oxide, which is first patterned using a standard photoresist
    3. KOH will slowly etch most hard mask materials, so if a deep silicon etch is being performed, the hard mask material must be of sufficient thickness to survive the etching process (see Slide 6)

- Etch Stops
- If a wet etching process has been well characterised, then it should be possible to etch features of a certain depth knowing the etching rate
  - In practice, this is more difficult than it sounds
    - The effective concentration of the etchant may decrease with use
    - When does the etch begin and end?
    - Some wetting time may be necessary and certainly some etchant removal time
  - Therefore, if the depth of a feature is a critical parameter, some method of precisely controlling the end of an etch – an ***etch stop*** process – will be necessary
- ***Dielectric etch stop***
  - Dielectrics, such as silicon nitride, tend to have a reduced etch rate compared to silicon
  - A layer may then be introduced underneath the layer to be etched to ensure that the etch terminates at the correct depth
  - However, this requires the use of an extra material (and hence deposition step) in the process

- ***Doping selective etching (DSE)***
  - Silicon which has been heavily doped with boron to a concentration of ~10^{26} m^{-3} has a significantly reduced anisotropic etch rate
  - Therefore, an etch of a low doped p-type or n-type silicon layer will naturally halt on a heavily boron doped layer, resulting in a very smooth surface
  - However, the addition of boron tends to cause a significant intrinsic stress in the silicon, which limits the use of these layers as mechanical components

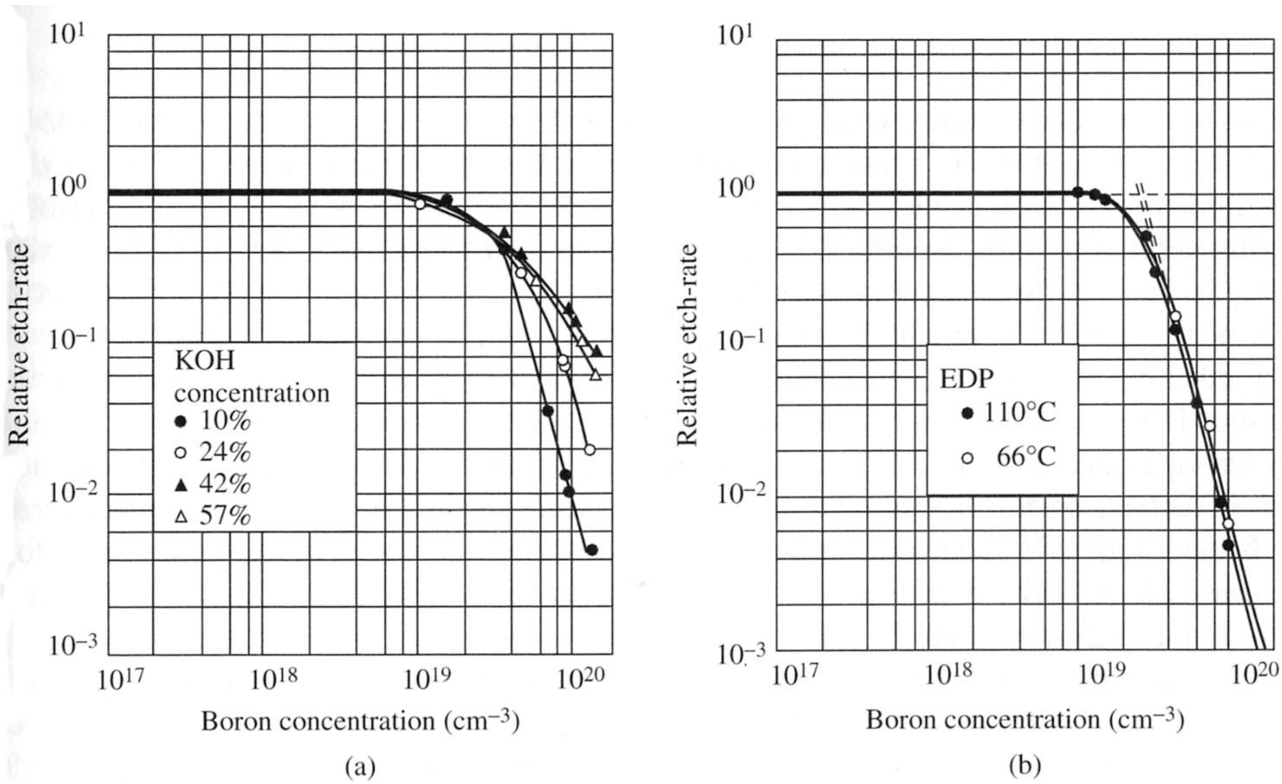
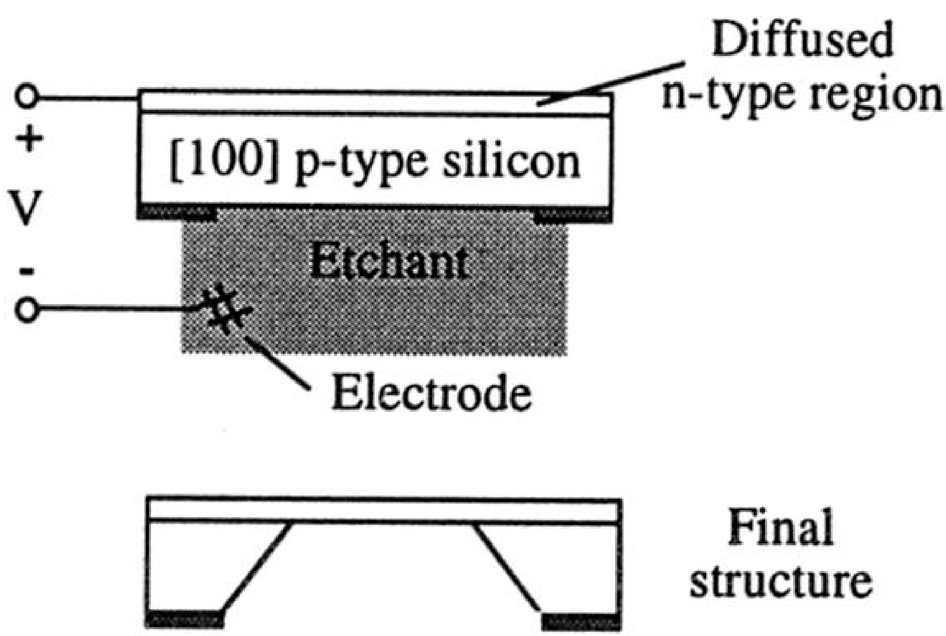


Figure 5.8 Boron etch-stop properties for (a) KOH and (b) EDP etchants

- ***Bias selective etching (BSE)***
  - This is otherwise known as an electrochemical etch stop
  - A positively biased silicon wafer will be oxidised in an etchant solution to form a protective oxide layer which will prevent etching
  - A current is required for the oxide to form, therefore, a reverse biased pn junction in the solution will not be able to form a passivation layer until all of the p or n-type material has been removed
  - At this point a current may flow, and the silicon surface will quickly oxidise, stopping the etch at the change in doping density



Dry Etching

- An alternative to wet etching of materials is the use of gas phase etchants
  - These so-called dry etching processes have the advantage that the use of a continuous flow of gas naturally removes unwanted reaction products from the surface
  - It also ensures a constant etch rate, as used etchant is constantly replaced
  - The etching process may be quickly terminated by pumping away the reactant gases, allowing a more accurate determination of etch time
  - Residual gas analysis of the reaction products may be used to determine when a particular layer has been fully etched
  - The danger of surface tension in a liquid breaking mechanical micro-components is removed

- Vapour Etching
- Xenon difluoride (XeF_2) is a highly selective vapour etchant for silicon
  - It requires no excitation, and does not etch silicon dioxide or most metals
  - It is an isotropic etch and so may be used in conjunction with sacrificial polycrystalline silicon to produce released surface structures
  - The reaction proceeds according to

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

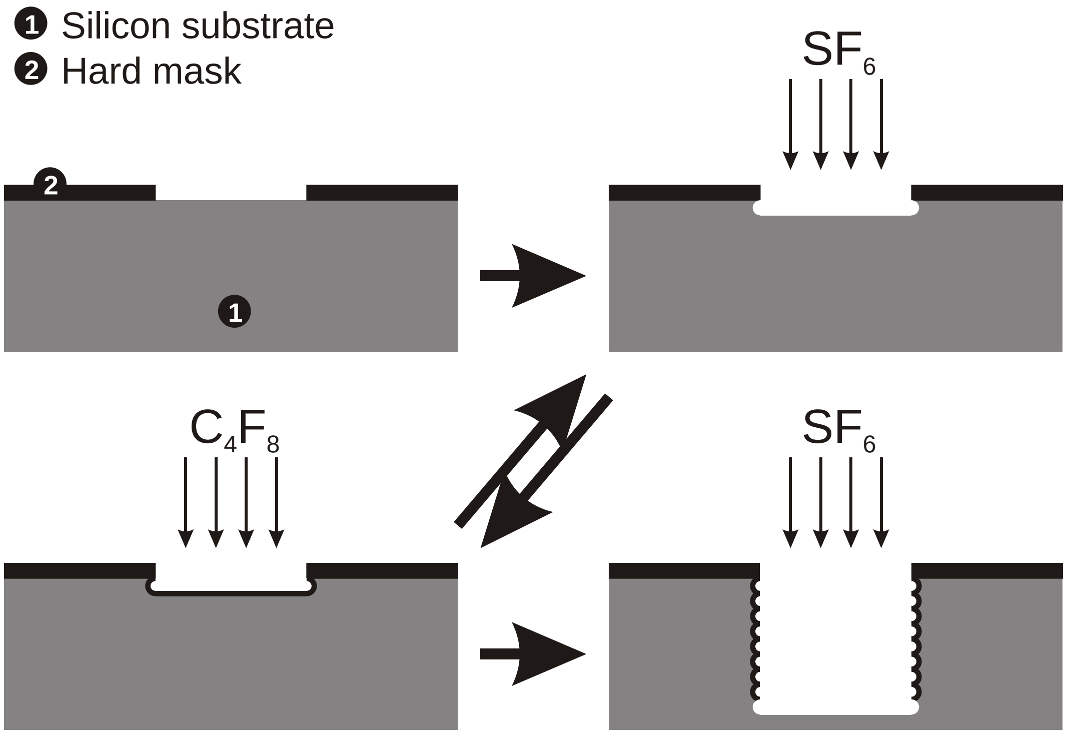
  - Etching normally takes place under a clean vacuum as XeF_2 will react with water, and so the sample should also be dehydrated prior to etching
  - The etch takes place at a pressure between 1Torr and the vapour pressure of XeF_2 (~3.8 Torr at 25° C)
  - Silicon can be etched at a rate of ~300 nm min^{-1}

- Reactive Ion Etching (RIE)
- In RIE, the reactant gas is excited to form a plasma which contains the reactive species required to perform the etch
  - The bombardment of the surface top be etched by ions from the plasma can lead to sputter enhancement of the etch rate
  - Although there are many plasma sources for performing RIE, the most common is rf-RIE
    - This system is identical to an rf-PECVD system (as used for a-Si:H deposition – see Lecture 9, Slide 17) however, the substrate is placed on the rf-driven electrode, as the energy of ions impacting this electrode is greater due to its negative self-bias with respect to earth

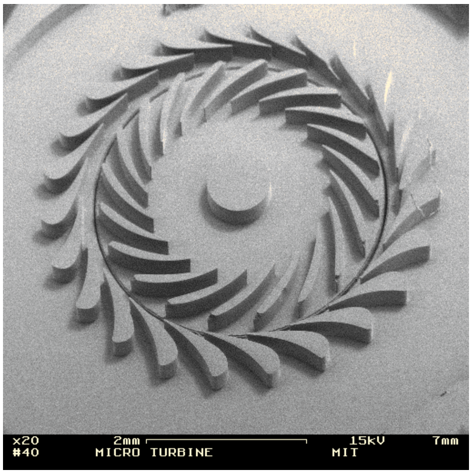
Material	Etch Gas
c-Si, a-Si, poly-Si	CF_4, SF_6
Silicon oxide	CF_4/H_2
Silicon nitride	CF_4/O_2
Organics	O_2, O_2/CF_4, SF_6
Aluminium	BCl_3

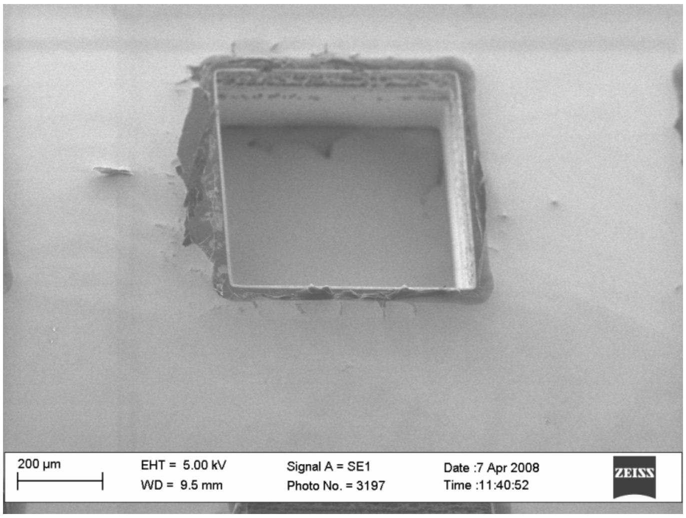
- At high pressures, ions crossing the plasma sheath undergo many collisions, and so strike the etch surface with a broad range of incident angles, and a fairly isotropic etch results
  - SF_6 makes a particularly good isotropic etch for silicon
  - The high pressure also means that the flux of reactant species is high and the etch rate is also increased
- At low pressures, ions are accelerated across the sheath without collision, and so tend to hit the etch surface at close to normal incidence
  - Side walls are therefore only weakly etched, and an anisotropic etch results
  - CF_4 makes a particularly good anisotropic etch for silicon as it also coats the side walls with a protective fluorine polymer, which is only removed by ion bombardment
  - A thin fluorine polymer layer may sometimes be left even on the etched faces at the end of a CF_4 plasma etch, and so O_2 is often added to the gas mixture to remove this polymer layer

- Deep Reactive Ion Etching (DRIE)
- Standard RIE tends to produce etch rates between 10 and 100 nm min^{-1}
  - Whilst this is sufficient for surface micromachining, it is far to slow to allow a layer hundreds of µm thick to be etched
  - DRIE received an impetus thanks to research carried out at Bosch, where a cyclic process involving two important stages was developed for deep isotropic etching
  - In the first stage of the BOSCH process, a dense SF_6 plasma is used to etch a thin layer of silicon
  - In the second stage, a C_4F_8 plasma is used to deposit a thin fluorine polymer on the etched surface
  - When SF_6 is reintroduced, it preferentially removes the polymer from the bottom of the etch structure, exposing the silicon in this region and allowing the etch to proceed
  - The sidewalls, however, remain protected and are not etched



- In this way, deep structures may be produced with vertical sidewalls at an etch rate of up to 20 μm min^{-1} in bulk c-Si
- DRIE has enabled the production of a range of new 3D microsystem structures, including the MIT microturbine





http://www-mtl.mit.edu/mtlhome/6Res/AR1999/AR99-MEM.pdf

Other Etching Techniques

- Both dry and wet etching techniques require some means of protecting certain areas of a sample which must not be etched, and this normally requires photolithography
  - However, several techniques exist for removing material without the need for prior patterining
- In ***ion milling*** systems, a focussed beam of Ar (or other suitable) ions is directed at a substrate allowing material to be locally removed by sputtering
- In ***laser micromachining*** systems, a high power laser pulse is focussed on the material to be removed
  - The material is locally heated and sublimes, allowing a structure to be formed
- Whilst such techniques are good for prototyping, direct writing of patterns is slow and not commercially acceptable