Plasma and Dry Micro/Nanotechnologies
8. Etching

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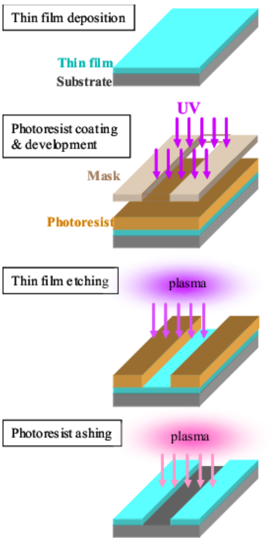
Outline

8.1 Motivation - Lithography process flow

Microlithography is a technique that creates microstructures after given geometrical template:

- Lithography is usually applied to shape a thin film $\Rightarrow$ deposition of thin film
- Photosensitive material (resist) is coated on the material that should be shaped
- Resist is irradiated through a mask, by projection of UV image or by directed electrons (photolitography or electron lithography)
- Resist development:
  - positive resist: soluble in developper at the irradiated places
  - negative resits: unsoluble in developper at the irradiated places
- Etching of the film through photoresist pattern
- Rest of the resist is removed



lithography patterning with positive resist

Photolithography - step details

- creation of the mask layout on a computer
- generation of a photomask
  a sequence of photographic processes (using optical or e-beam pattern generators) that results in a glass plate that exhibits the desired pattern in the form of a thin (≈100 nm) chromium layer.
- deposition of thin film (discussed later)
- spin-coating of a photoresist (positive or negative)
  polymeric photosensitive material spun onto the wafer in liquid form (an adhesion promoter such as hexamethyldisilazane, HMDS, is usually used prior to the application of the resist). The spin speed and photoresist viscosity determine the final resist thickness, which is typically between 0.5–2.5 μm. Due to the better process control that can be achieved for small geometries, the positive resist is most commonly used in VLSI processes.
- soft-baking (5–30 min at 60–100 °C) in order to remove the solvents from the resist and to improve the adhesion.
- mask alignment to the wafer
- exposure of photoresist to a UV source - photoresist is developed in a process similar to the development of photographic films
- hard baking of the resist (improvement of adhesion)
  20–30 min at 120–180 °C
- etching of underlying thin film through created pattern on wafer
- removal of the photoresist in acetone or another organic removal solvent

Techniques for Photolithography

Three different exposure systems (depending on the separation between the mask and the wafer):

1. contact - better resolution than the proximity technique **but constant contact of the mask with the photoresist reduces the process yield and can damage the mask**
2. proximity
3. projection - uses a dual-lens optical system to project the mask image onto the wafer $\Rightarrow$ one die exposed at a time $\Rightarrow$ step and repeat system to completely cover the wafer area. **The most popular microfabrication system yielding superior resolutions to the contact and proximity methods.**

The exposure sources used for photolithography depends on the resolution.

- above 0.25 μm minimum line width $\Rightarrow$ high-pressure mercury lamp (436 nm g-line and 365 nm i-line),
- between 0.25 and 0.13 μm $\Rightarrow$ deep UV sources such as excimer lasers (248 nm KrF and 193 nm ArF),
- below 0.13 μm regime $\Rightarrow$ extensive competition between e-beam, X-ray and extreme UV (EUV) (with a wavelength of 10–14 nm)

8.2 Motivation - Etching and Substrate Removal

Classification of Etching/Sputtering Processes

Basic classification:

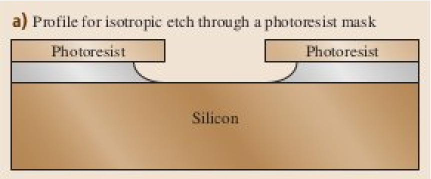
- wet etching
- dry etching

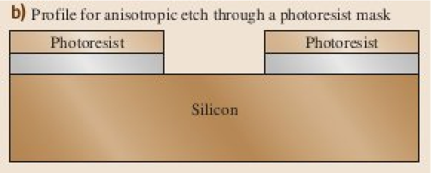
Classification according to the type of process:

- ion sputtering
- chemical etching
- plasma etching

Two important properties of etching:

- selectivity - degree to which the etchant can differentiate between the layer to be etched and the masking layer or underlaying material
- directionality - istropic versus anisotropic etching





Properties of Etching/Sputtering Processes

ion sputtering

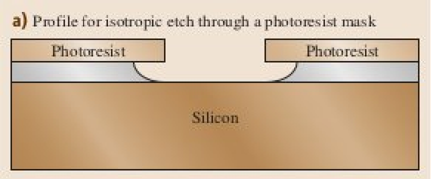
- purely physical approach, removal by energy transfer
- slow process, no selectivity
- ions are directed by electric field, i.e. anisotropic process

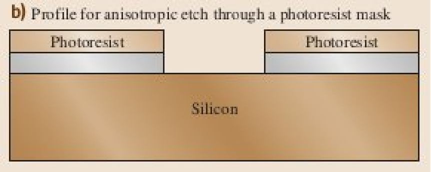
chemical etching

- purely chemical processes that requires aggressive chemicals and/or elevated temperature for reaction activation
- can be very fast, selective
- chemical reactions with surface are not directed, i.e. isotropic process

plasma etching

- combination of physical and chemical approaches
- directional process





8.3 Wet Etching

- isotropic process (except for crystalline materials) $\Rightarrow$ lateral undercut, minimum feature size $> 3\,\mu$m
- superior selectivity to the masking layer as compared to dry techniques

Historically, wet etching techniques preceded the dry ones. Still important for micro/nanofabrication in spite of their less frequent utilization in VLSI technology.

Etching of SiO_2

- etchant - dilute (6:1, 10:1 or 20:1 by volume) or buffered HF (BHF: $HF+NH_4F$) solutions
- masking materials - photorezist or silicon nitride
- etch rate $\approx$ 100 nm/min in BHF

Etching of Si_3N_4

- phosphoric acid $(H_3PO)_4$ at 140–200 °C
- masking materials - silicon oxide
- not commonly used due to the masking difficulty and nonrepeatable etch rates

Etching of metals - Al, Cr, Au various etchants combining acid and base solutions, commercially availble

Wet Chemical Etching

Anisotropic and isotropic wet etching of crystalline (Si and GaAs) and amorphous (glass) substrates is an important topic in micro/nanofabrication. The realization of anisotropic wet etching of c-Si is considered to mark the beginning of micromachining and MEMS fabrication.

Isotropic etching of c-Si

- $HF/HNO_3/CH_3COOH$ etchant - "HNA" stands for hydrofluoric acid (HF), nitric acid (HNO_3) and acetic acid (CH_3COOH). HNO_3 oxidizes Si, HF dissolves the oxide, CH_3COOH prevents the dissociation of HNO_3
- masking materials - SiO_2 for short etch time otherwise Si_3N_4
- dopant selectivity - etch rate drops at lower doping concentrations ($< 10^{17}\ cm^{-3}$ n- or p-type), it can be as etch-stop mechanism but it is not widespread due to its difficulty

Isotropic etching of glass

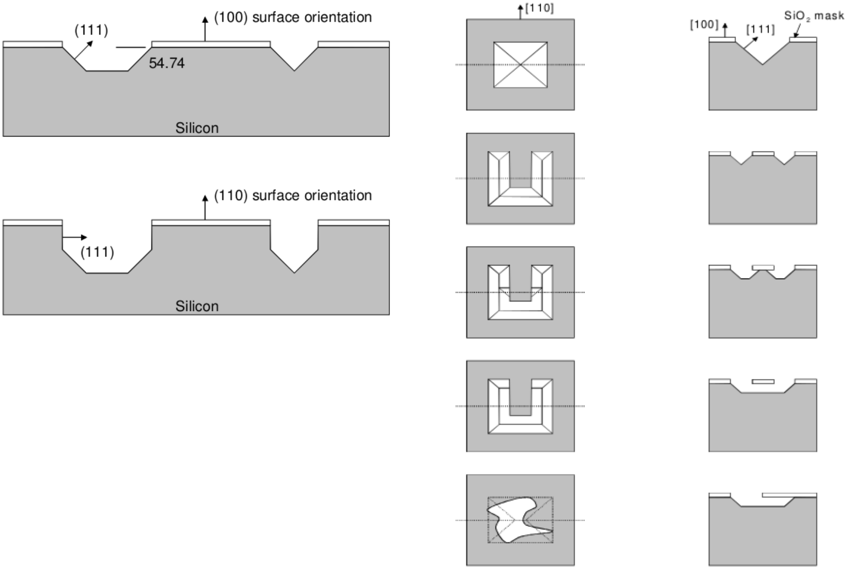
- etchant - HF/HNO_3
- masking materials - Cr/Au for shorter time, long etching requires a more robust mask (bonded Si)
- etching results in rough surfaces, used in fabrication of microfluidic components (mainly channels)

Wet Chemical Etching

Anisotropic etching of c-Si

- three possible anisotropic etchants attacking c-Si along preferred crystallographic directions:
  - potassium hydroxide (KOH),
  - ethylenediamine pyrocatechol (EDP - a typical formulation consists of ethylenediamine NH_2-CH_2-CH_2-NH_2, pyrocatechol $C_6H_4(OH)_2$, pyrazine $C_4H_4N_2$ and water)
  - tetramethyl ammonium hydroxide (TMAH)
- etch rate $\approx 1\ \mu$m/min at temperature 85–115 °C
- etch rate slowest for (111) planes $\Rightarrow$ used to create beams, membranes and other mechanical and structural components,
  markedly reduced in heavily ($> 5 \times 10^{19}$ cm^{-3}) boron-doped (p^{++}) regions
- etching chemistry is not quite clear: Si oxidation at surface and reaction with with hydroxyl ions (OH^-) creates soluble silicon complex (SiO_2OH^{2-}
- masking materials - SiO_2 and Si_3N_4 (superior for longer etch times)

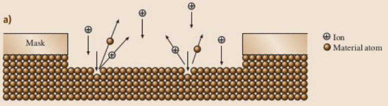
Examples of Si Anisotropic Etching



8.4 Dry Etching

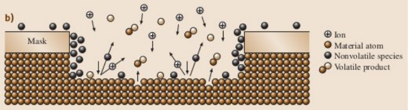
Types of Directional Dry Etching

ion sputtering (milling)



- pressure 0.01 – 0.1 Pa, Ar^+
- etch rate few nm/min
- poor selectivity (close to 1:1 for most materials)

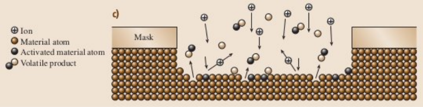
high-pressure plasma etching



- pressure 15 – 500 Pa
- highly reactive plasma species produce volatile molecules
- nonvolatile species are removed by low-energy ions

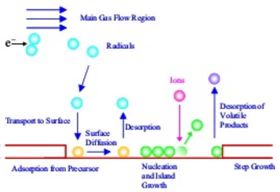
→ directional etching due to passivation of side walls by nonvolatile species

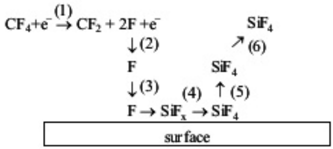
reactive ion etching (RIE)

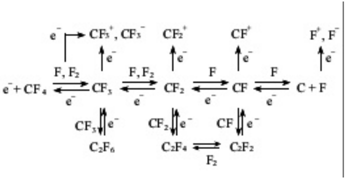


- pressure 1 – 10 Pa
- reactive species react only with activated atoms of material, activation achieved by the collision with an incident ion

Principles of Plasma Etching – Plasma Chemistry







F. Chen, 2003, Lecture notes . . . , p. 167

1. Creation of reactive species within plasma phase by electron–neutral collisions

$$e^- + CF_4 \rightarrow CF_3 + F + e^-$$

2. Transport of reactive species from plasma to substrate
3. Adsorption of reactive species on surface (physisorption or chemisorption)
4. Surface or volume diffusion of reactants, formation of desorbing species

$$F^* + SiF_x \rightarrow SiF_{x+1}$$

5. Desorption of product species

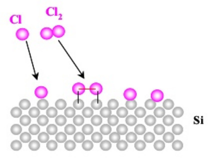
$$SiF_{4(s)} \rightarrow SiF_{4(g)}$$

6. Transport of product species into plasma
7. Simultaneous re-deposition of etching products

Principles of Plasma Etching - Spontaneous Etching

Principles of Plasma Etching – Spontaneous Etching

Neutral species from plasma interact with solid surface to form volatile products **in the absence of energetic radiation** (ion bombardment, UV radtiation)



Etching rate follows **Arrhenius relationship** because it is limited by surface reaction kinetics:

$$ER_s = k_o e^{\left(-\frac{E_a}{KT}\right)} Q$$

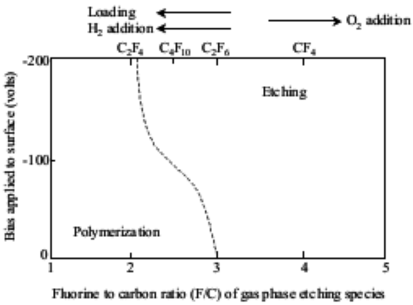
Q flux of reactive species, *T* substrate temperature, k_0 preexponential factor, E_a **activation energy**

Typically, Langmuir-Hinschelwood mechanism (reaction between chemisorbed species) - creation of free radicals in plasma eliminates chemical barrier for chemisorption

Neutral	Substrate	Q (#/cm^2/s)	k_o (Åcm^{2}s/#min)	E_a {eV}
Cl	Poly-Si	6×10^{19}	2.57×10^{-14}	0.29
F	Si<100>	2.3×10^{19}-1.1×10^{22}	3.59×10^{-15}	0.108

Because of higher activation energy, etching yield by atomic Cl is two orders of magnitude lower. It is consistent with high energy barrier for penetration of Cl into Si (13 eV) compared to F (1 eV)

Principles of Plasma Etching - Spontaneous Deposition

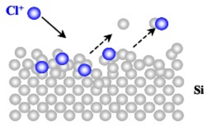


Concept of the carbon/fluorine ratio to help quantify the conditions under which polymer formation occurs.

Principles of Plasma Etching - Effect of Ions

Principles of Plasma Etching – Effect of Ions

chemical sputtering



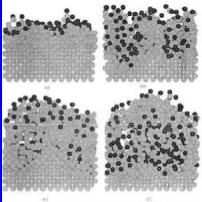
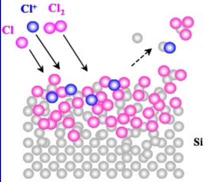
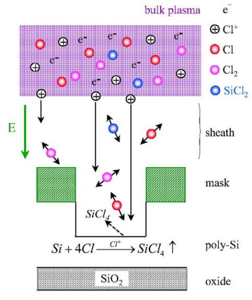


Fig. 13. Molecular dynamic simulation of Cl+ interacting with Si [Barone and Graves].

ion-enhanced plasma etching





- highly reactive radicals , e.g. atomary chlor, created in plasma react with surface producing gaseous products
- plasma ions bombards the surface (acceleration through plasma sheath)

- removal of surface contamination that block etching
- contribution to etching kinetics

Types of Directional Dry Etching

Types of Directional Dry Etching

deep reactive ion etching (DRIE)

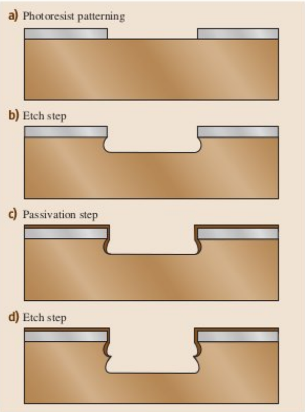


Fig. 8.17a–d DRIE cyclic process: (a) photoresist patterning, (b) etch step, (c) passivation step, and (d) etch step

- two step cycle (see fig.)
- aspect ratio 30 : 1
- etch rate of Si = 2-3 μm/min

Silicon DRIE:
etching step - SF_6/Ar
passivation step - nCF_2/Ar (50 nm teflon-like polymer deposited on side walls)

Table 8.1 Typical dry etch chemistries

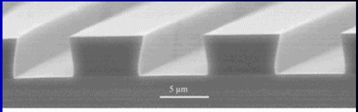
Si	CF_4/O_2, CF_2Cl_2, CF_3Cl, $SF_6/O_2/Cl_2$, $Cl_2/H_2/C_2F_6/CCl_4$, C_2ClF_5/O_2, Br_2, SiF_4/O_2, NF_3, ClF_3, CCl_4, $C_3Cl_3F_5$, C_2ClF_5/SF_6, C_2F_6/CF_3Cl, CF_3Cl/Br_2
SiO_2	CF_4/H_2, C_2F_6, C_3F_8, CHF_3/O_2
Si_3N_4	$CF_4/O_2/H_2$, C_2F_6, C_3F_8, CHF_3
Organics	O_2, CF_4/O_2, SF_6/O_2
Al	BCl_3, BCl_3/Cl_2, $CCl_4/Cl_2/BCl_3$, $SiCl_4/Cl_2$
Silicides	CF_4/O_2, NF_3, SF_6/Cl_2, CF_4/Cl_2
Refractories	CF_4/O_2, NF_3/H_2, SF_6/O_2
GaAs	BCl_3/Ar, $Cl_2/O_2/H_2$, CCl_2F_2/O_2/Ar/He, H_2, CH_4/H_2, $CClH_3/H_2$
InP	CH_4/H_2, C_2H_6/H_2, Cl_2/Ar
Au	$C_2Cl_2F_4$, Cl_2, $CClF_3$

Pros and Cond of Plasma Etching

Pros and Cons of Plasma Etching

Most of dry etching applications are plasma based.

\+ more anisotropic than chemical etching (smaller undercuts allow smaller lines to be patterned, etching of high-aspect-ratio vertical structures)



Resist with typical undercut on a Si substrate

\+ higher etch rate due to synergy of chemical etching and ion bombardment

\- lower etching selectivity

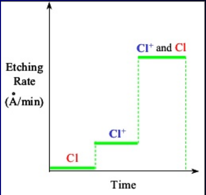


Fig. 22. Ion-enhanced etching increased the etching rate by order(s) of magnitude.