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Etching





Lecture 7 Etching



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Etching: Basic Terminology



- Etching of thin films and sometimes the silicon substrate are very common process steps.
- Usually selectivity, and directionality are the first order issues.

Etching - Overview

- Basic Terminology
- Wet Etching
- Dry / Plasma Etching
 - Mechanisms
 - Example
 - Reactor Designs
- Summary and Appendix

Etching: Basic Terminology

- 1. Etch rate
- 2. Selectivity
- 3. Anisotropy

4. Uniformity / Homogeneity

Etching: Basic Terminology

Etch rate: r

- Speed at which ethcing occurs
- Typical unit: r [nm/min]

Selectivity : S

Ratio of two etch rates

Example 1:

$$S = \frac{r_1}{r_2}$$

r

SiO₂ etching with hydrofluoric acid (HF): SiO₂+ 6 HF \rightarrow H₂SiF₆ + 2 H₂O

A. Determine the etch time for a 1,2 μm thick SiO_2 film

with $r_{SiO2} = 400 \text{ nm/min} \rightarrow 3 \text{ min}$.

B. How thick should the resist mask be if the selectivity is $S_{SiO2/resist} = 4$?



Etch rate and selectivity are crucial for defining masks! (Photo- or "Hard"masks)

BOE : buffered oxide etching BHF: buffered HF NH_4F buffer: Help to prevent depletion of F- \rightarrow decrease etch rate of photoresist

Etching: Basic Terminology Anisotropy A

Isotropic etching removes material equally in all directions
 → Undercut of the mask



Anisotropic etching removes material only perpendicular to the surface
 → accurate transfer of the mask pattern

Anisotropy:
$$\frac{\text{vertical etch rate - horizontal etch rate}}{\text{vertical etch rate}}$$
 $A = 1 - \frac{r_{hor}}{r_{vert}}$

Etching: Basic Terminology *Uniformity / Homogeneity*

Measures the distribution of the etch rate

□ Wafer to wafer, esp. for multi-wafer processing

□ Across one wafer (e.g. center vs. edge)



□ Has to be considered when determining etching time (e.g. overetching)

Production: Matching production tools (esp. litho and etching)



Etching Performance Parameters

Etch Rate <i>R</i>	The film thickness being etched per unit time. <i>R</i> has significant effects on throughput.
Etch Uniformity	Variation of etch rate throughout one wafer, multiple wafers or multiple batches of wafers
Selectivity S	The ratio of the etch rates between two different materials
Anisotropy A	Etching directionality A=0, isotropic; A=1, anisotropic
Undercut	Unilateral overetching

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Example 1: Etch SiO₂ using HF

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

In practice, BOE : buffered oxide etching or BHF: buffered HF

NH₄F buffer: Help to prevent depletion of F⁻ and decrease etch rate of photoresist

Isotropic

Example 2: Ecth Si using HNO_3 and HF (HNA) Si + HNO₃ + 6HF \rightarrow H₂SiF₆ + HNO₂ + H₂O + H₂

Example 3: Ecth Si₃N₄ using hot phosphoric acid

 $Si_3N_4 + H_3PO_4 + H_2O \rightarrow NO \uparrow + NO_3^- + H_2PO_4^- + H_2SiO_3$

Wet Etching: ExamplesExample 4: Etch Si using KOHAnisotropicSi $+ 2OH^{-} + 4H_2O \Rightarrow Si(OH)_2^{++} + 2H_2 + 4OH^{-}$

Anisotropic wet etching results from surface orientation



Wet Etching: Examples

Example 3: Etch Si using KOH



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Wet Etching: Examples

Example 3: Etch Si using KOH



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Self-Limited

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Wet Etching: Applications

MEMS (MicroElectroMechanical Systems) Made from Si Anisotropic Wet Etching



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Wet Etching: Drawbacks

In the manufacture of large-scale electronic ICs, wet etching is being replaced by dry etching.

- (1) Wet etching is mostly isotropic.
- (2) Wet etching has poor resolution.
- (3) Wet etching depends on a lot of corrosive chemicals, which are harmful to human bodies and environments.

(4) Wet etching needs a large number of chemical reagents to wash away the residues. Non-economical!!

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Etching: Requirements at the Nanoscale

Etch Requirements at the Nanoscale:

- 1. Obtain desired profile (sloped or vertical)
- 2. Minimal undercutting or bias
- 3. Selectivity to other exposed films and resist
- 4. Uniform and reproducible
- 5. Minimal damage to surface and circuit
- 6. Clean, economical, and safe





Etching: Requirements at the Nanoscale

	Reactive neutral molecules	Ions (z.B. Ar+)	
	chemical	physical	
Selectivity	++		
Anisotropy	(<<1)	++ (~1)	
Examples	liquid, steam or plasma	Ion bombardment ("sputter")	

How can we combine chemical and physical components?

Plasma contains neutral radicals AND positive lons!

Plasma

Plasma

The 4th aggregate state (in increasing excitation)

solid	liquid	gaseous	PLASMA
Ice H ₂ O	Water H ₂ O	Steam H ₂ O	lonized Gas H ₂ → 2H ⁺ + 2e ⁻
T < 0°C	0°C < T < 100°C	T > 100°C	T > 100000°C
No.			
atoms / molecules are fixed in the crystal lattice	atoms / molecules can move freely as a network	atoms / molecules can move freely, large distances	lons and electrons noy bound, very large distances

Plasma Generation

Application relevant generation of plasma in a parallel plate reactor



- Anode grounded
- Cathode connected to RF generator via impedance matching network
- High electric field ionizes gas molecules \rightarrow Plasma!
- "Fast" electrons follow RF field \rightarrow positive ions determin plasma potential
- A smaller electrode leads to a higher voltage difference compared to plasma



- Dissociation: Partitioning a molecule into components, e.g. free radicals
- Ionization: Further generation of free electrons and charged molecules
- Excitation: excited molecules relax and emit Photons ("glow")
- Recombination: Radicals and molecules recombine

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• Typically there are about 10^{15} cm⁻³ neutral species (1 to 10% of which may be free radicals) and 10^{8} - 10^{12} cm⁻³ ions and electrons

• In standard plasma systems, the plasma density is closely coupled to the ion energy. Increasing the power increases both

- There are three principal mechanisms
 - chemical etching (isotropic, selective)
 - physical etching (anisotropic, less selective)
 - ion-enhanced etching (anisotropic, selective)
- Most applications today try to use the ion-enhanced mechanism (which provides in fact more than the sum of its components).

1. Chemical Etching

- Etching by reactive neutral species, such as "free radicals" (e.g. F, CF₃)
- Additives like O_2 can be used which react with CF_3 and reduce $CF_3 + F$ recombination \rightarrow higher etch rate



2. Physical Etching or "Sputter Etching"

- Purely physical etching
- Highly directional (ε field across plasma sheath)
- Etches almost anything
- Poor selectivity: all materials sputter at about the same rate
- Pure sputter etching uses Ar+ \rightarrow Damage to wafer surface and devices can occur:
 - (a) trenching ion
 - (b) bombardment damage, radiation damage, redeposition of photoresist
 - (c) charging
- These damages can occur in any etch system with a dominant physical etching component



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3. Ion Enhanced Etching or Reactive Ion Etching (RIE)

• It has been observed that chemical and physical components of plasma etching do not always act independently - both in terms of net etch rate and in resulting etch profile.



Example:

• Etch rate of silicon as XeF₂ gas (not plasma) and Ar⁺ ions are introduced to silicon surface. Only when both are present does appreciable etching occur

- Etch profiles can be very anisotopic, and selectivity can be good
- Many different mechanisms proposed for this synergistic etching between physical and chemical components. Two mechanisms are shown below:



• Ion bombardment can enhance etch process (such as by damaging the surface to increase reaction, or by removing etch byproducts)

• Ion bombardment can remove inhibitor that is an indirect byproduct of etch process (such as polymer formation from carbon in gas or from photoresist)

• Whatever the exact mechanism (multiple mechanisms may occur at same time):

- need both components for etching to occur.
- get anisotropic etching and little undercutting because of directed ion flux.
- get selectivity due to chemical component and chemical reactions.
- \rightarrow many applications in etching today

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Si, Si₃N₄ and SiO₂ Etching

$$Si+4F^* \rightarrow SiF_4\uparrow SiO_2+4F^* \rightarrow SiF_4\uparrow +O_2\uparrow Si_3N_4+12F^* \rightarrow 3SiF_4\uparrow +2N_2\uparrow$$

- ✓ CF_x (x≤3) etches SiO₂ or Si₃N₄ faster than Si.
- ✓ Adding a little O_2 into CF_4 may increase its etch rates for Si, SiO₂ and Si₃N₄

10% O₂ achieves the maximum Si/SiO₂ etch rate ratio

Additive gases can improve selectivity



✓ CF_x (x≤3) etches SiO₂ or Si₃N₄ faster than Si.

✓ Adding a little H_2 in CF₄ can increase the concentration ratio of CF_x : F* and hence increase the etch rate ratios of SiO₂ : Si and Si₃N₄:Si.



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Increasing F/C by adding O₂ can increase etch rate Decreasing F/C by adding H₂, etching tends to form polymer film

Concept Test 8

7.1: A plasma etch process can be described with the following terms: *Etch Rate – Selectivity - Anisotropy – Uniformity*A plasma etch tool has the following process parameters: Pressure,
Temperature, Gas composition, Gas flow, Substrate bias, RF power.
Which of the following statements are true:

- A. Pressure affects anisotropy and rate.
- B. Temperature affects mainly the ion driven component.
- C. The gas composition affects mainly the etch rate.
- **D.** Gas flow affects mainly the chemical component.
- E. Substrate bias affects mainly the chemical component.
- F. RF power affects mainly the etch rate.

Concept Test 8 Etch Rate – Selectivity - Anisotropy - Uniformity

- Pressure (Anisotropy and Rate: collisions, mean free path)
- Temperature (All: chemical component)
- Gas mixture (All: chemical component)
- Gas flow (Rate and Selectivity: more gas → more chemistry; Uniformity: in connection with chamber geometry)
- Substrate bias (physical component in HDP tools)
- RF power (rate: plasma density, anisotropy: substrate bias)
- Chamber geometry (usually not a parameter)

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RIE Example: Highly Selective Silicon Etch Process



RIE Example: Highly Selective Silicon Etch Process

Solution: Gate electrode etch process for silicon MOSFET

HBr + O₂ based plasma process in Oxford RIE Etcher

- + Etch product: Si + Br = SiBr (volatile)
- + O_2 addition to increase selectivity
- + Sidewall passivation with SiOBr (anistropy!)
- HBr is corrosive and highly poisonous

Process development: Optimizing process parameters

e.g. Pressure [mTorr] O₂-Admixture RF power Plasma power Gas flow

RIE Example: Highly Selective Silicon Etch Process Process development: Optimizing process parameters

e.g. Variation of chamber pressure [mTorr]

Fixed parameter: gas mixture: 2% O₂ in HBr



Preliminary result:

Rate too high (r_{SiO2min} = 3.7 nm/min)

Further increase of pressure not feasible \rightarrow loss of anisotropy



New optimization approach:

Increase of O₂ admixture

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RIE Example: Highly Selective Silicon Etch Process Process development: Optimizing process parameters

e.g. Variation of chamber pressur [mTorr]

NEW parameter: gas mixture: increase from $2\% O_2$ in HBr to **5%**



Result:

Rate optimized ($r_{SiO2min} \sim 0 \text{ nm/min}$)

Next steps:

- Check polysilicon etch rate r_{Si}
- Check anisotropy
- If needed: further optimization:
 - RF power
 - Plasma power
 - Gas flow...

RIE Example: Highly Selective Silicon Etch Process Result: highly selective, anisotropic HBr/O₂ RIE process



Scanning Electron Microscope (SEM) Image:

- 26 nm Poly-Si Gates
- Etch stop on 3 nm SiO₂



Optimized HBr/O₂ Process fulfils all requirements

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Optical Endpoint Detection

Determining the Etch Time

Recommended Wavelengths for Monitoring Endpoint

Etch Application	Film Type	Species	Wavelength
Contact & Spacer	Oxide over Si poly or silicide	со	483.5nm
	Childe over on polyr or sincide	CF2	270 nm
Via	Oxide over metal	со	438.5nm
		CF2	270 nm
Stack	Oxide over nitride	со	438.5nm
	Oxac over mende	CN	386.5nm
Isolation	Nitride over oxide	CN	386.5nm
Patterned Poly	Poly over ovide	Cl, Br	470.5nm
		Br	312.5nm
Patterned Wsi2	Wsi2 over poly or oxide	F	441.5nm
Patterned TiSi2	TiSi2 over poly or oxide	Cl, Br	470.5nm
Patterned MoSi2	MoSi2 over poly or oxide	Cl, Br	470.5nm
Patterned Al	Al-Si-Cu over barrier metal or oxide	Al	396 nm



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Source: http://www.findmems.com/bosch/mems-bosch-automotive-applications-and-beyond

Active Etch Step: SF₆ isotropic etch

Passivation Step: C_4F_8 inhibitor layer \rightarrow Thin layer at Si sidewalls

Figure 1. (*a*) Ideal (or targeted) profile of the etched trench by employing the Bosch process. (b) Real profile of the etched trench by employing the Bosch process. (c) The periodic cycles in the Bosch process.

Etching

active time

Passivation

active time

(c)

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Different configurations have been developed to make use of chemical, physical or ion assisted etching mechanisms.

Barrel Etchers

- Purely chemical etching
- Used for non-critical steps, such as photoresist removal ("ashing")



Parallel Plate Systems - Plasma Mode

- Electrodes have equal areas (or wafer electrode is grounded with chamber and larger)
- Only moderate sheath voltage (10-100 eV), so only moderate ionic component
- Strong chemical component
- Etching can be fairly isotropic and selective



Parallel Plate Systems - Reactive Ion Etching (RIE) Mode

- For more directed etching, need stronger ion bombardment
- Wafers sit on smaller electrode (RF power there)
- Higher voltage drop across sheath at wafers.(100-700 eV)
- Lower pressures are used to attain even more directional etching (10-100 mtorr)
- More physical component than plasma mode for more directionality but less selectivity



High Density Plasma (HDP) Etch Systems

• Uses remote, non-capacitively coupled plasma source (Electron cyclotron) resonance - ECR, or inductively coupled plasma source - ICP)

- Uses separate RF source as wafer bias. This separates the plasma power (density) from the wafer bias (ion accelerating field)
 - Very high density plasmas (10¹¹-10¹² ion cm⁻³) can be achieved (faster etching)
 - Lower pressures (1-10 mtorr range) can be utilized due to higher ionization efficiency (\rightarrow longer mean free path and \rightarrow more anisotropic etching)
 - These systems produce high etch rates, decent selectivity, and good directionality, while keeping ion energy and damage low



Widely used today!



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Summary: Plasma Etching







Summary of Key Ideas

- Etching of thin films is a key technology in modern IC manufacturing.
- Photoresist is generally used as a mask, but sometimes other thin films also act as masks.
- Selectivity and directionality (anisotropy) are the two most important issues. Usually good selectivity and vertical profiles (highly anisotropic) are desirable.
- Other related issues include mask erosion, etch bias (undercutting), etch uniformity, residue removal and damage to underlying structures.
- Dry etching is used almost exclusively today because of the control, flexibility, reproducibility and anisotropy that it provides.
- Reactive neutral species (e.g. free radicals) and ionic species play roles in etching.

• Generally neutral species produce isotropic etching and ionic species produce anisotropic etching.

• Physical mechanisms:

- Chemical etching involving the neutral species.
- Physical etching involving the ionic species.
- Ion-enhanced etching involving both species acting synergistically.



Appendix: Plasma Etching in Silicon Technology

Common etchants used for various films in silicon technology.

Material	Etchant	Comments
Polysilicon	SF ₆ , CF ₄	Isotropic or near isotropic (significant undercutting); poor or no selectivity over SiO ₂
	CF_4/H_2 , CHF_3	Very anisotropic, non-selective over SiO ₂
	CF_4/O_2	Isotropic, more selective over SiO ₂
	HBr, Cl_2 , $Cl_2/HBr/O_2$	Very anisotropic, most selective over SiO ₂
Single crystal Si	same etchants as polysilicon	
SiO ₂	SF_6 , NF_3 , CF_4/O_2 , CF_4	Can be near isotropic (significant undercutting); anisotropy can be improved with higher ion energy and lower pressure;
		poor or no selectivity over Si
	CF_4/H_2 , CHF_3/O_2 , C_2F_6 , C_3F_8	Very anisotropic, selective over Si
	CHF ₃ /C ₄ F ₈ /CO	Anisotropic, selective over Si_3N_4
Si_3N_4	$\mathbf{CF}_4/\mathbf{O}_2$	Isotropic, selective over SiO ₂ but not over Si
	$\mathbf{CF}_4/\mathbf{H}_2$	Very anisotropic, selective over Si but not over SiO ₂
	$CHF_{3}/O_{2}, CH_{2}F_{2}$	Very anisotropic, selective over Si and SiO ₂
Al	Cl ₂	Near isotropic (significant undercutting)
	Cl,/CHCl,, Cl,/N,	Very anisotropic;
	2 3 2 2	BCl, often added to scavenge oxygen.
W	CF ₄ , SF ₆	High etch rate, non-selective over SiO ₂
	Cl ₂	Selective over SiO ₂
Ti	Cl ₂ , Cl ₂ /CHCl ₃ , CF ₄	
TiN	Cl ₂ , Cl ₂ /CHCl ₃ , CF ₄	
TiSi ₂	Cl ₂ , Cl ₂ /CHCl ₃ , CF ₄ /O ₂	
Photoresist	O ₂	Very selective over other films