Plasma Etching

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Overview

• Difference between plasma deposition and etching
• Plasma etching mechanisms
• Anisotropic and isotropic etching
• Redeposition and self-passivation
• DRIE
• Application examples
Plasma etching summary

- Plasma has ions and excited species of reactive gases
- Reactive ions are directed to the surface by electric fields
- Chemical reactions take place at the surface and eat away the material
- Sputtering can also etch away material
- Reaction products are removed in gas form
- DRY ETCHING: reactants are gaseous and solid
WHY PLASMA ETCHING

Advanced IC Fabrication with small geometries requires precise pattern transfer

Geometry in the 1.0-3.0 micrometer range is common

Current exposure tools allow creation of submicron patterns

Line widths comparable to film thickness

Some applications require high aspect ratio

Some materials wet etch with difficulty

Disposal of wastes is less costly
## Materials and Gas Systems

<table>
<thead>
<tr>
<th>Materials</th>
<th>Etch chemistry</th>
<th>Reaction products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>CF(_4), SF(_6), HBr, Cl(_2), NF(_3), HI</td>
<td>SiF(_4), SiCl(_4), SiF(_2), SiCl(_4), SiBr(_4), SiI(_4)</td>
</tr>
<tr>
<td>SiO(_2), Si(_3)N(_4)</td>
<td>CHF(_3), C(_4)F(_8), C(_2)F(_6), SF(_6), NF(_3)</td>
<td>SiF(_4), CO, CO(_2)</td>
</tr>
<tr>
<td>Al</td>
<td>BCl(_3), HCl, Cl(_2)</td>
<td>Al(_2)Cl(_6), AlCl(_3)</td>
</tr>
<tr>
<td>W</td>
<td>SF(_6), CF(_4), NF(_3) Cl(_2), O(_2)</td>
<td>WF(_6) WOCI(_x)</td>
</tr>
<tr>
<td>Ti, TiN</td>
<td>Cl(_2)</td>
<td>TiCl(_4)</td>
</tr>
<tr>
<td>Polymers</td>
<td>O(_2), O(_2)/CF(_4), SO(_2)</td>
<td>CO, H(_2)S, CO(_2), HF, H(_2), H(_2)O</td>
</tr>
<tr>
<td>InP, HgCdTe</td>
<td>CH(_4)/H(_2)</td>
<td>In(CH(_3))(_3), PH(_3), Cd(CH(_3))(_2)</td>
</tr>
<tr>
<td>GaAs</td>
<td>Cl(_2), BCl(_3)</td>
<td>Ga(_2)Cl(_6), AsCl(_3)</td>
</tr>
</tbody>
</table>
Periodic Table of the Elements

Halogens

Atomic masses in parentheses are those of the most stable or common isotope.
Prior to etch

film to be etched

substrate

resist

after etch

film to be etched

substrate

resist

No process is ideal, some anisotropic etches are close.
Selectivity = \frac{\text{Etch rate of film to be etched}}{\text{Etch rate of substrate}}

Etch rate ratio = \frac{\text{Etch rate of film to be etched}}{\text{Etch rate of Mask}}
Degree of Anisotropy

\[ A_f = 1 - \frac{l}{h_f} = 1 - \frac{R_l t}{R_v t} = 1 - \frac{R_l}{R_v} \]

- For isotropic etching: \( R_l = R_v \) and \( A_f = 0 \)
- For anisotropic etching: \( R_l = 0 \) and \( A_f = 1 \)
# Types of Dry Etching Processes

<table>
<thead>
<tr>
<th>Types of Etching</th>
<th>Methods</th>
<th>Geometry</th>
<th>Selectivity</th>
<th>Excitation Energy</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas/vapor Etching</td>
<td>Chemical</td>
<td>Isotropic</td>
<td>Very high</td>
<td>none</td>
<td>High (760-1torr)</td>
</tr>
<tr>
<td>Plasma Etching</td>
<td>Chemical</td>
<td>Isotropic</td>
<td>High</td>
<td>10's to 100's of Watts</td>
<td>Medium (&gt;100 mtorr)</td>
</tr>
<tr>
<td>Reactive ion Etching</td>
<td>Chemical &amp; Physical</td>
<td>Directional</td>
<td>Fair</td>
<td>100's of Watts</td>
<td>Low (10-100 mtorr)</td>
</tr>
<tr>
<td>Sputtering Etching</td>
<td>Physical</td>
<td>Directional</td>
<td>Low</td>
<td>100's to 1000's of Watts</td>
<td>Low (~10 mtorr)</td>
</tr>
</tbody>
</table>

(1 torr = 1 mmHg)
RF-Plasma-Based Dry Etching

- A plasma is fully or partially ionized gas composed of equal numbers of positive and negative charges and a different number of unionized molecules.
- A plasma is produced when an electric field of sufficient magnitude is applied to a gas, causing the gas to break down and become ionized.

\[
e^- + CF_4 \rightarrow CF_3^+ + F + 2e^-
\]
Capacitive and Inductive Coupling

- Most low and medium plasma density reactors utilize capacitive coupling while high density plasmas can be generated by inductively coupled, electron cyclotron resonance (ECR) and some high frequency capacitively coupled reactors.

- The capacitive coupling requires a high capacitance between the electrode and the plasma (*large amplitude RF voltages*).

- The inductive coupling requires a high inductance between a coil and the plasma (*large RF currents*).

- Capacitive coupling results in a high energy ion bombardment while the ion bombardment energy is much lower in inductively coupled discharges.

- In a capacitive discharge, the periodic electron current flow to the electrode causes a modulation of the plasma potential.

- In an inductive discharge, the time varying current induces a time-varying magnetic field which induces a time varying electric field that can sustain the plasma.
Reactive and Condensable Species

Neutral species that arrive at the wafer surface can stick to the surface and react. Depending on the sticking coefficients and reaction probabilities, reactive and condensable species can be distinguished among the species in the feed gas and the reaction products. The balance between reaction and condensation influences the etch profile.

**Reactive species:**
- React chemically with surfaces.
- Reactions are not very temperature sensitive because of low activation energies for the reactions.
- Surface coverage is typically saturated at a few monolayers.

**Condensable species:**
- Form liquid or solid films on surfaces.
- Surface coverage dependents strongly on the substrate temperature.

**Examples at room temperature:**
Halogen atoms: reactive but not condensable
CF₄, CHF₃, SF₆: not reactive, not condensable
N₂, H₂, O₂: not reactive, not condensable
Plasma by products: usually not reactive, condensable when non volatile
Polymer precursors (CₓFᵧ): both condensable and reactive
Etch Mechanism

• Generation of etching species
  - Without generating the etching species, etching will not proceed

• Diffusion to surfaces
  - Etching species must get to the surface to react with the thin or substrate molecules.
  - The mechanics of getting to the surface can limit aspect ratio, undercutting, uniformity.

• Adsorption
  - Can also affect aspect ratio.

• Reaction:
  - Strong function of temperature (Arrhenius relationship).
  - Obviously affect the etch rate.

• Desorption
  - Can stop etch if the reacted species is not volatile.

• Diffusion to bulk gas
  - Can lead to non-uniform etching due to dilution of un-reacted etching species.

The slowest dominates !!!
Overview of Plasma Etch Mechanisms I

1. **Chemical etching:** Spontaneous, isotropic, very selective.
2. **Ion enhanced etching:** Neutrals and ions involved, ion energy needed to stimulate chemical reaction or to remove reaction products. Anisotropic and selective.
3. **Physical etching:** Anisotropic and non-selective.
4. **Trenching:** Caused by ion deflection from sidewalls (surface scattering or influence of electric field of charged mask / sidewall).
5. **Sidewall passivation:** Deposition of non-volatile materials: Etch byproducts, surface reactions with certain feed gas additives, mask material. Removed from horizontal surfaces by ion bombardment.
6. **Mask erosion:** Caused by ion bombardment / sputtering.

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Gas Phase Etch

Reactive Gas
- Gas adsorbs on the surface, diassociates, and then reacts

Xenon Difluoride Etching

\[ \text{XeF}_2 \xrightarrow{\text{Adsorb}} \text{Xe} + 2 \text{F} \]

Particular features of XeF\(_2\) etching
- extremely selective
- fast etch rate
- isotropic
Etch mechanisms of silicon in HBr and Cl2 plasmas (I)

- Chlorinated or brominated layer
- Amorphized layer

Determination by spectroscopic ellipsometry (SE)

Graphs showing:
- Amorphized layer thickness vs. bias power (W) for HBr and Cl2
- Halogenated layer thickness vs. bias power (W) for HBr and Cl2

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Dry Etching Si/SiO2 in F-Based Gases and Plasmas

- Prominent etch chemistry in ICs & MEMS
- $\text{CF}_4$ does not etch Si (does not chemisorb) but $\text{F}_2$ gas will etch Si with etch products $\text{SiF}_2$ and $\text{SiF}_4$
- Plasma is needed to generate F that must penetrate Si$_2$F$_2$-like surface
Overview of Plasma Etch Mechanisms II

Anisotropic plasma etching has two components, chemical etching (neutrals and radicals of the plasma) and physical bombardment (ion assisted etching reactions).

VLSI plasma etch processes are characterized by a varying significance of the chemical and physical components. Aluminum etching is a very chemical etch while SiO$_2$ etching has a very strong physical component. Silicon etch has strong chemical and physical components.

To understand plasma etching mechanisms and improve processes, it is essential to describe these two components and the synergy existing between these two components:

Setup of the classical experiment to proves the synergy of chemical and physical components in plasma etching:


http://content.aip.org/JAP/AU/v50/i5/3189_1.html

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Controlling Anisotropy

Anisotropy can depend on mean free path, or on DC plasma bias.

- Increasing mean free path (generally) increases anisotropy
- Increasing DC bias (generally) increases anisotropy
**Dry Etching Spectrum**

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Physical (Sputtering)</th>
<th>Energy</th>
</tr>
</thead>
</table>
| Low <100 mTorr | Momentum Transfer  
             Directional Etch Possible  
             Poor Selectivity  
             Radiation Damage Possible | High Energy |
| 100 mTorr | **Reactive Ion Etching**  
             Physical and Chemical  
             Variable Anisotropy  
             Variable Selectivity |          |
| 400 mTorr | **Chemical Plasma Etching**  
             Fast  
             Isotropic  
             High Selectivity  
             Low radiation Damage | Low Energy |
Increase of Degree of Anisotropy
Formation of Sidewall Passivating Films

- Formation of nonvolatile fluorocarbons that deposit on the surfaces (Polymerization)
- The deposit can only be removed by physical collisions with incident ions
- Fluorocarbon films deposits on all surfaces, but the ion velocity is nearly vertical. As a result, as the etching proceeds there is little ion bombardment of the sidewalls and the fluorocarbon film accumulates
- Adding hydrogen encourages the formation of the fluorocarbon films because hydrogen scavenge fluorine, creating a carbon-rich plasma (same thing happened when C_2F_6 is used instead of CF_4)
- Less accumulation is observed on SiO_2 than Si surfaces
- Tradeoff between Si/SiO_2 selectivity and Anisotropy
Sidewall passivation layer formation (I)

At room temperature etch anisotropy is always obtained thanks to the formation of a sidewall passivation layer:

The sidewall passivation layer can be formed by different mechanisms:

1) Mask etch products sputtered into the plasma gas phase by energetic ion bombardment and get re-deposited on the feature sidewalls.

2) Condensation of some molecules or atoms originating from the dissociation of the feed gas stock.

3) Etch by products dissociation in the gas phase leading to the formation of partially volatile or non volatile etch by products which get re-deposited on the feature sidewalls.

4) Direct line of sight deposition of non volatile etch by-products.
Sidewall passivation layer formation (II)

Chamber walls

Plasma

Resist etch products (ex: Al etching)

Etched by-products

Etched surface

Gas chemistry leading to the condensation of species on the sidewalls (Example: fluorocarbon gas in oxide etching)

Mask

Passivation layer

Etched by-products redeposition (line of sight)
Sidewall passivation layer formation (III)

Resist mask

Re-deposition of resist etch products on the Al sidewalls generating a carbon-based passivation layer

Al

C\textsubscript{x}Cl\textsubscript{y}

Resist mask

Condensation of CF\textsubscript{x} species from the fluorocarbon gas on the oxide sidewalls and re-deposition of resist etch products both contribute to the CF\textsubscript{y} passivation layer formation

SiO\textsubscript{2}

C\textsubscript{x}F\textsubscript{y}

Resist mask

Re-deposition of silicon etch products from the plasma gas phase and direct line of sight deposition of silicon etch products

Si

SiO\textsubscript{x}
Etching Profiles

- **Anisotropic Etching**
  (ideal sidewall passivation)

- **Tapering**
  (strong sidewall passivation)

- **Bowing**
  (ion trajectory distortion, mostly in dense areas)

- **Undercutting**
  (spontaneous etching)

- **Notching**
  (ion trajectory distortion and chemical etching)
Spontaneous Etching Reactions in Plasma Etching
- Silicon Etching with Fluorine Radicals -

Silicon etch rate is driven by radical concentration in the gas phase. Higher source power leads to deeper SF$_6$ dissociation and more free fluorine. Higher SF$_6$ flow reduces the concentration of reaction products in the gas phase. For very high source power / SF$_6$ flow combinations, the etch rate saturates, indicating that surface processes are becoming rate limiting.

SF$_6$ plasma, no additives.
10 mTorr pressure.
No bias power.

Spontaneous or chemical etch processes are typically isotropic because the lack of ion bombardment does not allow the formation of a sidewall passivation.
The Role of Ion Bombardment in Plasma Etching
- Anisotropy -

Ion bombardment enhanced etch:
- Ion enhanced chemical reaction
- Ion induced damage and mixing
- Chemical sputtering

Etch by-product removal:
- Physical and chemical sputtering
- Enhanced sidewall passivation formation due to backspattering of non volatile etch products

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The Role of Ion Bombardment in Plasma Etching

When a surface is exposed to ion bombardment, atoms and molecules can be ejected. This is called **Sputtering**.

**Physical sputtering** is a non-selective phenomenon (materials of different nature can be sputtered at similar rates). It is also a directional phenomenon which helps in obtaining anisotropic etching profiles.

**Ion induced damage and mixing**: Ion bombardment may favor neutral dissociation at the surface and increase the number of adsorption sites by generating some surface roughness and generating dangling bonds.

**Ion enhanced chemical reaction**: Ion bombardment may favor the formation of etch products.

**Chemical sputtering**: Ion bombardment may favor the desorption of etch by products.

**Ions as a source of reactants**: Ions get neutralized when they reach the surface, they become an additional source of reactive species.
The Role of Ion Bombardment in Plasma Etching
- Factors Influencing Anisotropy -

**Ion energy flux** (ion density and ion energy): Primarily responsible for the etch anisotropy in plasma etching. In general an increase in ion energy flux leads to a better anisotropy.

**Neutral to ion flux ratio**: The lower the neutral to ion flux ration the better the anisotropy.

**Natural species reactivity**: Probability for spontaneous reaction of neutral species to react with the surface.

**Deposition rate** for non-volatile etch products forming a passivation layers at the feature sidewalls.

**Substrate temperature**: Influences neutral species reactivity and reaction product deposition.
In this classical experiment, the silicon etch rate increased by one order of magnitude when the ion beam is turned on. This shows the importance of the ion/neutral synergy in plasma etching.

The reaction of XeF2 with silicon is described by the following reaction scheme:

\[
\begin{align*}
XeF_2(g) & \rightarrow XeF_2(p) \\
XeF_2(p) + Si(s) & \rightarrow Xe(g) + SiF_2(s) \\
XeF_2(p) + SiF_2(s) & \rightarrow Xe(g) + SiF_4(g) \\
SiF_2(s) & \rightarrow SiF_2(g) \text{ (over 600K)}
\end{align*}
\]

Enhanced by ion bombardment

For more information on the reaction of XeF2 with silicon see website of TU Eindhoven:
http://www.phys.tue.nl/aow/Pages/Research/spontaneous_etching.htm
Spontaneous Etching Reactions in Plasma Etching
- Formation of Free Radicals: CF₄ -

Effect of Additives: Adding of O₂ to CF₄

![Graph showing the effect of O₂ on etch rate and line intensity](image)

Formation of free F:

\[
\text{CF}_4 + e \rightarrow \text{CF}_3 + F + e
\]

Addition of O₂ - Suppression of radical recombination:

\[
\text{CF}_3 + F \rightarrow \text{CF}_4
\]

But:

\[
\text{CF}_2 + O \rightarrow \text{COF} + F
\]

\[
\text{COF} + O \rightarrow \text{CO}_2 + F
\]


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Silicon to nitride selectivity for a SF6 plasma is shown as a function of $V_{dc}$. The lower $V_{dc}$, the more chemical the etch. The results show that nitride requires ion bombardment to be etched in a fluorine based plasma while silicon etches spontaneously. Therefore very high selectivities can be obtained by reducing the ion component of the etch. Decoupled ICP or ECR plasma sources and downstream reactors are suited for this application.
Charging effects in plasma etching (I)

Introduction

Charging effects during plasma etching of high aspect ratio structures can cause:
- gate oxide degradation during gate etching
- profile deformation issues such as notching or bowing

The origin of this phenomenon is due to the difference in directionality between ions and electrons when they cross the plasma sheath and interact with three dimensional structures.

Charging effects become important for aspect ratios higher than 2:1.
Charging effects in plasma etching (III)

Ion and electron fluxes onto large open areas are equal.

Any vertical surface on the wafer (feature sidewall) screens a part of the electron flux: the net flux of electrons arriving on the surface decreases. In contrast, the ion flux is not impacted. If the surface at the bottom is an insulator, it charges positively, possibly leading to a partial deviation of the ion flux. If the mask is an insulator, it will charge negatively.

For two adjacent sidewalls are present (space between two lines or trenches), the shadowing effect becomes even more pronounced. The insulator between the lines will be charged even more.

Adapted from Hwang and Giapis, JVST B15, 70, (1997)
Charging effects in plasma etching (VI)
Simulation of charging effects during a polysilicon gate etch process

The very strong peak potential that develops close to the edge of the structure induces an ion trajectory distortion. Close to the edge of polysilicon, ions never reach SiO₂ at the bottom. They get deflected by the high potential at the bottom that develops on the SiO₂ surface and reach the polysilicon sidewalls. There, the ions can generate some etching if their energy is high enough to punch through the passivation layer.
Plasma Potentials and Excitation Electrode Voltages

Purely capacitive sheath behavior.
V(t) - excitation electrode voltages
V_p(t) - plasma potentials

dc coupled

capacitively coupled

Typical Plasma Etch Configuration

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Electron and Ion Fluxes to Reactor Electrodes
- asymmetric reactor, small electrode powered -

- Diagram showing the current to the excited electrode and chamber walls, with positive ion current indicated.
- Pulses of electron current are shown with equal area.
- Graphs of $V_p(t)$ and $V(t)$ with $V_{dc}$.
The Trenching Phenomenon

Profile trenching is caused by ion bombardment.

Ions arriving at grazing angles on the feature sidewalls get reflected and accumulate leading to a localized higher etch rate.

This effect is well known in sputter etching and in plasma processing.

At least two possible explanations for trenching can be found in the literature:

1. Ion scattering from sloped sidewall surfaces
   H.H. Sawin; J. Appl. Phys. 70 (1991) 5314 and others)

2. Ion deflection due to differential charging of microstructures
   72 (1998) 1294 and others)
Mirotrenching: Chemistry Effect

Source power: 500 W
Cathode power: 80 W

500 nm PECVD HM / bulk silicon
P < 10 mTorr

HBr(50)-He(40)  Cl₂(50)-He(40)  HCl(50)-He(40)

⇒ Severe trenching with pure chlorine chemistry in a bias power range of less than 100 W
⇒ Directed by the angular distribution of ions impacting and scattering the evolving feature
⇒ Alternative explanation: Presence of fast protons neutralises the negative charging of the mask (HBr and HCl)

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Microtrenching: Ion Deflection


Authors found microtrenching to be influenced by the direction of a weak magnetic field.

This field changes only the angular distribution of the electrons. The ions are too immobile.

This result strongly support the differential charging mechanism.
Controlling Polymerization through F/C-Ratio

- Higher F/C-ratio leads to more etching
- Lower F/C-ratio leads to more polymerization
- Can be determined by the gas used
- Adding H₂ consumes F – leads to polymerization
- Adding O₂ consumes C – leads to etching
Damage in Reactive Ion Etching (RIE)

- Typical ion flux of $10^{15}$ ions/cm$^2$ are delivered at energies of 300 to 700 eV in a RIE.

- After a typical etch in a carbon containing RIE, the top 30 Å is heavily damaged, with an extensive concentration of Si-C bonds.

- RIE processes done in a hydrogen-containing ambient also have Si-H defects that can be observed as deep as 300 Å.

- Hydrogen may penetrate several microns into the surface where it can deactivate dopants in the substrate.
Temperature effects in plasma etching

Wafer surface temperature depends on:
- Chuck temperature
- Ion density and ion energy
- Exothermicity of the etching reaction

Surface temperature influences etching processes:
- Reaction probabilities of incident species depends on substrate temperature
- Vapor pressure of etch products is temperature dependent
- Re-deposition of reaction products on feature surfaces depends on temperature

Major issues associated with the variable temperature:
- Temperature is difficult to control in plasma processes
- Substrate temperature is difficult to monitor
Temperature effects in plasma etching
- Selectivities and profile control -

At very low temperature, silicon etch rate in SF$_6$ based plasmas is not impacted.

- SiO$_2$ and photoresist etch rates decrease strongly for decreasing temperatures

- Spontaneous etching reaction between fluorine atoms and silicon are frozen for temperatures below -90°C (no under cut below an SiO$_2$ hard mask).

From: “Low-temperature reactive ion etching and microwave plasma etching of silicon”
S. Tachi, K. Tsujimoto, S. Okudaira
BOSCH ICP (PLASMA THERM)

The Bosch process uses two chemistries, one to generate polymers and the other to etch silicon. The etch machine switches between the two every few seconds to ensure that the sidewalls are covered with polymer allowing fast, deep trench etching. (the substrate is on a chuck that is cooled by liquid nitrogen.

- 5μm spaces
- 200μm etch depth
- 40:1 aspect ratio
- 2μm/min Si etch rate
- >75:1 selectivity to photoresist
Examples
Dry Etching Organic Films

- $O_2$ plasmas can remove organic films with high selectivity
- Adding $CF_4$ can increase etch rate and lowers variation
  - but selectivity can be reduced if too much is added
PLASMA STRIPPING

Goal: Complete removal of resist without damage

Problem: Conventional ashing may not work because of:
- Resist Hardening in High Dose Implants and in Syilation Residues and polymers from plasma processes
- Metals remain behind in resist

More Aggressive Plasma Processes can Damage Devices
- Ion Bombardment in RIE and even in barrel etchers
- Oxide charging
- UV and soft x-ray

Solutions: Enhance plasma density, microwave, magnetic
- Temperature control in downstream etchers
- Use H2 for removing phosphorus implanted resists
Examples
Examples
Loading Effects and Aspect Ratio Dependent Etching

**Macroscopic Loading:**
- Etch rate decreases when the total area of the material to be etched decreases
- Effect is caused by the consumption of reactive species produced by the plasma during the etching process

**Microscopic Loading:**
- Identical features are etched with different rates depending on their position with respect to open area features (dense areas, semi dense areas, open areas)

**Aspect Ration Dependent Etching (ARDE):**
- Features with a high aspect ration (depth/width) have a higher etch rate then those with a small aspect ratio (normal ARDE). Under certain process conditions, this effect can be reversed (reverse ARDE)
This effect is attributed to a localized depletion of etching species caused by the etching process itself.

Processes with strong macroloading typically also exhibit significant microloading.
Aspect Ratio Dependent Etching (ARDE)

Feature dimension strongly influence the etch rate. Typically large open areas etch faster than densely packed features (normal ARDE).

Possible mechanisms for aspect ratio dependent etching rates:
(Gottscho, Jurgensen, Vitkavage, J. Vac. Sci. Technol. 10, 2133 (1992))


2. Ion shadowing (Shaqfeh, Jurgensen, J. Appl. Phys. 66, 4664 (1989)).

3. Neutral shadowing (Giapis, Scheller, Gottscho, Hobson, Lee, Appl. Phys. Lett. 57, 983 (1990)).


Also to be considered for highly selective oxide etching:
