Lecture 11

Etching Techniques

Reading:

Chapter 11

Etching Techniques

Characterized by:

1.) Etch rate (A/minute)

2.) Selectivity: S=etch rate material 1 / etch rate material 2   is said to have a selectivity of "S" for material 1 over material 2.

3.) Anisotropy:

$$A = 1 - \frac{\text{Lateral Etch Rate}}{\text{Vertical Etch Rate}}$$

4.) Under cut: If 0.8 um lines result from an etch using 1 um photoresist lines as a mask, it is said that the process bias is 0.1 um for that particular etch.

Mask
Chrome

Lithography bias

Photoresist

Oxide

Wafer
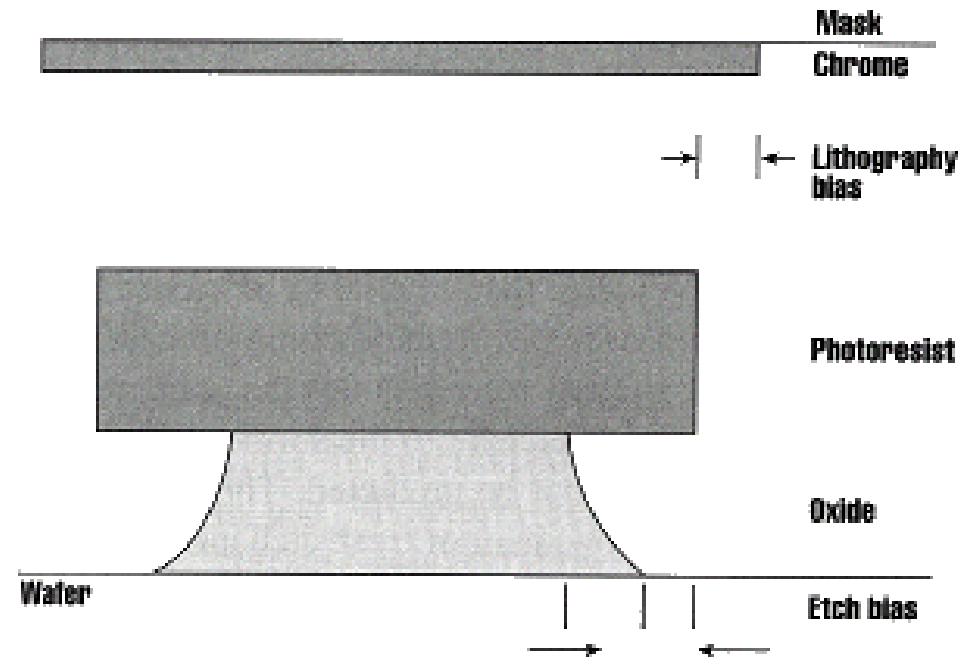
Etch bias

Figure 11-1   Typical isotropic etch process showing the etch bias.

Controlling Anisotropy

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

•Increasing mean free path (generally) increases anisotropy

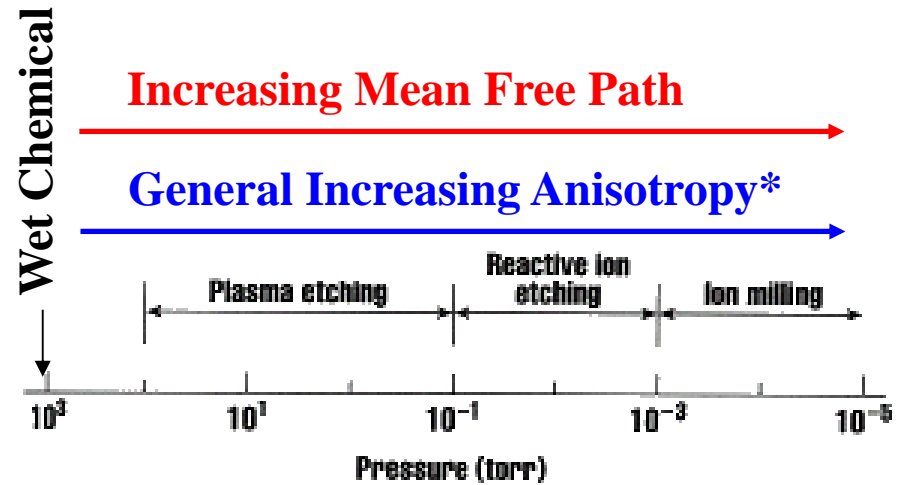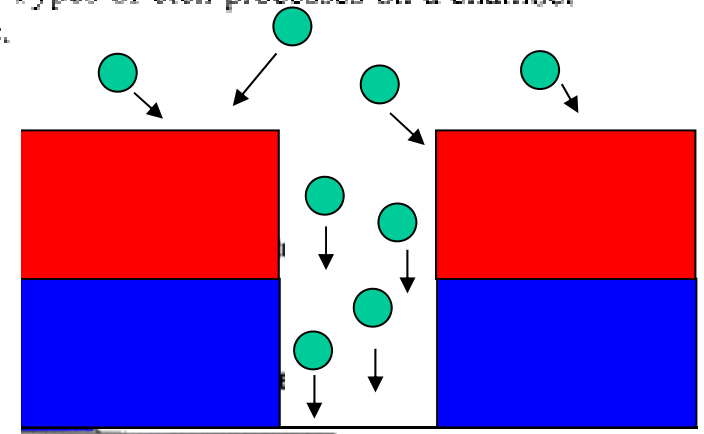**•Increasing DC bias (generally) increases anisotropy**
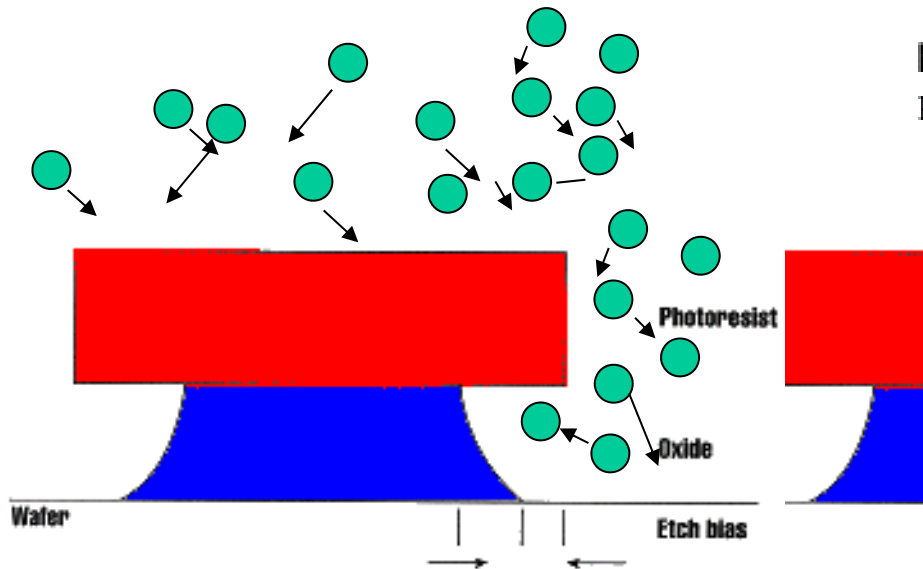

Figure 11-2 Types of etch processes on a chamber pressure scale.

* Some wet and plasma chemistries can have high anisotropy by using the chemistry to etch preferred crystalline planes.

Common Etching Techniques

Etching can be characterized by how much of the process is:

Chemical: Using the chemistry of the etch to remove material into a solution (liquid or gaseous solution)

Sputtering: In plasma systems, Ions can be accelerated fast enough so as to "Ram" into the surface, "knocking out" atoms/molecules

Many etching techniques use both chemical and sputtering.

1.) Wet Chemical Etching:
> Advantages: Cheap, almost no damage due to purely chemical nature, highly selective
> Disadvantages: poor anisotropy, poor process control (temperature sensitivity), poor particle control, high chemical disposal costs, difficult to use with small features (bubbles, etc...).

Advantages Common to all of the following: Low chemical disposal, temperature insensitivity, near instant start/stop (no drips, etc..), applicable to small features (gas permeation of small features).

2.) Plasma Etching:
> Advantages: Moderately anisotropic using sidewall polymerization techniques (discussed later) , can be selective
> Disadvantages: Ion damage, residue

3.) Reactive Ion Etching:
> Advantages: Highly anisotropic using sidewall polymerization techniques, can be selective but less so than plasma etching due higher DC bias and longer mean free path.
> Disadvantages: High ion damage, residue

4.) Ion Milling:
> Advantages: Extremely anisotropic, Independent of material composition (useful in quaternaries).
> Disadvantages: Extremely high ion damage, non-selective, residue

Wet Chemical Etching:

Process requires:
1.) Movement of etchant species toward the wafer surface
2.) Reaction at the surface
3.) Movement of reactant products away from the surface
Any one of the above three steps can be the etch rate limiting step

2 important Wet Etch Concepts:
A.) Buffering the solution to maintain constant etch rate with time:
Consider etching of SiO_2

$$SiO_2 + 6HF \rightarrow H_2 + SiF_6 + 2H_2O$$
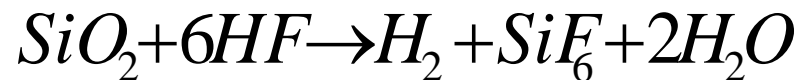
But as the HF is depleted (used up) from the solution the etch rate would change. Thus, a Buffering solution is added that controls the HF concentration as:

$$NH_4F \Leftrightarrow NH_3 + HF$$

The HF concentration remains "saturated". As HF is consumed etching SiO_2, the above reaction replaces the HF, keeping the etch rate constant.

Wet Chemical Etching:

B.) Oxidation/Reduction Reactions

Many chemical etchants use oxidation reactions to oxidize the surface followed by (simultaneously) reduction reactions to "reduce" the oxidized material (moving it into solution). Sometimes the chemicals used to oxidize and reduce are diluted in water or other solutions (acetic acid, ethylene glycol, etc…)

Example: Use oxidizing agents such as nitric acid (HNO_3)to oxidize material (Si) with HF to remove the oxide. Acetic acid ($HC_2H_3O_2$) is used to dilute the solution. If the solution is to be 10% HF, 40% nitric acid and 50% acetic acid, what is the etch rate?

      Two determine etch rate

1.) Draw a line from 10% HF parallel to the side of the triangle counterclockwise to the HF side,

2.) Draw a line from 40% nitric side parallel to the side of the triangle counterclockwise to the nitric side

3.) Draw a line that goes from the 50% Acetic point to the intersection of the previous two lines

====> less than 7.6 um/minute (lowest value on the plot)
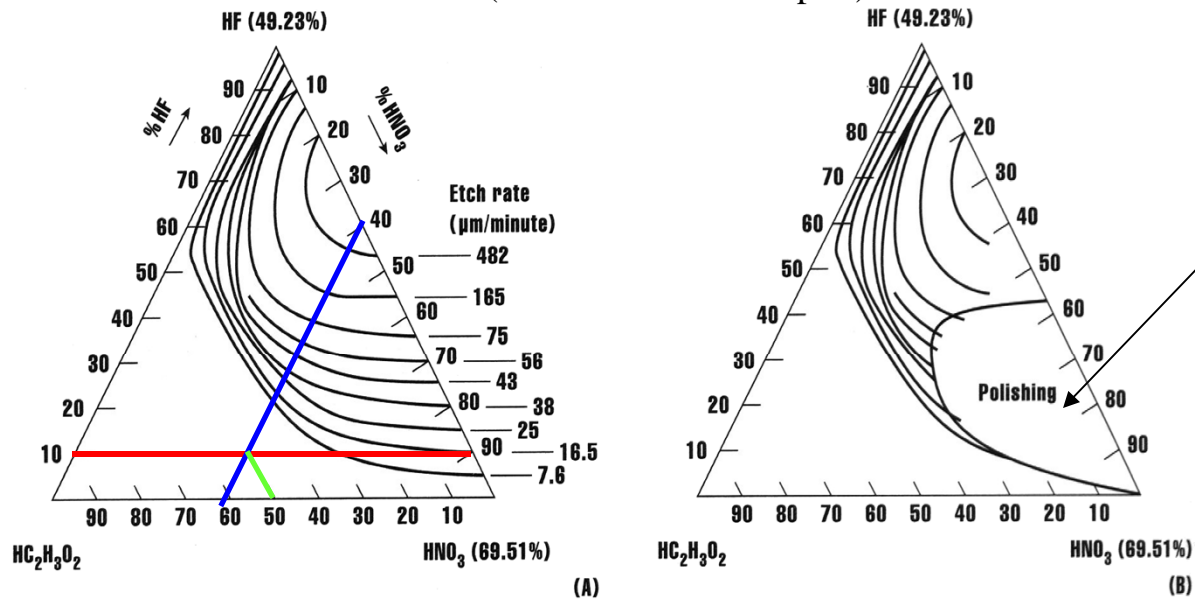
For Si, regions exist where the reduction reaction is so slow, the surface is very planar and ends up being "polished " after the etch.

Figure 11-5 The etch rate of silicon in HF and HNO_3 (after Schwarz and Robbins, reprinted by permission of the publisher, The Electrochemical Society Inc.).
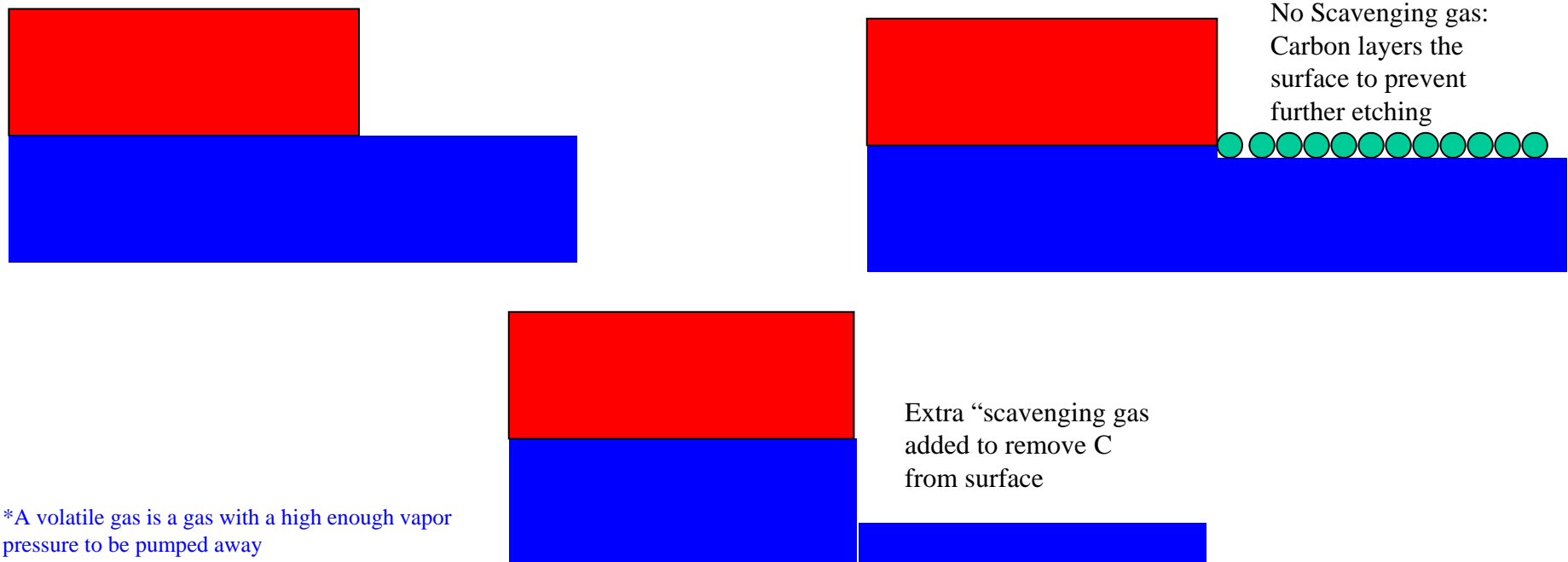
Plasma Etching:

Consider a reaction of CF_4 and Silicon. It is desired to replace C with Si to form a volatile* Si gas SiF_x. This requires the breaking of C-F (supplying 105 kcal/mole or 4.52 eV/molecule) and Si-Si (supplying 42.2 kcal/mole or 1.82 eV/molecule) bonds and the formation of Si-F bonds ("consuming" 130 kcal/mole or 5.6 eV/molecule). ===> CF_4 will not etch Si directly due to excessive energy requirements.

We can aid this process to get the CF_4 to etch Si, by:

A.) Pre-breaking the C-F bonds via the plasma, lowering the net energy required at the surface

B.) Pre-breaking the surface Si-Si bonds via the ion bombardment, lowering the net energy required at the surface

If both of these are done, it only takes 17 kcal/mole (0.73 eV/molecule) to form Si-F bonds.

Consider what happens to the Carbon? Without the addition of a "scavenging gas" (discussed in a moment), the C merely exchanges with the Si until complete C coverage occurs and the reaction stops (assuming no ion bombardment, see below).

No Scavenging gas: Carbon layers the surface to prevent further etching

Extra "scavenging gas added to remove C from surface

*A volatile gas is a gas with a high enough vapor pressure to be pumped away

Georgia Tech

ECE 6450 - Dr. Alan Doolittle

Plasma Etching:

Tailoring gas Chemistry for Selectivity vs Anisotropy:

Consider the addition of oxygen (O_2) to the plasma:

C can be removed by forming CO and CO_2 gases which are easily pumped away (higher vapor pressure than solid C or CF_x gas). This decreases the amount of C available to form CF_x radicals, increasing the relative F concentration in the plasma, increasing the etch rate. However, the oxygen can create SiO_2 on the surface which etches slower in the CF_4 chemistry. Si etch rates peak at about 12% O_2 due to formation of SiO_2 on the surface at high oxygen levels. Adding small amounts of O_2 increases the Si over SiO_2 selectivity at the expense of anisotropy.
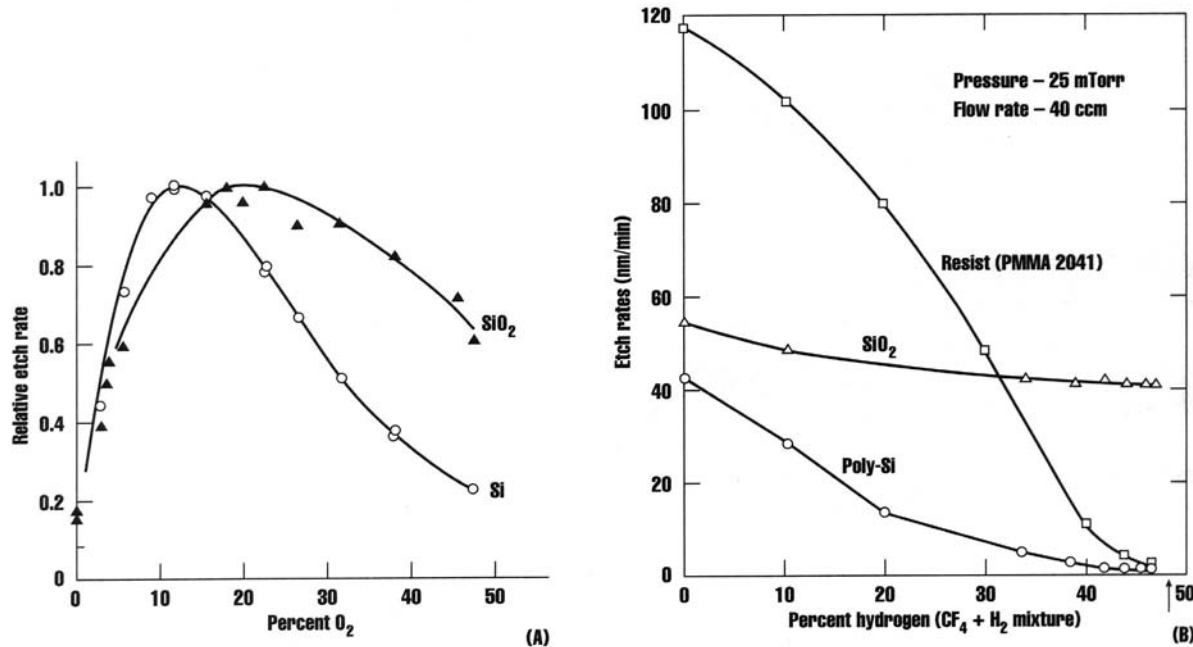
Figure 11-11 Etch rate of Si and SiO_2 in (a) CF_4/O_2 plasma *(after Mogab et al., reprinted by permission, AIP)*, and (b) CF_4/H_2 plasma *(after Ephrath and Petrillo, reprinted by permission of the publisher, The Electrochemical Society Inc.)*
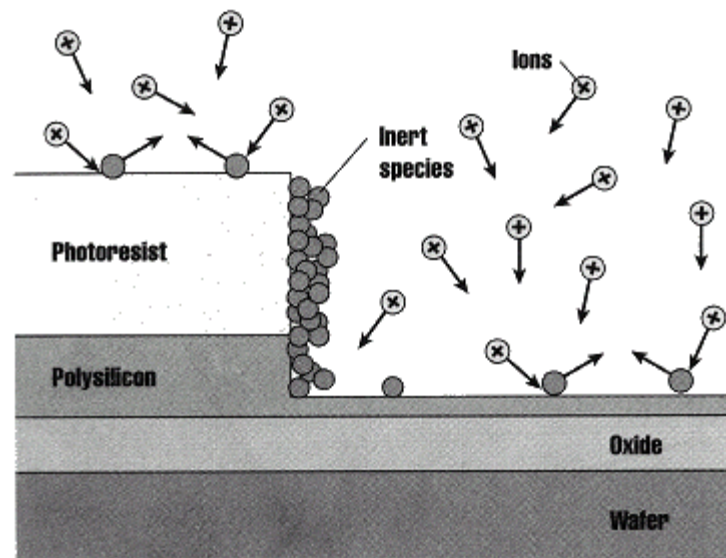
Plasma Etching:

Polymerization:

By adding hydrogen to the plasma, the fluorine content of the plasma is scavenged* (F+H->HF where HF has a higher vapor pressure and thus, is pumped away faster) and CF_X forms. This fluorocarbon residue, CF_X, can be deposited preferentially on the sidewalls, enhancing anisotropy by forming a lateral etch mask. These fluorocarbons are not easily removed by the plasma chemistry, and thus, must be "sputtered" by ion bombardment. Since the E-field is perpendicular to the wafer surface, minimal fluorocarbon etching of sidewalls occurs while deposition on the flat portions of the wafer are easily removed.

In terms of gas chemistry, adding H_2 does the opposite of adding O_2. Adding small amounts of H_2 increases SiO_2 etch anisotropy.

Figure 11-10 Schematic diagram of a high pressure anisotropic etch showing the formation of sidewall passivating films.

Scavenged: When a gas is introduced to intentionally remove another species (gas or solid compound) this introduced gas is called a scavenging gas.

Problems experienced in practice:
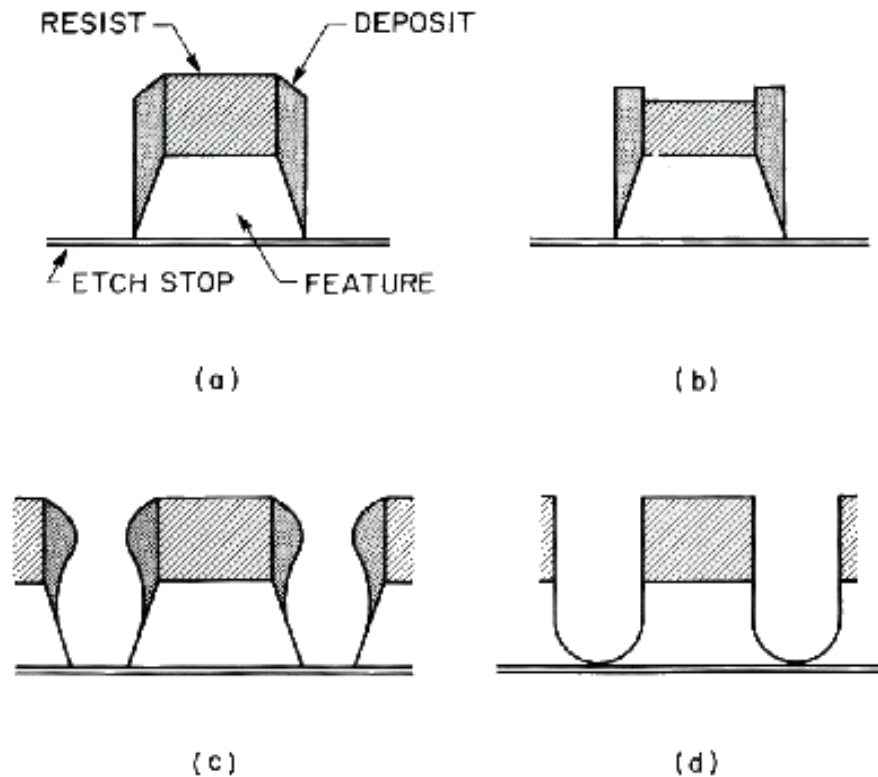
FIGURE 13
Some feature profiles that can be caused by deposition during anisotropic etching. (a) A trapezoidally shaped deposit caused by a uniform deposition rate which can result from widely spaced features. (b) This same type of deposit can result in "horns" if the resist etches faster than the deposit. (c) Inwardly bowed walls can be caused by a plasma source of deposit on closely spaced features. (d) Rounded bottoms can be caused by redeposition, which has a much higher rate toward the bottom of a small etching area. Such rounding is often observed for submicron window etches and is removed during an overetch, leaving vertical walls.

Summary of Plasma Etch Chemistry using CF_4 to etch Si

Material = Si Condition	Etch Rate	Anisotropy	Selectivity Si over SiO_2
F-Rich (O_2 added)	Increased	Decreased	Increased
C-Rich	Decreased	Increased	Decreased

Material = SiO_2 Condition	Etch Rate	Anisotropy	Selectivity SiO_2 over Si
F-Rich	Increased	Decreased	Decreased
C-Rich (H_2 added)	Decreased (only slightly since HF etches SiO_2)	Increased	Unchanged

Effect of reactor loading

Depletion of the reactant gas by increased surface area is sometimes a problem. (Lab conditions and multi-wafer systems). The etch rate can be determined as,

$$R = \frac{Ro}{1 + kA}$$

where Ro is the empty chamber etch rate, A is area of wafers loading into the reactor, and k is constant that can be reduced by increasing gas flows at constant pressure

Plasma Process Monitoring

Emission Spectroscopy: Observing the intensity of individual plasma lines resulting from molecular recombination events. These events can be very weak so sensitive equipment is required.

Interferometry: Requires large unpatterned areas.

Reactive Ion Etching

Designed to give better control of Selectivity and Anisotropy independently:

Characteristics:

1.) Lower operating pressures result in higher anisotropy (longer mean free path allows more directed acceleration of ions)

2.) A DC bias enhances ion bombardment energy, resulting in some sputtering and chemical catalyst effect.

3.) A sidewall polymerization gas (BCl_3, CCl_4 etc...) is added to enhance anisotropy. The enhanced sputtering features of RIE insure "mostly" or "only" sidewall polymerization.

More damage occurs: Many III-V processes can not tolerate this damage.

Some unintentional deposition of the polymerization gas can result in defects if conditions are not optimized.
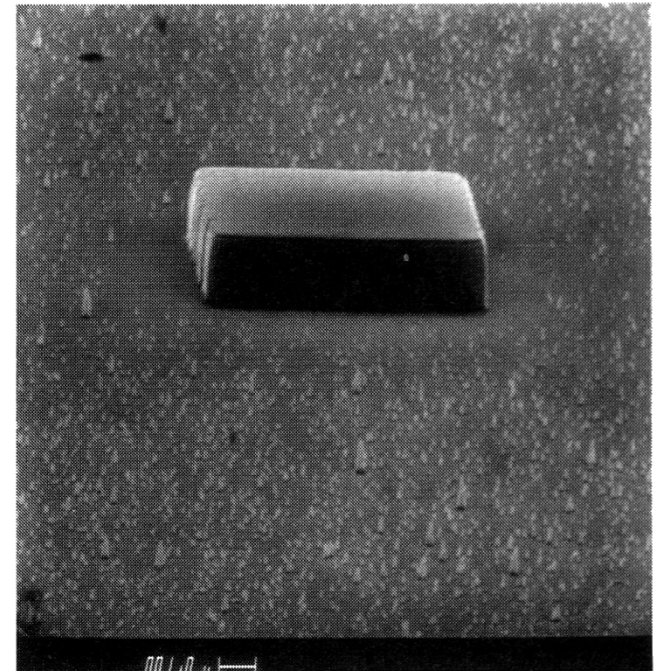
FIGURE 21
An SEM of unetched residue, or "grass," around a patterned feature.