Etching and Pattern Transfer (1)

OUTLINE

• Basic Concepts of Etching
• Wet Etching
• Specific Wet Etches
  – Silicon
  – Silicon Dioxide
  – Aluminum
• Dry (Plasma) Etch
  – Review of Plasmas

Reading Assignment: Plummer, Chapter 10

Introduction

• Etching is selective removal of thin film(s) resulting in a desired thin film(s) pattern
• The Etch Mask is usually photo-resist or oxide/nitride
• Multi-layer structures can be etched sequentially using same masking layer
• Etching can be done in either “wet” or “dry” environment
  – Wet etching = liquid etchants
  – Dry etching = gas phase etchants in a plasma.

Plummer, Fig. 10-1
Basic Concepts

- Etching process consists of three steps
  - Mass transport of reactants (through a boundary layer) to the surface to be etched
  - Reaction between reactants and the film(s) to be etched at the surface
  - Mass transport of reaction products from the surface through the boundary layer

- Etching is usually done using liquid phase or gas phase reactants
  - **liquid phase (wet) etching** — reaction products soluble in solvent or gaseous
  - **gas phase etching** — reaction products gaseous / sublimation temperature

Definition of Terms

- Etch profiles do not have perfect straight walls under the edge of the mask
- Etching occurs both vertically and laterally
  - Undercutting of photoresist mask and non vertical sidewall
- Erosion of resist could also occur
  - More lateral etching of resist
- Etchant could attack substrate leading to changes in profile

Plummer, Fig. 10-2
Definition of Terms

- Anisotropic etching is the preferred process
- Step coverage problems ??

Etch Figures of Merit

<table>
<thead>
<tr>
<th>Etch Rate (R)</th>
<th>Rate of film removal, typically 1000 Å/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etch Uniformity (U)</td>
<td>% change in etch rate across a wafer, lot, etc</td>
</tr>
<tr>
<td>Selectivity ($S_{film}/S_{mask}$)</td>
<td>Ratio of the etch rate of various materials e.g. Film to PR $S_{film}$ : Film to mask selectivity; $S_{mask}$ : Film to substrate selectivity</td>
</tr>
<tr>
<td>Anisotropy, A</td>
<td>Measure of directionality of the etch. $A=1$ corresponds to perfect anisotropic etch $A=0$ corresponds to isotropic etch</td>
</tr>
<tr>
<td>Undercut</td>
<td>Measure of the lateral extent of the etch per side</td>
</tr>
<tr>
<td>Substrate Damage</td>
<td>Physical and/or chemical damage of the substrate.</td>
</tr>
</tbody>
</table>
Etch Figures of Merit

**Uniformity**
\[ U = \frac{R_{\text{high}} - R_{\text{low}}}{R_{\text{high}} + R_{\text{low}}} \]
- \( R_{\text{high}} \): maximum etch rate
- \( R_{\text{low}} \): minimum etch rate

**Selectivity**
\[ S_{\text{fm}} = \frac{R_{f}}{R_{m}} \]
\[ S_{\text{fs}} = \frac{R_{f}}{R_{s}} \]
- \( R_{f} \): film etch rate
- \( R_{m} \): mask etch rate
- \( R_{s} \): substrate etch rate

**Anisotropy**
\[ A = \frac{R_{\text{vertical}} - R_{\text{lateral}}}{R_{\text{vertical}}} \]
- \( R_{\text{vertical}} \): vertical etch rate
- \( R_{\text{lateral}} \): lateral etch rate

Etch Process Control

- End point detection usually done by monitoring color of film or reaction product species
  - Interferometry to monitor film thickness
  - Optical spectroscopy to monitor reaction products
- Mask dimensions erode during etch especially dry etch
  - Need to account for mask erosion
- Usually need to each to clear + over-etch (typically 5-10%)

![Fig. 10.4: Illustration of etch bias and overetch. In a, the etch bias, \( b \), is shown for a given etch depth, \( d \). In b, overetching is illustrated where etching is continued even after the etch depth, \( d \), equals the film thickness, \( s \).](image)

*Plummer, Fig. 10-4*

![Fig. 10.5: Illustration of mask erosion. In a, there is an idealized rectangular mask and isotropic etching of the mask and the substrate. In b, there is a sloped mask and anisotropic etching. In both cases, more lateral etching of the substrate occurs as a result of the mask erosion, or erosion.](image)

*Plummer, Fig. 10-5*
Wet Etching

How?

Simply place the wafer in solution that attacks the film to be etched but not the mask (resist).

- Diffusion reactive species from the liquid bulk through the boundary layer to the surface of wafer
- Reaction of species at the surface to form solvable species
- Diffuse reaction products away from the surface through the boundary layer into the bulk of the liquid

Advantages
High selectivity because it is based on chemical processes

Disadvantages
Isotropic, poor process control and particulates

Wet Etching Examples

Silicon Dioxide

\[ \text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \]

Silicon

\[ \text{Si} + 2\text{HNO}_3 \rightarrow \text{SiO}_2 + 2\text{HNO}_2 \]
\[ \text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \]

- Preference is to have it reaction rate controlled because
  - Etch rate can be increased by temperature
  - Good control over reaction rate – temperature of a liquid is easy to control
- Mass transport control will result in non-uniform etch rate
  - Boundary layer un-even
- Etchant is stirred to minimize boundary layer and thus make etching reaction rate controlled
- Etch rate is a function of temperature, specific reaction and concentration
Isotropic Wet Etches

**Silicon Dioxide**

- Etch is isotropic and easily controlled by dilution of HF in H₂O
- Thermal oxide etches at
  - 1200 Å/min in 6H₂O:1HF
  - 300 Å/sec or 1 micron/min in 49% by weight HF
- Doped/deposited oxide etch faster in HF
- Selectivity to silicon S₁ᵦ > 100
- Buffered HF (BHF) or Buffered oxide etch (BOE) provides consistent etch rates
  - HF is consumed and the etch rate drops
  - Serious process control issue
  - Solution: HF buffered with NH₄F to maintain HF concentration 6NH₄F:1HF

\[
\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2 \cdot \text{SiF}_6 + \text{H}_2\text{O} \rightarrow \text{H}_2 \uparrow + \text{SiF}_6 + 2\text{H}_2\text{O}
\]

**Silicon Dioxide Etch Rate**

- Etch rate of SiO₂ - 300 Å/min
- Etch rate of Si₃N₄ - 5-15 Å/min
- Very good selectivity of oxide to nitride
- Silicon nitride etches in 49% HF at room temperature at about 500 Å/min
- Phosphoric acid at 150 °C [140-200 °C] etches Si₃N₄ at fairly fast rate
  - Etch rate of Si₃N₄ - 100 Å/min
  - Etch SiO₂ - 10 Å/min
  - Selectivity of Si₃N₄ over SiO₂ : S = 10
  - Selectivity of Si₃N₄ over Si: S=30

**Silicon Nitride**

- Silicon Nitride is etched very slowly by HF solutions at room temperature, for example 20:1 BOE @20 C
  - Etch rate of SiO₂ - 300 Å/min
  - Etch rate of Si₃N₄ - 5-15 Å/min
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  - Selectivity of Si₃N₄ over Si: S=30

**Phosphoric Acid Etch Rate**
Isotropic Etches

Silicon

• Silicon is etched in two steps by nitric acid and hydrofluoric acid mixtures
• Use oxidant to oxidize silicon to form silicon dioxide followed by HF etch of silicon dioxide
  – Oxidation: HNO₃ → SiO₂
  – Reduction: HF → SiF₆
• Acetic acid (CH₃COOH) is often used as diluent instead of water
• Excess nitric acid results in a lot of silicon dioxide formation and etch rate becomes limited by HF removal of oxide
  – Polishing etch

This can be broken down into anodic and cathodic reactions and an electrochemical etch can be configured.

**Anodic Reaction**

\[
\begin{align*}
\text{Si} + 2\text{H}^+ &\rightarrow \text{Si}^{2+} \\
\text{Si}^{2+} + 2(\text{OH}^-) &\rightarrow \text{Si(OH)}_2 \\
\text{Si(OH)}_2 &\rightarrow \text{SiO}_2 + \text{H}_2 \\
\text{SiO}_2 + 6\text{HF} &\rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}
\end{align*}
\]

**Cathodic Reaction**

\[
\begin{align*}
\text{HNO}_2 + \text{HNO}_3 &\rightarrow \text{N}_2\text{O}_4 + \text{H}_2\text{O} \\
\text{N}_2\text{O}_4 &\rightleftharpoons 2\text{NO}_2 \\
2\text{NO}_2 &\rightleftharpoons 2\text{NO}_2 + 2\text{H}^+ \\
2\text{NO}_2 + 2\text{H}^+ &\rightleftharpoons 2\text{HNO}_2
\end{align*}
\]
Isotropic Etches

Silicon

- Doping selective etches developed for detecting pn junctions and for etch stops
  - 1HF:3HNO₃:8CH₃COOH etches heavily doped silicon (>10¹⁹ cm⁻³) but does not etch lightly doped silicon
    - \( R_{\text{heavy-doping}} = 15R_{\text{light-doping}} \)
  - Ethylenediamine-pyrocatechol-water etches lightly doped silicon but does not attack heavily doped p-layers
- Defect Selective Etch form etch pits at dislocations, stacking faults and precipitates
  - Defect density observable by optical microscopy after staining

Anistropic Etch

Silicon

- Orientation selective etch of silicon occur in hydroxide solutions because of the close packing of some orientations relative to other orientations
  - Density of planes : <111> > <110> > <100>
  - \( R_{\langle 100 \rangle} < R_{\langle 110 \rangle} < R_{\langle 100 \rangle} \)
- <100> direction etches faster than <111> direction
  - \( R_{\langle 100 \rangle} = 100 R_{\langle 111 \rangle} \)
  - It is reaction rate limited

\[ 23.4\text{KOH} : 13.5 \text{IPA} : 63\text{H}_2\text{O} \]
Isotropic Etch
Aluminum

- Aluminum etches in water, phosphoric, nitric and acetic acid mixtures
- Converts Al to Al₂O₃ with nitric acid (evolves H₂)
- Dissolve Al₂O₃ in phosphoric acid
- Gas evolution leading to bubbles
- Local etch rate goes down where bubble is formed
  - Non-uniformity

16H₃PO₄ : 2H₂O : 1HNO₃ : 1CH₃COOH

Table of Wet Etches

<table>
<thead>
<tr>
<th>Material</th>
<th>Etchant</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>HF (49%)</td>
<td>- etches Si slowly (i.e. will etch Si very slowly in comparison)</td>
</tr>
<tr>
<td></td>
<td>NH₄FHF (6:1)</td>
<td>- etch rate depends on film density, doping</td>
</tr>
<tr>
<td></td>
<td>Buffered HF or &quot;BHF&quot;</td>
<td>- about 1/20th the etch rate of straight HF</td>
</tr>
<tr>
<td></td>
<td>16H₃PO₄ : 2H₂O : 1HNO₃ : 1CH₃COOH</td>
<td>- small non-uniformity on nitride, doping</td>
</tr>
<tr>
<td>B</td>
<td>BHF (98%)</td>
<td>- etch rate depends strongly on film density, O₂</td>
</tr>
<tr>
<td></td>
<td>B₂H₆ : H₂O (boiling @ 180-190°C)</td>
<td>- selective to SiO₂</td>
</tr>
<tr>
<td></td>
<td>HF : (1% HNO₃ : 1% CH₃COOH) (98:2:1)</td>
<td>- requires oxide mask</td>
</tr>
<tr>
<td>Al</td>
<td>H₂SO₄ : H₂O₂ : H₂O₂ (1:1:1)</td>
<td>Selective to Al, SiO₂, and phosphorous</td>
</tr>
<tr>
<td>Poly-silicon</td>
<td>HNO₃ : HF : H₂O₂ (30:20:1)</td>
<td>- etch rate depends on etch/oxidation composition</td>
</tr>
<tr>
<td>Single-crystal Si</td>
<td>HNO₃ : HF : H₂O₂ (30:20:1)</td>
<td>- etch rate depends on etch/oxidation composition</td>
</tr>
<tr>
<td>Y</td>
<td>Y₂O₃ : H₂O : (H₂O₂ + H₂O) (1:1:1)</td>
<td>- crystallizes/crystallizes slowly, relative rich rate: 0.19/38.4/11.1</td>
</tr>
<tr>
<td>Ti</td>
<td>TiCl₄ : HCl : H₂O₂ (1:1:1)</td>
<td>Selective to TiCl₄</td>
</tr>
<tr>
<td>TiO₂</td>
<td>TiCl₄ : HCl : H₂O₂ (1:1:1)</td>
<td>Selective to TiCl₄</td>
</tr>
<tr>
<td>Photonet</td>
<td>H₂SO₄ : H₂O₂ : C₂H₅OH</td>
<td>For wafers without metal</td>
</tr>
<tr>
<td></td>
<td>H₂SO₄ : H₂O₂ : C₂H₅OH</td>
<td>For wafers with metal</td>
</tr>
</tbody>
</table>

Table 16.1: Common wet reactive etch recipes for removing this film used in IC fabrication.
Summary of Wet Etches

- Wet etches are selective isotropic and fast
  - Usually reaction rate limited

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple &amp; Fast</td>
<td>Undercutting</td>
</tr>
<tr>
<td>Selective</td>
<td>Strain at interface can enhance undercutting and lift-off film</td>
</tr>
<tr>
<td>Reproducible</td>
<td></td>
</tr>
</tbody>
</table>

Example I

Etch 1 micron of SiO₂ on Si with \( R_{\text{oxide}} = 4000 \, \text{Å/min} \), \( S_{\text{fs}} = 25 \)

Etch is for 3 min. How much Si is etched?

\[ R_{\text{Si}} = \frac{R_{\text{oxide}}}{S_{\text{fs}}} = 160 \, \text{Å/min} \]

*Note that Si is exposed only after oxide is etched completely*

**Time to etch oxide is**

\[ t_{\text{oxide}} = \frac{10,000 \, \text{Å}}{4000 \, \text{Å/min}} = 2.5 \, \text{min} \]

Silicon is exposed for \( t_{\exp} = 3.0 - 2.5 \, \text{min} = 0.5 \, \text{mins} \)

Amount of silicon etched is \( 160 \times 0.5 = 80 \, \text{Å} \)
Example II

- 0.5 micron of oxide layer is etched to achieve equal structure widths and spacings.
- The etch process has anisotropy of 0.8.
- If the distance between the mask is 0.35 micron, what structure spacings and widths are obtained?

\[
W_m = W_i + 2b = W_i + 2x_i(1 - A_i)
\]
\[
x = 2W_i - W_m
\]
\[
x = 2W_i - [W_i + 2x_i(1 - A_i)]
\]
\[
W_i = x + 2x_i(1 - A_i)
\]
\[
W_f = 0.35 \mu m - 2 \times 0.5 \mu m(1 - 0.8) = 0.55 \mu m
\]
\[
A_i = 1 - \frac{b}{x_i}
\]

Chemical Mechanical Polishing I

- Chemical Mechanical Polishing is used to planarize surfaces by removing bumps and micro-protrusions
- Similar to lens polishing or wood polishing with sandpaper
- Uses a chemical slurry which contains etchants and abrasives. It essentially combines chemical and physical components of etching
- Anisotropic because of its tendency to flatten surfaces
- Wafers on a rotating carrier are brought into contact with a polishing pad on a rotating table
Chemical Mechanical Polishing II

- The polishing rate is a function of
  - Down pressure
  - Table rotating speed
  - Wafer rotation speed
  - Slurry flow rate
  - Slurry concentration, particle size and components
  - Polishing pad stiffness and graininess
- Polishing dielectrics, oxides, poly-silicon, copper for
  - Shallow trench isolation (STI) & interconnects

Gas Phase (Plasma) Etching

Plasma etching has largely replaced wet etching in IC technology because of the directional etching possible with plasma etch systems

- Directional etching — presence of ionic species in the plasma & the electric field
- Systems can be designed so that reactive chemical components or the ionic components dominate
- Plasma systems use a combination of ionic and reactive chemical species acting in a synergistic manner
  - Etch rate that is much faster than the sum of individual etch rates when they are acting alone

Reactive chemical component of plasma etching often has high selectivity
Ionic component of plasma etching often has directionality
Utilizing both components, directionality could be achieved while maintaining an acceptable selectivity
Review of DC Plasmas

- Plasma is partially ionized gas
- Application of voltage across two electrodes in a gas results in an arc and generation of ions and electrons
- Ions collide with the cathode generating secondary e-
- e- accelerated towards the anode gaining energy
- Energetic e- collide with neutral molecules generating more ions, e- and excited radicals.

Pressure: 200 mTorr – 1 Torr
Energy: DC Voltage Source (≈100 V/cm)

Review of RF Plasmas

- Application of RF electric field across two electrodes ionizes atoms/molecules producing positive ions and free electrons creating a plasma
- Voltage bias develops between the plasma and electrodes because of the difference in mobilities (masses) of electrons and ions
- Plasma is positively biased with respect to the electrodes

Pressure: 1 mTorr – 1 Torr
Energy: RF Source @ 13.56 MHz
RF Plasma Potential Profile

- Sheaths form next to electrodes and voltage drops occur at sheaths corresponding to dark region
- Electrodes capacitively couple to plasma
- Ions respond to the average sheath voltage while the electrons respond to instantaneous voltage
- If electrodes have equal areas, the voltage drop at the sheaths are symmetrical
- If the electrodes have unequal areas, the voltage drop between the sheaths and the electrodes are asymmetrical with a much larger voltage drop occurring at the smaller electrode
  - Two capacitors in series

Plummer, Fig. 10-8

Plasma Reactions

For a plasma with inlet flow of molecule AB, Plasma processes are:

**Dissociation**

\[ e^* + AB = A + B + e \]

**Atomic Ionization**

\[ e^* + A = A^+ + e + e \]

**Molecular Ionization**

\[ e^* + AB = AB^+ + e + e \]

**Atomic Excitation**

\[ e^* + A = A^* + e \]

**Molecular Excitation**

\[ e^* + AB = AB^* + e \]

Plummer, Fig. 10-9
Plasma Reactions

- A*, AB*, e* refer to particles whose energy are much above the ground state
- Molecular fragments and dissociated atoms are very reactive (they are called radicals)
- Plasma consists of about 1% radicals and 0.01% ions
  - $10^{15}$ cm$^{-3}$ neutral species
  - $10^9$ – $10^{12}$ cm$^{-3}$ ions and electrons
  - $10^{12}$ – $10^{14}$ cm$^{-3}$ reactive neutral species
- Plasma density and ion energy are closely coupled

Summary of Today’s Lecture

- We studied the basic concepts of etching
  - Mass transport to reaction surface
  - Reaction at the surface
  - Mass transport of reaction products away from the surface
- We defined the metrics of pattern transfer
  - Selectivity (film/substrate, resist/film)
  - Anisotopicity
  - Mask bias, etch bias
  - Non-uniformity + overetches
- We reviewed DC & RF Plasmas
  - Plasma reactions