Lecture 10

Microfabrication – Pattern Transfer (III)

- Wet Etching
  - Isotropic Wet Chemical Etching
    - Selected Wet Etchants and Selectivity
    - Surface Micromachining Material Systems
    - Design of Surface Micromachining Process
    - Etch Selectivity in Surface Micromachining
    - Stiction in Fabrication
    - Surface Micromachining Materials
    - Silicon Isotropic Wet Etching

Wet Chemical Etching

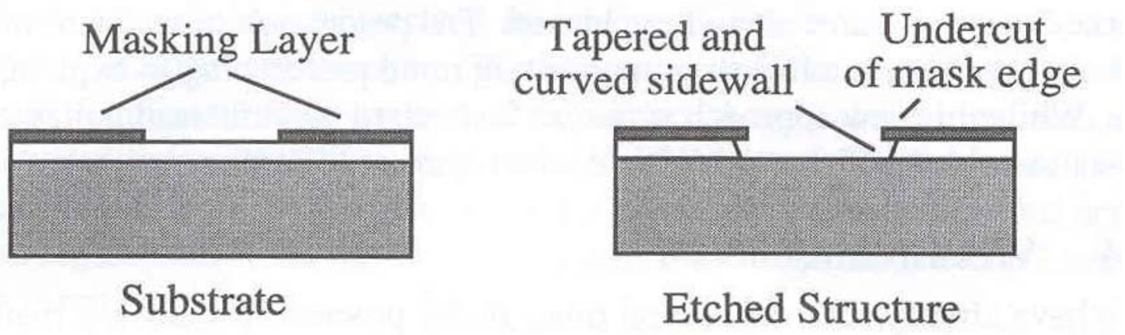
- **Wet Chemical Etching:** Immersion of the patterned substrate in a suitable liquid chemical, and the etchant attacks the exposed region and leaves the protected region alone.
- The rate of etching and the shape of the resulting etched feature depend on many thing:

1. the type of substrate,
2. the specific chemistry of the etchant,
3. the choice of masking layer and the tightness of its adhesion to the substrate,
4. the temperature (which controls reaction rates), and
5. whether or not the solution is well stirred (which affects the rate of arrival of fresh reactance at the surface).

- Depending on the temperature and mixing conditions, the etching reaction can be either
- *reaction-rate controlled*, dominated by temperature, or
- *mass-transfer limited*, determined by the supply of reactants or the rate of removal of reaction products.

Isotropic Wet Etching

- Most wet etching is isotropic, in that the rate of material removal dose not depend on the orientation of the substrate. **Isotropic etching.**
- When etching single-crystal substrates with certain etchants, orientation-dependent etching can occur. It is called **anisotropic etching**.



Because the wet-etching is isotropic, the mask is undercut, the side wall is typically papered and curved.

- Adhesion of the mask to the thin film is also important.
- If the adhesion is weak, enhanced etching can actually occur at the film-mask interface, exaggerating the sloping of the sidewall.
- Such tapered sidewalls can be an advantage when attempting to cover the etched feature with an additional film. Perfectly vertical steps are harder to cover.

Selected Wet Etchants and Selectivity

- **Etch rate :** Speed of etching for the desired materials.
- **Selectivity :** Discrimination between the etched materials and the un-etched materials.
- HF etches silicon dioxide, but also etches silicon nitride slowly.
- If silicon nitride is the mask material, one must be concerned with how long it it must remain exposed to the etchant.
- In surface micromachining, where long etch times may be required to remove all of the oxide beneath structural elements, the etch selectivity of protective layers is important.

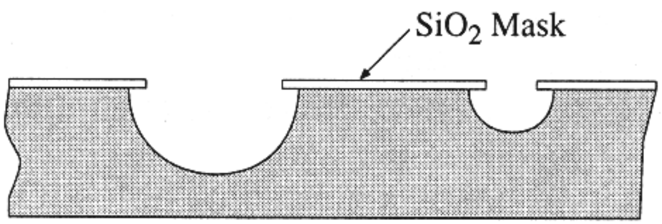
Table Selected wet etchants

Material	Etchant
Thermal or CVD silicon dioxide	Buffered hydrofluoric acid (5:1 NH_4F: conc HF)
Silicon nitride	Hot phosphoric acid
Polysilicon	KOH or ethylene diamine/pyrochatecol (EDP)
Aluminum	PAN (phosphoric, acetic, nitric acids)
Copper	Ferric chloride
Gold	Ammonium iodide/iodine alcohol

Stirring of Isotropic Wet Etching

- 等方性 식각은 모든 방향으로 같은 속도로 이루어지나, 가늘고 긴 통로에서는 반응의 확산이 제한되기 때문에 속도가 느려진다.
- 그런 경우, 식각액의 교반(stirring)이 식각 속도나 식각된 구조물의 형상을 좋게 해준다.
- 교반을 잘 해주면 거의 반구에 가까운 면을 얻을 수 있는데, 이는 교반이 반응액이나 생산물을 잘 수송해서 식각 속도를 높여주고 수송을 균일하게 해주기 때문이다.

ISOTROPIC WET ETCHING: AGITATION



ISOTROPIC WET ETCHING: NO AGITATION

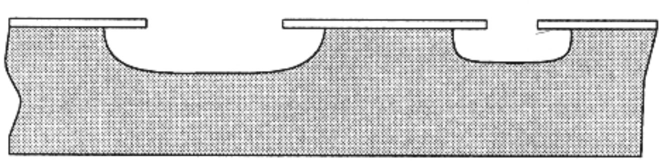
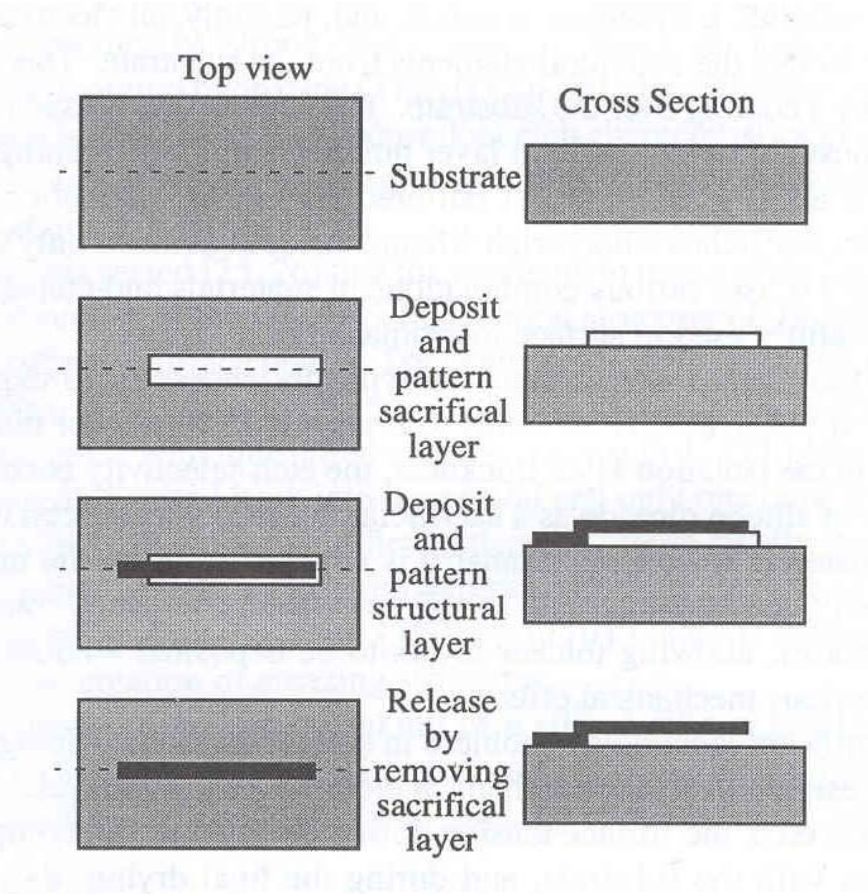


Illustration of isotropic etch cross sections showing the effects of mask geometry and agitation. Note that this type of etchant is an option for silicon and is, in general, the only wet etch option for glasses. After Petersen(1982).

Surface Micromachining Material Systems

- A sacrificial layer is deposited and patterned on a substrate.
- Then, a structural material is deposited and patterned so that part of it extends over the sacrificial layer and part of it provides an anchor to the substrate.
- Finally, the sacrificial layer is removed, leaving a cantilever beam of the structural-layer attached at one end to the substrate.



Illustrating surface micromachining: the use of an isotropic wet etchant to remove a sacrificial layer beneath a cantilever beam.

Design of Surface Micromachining Process

- Enormous flexibility in the design of surface micromachining process.
- One needs three or four different materials:

(1) a substrate (or a suitable thin-film coating over a substrate to provide the anchoring surface),
(2) a sacrificial material,
(3) a structural material,
(4) and an electrical insulation material (isolation the structural elements form the substrate).

- The etchant that is used to release the structure must etch the sacrificial layer quickly, and the remaining layers very slowly, if at all.
- For example, 5:1 buffered HF etches thermal oxide at about 100 nm/min, but etches silicon-rich silicon nitride at a rate of only 0.04 nm/min.

Table Surface micromachining material systems

Structural	Sacrificial	Release Etch	Isolation	Ref.
Polysilicon	SiO_2	Buffered HF	Si_3N_4 + SiO_2	[20]
Polyimide	Aluminum	PAN Etch	SiO_2	[21]
LPCVD Si_3N_4 + Al	Polysilicon	XeF_2	SiO_2	[22]
Aluminum	Photoresist	Oxygen plasma	SiO_2	[23]

Etch Selectivity in Surface Micromachining

- During the release etch, when it is typically necessary to exploit the undercutting of the structural elements to remove thin films over distances large compared to the isolation-layer thickness, the etch selectivity becomes critical.
- In the case of silicon dioxide as a sacrificial material with silicon nitride as the isolation material, if the stoichiometry is adjusted to make the nitride silicon rich, not only does the etch rate in HF decrease significantly, but its residual stress decreases, allowing thicker layers to be deposited without cracking or other deleterious mechanical effects.

Stiction in Fabrication

- The unintended adhesion of released mechanical elements to the substrate.
- When using a wet release etch, the surface tension during drying can pull compliant beams into contact with the substrate, and during the final drying, they can adhere firmly together.
- **Methods of avoiding stiction** include

  (1) the use of self-assembled molecular monolayers (SAM's) to coat the surfaces during the final rinse with a thin hydrophobic layer, reducing the attractive force,

  (2) the use of vapor or dry-etching release methods, such as XeF_2,

  (3) various drying methods (freeze drying and drying with supercritical CO_2) that remove the liquid without permitting surface tension to act,

  (4) temporary mechanical support of the movable structure during release using posts of photoresist or some other easily removed material.

Surface Micromachining Materials

- The most widespread material system used to date is silicon-rich silicon nitride as a coating on an oxidized silicon substrate to provide electrical isolation and an anchor, silicon dioxide as the sacrificial layer, polysilicon as the structural material, and buffered HF as the etchant.
- This combination is used in Analog Devices surface micromachined accelerometers.
- The use of LPCVD Si_3N_4 with aluminum electrodes as the structural material, polysilicon as the sacrificial layer, and the vapor etchant XeF_2 as the release etch is used in the Silicon Light Machine optical projection display.
- Texas Instruments uses aluminum as the structural material in their projection display, with photoresist as the sacrificial material removed by plasma etching.

HF / HNO_3 / Acetic Acid ("HNA")

- HNA : a mixture of HF, HNO_3, CH_3COOH.
- HNO_3 : 실리콘을 산화.
- HF : HF의 fluoride ion은 용해 가능한 silicon compound인 H_2SiF_6를 생성.
- *Acetic acid* : HNO_3가 NO^-_3 나 NO^-_2로 분해하는 것을 막고, 실리콘의 산화에 직접적으로 관여하는 성분을 만들어 준다.

$$N_2O_4 \leftrightarrow 2NO_2$$

- 초산이 없더라도 NO_2가 없어질 때까지 잠시 식각이 된다.
- 식각 화학식은 복잡하나, 식각 속도는 용액의 조성과 silicon doping에 영향 받는다.

$$18HF + 4HNO_3 + 3Si \rightarrow 2H_2SiF_6 + 4NO_{(g)} + 8H_2O$$

- 이 식각액의 단점은 SiO_2를 비교적 빠른 속도 (30~70 nm/min)로 상하게 한다는 것이다.
- Light doping ($<10^{17}$ cm^{-3} n- or p- type)된 영역은 heavily doped region보다 150 배 정도 더디게 식각 된다는 점에 유의해야 한다.

(continued)

HF / HNO$_3$ / Acetic Acid (“HNA”)

- 단결정 실리콘 습식 식각의 기본 원리.
  - (1) Si에 hole이 주입되어 Si^{2+}나 Si^{+}를 생성.
  - (2) Si^{2+}에 OH^{-}가 붙어서 $Si(OH)_2^{2+}$ 를 생성.
  - (3) hydrated Si (Silica)가 용액의 복잡한 용제와 반응.
  - (4) 반응 생성물이 용액에 용해.
- 이런 식각에서는 hole 공급원, OH^{-}, 복잡한 용제가 필요하다. Hole을 만드는 화학 반응은 화학식에서 전자를 다른 변으로 옮기는 것에 지나지 않는다.

$$2e^{-} + HNO_2 + HNO_3 + H_2O \rightarrow 2HNO_2 + 2OH^{-}$$

다른 표현으로 ($+2h^{+}$)

$$HNO_2 + HNO_3 + H_2O \rightarrow 2HNO_2 + 2OH^{-} + 2h^{+}$$

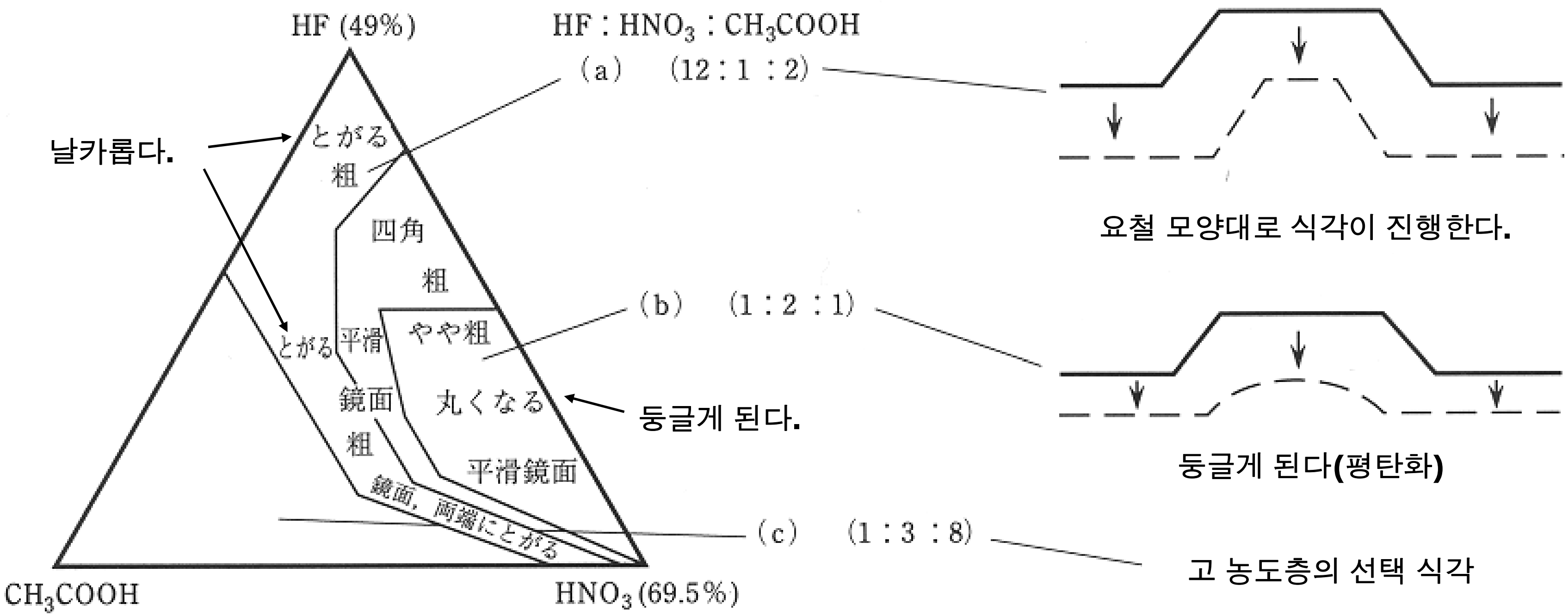
이것은 전기화학 반응이고, 이 식각이 기본적으로 전하 이송에 의한 공정이므로 dopant type/concentration 그리고 외부에서 가해 주는 전위가 식각 공정에 영향을 주게 된다.

Table of HNA Etchant Formulations

Table of HNA etchant formulations, assuming standard acid concentrations (note that water or acetic acid can be used) and their properties. From Petersen (1982).

Etchant (Diluent)	Reagent Quantities	Temp. °C	Etch Rate (µm/min)	(100)/(111) Etch Ratio	Dopant Dependence	Masking Films (etch rate)
HF	10 ml				$\leq 10^{17}$ cm^{-3} n or p reduces etch rate ≈150 ×	
HNO_3	30 ml	22	0.7 to 3.0	1:1		SiO_2 (30 nm/min)
(water, CH_3COOH)	80 ml					
HF	25 ml					
HNO_3	50 ml	22	4	1:1	no dependence	Si_3N_4
(water, CH_3COOH)	25 ml					
HF	9 ml					
HNO_3	75 ml	22	7	1:1	---	SiO_2 (70 nm/min)
(water, CH_3COOH)	30 ml					

HNA Isotropic Etching



HF-HNO$_3$ 계 etchant에 의한 실리콘의 등방성 식각