

Silicon Micro- & Nanofabrication Part 2 – Deposition & Wet Etching

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Thin Films

- **Thermal Silicon Oxide (Discussed last week)**

- Amorphous material.
- Insulating layer.
- Mask
- Sacrificial layer.
- Impurities such as Na⁺ and K⁺ diffuse through it.
- Most dopants except Ga diffuse poorly through it.
- Thicknesses usually less than 1 μm are produced.

- **Silicon Dioxide (SiO₂) by CVD**

- Insulator between conducting layers.
- Diffusion and ion implantation masks.
- Sacrificial material.
- **Chemical Vapor Deposition** (deposition of a solid on a heated surface from a chemical reaction in the vapor phase.)



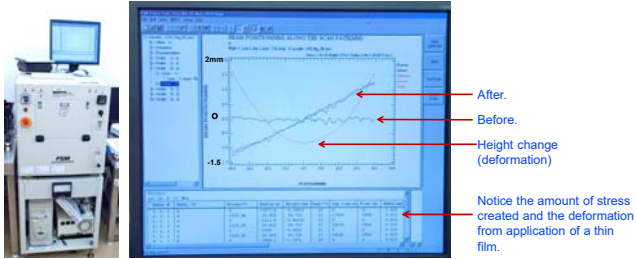
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- **Polysilicon Films (high-purity form of silicon with many silicon atoms)**

- Initially amorphous but may crystallize during deposition.
- **Transition from small grains at the film/substrate interface to columnar crystallites on top.**
- Dopants, impurities and temperature influence crystal orientation.
- Dopants decrease resistivity to produce conductors and control stress.
- Can be doped by diffusion, implantation, or by the addition of dopant gases during deposition.
- **Piezoresistive sensor elements may be fabricated from polysilicon.**
- **Low Pressure Chemical Vapor Deposition (LPCVD).**

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Thin Film Stress Gage...



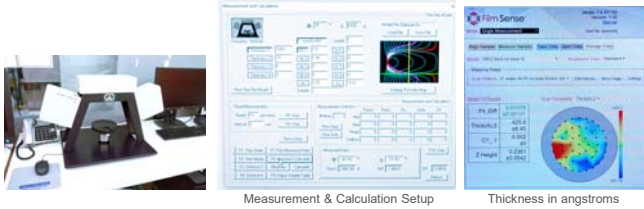
● Silicon Nitride (Si_3N_4)

- Amorphous
- Insulator between conducting layers.
- Excellent water and ionic barrier.
- Can not be directly put on silicon.
- May be put on a silicon dioxide layer.
- Highly selective etch rates.
- Hard material that may be used for structural purposes.
- Useful in high temperature applications.
- An important mechanical membrane and isolation/buffer material.
- CVD Techniques

● Phosphosilicate Glass (PSG)

- PSG and borophosphosilicate glasses (BPSG) soften and flow at lower temperatures, enabling smoothing of topography.
- Etch faster than silicon dioxide, hence more suitable sacrificial layer.
- Dielectric between conducting metal layers.
- Gettering – a process to remove impurities (e.g. alkali ions) and improve flow capabilities.
- Passivation coat to provide mechanical protection
- Creating by addition of phosphine to the gas stream.

Ellipsometer...



Ellipsometers give *non-contact thickness* and *refractive index* measurements of thin transparent and semi-transparent films to *sub-angstrom precision*. It is based on the change of polarization upon reflection or transmission.

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• Metal Films

- Aluminum and tungsten are commonly used.
- Metals with high reflectivity include Al (aluminum) and Au (gold).
- Metals with high mass density include W (tungsten), Au (gold) and Pt (platinum).
- Metals with specific adsorption and adhesion characteristics include Pd (palladium), Ir (iridium), Au (gold) and Pt (platinum).
- Tungsten will nucleate on Si or metal surfaces, whereas it does not adhere well on dielectric materials such as SiO_2 and Si_3N_4 . (They generally require us of a conformal TiN/Ti bilayer for a diffusion barrier to promote adhesion with CVD).
- CVD and PVD (Physical Vapor Deposition) techniques.

1. Kim S-D, Heun Kim C. Defect formation of chemical vapor deposited tungsten on rapid thermal annealed TiN/Ti. *Thin Solid Films*. 2008;07/31/2008:516(18):6310-6314. doi:https://doi.org/10.1016/j.tsf.2007.12.141.

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Thin-Film Deposition Processes

1. **Chemical Vapor Deposition**
 - Chemical vapor deposition is the deposition of a solid on a heated surface from a chemical reaction in the vapor phase.
2. **Physical Vapor Deposition**
 - Material is transported in vapor form from a source to a substrate through a vacuum or low-pressure gaseous environment:
 - Evaporation,
 - Sputtering,
 - Arc vapor deposition
 - Laser ablation,
 - Ion plating.
3. **Epitaxial Deposition**
 - A single crystal layer can be deposited onto the surface of a substrate wafer.

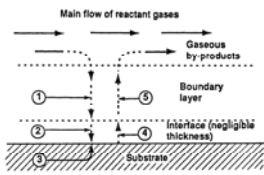
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Chemical Vapor Deposition (CVD)

- Chemical vapor deposition is the **deposition of a solid** on a heated surface from a **chemical reaction in the vapor phase**.
- Like PVD, the deposition species are atoms or molecules or a combination of these.
- **Advantages:**
 - High throwing power for ease of filling deep recesses, holes and other three-dimensional shapes;
 - Deposition is not limited to line-of-sight;
 - Coatings up to several centimeters can be realized;
 - Ultrahigh vacuums are not necessary; and
 - Co-deposition of elements or compounds is achievable
- **Disadvantages:**
 - Use of temperatures above 600°C.
 - Requirement for chemical precursors with high vapor pressure and toxicity,
 - Toxic by-products.

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CVD Process...



1. Reactant gases enter the reactor by forced flow.
2. Gases diffuse through the boundary layer.
3. Gases come in contact with the surface of the substrate.
4. Deposition takes place on the surface of the substrate.
5. Gaseous by-products are diffused away from the surface

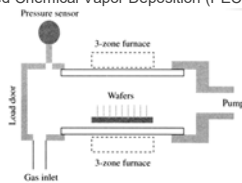
(Boundary layer is a few to tens of micrometers – and is flow, pressure, temp. dependent.)

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Pierson H.G. Handbook of Chemical Vapor Deposition (CVD): Principles, Technology, and Applications, 2nd ed. William Andrew Publishing/Noyes, Norwich, N.Y. (1999).

Methods...

- **CVD Deposition Methods.**
 - Atmospheric Pressure Chemical Vapor Deposition (APCVD).
 - Low-Pressure Chemical Vapor Deposition (LPCVD).
 - Plasma-enhanced Chemical Vapor Deposition (PECVD).



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Image courtesy of Gardner JW.

Feature of the CHA E-beam Evaporator...

- Operates in a high vacuum of 10^{-6} Torr. (Really small pressure!)
- Can accommodate up to six crucibles at once .
- Planetary wafer holder that can hold up to 18, 100 mm wafers.
- Has a quartz crystal microbalance for monitoring deposition rate and thickness
- PLC automation with a touchscreen interface for monitoring and controlling the system. (Programmable Logic Controllers)
- Limitation: Line of sight deposition can't completely coat complex geometries.

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Metals for Evaporation in Graphite Crucibles...



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Alternatively, Sputter Deposition (PVD)...

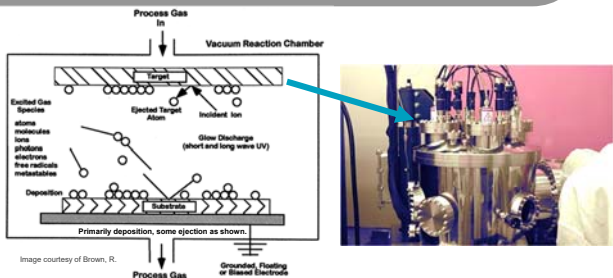
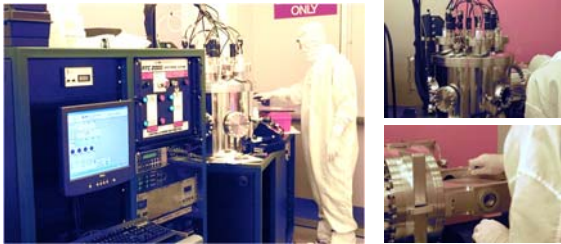


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Sputtering Equipment...



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DC metal Sputter System –
Aluminum, Titanium and Niobium.

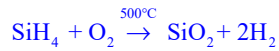


Cluster Sputter System.

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Some Example Select Thin-Films

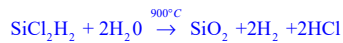
- SiO₂ can be deposited with CVD by reacting silane and oxygen in a LPCVD reactor as shown:



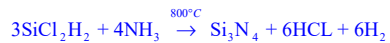
- SiO₂ can be deposited with LPCVD by decomposing tetra-ethyl-ortho-silicate, Si(OC₂H₅)₄, also known as TEOS. This is vaporized from a liquid source.

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- SiO₂ can also be deposited with LPCVD using dichlorosilane:



- Si₃N₄ can be deposited with LPCVD using dichlorosilane and ammonia:



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CVD Thin-Film Properties...

- There are three factors that control the nature and properties of the deposit:
 - Epitaxy
 - Gas-phase precipitation
 - Thermal expansion
- CVD structure can be controlled by manipulation of temperature, pressure, supersaturation and the CVD reaction.
- Ceramics, including SiO₂, Al₂O₃, Si₃N₄ and most dielectrics are amorphous.
- Metal deposits tend to be crystalline.

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Atomic Layer Deposition (ALD)



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Materials That Can Be Deposited...

- **Oxides:** Al_2O_3 , HfO_2 , SiO_2 , TiO_2 , SrTiO_3 , Ta_2O_5 , Gd_2O_3 , ZrO_2 , Ga_2O_3 , V_2O_5 , Co_3O_4 , ZnO , ZnO:Al , ZnO:B , $\text{In}_2\text{O}_3\text{:H}$, WO_3 , MoO_3 , Nb_2O_5 , NiO , MgO , RuO_2
- **Fluorides:** MgF_2 , AlF_3
- **Organic-hybrid materials:** Alucone
- **Nitrides:** TiN , TaN , Si_3N_4 , AlN , GaN , WN , HfN , NbN , GdN , VN , ZrN
- **Metals:** Pt , Ru , Pd , Ni , W
- **Sulfides:** ZnS

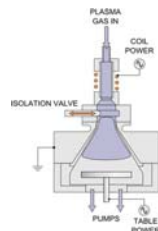


Image courtesy of Oxford industries

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Select ALD Features...

- 100% film density guarantees ideal material properties.
- Insensitive to dust (grows underneath dust!).
- Oxides, nitrides, metals, semiconductors possible (Cambridge Nanotech provides standard recipes).
- Amorphous or crystalline depending on substrate and temperature.



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Cambridge NanoTech Inc.

More ALD Features...

- Digital thickness control to atomic level (no rate monitor needed, just set the number of atomic layers).
- Perfect 3D conformality, 100% step coverage: uniform coatings on flat, inside porous and around particle samples.
- Low defect density.
- Gentle deposition process for sensitive substrates, no plasma.
- Low temperature deposition possible (RT-400C).
- Low stress because of molecular self assembly.

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Cambridge NanoTech Inc.

Ion Implantation

- In ion implantation, the dopant element is ionized, accelerated to a kinetic energy of several hundred keV, and then driven into the substrate.
- The electrical conductivity of an intrinsic semiconductor can be increased through doping. The charge carrier density can be increased through impurities of either higher or lower valence.
- Doping can be used to control etching by reducing etch rates.
- Sources for *n*-type doping include antimony, arsenic and phosphorous; and for *p*-type doping, boron.

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Chemical Etching

- Anisotropic etchants (potassium hydroxide, ethylene diamine pyrochatechol, and tetramethyl ammonium hydroxide):
 - Etch silicon preferentially along preferred crystallographic directions.
 - Show a reduction of etch rate in heavily doped *p*-type regions.
- Boron typically is incorporated using ion implantation for this purpose.

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Wet Bulk Surface Micromachining

- In wet bulk micromachining features are sculptured in bulk materials like silicon, quartz, sapphire, ceramics, SiC, GaAs, InP and Ge by orientation independent (isotropic) or orientation-dependent (anisotropic) **wet etchants**.
- Integrated circuits typically have **aspect ratios** of 1-2, while in BioMEMS the ratio may be up to 400.

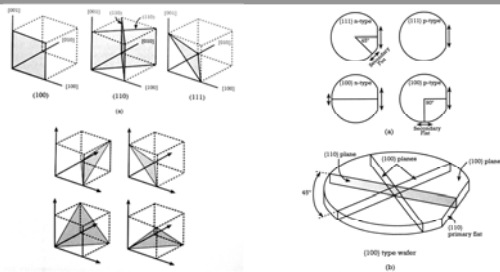
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Recall Silicon Crystal Orientation...

- Orientation is important because of different characteristics and etching speeds in different planes and resulting etching angles.
 - The (111) plane has the highest atom packing density and is relatively non-etching compared to the others.
 - The angles between planes, {100} and {110} are 45 or 90 degrees, between {100} and {111} are 54.74 degrees, and between {111} and {110} planes 35.26, 90 or 144.74 degrees.

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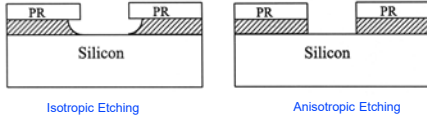
and the Miller Indices...



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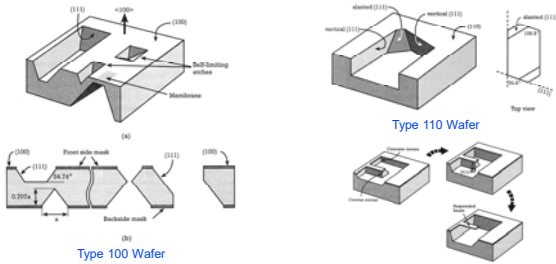
Images courtesy of Madou M.

and Isotropic vs. Anisotropic Etching...



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Resulting in the following Geometric Shapes...

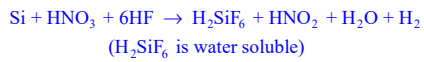


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Images courtesy of Madou M.

Isotropic Etching Agents...

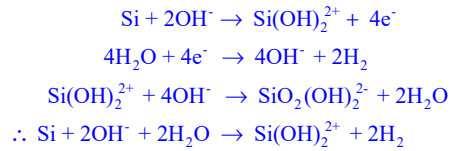
- **Isotropic** etchants are usually **acidic**, and lead to rounded features (**HNA** = HF (hydrofluoric acid) + HNO₃ (nitric acid) + CH₃COOH (acetic acid)):



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Anisotropic Etching Agents...

- Anisotropically etchants are alkaline:



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Structural Element/Sacrificial Layer/Etchant

- Common structural elements include polysilicon, polyimide, silicon nitride and tungsten.
 - The polysilicon and its sacrificial layer, silicon dioxide can be applied by LPCVD. Silicon dioxide can be etched away with hydrofluoric acid (HF) solution without etching the polysilicon.
 - Polyimide can be used with aluminum as the sacrificial layer, the latter being dissolvable with acid-based etchants.
 - Silicon nitride is both a good structural material and electrical insulator. Polysilicon can be used as the sacrificial layer, in which case KOH and EDP can be used as the etchants.

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- Tungsten can be applied by CVD over silicon dioxide (with a suitable conformal TiN/Ti bilayer to promote adhesion)¹, and again HF is a suitable etchant to remove the silicon dioxide sacrificial layer.
 - With ALD there are techniques to place tungsten on a hydroxylated silica (SiO₂) surface using repeated exposures to disilane (Si₂H₆) and tungsten hexafluoride (WF₆).²
 - Various other substrates have been studied using the two phases of tungsten, alpha (stable) and beta (metastable).³

1. Eam J.W, Nelson C.E, Grubbs R.K, George S.M. Nucleation and growth during tungsten atomic layer deposition on SiO₂ surfaces. *Thin Solid Films*. 2001;05/01/2001:386(1):41-52. doi:https://doi.org/10.1016/S0040-6090(01)00762-3.
2. Kim S.D, Hwan Kim C. Defect formation of chemical-vapor deposited tungsten on rapid thermal-annealed TiN/Ti. *Thin Solid Films*. 2008;07/31/2008:516(15):6310-6314. doi:https://doi.org/10.1016/j.tsf.2007.12.141
3. Lee J-S, Cho J, You C-Y. Growth and characterization of alpha and beta phase tungsten films on various substrates. *Journal of vacuum science & technology A: Vacuum, surfaces, and films*. 2016;34(2):doi:10.1116/1.4936291

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Stiction and Critical Point Dryer

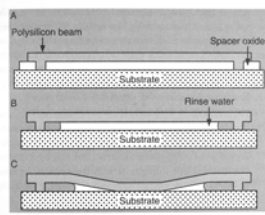


Image courtesy of Madou M.



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Atomic Force Microscopy Measurement

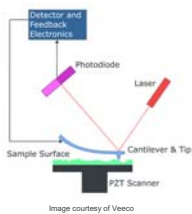
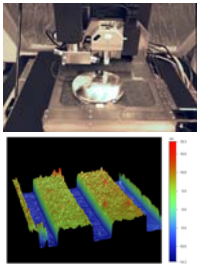


Image courtesy of Veeco

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Substrate Bonding

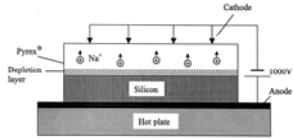
1. Silicon Direct Bonding (or Fusion Bonding)
 - Silicon to Silicon
 - Silicon on Insulator (SOI)
 - No intermediate layers
 - Requires heating (450°)
2. Anodic Bonding
 - Silicon to Glass (Pyrex 7740)
 - Intermediate Adhesive Layers
3. Lasers

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Wafer Bonding



Wafer bonder - anodic or direct (fusion).



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Key Points

- Important thin-films to remember:
 - Thermal Silicon Oxide,
 - Silicon Dioxide (SiO_2),
 - Polysilicon,
 - Silicon Nitride (Si_3N_4),
 - Phosphosilicate Glass (PSG),
 - Metal films (e.g., tungsten and aluminum).
- Thin films may be produced by the following methods:
 - Thermal oxidation,
 - Physical Vapor Deposition,
 - Chemical Vapor Deposition,
 - Epitaxial Deposition,
 - Atomic Layer Deposition (ADL).

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- Ion implantation may be used to
 - Improve electrical conductivity,
 - Control etching characteristics.
- Wet bulk micromachining incorporates:
 - Isotropic and anisotropic etching,
 - 3-D structure and sacrificial layers.
- Characterization can be done with Atomic Force Microscopy
- Wafer bonding can be done by these two techniques:
 - Silicon direct (or fusion) bonding,
 - Anodic bonding.

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