Classification of Film Deposition Technologies

a) **Physical**
   - **Vacuum Evaporation:**
     1) a vapor is generated,
     2) the vapor is transported from the source to the substrate,
     3) the vapor is condensed to a solid film on the substrate.

   Source: resistance-heated filaments; crucibles heated by conduction, radiation or rf-induction; arc (Thermal Evaporation); exploding wires; electron beams (Electron-beam Evaporation); or pulsed laser (Pulsed Laser Abalation).

   - **Molecular Beam Epitaxy (MBE):** finely controlled method for growing single-crystal epitaxial films in a high vacuum ($10^{-11}$ torr). The films are formed on single-crystal substrates by slowly evaporating the elemental or molecular constituents of the film from separate Knudsen effusion source cells (deep crucibles in furnaces with cooled shrouds) onto substrates held at a temperature appropriate for chemical reaction, epitaxy, and re-evaporation of excess reactants. Fast shutters are interposed between the sources and the substrates. By controlled these shutters, one can grow superlattices with precisely controlled uniformity, lattice match, composition, dopant concentrations, thickness, and interfaces down to the level of atomic layers.

   Schematic cross-section of a typical MBE growth chamber

   Advantages: complex layers or superlattices, low temperature requirement epitaxy (Si: 400 - 800°C, GaAs: 500 - 600°C).
Disadvantages: limited product throughput, complex operation, expensive equipment.

b) Chemical

**Gas-phase Chemical Process**

- **Thermal Forming Processes:**
  - **Thermal oxidation:** substrate itself provides the source for the metal or semiconductor constituent of the oxide (SiO₂/Si)
  - **Thermal nitridation** etc

- **Ion implantation:**
  Mainly used to form silicon-on-insulator structures by implanting large dose of atomic or molecular oxygen ions in single crystal silicon substrates to produce a buried oxide layer with sharp interfaces after annealing.

- **Chemical Vapor Deposition (CVD):**
  Materials synthesis process whereby constituents of the vapor phase react chemically near or on a substrate surface to form a solid product. Chemical reaction types basic to CVD include pyrolysis (thermal decomposition), oxidation, reduction, hydrolysis, nitride and carbide formation, synthesis reactions, disproportionation, and chemical transport. Most CVD processes are chosen to be heterogeneous reactions (take place at the substrate surface) rather than homogeneous reactions (take place in the gas phase). CVD involves at least 3 steps:
  1) Arrival: bulk transport of reactants into the process volume, gaseous diffusion of reactants to the surface, absorption of reactants onto the surface,
  2) Surface reaction: surface reaction (reaction can also take place in the gas volume immediately above the surface), surface diffusion, crystal lattice incorporation, and

**Reactors:** allow transport, provide activation energy, maintain a specific system pressure and temperature, allow the chemical processes for film deposition, and remove the by-product.

**Temperature:** hot-wall reactors (tubular in shape) are for exothermic process (semiconductors) and cold-wall reactors (bell-jar) for endothermal processes (silicon from halides). Heating is accomplished by rf induction or high-intensity radiation lamp.

**Pressure:** the reduced operating pressure increases the mean-free path of the reactant molecules which allows a closely spaced wafer stacking. This allows a greatly increased throughout and hence a lower product cost.
Principal CVD reactor geometries for silicon epitaxy.

Different types of CVD:
Atmospheric-pressure CVD (APCVD), Low-pressure CVD (LPCVD), Metalorganic CVD (MOCVD), Photo-enhanced CVD (PHCVD), Laser-induced CVD (PCVD) and Electron-enhanced CVD.

Liquid-phase Chemical Process

- Electro-process: based on the electrochemical processes (include anodization and electroplating) and/or chemical deposition processes (include reduction plating, electroless plating, conversion coating, and deposition).

  Electrolytic Anodization: an oxide film is formed the substrate. The anode reacts with negative ions from the electrolyte in solution and becomes oxidised, forming a nonporous and well-adherent oxide films. (Ta$_2$O$_5$/Ta, Al$_2$O$_3$/Al, TiO$_2$/Ti and Nb$_2$O$_5$/Nb).

  Electroplating: a metallic coating is electrodeposited on the cathode of an electrolytic cell consisting of a positive electrode (anode), a negative electrode (cathode), and an electrolyte solution (containing the metal ions) through which electric current flows.

  Chemical Reduction Plating: reduction of a metal ion in solution by a reducing agent added just before use. Reaction is homogeneous and deposition takes place everywhere in the solution. (Silvering of glass using silver nitrate and hydrazine).
Electroless (Autocatalytic) Plating: Selective deposition plating process in which metal ions are reduced to a metallic coating by a reducing agent in solution. Plating takes place only on suitable catalytic surfaces (substrates of the same metal being plated).

Electrophoretic Deposition: deposition of a film from a dispersion of colloidal particles onto a conductive substrate. The dispersion in a conductive liquid dissociates into negatively charged colloidal particles and position ions (cations), or the reverse. On application of an electric field between the positive substrate electrode (anode), the colloidal particles migrate to the substrate, become discharged, and form a film. (Black oxide on steel, Phosphate conversion coatings of iron with phosphoric acid).

Immersion (Chemical Displacement) Plating: deposition of a metal film from a dissolved salt of the coating metal on a substrate by chemical displacement without external electrodes. A more electronegative metal displaces from solution any metal is more electropositive (Tin coatings on copper).

- Mechanical Processes: deposit coatings from liquid media that are subsequently reacted chemically to form the inorganic thin film product are spraying, spinning, dipping and draining, flow coating, roller coating, pressure-curtain coating, brushing and off-set printing of reagent solution. Chemical reaction of the coating residue by thermal oxidation, hydrolysis or pyrolysis produces the desired solid film.

Liquid-phase Epitaxy (LPE): thermally-controlled over-growth of thin single-crystalline films of compound semiconductors and magnetic garnets from the melt on a single-crystal substrate.

Sol-gel Method: prepare metal oxide glasses and ceramics by hydrolyzing a chemical precursor to form a sol and then a gel, which on drying (evaporation) and pyrolysis gives an amorphous oxide. Upon further heat treatment crystallization can be induced.

C) Physical-chemical Process (Glow-discharge Process)
- Sputtering: the ejection of surface atoms from an electrode surface by momentum transfer from bombarding ions to surface atoms i.e. an etching process. This produces a vapor of electrode material and uses as a method of film deposition similar to evaporative deposition.

Glow Discharge DC Sputtering: uses a plate of the material to be deposited as the cathode electrode in a glow discharge. Films of pure metals can be deposited when using noble gas.
Reactive Sputtering: sputtering elemental or alloy targets in reactive gases to fabricate compounds.

Magnetron Sputtering: magnetic field transverse to the electric fields at sputtering-target surfaces. Higher deposition rate and secondary electrons could not bombard the substrates.

Ion Beam Sputtering: ion beams, produced in, and extracted from glow discharges in a differentially pumped system will be used.

RF Sputtering: for insulating target, it will be charged up until it repels any further bombardment. An ac current (frequencies of the order of 13.56MHz) is used so that the target would be alternately bombarded by positive ions and then by negative electrons in order to neutralize the charge.
**Bias Sputtering:** for high bombardment energies, re-sputtering will be occurred. To lower the energies, an electrical bias applied to the substrates to control the amount of ion bombardment.

- **Plasma Process:** some chemical reactions are accelerated at a given temperature in the presence of energetic reactive-ion bombardment. A metal to be oxidized, nitrided or carburized is made the cathode of a glow discharge and is simultaneously heated by radiant or rf-induction means.
  - Plasma oxidation
  - Plasma Nitridation
  - Plasma Anodization
  - Plasma Reduction
  - Plasma Polymerization
  - Microwave Electron Cyclotron Resonance (ECR) Deposition


<table>
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<tr>
<th>Method</th>
<th>Rate (Å/min)</th>
<th>Epitaxy 1-10</th>
<th>Stoichiometry 1-10</th>
<th>Temperature (°C) Substrate Anneal</th>
<th>Devices</th>
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<td>8</td>
<td>3</td>
<td>RT-700 500-700</td>
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<td>5</td>
<td>5</td>
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<td>RF Magneton</td>
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</tr>
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<td>Ion Beam Sputter</td>
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<td>Sol-gel</td>
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<td>2-8</td>
<td>9</td>
<td>RT 450-750</td>
<td>1-5</td>
<td>L</td>
<td>Multiple coating</td>
</tr>
<tr>
<td>MOD</td>
<td>3000 Å/C</td>
<td>2</td>
<td>9</td>
<td>RT 500-800</td>
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<td>High T$_{1/2}$</td>
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<td>MOCVD</td>
<td>50-1000</td>
<td>5</td>
<td>7</td>
<td>400-800 600</td>
<td>1-5</td>
<td>H</td>
<td>High T$_{1/2}$ (substrate)</td>
</tr>
</tbody>
</table>

Devices number: 1-Capacitor, 2-Memory cell, 3-Actuator, 4-Electro-optic, 5-Pyroelector, 6-SAW.
Material Characteristics

The desired material characteristics of the deposited films will be in most cases the decisive factor for the selection of a preferred deposition technology. In general,

Characteristics of thin films ≠ Characteristics of bulk materials

This discrepancy can be resulted from surface/volume ratio, and/or surface contamination, nucleation effects, surface mobility, chemical surface reactions, adsorbed gases, catalytic or inhibitory effects on films growth, surface topography, crystallographic orientation and stress effects.

- **Major physical and chemical parameters:**

1. **Electrical**
   - Conductivity/resistivity
   - Dielectric constant/dielectric loss/dielectric strength
   - Polarization/P-E loop
   - Permittivity
   - Stability under bias
   - Electromigration/leakage current
   - Radiation hardness

2. **Thermal**
   - Coefficient of expansion
   - Thermal conductivity
   - Thermal fusion temperature
   - Volatility and vapor pressure
   - Temperature variation of all properties
   - Stability or drift of characteristics

3. **Mechanical**
   - Intrinsic, residual and composite stress
   - Anisotropy
   - Adhesion
   - Hardness
   - Density
   - Fracture
   - Ductility
   - Elasticity

4. **Morphology**
   - Crystalline or amorphous
   - Crystallite orientation
   - Surface topography
   - Structural defect density
   - Microstructure
   - Planarity
5. **Optical**
   - Refractive index
   - Absorption/transmission
   - Birefringence
   - Spectral characteristics
   - Dispersion

6. **Magnetic**
   - Saturation flux density
   - Coercive force
   - Permeability

7. **Chemical**
   - Composition/Impurities
   - Reactivity with substrates and ambient
   - Thermodynamic stability
   - Etch rate/corrosion and erosion resistance
   - Toxicity
   - Hygroscopicity
   - Impurity barrier or gettering effectiveness
   - Carcinogenicity

**Process Technology**
A wide variety of process technologies is available for the deposition of thin films (thickness: 1 nm to several micrometers). These technologies differ to a large degree in their physical and chemical principles of operation and in the commercially available types of equipment. Each process technology has been developed because it has unique advantages over others. However, each process technology has its limitations.

Several Important factors:
1) Stability and repeatability of the processes used especially in the large-scale manufacturing or semiconductor devices.
2) Uniformity both in thickness and composition.
3) Compatibility with the structures already built into the device.
4) High degree of flexibility.
5) Step coverage or conformality.
6) Cost.

Reference
Sol-gel Process

Sol-gel processing is currently one of the most actively studied processing techniques of oxides. In its simplest form, the sol-gel process involves four stages:

1) the preparation of a homogeneous precursor solution, usually metal alkoxides,
2) the deposition of a thin layer on the substrates,
3) simultaneous hydrolysis and polycondensation, and
4) the heating of this amorphous film.

• **Preparation of a homogeneous precursor solution**

There are two different ways to prepare precursor solution, either from inorganic precursor (i.e. inorganic salts in aqueous solution) or from metal alkoxide precursor (i.e. metal alkoxides in non-aqueous solvent, usually their parent alcohol).

**metal alkoxide:** easier to control the hydrolysis rate and condensation rate

**inorganic:** cheaper

**Synthesize metal alkoxides:**

1) Highly electropositive elements with valences up to three (alkali metal, alkaline earth, Lanthanons): react directly with alcohols.

\[ M + nROH \rightarrow M(OR)_n + \frac{n}{2} H_2 \]

For comparatively less active metals (Al or Be): a catalyst (iodine) is required.

2) Electronegative elements (boron, silicon and phosphorus); react of covalent halides with alcohol. This method, which employs the anhydrous chlorides as starting material, does not completely replace the halide when the central metal atom is less electronegative. In this case, use of bases such as pyridine or ammonia.

\[ \text{TiCl}_4 + 4\text{ROH} + 4\text{NH}_3 \rightarrow \text{Ti(OR)}_4 + 4\text{NH}_4\text{Cl} \]

3) Esterification of their oxyacids or oxides (acid ahydrides) with alcohol. The water produced in the reaction is removed continously.

\[ \text{B}_2\text{O}_3 + 6\text{ROH} \rightarrow 2\text{B(OR)}_3 + 3\text{H}_2\text{O} \]

4) Transesterification of alcoholysis reactions of lower alkoxides to produce higher alkoxides.

5) Reactions of dialkylamides of metals with alcohol.

\[ \text{Nb(NEt}_2\text{)}_4 + 4\text{ROH} \rightarrow \text{Nb(OR)}_4 + 4\text{Et}_2\text{NH} \]

In some case, the alkoxides formed are unstable and would precipitate out. A drying control chelating agent (DCCA) would be used.
For multi-component alkoxide solution, individual metal alkoxide sol is prepared. Precaution is required not to allow any pre-hydrolysis of the metal alkoxides before mixing. This is usually achieved by simple distillation of the solvent beforehand. Moreover, all the metal alkoxide sol formed should be kept under inert gas for storage. In the process of mixing, common solvent to all alkoxides is required. Reflux for several hours may be needed for complete mixing and the solution should then be concentrated to the desired concentration.

- **Deposition on Substrates**

Methods: Spin-coating, dipping coating, spraying, electrophoresis, thermoporeisis and sedimentation (settling).

Among all, spinning and dipping are the most extensively used. Dip-coating is divided into five stages: immersion, start-up, deposition, drainage and evaporation. The thickness of the deposition film is related to the position

![Five stages of the dip-coating process](image)

The moving substrate entrains liquid in a fluid mechanical boundary layer carrying some of the liquid toward the deposition region where the boundary layer split in two. The inner layer moves upward with the substrate, while the outer is returned to the bath.
A competition among as many as six forces in the film deposition region governs the film thickness and position of the streamline:

1) viscous drag upward on the liquid by the moving substrate,
2) gravity force,
3) resultant force of surface tension in the concavely curved meniscus,
4) inertial force of the boundary layer arriving at the deposition region,
5) surface tension gradient, and
6) the disjoining or conjoining pressure (important in films of thickness less than 1 µm).

When the liquid viscosity ($\eta$) and substrate speed ($U$) are high enough to lower the curvature of the meniscus, then the deposited film thickness ($h$) is the thickness that balances the viscous drag ($\eta U/h$) and gravity force ($\rho gh$):

$$h = c\left(\frac{\eta U}{\rho g}\right)^{1/2}$$

Here the proportionality constant, $c$, is about 0.8 for Newtonian liquids. When the substrate speed and liquid viscosity are not high enough, as is often the case in sol-gel processing, this balance is modulated by the ratio of viscous drag to liquid-vapor surface tension ($\gamma_{LV}$) according to the following relationship derived by Landau and Levich:

$$h = 0.94\left(\frac{\eta U}{\gamma_{LV}}\right)^{1/6}\left(\frac{\eta U}{\rho g}\right)^{1/2}$$

Some modifications should be made when taking into account film shrinkage due to evaporation and partial sintering. This equation fairly describes the situation for polymeric systems. However, for sols composed of mutually repulsive and monosized particles which tend to order as $U$ increases, the equation seems to deviate from the predicted behaviors.
Hydrolysis and Condensation

In general, metal alkoxides are very active due to the presence of highly electronegative OR groups that stabilize M in its highest oxidation state and render very susceptible to nucleophilic attack.

Mechanisms

In the absence of catalyst, for coordinatively saturated metals, hydrolysis and condensation both occur by nucleophilic (SN) mechanisms. They involve (i) nucleophilic addition (AN), (ii) proton transfer from the attacking molecule to an alkoxide or hydro-ligand within the transition state, (iii) removal of the protonated species as either alcohol (alcoxolation) or water (oxolation).
When \( N - z > 0 \), condensation can occur by oxolation,

![Image showing the mechanism of oxolation](image)

**Reaction rate**

**Choice of precursor:** The thermodynamics of hydrolysis, alcoxolation and oxolation are governed by the strength of the entering nucleophile, the electrophilicity of the metal, and the partial charge and stability of the leaving group. That is, these reactions are favored when the partial charge of oxygen, \( \delta(O) \ll 0 \), \( \delta(M) \gg 0 \), and \( \delta(H_2O) \) or \( \delta(ROH) > 0 \).

Another factor that influences reaction kinetics is the degree of oligomerization (molecular complexity) of the metal alkoxides. The molecular complexity depends on the nature of the metal atom. Within a particular group, it increases with the atomic size of the metal, thus explaining the tendency of divalent transition metal alkoxides (Cu, Fe, Ni, Co and Mn) to polymerize rendering them insoluble. Oligomerization also depends on the alkoxide ligand, for example, (i) Ti(OEt)\(_4\) exhibits an oligomeric structure, whereas Ti(OPr)\(_4\) remains monomeric; (ii) partial hydrolysis of Zr(OPr)\(_n\)\(_4\) dissolved in the polar, protic solvent, n-PrOH, results in a precipitate, whereas homogeneous gels are obtained by hydrolysis of Zr(OPr)\(_n\)\(_4\) dissolved in non-polar, a protic solvents such as cyclohexane. These differences reflect the influence of molecular complexity on the hydrolysis kinetics: alkoxy-bridging occurs in cyclohexane allowing controlled hydrolysis whereas alcohol association (rather than alkoxy bridging) occurs preferentially in nPrOH resulting in rapid hydrolysis and formation of a highly condensed product.

The size and electron-providing/electron-withdrawing characteristics of the organic ligand also affect the hydrolysis and condensation kinetics.

**Acidity:** kinetics are determined by the transfer ability of the proton, so a greater acidity of the proton would reduce the associated activation barriers and enhance the kinetics.
Annealing

Annealing is a process by which an amorphous gel crystallizes to give a crystalline one. During heating, structural evolution occurred and could be classified into three regions.

I) Weight loss and little shrinkage of the gel. This weight loss corresponds to the endothermal attributed to the desorption of physically adsorbed water (or perhaps residual solvent) while the shrinkage results from the increase in surface energy caused by the desorption of water or alcohol. The resulting linear strain, $\varepsilon$, is

$$\varepsilon = (1 - \nu) S \rho_s \frac{\Delta \gamma}{E}$$

where  
$S$ = surface, 
$\rho_s$ = skeletal density, 
$\Delta \gamma$ = change in specific surface energy, 
$\nu$ = Poisson's ratio and 
$E$ = Young modulus of the skeleton.

II) Weight loss and shrinkage in this region are attributed primarily to the removal of organics (weight loss), polymerization (shrinkage and weight loss), and structural relaxation (shrinkage). Continued desorption and dehydroxylation that increases surface energy, $\gamma$, by about a factor of 2, should result in an addition cailary strain in above equation of $\approx 1\%$. This only represents a minor contribution to the shrinkage in this region.

III) Region III commences in the vicinity of $T_g$ for the corresponding melt-prepared glass, and shrinkage occurs with little weight loss.
Advantages of Sol-gel method

- High homogeneity (particulate-free)
- Easy composition control (stoichiometric ratio) with high purity
- Film uniformity over large area and versatile shape
- Low processing temperature
- Low cost (equipment)

Industrial applications

- Effects of the processing parameters
  
  1) Solvent: Solvent with more bulky ligands due to the steric hindrance may result in better control in the rate of hydrolysis and condensation. For example, 2-methoxyethanol instead of ethanol with advantages of simple distillation and easier in storage.

  2) Crystalline temperature: (differential thermal analysis (DTA), thermogravimetry (TG) and XRD)

  powder:
  Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$(SBN) powder starts to crystallize at about 630°C
  melting point of single crystal
  ~1700°C
  solid state reaction method ~1400°C
powder:
28.7° and 31.1° peaks indicate the co-existence of orthorhombic and tetragonal phase at low annealing temp. (pure tetragonal phase at 120°C)

thin film:
that predicted by DTA and phase transition occurs at 700°C (substrate effect)

Lattice matching effects
enhanced orientation to (001) plane in MgO
enhancement in (121) and (131) planes for sapphire orthorhombic phase was preferred in the case of corning glass

Novel route for epitaxial growth of thick SBN films
PLD: excellent crystallinity, not good for thick films
Sol-gel: good for thick films, OK crystallinity
A PLD - Sol-gel hybrid technique to fabricate SBN films
Thickness of sol-gel films ~1.2 µm, PLD layer ~100 nm.
Dr. C. L. Mak

0-2θ scan: stronger intensity rock curve: 0.7° (a) and 2.3° (b) Pole figure: SBN inter-grown at an orientation 18.5° on MgO substrate

Therefore, films with a PLD self-template layer showed excellent epitaxy and densely packed grain morphology

Generalize to prepare other high-quality multi-component thick oxide films on Si

Choice of substrate has an important influence on the orientation of the films

4) **Thickness effect** (XRD)

stack of dip-coated layers thicker film: preferred and better oriented (001) layers, increased grain size and decreased porosity prolonged annealing shows no apparent effects on these structural changes
progressively improved sol-gel films can be produced by increasing the number of dip-coated layers as compared to other physical deposition

5) **Annealing atmosphere**: for oxide, usually annealed in oxygen would enhance the quality of the films.

6) **Stoichiometric composition**: the composition ratio would affect the phase and structure of the films which would affect its structural properties.

- **Applications**

  Ferroelectric materials
  - Ferroelectricity (spontaneous polar)
  - Pyroelectricity (thermal)
  - Piezoelectricity (stress/strain)
  - Dielectric
  - electro-optics

  Ferroelectric nonvolatile memory (FNVM)
  - infrared sensor
  - actuator
  - capacitor
  - waveguide modulator

Thin films
- Trend toward miniaturization
- Designing advantages:
  - Large geometrical flexibility and ease of integrating with other IC
  - Lower cost
- Properties unique to thin films
SEN powders/ films prepared by Sol-gel method

\[
\text{Barium} \quad \text{Niobium (V) chloride} + \text{Potassium hydroxide} \\
\downarrow \quad \downarrow \\
+ 2\text{-methoxylethanol} \\
\downarrow \quad \downarrow \\
\text{Strontium methoxyethoxide} \quad \text{Barium methoxyethoxide} \quad \text{Niobium methoxyethoxide} \\
\downarrow \quad \downarrow \\
\text{Reflex} \\
\text{Strontium Barium Niobate Sol} \\
\downarrow \\
\text{Spin coated on the substrate then anneal at 700°C} \\
\downarrow \\
\text{Strontium Barium Niobate Film}
\]
Vacuum Coating

History:
1857  Faraday exploded metal wire in an inert atmosphere
1887  Nahrwold deposited platinum films using Joule heating
1955  Development of vacuum equipment to allow industrial applications e.g.
      antireflection coatings, front-surface minors, interference filters, sunglasses,
      decorative coatings on plastics and textiles

Uncoated substrates are placed in a large vacuum chamber capable of achieving a
vacuum of at least 10-6 torr. At the bottom of the chamber is a source of the film material
to be vaporized as shown. The substrates are mounted on a series of rotating carousels,
arranged so that each substrate sweeps in planetary style through the same time-average
volume in the chamber.

Schematic view of a typical vacuum deposition chamber

Three distinguishable steps:
1)  Transition of a condensed phase (solid or liquid) into the gaseous state,
2)  Vapor transversing the space between the evaporation source and the substrate at
    reduced gas pressure,
3)  Condensation of the vapor upon arrival on the substrates.
• Thermal evaporation

The simplest type of source of vaporized material relies on resistive heating of a thin folded strip (boat) of tungsten, tantalum, or molybdenum by a high direct current. Small amounts of the coating material are loaded into the boat. A high current (10-100A) is passed through the boat, which undergoes resistive heating. The coating material is then vaporized thermally. Because the chamber is at a greatly reduced pressure, there is a very long mean free path for the free atoms or molecules, and the heavy vapor is able to reach the moving substrates at the top of the chamber. Here it condenses back to the solid state, forming a thin and uniform film.

Pros: simple and cheap, good for most volatile material, coatings of excellent quality can be produced if they are deposited on a hot substrate.

Cons: some substrates can react with the hot boat which can cause impurities, most metal oxides cannot be vaporized due to a high melting temperature.

• Electron bombardment

This method is capable of vaporizing even highly involatile materials, such as titanium oxide and zirconium oxide. Using large cooled crucibles precludes reaction of the heating material with the metal of the boat. A high flux of electron gun (1A at 10 kV) is aimed at the film material contained in a large, water-cooled, copper crucible. Intense local heating melts and vaporizes some of the coating material in the center of the crucible without causing undue heating of the crucible itself. For particularly involatile materials, the electron gun can be focused to intensify its effects. Careful control of temperature and vacuum conditions ensures that most of the vapor is in the form of atoms or molecules, as opposed to clusters. This produces a more even coating.

Ion-assisted bombardment is a coating technique that can offer unique benefits under certain circumstances. Ion assist during coating leads to a higher atomic or molecular packing density in the thin film layers. This results in a higher refractive index and, most important, superior mechanical characteristics. (specifically, the lack of voids in the more efficiently packed film means that it is far less susceptible to water-vapor absorption. Water-vapor absorption can change the refractive index and mechanical properties.) Ion-assisted coating can be also used for cold processing. Eliminating the need to heat parts allows cemented to be safely coated.

• Applications:
1) Single-layer MgF$_2$ on fused silica antireflection coatings

The substrate (glass, quartz) is coated with a thin layer of material so that reflections from the outer surface of the film and the outer surface of the substrate cancel each other by destructive interference. The intensity of the transmitted beam is correspondingly increased so that, ignoring scattering and absorption,

\[
\text{Incident energy} = \text{reflected light} + \text{transmitted energy}
\]
Two requirements create an excellamation of reflected beams with a single layer coating. The reflections are exactly 180 degrees out of phase, and they have the same intensity. In order to achieve the correct phase for cancellation, the thickness of the single layer antireflection film must be an odd number of quarter wavelength.

There is a $\pi/2$ phase shift for reflections at both interfaces because they are low to high index medium interfaces. These identical phase shifts cancel each other out. The net phase shift between the reflections is therefore determined solely by the optical path difference $2t \times n$. The phase shift is therefore $2tn/\lambda$. Hence the thickness is usually set to be $\lambda/4$ resulting in the phase shift of 180 degree.

For refractive index, the intensity of a reflected beam from a single surface, at normal incident, is given by

$$\left(\frac{1-p}{1+p}\right)^2 \times \text{the incident intensity}$$

where $p$ is the ratio of the refractive of the refractive indices of the two materials at the interface. For the two reflected beams to be equal in intensity, it is necessary that $p$ be the same at both the interfaces, i.e.

$$\frac{n_{\text{air}}}{n_{\text{film}}} = \frac{n_{\text{film}}}{n_{\text{substrate}}}$$

Since the refractive index of air is 1, the thin antireflection film ideally should have a refractive index of $(n_{\text{substrate}})^{1/2}$. For glass, the refractive indices are between 1.5 to 1.75, so the refractive index of the film should be ~1.3. MgF₂ is a good choice.

Amorphous MgF₂:

$$n(\lambda) = \frac{1}{2}(n_0 + n_e)$$
where ordinary index $n_o(\lambda) = 1.36957 + \frac{3.5821 \times 10^{-3}}{\lambda - 0.14295}$

and extraordinary index $n_e(\lambda) = 1.381 + \frac{3.7415 \times 10^{-3}}{\lambda - 0.14947}$

2) Multilayer antireflection coatings (MgF$_2$/MgO/glass)

This coating is used as an alternative to the single-layer antireflection coating. It was develop because of the lack of suitable materials available to improve the performance of single-layer coatings. In a two-layer coating (quarter/quarter coating), the first reflection is cancelled by interference with two weaker reflections.

Interference in a typical quarter/quarter coating

The formula for exact zero reflectance for such a coating is

$$\frac{n_1^2 n_3}{n_2^2} = n_{\text{air}} = 1$$

These two-layer antireflection coating is the simplest type of the V-coatings used in monochromatic applications e.g. nontunable laser.
3) Broadband antireflection coatings

In order to have a flat spectral response, transmitting optics used in polychromatic radiation are coated with a broadband antireflection coatings.

4) Metallic high-reflection coatings (Al, Ag, Au)

**Optical Properties**

When a material is illuminated with light, there are three processes that can occur: absorbed, transmitted or reflected.

Optical properties will derive from the effect of all the energy loss mechanisms that can result from the interaction between the light and the charges contained in the materials.

- a) tight bounded electron e.g. inner shell,
- b) loosely bound e.g. outer shell
- c) free electron e.g. conduction electron

**Refractive index**

1) The electric vector of the wave force the charges to be displaced,
2) oscillating em wave produces an oscillating induced dipoles,
3) assuming negligible energy loss by the oscillating dipoles, then the dipoles will eventually re-radiate at the same frequency
4) the presence of the charge (b and c) delays its transmission and does not cause any energy loss (transparent)
5) this delaying action reduces the effective velocity of the light.

\[ n = \frac{\text{velocity of light in vacuum}}{\text{velocity of light in the material}} \]

The greater the polarization the more will be the delaying action, and hence the greater the value of \( n \).

\[ n = \sqrt{\varepsilon_r} \]

General principles:

- 1) dense material more electrons per atom larger \( n \)
- 2) more polarizability has larger \( n \)
  (glass: 1 ~ 2; semiconductor: 3 ~ 6)
- 3) only right at frequencies for which the material is transparent

**Dispersion**

As a result of the frequency dependence of \( \varepsilon_r \) in the optical region (relaxation process), the refractive index is dependent on frequency. This is referred to as optical dispersion. Each charge can be characterized by a natural resonant frequency.
\[ \nu_0^2 = \frac{G}{4\pi^2 m} \]

For frequencies well below resonance the induced dipoles have little difficulty in following the applied the applied field whereas above it there will be very little polarization since the variations in the electric field will be too rapid. For the normal dispersion, as the optical frequency is increased towards the electron resonant frequency, the greater will become the amplitude of the excited motion. As a result the amplitude of the oscillatory polarization produced will increase with frequency with a consequent increase in the refractive index.

\[ n^2 = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \]

In the immediate vicinity of a resonance frequency the refractive index decreases with frequency. This property is not normally utilized for instrumentation and is termed anomalous dispersion.

Schematic representation of the frequency dependence of refractive index

As frequency is increased, first the permanent, then the ionic and finally the electronic dipoles become unable to respond.

Method to measure the refractive index
1) Brewster's angle for refractive index
   In vacuum, we have at Brewster's angle \( \theta_B \)
   \[ \tan \theta_B = n_2 \]
   where \( n_2 \) is the refractive index of film. At this angle the parallel component of the light reflected at the air-film interface vanishes. In this case, the reflected radiation is completely plane polarized with polarization vector perpendicular to the plane of incidence.

2) Variable angle Spectroellipsometry
   Ellipsometer is a highly sensitive and accurate optical instrument that is nowadays widely used to measure the refractive index of thin film and its thickness in integrated circuit fabrication. The accuracy in measuring film thickness can be up to 0.007 nm (0.07 Å). In addition, ellipsometer can be used to measure the refractive index of bulk for jewellery examination. A typical ellipsometer as shown in the following
Dr. C. L. Mak

A figure consists of a collimated monochromatic light source, a rotatable polarizer, a compensator (usually a quarter-wave plate, axis at ±45° to the plane of incidence), a specimen holder, a rotatable analyzer and a photo detector.

For optical thin film: The ratio in complex amplitude reflectively of the p-component (parallel to the plane of incident) and s-component (perpendicular to the plane of incident) of a parallel beam of light incident at an angle \( \phi \) on a transparent film (with refractive index, \( n \) and thickness, \( d \)) overlaid on a transparent substrate (with refractive index, \( n_s \)) is given by:

\[
\frac{R_p}{R_s} = \left| \frac{R_p}{R_s} \right| e^{i\Delta} \quad \text{where} \quad i = \sqrt{-1}
\]

\[
= \tan \psi e^{i\Delta}
\]

\[
= \frac{(r_{p01} + r_{p12} e^{-i\phi})(r_{s01} + r_{s12} e^{-i\phi})^{-1}}{(1 + r_{p01} r_{p12} e^{-i\phi})(1 + r_{s01} r_{s12} e^{-i\phi})^{-1}} \quad ....(1)
\]

where \( \psi \) is the amplitude ratio;
\( \Delta \) is the phase difference;
\( r_{p01}, r_{s01}, r_{p12}, r_{s12} \) are Fresnel coefficients at the air-film and film substrate interfaces.

and \( \theta = 4\pi d \sqrt{n^2 - \sin^2 \phi} / \lambda \) \quad ....(2)
Separating equation (1) into real part and imaginary part and on further simplification, we obtain:

\[ \tan \psi \cos \Delta = \frac{a_p + b_p \cos \theta (a_s + b_s \cos \theta) + c_p c_s (1 - \cos^2 \theta)}{(e_p + d_p \cos \theta)(f_s + d \cos \theta)} \quad \ldots \ldots (3) \]

\[ \tan \psi \sin \Delta = \frac{c_p (a_p + b_p \cos \theta) - c_s (a_s + b_s \cos \theta)}{(e_p + d_p \cos \theta)(f_s + d \cos \theta)} \sin \delta \quad \ldots \ldots (4) \]

The parameters \( a_p, a_s \ldots \) and \( f_s \) have a mathematical relation in terms of \( r \). \( \delta \) is the phase difference between the electric field vector components with one parallel to the plane of quarter wave plate and the other perpendicular to it.

By rearranging equations (3) and (4), we can obtain two separate equations: one for \( \Delta \) and the other for \( \psi \), both in terms of film thickness, \( d \), and refractive index of film, \( n \). The equations are extremely complicated and their solutions can only be found by using a computer.

Certain settings of the polarizer cause the reflected light from the specimen to become linearly polarized. The analyser is then rotated to a position where almost no light reaches the photo-detector, giving the lower reading (or observe by naked eyes until minimum intensity is observed). From the angular settings of the polarizer (P) and analyser (A) at this condition, the ellipsometric parameters \( \Delta \) and \( \psi \) are derived respectively. There are two settings of polarizer (P\(_1\), P\(_2\)) and analyser (A\(_1\), A\(_2\)) which can cause null intensity.

For a perfect compensator (a quarter-wave with \( \delta = 90^\circ \)), the relation between polarizer P and, analyser A settings, with \( \Delta \) and \( \psi \) respectively become rather simple:

\[ \Delta = 90^\circ - 2P_2 = 270 - 2P_1 \quad \ldots \ldots (5) \]

\[ \psi = 180^\circ - A_2 = A_1 \quad \ldots \ldots (6) \]

\( \Delta \) and \( \psi \) can be found by measuring \( A_1, A_2, P_1 \) and \( P_2 \). On the other hand, a series values of \( \Delta \) and \( \psi \) can be calculated by computer from a series of preset values of \( n \) and \( d \). Compared the experimental values of \( \Delta \) and \( \psi \) with these calculated values, the refractive index \( n \) and the thickness \( d \) can be estimated.

For film-free substrate: \( n_s = n - ik \)

and \( k \) is the extinction coefficient and is related to absorption coefficient \( \alpha \) (in units of cm\(^{-1}\)) by

\[ k = \alpha \lambda / 4 \pi \]

The following relationships hold:

\[ n^2 - k^2 = a \quad \ldots \ldots (7) \]
\[ 2nk = b \quad \text{.....(8)} \]

where

\[ a = \frac{t^2(\cos^2 \omega - \sin^2 \omega \sin^2 \Delta)}{(1 + \sin 2\omega \cos \Delta)^2} \]

\[ b = \frac{\sin 4\omega \sin \Delta}{(1 + \sin 2\omega \cos \Delta)^2} \]

\[ t = \sin \varphi \tan \varphi \]

By solving equations (7) and (8) and eliminating negative roots, \( n \) can be found directly as:

\[ n = \pm \sqrt{\frac{a \pm \sqrt{a^2 + b^2}}{2}} \quad \text{.....(9)} \]

\[ k = \frac{b}{2n} \quad \text{.....(10)} \]

**Applications**

Spectroellipsometric study of KNSBN films
- study the optical properties/surface roughness as a function of sol concentration
- single layer, sol concentration 0.03M ~ 0.18M

\[
k(E) = \frac{A(E_g - E)^2}{E^2 - BE + C} \quad n(E) = n_w + \frac{A(-B^2E + 2E_gBE - 2E^2E + 2CE + E_gB + BC - 4E_gC)}{\sqrt{4C - B^2} \left(E^2 - BE + C\right)}
\]

<table>
<thead>
<tr>
<th>Sol concentration</th>
<th>0.03 M</th>
<th>0.06 M</th>
<th>0.09 M</th>
<th>0.12 M</th>
<th>0.15 M</th>
<th>0.18 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_w )</td>
<td>1.396</td>
<td>1.170</td>
<td>1.469</td>
<td>1.316</td>
<td>1.264</td>
<td>1.402</td>
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<tr>
<td>( \varphi )</td>
<td>0.033</td>
<td>0.050</td>
<td>0.075</td>
<td>0.099</td>
<td>0.105</td>
<td>0.104</td>
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<tr>
<td>( \beta )</td>
<td>9.28</td>
<td>9.40</td>
<td>10.08</td>
<td>11.09</td>
<td>10.38</td>
<td>10.37</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>21.87</td>
<td>23.69</td>
<td>27.01</td>
<td>34.88</td>
<td>28.17</td>
<td>28.04</td>
</tr>
<tr>
<td>( \Delta E )</td>
<td>1.92</td>
<td>1.79</td>
<td>1.84</td>
<td>1.86</td>
<td>1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>( d_0 )</td>
<td>29</td>
<td>60</td>
<td>69</td>
<td>87</td>
<td>89</td>
<td>105</td>
</tr>
<tr>
<td>( d_1 )</td>
<td>2</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Void percentage ( f )</td>
<td>10</td>
<td>40</td>
<td>45</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

\[ (1 - f) \frac{n_b^2 - n_s^2}{n_b^2 + n_s^2} + f \frac{1 - n_s^2}{1 + n_s^2} = 0, \]
refractive index increases with energy and sol conc.
fitting thickness checked with surface profiler $d_v/d_0$ increases with sol conc. → rougher; checked with AFM $d_v(\mathrm{SE}) \sim 0.06R_q^2 + 0.5R_q + 0.1$ nm in amorphous semicond.: $d_v(\mathrm{SE}) \sim 1.5R_q + 0.4$ nm

Reference