

# I. Preliminary

## I.1 Sample Preparation for TEM

Suppliers for TEM: Ernest F. Fullam; Ted Pella(PELCO); SPI; Ladd Industries; and Polaron etc.

### ***I.1.1 Geometry of a TEM sample:***

Thickness in beam direction:  $\leq 200\text{nm}$  for 100 KeV

For examples: Al  $\leq 600\text{nm}$ ; Fe  $\leq 200\text{ nm}$  and Au  $\leq 100\text{nm}$  for 100 KeV

The thickness of sample for 1 MV TEM is about 2.5 times greater than that of 100KeV.

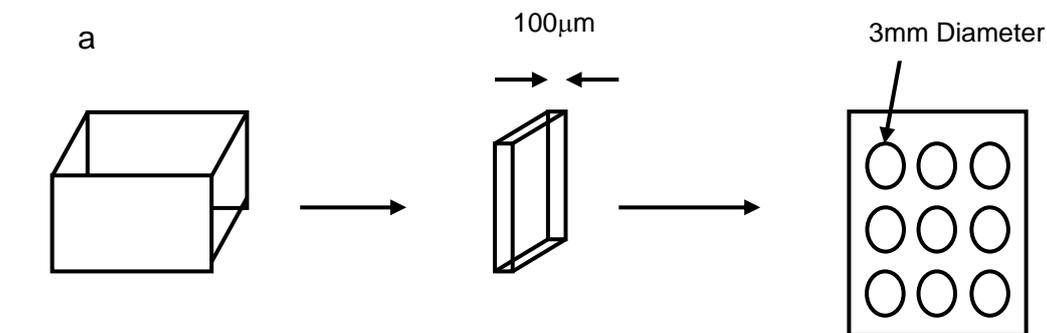
The thickness of sample depends on (a) Resolution desired and (b) features of interest.

Diameter of TEM specimen:

- Standard  $< 3.05\text{ mm}$
- Specific  $< 2.3\text{ mm}$  (This can thin more of sample and is good for ferromagnetic materials. It is also good for HREM)

### ***I.1.2 How to achieve this geometry?***

(A) Bulk Sample



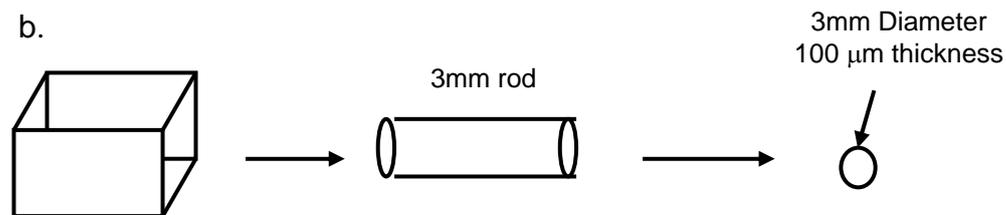
(1) Punch

(2) Ultrasonic Cutter

(3) Slurry Driller

This technique will introduce mechanic strain. It is good for X-ray, structure and image analysis.

The other way;



(1) Diamond Saw

(2) Electro Discharge Saw

We can also use the roller to roll metal down to 100  $\mu\text{m}$  foil and use the method in (A) to make 3mm diameter of TEM specimen.

(B) Brittle Bulk Materials

(1) As (A)a. above.

(2) Crash and sprinkle the particulates onto a support film.

(C) Non-Bulk Samples

(1) Particulates, powders, and fibers

< 200 nm : sprinkle onto a support film

> 200 nm : embed to make bulk composite

Note: The embedding material should be as similar to particulate as possible.

(2) Thin films

Deposit onto a removable substrate.

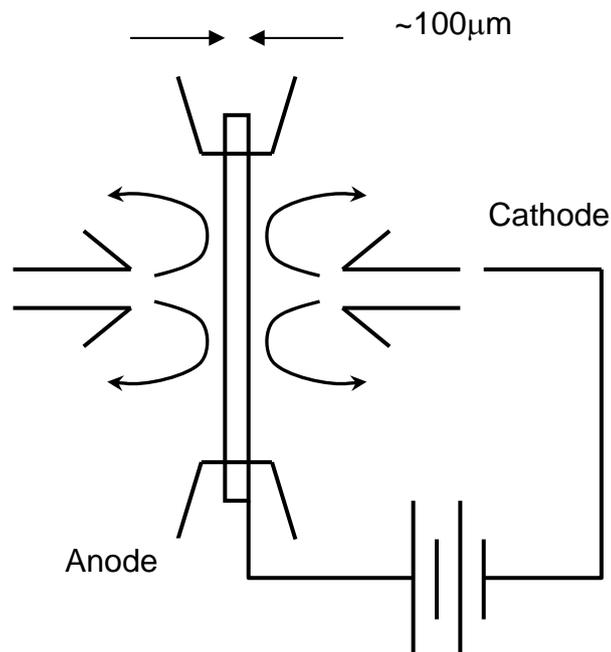
For examples:

- (a) Acetate film: can remove by acetone vapor.
- (b) Rock salt: soluble in water and can cleaves on [100] or other crystal orientation.
- (c) Metals film: Cu can dissolve in diluted  $\text{HNO}_3$ .

### ***1.1.3 Thinning:***

#### (1) Electrochemical Polishing (but not etching)

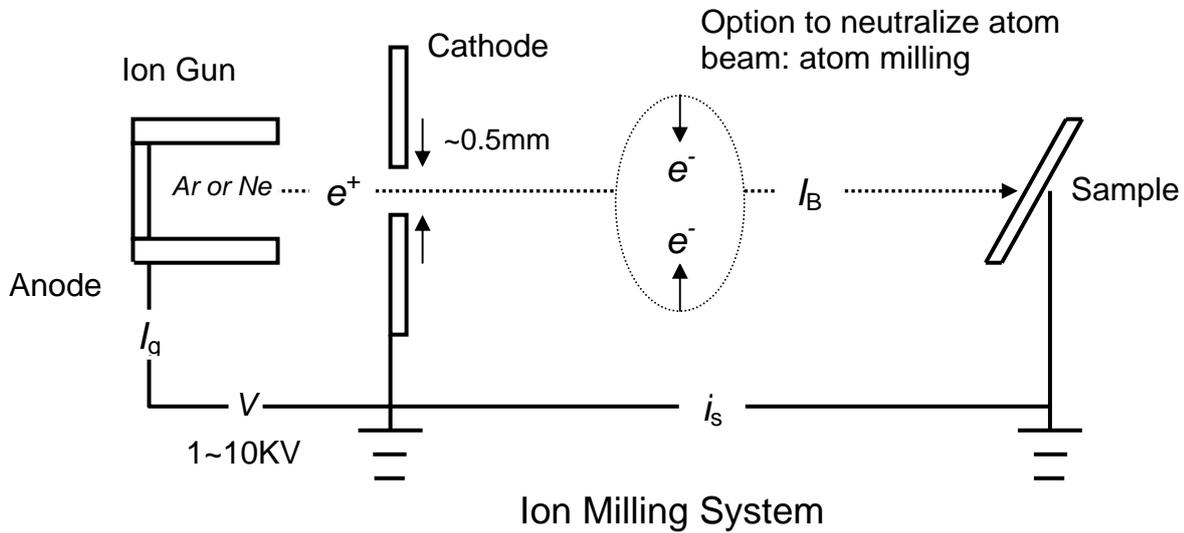
- Can get acres of thin area.
- High quality thin area.
- Fast < 30 minutes



#### (2) Chemical Polishing

Same above without electrodes.

### (3) Ion Milling



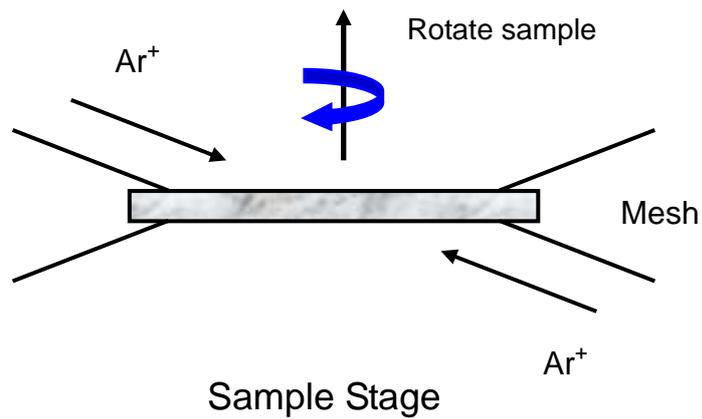
$i_g$  : gun current

$i_s$  : specimen current

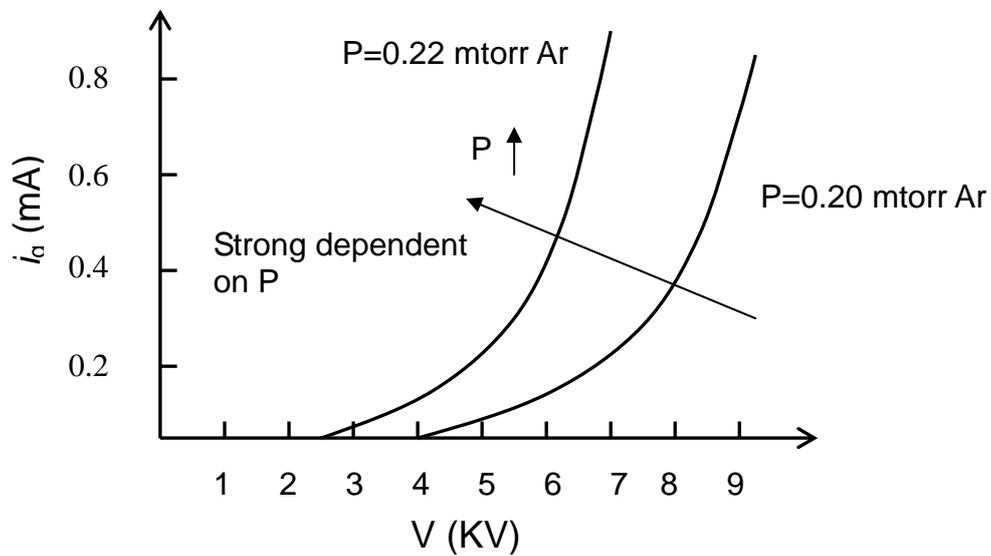
$i_B$ : Beam current

typical :  $i_g=0.5$  mA and  $i_s = 50$   $\mu$ A

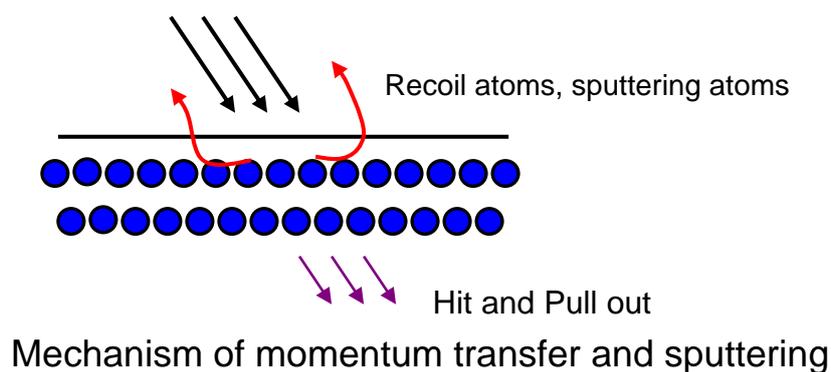
Note: Cathode is bombarded by ions and is replaced after ~100 hours.



The number of ions in plasma depend on V and pressure in gun.



- The sputtering is the removal materials from a target as a result of interaction of incident ions and atoms in sample.
- Monentum transfer from ions to target atoms is the most important process in sputtering.



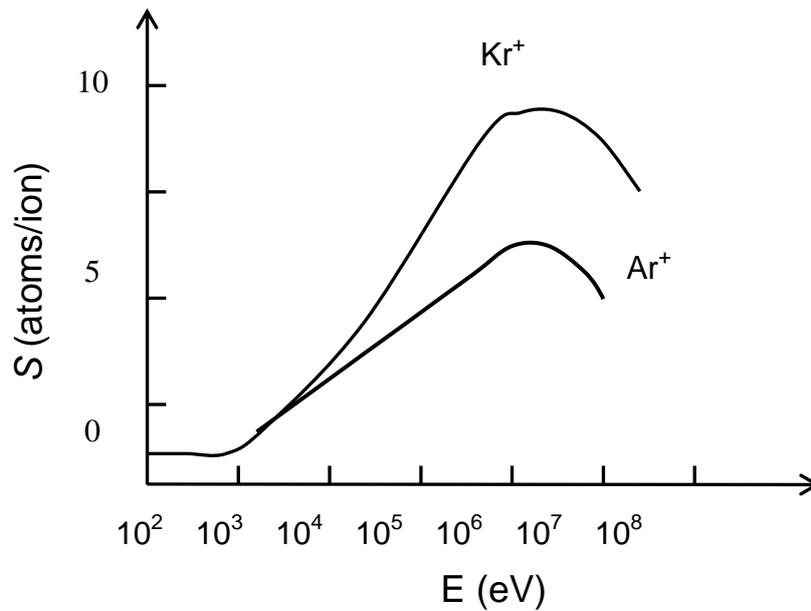
S = sputtering yield or rate

$$=1.3 \times 10^{10} n_0 \sigma E (M_1 M_2 / (M_1 + M_2)) \exp(-10.4 V M_1 E_B / (M_1 + M_2))$$

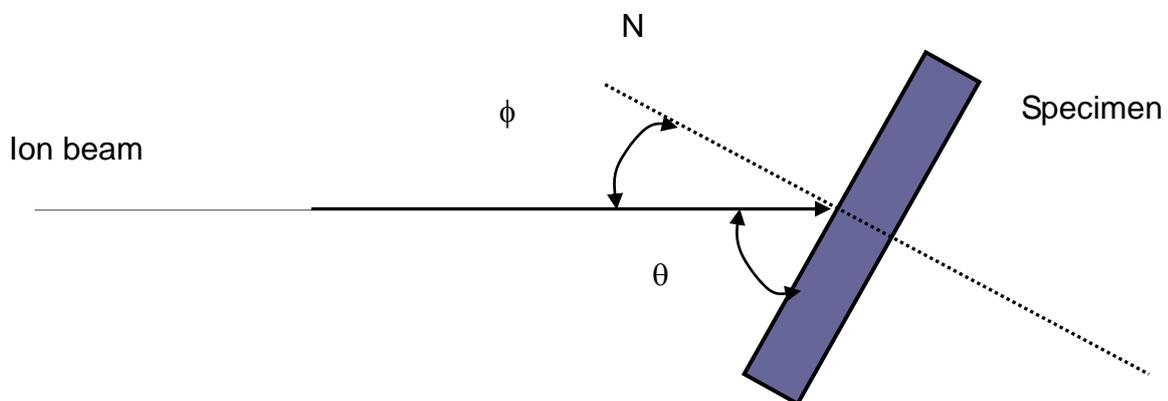
Where  $M_1$  : ion atom mass,  $M_2$ : target atom mass,  $n_0$ : # atoms/volume

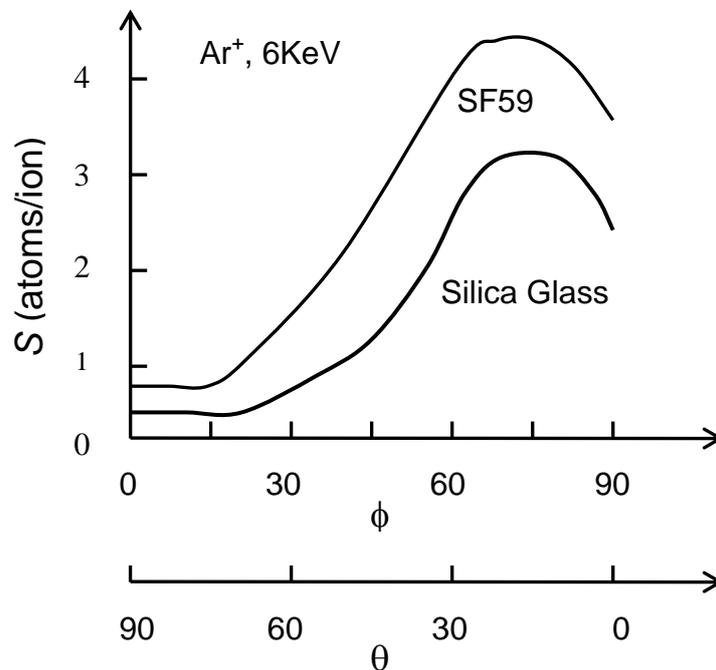
(target),  $\sigma$ : collision cross section,  $E$ : ion energy and  $E_B$ : energy of sublimation.

Note: cathode materials  $E_B$  large will provide long lifetime of cathode due to decrease the  $S$ .



The sputtering angle will also affect the sputtering rate.





Sputtering rates are greatest at  $\theta \sim 15^\circ$  and  $E \sim 8 \text{ KeV}$ . But 8 KeV  $\text{Ar}^+$  produces radiation damage that induce the vacancies and voids.

Typical sputtering angles will be;

$\theta = 15^\circ$ , for maximum sputtering rate

- ◆ early rapid thinning
- ◆ maximum beam damage
- ◆ maximum surface irregularity

$\theta = 10^\circ$ , for small wedge angle, low sputtering rate

- ◆ radiation damage is limited to  $\sim 10 \text{ nm}$  from surface
- ◆ usually useful for remove by final thinning

Thought, there are two processes for thinning;

After  $15^\circ$  thinning at  $E \sim 5\text{-}6\text{KV}$ ,  $\rightarrow$  Fast remove thickness

- Cause radiation damage
- Unwanted oxide or contamination

After 10° thinning at E~1-2KV, →Final thinning

- Fine the surface

Due to the slow process of ion milling ( typical 1 μm/gun/hour), the dimpling the sample thickness to < 10 μm is required to reduce the contamination. The ion milling tend to etching the sample, thus, the start with polished surface of sample and reducing the milling time are important.

### ***1.1.4 Supplement of Microscopy Specimen Preparation Techniques***

#### **1. Introduction**

Scanning electron microscopy, optical microscopy and transmission electron microscopy require special specimen preparation techniques. These include ultramicrotomy (i.e. thin sectioning), sputtering (i.e. of a thin metal film), electropolishing, ion milling and various mechanical cutting/polishing techniques.

In general, the sample should consist of either particles dispersed in a liquid, or solid materials. The dispersions are usually sprayed onto a suitable substrate and coated with a conductive film as described below. Appropriate specimens from solid samples are prepared by applying one or several of the techniques described in the next section.

#### **2. Principle**

##### **A. Cutting/Mechanical Polishing Techniques**

Specimen preparation for electron microscopy often includes the use of a diamond wheels cutter. This consists of a thin metal wheel with a

diamond abrasive coating. Adjusting the rotating speed of the wheel controls the cutting speed. In this way sub-millimeter specimens can be cut with minimum damage.

Mechanical polishing is used to prepare the surface of specimens for microscopical observation. It is also used as a relatively fast way to pre-thin samples. The polishing is done on an automated unit consisting of a rotating wheel and a jig for applying suitable pressure to the sample. Polishing materials including abrasive papers and cloths impregnated with diamond or alumina compounds are used to obtain a lustrous surface.

## B. Vacuum Evaporation and Sputtering

Thin conduction film can be deposited by either vacuum evaporation or by sputtering from a target material onto a substrate.

In vacuum evaporation the source direct heating evaporates materials. The substrate, which is normally at ambient temperature, is rotated during the evaporation procedure to obtain a uniform deposition. Gold and carbon are most commonly used, but other materials such as platinum or palladium are also employed as evaporation sources.

In sputtering, the sample is placed in an inert gas atmosphere (e.g. Ar). A high voltage is applied to cause ionization of the gas. The ions are propelled towards a suitable target, such as a thin gold foil. This causes gold atoms to be knocked off and to be redeposited onto the surface of the sample. In most cases, the films that are deposited are in the range of 10 to 50 nm thick.

## C. Ultramicrotomy

Thin sections for optical and for transmission electron microscopy are prepared by microtomy. The sample is mounted on a motor driven stage. Downward movement of the specimen causes it to contact a knife-edge. The knife itself is made out of glass or of a diamond single crystal. Often

the sample is embedded in an epoxy resin for ease of handling and for stability.

In ultramicrotomy a sensitive mechanism controls the advance of the specimen tip towards the cutting edge of the knife and thus the thickness of the sections. Typically sections with thickness in the range of 50 to 100 nm are obtained which are then collected on suitable electron microscope grids or onto glass slides.

If the specimen under question is too soft at room temperature, such as polyethylene, cryomicrotomy is used. In this case a special attachment cools the specimen and the knife down to - 160 °C. In this way the distortion of the specimen during sectioning is minimized.

#### D. Ion Milling

Ion Milling is a technique used to thin specimen (e.g., ceramics or metals) for transmission electron microscopy. In this technique a beam of Ar ions impinges on a rotating specimen. As a result of head-on collisions the Ar ions will knock out atoms from the specimen leading to a gradual decrease in thickness. As soon as perforation occurs, the beams are stopped and the specimen is transferred to the electron microscope for examination. A thin, electron transparent area is usually found near the periphery of perforation.

Because the rate at which ion milling progresses is only of the order of a few microns per hour the initial thickness of the specimen must be reduced by mechanical polishing to less than 70 nm.

#### E. Electropolishing

Electropolishing is used to thin metallic specimens, which might be affected by the heating effects during ion milling. During electropolishing, a mechanically thinned specimen is immersed in an acid electrolyte. A potential is applied between the specimen and two parallel plate cathodes

positioned on opposite sides of the specimen. As a result of the electrochemical reaction, specimen dissolution occurs. When a small perforation forms the reaction is stopped; the specimen is rinsed and examined in the microscope.

The temperature of the electrolyte, the voltage and the concentration of the electrolyte are variables, which will affect the uniformity with which the specimen dissolves.

### 3. Experimental Procedures

#### A. Materials

- a. Bakelite mounting materials
- b. Sand papers
- c. Electropolisher and etching apparatus
- d. Stainless sheet.

#### B. Technique

##### a. Preparation of metal sample:

(a) Cut of a 1 cm square of metal sheet and mount this piece in Bakelite.

(b) Polish and grind metal surface using rough grinder down through sand papers, turning sample to orient scratches.

(c) Slurry drill sample into a 3 mm diameter.

##### b. Electropolishing

(a) Prepared polishing solution: 45%  $\text{H}_3\text{PO}_4$  + 30%  $\text{H}_2\text{SO}_4$  + 25% Water

(b) Set up sample in the sample holder of electropolisher.

(c) Immerse the sample holder into the electrolyte.

(d) Turn on the power and slowly increase the voltage to 10 V. The

amperage should be below 1 amp. If it is above 1 amp, instead of turning down the voltage, use an ice bath to cool down the electrolyte.

(e) Continue polishing the sample and stop after hearing the warning sound. The warning sound is design to notify you when a small perforation forms in the sample.

(f) Remove the sample holder and rinse in the distilled water.

(g) Take out the sample and dry out using alcohol.

(h) Observe your sample in the optical microscopy to examine the sample.

### C. Questions

(a) How to select the electrolyte use in the electropolishing?

(b) Is there any differential etching occurs? How to prevent it?

(c) Write down the procedures of TEM sample preparation.

(d) Are there any step you must notice to prevent the sample damage?

## I.2 Vacuum Concepts and Technology

### **I.2.1 Properties of a gas**

The mean free path for particles of size  $d_o$  was derived by Maxwell,

$$\lambda = \frac{1}{\sqrt{2}\pi d_o^2 n} = \frac{kT}{\sqrt{2}\pi d_o^2 P}$$

where  $n$  is the particle density ( $N/V$ ), and the ideal gas law,  $P=nkT$ , has been used.

For a mixture of e's and molecules, this relation becomes,

$$\lambda = \frac{4}{\pi(d_e + d_o)^2 n(1 + \frac{m_e}{m_o})^{1/2}} = \frac{4kT}{\pi(d_e + d_o)^2 P(1 + \frac{m_e}{m_o})^{1/2}}$$

where  $d_e$ = diameter of electron,  $m_e$ = mass of electron, etc.

Using  $d_o=3.7 \times 10^{-10}$  m,  $m_o=28.7$  g/mole for air, then ,

$$\lambda = \frac{0.038}{P} \quad \text{for } \lambda \text{ in meters and } P \text{ in Pa.}$$

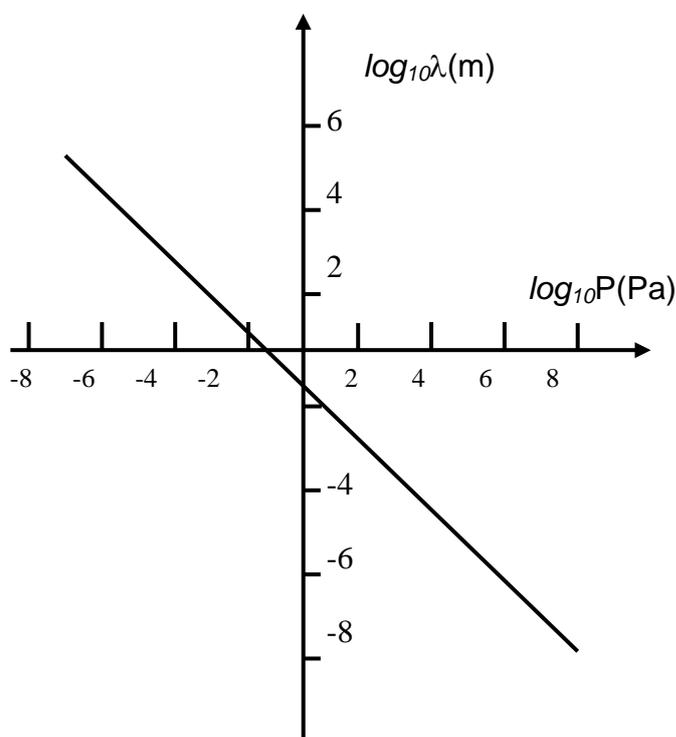
Comparing this result with  $\lambda = \frac{0.066}{P}$  from O'Hanlan for collisions of air molecules is quiet similar..

The low pressure properties of air can be list as following;

Pressure (Pa)	n (m <sup>-3</sup> )	d(m)	λ(m)	Γ(m <sup>-2</sup> -s <sup>-1</sup> )
1.01x10 <sup>5</sup> (760 Torr)	2.48x10 <sup>25</sup>	3.43x10 <sup>-9</sup>	6.5x10 <sup>-8</sup>	2.86x10 <sup>27</sup>
100(.75 Torr)	2.48x10 <sup>22</sup>	3.44x10 <sup>-8</sup>	6.6x10 <sup>-5</sup>	2.83x10 <sup>24</sup>
1(7.5 mTorr)	2.48x10 <sup>20</sup>	1.60x10 <sup>-7</sup>	6.6x10 <sup>-3</sup>	2.83x10 <sup>22</sup>
10 <sup>-3</sup> (7.5x10 <sup>-6</sup> Torr)	2.48x10 <sup>17</sup>	1.60x10 <sup>-6</sup>	6.64	2.83x10 <sup>19</sup>
10 <sup>-5</sup> (7.5x10 <sup>-8</sup> Torr)	2.48x10 <sup>15</sup>	7.41x10 <sup>-6</sup>	664	2.83x10 <sup>17</sup>
10 <sup>-7</sup> (7.5x10 <sup>-10</sup> Torr)	2.48x10 <sup>13</sup>	3.44x10 <sup>-5</sup>	6.6x10 <sup>4</sup>	2.83x10 <sup>15</sup>

Where n: particle density; d: average molecular spacing, λ: mean free path, and Γ: particle flux on a surface. T=22°C.

A typical electron microscope is on the order of one meter long. The minimum operating pressure with λ >1m is P < 0.038/1m = 0.038 Pa or P ≤ 10<sup>-2</sup> Pa.



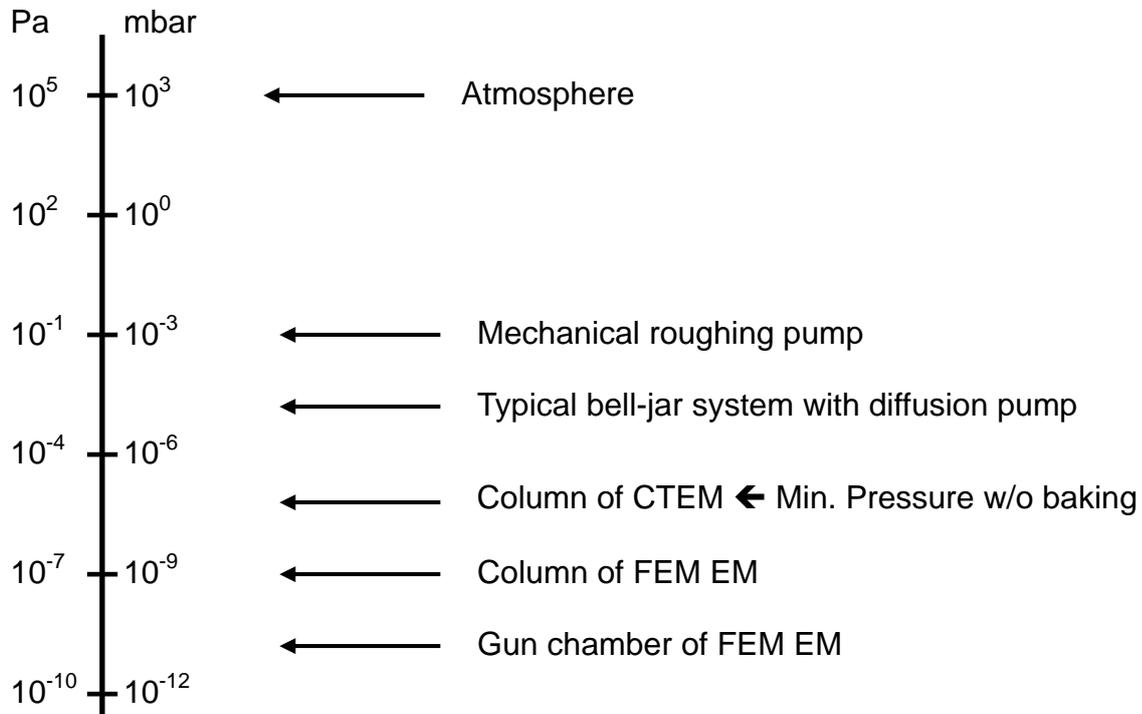
## 1.2.2 Production of vacuum

A vacuum pump is a gas pump designed to operate at lower than atmospheric pressures. A vacuum system consists of pumps and a chamber connected by piping and ductwork. The low pressure in the chamber is maintained by the continued flow of gases from the chamber to the pumps, where they are entrained or expelled into the atmosphere.

The pressure range can be classification as :

Degree of Vacuum	Pressure Range (Pa)
Low	$10^5 > P > 3.3 \times 10^3$
Medium	$3.3 \times 10^3 > P > 10^{-2}$
High	$10^{-1} > P > 10^{-4}$
Veryhigh	$10^{-4} > P > 10^{-7}$
Ultrahigh	$10^{-7} > P > 10^{-10}$
Extreme Ultrahigh	$10^{-10} > P$

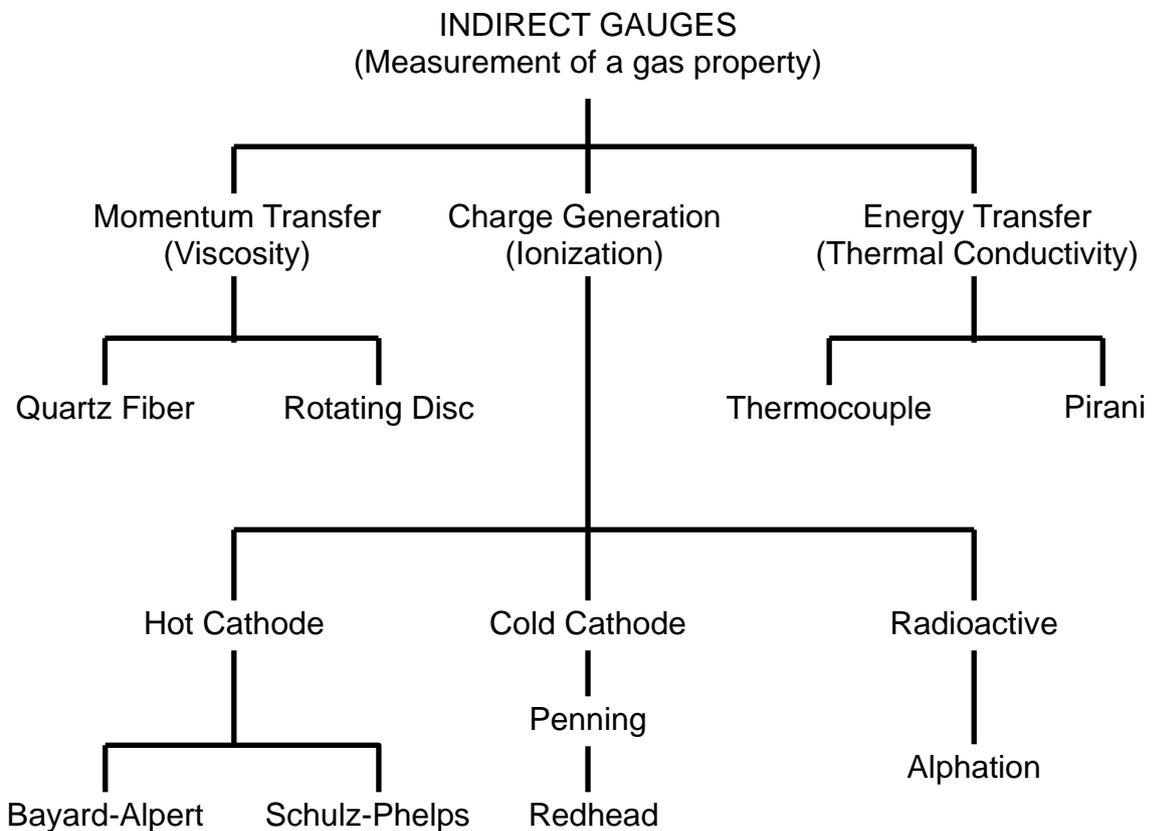
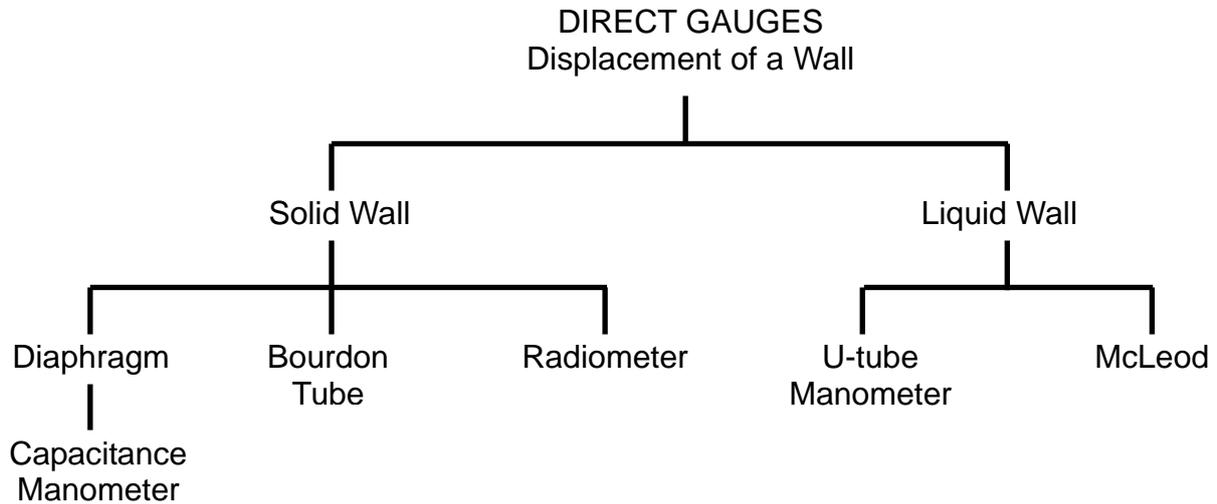
From "Dictionary for Vacuum Science and Technology", M. Kaminsky and J. M. Lafferty



Typical pressure range related to vacuum systems

### 1.2.3 Measurement of vacuum

Classification of Pressure gauges is shown as following;



Units of pressure can be listed as following:

$$\text{Pa} = \text{N/m}^2$$

$$1 \text{ atm} = 101,323.2 \text{ Pa} \sim 10^5 \text{ Pa}$$

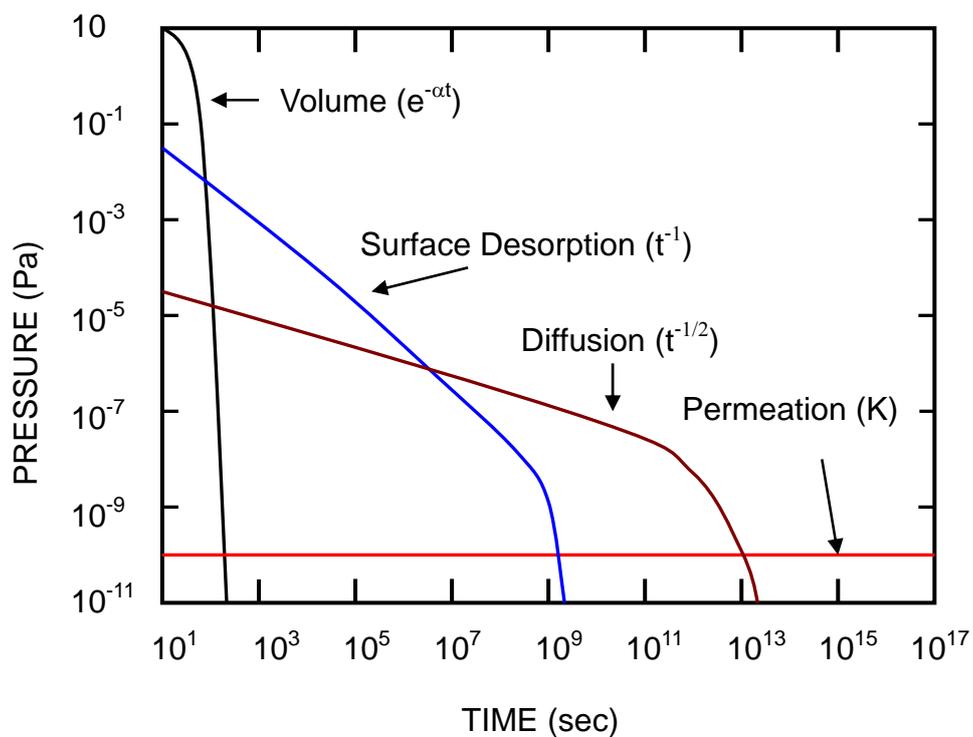
$$1 \text{ bar} = 1 \text{ atm} = 10^5 \text{ Pa}$$

$$1 \text{ mbar} = 10^{-3} \text{ atm} = 100 \text{ Pa}$$

$$1 \text{ torr} = 1 \text{ mmHg} = 1/760 \text{ atm} \sim 1.3 \text{ mbar} \sim 130 \text{ Pa}$$

$$1 \text{ micron} = 1 \text{ } \mu\text{mHg} = 10^{-3} \text{ torr} \sim 10^{-6} \text{ atm}$$

Rate limiting steps during the pumping of a vacuum chamber;



### 1.2.4 Materials for vacuum contamination

