Biomedical Ultrasound: Fundamentals of Imaging and Micromachined Transducers

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Lecture: 19
Thermal Evaporation theory

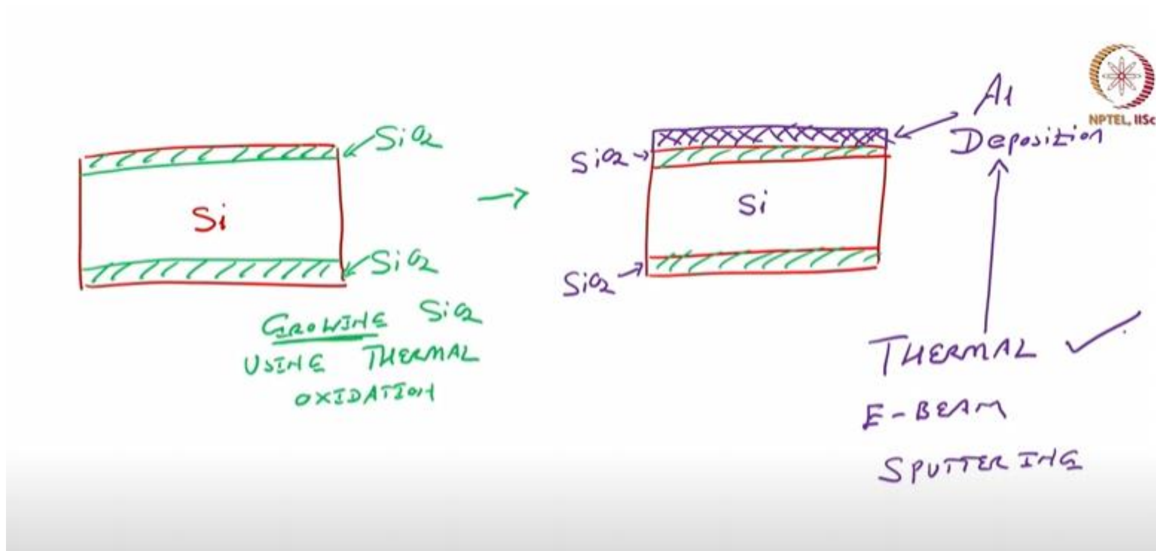
Hi, welcome to the lecture on physical vapor deposition techniques. In physical vapor deposition techniques there are 3 types,

1. thermal evaporation
2. e beam evaporation
3. sputtering.

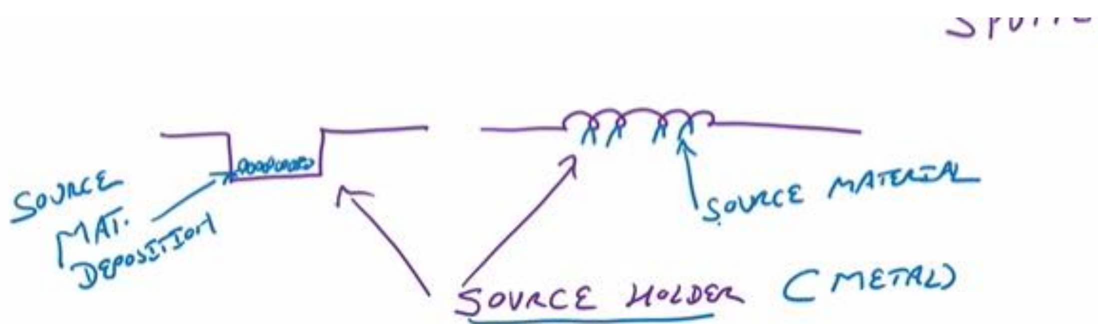
Now let us go one by one and understand what each technique holds for us and how to use this particular thermal evaporation tool, electron beam evaporation tool and sputtering tool to deposit metals, semiconductor and insulators.

So, as I have told you earlier, we also have a lab component included into this particular course and thus we have recorded lab sessions for each tool that I am going to talk here in terms of physical vapor deposition (PVD).

So let me draw a silicon wafer cross section. We have already seen how silicon dioxide can be grown using silicon using thermal oxidation on silicon wafer. So, we have thermally grown SiO_2. Thermal oxide can be two types wet oxidation and dry oxidation. After this, if I want to deposit a metal on to this particular oxidized silicon wafer thenwe will have to use a deposition technique. For SiO_2, I have used the word growing using thermal oxidation technique. But here, I am using the term, depositing. So, now we are depositing a material on to the oxidized silicon substrate. Let us say this is aluminum so we call it aluminum deposition. We have a silicon substrate, SiO_2 as an oxide layer and then deposition using one of the technique. The reason of oxide layer on silicon is to avoid any short circuit with the metal layer that we are depositing using one of the technique. Now the techniques of deposition can be thermal evaporation, electron beam evaporation and sputtering. So, today's lecture we look into the thermal evaporation and as the name says there would be a thermal energy that is used to evaporate a material of our interest.

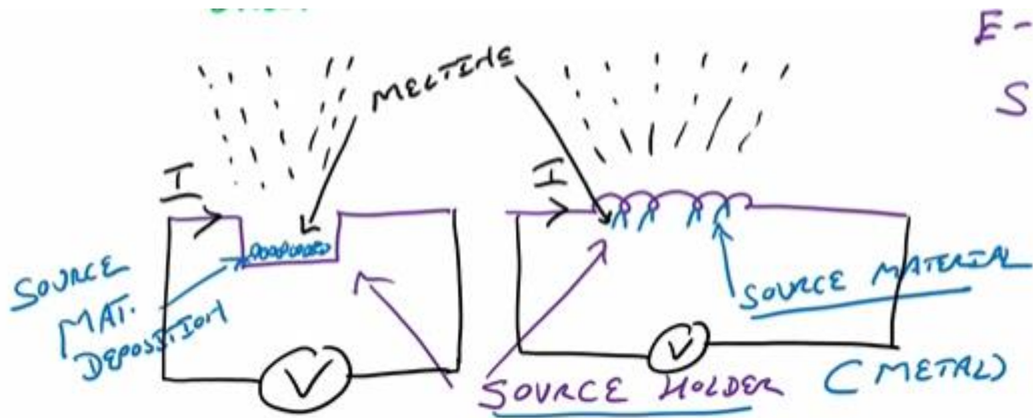


So, the following two drawings shows the source holder on which we load the source that we want to evaporate. It can be beads, chunks of metal,or wire that we can load on to this particular coil. The one in blue color is the material for deposition, or source material.

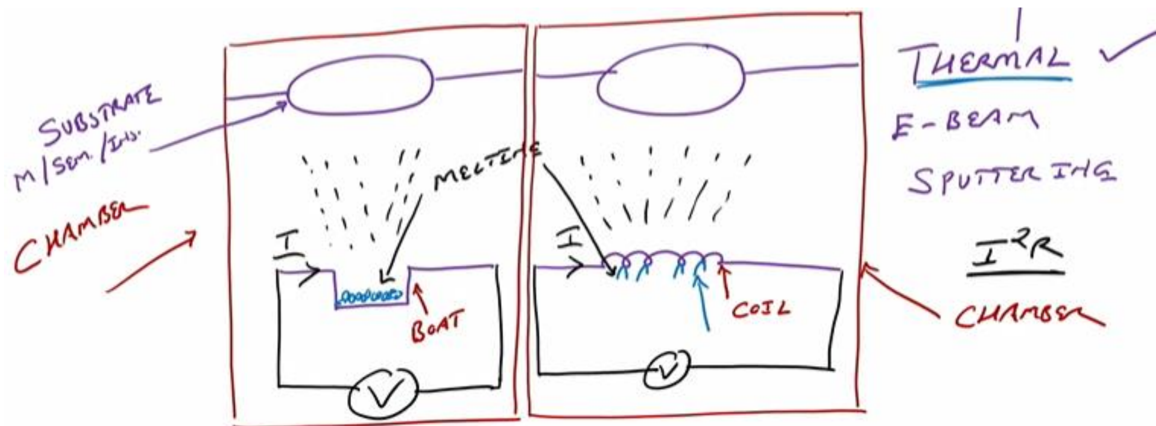


The source holder is always a metal. Source material can be semiconductor, metal or insulator. There is a limitation of thermal evaporation that we cannot deposit insulator that we will understand in some time, but right now the way to evaporate this particular source material is applying the voltage across the source holder or you can say across the source.

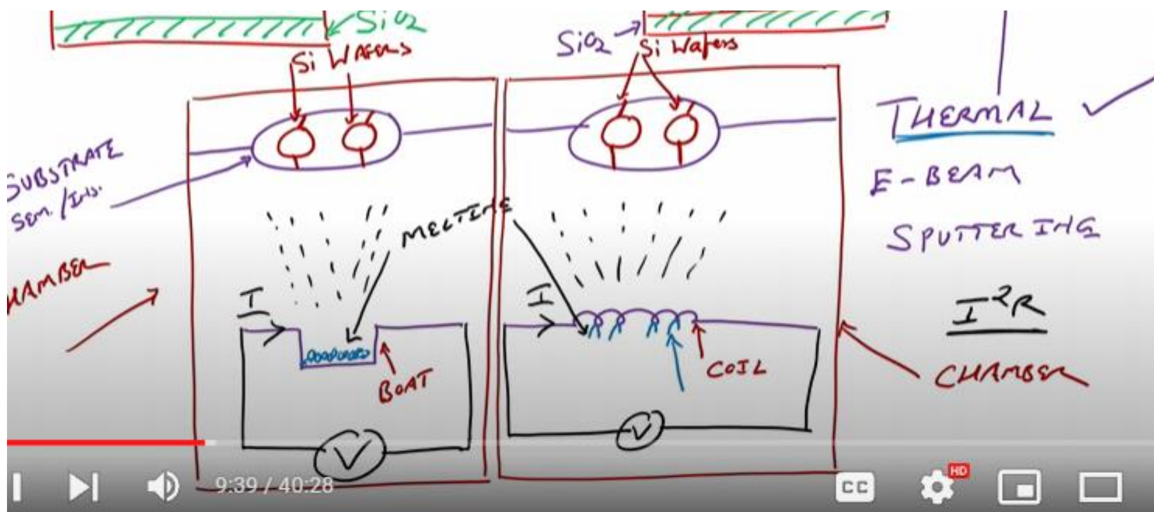
If you apply a voltage, current will flow through the source holder, because it is a metal. When the current flows through the source holder there will be I^2R heat. This is also called as as Joule heating. Now when you apply a current and when there is I^2R heating, the material which is loaded on to the source holder will start melting because of the heating. So, the source material will start melting and if you keep the heating on, it will start evaporating



Once it evaporates it will coat the entire chamber. Let me draw a chamber for you. The difference between both the chambers is that in the left one, we have used a boat as the source holder, and in the right figure, we have used a coil as the source holder. Then we load the source on to the substrate holder. Substrate again as we know can be metal, semiconductor or insulator For example, polymer can be used as a substrate, silicon can be used as a substrate, glass can be used as a substrate. We can use anything as a substrate.

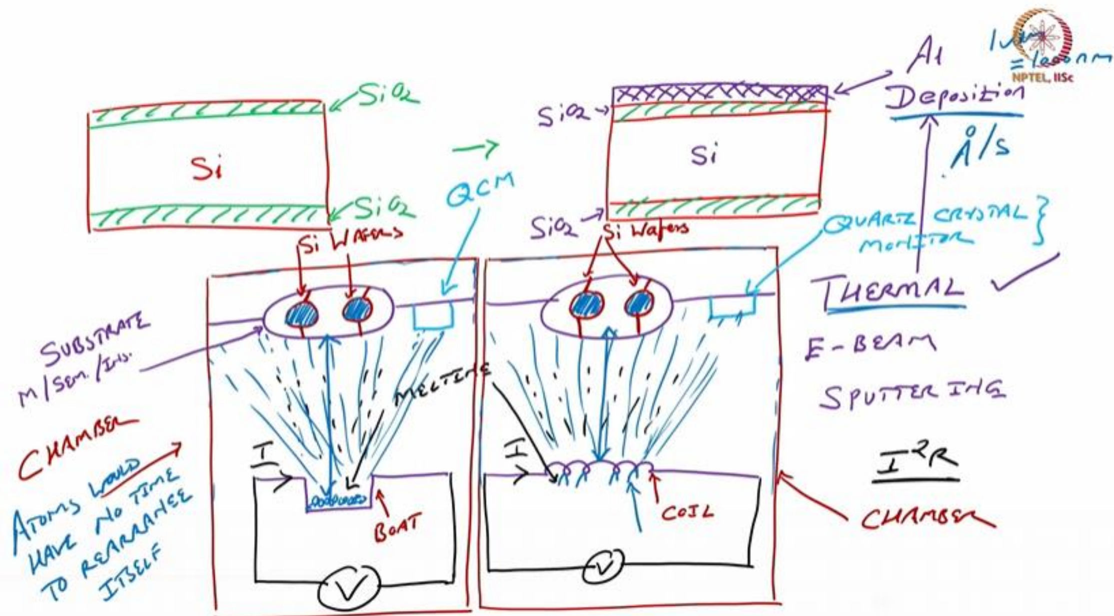


Let us take a silicon wafer as the substrate, I am showing two silicon wafers on each side as the substrate, and securing it with a pin, so that it does not fall.



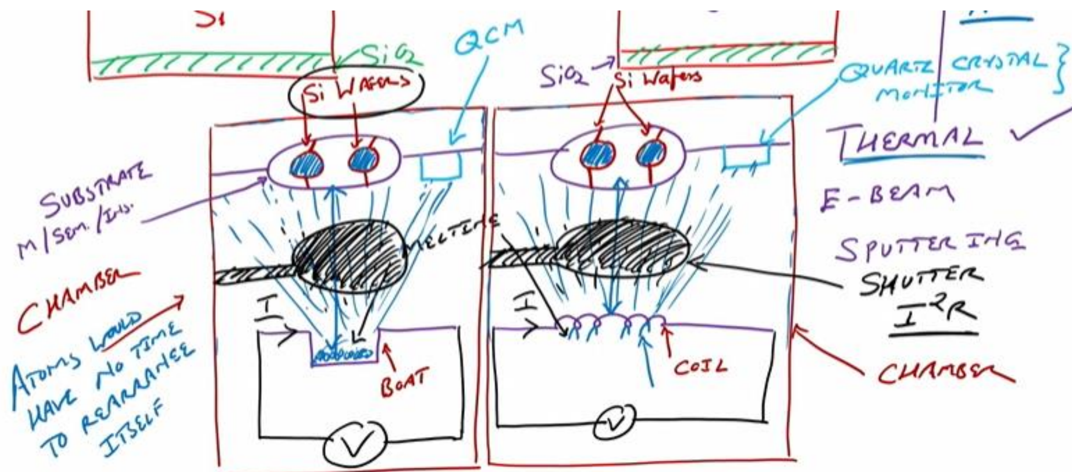
Now, the next thing is that the melted source material will evaporate and will start coating the wafer and it will also coat the walls. The metal starts depositing on to our silicon wafer. So, you can see that the atoms would have no time to rearrange itself because it is a fast the technique. It is so fast that atoms would not have enough time to rearrange itself.

If I say that we need to deposit 1 micrometer or 1000 nanometer of aluminium, how would I know it is 1 micrometer? So, we require another tool that is integrated inside this particular chamber and that tool is called as quartz crystal monitor (QCM. This QCM works on the principle of piezoelectric. So, what is piezoelectricity? When you apply a pressure there is change in voltage or when you apply a voltage there is change in pressure, that is the piezoelectric effect.



Now, this QCM is used because the material that we are evaporating will also get deposited on to the QCM. Maximum deposition is vertically right above the sample holder, because of the basic cosine law. So, the question for you is why we are loading exactly at 90 degree, and how it compares with source material being present at other angles, compared to the substrate. Now when the QCM is deposited by the material, the vibration frequency would change, and the machine is already programmed to understand what is the deposition rate in Angstrom per second. So, based on the deposition of the material on the QCM we can see the corresponding change in a display in terms of Angstrom per second. So, that is how we can understand when to stop the thermal evaporation as soon as 1 micrometer is deposited.

But another question is, that if you apply a voltage and the current starts flowing how will you control the time in which evaporation should start because as soon as this melts the material is loaded. So, we need to first understand that the material is completely melted and only then should we should start evaporation. So, there is one more tool within this called as a shutter. This is a metallic plate which is between source and substrate. The role of this plate is to block the evaporated material from reaching the silicon wafers until All material is melted. We remove this shutter only when we see that the material that we have to evaporate is completely melted and is now ready to evaporate.



So, then we can remove the shutter from the path and the evaporated material can now deposit on the substrate.

Now, the next thing is there is something called mean free path. We need to have this mean free path high, so, that when the material which is melted evaporates, it will not collide with the molecules present in the atmosphere. So, how long can the evaporated molecule travel before the collision happens with the molecules present in the atmosphere. This is mean free path. If the molecule can travel longer without collision, then the deposition becomes better. For this, we need to create vacuum using vacuum pumps. There are two pumps that are used in this thermal evaporation: Primary pump and

secondary pump. Primary pump is generally a rotary pump. Secondary pump can be oil based pump, turbo molecular pump or any other pump that can help us to improve the vacuum. The role of the primary pump (rotary pump) is to get vacuum about 10^{-2} -10^{-3} Torr.

The secondary pump role is to get us vacuum from 10^{-4} or greater than 10^{-3} all the way to 10^{-7} Torr. Since we deposit the material in the presence of vacuum this physical vapor deposition techniques, whether it is thermal or e- beam or sputtering is also called vacuum deposition.

The next thing is, if I say vacuum it means that there should be some gauge to help me to know what is the vacuum level. So I require 2 gauges, one of which is called as pirani gauge and second which is called as penning gauge. Pirani gauge is used for vacuum in the order of minus 2 to minus 3, penning gauge is used for vacuum of order of minus 5 to minus 6 Torr. So, now we have deposited aluminum using thermal evaporation.

So what can be the limitation here? The limitation of this particular system is that we have to rely on applying the thermal energy to the source material so that it gets melted and starts depositing. That means my melting point of source holder should be very high compared to melting point of source material. When this particular case is not satisfied then the source holder will also start to evaporate. Let us say here we are depositing aluminum. This is fine because the melting aluminum is really low. But let us say instead of aluminum, I use silicon dioxide. The melting point of silicon dioxide is extremely high and the melting point of the source holder will be approximately equal to silicon dioxide.

That means that both the source holder and the source material will start evaporating, and that is what we do not want. We only want the material loaded on to the source to evaporate and not source holder itself. So in such a case, we cannot use thermal evaporation. Let us now focus on few slides which will show you different kind of deposition system with the focus on thermal evaporation..

So on this slide you see 3 systems 1, 2 and 3. One is electron beam evaporation system and another are thermal evaporation automated and semi automated systems.

PVD: Physical Vapor Deposition

- **Physical methods produce the atoms that deposit on the substrate**

Evaporation

Sputtering

- **Sometimes called vacuum deposition because the process is usually done in an evacuated chamber**

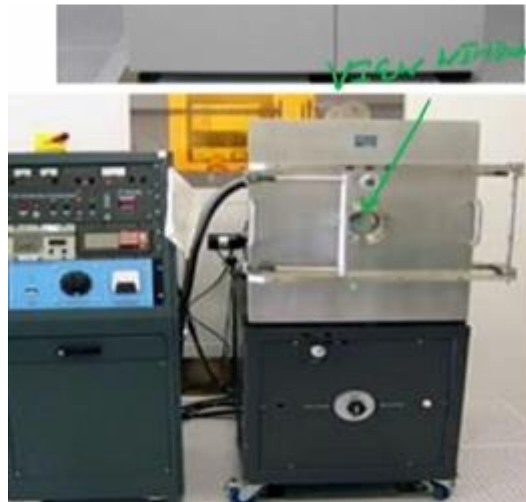
Generally, PVD is used for depositing metals.

Dielectrics can be deposited using specialized equipment

So, in general physical deposition methods or physical methods produce the atoms that deposit on the substrate and we have two techniques evaporation and sputtering. In evaporation we have thermal evaporation and e-beam evaporation which is electron beam evaporation and then we have sputtering. This process is also called vacuum deposition because the process is usually done in an evacuated chamber Generally PVD is used for depositing metal, dielectrics can be deposited using specialized equipment.

However, there are lot of materials in which the melting point of the source material is less than melting point of the source holder. Then we can use PVD without any worry.

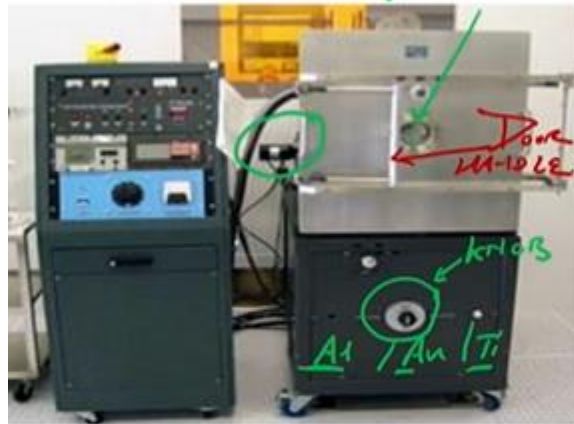
Now, let us understand the what are some of the things within this photograph. So, I will try to explain it to you. This one is a view window from which we can see the substrate and the source itself.



This one is to change the substrate. If you are we want to have aluminum, and then you want to deposit gold, and then titanium. So, can it can be 1 substrate or 2 substrate or 3 substrate or 4 substrate. So, we can select any source material depending on which material you want to deposit on to the substrate.

Now, this is a gauge which can be penning gauge or pirani gauge. I am not sure which type this is because I cannot see the second gauge. If I see the second gauge then I can tell you which one is this one.

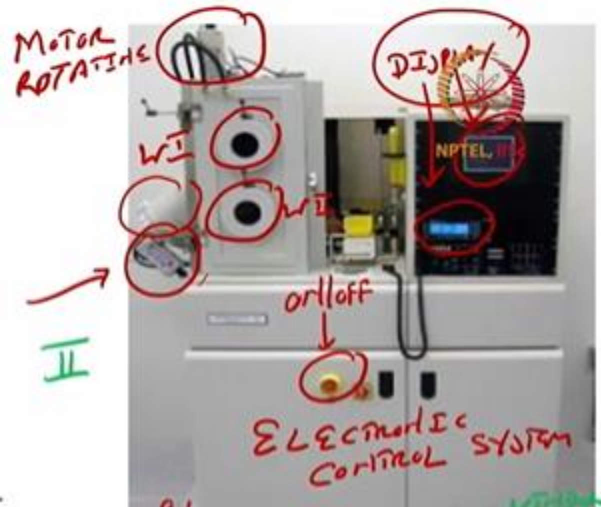
This is a door handle for the chamber. So, when you purge the air to kill the vacuum you can use the door handle to open the chamber.



Now, you can see this red color display, this is your thickness monitor, quartz crystal monitor or thickness monitor generally gives the deposition rate in terms of angstrom per second.

Then there is a variac. And a current meter to show the current in terms of amperes. There is also a vacuum pump and another control electronics right.

Now let us see the figure 2, where we have 2 viewing windows window 1 for substrate and window 2 for source. We have a motor for rotating. We have two displays and then we have electronic control system On the back side is the connection to the high vacuum pump or the turbo molecular pump. Again there is a gauge for measuring the vacuum.



Why do we call this as a semi automatic system, because we can load all the parameters. For example, if I want 1 micrometer thick metal, then the shutter will close automatically as soon as 1 micron is reached. The deposition rate of the material can be set, and automatically the voltage that is required to heat the material will be given to the boat. So, it is semi automatic because we have to feed the information and then it will happen. Again we have to kill the vacuum by purging the air and we can open the chamber. That is why we call it a semi automated system.

If you see this first system, you can see the turbo pump, viewing window for substrate, viewing window for source, the on off switch, the thickness monitor, the gauges, the control electronics. This particular tool is not a thermal evaporation, but a electron beam evaporation and we will see in one of the lecture about electron beam evaporation.

So, let us go to the next one. So, in evaporation techniques of physical vapor deposition, a vacuum chamber is pumped down to less than 10^{-5} Torr. Evaporation atoms from the source condense onto the surface of the wafer.

The heater can be resistive type, generally tungsten filament is used and it heats up as current flows, either filament coil or we can use a substrate or source holder. Amongst the evaporation technique the popular one is electron beam evaporation system in which high energy electron beam is focused on the source material in crucible using magnetic fields Last is depending on the method of evaporation and hardware, evaporation techniques can be categorized as thermal evaporation or electron beam evaporation.

Now, let us understand mean free path. I told you mean free path is given by lambda and it is nothing but the average distance a molecule travels before it collides. When we melt the material, it will travel towards the substrate, it collides with what other molecules in the atmosphere. So, we require vacuum. So, in other words after melting how far the vapor travels in the chamber before it hits a residual gas molecule and that can be given by this equation

$$\lambda = \frac{kT}{\sqrt{2}\pi P d^2}$$

Where,
T = Absolute temperature of the chamber
D = Gas molecule diameter
P = Pressure
k = Boltzmann constant

So, let us take an example of mean free path calculation suppose a nitrogen gas molecule whose diameter is 3 Angstrom (d is known) and temperature chamber is 300 Kelvin. So, T is also known. Calculate the mean free path of the gas.

Mean Free Path - Example

- Consider a nitrogen gas molecule whose diameter of 3Å and the temperature of the chamber is 300 K. Calculate the mean free path of the gas
- Given:

d = 3Å and T = 300 K

$$\lambda = \frac{kT}{\sqrt{2}\pi P d^2} = \frac{0.00777}{P\ (torr)}$$

If $P = 10^{-6}$ Torr, then $\lambda = 78$ m

i.e. The gas molecule can travel for 78m without any collision with other molecule

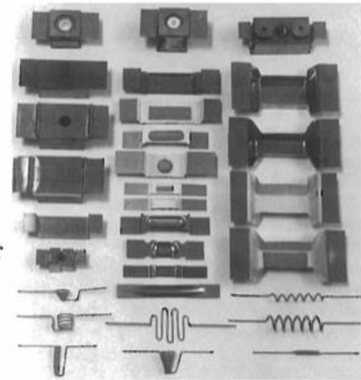
Now, we know k is Boltzmann constant. So, it is easier for us to put the value. We have d, we have T, we do not have pressure value. So, let us assume that the pressure is 10^{-6}. Depending on the assumption of 10^{-6} or 10^{-5} , the overall result will come differently. So, here, if we consider P equals to 10^{-6} Torr, and if we place all the values in the equation we get lambda of 78 meters.

That means the gas molecule can travel for 78 meter without any collision with other molecule.

Let us understand the heated evaporation sources and what are the different kind of sources available. There can be tungsten wire sources, refractory metal sheet sources, sublimation furnace sources, crucible sources. Depending on what kind of material you want to evaporate you can use different kind of sources as shown in this particular example.

Resistance – Heated Evaporation Sources

- **Tungsten Wire Sources:**
  - Tungsten is used as crucible material.
  - These evaporant wets W and retained by surface tension.
- **Refractory Metal Sheet Sources:**
  - Tungsten, tantalum, and molybdenum sheet metal sources
  - Used for poor wetting evaporants or powders.
- **Sublimation Furnaces:**
  - Evaporation of sulfides, selenides, and some oxides as pellets
  - Evaporation from these sources tend to be constant over extended periods of time.
- **Crucible Sources:**
  - Cylindrical cups of Al_2O_3, BN, graphite, and refractory metals
  - Normally heated by external tungsten wire heating elements.
  - Sometimes, high-frequency induction rather than resistance heating is also used.



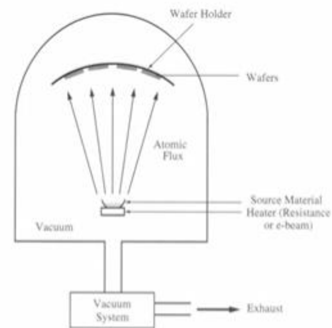
For example, we can use tungsten wire for a crucible or we can use tantalum or molybdenum when it is a refractory metal. We can use selenides or sulphides or some oxides as a pellets when it is sublimation furnaces. We can use Al2O3, BN, graphite and refractory material as crucible sources. So, instead of just resistance heating we can use high frequency induction heating.

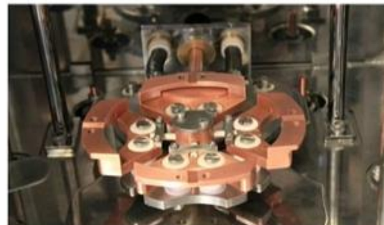
So, coming to thermal evaporation it relies on thermal energy applied to a crucible or a boat to evaporate atoms and this atoms will evaporate and deposit on to the wafers.

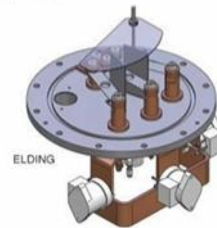
Thermal Evaporation

- Rely on thermal energy supplied to the crucible or boat to evaporate atoms
- Evaporated atoms travel through the evacuated space between the source and the sample and stick to the sample
- Surface reactions usually occur very rapidly and there is very little rearrangement of the surface atoms after sticking

Thickness uniformity and shadowing by surface topography, and step coverage are issues

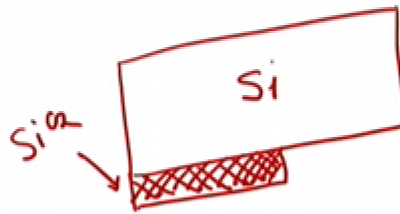




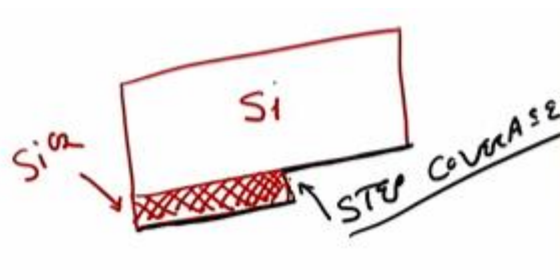


Surface reaction usually occur very rapidly and there is very little rearrangement of the surface atoms after striking. Thickness, uniformity and shadowing by surface topography and step coverages are the main issues. So, thickness is an issue because you have to be very particular about when to close the shutter.

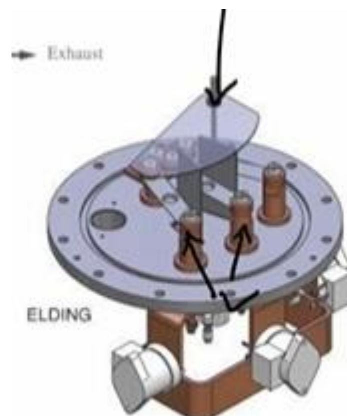
What is step coverage? Suppose, I have the silicon wafer and on silicon wafer, I have a material which I have pattern like this using photolithography which is one of the technique we will see in this course as well. So, there is silicon and there is silicon dioxide.



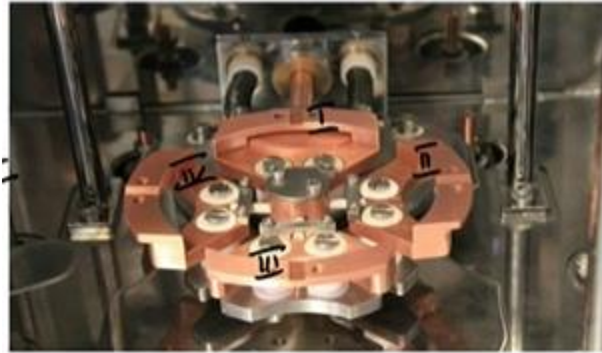
Now, if I want to deposit a metal it will get deposited uniformly on to the flat regions, and the step like region will not be covered that uniformly. This step coverage is poor in case of thermal evaporation.



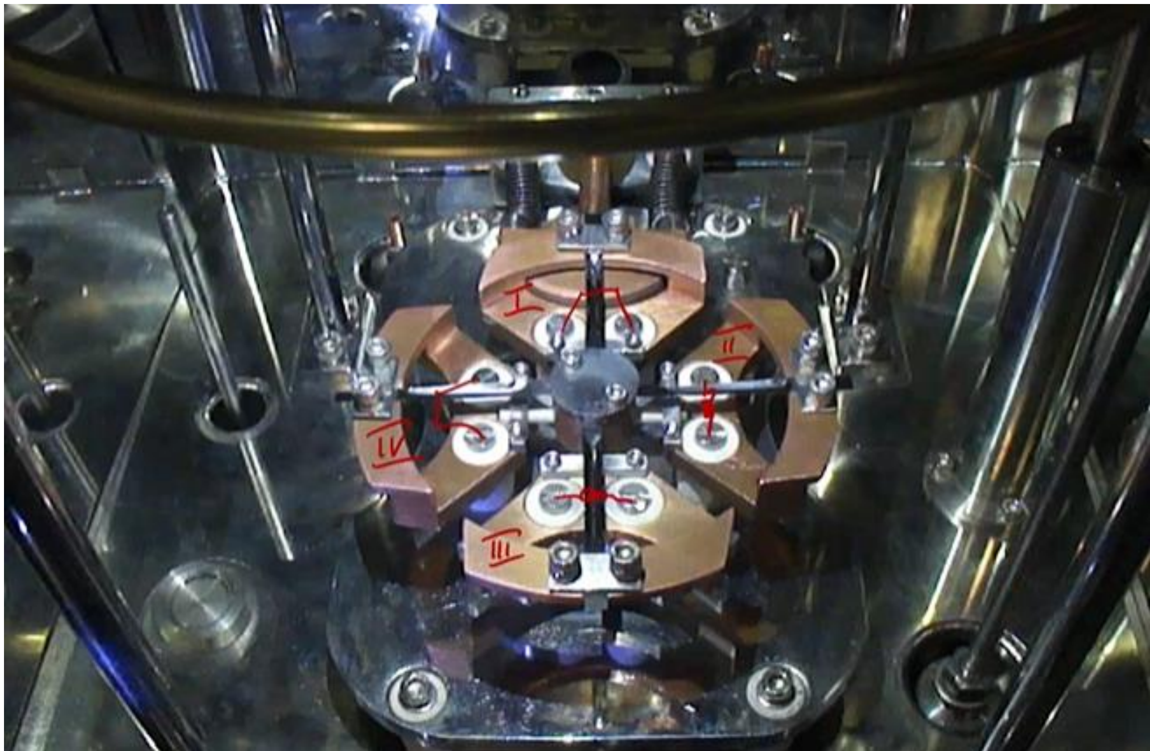
This particular slide shows a shutter, the electrodes for applying voltage.



The figure below has four sources, and four different sources can be evaporated.



We can also see a zoomed in view from within the chamber, and how source can be loaded between these 2 electrodes So we can have 4 sources. 1, 2, 3, 4 that we can load. So, one boat or one coil in each source holder.



Now, if you want to deposit an alloy you want to understand what is the binding energy of materials. The binding energy of alloy is different than binding energy of the atoms in a metal. And if you consider A and B as two different metals and AB as an alloy then activation energy of AB bond is different than the activation energy of only AA or BB bonds. So, metals can be considered as a solution of the two materials that means mixture of two different materials.

Partial pressure of A in AB at temperature T is not equal to partial pressure of pure A at T ie. $P_A(0)$. So, similarly for B, the partial pressure of B in AB is different than partial pressure of pure B. So, if you want to find out the flux ratio from the P_A and P_B equation, then we can find it out based on the atomic weight of B and A respectively. It also depends on the partial pressure of the chamber and it also depends on the bond activation energy of each material or metal. So, the vapor pressure as well as film compression depends on temperature and properties of the material. So, in case of alloy it is difficult to use thermal evaporation and we have to go for two source evaporation techniques.

Thermal Evaporation of Alloy

- Binding energy of metals in alloy is different than that of binding energy of atoms in metal.
- Generally, metal atoms are less tightly bound than atoms in an inorganic compound constituents tend to evaporate independently depending on temperature and enter vapor phase as independent atoms.
- Consider, A and B are two metals and A-B is an alloy. Activation energy of A-B bond is different from activation energies of A-A and B-B bonds.
- Metallic melts can be considered as a solution of the two materials.
- Partial pressure of A in AB at temperature T, $p_A \neq$ partial pressure of pure A at T, $p_A(0)$
- Similarly, for B, partial pressure of B in AB is different from pure B.
- $p_A = \gamma_A X_A p_A(0)$ where, γ_A is activity co-eff and X_A is mole fraction of A
- Similarly, $p_B = \gamma_B X_B p_B(0)$ where, γ_B is activity co-eff and X_B is mole fraction of B
- Flux ratio, $\frac{\Phi_A}{\Phi_B} = \frac{\gamma_A X_A p_A(0)}{\gamma_B (1-X_A) p_B(0)} \sqrt{\frac{M_B}{M_A}}$ where, M_B and M_A are atomic weight of B and A respectively
- The vapor pressure as well as film composition depends on temperature and properties of materials.

Wee will end the lecture on thermal evaporation here and in the next class we will look at the electron beam evaporation. Till then you just look into the slides and if you have any question you can ask us using the NPTEL forum. Till then take care. Bye for now.