Materials Chemistry

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Module - 2
Lecture - 4
Sputtering Deposited Thin Films and Applications

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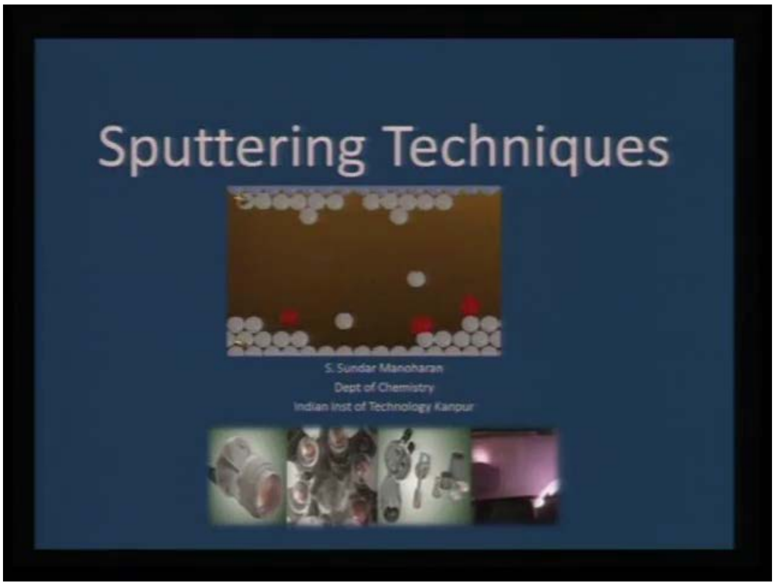

Sputtering Techniques

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In this module, we have already seen the principle behind molecular beam epitaxy and pulse laser deposition and pulse electron deposition. And in today's lecture I am going to specifically deal with the issues concerning sputtering technique, which is by and large a very useful material synthetic tool. Variety of compounds have been fabricated using this sputtering technique. Therefore, we are going to look little bit into the principle behind it, because this is one of the fairly well known and used by almost all the research groups across the world. But yet this has it is own novel features.

So, in today's lecture we will single out some of the aspects that underplay the importance of sputtering and also look at few examples. As you would see from animation that the process can be as simple as one atom knocking the other atom and in the process you can selectively deposit an atom, which is on the upper side. So, we will look into the details of this shortly.

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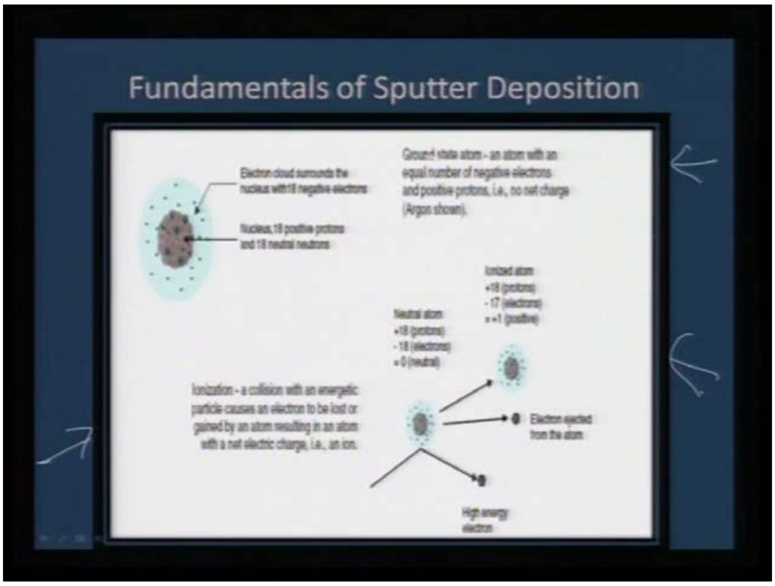

Fundamentals of Sputter Deposition

Ground state atom - an atom with an equal number of negative electrons and positive protons, i.e., no net charge (Argon shown).

Ionization - a collision with an energetic particle causes an electron to be lost or gained by an atom resulting in an atom with a net electric charge, i.e., an ion.

What is exactly the fundamental issue regarding sputter deposition. If you take any atom largely they are and does not have any charge whereas if you keep this under an electron cloud or in the influence of a very high electric field. Then this neutral atom actually gets ionized which we can see here, it gets ionized into energetic particles which actually loses either an electron or takes an electron. And therefore, this atom will have a net electric charge and this ionized atom, can actually be selectively placed on a particular substrate which happens to be an electrode. So, this is fairly a simple process of ionizing one atom, and using that atom to go and hit against another target material, and as a result we can get the necessary process carried out.

So, if you look at this simple cartoon of this sputter deposition what we see here, under a influence of a high voltage any atom which is ionized into a ion. Actually will form a plasma between two electrodes, one electrode can be one of the material which is the target material and the other electrode can be the substrate. So, you have a target and the substrate and in between you create a plasma, and this is what we call as a plasma cloud and this plasma cloud is composed of both positive ions as well as negative ions.

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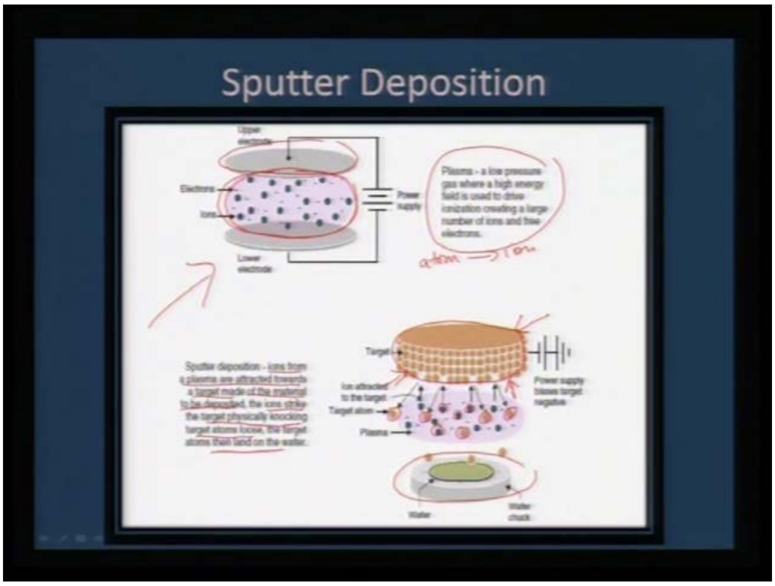

Sputter Deposition

Plasma - a low pressure gas where a high energy field is used to drive ionization creating a large number of ions and free electrons.

atom → Ion

Sputter deposition - ions from a plasma are attracted towards a target made of the material to be deposited, the ions strike the target physically knocking target atoms loose, the target atoms then land on the wafer.

And how this will happen when you create a plasma you need two things, one is a low pressure gas and a high energy field. So, this combination of a low pressure gas and a high energy field will result, in a plasma, which is composed of electrons as well as positive ions. So, if we have suppose this upper electrode as the target material and if it is biased such a way this acts like a cathode.

Now, what will happen all these positive ions what we have generated here in the plasma, this will go towards the cathode. And this will get bombarded or it will collide a fast collision will be there and this depends on the ion energy that you would generate. So, higher the field then you increase the ionic energy, so they will go at a rapid rate and knockout all this target atoms, from the target and these target atoms actually can be deposited on a wafer which is your substrate. So, this is the mechanism where ion from the plasma are attracted towards a target, made of the material to be deposited. And the ions strike their target physically knocking target atoms loose and the target then lands on the desired substrate. So, this is a simple process.

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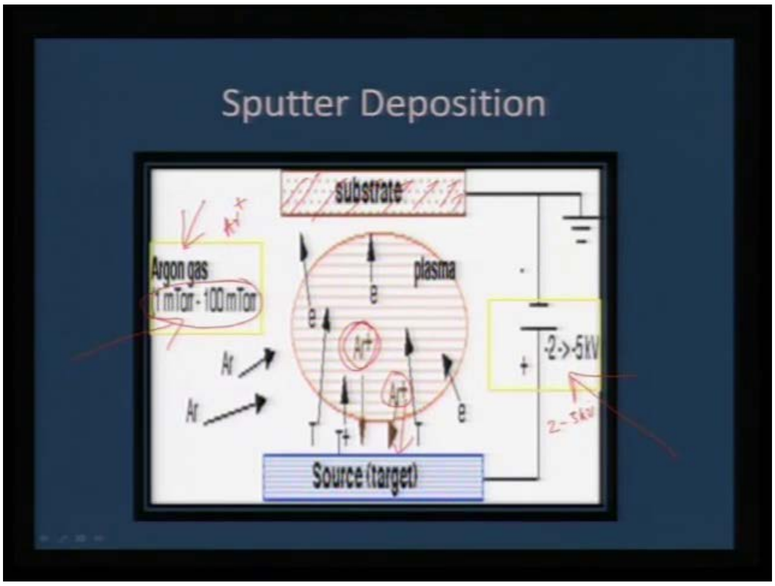

Sputter Deposition

Now, in this whatever is happening it is mainly governed by two parameters, one is the voltage that you apply and the gas that you use or the pressure of the gas that you employ. So, in most cases it is argon gas which is used as a sputtering ion because at lower pressure and at very high electric field, they easily ionize into argon plus and then they get they get generated as a r plus. And then they can go and strike on the source then the ablated material actually goes and falls on the substrate here. So, this is a very catchy parameter where you play around with 1 millitorr to 100 millitorr of argon gas pressure and the workable range is 2 to 5 k v you will come to this shortly from now.

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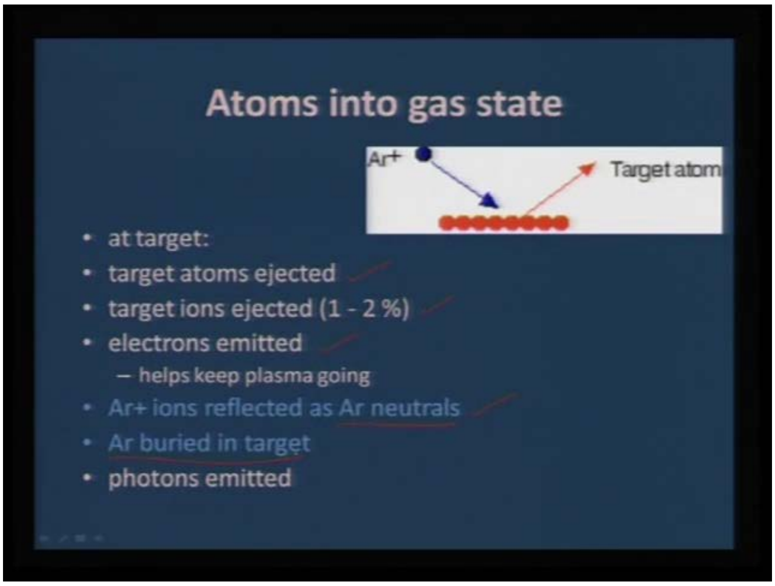

Atoms into gas state

- at target:
- target atoms ejected
- target ions ejected (1 - 2 %)
- electrons emitted
  - helps keep plasma going
- Ar+ ions reflected as Ar neutrals
- Ar buried in target
- photons emitted

So, when atoms go into a gas state what all is important, number one at the target, target atoms are ejected and the target ions are ejected to the extent of 1 to 2 percent, which means it is not a bulk phenomena what is happening you are only ejecting out the surface ions or atoms. And electrons are actually emitted during the process, which helps the plasma going. So, the you have a sustained plasma as long as you want and when the electric field is on this plasma will be sustained.

Because, electrons are also emitted and this will go to the anode and another thing that happens here is, argon ions they give back the energy and they will come back as neutral argon. Therefore, argon is also confined within the system and sometimes, depending on the ion energy argon can also be buried which is nothing but you are implanting ion into the depositing film. And photons are also produced during this process.

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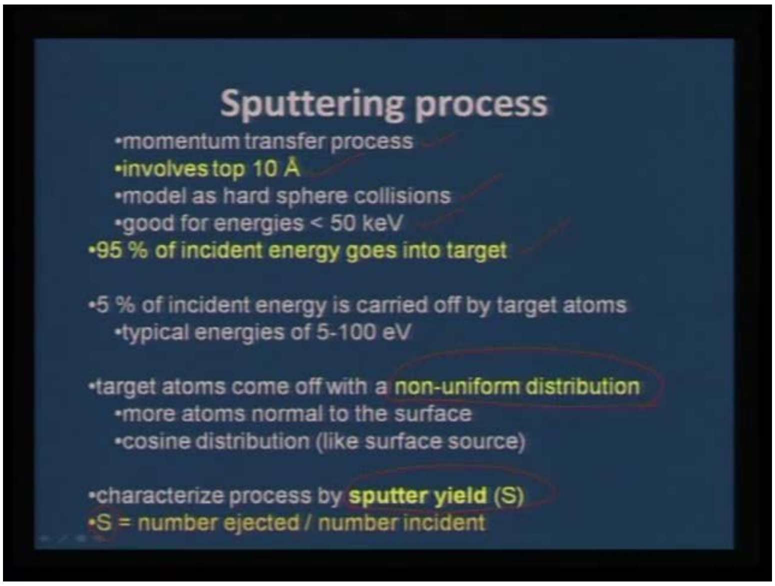

Sputtering process

- momentum transfer process
- involves top 10 Å
- model as hard sphere collisions
- good for energies < 50 keV
- 95 % of incident energy goes into target

- 5 % of incident energy is carried off by target atoms
  - typical energies of 5-100 eV

- target atoms come off with a non-uniform distribution
  - more atoms normal to the surface
  - cosine distribution (like surface source)

- characterize process by **sputter yield** (S)
- S = number ejected / number incident

Now, in this sputtering process what is the parameters that we need to have in mind and what is this in effect, tries to convey to us. First of all it is a momentum transfer process, it is not a chemical reaction one ion with lot of kinetic energy coming and impinging on the surface of another target ion. And those atoms are actually removed, forcibly by the argon ions as a result top 10 angstrom of the atomic layer is actually replaced by argon atoms.

So, it is mostly a hard spear collision model and that is what we saw in the first cartoon also it is merely a collision process. And the energies involved are less than 50 k e V and

95 percent of the incident energy goes into the target, where 5 percent of the incident energy is carried off by the target atoms. And another thing here is, that it is a non-uniform distribution.

Because, it randomly goes the way you position your target, the way you position your argon source, and the argon pressure, and the electric field that you apply everything brings about a non-uniform distribution. Therefore it takes a skill to optimize on the growth process. And usually when we think of sputtering, we talk about sputter yield which is called as S. So, and this S is nothing but the number of atoms ejected over the number of atoms incident, and the if you want to maximise on this then you need to vary some of the parameters. Therefore, whenever we talk about sputtering usually we think we refer to a sputter yield.

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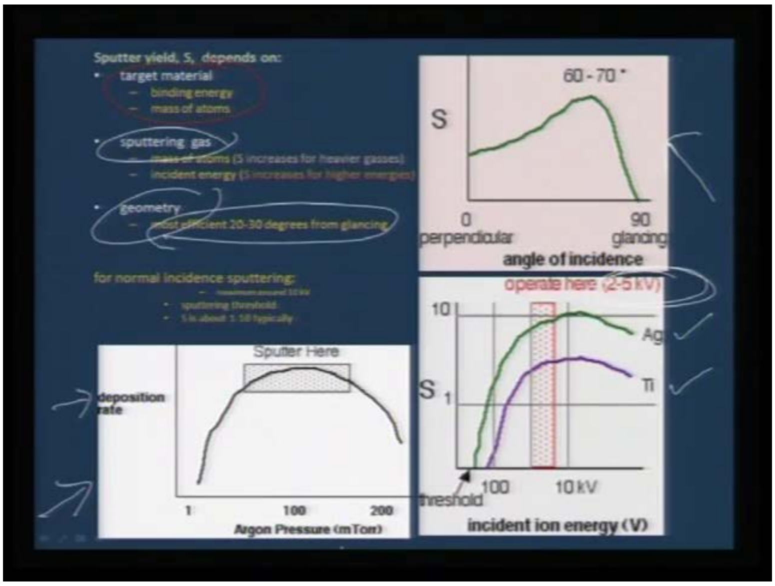

Sputter yield, S, depends on:
- target material
  - binding energy
  - mass of atoms
- sputtering gas
  - mass of atoms (S increases for heavier gasses)
  - incident energy (S increases for higher energies)
- geometry
  - most efficient 20-30 degrees from glancing

for normal incidence sputtering:
- maximum around 10 kV
- sputtering threshold
- S is about 1-10 typically

So, sputter yield actually depends on few parameters target material, sputtering gas and geometry in which it is aligned. These three cartoons will tell us what exactly this means, in this cartoon the sputter yield is actually plotted against the glancing angle of incidence. So, your argon is actually oriented to the target and how it is positioned the glancing angle, will tell you what sort of sputtering yield you will achieve as you see here it keeps on going up to 60 degree, 60 degrees of glancing angle.

But, what is optimised is that when you have a geometry of 20 to 30 degrees glancing then you get maximum sputtering yield. So, this is one parameter that we need to bear in mind and also, if you make a plot of sputtering yield versus incident ion energy you would see that there is a threshold, which is minimum beyond which you can actually knock out the atoms and that is of the order of 100 volts, nearly 100 volts.

So, minimum threshold energy is needed for the ions to come out of the target and this is a plot for silver and for titanium, where you can clearly see that it is workable around this region. So, 2 to 5 kilovolt is the operational voltage that is needed and also if you look at the deposition rate, versus argon pressure you can clearly see that it is at the maximum around 100 millitorr. So, irrespective of the chamber size these are some of the governing principles which has been standardized over many experiments.

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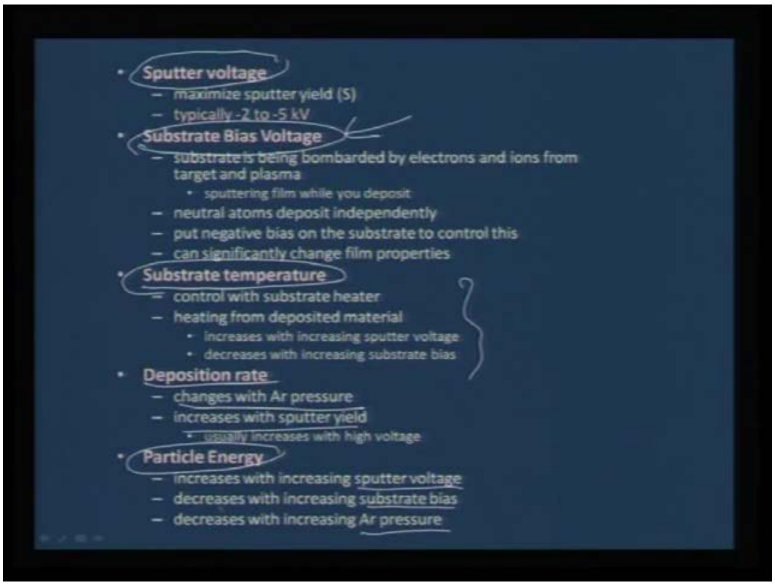

- **Sputter voltage**
  - maximize sputter yield (S)
  - typically -2 to -5 kV
- **Substrate Bias Voltage**
  - substrate is being bombarded by electrons and ions from target and plasma
    - sputtering film while you deposit
  - neutral atoms deposit independently
  - put negative bias on the substrate to control this
  - can significantly change film properties
- **Substrate temperature**
  - control with substrate heater
  - heating from deposited material
    - increases with increasing sputter voltage
    - decreases with increasing substrate bias
- **Deposition rate**
  - changes with Ar pressure
  - increases with sputter yield
    - usually increases with high voltage
- **Particle Energy**
  - increases with increasing sputter voltage
  - decreases with increasing substrate bias
  - decreases with increasing Ar pressure

So, apart from those three important parameters, sputter voltage and bias voltage is also important. Because, if you want the argon ions to travel towards the target material, then you need to have the bias voltage also regularized only then you can actually draw the argon atoms towards the cathode. So, bias voltage is important where you keep the target material negatively biased, so that the positive argons can come and hit the target.

And another thing that is important, specially when we think about making a film using sputtering it is substrate temperature, most of the compounds require some slight heating. Therefore, this substrate temperature is very important and as you would see in the following examples, silicon technology is mostly a sputtering technology and therefore, in silicon technology we use mostly room temperature. But, when we look for oxides and other refractory materials, if you want a crystalline film you need to regulate on the substrate temperature. Then the deposition rate is also important, which changes with argon pressure and these increases with the sputter yield. And again the particle energy, which is dependent both on the sputter voltage, substrate bias and argon pressure all these are important parameters.

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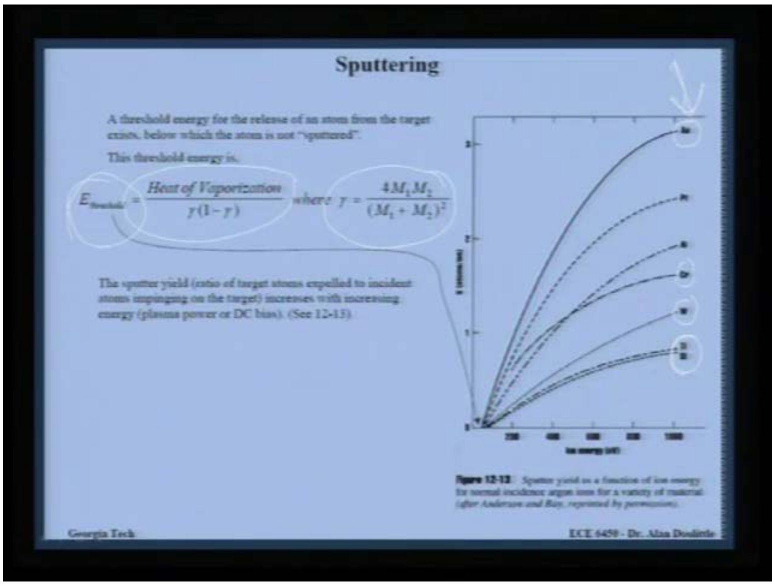

Sputtering

A threshold energy for the release of an atom from the target exists, below which the atom is not "sputtered".

This threshold energy is,

$$E_{threshold} = \frac{Heat\ of\ Vaporization}{\gamma(1-\gamma)} \quad where\ \gamma = \frac{4M_1M_2}{(M_1+M_2)^2}$$

The sputter yield (ratio of target atoms expelled to incident atoms impinging on the target) increases with increasing energy (plasma power or DC bias). (See 12-13).

Figure 12-13: Sputter yield as a function of ion energy for normal incidence argon ions for a variety of material (after Anderson and Bay, reprinted by permission).

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ECE 6450 - Dr. Alan Doolittle

In sputtering as I mentioned to you that this E threshold is the energy which is minimum to knockout the ions or atoms from the target. As you would see here, you can achieve this at relatively great ease for silicon and even for tungsten and other metals whereas, heavier metals like, platinum, gold you know require they give a very good yield with very high ion energy. And this is one of the reason in most of our experiments, where we would like to do characterization using gold coated samples, this is the philosophy behind that, that easily we can get a larger sputter yield at a relatively lower ion energy.

Therefore in most of the samples, where we study scanning electric and microscopic images, for non-conducting samples, biological samples, polymeric samples. Usually we do gold coating, compared to any other metal although other metals are relatively very cheap, the sputter yield at a relatively faster rate is determined only for gold. And this E threshold is actually related to heat of vaporization, and to the gamma factor. So, depending on this we can try to calculate the energy threshold for many metals.

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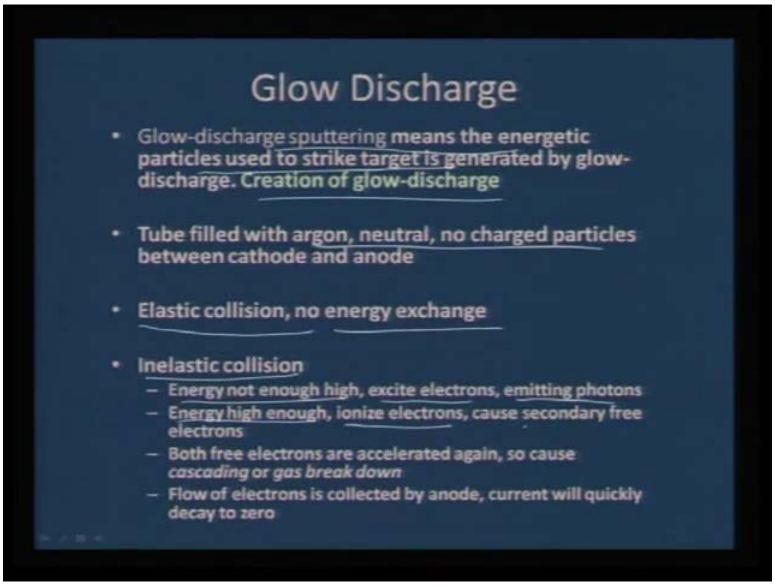

Glow Discharge

- Glow-discharge sputtering **means the energetic particles used to strike target is generated by glow-discharge.** Creation of glow-discharge
- **Tube filled with argon, neutral, no charged particles between cathode and anode**
- **Elastic collision, no energy exchange**
- **Inelastic collision**
  - **Energy not enough high, excite electrons, emitting photons**
  - **Energy high enough, ionize electrons, cause secondary free electrons**
  - **Both free electrons are accelerated again, so cause *cascading* or *gas break down***
  - **Flow of electrons is collected by anode, current will quickly decay to zero**

When we look at the sputtering phenomena as a whole, it is actually a glow discharge which is happening. This glow discharge can either bring about a sputtering process or it can bring about a plasma, which can actually bring about several other reactions. So, we will dwell little bit into what this glow discharge is, the glow discharge sputtering means energetic particles used to strike target.

And it is generated by glow discharge, which has to be created and this discharge need not necessarily be ionic, it can be neutral or no charged particles can also be produced between the cathode and the anode. If that is not a charged particle, then there would not be any inelastic collision, it will be elastic collision where no energy exchange is taking place. But, if it is a inelastic collision then energy is not very high, then it will only excite electrons and emit photons nothing will come out. But, if energy is high enough then it will ionize electrons and cause secondary free electrons to come.

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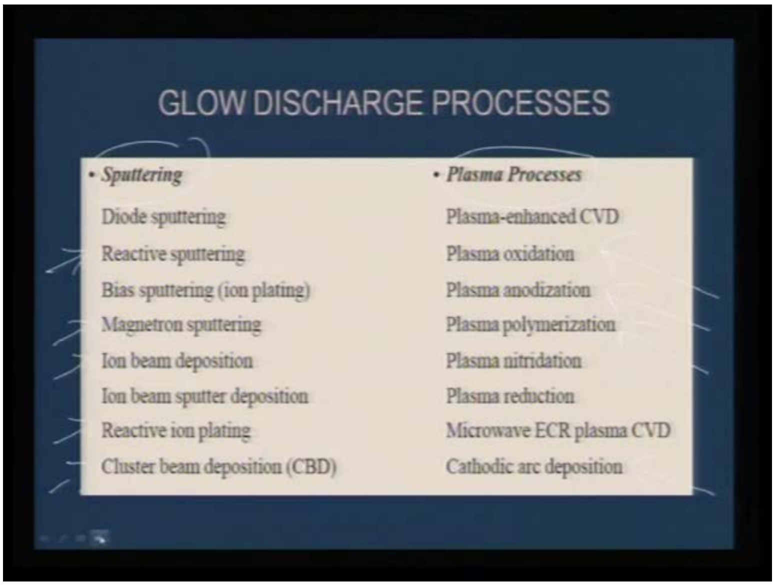

GLOW DISCHARGE PROCESSES

- *Sputtering*
  - Diode sputtering
  - Reactive sputtering
  - Bias sputtering (ion plating)
  - Magnetron sputtering
  - Ion beam deposition
  - Ion beam sputter deposition
  - Reactive ion plating
  - Cluster beam deposition (CBD)
- *Plasma Processes*
  - Plasma-enhanced CVD
  - Plasma oxidation
  - Plasma anodization
  - Plasma polymerization
  - Plasma nitridation
  - Plasma reduction
  - Microwave ECR plasma CVD
  - Cathodic arc deposition

So, in such a situation you can actually look for two different type of processes to happen, one is sputtering process. If we have a very high energy, then we will be able to ionize or it could be simply a plasma process and therefore, there are two sets of processes which are possible, using a glow discharge process. And based on this principle several other techniques have been developed, if you are talking now about sputtering then we can talk about reactive sputtering, magnetron sputtering, ion beam sputtering, reactive ion plating cluster beam deposition.

So, many approaches are developed based on the simple philosophy of a sputtering, but if it is only the interaction of your material with the plasma. Then we have plasma oxidation then anodization, polymerization, nitridation and cathodic arc deposition all these are possible using the plasma process. So, we will look at some of the examples we may not be able to go one by one, but specifically bring out some differences between each of these techniques, so that we can understand how different materials can be deposited using different approaches.

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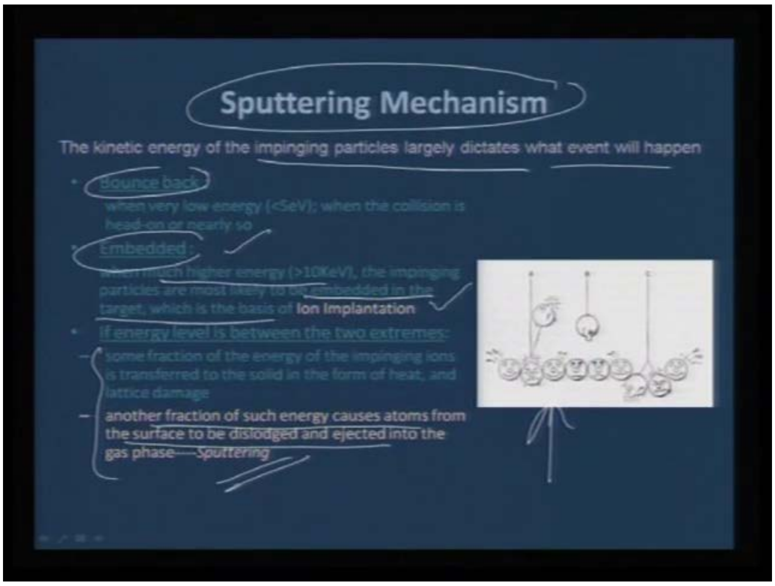

Sputtering Mechanism

The kinetic energy of the impinging particles largely dictates what event will happen

- Bounce back:
  when very low energy (<5eV); when the collision is head-on or nearly so
- Embedded:
  when much higher energy (>10KeV), the impinging particles are most likely to be embedded in the target, which is the basis of **Ion Implantation**
- If energy level is between the two extremes:
  - some fraction of the energy of the impinging ions is transferred to the solid in the form of heat, and lattice damage
  - another fraction of such energy causes atoms from the surface to be dislodged and ejected into the gas phase—*Sputtering*

Now, in the sputtering mechanism actually few things can happen based on the kinetic energy of the impinging particles, which largely will dictate whether the sputtering is going to be fruitful, and whether the sputter yield will be at it is maximum. One is bounce back, when the energy is very low then the collision will be head on and it will not really knock out the electron from the target. Number two, if the energy is very high then the argon ions can actually impinge into the target material and as a result they can get embedded in the target, which is the basis of ion implantation.

In fact, ion implantation itself is a big technique, we can modify the surfaces, we can do many chemical reactions on surfaces by mere ion implantation technique, which is a big research field in itself. And this is achieved only when the energy is greater than 10 k e V some if the energy level is actually between two extremes, it is neither low energy, nor higher. Then two thing can happen, one is some fraction of the impinging ions is actually transferred to the solid in the form of heat. Another fraction of such energy causes atoms from the surface to be dislodged and ejected into the gas phase which is nothing but sputtering.

So, we are actually talking about sputtering in the regime where the energy kinetic energy of the particles or the impinging particles or neither low nor very high. And this is the situation, what is actually mentioned in this interesting cartoon where you if you have a head on collision then necessarily it does not knock out. If it is having higher energy then it is getting actually buried, so several processes can happen.

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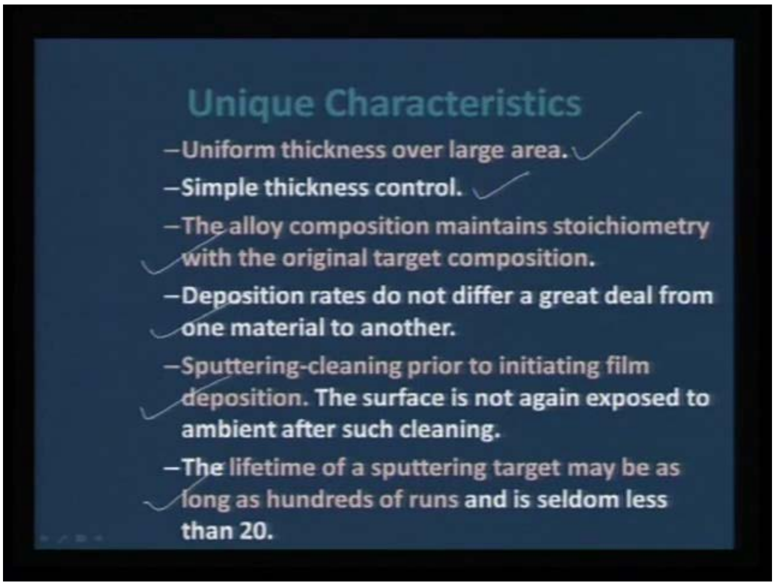

Unique Characteristics

- Uniform thickness over large area.
- Simple thickness control.
- The alloy composition maintains stoichiometry with the original target composition.
- Deposition rates do not differ a great deal from one material to another.
- Sputtering-cleaning prior to initiating film deposition. The surface is not again exposed to ambient after such cleaning.
- The lifetime of a sputtering target may be as long as hundreds of runs and is seldom less than 20.

And the unique characteristics of this sputtering process is that you get a uniform thickness over large area. And this is one technique which will stand out compared to all the other sophisticated techniques that we have seen, in terms of thin film deposition namely MBE, PLD and PED. Although those are extremely sensitive to the system that we are trying to deposit or the materials we try to ablate, the main feature of sputtering is that you can go for a very large area I will show you some cartoons on that simple thickness control there is no problem.

Then alloy compositions can easily be made into thin films because you essentially retain the same composition. Deposition rates can be tailored, sputtering cleaning has to be done before we initiate a film deposition, this is one intricate issue compared to MBE sputtering can actually bring a big mass of material. As a plasma, as a result before and after each cycle of deposition a thorough cleaning is needed for sputtering that makes this method a very involved one. And if you look at the target, what we have and how much we can sustain this target for deposition, you can at least run up to 100 cycles of or 100 runs you can easily do with this sputtering instrument.

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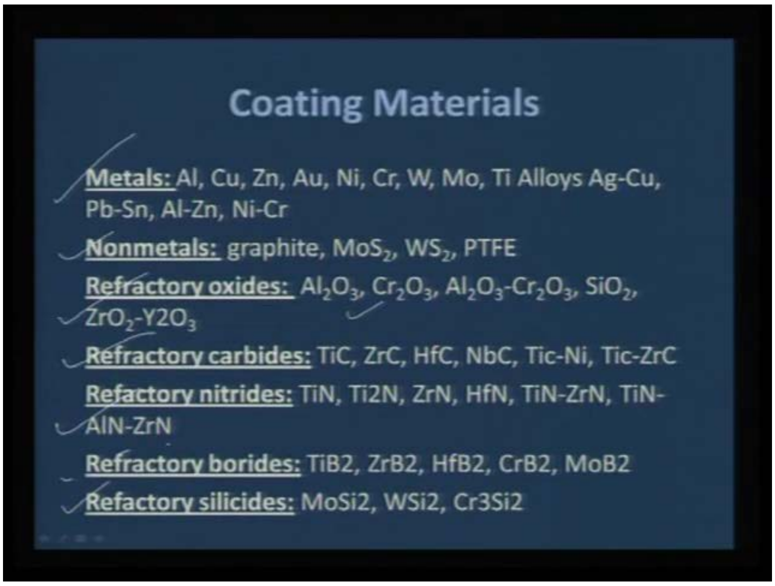

Coating Materials

Metals: Al, Cu, Zn, Au, Ni, Cr, W, Mo, Ti Alloys Ag-Cu, Pb-Sn, Al-Zn, Ni-Cr

Nonmetals: graphite, MoS_2, WS_2, PTFE

Refractory oxides: Al_2O_3, Cr_2O_3, Al_2O_3-Cr_2O_3, SiO_2, ZrO_2-$Y2O_3$

Refractory carbides: TiC, ZrC, HfC, NbC, Tic-Ni, Tic-ZrC

Refactory nitrides: TiN, Ti2N, ZrN, HfN, TiN-ZrN, TiN-AlN-ZrN

Refractory borides: TiB2, ZrB2, HfB2, CrB2, MoB2

Refactory silicides: MoSi2, WSi2, Cr3Si2

The materials which are actually coated by sputtering is a endless list, as you would see here almost the whole spectrum of compounds can be made, starting from metals. Any metals and the combination of metals as alloys or even non metals, graphite's molybdenum sulphide, PTFE can be made or refractory oxides, like alumina, chromia and other mixer oxides, composites can be made, carbides can be made, nitrides can be made.

In all these cases all you need to do is make a combination of argon with another gas, which will actually ensure the carbon formation or nitrogen formation. In the case of oxides we need to flush little bit of oxygen, along with argon then you get oxide. And then of course, the most rugged ones like borides and silicides can be made using sputtering. So, as you see from this list it is convincing to know that it is independent of the nature of the target material, whether it is metallic or refractory anything can be coated, which is actually a limitation in the case of MBE, PED or PLD.

This is a cartoon, which tells you the nature of deposition or the magnitude of the deposition. This is a PVD sputtering tool and as you would see here, all this are big wafers and together in one single run, you can make such big wafers coated therefore, you are talking about a scalar process which is much, much simpler compared to the other high vacuum techniques.

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PVD Sputtering Tool

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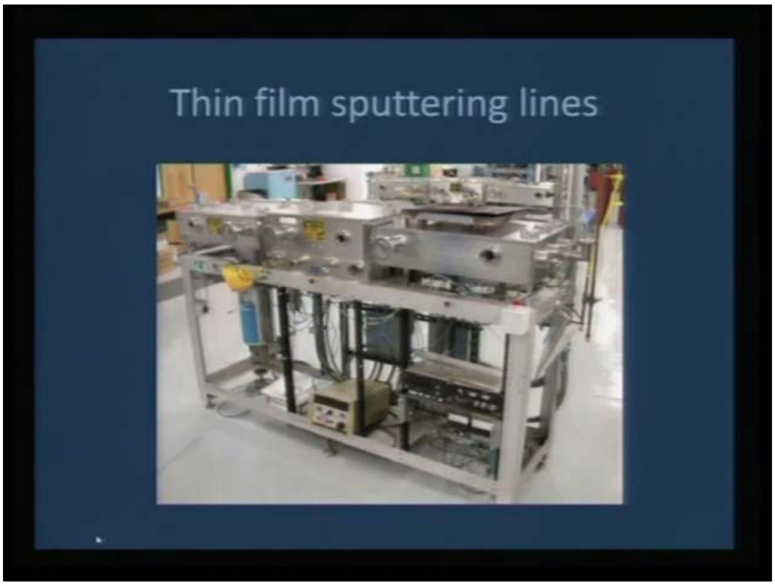

Thin film sputtering lines

And this is one of the thin film sputtering lines, not just this we can even make a series of this into 6, 7 lines. So, scale up and transforming this into industrial process is very, very easy and in fact the silicon technology either you talk about solar cells or you talk about computer devices. The most adaptable technique as of now in the industry is the sputtering technique, because you can make large wafer depositions.

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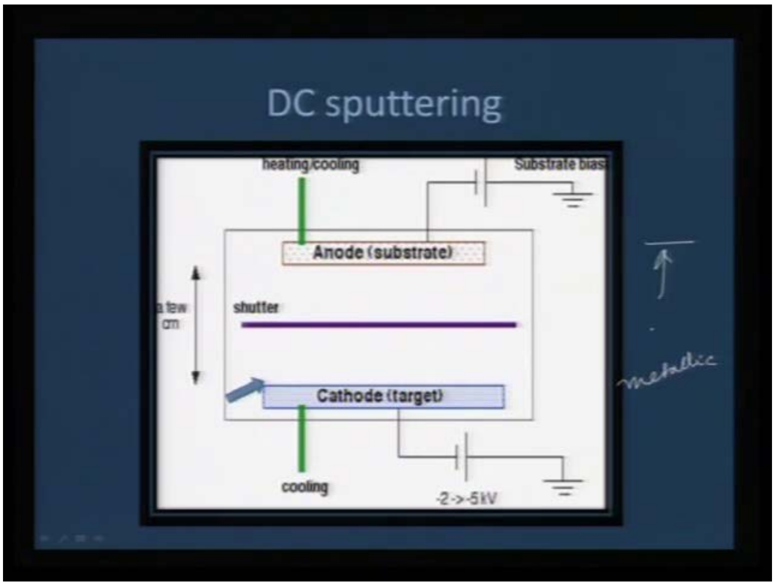

DC sputtering

Now, I want to bring some contrast between different sputtering techniques that I had mentioned, one is the DC sputtering. In DC sputtering as I told you here the cathode has to be a metallic compound, DC sputtering therefore, target cannot be anything other than a metal. So, this is one of the binding principle of a DC sputtering, so once the target is actually knocked out and then it goes to the anode and in the anode all the positive ions go and get deposited.

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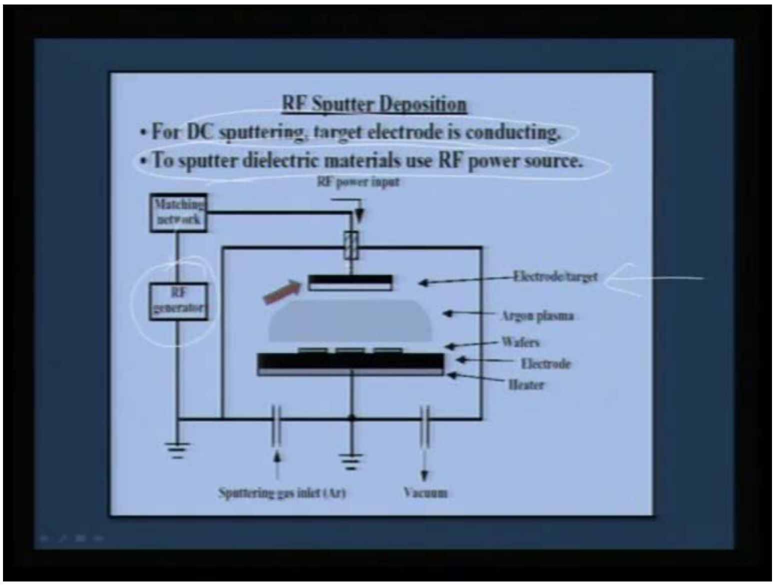

RF Sputter Deposition

- For DC sputtering, target electrode is conducting.
- To sputter dielectric materials use RF power source.

When we look at RF sputter deposition, there is a difference between DC and the RF. Because, in RF you do not necessarily need to have a material which is metallic, in that case what you do to sputter dielectric materials, we can actually use a RF source. We do not need to worry about it because; the limitation for DC sputtering is it has to be metallic whereas, for dielectric materials you use a RF generator which is actually grounded to your anode as a result you can deposit any sort of material using the sputtering technique. So, this is the main difference between the DC sputtering and RF sputtering.

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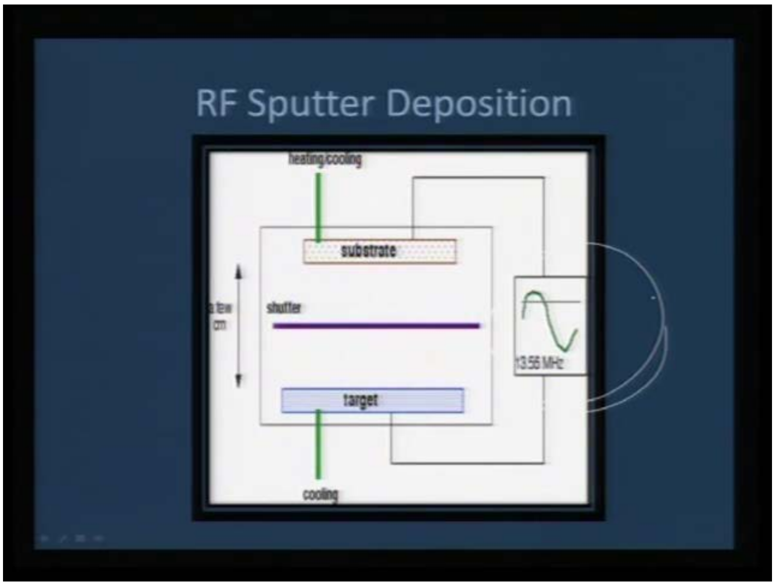

RF Sputter Deposition

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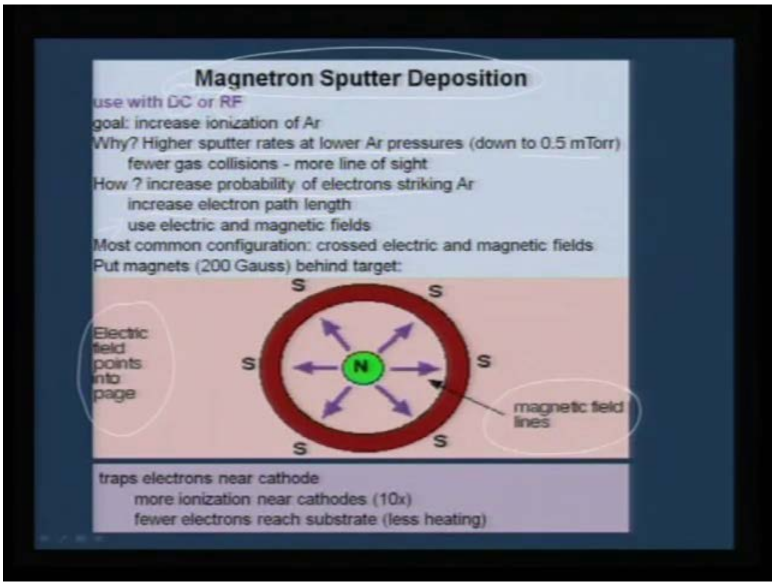

Magnetron Sputter Deposition

use with DC or RF
goal: increase ionization of Ar
Why? Higher sputter rates at lower Ar pressures (down to 0.5 mTorr)
    fewer gas collisions - more line of sight
How ? increase probability of electrons striking Ar
    increase electron path length
    use electric and magnetic fields
Most common configuration: crossed electric and magnetic fields
Put magnets (200 Gauss) behind target:

traps electrons near cathode
    more ionization near cathodes (10x)
    fewer electrons reach substrate (less heating)

So, the issue is emphasized here, you do not have to worry about the target being metallic you can do it through a RF generator. Now, we can also improvise on the deposition by using magnetron sputter deposition, this is actually employed along with either DC or RF because magnetron sputtering is very well known and it is established. Now, what is the goal it is to increase ionization of argon because in a very high field there could be saturation where after a certain time there would not be any deposition that is possible. So, we can actually use a magnet magnetic field to influence it.

So, this is what is shown here when there is a strong electric field then this magnetic field can actually influence the trajectory of your argon ions. So, why do we do that higher sputter rates at lower argon pressures can be achieved, even down to 0.5 millitorr and how it happens, the increase possibility of electrons striking argon, as a result there is increase electron path length and this we can achieve using electric and magnetic fields.

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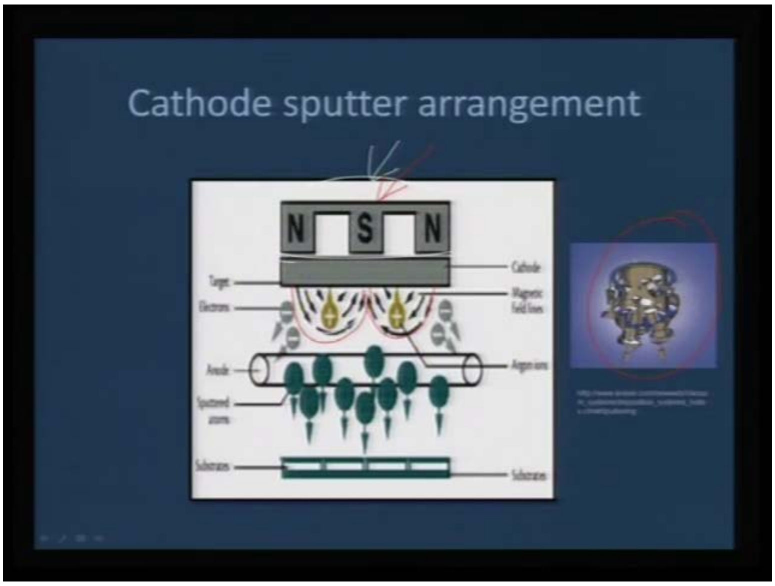

Cathode sputter arrangement

So, in magnetron sputtering what you would try to do is, behind the target we try to place this magnetic field. And as a result what would happen, there is a magnetic field line which is generated here and this magnetic field line will confine, the argon going only to a particular region. As a result the flow of the knocked out atoms will be synchronized and this can be enhanced by a simple modulation, where you try to keep a magnet behind the target. And that is the principle of magnetron sputtering, and there are several companies which actually sells such assembly for magnetron sputtering.

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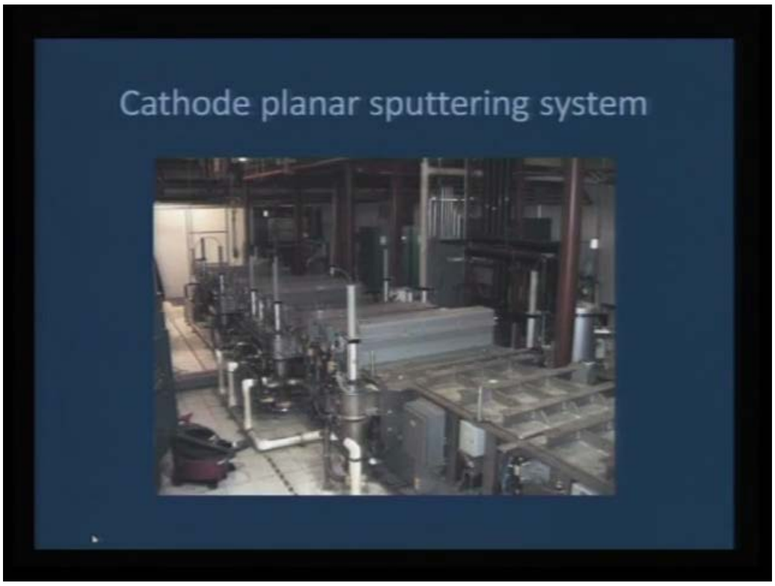

Cathode planar sputtering system

And as you would see here, this cathode planar sputtering is also a form of magnetron sputtering, how big this deposition unit can be you can easily scale it up to a industry level.

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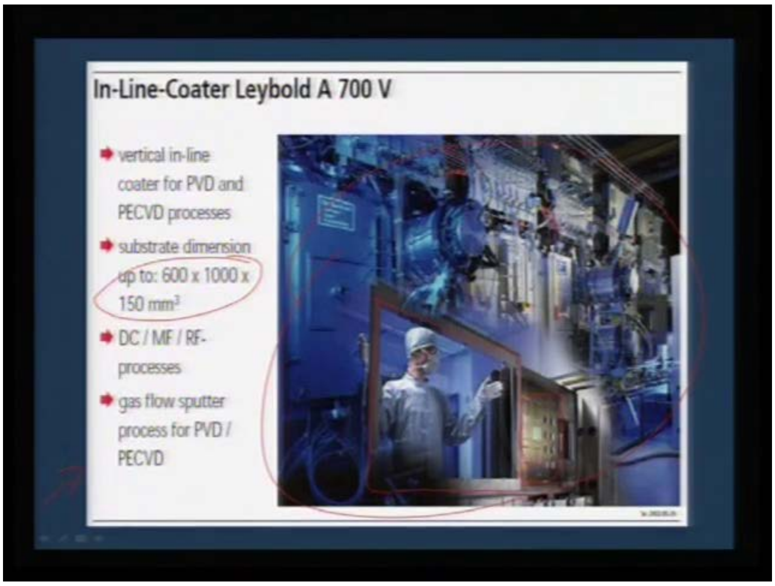

In-Line-Coater Leybold A 700 V

- vertical in-line coater for PVD and PECVD processes
- substrate dimension up to: 600 x 1000 x 150 mm³
- DC / MF / RF-processes
- gas flow sputter process for PVD / PECVD

And this is another cartoon, which tells us why sputtering technique is still the most coveted as far as industries are concerned. If you take a look at the dimension of this substrate, which this person is holding actually this is the big frame, which can be deposited either a glass material or any substrate can be housed as huge as that, which is absolutely impossible using any other vacuum technique. And the dimension here, is actually 600 mm by 1000 mm by 150 mm.

So, you can actually go for very large size depositions using sputtering techniques as you would see here, from this cartoon it is a very involved assembly it is not simple. But, then the versatility of bringing large area depositions is huge and you would see here, there are lot of mask here. So, you can mount your substrate and then push it selectively you can do patterning or deposition at your ease.

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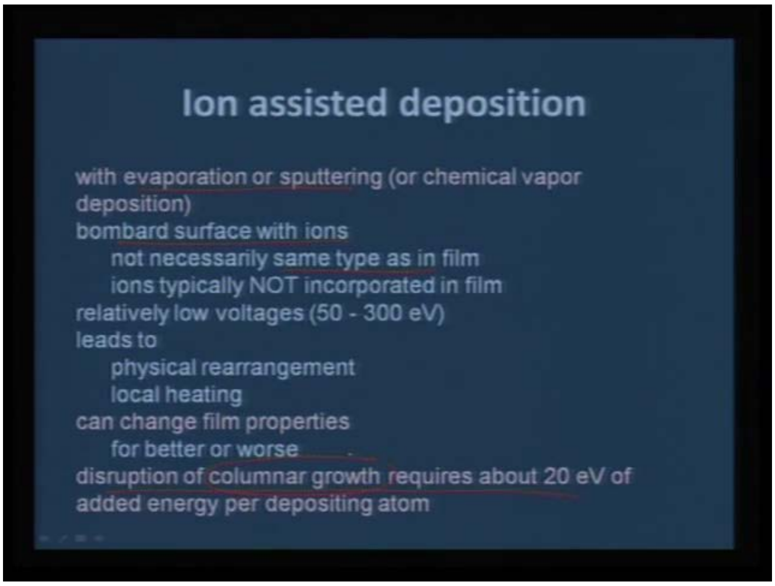

Ion assisted deposition

with evaporation or sputtering (or chemical vapor deposition)
bombard surface with ions
  not necessarily same type as in film
  ions typically NOT incorporated in film
relatively low voltages (50 - 300 eV)
leads to
  physical rearrangement
  local heating
can change film properties
  for better or worse
disruption of columnar growth requires about 20 eV of added energy per depositing atom

So, there are other forms of sputtering other than DC magnetron sputtering this is called ion assisted deposition. Here, with evaporation or sputtering we can actually bombard surface with ions. So, we can parallely there are two things happening here, ions actually argon ions knock out the material, along with that you can pump in some other ions, not necessarily the same type. And therefore, you can try to see the influence of this ion assisted deposition, in some cases it is also called soft landing techniques, where you can try to modulate the growth process.

Because, sometimes the roughness that it brings will be very high. So, to improve on the smoothness of the film you can actually bring out a ion assisted deposition mainly to improve on the smoothness of the film, and to avoid the columnar growth of the growing film. So, this is another approach that has been introduced which is called as ion assisted.

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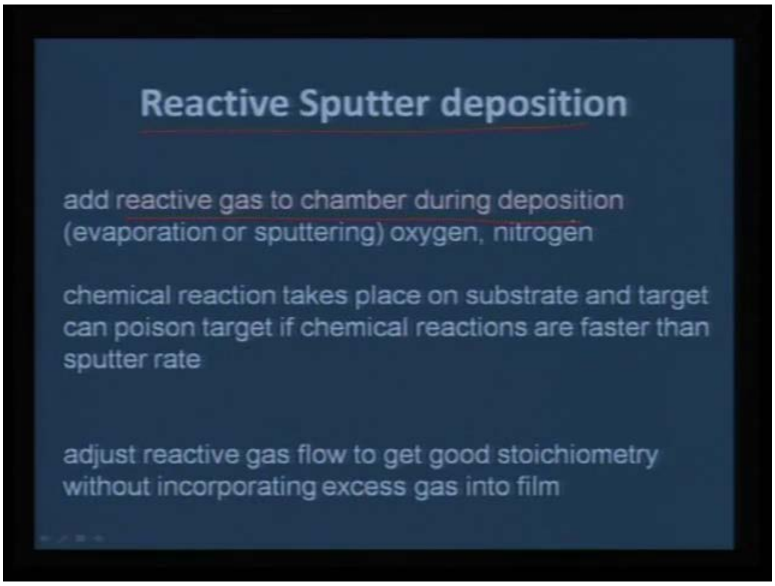

Reactive Sputter deposition

add reactive gas to chamber during deposition (evaporation or sputtering) oxygen, nitrogen

chemical reaction takes place on substrate and target can poison target if chemical reactions are faster than sputter rate

adjust reactive gas flow to get good stoichiometry without incorporating excess gas into film

And then there is another sputtering technique called reactive sputter deposition. Where your reactive gas to chamber during deposition is actually brought in, that is oxygen or nitrogen as I told you, if we are aiming at a oxide. Then you bring in oxygen along with argon or nitrogen, along with argon for making nitrates. So, by this way we can try to achieve a wide spectrum of compounds.

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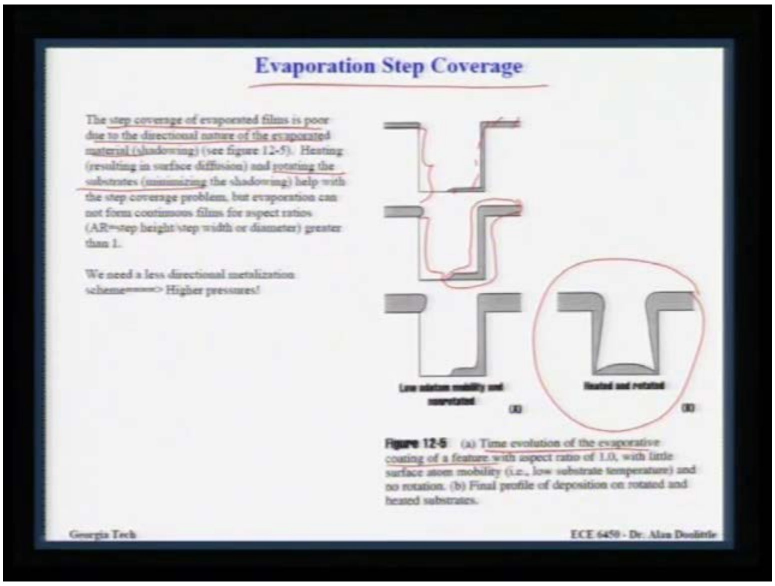

Evaporation Step Coverage

The step coverage of evaporated films is poor due to the directional nature of the evaporated material (shadowing) (see figure 12-5). Heating (resulting in surface diffusion) and rotating the substrates (minimizing the shadowing) help with the step coverage problem, but evaporation can not form continuous films for aspect ratios (AR=step height/step width or diameter) greater than 1.

We need a less directional metalization scheme=====> Higher pressures!

Figure 12-5 (a) Time evolution of the evaporative coating of a feature with aspect ratio of 1.0, with little surface atom mobility (i.e., low substrate temperature) and no rotation. (b) Final profile of deposition on rotated and heated substrates.

Georgia Tech

ECE 6450 - Dr. Alan Doolittle

One of the issue that we need to address, as far as a sputtering process is concerned is the evaporation step coverage. As you would see here, the step coverage of evaporated film is poor due to directional nature of the evaporated material as you would see from this cartoon, either we can heat the substrate in order to bring about a uniform coverage or the most important thing that we need to, adopt here is rotating the substrate. Because, as I told you the glancing angle of the target to substrate is very important.

And therefore, if we rotate the target then the growth mode can be increased. For example if this is a step height the and if it is focused only on a one direction, then the deposition is only happening and this place is left out. And this thickness of the film may keep growing, even without anything forming on this value. So, the best way to do that is to rotate and heat the substrate. So, that you can get a uniform step coverage and this is what is mentioned in the cartoon the time evolution of the evaporating coating, and lot of other modifications can also be brought in therefore, this is one of the serious issue as far as sputtering process is concerned.

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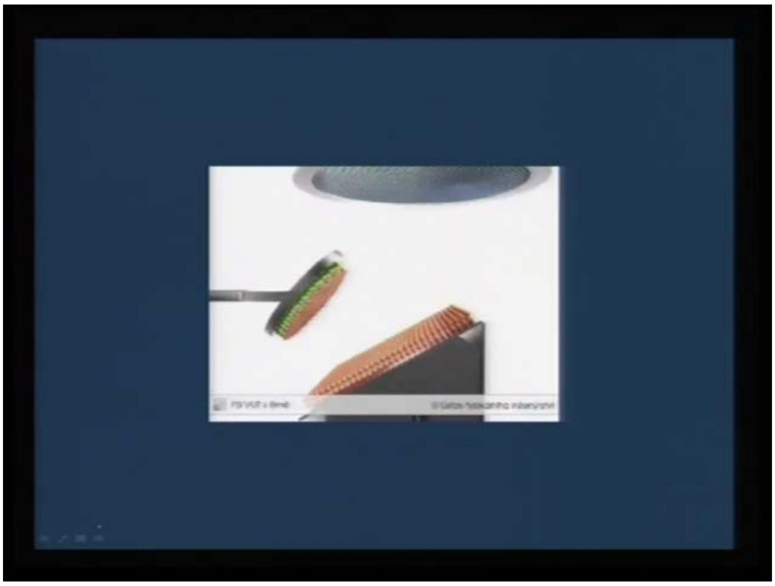

This is animation that will tell you the versatile nature of this sputtering process, as you would see here just by rotating or flipping the target, you can actually make multilayer’s with these. And without breaking the vacuum, you can see both the green ones and the orange ones can be deposited with these. So, one of the main advantage of this sputtering process is you can do a variety of layer thickness, and you can change the material within the sample or within the chamber without breaking the vacuums. Therefore, this is much more friendly than the other vacuum techniques that we have seen earlier.

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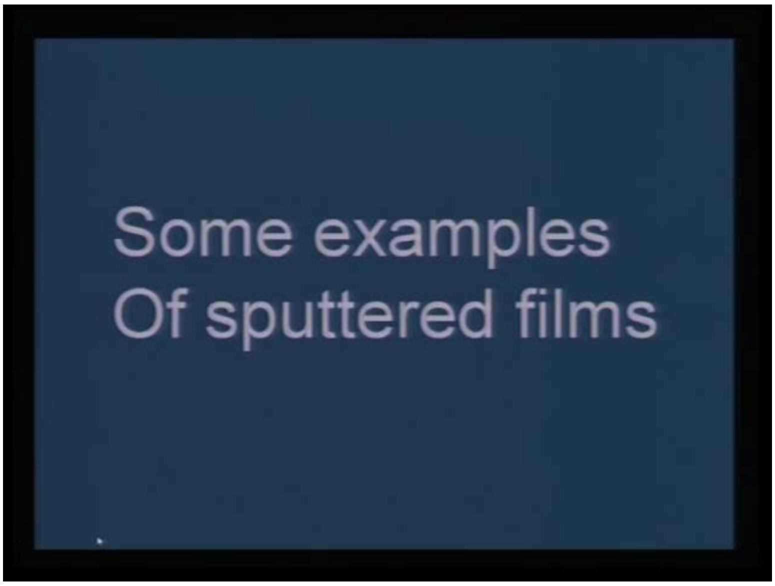

Some examples
Of sputtered films

I will also show some examples of sputtered films and try to bring in some issues related to the growth process, of different material using the sputtering process.

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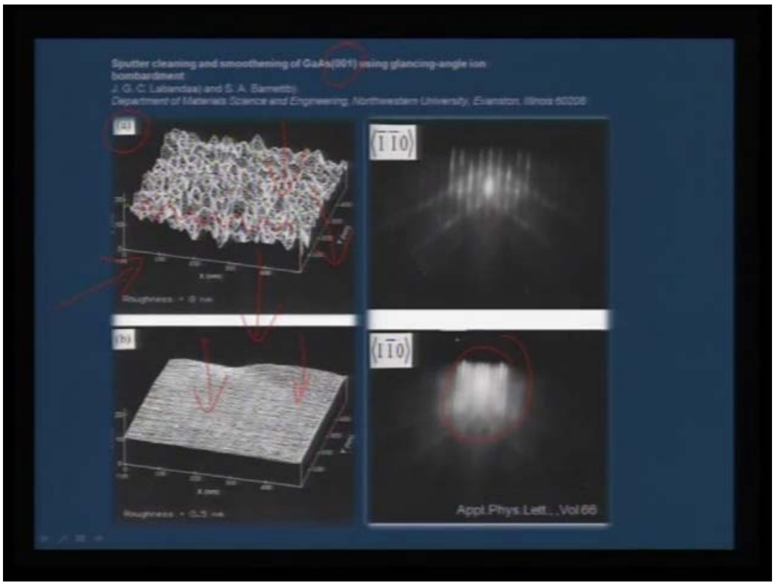

Sputter cleaning and smoothening of GaAs(001) using glancing-angle ion bombardment
J. G. C. Labanda(a) and S. A. Barnett(b)
Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

This is an example, of how gallium arsenide actually is deposited. And in this case you can see, the surface which is seen in cartoon a this is before sputtering and if you look at this surface of gallium arsenide, you can see there is, so much of roughness here on the surface and this is up to 8 to 10 nanometre. So, if you are going to put any film on this gallium arsenide, then the growth mode is actually going to mimic the surface roughness of your substrate.

So, it is a protocol that when you are going for any sputtering process or any deposition for that matter, the first protocol is to sputter and clean the film. So, that a flat surface is generated and in this case you can see, this is the diffraction pattern of your gallium arsenide 100 surface. Actually showing these streaks of these diffraction spots, after stuttering and if this surface is actually not sputtered, then you would not get these streaks very sharp. In other words you cannot actually monitor the growth process effectively.

So, even in MBE or PLD which are very sophisticated techniques, the first protocol that one would like to evolve with is to use a sputtering mechanism by which in situ you first clean it in a very high vacuum environment. So, as you would see here after sputtering the same gallium arsenide film is showing a very flat terrace. So, to grow film on this surface is going to mean quite a lot on the growth process compared to this one. Therefore, sputtering by itself it is a unique technique, but then even in sophisticated techniques like MBE or PLD, the first protocol that one would adopt is to use a sputtering mechanism, by which you can readdress this roughness before you start depositing any films.

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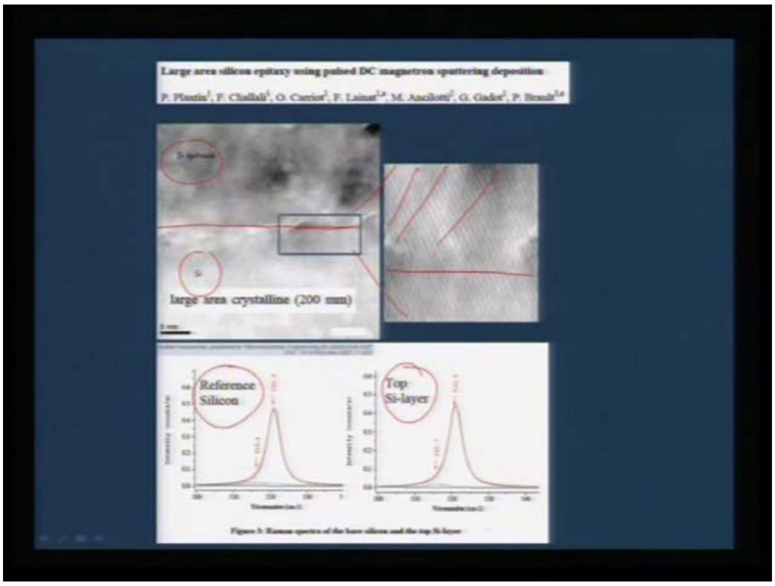

Large area silicon epitaxy using pulsed DC magnetron sputtering deposition

P. Plantin[1], F. Challali[1], O. Carrier[1], F. Lainat[1,#], M. Ancilotti[2], G. Gadot[2], P. Brault[1,#]

Figure 3: Raman spectra of the bare silicon and the top Si-layer

And you can see as another example, large area silicon expitaxy using pulsed DC magnetron sputtering deposition. And in this case this is a homo epitaxy, where silicon is actually deposited over silicon. And if you look carefully into this region, this is where the interface is and you would not really make a clear distinction between the single crystalline silicon, versus the silicon that is deposited.

Mainly because it is homo epitaxy number one also this highlights how DC magnetron sputtering can be very important. And if we actually blow up this range, you would see here that there is a very excellent epitaxial growth of the coated silicon over the substrate silicon. So, this is a very convincing proof that silicon can be deposited at ease and single crystalline, silicon can also be deposited and to substantiate the case, we can actually take a reference silicon and do the Raman spectra. And as you clearly see, both the Raman spectra of the substrate silicon as well as the top silicon layer, they show exactly the same Raman spectra showing that you can even get epitaxial growth without any problem.

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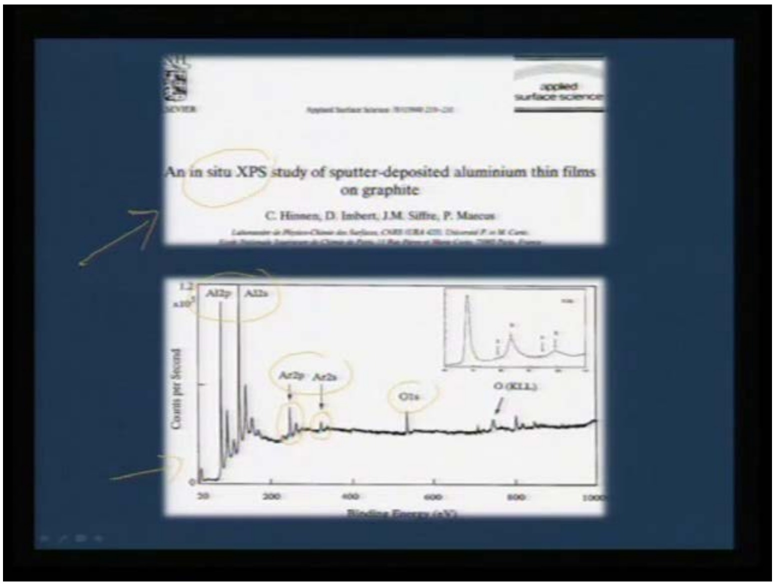

applied surface science

An in situ XPS study of sputter-deposited aluminium thin films on graphite

C. Hinnen, D. Imbert, J.M. Siffre, P. Marcus

As another example let us take the case of the XPS study of sputter deposited aluminium, thin films on graphite. As you would see, from this cartoon that we do not use sputtering just for removal of any atoms just for film deposition, but it is also possible for us to evaluate or to quantify how much of the layer thickness that we can grow. So, XPS we can do a quantitative analysis to find out, whether the sputtered deposited film is of the required thickness.

So, this is a in situ reaction between the film process as well as XPS. And this is the survey spectrum of XPS that we see where, the reflections due to oxygen, argon and aluminium is seen here. And as you see that aluminium is coated substantially at the same time, we also see the nature of this film growth where definitely there is some signature of argon that is present. So, if we want to remove argon from the embedded films in which argon atoms are embedded, then it is possible for us to heat the graphic little bit, so that this argon can actually come out.

So, there are several hybrid approaches where we can try to monitor the growth process of these sputtered films. And this is one of the very useful technique that is XPS to map whether, you have got the required amount of the material that is deposited, and as you would see here. In spite of that there is still some trace of oxygen that is left, which gives a clue that when you are trying to deposit aluminium film, there will always be some amount of residual oxygen that will be stuck to the film. So, this is one way to quantify the purity of the film.

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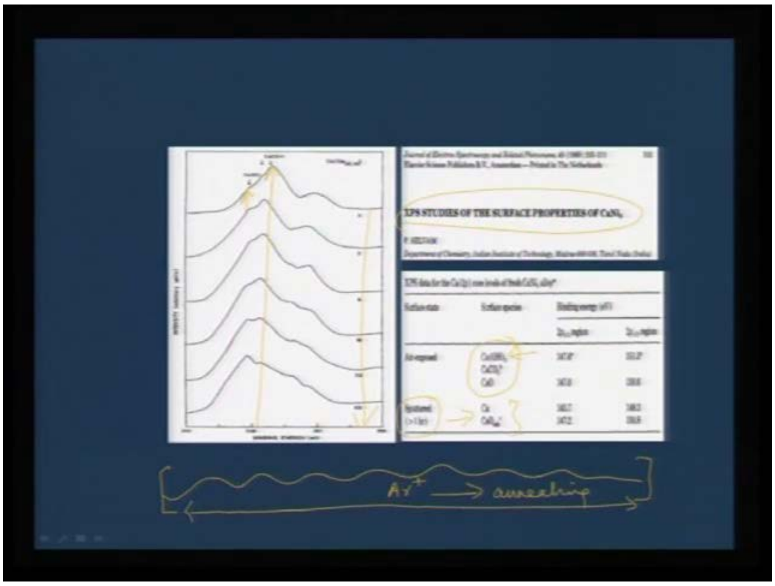
XPS STUDIES OF THE SURFACE PROPERTIES OF CaNi$_5$

And here again, there is another a example of how XPS studies can be used for calcium nickel alloy, this is s CANI five alloy. And this alloy before sputtering, actually gives a very different feature as you would see here, this is the peak corresponding to calcium two plus whereas, this is the peak corresponding to calcium oxide. And with the sputtering time over 0 to 65 minutes, you can see the shape of this curve changing.

And if you map the calcium two plus peak, it is actually fading completely with more and more time of sputtering. What it means that in this calcium nickel alloy there is a definite composition of calcium hydroxide that is sticking, calcium carbonate is there and also calcium oxide is there. And you would also find out that above one hour of over one hour of sputtering, you can almost remove all the hydroxide and carbonates. And this is one of the issue that would confront any of our study or growth process, because any metal or alloy will have a substantial amount of carbonates or hydroxides sticking to it. So, if you want to grow any particular film over a substrate, it is always better as a protocol to use sputtering, so that you can get this. Now, sputtering also will bring about roughness like this because you are knocking out at least 9 to 10 nanometres of the film thickness or the surface, with the argon ions.

Therefore, when we try to sputter with the argon ions, it should always be followed by a annealing process. So, when you do the annealing process what will happen this will actually become a very flat terrace. So, sputtering alone is not the issue when we want to make a very nice surface you should always go for argon sputtering, followed by a sustained annealing process. So, this cartoon clearly gives a clue to how the hydroxides and carbonates can contaminate the surface of any alloy surface.

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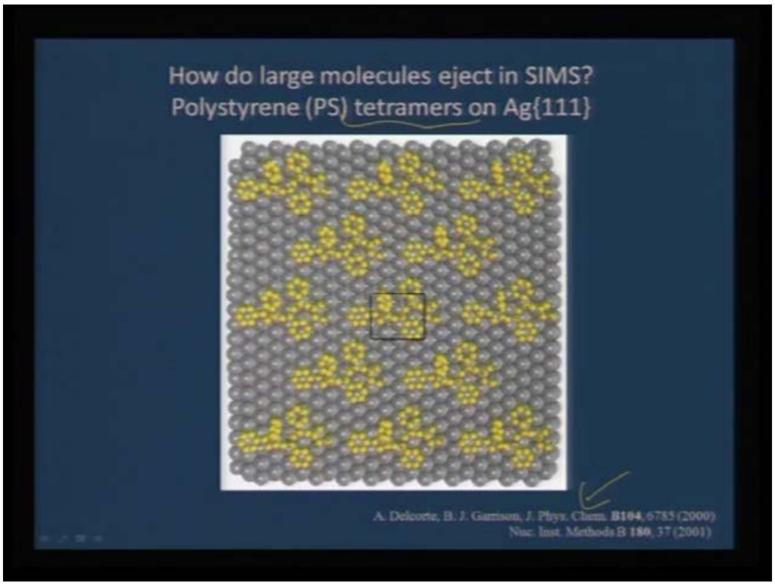

How do large molecules eject in SIMS?
Polystyrene (PS) tetramers on Ag{111}

A. Delcorte, B. J. Garrison, J. Phys. Chem. **B104**, 6785 (2000)
Nuc. Inst. Methods B **180**, 37 (2001)

This is another example, which has been quoted in JPC by this group, where they have tried to map the sputtering process for SIMS, this is secondary ion mass spectroscopy. And this is a very nice article, where polystyrene is actually deposited on silver 111 and if you want to quantify this result, using SIMS which will give you precisely the nature of or the constituents of this polymers, which are there. And specially if you want to know, what set of polymeric units are coming, secondary ion mass spectroscopy is a very good tool. And if you try to do the sputtering here, then you would find out that selectively this polymeric units will be coming out, it may be dimer, it may be trimer, it may be tetramer.

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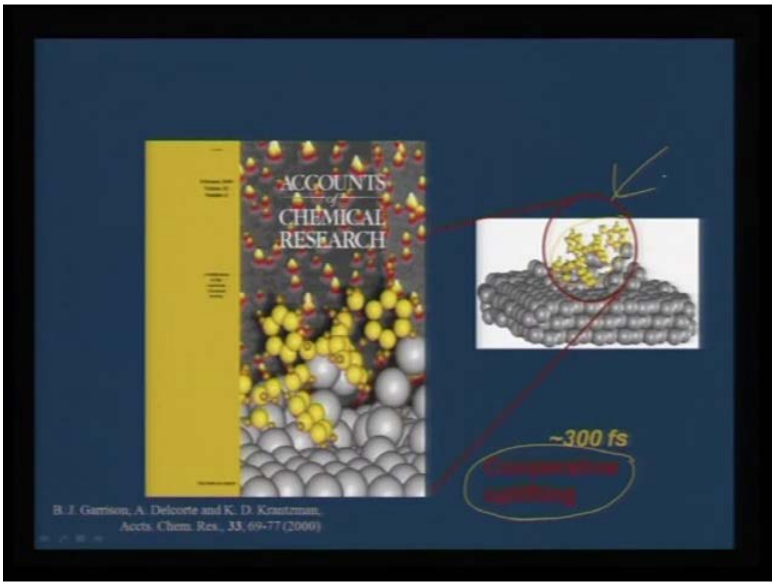

B. J. Garrison, A. Delcorte and K. D. Krantzman,
Accts. Chem. Res., 33, 69-77 (2000)

So, SIMS is a very good tool to study the nature of occlusion and this is has been actually published in accounts of chemical research. Unfortunately I am not able to show you the animation for this, but what is actually told, is that these are actually coming out as tetramers in the mass spectroscopy. So, when there is sputtering happening they do not come out as individual molecules, but they actually come out as tetramers. So, simple sputtering, but then this the notion of sputtering is actually used in a characterization tool, where it is not actually forming any film. But, it can become a very useful tool to analyse the selectively how adhesion is happening between a inorganic and polymer interface. So, this is a very good example where sputtering has proved to be a useful tool, to analyse the mechanism of adhesion.

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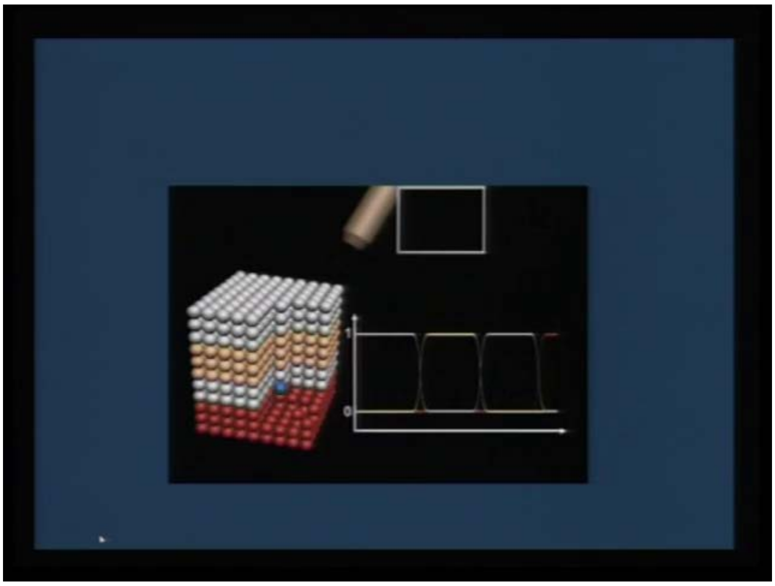

And this is a cartoon that will tell you, how we can map this what you see in this cartoon is a multilayer, with the different scales of atomic layers. And as you see here, when your argon ion is actually used to sputter the surface, first this top layer is getting etched or removed and in that case, you see both the layers actually coming out. Now, once the sputtering goes to the second layer you can see the first layer is actually coming down and the second layer is picking up.

You would see, as the grey scale top layer is vanishing and once the organ starts, hitting the second layer. The progression of this graph would change you can see that now the top layer is actually coming down in intensity whereas, the second layer is actually growing in intensity it is actually plotted in zero one scale. So, that gives a measure of the thickness of your first layer, how much is there and then you can keep going further because your second layer is going to deplete and the third layer is going to come.

So, this second layer which is actually showing maxima is now going to decrease as you see here, it is decreasing and the third layer is actually picking up. So, this is a depth profile that we can use sputtering to evaluate the thickness of your multilayer, and also it will tell if it is a inhomogeneous growth, then there will be a mixture of two things happening. So, the profile will tell us whether it is a very sharp interface or not the way it is going. Now, the red layer is coming out then you can see that that is picking up. So, this is the principle by which SIMS is used, secondary emission ion mass spectroscopy is actually a very nice tool. Where actually sputtering is the underlying principle that is used for evaluating the composition of different metal ions present in you sample.

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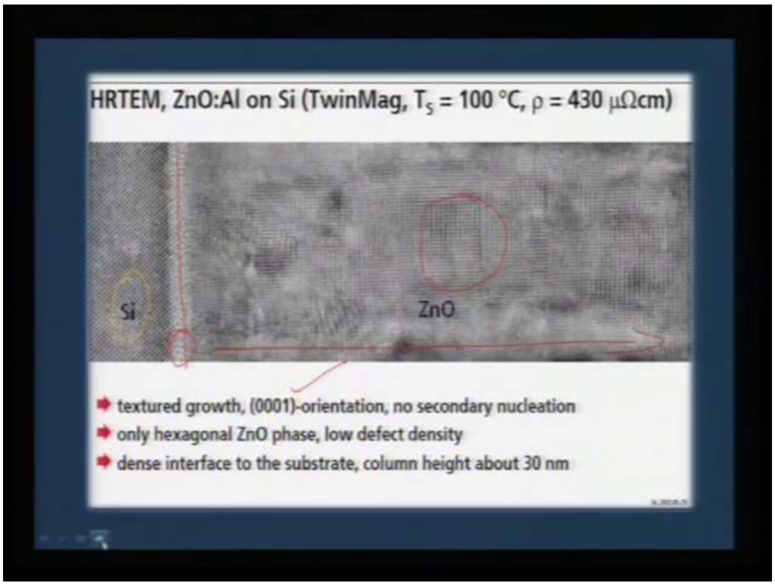

HRTEM, ZnO:Al on Si (TwinMag, T_S = 100 °C, ρ = 430 μΩcm)

- textured growth, (0001)-orientation, no secondary nucleation
- only hexagonal ZnO phase, low defect density
- dense interface to the substrate, column height about 30 nm

There are other useful examples, where sputtering is not merely a assisting tool, but it is also a very good processing tool. Here in this case very nice interface between silicon and zinc oxide is shown here, this is the interface and as you would see the there is some problem between the silicon and the interface. And this is mainly coming due to silica that amorphous silica is there, never the less once the zinc oxide starts growing over the thickness range you can see how oriented zinc oxide planes are placed.

So, you can get a textured growth along this 0001 orientation, no secondary inclusions are there only hexagonal zinc oxide phase with a very low defect density is there. So, sputtering can be used for oriented films. And this is again another example, where you can try to deposit zinc oxide with ease even in a different contour of your substrate. So, you can see in this depth also the TEM is given, so you can very clearly grow a uniform zinc oxide film.

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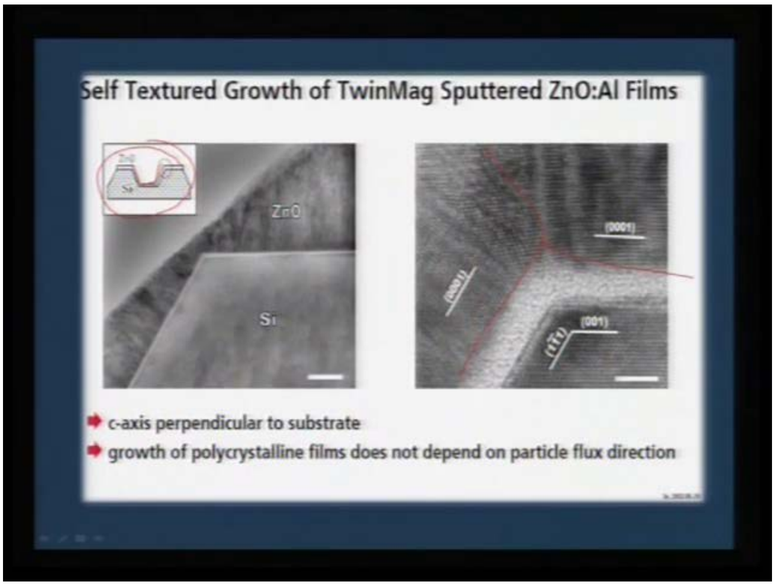

Self Textured Growth of TwinMag Sputtered ZnO:Al Films

- c-axis perpendicular to substrate
- growth of polycrystalline films does not depend on particle flux direction

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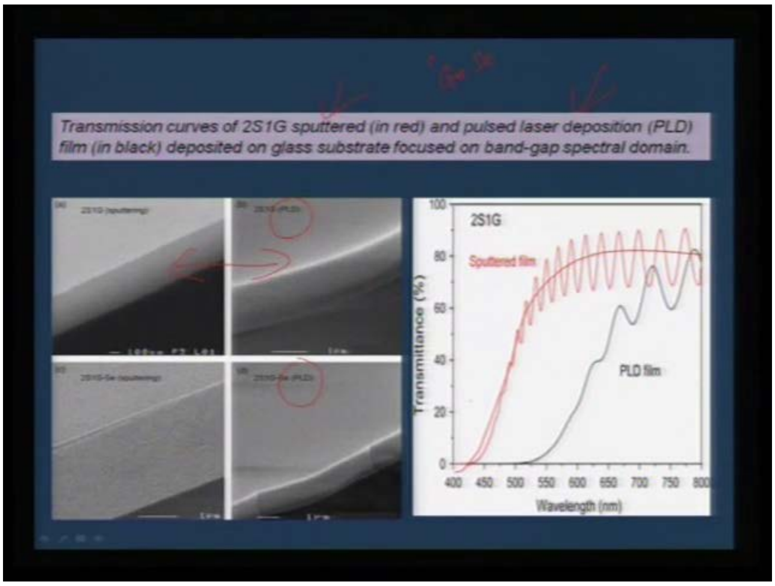

Transmission curves of 2S1G sputtered (in red) and pulsed laser deposition (PLD) film (in black) deposited on glass substrate focused on band-gap spectral domain.

And here is one cartoon just to give a comparison between where sputtered film, stands in comparison with other sophisticated techniques. For example, the most competing one along with the sputtering is PLD. Because, PLD can also be used for variety of materials and a comparison between the PLD deposited and the sputtered film, does give a impression that almost same roughness is there, and you can grow a very good film.

But, nevertheless it is interesting to see from the transmittance for this particular germanium selenide film that the transmittance is much better in the case of sputtered film. Because, you get a transmittance of 80 and it is really showing, a very steep fall compared to PLD, what it means is. Although PLD shows the roughness to be minimum, but then the transmittance is a good measure of the quality of the film and also the germanium and selenium ratio, and looks to be that the sputtered film has a much better chemical homogeneity, as far as this particular system is concerned.

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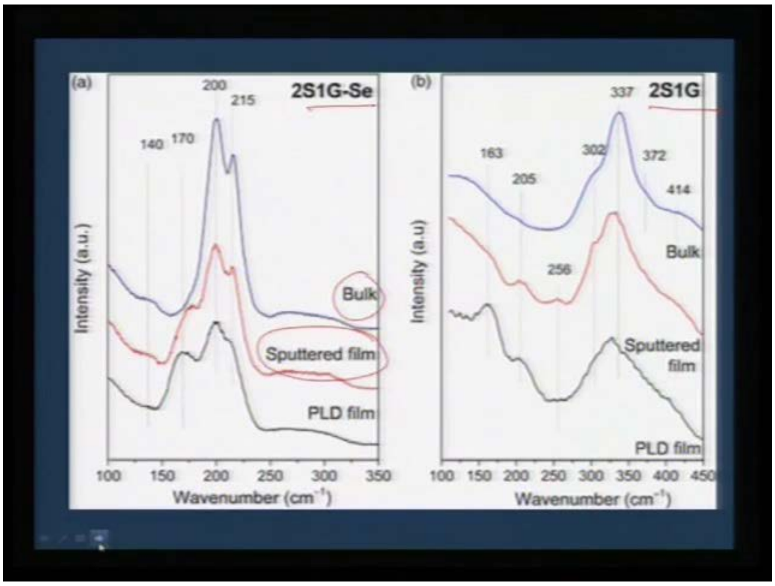

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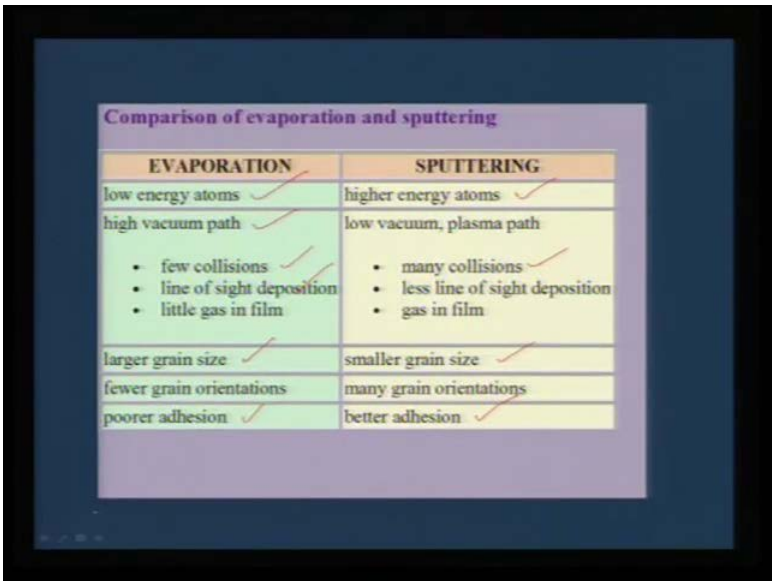

Comparison of evaporation and sputtering

EVAPORATION	SPUTTERING
low energy atoms	higher energy atoms
high vacuum path • few collisions • line of sight deposition • little gas in film	low vacuum, plasma path • many collisions • less line of sight deposition • gas in film
larger grain size	smaller grain size
fewer grain orientations	many grain orientations
poorer adhesion	better adhesion

And again the Raman spectra for the same, germanium selenide which is compared these sputtered films shows the Raman signal, which is much more closer to the bulk compared to PLD. So, in terms of the efficiency sputtering a sputtered film seems to be of a comparable quality compared to PLD.

So, just want to make one last conclusion or comparison between evaporation techniques and sputtering. We have seen one example of PLD, something similar in nature to sputtered film is the evaporation technique, where you take any metal to near to it is melting point because of the vapour pressure those are actually driven to the substrate and they form a film. So, in evaporation technique also you can either get a nucleated growth or a two dimensional growth, depending on the material.

But, one would see that compared to evaporation sputtering has it is own advantage, what are they in evaporation they these are actually the ions that are coming are of low energy. Therefore, it is a milder technique whereas, in sputtering the atoms that are coming out of the target are of higher energy, and even vacuum path you can see very few collisions and line of sight deposition is there.

But, sputtering is a many collision process. So, it is a momentous growth process and look at the texture of the film this is of larger grain size, smaller grain size therefore, the surface roughness will be much more lesser in sputtering compared to evaporation and you get a very better adhesion compared to evaporation technique. So, in many ways sputtering technique has it is own advantage, and they ease with which we can sputter brings about a extremely new and costly improvisation, where we can actually go for a combined technique, where sputtering can be the basic tool, but we can achieve several multilayer structures also using sputtering without much intricate instrumentation.

So, we have seen on the whole starting from a high vacuum technique that is MBE where we work at very high, vacuum deposition to one of the lowest vacuum rated deposition tool that is sputtering. In sputtering usually we play around at millitorr whereas, in MBE we are working at a very high base pressure. So, between these extremes we have seen, several issues that confront the film growth or material processing. And one can use this to the maximum advantage, specially sputtering technique mainly, because of it is versatility where we can go for a very large area deposition. So, with this we can stop.