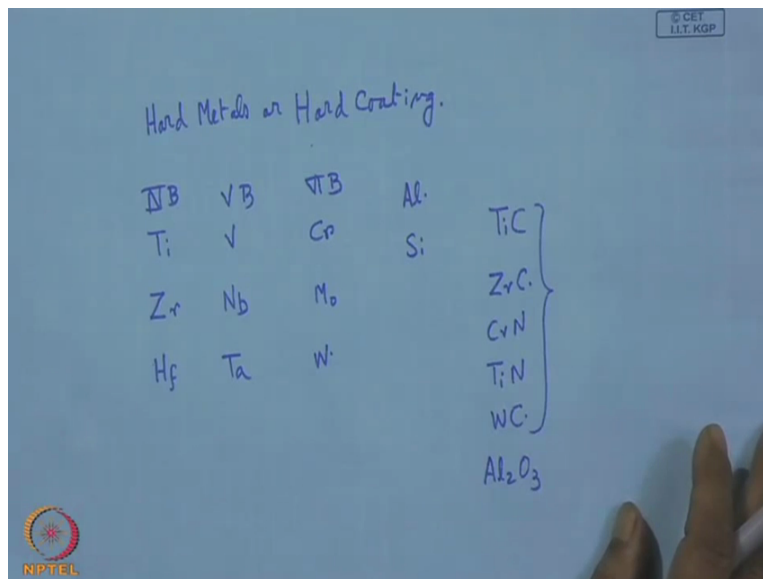


**Technology of Surface Coating**  
**Prof. A. K. Chattopadhyay**  
**Department of mechanical engineering**  
**Indian institute of technology Kharagpur**  
**Module 1**  
**Lecture no 12**  
**Reactive evaporation depositions**

Reactive evaporation depositions. We already know of the simplest and oldest process and what we have seen further to this that using a filament made of tungsten or tantalum as a heating source as a resistant heater, it will be easy to evaporate some low melting point metal or alloy and that is just for metallisation purpose but if we like to have wider use of this evaporation process.

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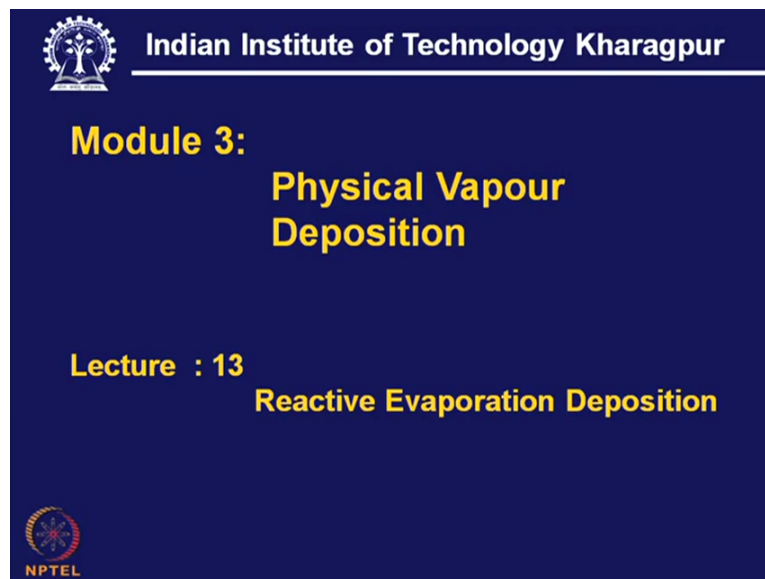



Say for example we are interested immediately in interest may be directed along this use of this what we called hard metals or hard coating and we know that it is needless to say that this titanium, zirconium, hafnium from group 4B 5B we have here vanadium, niobium, tantalum and also here we have 6B chromium, molybdenum and tungsten in addition to that we have aluminium, we have silicon for example, so what will be our goal from the engineering point of view to have one of the compound or what we know as hard coating that if we can produce out of this metal and that is no more this element but these are the carbides, carbides of all those bearing aluminium or we can have nitride, we can have boride or even oxide.

So the question comes here and if we are interested in titanium carbide or zirconium carbide or chromium nitride or titanium nitride or tungsten carbide, how we can deposit this thing or say for example aluminium oxide something like that so these are the material of immediate interest because they have those required properties means hardness, high temperature hardness, wire resistance, low friction many of those can offer low friction and high wire resistance and most importantly chemical stability, oxidation resistance and so many properties which are definitely attractive from the standpoint of mechanical function of this material.

So the question here rises whether we can use this evaporation, evaporation process that means this vacuum evaporation followed by condensation and deposition whether we can apply directly those processes for this kind of compound which are found by this group of elements and that is the point to be noted and considered.

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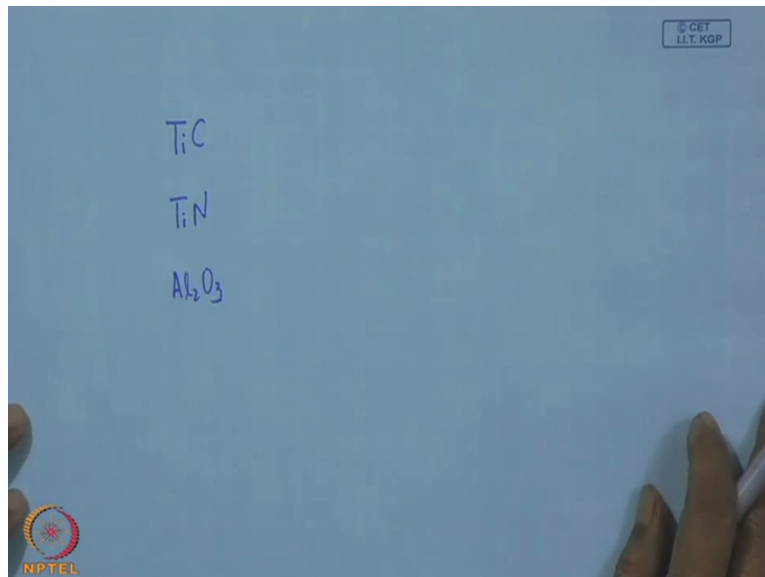
**Module 3:**  
**Physical Vapour  
Deposition**

**Lecture : 13**  
**Reactive Evaporation Deposition**

 NPTEL



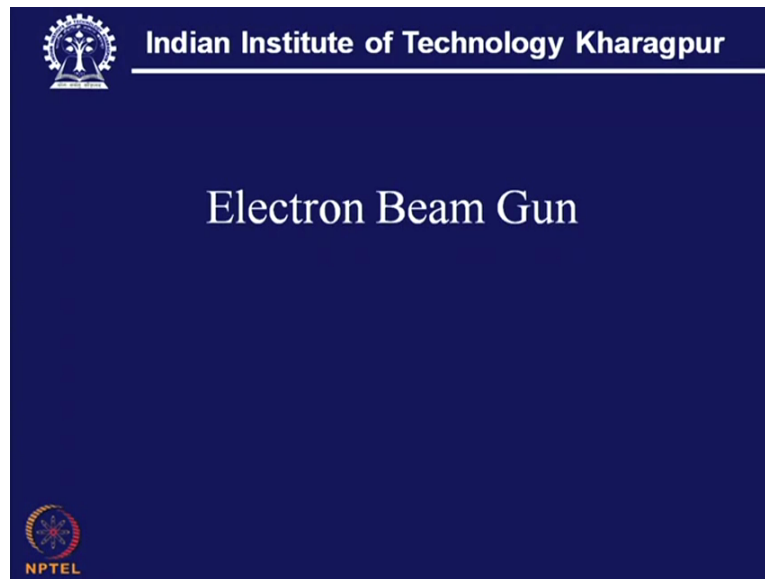
## Direct Evaporation



So here what we find that reactive evaporation decomposition but 1<sup>st</sup> of all let us look into the direct evaporation, so direct evaporation means here that we have to have a heat source, heating source and in that case directly this will be evaporated or titanium nitride will be evaporated or aluminium oxide will be evaporated but here the question is that this material must melt and then starts evaporating that means it can be straight solid to vapour or solid, liquid to vapour this path also it can follow but the main issue here is the energy density or the power density of the heat source.

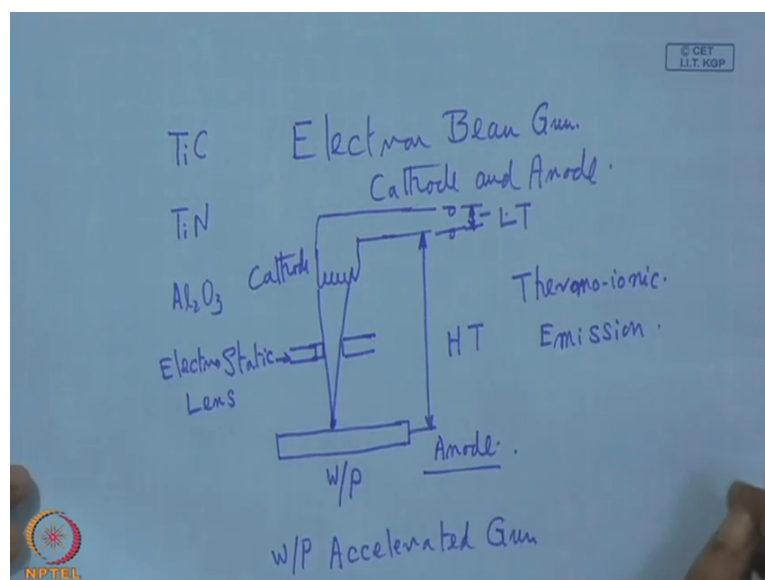
Now in this case what we find that normal filament, simple filament which are very simple in their construction it can be in the form of a boat or a foil or it can be a wire forming a basket within which we can place a crucible but this will not give the required power density for melting or vaporisation of this thing and as a result the process is limited by its power density.

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Now here comes the electron beam gun, so this electron beam gun as a replacement of this filament which can be a foil or it can be a wire, that electron beam gun that means it is actually an electron emitter, so this electron emitter will have emission of electron and which will be finely focused on the surface of the substrate or the surface of the material to be evaporated and in that case we expect a high power density and that can be used for melting and evaporation of the material.

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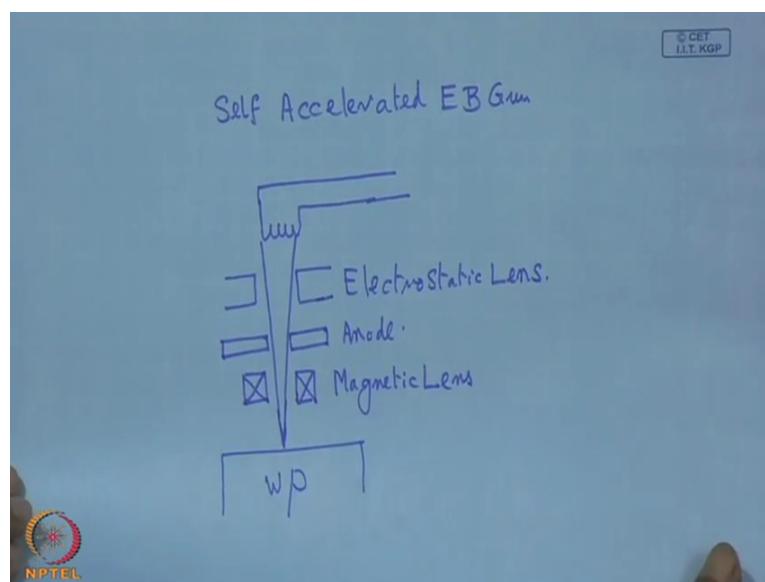


So basically this electron beam gun, beam gun it is actually it consist of just cathode and anode these are the essential elements in the construction of this electron gun, so we can put it like this. Say this is one wire here in the form of wire and here we have what we call this

substrate or the workpiece, this is the workpiece and here what we have? This is called workpiece accelerated, workpiece accelerated gun and between this 2 we have low tension supply, so between these 2 we have LT supply but between this 2 we have high tension supply, so that is the high tension supply, so this is just for heating this oil or this wire and because of this there will be thermo-ionic emission.

Thermo-ionic emission and with this emission, we can have a finely focused, so this is just like a focusing coil, it can be an electrostatic lens, electrostatic lens which will do the necessary focusing and through this we can have this beam which is finely focused and that will be useful for melting or evaporation of this, so this is actually workpiece accelerated gun that means the high tension is applied between this cathode, so this is cathode and this is going to be the anode in this case.

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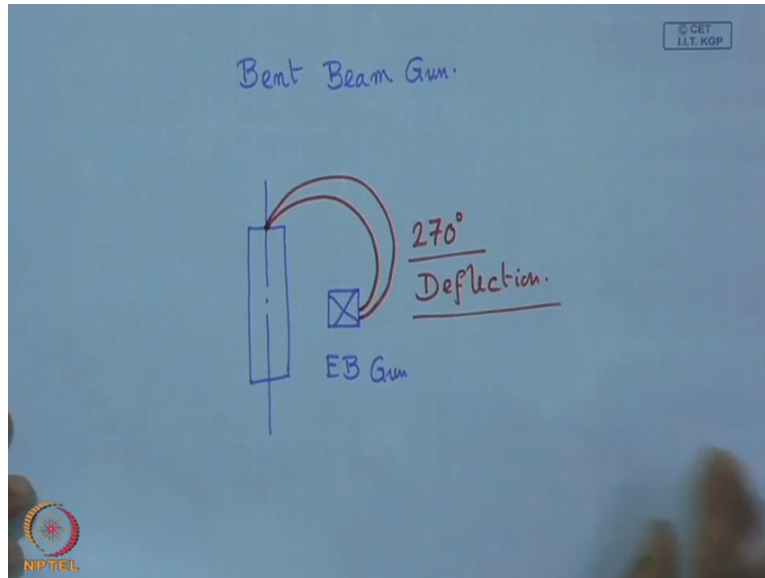


You have another option that is called self-accelerated gun, self-accelerated gun EB gun, so in this case we do have this wire which is functioning as the cathode and here of course we have the lenses focusing lenses electrostatic lens and then we have one aperture and through this again we have this focused beam and that can be incident, so it is an incidental beam and that is going to fall on this workpiece and here we can have one magnetic lens also that is for deflecting this beam, so this is magnetic lens and this is just one plate with one hole one slit, so this is anode and this is one electrostatic lens.

So this this is self-accelerated electron gun, so the advantage of this will be that it can be, it is more flexible in in determining this deposition rate and the evaporation rate, so those are

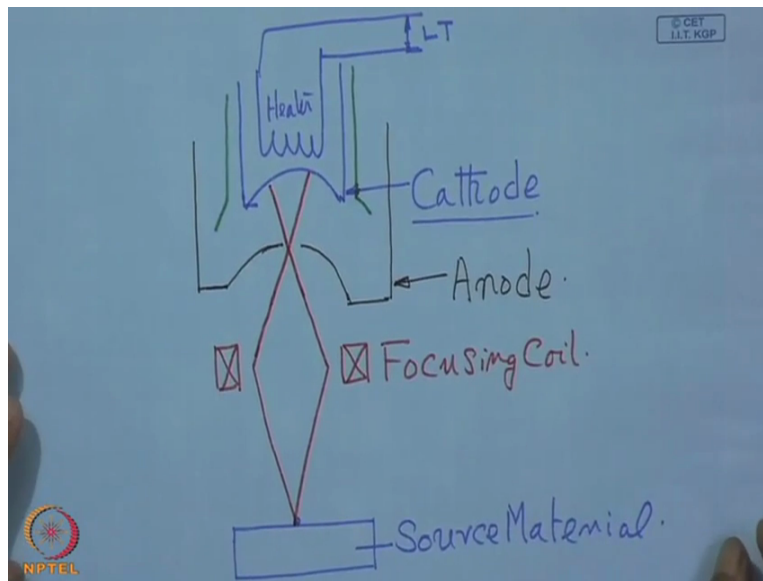
better handled by this and also this magnetic lens and be used for deflecting this beam, so over this inter-source we can have uniform melting and evaporation of the materials.

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So we have this electron beam gun and accelerated beam gun and then what we have what we call bent beam gun, so bent beam gun means suppose we have one source in the form of a rod. This is the material in the form of a rod and here we have this electron beam gun, this is the EB gun and here it is just not the focused beam will fall on the surface but it will be deflection of this electron stream that means this will be a something like this, so it is actually 100 270 degree deflection, it is 270 degree deflection that will be done to have proper location and focusing of this point over the surface, so this is one thing very useful for all this vacuum evaporation process, so it is call bent beam gun, it is also electron beam.

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Then we have what we called piercing gun, so here what we have just we have the cathode in the form of a disk and behind this we have the heater and that is also low tension that is low tension and here we have a shield, so this is the heater, this is the cathode and then what we have here we have shielding and then what we have here, this is actually the anode, so we can show this anode just like this, it is also have having an aperture in the central position something like this, so this is anode. So what we expect here that this electron beam that will emerge emit, it starts emitting from the surface and here we have the focusing coil and this is going to be the piece.

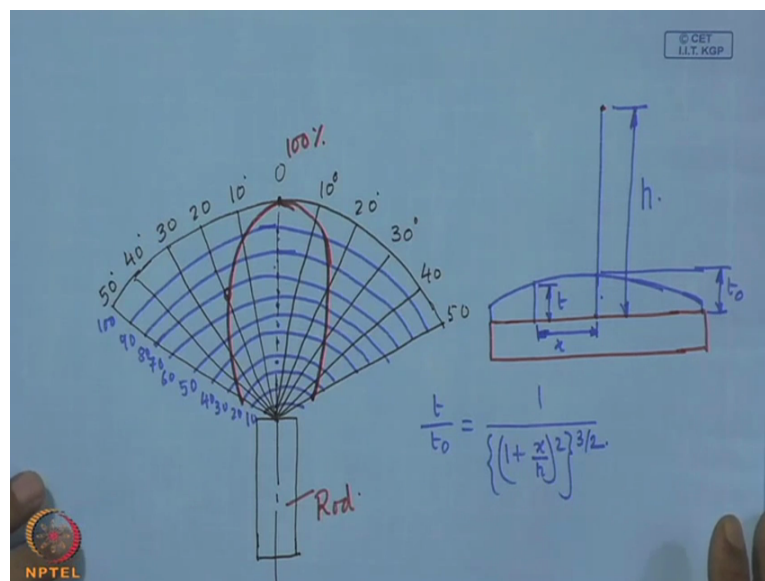
It may be the source material which is placed and that here it can be pinpointed and that is the source material which needs to be evaporated. So this is piercing gun which can be used for this evaporation purpose. So cathode, heater and between these 2 anode and this this heater, we can also have this high tension, so this will be just an emitter of electron and from that this will be finally it will arrive on the surface and do the necessary melting or evaporation. So this is about the use of gun, the main idea here is to obtain a high-power density and that is done by this electron gun.

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However though we use this electron gun but we are not free of 1 problem and that is the problem of variation of coating thickness.

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Now this can be illustrated one can immediately understand, suppose if we have just one rod it is a cylindrical rod and which is having this orientation, it is a vertical orientation and over that this is the distance over which, so this is the position and let us assume that this is 0 degree and if we just try to show that this is just we can have segmentation here, so 10, 20, 30, 40 and 50 degree, so that is the angle of divergences. Similarly we can also write we can also show in this direction, so this is also 10, 20, 30, 40 and 50.



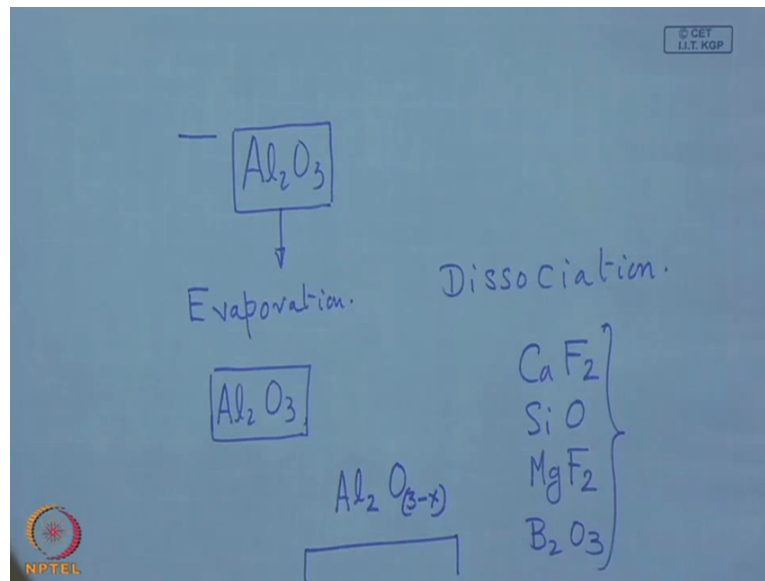
Now what we can show further to this, this is something interesting in that, so what we can see here that if we show with this diagram these are just subdivisions of this distance, this way we can see, so we have segmentation, okay we have this segmentation. Now if we consider this as hundred percent here, so this is just 10, 20, 30, 40, 50, 60, 70, 80, 90 and that is 100 percent. Now what is the significance of this diagram? Significance of this diagram would be evident if we just superimpose another distribution, so it will be something like this.

So this is so what we have shown by this red mark that is very important that means when it is just above this rod that is the evaporant, then just vertically above we have 100 percent coating thickness. Now when we have divergences of angle by 10 degree, it becomes 90 percent. When it is 20 degree it becomes, this is 80 this is 90, 70 and this is 60 percent. Similarly when it becomes 50 degree divergent angle then it becomes just 20 percent, so this way we can see the variation in thickness and this variation of thickness that becomes stiffer when we use an electron beam gun it becomes stiffer.

Now another way it can be also express if we have a point source and with that point source if we have a substrate here which is the receptor surface then we can also have this variation in coating thickness which can be also expressed by one relation and say this is the variation and this is actually the distance which is given by  $h$ , so that is the distance  $h$  and here the thickness is thickness is  $t$ , so thickness is  $t_0$ , so and say at a distance  $x$  from this point at a distance  $x$ , this thickness this is actually  $t$ , so another relation we can also write that is also given by  $1 + x^2/h^2$  to the power  $3/2$  and from this also we get another relationship that means this value of  $t$  that will be less as the value of  $x$  is increasing.

So this is actually a basic problem with this source but to improve this situation little bit what can be done? We can have some gas scattering by introducing argon gas and thereby it will be no more a line of sight and at the same time we can have some kind of mechanical movement, it can be reciprocatory, it can be a rotary, it can be a sun planetary moment, it can be 3 stage or 4 stage rotation that means sun, planets and satellite moment, so within the system it is a mechanical device mechanism which can be incorporated to improve this so called stiff variation in coating thickness and that can be properly handle. So this is one dimension of the problem however what we find limitation of direct evaporation. What we mean by this?

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That means if we are interested say for example aluminium oxide coating direct evaporation that means this material will be melted, evaporated and then that will again be deposited, it will arrive on the surface of the substrate there it get condensed and finally it is available obtained in the form of a film. So solid to solid, so it is solid in the bulk form and now it is the solid in the film form in the coating form, so this only its formation changes but it remains solid. Now there are some of the materials, so what is the requirement? Requirement is very clear on one side we have evaporation and on the other side we may have unfortunately disassociation.

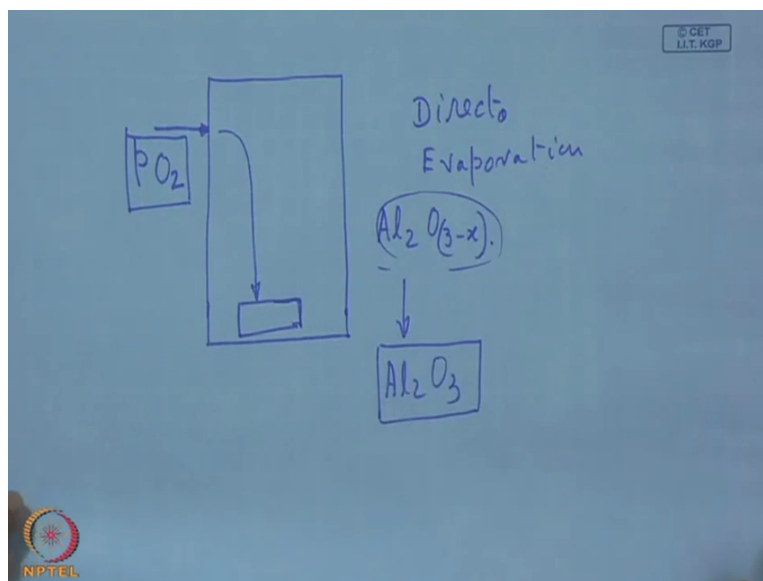
Now the temperature in question, where this evaporation takes place it depends upon also the vapour pressure and the material, basic material property, so once we know this thing at any cost this evaporation point that should not be above this dissociation point that means evaporation temperature should be always below this dissociation temperature otherwise what is going to happen? This aluminium that will split, this aluminium and oxygen that will that is called fragmentation and then they will arrive here as aluminium and oxygen and they can combine and during this combination that is the point where we may face problem.

We have seen there are certain materials say calcium fluoride, S i o then magnesium fluoride, B 2 O 3 boron oxide these are some of the materials means there can be many more but this is just by way of illustration what we can, what we like to say here that for this material, we can handle this evaporation very easily and this dissociation will not occur and it will not create any problems, so evaporation can be done very easily much before the dissociation takes place but for other material this is not that easy and in that case what we can what we end up

with say for example aluminium oxide when it is a solid, it undergoes evaporation and finally it comes like a condensed on the substrate and there we have it is no more aluminium oxide but it is aluminium  $Al_2O_3$  minus  $x$ .

So this is actually the final outcome if we go for this direct evaporation and that is becomes the basic problem and root of the problem is obvious that means the sticking coefficient of oxygen evaporation rate of oxygen and then the ability to combine with the surface, so these are the basic things which are actually responsible for this substoichiometric result on this aluminium oxide, so this is actually a major issue.

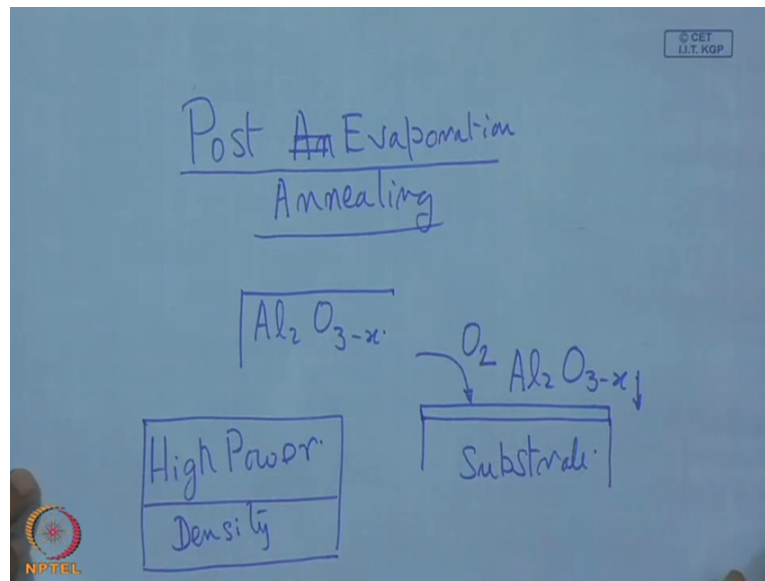
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Now to get rid of this what is normally done? Normally what is done, we have to have one chamber that is the evaporation chamber and within this evaporation chamber what is done, we have to inject  $O_2$  while this aluminium oxide is being evaporated, so this deficiency of oxygen during this condensation of this aluminium oxide what we see from that, so this is the substrate, so this oxygen will arrive here and that will actually make up this deficiency of  $3$  minus  $x$ .

So we need to have supply of  $O_2$  with a with a controlled partial pressure so that ultimately when it is a direct evaporation though it is a direct evaporation finally we end up with just not with this one but  $Al_2O_3$ . This is one way we can handle this problem another one is what we called so it is supply of  $O_2$  in a controlled manner that means with a controlled partial pressure, so here  $p_{O_2}$  has to be properly determine and that should be admitted to have to make up this deficiency.

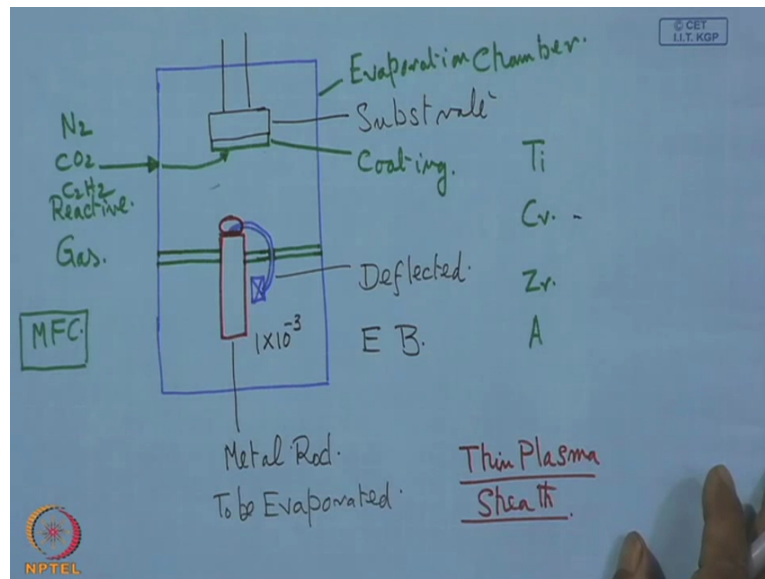
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Another one is called post annealing post annealing, so post evaporation annealing so this is also not uncommon and sometimes it is done also, so  $Al_2O_{3-x}$  so that will go, so that means this is a coating which is having... this is a substrate and this is a coating with  $Al_2O_{3-x}$  and here on this we have... this is done after this deposition, here also we can have supply of  $O_2$  so that this  $x$  value will fall and it will come to 0 and finally we get a  $Al_2O_3$ , so this substoichiometric formation of the coating that is one of the major problem.

Another one also we cannot just ignore this that means melting of this compound which is ceramic already known for its high melting point and other characteristics, so for melting and evaporation what we need? We need high power density, so for those we need high power density and sometimes it may not be that convenient to handle this thing, so for that what we need? We need another process what we call reactive evaporation. So this reactive evaporation what can be done in this case?

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We can have a material in this form say this is the vacuum chamber and here what we have? This is the feeder rod that means the metal which you need to evaporated and that is fade in this way and here this is actually a separator, so the separator is useful in that, so here what we have? We have one electron gun and with this electron gun we can deflect this beam and it will be allowed to pass through this slid and this is a separator and this separator is used and here what we have in addition to this? This is actually the substrate, say this is the metal rod, metal rod to be evaporated and that is the deflected electron beam.

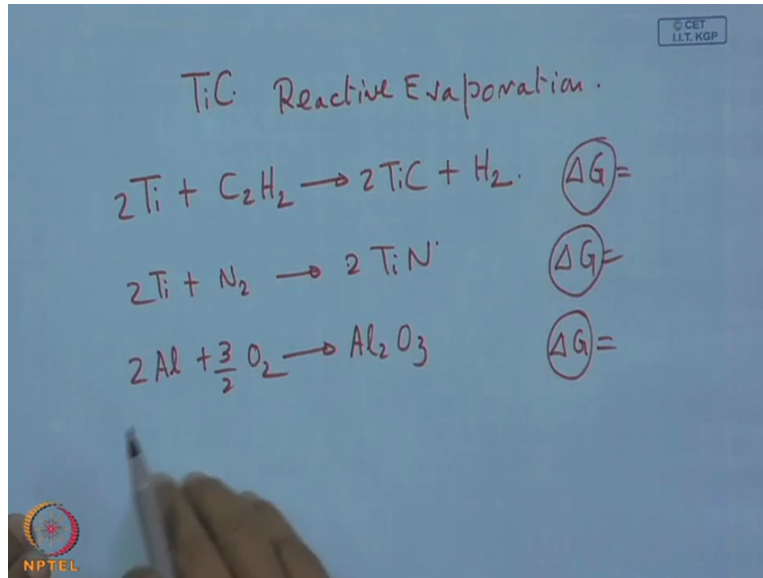
Now here we can maintain 2 pressure because this is the electron gun and where we need the pressure of better than  $10^{-3}$  but here to have now to have this evaporation it is just not evaporation, it is actually reactive evaporation, so what we need here this deposition of the material and this is just the coating and this coating may be this is the metal and from this side we have one reactive gas. Reactive gas, say we can say we can have here for example titanium, chromium or zirconium or even aluminium say for example and on this side we can have a reactive gas it can be  $N_2$  it can be  $CO_2$  or it can be  $C_2H_2$ .

So when this we can have a reaction the vapour is actually arriving here and this gas which will be admitted that will also arrive here and as a result we expect reaction to occur on the surface and definitely with that we can have a reaction product that means it is a reactive layer of this compound and which need not to be directly evaporated. Obviously what we have to have, control of this partial pressure, so naturally this one it has to, it must have this is the vacuum system, so this is actually the evaporation chamber.

So what is to be maintained here all these gases which are admitted for that we need MFC that means the mass flow controller which will allow the calculated quantity of material into this chamber and at the same time the pressure is maintained on the downstream side by proper throttling of the valve on the downstream side followed which following which what we have all the entire vacuum system, so here actually we have a pool of material. In fact since it is the electron so what we have in case in this case we have a thin plasma sheath, so on this top of that on the top of that we have a thin plasma sheath just in this top of the molten pool, so it is actually a pool formation, so here we have a thin plasma sheath so this way we can also have reactive evaporation. So this will solve our problem and we can get very easily the coating of choice and which can be mostly comes from those compounds of the hard metals.

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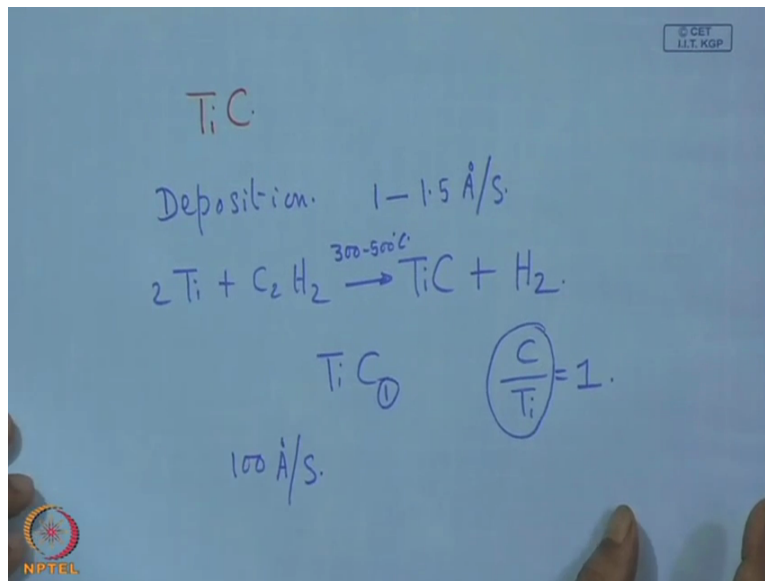




However the problem this reactive sputtering whatever we have just now discussed, this is also not free of problems. Free of problem mean say we are interested in deposition of TiC by reactive evaporation, so obviously most reasonably we like to have this titanium vapour plus say supply of acetylene and that can give us 2 TiC with liberation of hydrogen. Experience shows but this way we can also have say Ti plus N<sub>2</sub> we can have 2 TiN. Similarly Al plus 3 O<sub>2</sub>, 2 Al we can also have Al<sub>2</sub>O<sub>3</sub>.

What is really important here delta g of all this reactions this delta g this value so whether this value is highly negative or not so highly negative that will give a clear message clear information with what ease, it is actually the ease or difficulty of the reaction we have to carry forward the reaction in this direction, so whether it is the ease of the reaction or the difficulty of the reaction, so here this delta g value we have 2 determined for each reaction considering this pre-energy change from this side to that, so which one is stable, so these issues must be taken into consideration. Now when that is decided we can see that whether it is easy to have this reaction or it is just really difficult to have such kind of reaction or formation of the coating.

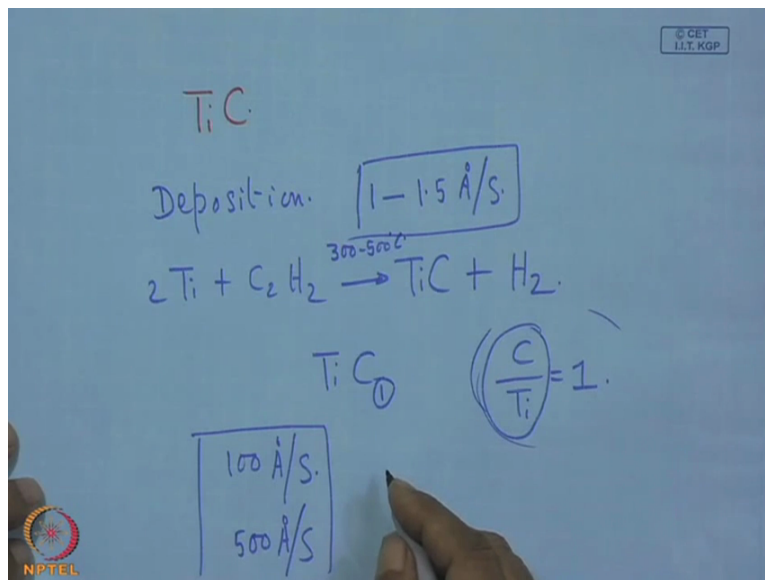
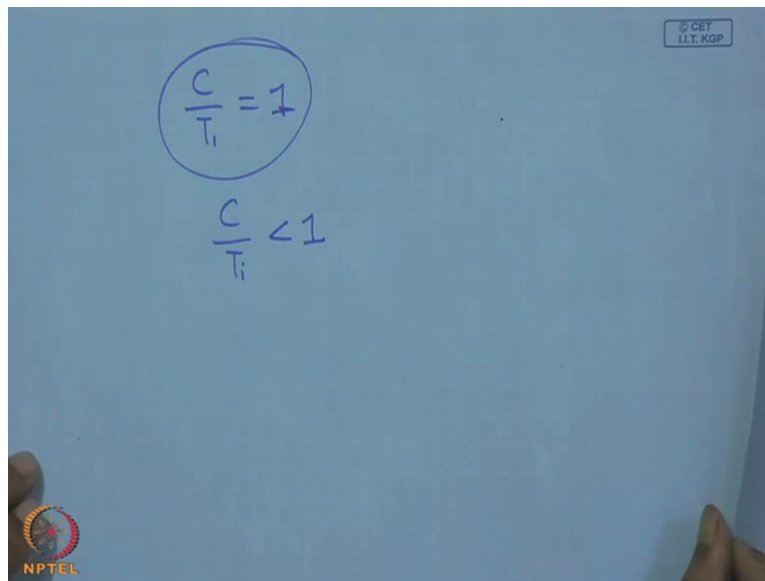
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Experience say that from this all investigation that there is getting TiC with a lower deposition rate, low deposition rate. Low deposition rate say for example 1 to 5 angstrom per second this is a low deposition rate and that is possible just by this Ti C 2 H 2, 2 Ci and this is TiC plus H 2 that is possible in the range of 300 to 500 degree centigrade and with TiC that means this value is 1. So we here C by Ti that is equal to 1, so that is of our immediate interest that ketone to enone ratio whether that is one or less than 1 but now if you like to push this deposition rate, so here it is 1 to 1.5, suppose we like to push it in the order of say 100 angstrom per second or example or it can be save in 500, then that is the beginning of the problem and there we to push this thing we have to also increase the rate of evaporation of titanium here and also the flow rate of C 2 H 2 that is also that has to be also done.



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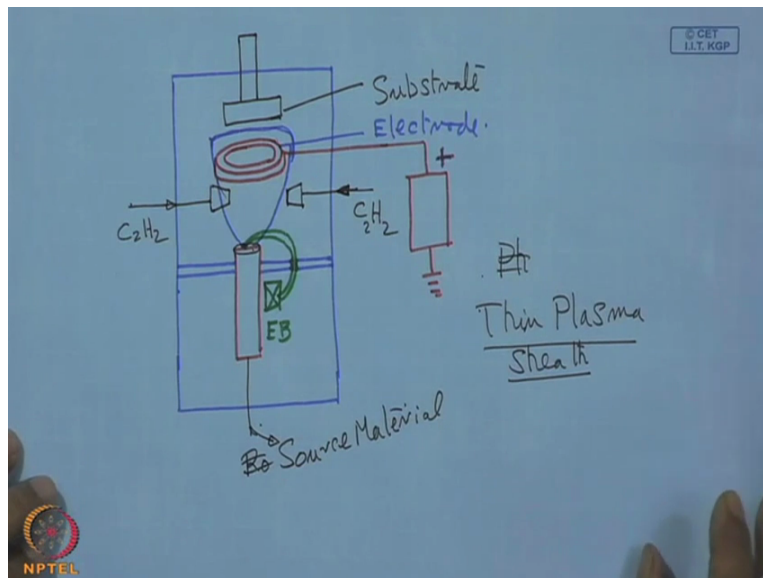


But in this case our experience is that with that we never get a C by Ti equal to 1 but this this hardly we can achieve but in most of the cases that is going to be less than 1 means in this case the free energy of formation of the activation energy that is not favouring the formation of this particular titanium carbide and for that we have to find out another path or another route to solve this problem and that is known as activated reactive evaporation. That means in simple language what we have to do here that to activate those things that means ionisation of this metal and gas. In this case what we see it is just in the atomic state, this reaction is going to take place, so this is thermally activated.

Now what is done in this case, we can also mention that if we like to have this is in this may be with such a high rate compared to this is a very low rate and this is reasonably high, so in

that case if we like to have this kind of thing, we must increase the temperature but then the basic purpose of this PVD say evaporation that is actually lost because here the whole idea is not to raise the temperature of the substrate which are temperature sensitive and in that case the we cannot handle the substrate and the substrate will be damaged thermally, so that is just not possible.

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So we have to we (43:46) to activate the whole process and that is known as activated reactive evaporation and with this activated reactive evaporation, we have to have certain modification in the evacuation chamber, so this is the evacuation this is the vacuum chamber or say this is the deposition chamber, so here we have a separator so here we have the rod that means the feeding rod which is supplying the stream of metal and then we must have the

separator here, we have this slit and then what we have here we have this electron beam gun EB and with this EB we can focus this stream and this is actually a bent beam gun, so it is focused here and the location of the substrate, substrate must be also located here that is the location of the substrate, so this is the location of the substrate.

Now what we have, here we have one like it is like a burner which is supplying this gas, so the gas can be admitted from this side and here we have a burner like thing. So it is something like a burner from each side we have this burner, so this is actually radially arranged. So gas is supplied radially so this is actually the front view, so this is actually the supply gas that means this reactive gas, so this reactive gas is supplied radially from each direction, so this is the supply of the gas but what is important here that here we must have one electrode and this is this looks like ring, it looks like a ring that means this is almost like a ring.

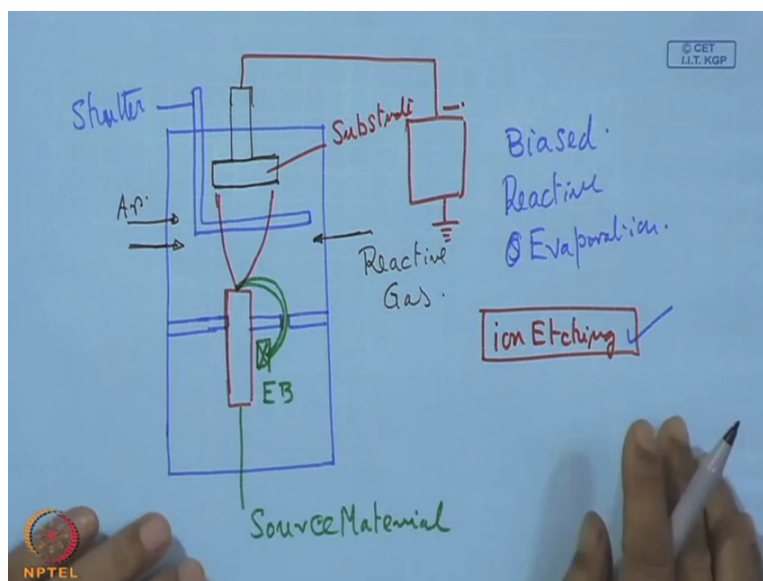
This is one electrode which is actually positively biased, so gas supply this is actually the substrate, so only the thing what has been changed here, modified that this is the actually the source material, so that is the source material, so this way what we can see here that this electrode which is positively biased that means what we have in here, we have a plasma sheath just here we have a plasma sheath, thin plasma sheath and there we have this secondary electrons which will be drawn in this reaction zone, so this is actually the reaction zone, so what we all so want to like to have that means in this zone, in this zone that is actually the reaction zone.

So here what we like to have this stream of metal vapour and the stream of this reactive gas those will have some kind of collisional ionization that means this electrons secondary electrons at will be drawn in this reaction zone by this positively biased probe and that is one electrode, so this is electrode, so which is going to have which is going to attract the secondary electrons, low-energy electrons here and this electrons while it being attracted they will have collision with the stream of metal vapour and this gas thereby it can be ionised.

So both this reactive gas it can be it can be acitlyn, it can be nitrogen, it can be hydrogen sulphide, it can be even carbon dioxide whatever may be the ultimate compound we are interested in that get will be also ionised and in this ionised form their ability to react that will be easy and then it simply facilitates this reaction to occur at a much lower temperature which otherwise could not have been possible. Had not been only thermally activated, so by this what we are doing, just by bringing a probe, okay by just bringing this probe what we are

going to do here, just getting the secondary electrons which ionises this reactive gas and this stream of metal vapour, so in that ionised state this 2 reactive spaces has a better chance to react and with the formation of stoichiometric titanium carbide even with a high rate. So that is the advantage of activated reactive evaporation.

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Now what we have also biased evaporation, in this biased evaporation what we have, we can also have little modification of this chamber, so we have to have the vacuum system here also we have the separation this is the partition we do have here this feeder rod that means the filler material which can be evaporated by this electron beam and this is the electron beam which will be deflected through 270 degree, so this is EB that is the source material, so it is

separating to chamber and here at the top what we have that is the substrate placed and here we can have either reactive gas or it can be just gas also another gas for this plasma.

So this is reactive gas and also we have admittance of argon which has to be used for initiation of this plasma. Now what is the specialty of this process? Here of course the substrate has to be negatively biased. Substrate, so this is the substrate so we have this vapour flux which can go on this side however what we can do just by negative polarisation, we can also have this argon ion which will be splitted by this secondary electron this is the cell this chamber valve if this acts like anode, then the secondary electron that will be attracted and in the process this argon neutral which is present here that will be splitted and this argon will be splitted as so into electron and argon ion.

Now this argon ion and we attracted over the surface and it will do the necessary impingement, so it is going to strike the surface. Now what are those advantages? The advantages are many (53:39) number 1 it is very similar what we call ion etching, ion etching what we use in sputtering but this is not a sputtering, so material stream that is generated by this vapour flux by this by this electron beam however the substrate can be cleaned before evaporation, so in C 2 we can have a high-quality surface and is almost a virgin surface free of all sort of contaminant and also oxide layer and after that, so here reasonably we must have 1 shutters between these 2.

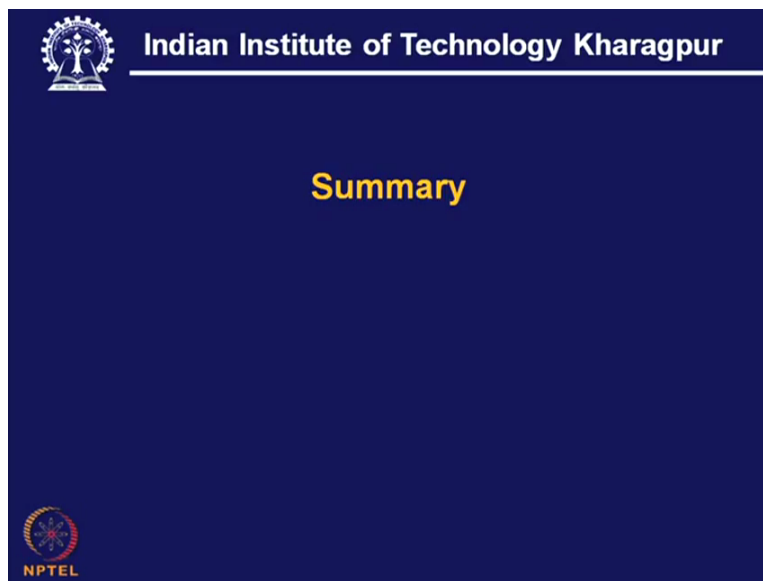
So this is going to be a shutter blocking this flow of flux so this is actually one shutter, so what can be done so at the very beginning this argon ion that will cause sputtering of the top surface of the substrate thereby that surface will be clean and that material may be deposited on the shutter, so once that etching period is over, we can remove this one and then this vapour flux that will be falling on the surface and this becomes a receptor surface but during this period also we can keep the substrate bias in but during ion etching the bias voltage will be more however during the deposition process buyers should be kept at a low rate so that sputtering, this deposited material which is evaporated and condensed that should not be totally resputted and the material should not be totally eroded, so during the evaporation process we can also have, we can also have some kind of substrate biasing and here we can have this argon ion impingement.

Here the whole idea is to have densification of the coating this is number 1 if there are some loose particle that can be also pulled out that can be removed from there and then also we can neutralise some of the stress for some reason if there be any tensile stress and also if it is

necessary some residual compressive stress of course in a very controlled manner that can be also induced on the surface.

So the whole idea here is that modification of the surface it is the same material which can be deposited without biasing and now with biasing we can have the basic morphology of the substrate whether it is a columnar grain whether it is an open column or porous column or it is a dense column we can also try to transform into (( ))(57:09) structure and energy available will be useful but this can be also extended for reactive sputtering, so reactive sputtering that will be also reactive evaporation, evaporation that means that is going to be biased reactive evaporation, so the material which will be deposited, this flux of metal and then we have the reactive gases and then we have this ion energy of this argon which is impinging on the surface and that will facilitate formation of this reaction product in the form of a film on the surface good and adequate property requirement.

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So in summary what we can summarise immediately that reactive sputtering is essential when the direct sputtering is difficult because of the lack of stoichiometry it is because of the simple reason that the metal and non-metal part, they cannot combine in the stoichiometric form and as a result there is a substoichiometric formation in the product of this evaporation and this can be handled by reactive evaporation but in some reactive evaporation what we have seen that because of this limitation of this reaction and the free energy restriction, the activation energy restriction, the reaction cannot be conducted with the result of stoichiometric formulation in that case by activate the materials in the ionic state this reaction can be conducted and this activation facilitate this reaction to occur. We have also seen that

this biased reactive evaporation or biased evaporation that helps by just ion impingement on the coated surface the film property and the morphology can be improved remarkably.