Technology of Surface Coating Professor A. K. Chattopadhyay Department of Mechanical Engineering Indian Institute of Technology Kharagpur Lecture No 18 Sputter Deposition of Nitride Coating

(Refer Slide Time: 0:22)



Okay today's topic is sputter deposition of nitride coating and this nitride, we mean the metal nitride coating of transition elements that means this titanium, zirconium, hafnium then we have vanadium, niobium, tantalum, tungsten, molybdenum and chromium. Now these transitional elements, they are known as good carbide former, oxide former, boride former and nitride former. Now these nitride coatings are well-known for their extraordinary

hardness, wire resistance, anti-welding property and so on. So these are extremely good candidate for all sort of mechanically functional surfaces, so that is well-known in art, so here the whole idea of this topic is to how to deposit this nitride of this elements by this sputtering.



(Refer Slide Time: 1:59)

Now sputtering means we have here 2 possibilities, say for example if we take titanium nitride as one example, then titanium nitride can be coated directly from a target and this target get can be made of titanium nitride as a powder metallurgy product and this is going to be a target. That means this will serve as a cathode for this sputtering device. Now here for sputtering this one we need adequate cathode current or say cathode power density which should be adequate for dislodgement and ejection of this titanium nitride in the form of a sputtered flux which will be intercepted by a substrate placed in front of it, so it will be intercepted by this.

However, the shortcomings are there these are the limitations, here we need high cathode power density that means cathode power should be quite high to cause this dislodgement and ejection of this titanium nitride and there should be another condition that this titanium nitride may also get dissociated during its flight from this target to the substrate and then it may combine. Now in the process it may happen, this is titanium nitride but it can happen to any of those elements and the compound forming this non-metal part which is nitrogen, oxygen or carbon and when it combines on the substrate surface, it may be deficient in this nitrogen, so we may end up with one such thing where x is less than 1.

So in that case we may need additional support or nitrogen supply within this chamber or post sputtering annealing of this compound, so that this deficiency of nitrogen can be made up in the post sputtering operation. So this we can identify 2 basic limitations one is requirement of high power density for the cathode and number 2 is that to get a stoichiometric compound of this particular metal when it combines with this oxygen, nitrogen, carbon or boron and that is why people have the 2nd option.

(Refer Slide Time: 5:25)



The option that means all these sputtered coating technologies, they have another option and that we know as advantage that is actually we call it is reactive sputtering. This is actually the reactive sputtering, now it has certain distinct advantage over direct sputtering, what are those?

(Refer Slide Time: 5:51)



Number 1 here we can illustrate this point if we have a simple sputtering chamber then instead of titanium nitride, just at the top we can have a cathode which is titanium and that is electrically separated and it will be connected to the negative polarity of the power supply and in front of it that is the substrate and this is also electrically isolated the chamber and this is also connected to this another power supply which has a negative polarity and this is also grounded, so this is negatively polarized, it is we know by now that this is substrate biasing which we may need before sputtering, during sputtering also but cathode should be negatively polarized from the very beginning and then what we have here, we have to admit argon from this side but in addition to that what we have to have, we have to have also entry of nitrogen, so there are technical peripherals, peripheral elements which should be added to the basic system.

So that metered quantity of argon and that of nitrogen can be admitted and the whole idea here is that, so whole idea is that when we have this sputtered flux of titanium, this is arriving here on the surface and at the same time we also expect this nitrogen which will be also on the side and there on the surface, on the substrate surface a necessary, a required reaction Ti plus N 2 that means this should take place and this reaction showed move in the forward direction and for that we need all the necessary things that means temperature, pressure then there is plasma excitation, initiation of the plasma and substrate biasing, so it is argon pressure, nitrogen partial pressure, polarisation of the main cathode that means titanium then polarisation of the substrate and maintaining the substrate with certain temperature.

So when we have a combination, right combination of this process variable, one would expect that this TiN formation that is going to take place right on the substrate surface and thereby synthesis of titanium nitride would take place and a titanium nitride coating architecture will build up on this surface, so this is exactly what we mean reactive sputtering. It is just by way of illustration in this case but it can be any nitride of hafnium, nitride of zirconium because these are the elements of group 4b and these are having the best chemical stability and that would be extremely useful for all functional requirements of this coating when it is put on a particular functional compound and or device.

So we understand here this is reactive sputtering and advantage of this reactive sputtering is that, in this case what we are having, so we are having here argon entry, nitrogen entry, polarisation and also what we have, we must have here one pumping system that means for evacuation, so this is just a module which should be attached to this. However, we must have proper temperature control because the temperature of the substrate that T, what we have shown here that T, this also should be properly monitored and more importantly the process pressure that means the pressure show there is a sense, there is a sensing element which is the pressure sensor and in addition to that just before this pumping system.

So this is the pumping system that is for maintaining this pressure pumping system here we must have one throttle valve, so this throttle valve should be motorised and this pressure sensor will send a signal and that is through amplification that will be fed here and so their it is going to be a motorised valve, so accordingly the throttle opening of this valve should be adjusted in in connection with the pressure p what is the said value? And it will this pressure sensor will monitor the pressure and that signal will be continuously fed this valve, throttle valve and this pressure is maintained, so this is one of the very important parameter of this whole process.

So this is just a schematic of this apparatus and in this side obviously we must have what we call MFC, we must have this mass flow controller on this side, so this is the mass flow controller this is the MFC for nitrogen and this is going to be the MFC for argon and on this side we supply from the bottle, from the cylinder that has to be arranged. So this is about the requirement of the sputtering apparatus, so the advantages is if we get back to this one, the advantage number 1 that this cathode current density that requirement is less in this case because it is just a metal and not a compound which is going to be sputtered.

So that energy, bond energy or the energy to cause this dislodgement and ejection that is going to be less than had it been just titanium nitride or any other compound and at the same time what we can have here that this can be graded structure and this graded structure means in this case, suppose this is the substrate, this is the substrate and on that substrate we can build very conveniently as per the requirement of graded structure and this graded structure simply means that over that it is just not a titanium nitride or it is just not a stoichiometric titanium nitride.

It can start with a nanometre level titanium, just a metallic titanium on this and gradually the percentage of titanium and nitrogen that can be properly controlled, so that finally it is going to be a graded structure with x value is gradually increasing and from titanium to titanium nitride, we can have a TiN x where the value of x, that value of x that will be gradually it will be keep on increasing and within this when we have a sufficiently grown layer and then this is just a, this is just a graduation of the property and over that very easily a stoichiometric TiN that can be built, so this is one of the greatest advantage of this reactive sputtering in comparison to a direct sputtering of a titanium nitride from a solid piece of titanium nitride cathode.

(Refer Slide Time: 16:43)



Now one issue that also can be considered here that means the requirement of this temperature, requirement of this temperature and that is one of the points of greatest interest and highest attention temperature. Now compared to CVD, when one compare CVD versus PVD immediately the thing what one should look for the temperature requirement, this is high temperature and this is low or moderate temperature. Now here what we understand this

is fully thermally activated and this is mostly plasma activated followed by little support from thermal activation that means if we consider this as the energy requirement for any reaction to take place.

In that case this is maybe 100 percent thermally activated and when we like to have one PVD process in PVD maybe we can find out that out of this energy requirement, we have apportionment and this apportionment maybe here and this part is because of the plasma activation and this is actually thermal activation and here the whole thing is thermally activated. So this is one of the greatest interest or attraction for PVD that this low temperature requirement is low and this particular PVD and in addition to that what we can say it is reactive sputtering which is very attractive and interesting process.

In that the temperature requirement is greatly reduced and this material or this process becomes very flexible in that it can take care of varieties of substrate material which are otherwise temperature sensitive. So this is one of the important issues which are properly addressed by PVD and in particular by this sputtering process. So this is important importance that is highlighted and during how to (())(19:34) issue or the subject topic, how this reactive sputtering, this principle which we have so far discussed, how we can put this thing in practice? So this can be done in this way we can have another illustration perhaps.

(Refer Slide Time: 20:00)



This is the target material target and just in front of it we have the substrate material, this is going to be the substrate, so this is substrate and this is the target and whole thing is placed within this chamber. Now how this process should start that is one very important thing, very

interesting thing, so just in front of it shutter is placed and what we are talking about, this is actually a single target machine, it is a single target but we can have conveniently we can have a single target machine, we can have a twin targets, dual target or a commercial 4 target machine, so that can be also conveniently used.

Now this is the actually the shutter, so how to initiate this process, so one thing one should look, careful look that that this entry point of this gas to initiate plasma or for excitation of plasma that is argon, that entry point or the point where it will be showered, so that is this shower or the nozzle will that should be placed very close to the target where as what we find that this entry of this reactive gas which is nitrogen or which can be CO 2 or some compound of boron but in this case it is nitrogen, it is directed and placed more towards the substrate. The whole idea here is that we want only titanium atom from this side and this will deflux will arrive on this side and nitrogen should be easily available very close to the substrate surface and this nitrogen need not to be placed near this surface of the target because it is not necessary and that the same time this is not also desirable.

The reason is as follows that if we have nitrogen on this side, we can have this target poisoning and we have immediately nitride formation on the target and then the sputtering rate and the requirement of energy everything will keep on changing and the whole principle or the idea behind reactive sputtering that will be totally (())(23:05). So here clearly the idea is that nitrogen should be available close to this surface of this substrate while argon should be very close to the target, so with this arrangement one can start the sputtering process and that, so this can be this power supply can be switched on this side, so this is negative polarity, there also we have a negative polarity. It can be RF or it can be DC or it can be even pulse DC that is one issue but this should be done by placing the shutter in front of this substrate, so now this shutter is separating the substrate from the target.

Now what we get now again this shutter this is a part of the body of the machine of the apparatus, so material ion flux that will be intercepted by this shutter, so this is actually what we call, what we call, actually target cleaning. So this is the 1st step, this is called target cleaning by this ion etching, so this is actually target cleaning, so this argon ion these are going to strike this surface of the target and it is actually a cleaning process, so if there be any contaminated layer for some reason that will be removed through this dislodgement and that flux is going to deposit on the shutter. At the same time what we can also do, now this argon should not be, nitrogen should not be injected this argon that can be also brought in on this

side and what is going to happen? That this side we have the shutter and at this point we do not have any activation of the substrate, so this is actually a passive substrate, it is not yet polarized. Now what we are going to do after this, after this actually the shutter will be removed.

(Refer Slide Time: 26:00)



So when we mentioned various steps of reactive sputtering of TiN, what we mean that step number 1 is target cleaning and once this is done say for 30 minutes or 15 minutes whatever may be the time span. After that this shutter will be opened or removed thereby what happens in this case now this ion flux is directed on the surface and at this point, we have to charge this shutter with this negative polarisation, so now with this negative polarisation what is going to happen? This titanium neutral that will become titanium ion and this titanium ion will be attracted towards the surface, so next step it is actually this flux of titanium ion that will be directed with towards this substrate by removing the shutter and here we have argon dislodgement by this this titanium dislodgement.

Say for example this is titanium target by this argon and then this titanium will be directed and since it is negatively polarized it will be titanium ion which will arrive with sufficient energy that has to be ensured that it arrives with sufficient energy and accordingly the polarisation that has to be also done. So it is actually the selection of this voltage which will cause that arrival of this titanium ion with sufficient energy and what it is going to do, very important step with this titanium this is called substrate etching. Substrate etching and we also call ion etching and this ion etching that we do that is done just by this titanium iron, so there are 2 things by this process the whole surface is less cleaned and other same time what is going to happen?

Now we have to produce a graded layer that means once these substrate etching that is done with the help of this titanium ion then actually we have to adjust this biased voltage of the substrate, biased voltage of the substrate, so that now no more ion etching should take place and there should not be a very seviour of vigorous ion etching, it can be mild biased so that the whole purpose of bias that is served but at the same time this titanium can deposit on the surface, so that is switching over to step number 3 and that step number 3 is now deposition of a layer of titanium, so this layer of titanium deposition that is the step number 3 and we are switching over from 2 to 3 just by changing the polarisation, the voltage that means this biased voltage which is required for iron etching and that just by reducing that one, so that this titanium is not just being removed or from this surface or driven out but it can be well-received and it can stick to that with mild biasing and with that we get a sub-layer of titanium and that is exactly called adhesion layer.

(Refer Slide Time: 30:39)



So this is the substrate, with the substrate we have actually a titanium layer and that is in nanometres level and on that actually starts the deposition of titanium nitride that means after few minutes of passing this titanium flux then it is actually the nitrogen which is which one can start admitting from this side, so it is nitrogen which will be also ionised and it is the continuous flux of titanium that is also arriving, so on the surface we have a titanium nitride.

So even if we compared this PVD, this reactive sputtering, this reactive sputtering, reactive sputtering process with a CVD, conventional CVD, if we reconsider then what we see here that directly say it is a carbide substrate, tungsten carbide and cobalt substrate, this is also going to be a tungsten carbide cobalt substrate, we can have by PVD, we can have by CVD but there will be difference is that, this is a tungsten carbide cobalt that is the composite over that, we must have a TiC and that TiC is just not a functional layer and this titanium carbide layer is a buffer layer which is just like a bridge between the substrate.

This is the CVD process between the substrate of tungsten carbide cobalt and the top titanium nitride and in between we can have certain thickness of titanium carbon nitride and finally we put this titanium nitride. What we see here? It is actually same tungsten carbide cobalt, it is a PVD process but we do not require TiC but what we require just a layer of titanium instead of titanium carbide on which we can have a deposition very easy deposition of titanium nitride and this titanium nitride is deposited on this buffered layer or adhesion layer of titanium.

(Refer Slide Time: 33:26)



So this way the various steps has to be carried out in sequence keeping all those parameters, parameters means this cathode voltage then the system pressure and also if it is an unbalanced magnetron and if provisions are there, then it is also the ion to atom this ratio of this incoming flux towards the substrate because it is very important to have one of the strongest interface which will be established just over the substrate surface and over this interface the whole architecture will be built. So this interface cleaning 1st is target cleaning that is on this target side, then using the target material for cleaning the substrate material then using that target material for having a nanometre level coating which is an adhesive layer and then finally switching over from this adhesive metal layer to the layer of nitride of that particular element, so we can find at least there are 4 steps in in getting this particular coating and in the 4th step it is actually the titanium nitride coating or any nitride of a metal coating that takes place in the 4th step.

(Refer Slide Time: 35:27)



Now important thing is the process variables, so here what we find that process variables are we can find out this is actually the cathode current, cathode current is one of the important process variables then comes the process pressure that means what is the pressure inside the temper inside the PVD chamber or the sputtering chamber, so this is process variable number 2. Number 3 as we have mentioned it is also the substrate temperature and obviously the choice would be the minimum possible substrate temperature which can satisfy all the requirements of the coating and obviously when it is a PVD and more in in particular when it is the sputtering.

So one should attempt to keep a very low temperature and that is one of the subject of investigation and research, how would be, how low the temperature could be in order that this substrate is totally free of any thermal damage and any temperature sensitive substrate can be covered under this sputtering technology and at the same time the synthesis of titanium nitride that is possible with all the required properties means hardness, adhesion with the substrate, low possible, stress in the coating, very good value of the growth rate and the functional property of the coating. So one would expect or desire to have all this required properties along with the one of the lowest possible temperature and that is going to be one of the main objectives of this sputtered coating technology.

(Refer Slide Time: 37:57)



So process variables we have mentioned let us look cathode current, actually it is cathode current but when we consider the cathode area then it becomes actually the cathode current density or in in what also we can mention this is the power density, so with a given cathode, we can also use cathode current as one of the parameters but importantly it is actually cathode current density and normally it is expressed in milliampere per square centimetre and from the previous discussion we already have understood that it is always the objective of this technology with all sort of modification and improvement, it is just augmentation of the this cathode current density or the substrate current density in the order of 10 to 20 milliampere per square centimetre with a low iron energy which is within the limit of hundred electron volt.

(Refer Slide Time: 39:28)



So when it is cathode current we can have a look how it is going to affect this process parameter, so one would be interested in the growth rate which will be given by micron per hour and if we just keep on changing the cathode current say reasonably say from 4 ampere to 8 ampere with a target of say 250 millimetre, it is a rectangular target by 125 millimetre which is quite reasonable and it is the observation that this growth rate is increasing because it is the ion energy which is available on this cathode surface and that increases the sputtering rate. However, what we also can find how this hardness will keep on changing, now this is going to be its value of hardness one would look into and this value of hardness with this cathode current.

So this is also have a rise in strength and it is because of this densification of the coating with this rise of temperature and it is actually the energy which is available and with that availability, we can have a densification of the coating and that is reflected in the adhesion of the coating. In we can also look into the stress in the coating that means the residual stress which will be compressive in nature and if we have this cathode current, we can also see that this is also our experience that this stress will keep on increasing because of the energy of the incoming flux and that induces residual stress which is compressive nature and this is actually negative. Then comes very important issue that this adhesion and in adhesion actually it is the critical load, this critical load which causes the detachment of the coating from the substrate and where a tendency has been observed like this.

Now this is actually fall of hardness sorry fall of interfacial strength. Now this can be because of 2 reasons one is that because of this higher level of energy available there could be some

intermixing at this interface that means, if this is the interface, this is the substrate and this is going to be the coating, so we have to look in that weather this high cathode current that is actually detrimental for this building up of the interface. Now this interface is actually developed at the very initial phase of sputtering and at this moment if we have too much of inter-diffusion which may lead to formation of a thick diffusion layer and a too much of reaction then that characteristics of this reaction layer is quite different from that of the coating and substrate. Additionally if it is becomes a brittle face then that can also cause this loss of strength, adhesion strength as a result we can see of falling tendency.

(Refer Slide Time: 44:04)



Partial pressure of nitrogen, now this partial pressure of nitrogen that is one way we can have a look here what is this partial pressure of nitrogen? That means with this partial pressure of nitrogen, the growth rate, now normally the partial pressure of nitrogen that one can keep between 1 into 10 to the power minus 5 torr to 1 into 10 to the power minus 3 torr and this is more or less very reasonable operation, operating range and here we have the growth rate and this growth rate one can find say this is one into 10 to the power minus 5 torr followed by 1 into 10 to the power minus 4 and 1 into 10 to the power minus 3.

So what we find here that this is actually the growth rate and when it comes in this enter this zone it all falls like this, it is having a rapid fall and then if we fix that this is the operational range, then it does not change much, so for all practical purpose, we can consider this as more or less it is just little slight fall but for all practical purpose we can ignore it and this is not going to be very significant but from this to this, this fall is actually it is there with this low-pressure of nitrogen, it is titanium and then this titanium is actually becoming titanium N x and when it is coming in the order of 1 into 10 to the power minus 4, then it becomes very close to titanium nitride that means N by Ti that is going to be almost 1 that is why here the growth rate which we can express in micron per hour, that can be affected by this change of partial pressure of this nitrogen and that is in torr.

Now with this partial pressure another thing also we can mention here which is also worth mentioning that this particular thing, this particular thing say this is actually ratio, atomic ratio of N by Ti. Now one would be interested to get is stoichiometric TiN and stoichiometric TiN means N by Ti should be very close to one and this is also our experience 1 into 10 to the power minus 5, if that is the point where deposition starts and then gradually changing this thing, one into 10 to the power minus 4 and if we can extend this sputtering over 10 to the power minus 3 and that is p N2 in torr that is partial pressure.

Then what also we can see this is also another thing that it comes, it rises like this and it comes very close to one and from this point, from minus 4 to minus 3 it is coming almost uniform, so this is one very interesting observation or TiN deposition that means it is very stable between 10 to the power minus 4 torr to 10 to the power minus 3 torr and that is the partial pressure of nitrogen, so within this zone even if we vary little bit then there will not be too much change in the stoichiometric relation of titanium nitride. However, if we consider titanium carbide say using titanium sputtered vapour flux and CH 4 as the reactive gas then the situation will be little different.

(Refer Slide Time: 49:10)



So this we can explain this way this is 10 to the power minus 4 torr, 10 to the power minus 3 and that happens to be the partial pressure of methane CH4 and that is in torr and here what we see this is actually C by Ti and what we can see, it is extremely narrow zone over which we can hold it is somewhere between 10 to the power minus 4 to minus 3 and where we can get a narrow zone, where we can have just C by T is equal to 1.

(Refer Slide Time: 50:01)



So this is also N by T is equal to 1 this is one of the best value for stoichiometric formulation and this is going to be C by Ti is going to be 1 but 1 cannot hold it with such a stability and just little variation in the partial pressure, one would expect, one would not expect this thing to be very stable but it will go like this very sharp that means in this zone C is greater than that of Ti in the coating. In practice one would see that it is actually TiC with substoichiometric value of x which is less than 1 and that is a dispersion of this TiC x in a matrix of carbon at means in this zone this carbon is actually separated out from methane and it does not combine with titanium that means here it is a very narrow zone over which one can hold this stoichiometric titanium carbide.

One can hold stoichiometric titanium carbide but beyond this point it will be a situation where we have TiC x dispersion where x is less than 1 and it is actually well dispersed in a matrix of carbon. So from this one can also see that is rather difficult to get stoichiometric titanium carbide by this reactive sputtering whereas getting TiN titanium nitride is not so difficult and it is so stable over certain range of partial pressure partial pressure of nitrogen. So this is one of the very important considerations one can find the basic advantage in reactive sputtering of titanium nitride and the difficulty also it is a difficulty of getting stoichiometric titanium carbide by the same reactive sputtering.

(Refer Slide Time: 52:38)





Now comes substrate temperature, now substrate temperature has one effect in that it is actually it is independent of this hardness value, this hardness value it does not change and here of course it is, what we are showing by a straight line, straight line means it is it is insensitive to this temperature and this temperature that was varied from 250 to 450 and that is this zone particularly in consideration of the substrate like steel family HSS, tool steel, Die steel and bearing steel, so these are the few materials which are taken into consideration and for this, this is one of the very interesting zone because the metallurgy of this materials are not affected here and this is one zone where this attempt has been made.

What was seen, what one could see during this temperature variation only the grain growth has taken place that means from 250 to 450 the grain size of this titanium nitride would have increased that was also in nanometres scale and another thing what was also observed, little fall of this compressive stress, that is the compressive stress which was little bit has fallen because of this rise of temperature it could have been relaxation of the stress at that particular temperature. However, hardness or LC value that means this critical normal load for the adhesion of the coating, it was not that effected by this change of temperature.

(Refer Slide Time: 55:02)



Then comes substrate bias, now this substrate bias has an immediate effect on all those process variables, so this is substrate bias, so this is actually the sputtering rate say it is R micron per hour, so what happens quite interesting that it is uniform over a certain range of bias it may start say from minus 10 volt and when it comes to minus 50 volt, it has a falling trend and it drops quite significantly that means sputtering rate is quite low. Sputtering rate is quite low because of the (())(55:48) from the substrate. However, when it was the hardness value, we can see this is a rising curve followed by a fall with these VS.

Similarly when it was critical load that also show a similar trend in this case what we can see that with this VS value, this compressive stress was quite high and at that point it attain the highest possible hardness densification of the coating. However, beyond this point it became quite brittle, so it became almost a brittle, so with induction of so much of compressive stress the coating became brittle, so it could be that with this brittle coating it could not show the same hardness and the indenter as an easy path for propagating the crack and indentation was easy and that was shown by this hardness, follow-up hardness.

This is LC critical normal load, so what happens with this increased of biased voltage, we have high energy, high amount of large amount of incoming flux which is striking the substrate surface with high energy and in this case if it is so that with this high energy, we can have some sort of interdiffusion and which is quite stronger and this interdiffusion or this bond formation, if it is quite severe or aggressive, in that case we may expect a thick diffusion layer at this interface and that may lead to follow-up this critical value of this crack for this crack propagation and it is because of the large amount of energy which is available and this interface. So this is also one point one should also look in, so finally what we see that it is actually the substrate bias, substrate cathode current, partial pressure of nitrogen, so these are the few things which are actually controlling the property of the coating.

(Refer Slide Time: 58:49)



So with that what we can say here that reactive sputtering of metal nitrate requires less cathode of density than direct sputtering of the same. It has also gained an advantage for building a graded architecture of the coating from right from the coating substrate interface that means with pure titanium with little bit of change in the amount of nitrogen with respect to titanium, we can reach a stoichiometric titanium nitride. The stoichiometric coating can be deposited at much low temperature than that required in CVD. Here with 250 or 300 around 400 it was possible to deposit TiN weather, where for normal CVD a temperature in the order

of 900 is necessary. The process parameters like cathode current, substrate bias, partial pressure of nitrogen that mainly controls the growth rate and other functional properties of this nitride coating.