Fundamentals of Materials Processing-2
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Module – 02
Thin Film Deposition
Lecture - 08
Sputtering

Welcome, this is lecture 8 of module 2 on Thin Film Deposition. In the previous 2 lectures, we discussed about plasma and plasma physics and in those lectures, we mainly concentrated on how to create plasma and how to sustain plasma and we also know that plasma consists of electrons, positively charged gas ions and also neutral species neutral gas atoms.

Now, in the following 2 or 3 lectures, we will discuss how to use this plasma for a physical vapor deposition process or PVD process called Sputtering.

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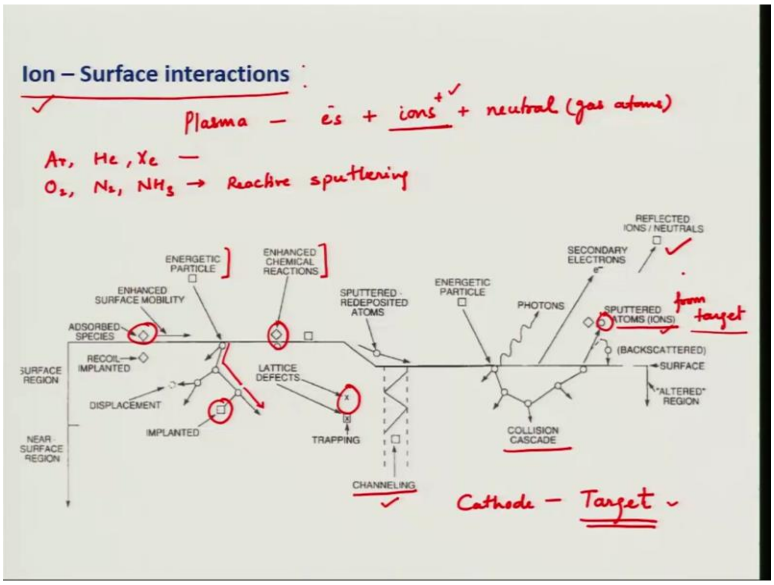

First look at what happens when ions which are in plasma interact with the surface. So, we start with ion surface interactions, remember when we are discussing physical vapor deposition techniques, we had discussed there are 2 different, 2 techniques or 2 broad categories – one was evaporation and second was sputtering. Evaporation was by heating the material and sputtering was mechanical mechanically removing the material from the source.

In the sputtering process, we will use these ions which are in plasma. So, our plasma has electrons plus ions most of them are positively charged plus neutral species neutral species of gas atoms that we are using to create plasma gas atoms we can use many types of gases, we can use noble gases like argon, helium, xenon, etcetera to create neutral plasma or we can use oxygen, nitrogen and sometimes ammonia these gasses to create plasma of these gasses or ions of these gasses which can be used for reactive sputtering.

Now, for sputtering process, we are mainly interested in these positively charged ions, what happens that if you recall our cathode which is negative electrode, all positively charged ions will be accelerated towards the cathode. So, in the electric field which is applied between in the 2 electrodes, now these positively charged ions which has certain some kinetic energy when they collide with the surface of cathode, there are many activities that happened on the surface some of these are that these energetic particles will go deep down into the surface of the cathode in this lecture and the lecture following these will called cathode as our target. Our cathode is our target on which we want to bombard these positively charged ions.

So, some of these will be just reflected, they will collide with the surface and will be reflected back some of them will displace the surface atoms of the target and get in planted, they will go deep down in to my cathode or target or a target they may also get adsorbed on the target if they have low energy they will just come close to the target and just sit there and do nothing they can also react with the target if we are using any ions of a reactive gas like oxygen, nitrogen etcetera then they might react with our target. And in various processes they might also create lattice defects in our target, they might also move lead down to a target by a process called channeling.

Channeling is the process when these positively charged ions find channel between 2 lattice planes of the target and then they feel low resistance due to the atoms because they are moving in between planes in between the planes of atoms of the target. They can just move without much resistance beat into the target and this is the process called channeling. Now the process we are interested in, this is called sputtering in which true of cascade of collisions, these ions will result in sputtering of the atoms or ions from target. So, it is the target material that we want to deposit as thin film and these energetic ions will transfer their energy their kinetic energy to the atoms or ions of the target material it will then come out of the surface and we can use these sputtered atoms to deposit thin films. We are mainly interested in the sputtered atoms.

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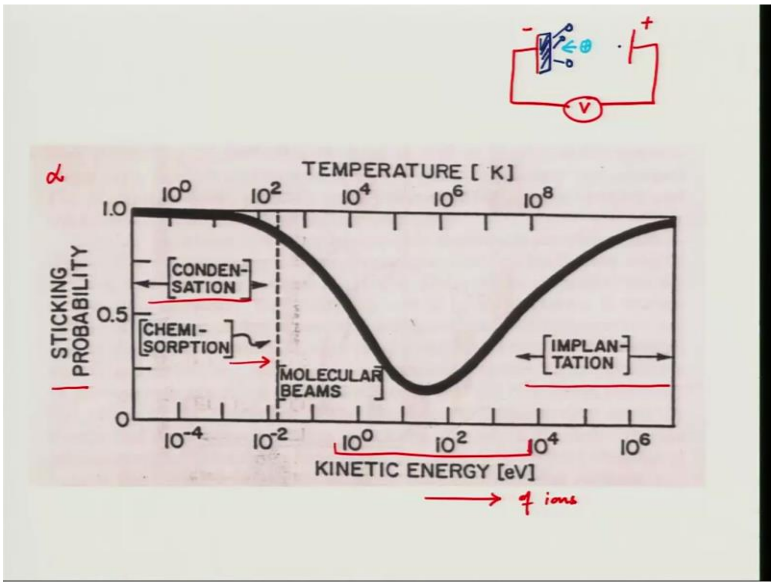

Now, let us have a look at the energy distribution of the ions in which many of these activities of ion surface interaction takes place. So, as you see on the y axis, we have a confession called sticking probability alpha and here we have kinetic energy of ions which are bombarding the surface of my target. We can see if the kinetic energy of these ions is very low in terms of electron volts then either they will just form a condensation they will just get fezzes out without any chemical interaction between the target and the ions on the surface of my target.

If they have slightly higher energy, they will they may form a chemical bond with the surface it may be van der Waals forces as well and they will get chemi-sorped. So, we are not interested in these low energy ions. If we increase the energy on the other hand then these ions will go deep inside the target material and get implanted there and stay there and that is why the sticking coefficient is very high because they are going inside the target and just sticking there on the left side they are just staying on the surface and a sticking there.

What we are interested in the energy range where the sticking probability is very low in these range where the sticking probability is low which means that these ions recalled from the surface. In the process of required the momentum transfer they transfer their energy to the atoms of the target and when we do that these atoms which are on the target surface will come out with certain kinetic energy and we can use these for thin film deposition.

We are interested in the energy range of around few 100 electron volts up to by sputtering process. So, we need to get our ions to these energies, remember we are discussing parallel plate geometry, right now give the applied voltage and we have a negative and positive electrode and our negative electrode is our target and our positively charged ions are accelerated towards this and result in this sputtering of these atoms from the target and we can keep our substrate at any place where they will reach and form a thin film and we have a plasma here in between these 2 electrodes.

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$$S = \frac{\text{\# of sputtered atoms}}{\text{\# of impinging ions}}$$

Table 3-4. Sputtering Yield Data for Metals (atoms/ion)

	Plasma species						
Sputtering Gas	He	Ne	Ar	Kr	Xe	Ar	Ar Threshold
Energy (keV)	0.5	0.5	0.5	0.5	0.5	1.0	Voltage (eV)
Ag	0.20	1.77	3.12	3.27	3.32	3.8	15
Al	0.16	0.73	1.05	0.96	0.82	1.0	13
Au	0.07	1.08	2.40	3.06	3.01	3.6	20
Be	0.24	0.42	0.51	0.48	0.35		15
C	0.07	—	0.12	0.13	0.17		
Co	0.13	0.90	1.22	1.08	1.08		25
Cu	0.24	1.80	2.35	2.35	2.05	2.85	17
Fe	0.15	0.88	1.10	1.07	1.00	1.3	20
Ge	0.08	0.68	1.1	1.12	1.04		25
Mo	0.03	0.48	0.80	0.87	0.87	1.13	24
Ni	0.16	1.10	1.45	1.30	1.22	2.2	21
Pt	0.03	0.63	1.40	1.82	1.93		25
Si	0.13	0.48	0.50	0.50	0.42	0.6	
Ta	0.01	0.28	0.57	0.87	0.88		26
Ti	0.07	0.43	0.51	0.48	0.43		20
W	0.01	0.28	0.57	0.91	1.01		33

How many atoms are being sputtered from the target? It is quantity that we defined as sputtering yield and sputtering yield depends on number of sputtered atoms divided by number of impinging ions.

For each ions that is bombarded on the surface of the target, how many atoms are being sputtered and of course, we would want that for each ion more and more number of atoms from the target are being sputtered so, that we can use them these sputtered atoms for thin film deposition. This table here gives an idea of different sputtering yields for different metals under different plasma gasses. So, these are my plasma gas or plasma species and these are or the or the sputtering gas and these are my metals or the target of which we make our cathode and these are a different energies and a comparison between argon at higher energy and the 0.5 kilo electron volt. So, you can see in some cases the sputtering unit is very high and in some other cases the sputtering yield is very low.

You can choose your plasma is species according to what you want to deposit and there is the threshold voltage for sputtering how much is the energy of the ion should be there so that you can start sputter and this threshold voltage depends on how strongly these atoms of the target are bonded together. So, at what energy if the ions are approaching they will be able to sputter and this is the quantity called threshold voltage and you can see that sputtering is for different metals in a same sputtering gas very very differently in a large scale. So, you should also keep into keep in mind that sputtering yield for different elements is different.

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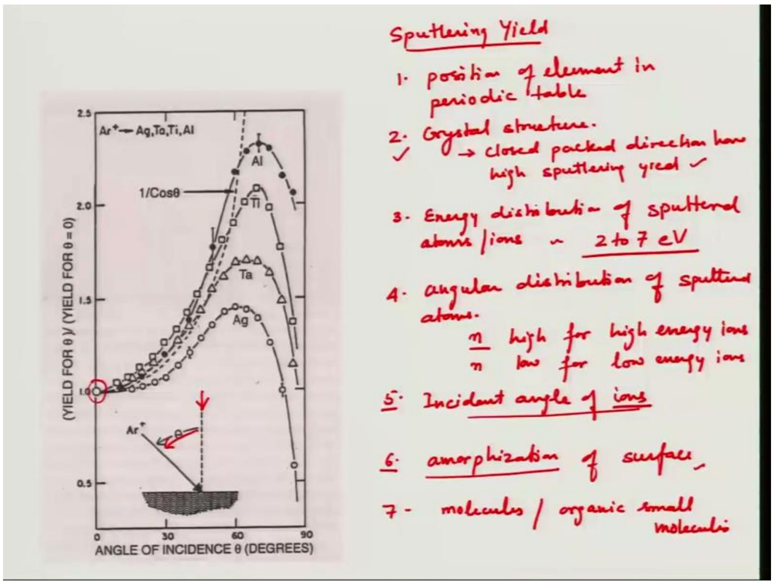

And what are these sputtering yields depend on that list down some of those properties; this sputtering yield depends on the position of element in periodic table, number 1. Number 2, it depends on the crystal structure and even in the same material the closed packed closed packed directions have high sputtering yield you can think of this that if you have a closed packed direction along which my ion is bombarding. So, it will interact with more atoms of the target or of that material and will able to transfer it is energy to more number of atoms and then our sputtering yield would be higher. Also depends on it also effects the energy distribution of a sputtered atoms or ions.

The sputtered species from the target can be can be atoms or ions or in some cases even molecules now the energy distribution because we do not want all these material to just come out of the surface and just sit there they have to have certain kinetic energy to move towards the surface or the substrate where we want to deposit the film. So, the energy distribution of sputtered atoms lies around 2 to 7 electron volts and of course, you can adjust this by adjusting the energy of the ions that you have bombarding on the surface or the target. It also depends on angular distribution of sputtered atoms.

These atoms when they came out of the target surface, there will have certain angle; they are not just coming out straight. So, there will be an angular distribution for high energy ions bombardment this distribution would be very narrow if you recall that the confession that we had used when we were describing the directionality of the source. So, n will be high, for high energy ions bombarding on the surface and n is the directionality and n will be low, for low energy ions. So, the energy of the ions will also define how spread out these atoms and ions coming out of the target will be other important parameter is incident angle of ions at what angle they are approaching these energetic ions are approaching the surface and this is very important because you can see in this graph here that how the yield where is with an angle theta and this is the yield for theta and yield for theta is equal to 0 means if you are coming state at the surface or the target.

If we are coming a state and your sputtering unit is one then if you increase the angle up to around 45 to 60 degrees, your sputtering yield increases and then it is starts to decrease then you are coming at very acute angle, so towards the surface. Now it should be evident then if ion is coming straight of the target, it will try to push the atoms of the material in deep inside and not will be able to remove these atoms from the surface and if the ion is approaching at an angle then it will just transfer its energy and you will be able to knock out the atoms from the surface. So, the sputtering yield increases and then if the angle is very narrow or from the normal to the surface it is close to 90 degree. Then they will just glance half from the surface and will not be able to transfer the energy. So, incident angle of ions is also very important.

Now when these energetic ions are being bombarded remember we had said that closed pack directions have more sputtering yield and the less closed pack directions have a different sputtering yield and this will also create different sputtering yields in different directions. But if in the process due to damage is created by this sputtered atoms creates an amorphous structure locally then the directionality and sputtering yield at different places will be same. So, if you have a polycrystalline material you would have certain atoms, certain grace which are oriented favorably some grains will be oriented unfavorably for sputtering.

But due to the first way of ions, it will try to create defects and amorphize the layer and then it the fact of crystal structure vanishes and then you guide uniform sputtering from entire surface of the target. So, this amorphization of surface happens during ion bombard argument. Now if you have your target at the higher temperature then you would be able to anneal these defects and then your target will become again polycrystalline. So, you can decide by if you want to do at room temperature or a higher temperature or you need an amorphized surface for sputtering or not for various depositions or different thin films.

You can also sputter molecules and sometimes you need organic small molecules have been reported now organic molecules of soft material, it is countered intuitive to thing that you will be able to sputtered these molecules. But in fact, you can under certain conditions you can also sputter these organic molecules from a target. So, this is about sputtering yield and how the sputtering process from at the target happens.

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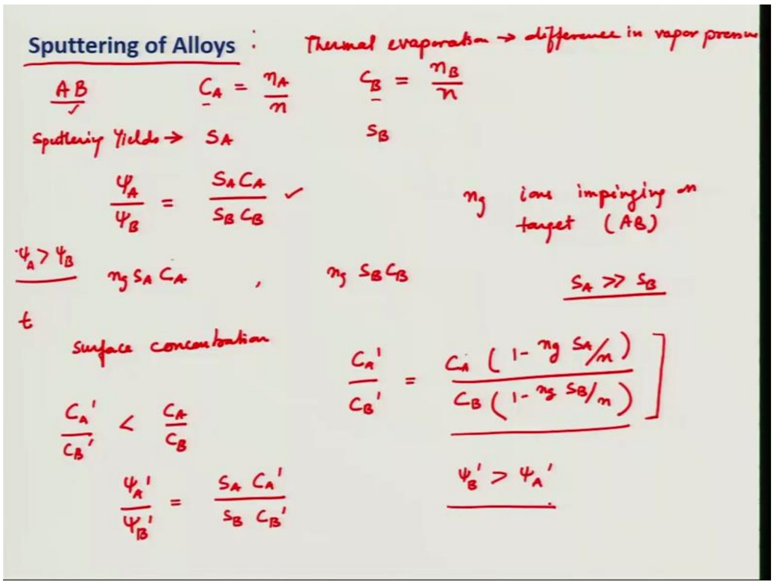

Now, the most important part it is sputtering of alloys, if you recall that when we were doing thermal deposition or thermal evaporation, we had said we cannot have maintain the stoichiometry for thin film deposition because of the different difference in vapor pressure in thermal evaporation, it is what that difference in vapor pressure.

Now here also we have if we take an alloy of A and B. So, this is my alloy of a composition, let us say C A and C B where C A is number of A atoms divided by total number of atoms and C is number of B atoms divided by total number of atoms. Now C A and C B will also have different sputtering yields for a given energy of ions. Energy of ion is fixed because our target is same of made of alloy called A B with certain composition, now sputtering yields are different S A and S B.

So, the sputtered flux will depend on the concentration and the sputtering yield these are the sputtering yields. So, the sputtered flux or the ratio of the flux psi, psi of A and psi of B will depend on S A C A and S B C B. If C A is higher, then for the same S A over S B, you will be more a sputtered or if the concentration of B is higher in the alloy then for the same for a same sputtering yields more B will be sputtered. So, in the flux of the material which is coming out and going to be deposited on the surface or substrate my psi A and psi B ratios like this.

Now, if ng atoms or ions are impinging on target which is alloy AB then the total atoms coming out of A and B would be ng S A C A and also ng S B C B because C A is concentration and the sputtering yield depends on number of ion impinging. Now say after certain time T sometime because let us assume that S A is much greater than SA. So, more of AB is sputtered if more of A is being a sputtered from the surface of the target then my target is getting which are in B. So, my concentration will change this is the surface concentration surface concentration will be C A dash over C B dash which is equal to C A. Now 1 minus and g S A over n and this is write by C B 1 minus ng S B over n for C A and C B was my initial composition, but after sputtering for some time T then some atoms of A and B have sputtered my surface concentration the ratio of the concentration will be like this.

Now if S is higher than SB, we know that C A dash over C B dash would be less than C A over C B and this is from A this expression because S A is higher C A over C B then C A dash over C B dash would be lower than C A over C B. So, my target is now which are in B. So, if you calculate the flux, again from this composition we will see that psi A dash over psi B dash will be equal to S A C A dash over S B C B dash. Now the sputtering will depend on the new composition and where C A dash over C B dash is this expression. Now if S A is higher than S B at some point psi B dash will be higher than psi A dash here psi A was higher than psi B. Now I have no sputtered flux for B.

Now, this change between higher flux of A and higher flux of B will eventually retain a steady state such that in a steady state. My composition becomes let us C A over C B dash is equal to C A S B over C B SA. So, this is my in a steady state and this is surface composition.

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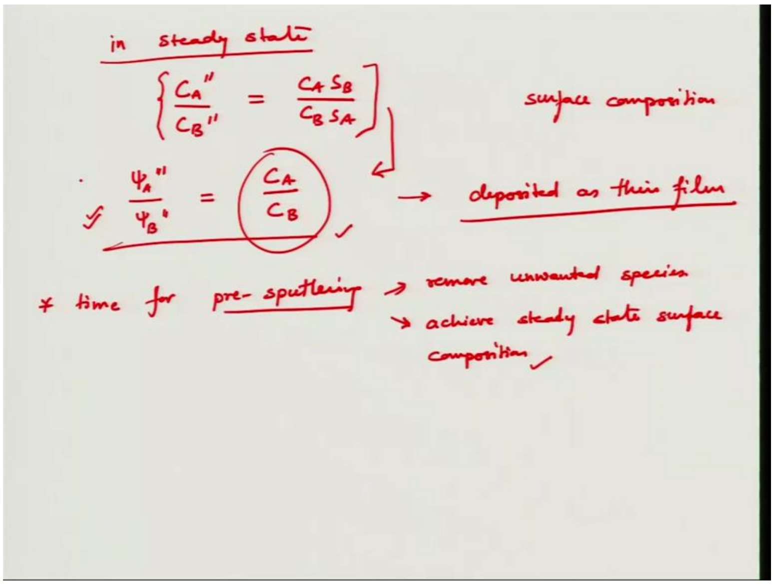

As steady state will reach where my surface composition will become this and then if I calculate the flux from this surface composition, I will get psi A double dash over psi B double dash will be equal to C A over C B from this surface composition.

Now, if I have this then I know because this is the flux ratio of material in the flux in the vapor fields. So, this is the composition deposited as thin film which was our goal to start with remember our target was this C A and C B and we wanted to deposit the film of the same ratio C A over C B and we have achieved that. But my surface composition is different surface composition not the target composition target composition is still C A over CB, but this instantaneous the dynamics between how much the sputtered rate and the composition will play outside that we will get a steady state deposition of the composition that you want.

Now you can see that you can use sputtering for a deposition of alloys without losing the sociometry, the only condition is where we should allow time for pre sputtering, pre sputtering means it has 2 reasons that first you can remove any thing that is deposited on the surface are adsorbed, any gasses, any unwanted, species remove that you are not depositing on a surface you are surface is blocked by a cover. So, your surface is blocked so that you are not depositing anything unwanted on your substrate and you are doing sputtering process here and so remove unwanted species and second achieve steady state surface composition and it will take maybe a minute of 5 minute of sputtering to reach this. So, the CD state surface composition which is this and you can calculate what would be the CD state surface composition.

Once you reach this steady state surface composition, we can remove the shutter in front of your substrate and allow this flux to be deposited on the surface or to the substrate that you want to deposit thin film. So, in this way this is a superior technique compared to thermal evaporation and this is we will see more benefits or more advantages of a sputtering process over thermal evaporation in the coming lectures and various ways of doing the sputtering process.

Thank you very much.