Surface Engineering for Corrosion and Wear Resistance Application

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Lecture – 46
Sputtering

Welcome to the 46th lecture of Surface Engineering; in the previous one, we discussed the process of physical vapor deposition, where we realized that we can always try to heat a material with reasonably low boiling temperature and high vapor pressures. So, that it goes into the vapor state and then obviously, the vapor would like to come back to the ground state which is the liquid or the solid state.

So, in the in the process it actually will be looking for a colder substrate and get deposited onto the colder substrate and that is how we can create few micrometer thick layers which we call till films on all kinds of materials or not necessarily conducting materials also non conducting materials. The whole process was based on heating the species that we want to coat. There are applications where exposing material to such high temperature is not always desirable.

In fact, we may require particularly for semiconductor industry we may require certain thin coatings to be developed which will not be exposed to any thermal activation at all because, that may damage the performance of the device. So, in a situation like that we adopt a special category of PVD which we call sputtering.

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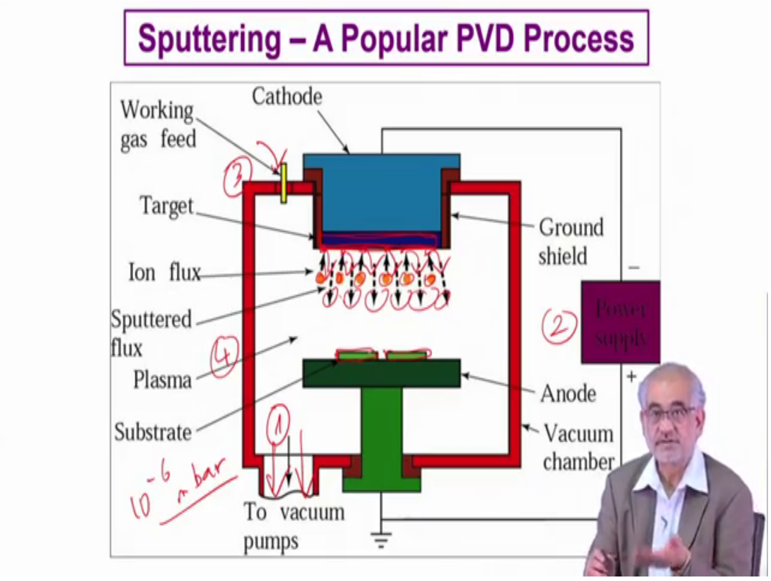

Sputtering – A Popular PVD Process

Now, sputtering is in simple words it is like you are here is a process, where you scoop the material from the surface literally atom by atom by way of shooting certain time little projectiles. And, in the process those scooped out species or atoms neutrals will find it is their way on to deposit onto colder substrate and that is the process of sputtering.

So, let us try and explain what exactly it is. So, first is we have a chamber we have an enclosed chamber which we which we can actually we need to evacuate. So, this is how we can pump down to very low pressure let us say typically 10 raise to minus 6 millibar pressure. So, after evacuation so there is no oxygen there is no other reactive gases inside very low pressure. So, now, we actually place the target. So, so this is the target which from which we want to take out maybe let us say aluminium or let us say maybe gold or maybe carbon or some other whatever is a desired material.

So, we place it over here and then also we have a stage on which we have our material which is to be coated. So, let us say this is the component that we want to coat. Now, we create an electrical circuit such a way that the target is connected to the negative electrode the cathode and component to be coated is connected, or is actually grounded or can be considered to be in the positive side the anode. So, we usually pulse at very high rate and when we pulse electrical current at very high rate then during the pulse on time the there will be. So, once we create a very high in the electrical bias inside the chamber and we would have back filled with certain amount of argon or usually argon.

So, the argon gets ionized and these ions actually get during the pulse on time the positive pulse they gets they get very highly accelerated charge they move at a very high velocity towards the negatively biased electrode the cathode. So, these are the these are the argon ions which are now energized at a very high velocity accelerated towards the cathode. And, when a heat the cathode when they heat the cathode here or here or wherever it is they will be able to dislodge some of the atoms sitting onto the surface.

Now we are we already studied that while discussing structure of solids that the surface atoms are indeed at relatively higher energy state than the atoms at the core and they have a higher reactivity because they enjoy a 1 degree of freedom compared to higher 1 degree of higher freedom then the atoms in the surface because they have atoms missing above or below the surface. So, these atoms which when they are heat by these projectiles individual projectiles of argon ions, they are some of them will actually experience an impact which will have an energy that can over the overcome the binding energy of the atom to the surface.

So, that would allow those few atoms to get detached from the surface. And so, they get detached and then they come out. So, when this process happens then you actually see a number of such atoms from the target surface to come out and these atoms actually now come and deposit onto the surface. So, the so you first heat the surface with very high velocity these large atoms and these atoms now come and deposit on to the surface.

So, this transport can actually be pretty fast. In fact, the whole if the PVD process takes let us say for a particular to deposit a particular thickness if it takes an hour here it can be done in few tens of a minute. So, it can be much faster. So, the important part is that stepwise we first have to evacuate, then we create this high potential difference between the 2 electrodes, we feed in certain gas which is usually argon then we create the plasma and now we are ready. So, once we start pulsing at very high rate then the this process of removing atom by atom from the surface and then bringing them onto the vapor or the substrate to be deposited, then they create a very thin coating.

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Sputtering – Salient Features

- ❑**Sputtering** involves **ejecting material/atoms** from a **"target"** (i.e. a **source**) onto a **"substrate"** (Si wafer)
- ❑**Ejected atoms** carry a **wide** (kinetic) **energy distribution**
- ❑Sputtering is usually conducted in **vacuum** or in an inert **gas atmosphere**, e.g. **argon**
- ❑**Produces a sharp substrate-deposit interface**
- ❑**Sputtered ions** (only a small fraction of ejected species) **ballistically fly** from target in *straight lines* and **impact** the substrate or chamber wall
- ❑**Re-sputtering** or **re-emission** of deposited material may happen during deposition due to **high energy bombardment or impact**
- ❑At higher gas pressure, ions **collide** with gas atoms (**moderator**) and **diffuse** to substrate or chamber wall and condense after a **random walk**
- ❑**Applications:** in ***semiconductor industry, coating (functional and decoration), surface analysis, fusion plasma and space physics***

So, the process depends upon this ejection of atoms from the surface and this surface of the targets. So, which is basically the source material and the ejected atoms should come and sit on the substrate that we want to coat. So, the ejected atoms depending upon whether the projectile is heating head on 90 degree directly normal or through a grazing angle. The kinetic energy of the ejected atom will greatly depend upon the energy with which the projectile had heat the surface and made it come out.

So, also it will depend upon the distance which it has to cover from the center to the periphery. So, there could be a wide distribution of energy and this because of this wide distribution energy there could be variation in thickness and even composition, if it is deposition if the sputtering is from an alloy. Anyway we need to create a vacuum and then backfill with an inert gas usually argon. The interface just like in the previous PVD process this is also nothing, but a PVD process will also be a sharp. So, you too create a sharp substrate deposit interface.

The sputtered ions which actually are only a fraction of the total number of ejected ions, will fly ballistically in other words they basically are dependent entirely upon the energy with which they are heat. So, there is no thermal activation here, and they will move in straight lines and then impact the substrate or the chamber wall. So, they can go and deposit on the chamber wall or they can come and sit onto the substrate whichever comes on their path of light.

But, if the momentum is fairly high then there could be a possibility of re sputtering or re emission of atoms from the substrate on which you are depositing; that means, you are now re-sputtering atoms from the substrate surface which you do not want. So, you have to control the energy very carefully. And this, so this high energy bombardment needs to be avoided. So, at higher gas pressure the ions can collide with the gas atoms, which is used as a moderator and diffuse to the substrate.

And when actually it heats and goes and sits inside it actually can create certain diffusion gradient and in the process it can actually move inside the substrate and proceed up to a certain depth. The applications could be typically in semiconductor industry for various kinds of functional and decorational coating. It can be used for surface analysis and also has wide application in fusion plasma and space physics. So, sputtering is used also to create a conducting coating or a non conducting coating. So, the applications can be multifaceted, but the most of the applications are in the semiconductor industry anyway.

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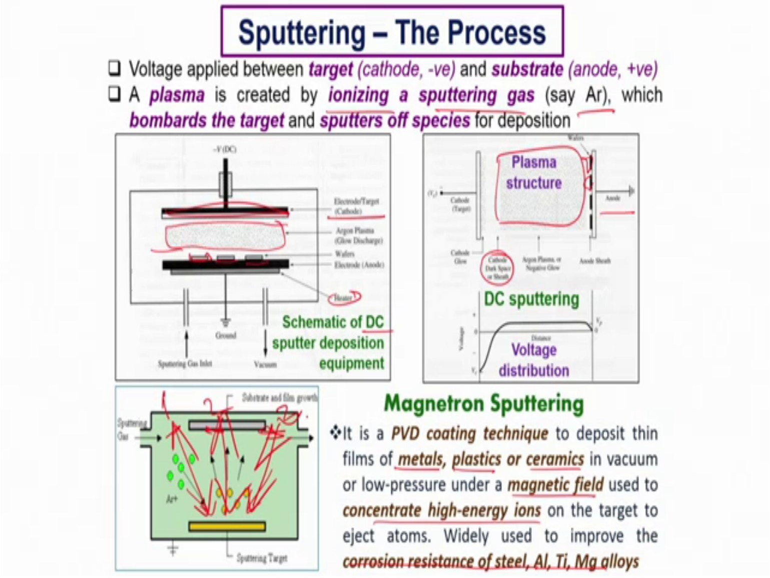

Sputtering – The Process

- ☐ Voltage applied between ***target*** *(cathode, -ve)* and ***substrate*** *(anode, +ve)*
- ☐ A ***plasma*** is created by ***ionizing a sputtering gas*** (say Ar), which ***bombards the target*** and ***sputters off species*** for deposition

Magnetron Sputtering

❖It is a ***PVD coating technique*** to deposit thin films of ***metals, plastics or ceramics*** in vacuum or low-pressure under a ***magnetic field*** used to ***concentrate high-energy ions*** on the target to eject atoms. Widely used to improve the ***corrosion resistance of steel, Al, Ti, Mg alloys***

So, the typical process would require that as I was saying that this is the target and these are the components on which you are depositing. Say for example, silicon wafers, you may have an auxiliary heater here, which actually allow certain diffusion of the deposit and the substrate below and in the process the sharp interface can be replaced with a fairly diffuse interface with a better bonding.

So, this argon plasma that you create is it covers the entire distance in between except thin layers, some kind of sheet which actually is divide of very high density of these ions. Now, the activation can be through direct current. So, in that case you call it simply dc sputtering you can also use high frequency inductively coupled radiofrequency plasma. So, it can be an RF sputtered RF induced sputtering, but the process remains the same that you actually will have a sputtering target which will take the heats of these argon ions will allow ejection of these species neutral species which go and sit on the surface of the cold substrate.

So, you can deposit metal you can deposit plastics or ceramics. So, that is the beauty you this actually independent of the chemical nature of the coating that you want to deposit. So, you use low pressure under a magnetic field to concentrate high energy ions this is typically done in case of magnetron sputtering, where the magnetron high flux magnets actually confine the plasma in a smaller region. And, in the process make the deposit more uniform and compositionally more correct.

So, the application wise you actually use it either for creating a conducting layer or an insulating layer or change the electrical resistance or the band gap you can also use it for improving the corrosion resistance or wear resistance and so on. You can even create it just as a possible substitute for let us say, galvanized you can create actually an cathodic or anodic layer to prevent corrosion and oxidation, but very thin and the advantage the other advantage is that you not exposing to any aqueous path you are not subjecting to any high temperature you are doing more or less at room temperature and most importantly you actually are able to maintain very thin precise layer.

So, this is the space I was talking about which is called the dark space or the sheet. So, you create a high density plasma all over so if this is the anode or the positive side on which you have placed your substrates to be coated. Let us say silicon wafers and this is the target from which you are actually extracting ions or making the argon ions heat the surface and dislodge atoms from this may be aluminium, may be carbon or any other material. So, there will be a little region in between which will have very low density and that is typically called the cathode dark space or sheet. the exact thickness and the location and the width of these region, largely affects the overall coating thickness and the uniformity of the coating.

One other thing is very important is that the if you can look at this substrate here or this substrate here they are tiny little much smaller compared to the overall dimension of the plasma that you create. And this is how you actually can make sure that there is uniform coverage and no shadowing effect no non uniformity. So, this plasma that we create is by ionizing a gas which is usually argon which I have already mentioned the reason why we use argon is because it does not have any solubility in the materials that we are using either as target or as the substrate.

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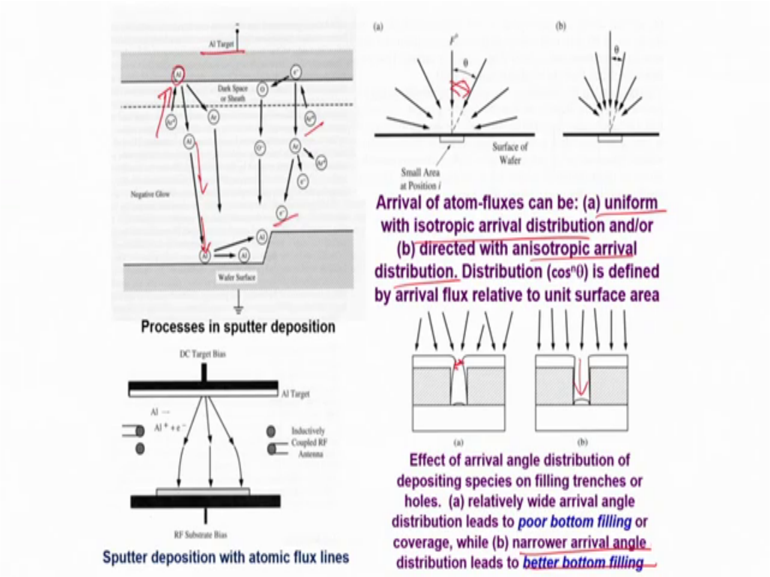

Processes in sputter deposition

Sputter deposition with atomic flux lines

Arrival of atom-fluxes can be: (a) uniform with isotropic arrival distribution and/or (b) directed with anisotropic arrival distribution. Distribution ($\cos^n\theta$) is defined by arrival flux relative to unit surface area

Effect of arrival angle distribution of depositing species on filling trenches or holes. (a) relatively wide arrival angle distribution leads to *poor bottom filling* or coverage, while (b) narrower arrival angle distribution leads to *better bottom filling*

So, like I was saying that here is a situation where let us say this is an aluminum target and this is a silicon wafer and we would like to create thin layers of aluminum in certain portions and not all over the surface. So, where we do not want aluminum to get deposited we will cover it up with a mask and rest of the regions will be exposed. So, we shoot argon ion and it dislodges and neutral aluminium and the aluminum arrives onto the surface like this. It can be a straight one like that or it actually can come through certain circuitry path some spiral path, but in the process it actually can heat the atmosphere inside the atoms inside and as since we are dealing with plasma so; obviously, we have these argon ions, cations and also we have electrons.

So, they actually the density of them actually will vastly control the rate and also the uniformity and the composition with which they arrive. So, this can be controlled like; obviously, one possibility is that you confine the plasma by way of applying high flux high power magnet and you in typically a magnetron and then you call it a magnetron sputtering. Similarly the frequencies of the sputtering can be changed from some normal level of using a normal electrical power supply to an RF couple power supply. In accordingly there could be certain differences.

So, this arrival will create the overall geometry or overall thickness and uniformity will govern that. So, what is important is that this angle theta actually at which the species is arriving is important. So, they can be uniform with isotropic arrival distribution or they can be directed with an isotropic arrival distribution. So that means, in certain cases I want a normal deposition with certain area coverage or I can make it an incline or arrival at an angle and there at the repulsion will be different and that may be required in a situation like this. So, in this kind of a situation if you want uniform deposition coming from the top, then these trenches here the opening being so small, may not be able to allow entry of sufficient number of atoms into the trenches. And in the process you get very poor coverage in the bottom of the trench.

On the other hand if you can create a directed deposition then actually you actually do see that the deposit here could be wider or more uniform. So, with the narrower angle of arrival you can have a better bottom filling or flooding with a wider angle of arrival you can have poorer bottom filling. So, this kind of geometry or consideration becomes assumes very important very very high importance when these dimensions are extremely small.

Now, generally when you are talking about a cutting tool or a large manufacturing device the dimensions are typically in millimeters if not centimeters, but when you are talking about a semiconductor device maybe as some reflector or maybe some photovoltaic device or some sensor. There these dimensions could be typically micrometer or even less than a micrometer. So, the arrival direction or the directionality of the flow of these atoms during sputtering becomes assumes very high importance.

So, in that case we may use either wider or shallower angle of deposition and that is how we can make sure that we actually can create wider coverage here. And not end up having incomplete coverage at the bottom of the trench like here. So, depending on the features that we want to develop and the dimension of the features we have to select the exact arrangements for deposition.

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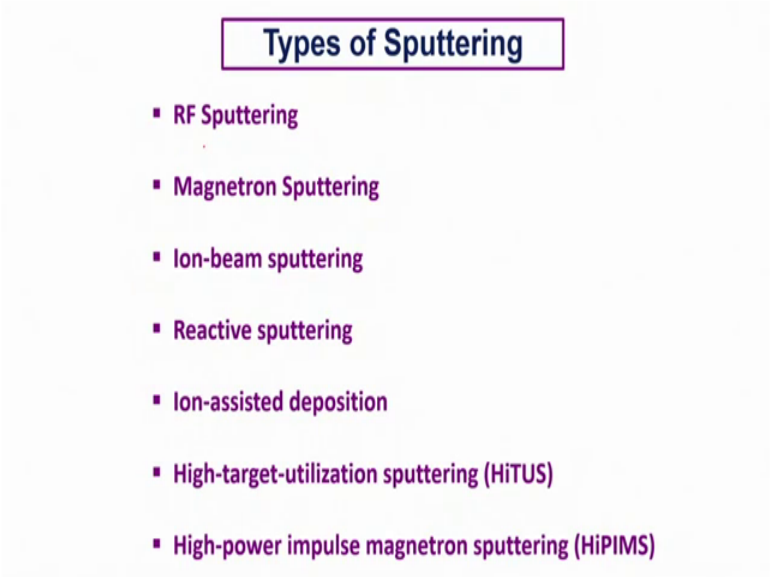

Types of Sputtering

- RF Sputtering
- Magnetron Sputtering
- Ion-beam sputtering
- Reactive sputtering
- Ion-assisted deposition
- High-target-utilization sputtering (HiTUS)
- High-power impulse magnetron sputtering (HiPIMS)

So, there could be various types of sputtering like I was saying that Radio Frequency couple sputtering; RF sputtering. Magnetron sputtering confined iron beam sputtering where we actually use an iron beam not just individual argon ions, but directed focused ion beam coming onto the target for sputtering. We can use we can allow entry of reactive gases and then create some kind of a situation where we create an oxide or a nitride or some other reaction layer onto the surface.

Similarly, deposition could be assisted by an ion beam. So, we actually where the ion beam is not a part of the same chamber it is created elsewhere and that ion beam can actually come and assist the deposition. We can create a separate tart a separate activation source for creating very high target utilization for sputtering also we can have a very high impulse or using a magnetic magnetron sputtering unit to create a very high impulse for deposition the deposition rate would be much higher in that case.

So, these are the various possibilities of sputtering the by and large the process remains the same that we actually create ions create a plasma we direct the plasma by way of negatively pulse negative pulses electrical pulses forced them to heat the surface of the target dislodge atoms eject atoms from those targets and those atoms will fly ballistically and then come on to the colder substrate and then deposit. And we actually can deposits multi layers or we can have multiple composition or we need not actually use the same target we can use multiple targets for example, in situations like this instead of having a single target covering the entire area we can have multiple targets here. And we actually can use the pulses let us say this is 1 2 3 we can sequentially create pulsing between this or this or this and in the process we can see deposition of 1 2 3 or A B C and in certain sequences.

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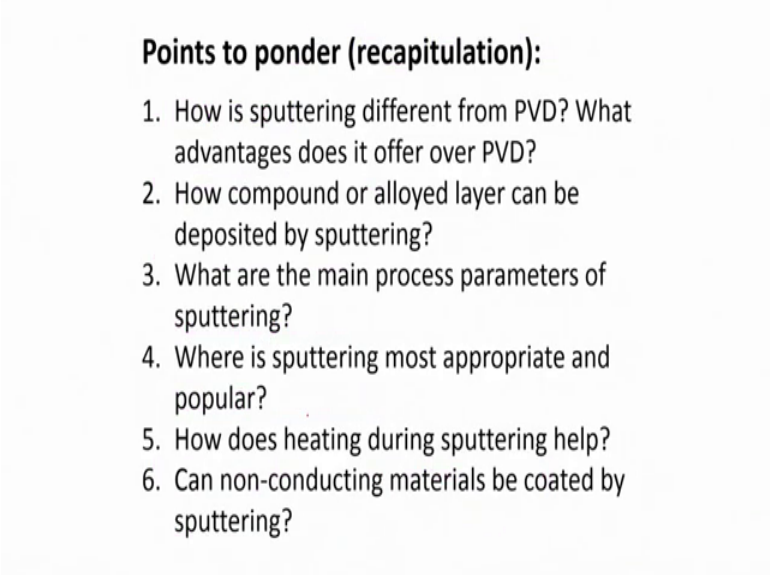

Points to ponder (recapitulation):

1. How is sputtering different from PVD? What advantages does it offer over PVD?
2. How compound or alloyed layer can be deposited by sputtering?
3. What are the main process parameters of sputtering?
4. Where is sputtering most appropriate and popular?
5. How does heating during sputtering help?
6. Can non-conducting materials be coated by sputtering?

So, time to recapitulate what we have discussed is a special type of PVD technique called sputtering. Wherein we actually use we take the material to the vapor state not by thermal evaporation, but by ion induced ejection, which is typically the process involving high velocity ions heating the target and ejecting some of the atoms in the form of neutral atoms. So, these atoms now fly and then come and sit and that is how we create a deposit layer.

The typical process parameters would be the distance the density of the plasma we create whether we are heating any we using any auxiliary heating process to heat the substrate during deposition then; obviously, the material that we use it is vapor pressure melting temperature vaporizing temperatures and so on. Then we also have to understand that the one of the biggest advantage is the fact that, we do not necessarily are this not an electrolytic process is not an electronic process. But, it is a process where we are using certain discharge and by way of creating a very large potential difference between two electrodes.

So, it can be used in special cases also for non conducting materials, even plastics can be quoted by sputtering provided we have what we have created certain provisions of having electrodes implanted onto the substrate on which we want to code. So, this is useful that we actually can be this is not just confined only to metals, but these useful to metal ceramics semiconductors polymers all kinds of engineering solids so.

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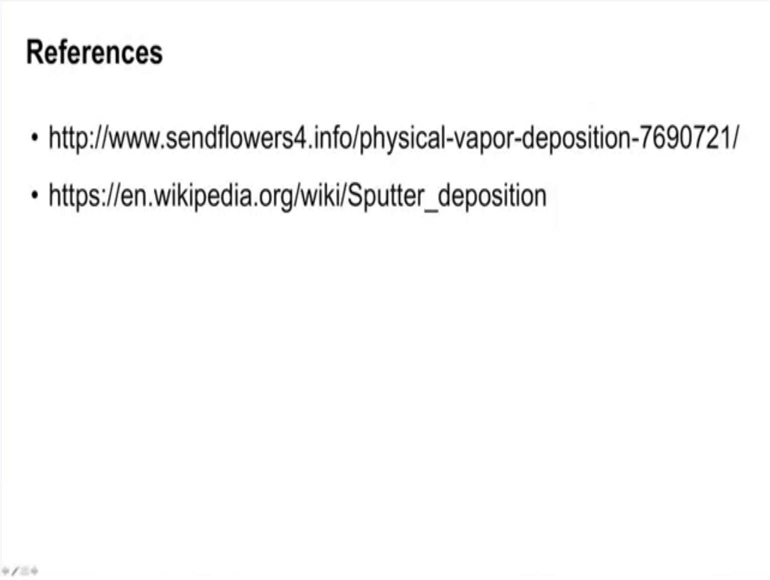

References

- http://www.sendflowers4.info/physical-vapor-deposition-7690721/
- https://en.wikipedia.org/wiki/Sputter_deposition

Thank you very much.