

Surface Engineering of Nanomaterials
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Lecture – 26
Thin Films for Surface Engineering of Nanomaterials

Hello. In this particular lecture we are going to discuss about the Thin Films for Surface Engineering of Nanomaterials. In last couple of lecture we have discussed about some kind of problems on based up wear, then abruption, then we have try to modify those problem, then we have discussed about several types of deposition techniques, then we have discussed about the modification of nanomaterials. So, in this particular lecture we are going to discuss about the thin films how it is helping for doing the surface modifications of particular materials.

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Thin Film:



- Thin film is a layer of substance or material on supporting substrate, ranging from nanometres to several micrometers in thickness.

Distinction: "Thin" Film - "Thick" Film:

- The limit between "thin" and "thick" films cannot generally be defined, although literature sometimes gives an arbitrary value of 1 μm . Basically, a film can be considered as "thin" when its properties are significantly different from the bulk.

For example:

- An Indium-Oxide film (In_2O_3), e. g., which can be used as temperature barrier coating due to its high transmission in the visible region and its high reflectivity in the infrared region (this is caused by optical interference effects) has to be approx. 300 nm thick. For optical applications this film can be considered as thin.



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So, here first before going to start let us know that; what is the definition of the thin films? So, at the onset let me discuss that thin films is a very very difficult to defined, because some people thing that 300 nanometers is the thin, some peoples are thinking at 2 nano meter is also thin. So, the thing is that its dependence upon the applications that whatever the application of that particular material based on that we can defined that materials whether it is thin or may be the thick. Because I will give some examples where you can find that in nanometer also there is some kind of materials which can act

as a thick. So, thin film is a layer of substance or material on supporting substrate ranging from nanometers to several micrometers in thickness. As I already told may be that size may be nanometer range may be sometimes it is in the micrometer range also.

So, distinction thin film or may be the thick film: the limit between thin and thick films cannot generally be defined because it is very difficult to say, although literature sometimes gives an arbitrary value of 1 micrometer. Basically, a film can be considered as thin when its properties are significantly different from the bulk, yes of course, Because in the subsequent slide will see that when we are making that thin film that it is giving the better properties, in terms of electrical, in terms of mechanical, in terms of thermal than the bulk or may be the thick film.

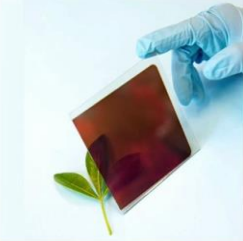
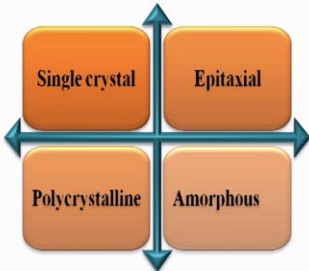
So, for example, an indium oxide film which can be used as temperature barrier, this one is the material coating due to its high transmission in the visible region and its high reflectivity in the infrared region; this is caused by optical interference effects has to be approx 300 nanometer thick. So, you can imagine that here 300 nanometer we are considering as a thin materials. For optical applications this film can be considered as thin, but when we are talking about particular this applications that 300 nanometer we are considering as a thin material.

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- If the same material would serve as insulator in a Josephson junction, 300 nm would be much too thick to allow Cooper pairs to tunnel through the oxide. For this application the In_2O_3 film should have a thickness of only 2 nm.

In other words, 'for one given application a film can be considered as thin while for another application the same film can be thick'.

Classification of "Thin" films on the basis of crystalline structure



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If the same material would serve as insulator in a Josephson junction, 300 nanometer would be much too thick to allow cooper pairs. Cooper pairs is not nothing but the material which we are using in between the two semi conducting layers. So, through the oxide for this application that indium oxide film should have a thickness of only 2 nanometer. So, now my one big question is that whether we going to say that 2 nanometer as a thin or thick or may be which one is thicker or may be which is the thinner whether 300 nanometers or may be the 2 nanometers; here are the answers.

In other words, for one given application as thin film can be considered as the thin while for another application as the same film can be knowing as a thick. So, it depends upon application to application. Somehow somewhere one film can be use as a thick somehow the same dimensions can be used as a thin. Classification of thin films on the basis of crystalline structure; so generally we can divide the thin films into four a classical division. One is called a single crystal, epitaxial, amorphous and the polycrystalline.


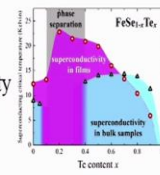
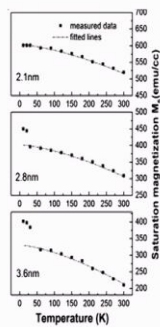
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Effects of "Thin" Films:

A microstructure which is different from the bulk (e.g. in respect to grain or crystallite size) the following effects may be observed:

- Increase corrosion resistance
- Improve hardness
- Enhance magnetic saturation induction
- Increase critical temperature of superconductivity
- Amplify optical absorption

Electro zinc plating

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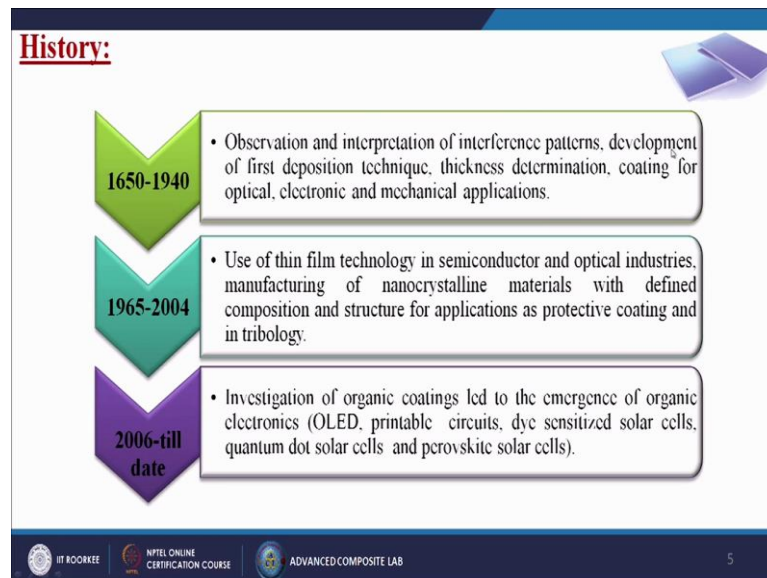
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So, effects of thin films. So, just in this particular slide I am going to discuss about if you are going to use those kinds of thin films; what are the advantages we are going to get. So, a micro structure which is different from the bulk. That means in respect to grain or crystallize size the following effects may be observed; increase corrosion resistance, improve hardness, enhance magnetic saturation induction which is nothing we are getting from this particular graph, in the right hand side it is giving the saturation

magnetization which is into the x axis; sorry which is into the y axis and the x axis is giving that temperature.

So, from this particular case you can see that when our thin film thickness is only around 2.1 nanometer it is giving the saturate magnetization values as around 600. So, when we are using our material as a thin that property is getting increased, so what it is doing it is increasing corrosion resistance improve hardness, increase critical temperature of super conductivity amplify the optical absorption. So, if we use the thin film then it can enhance so many properties than the thick film itself.

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Now, let us discuss about the history behind this. When people have started generally roughly people as to started using these kind of techniques in the year of 1650. So, from 1650 to 1940 observation and interpretation of interference patterns, development of first deposition techniques, thickness determination coating for optical, electronic and mechanical applications. People were working on this kind of things.

From 1965 to 2004 use of thin film technology in semiconductor and optical industries, manufacturing of nano crystalline material with defined composition and structure for applications as protective coatings and in tribology. People were working on these. And now people are working on this all kind of advanced materials from 2006 to till date. Investigation of organic coatings led to the emergency of organic electronics OLED

printable circuits, dye sensitized solar cells, quantum dot solar cells and parasitic solar materials and so on.

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Thin film growth process:

The deposition process of a film can be divided into three basic phases:

- Production of the appropriate atomic, molecular, or ionic species.
- Transport of these species to the substrate through a medium.
- Condensation on the substrate, either directly or via a chemical and/or electrochemical reaction, to form a solid deposit.

For example:

Chemical Vapor Deposition (CVD) Process

"The quality of thin film is highly dependent on deposition parameters such as temperature, pressure, time and so on."

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So, how we are doing this thin films or may be rather we can say how we are preparing this thin films, what is the growth mechanism over there. The deposition process of a film can be divided into three basic phases. So, first one is called the production of the appropriate atomic molecular or ionic species, so this one is the number one methods. Then second is that transport of this species to the substrate through a medium, so this is the second one. And last one is that condensation on the substrate either directly bio chemical or electrochemical reaction to form a solid deposit over there.

So, here this is the gas flow is going on, then the atoms is coming first abruptions on film (Refer Time: 07:12) is taking place, then nucleation of this atom is taking place, and the last one is that step flow growth means layer by layer it is forming and it is giving a coating on to the material surface.

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Some particular motives of thin film deposition:

- To maintain surface uniformity.
- To reduce the amount/mass of light absorbing materials.
- To decrease the weight and bulkiness of the materials.

Growth of a thin-film generally exhibit following features:

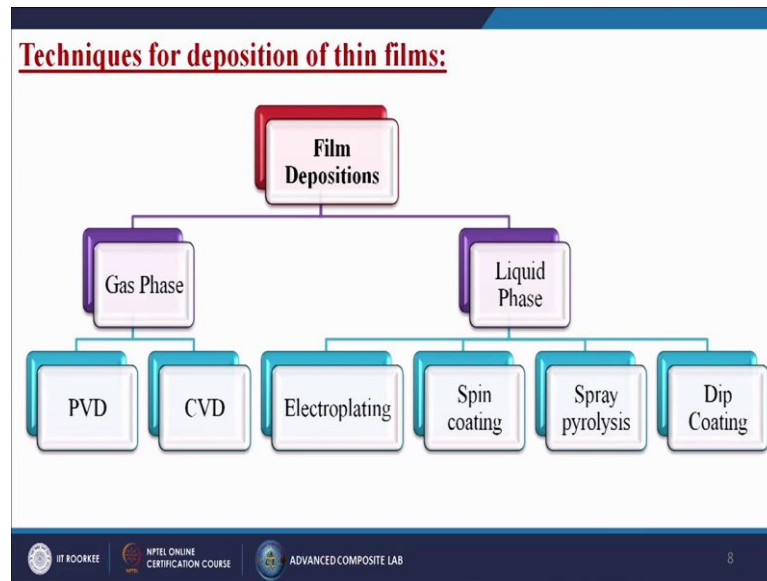
- The origin of thin films of all materials created by any deposition technique starts with a *random nucleation process* followed by **nucleation** and **growth stages**.
- Nucleation and growth stages are dependent upon various deposition conditions, such as growth temperature, growth rate, and substrate chemistry.

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So, some particular motives of thin film deposition; what are the logic that why we are going to use this kind of thin films for surface engineering. So, first is that to maintain the surface uniformity. So, we can get a homogeneous of surface (Refer Time: 07:42) over there smoothness of the surface will be good. To reduce the amount or mass of light observing materials; to decrease the weight and bulkiness of the materials, that means we are reducing the weight we are reducing the volume, but simultaneously we are ensuing the properties then the bulk film or the thick film.

Growth of a thin film generally exhibit following features. The origin of thin of all materials created by any deposition technique starts with a random nucleation process followed by nucleation and growth stages. Nucleation and growth stages are dependent upon various deposition conditions such as, growth temperature, growth rate, and substrate chemistry. So, the thing is that it depends upon our recommend that how many layer we are going to make to the substrate, what is the substrate condition, how much temperature can sustain this substrate and the thin films. So, it depends upon what property you are going to achieve, so depending upon that we can go for a single layer, we can go for a multiple layer deposition on to our substrate.

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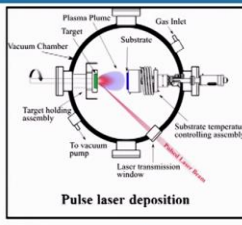
So, what are the techniques of deposition on thin films? Generally it can be divided into two parts: one is called the gas phase and other one is called the liquid phase. Gas phase generally you have discussing about the PVD process; physical vapour deposition process, and the CVD is call the chemical vapour deposition process. If you remember we have discussed the PVD process and our CVD process in details on lecture number 12 and lecture number 13.

And in this particular slide we are going to discuss about this kind of thinks into details, that is called the liquid phase which is divided into four parts; one is called the electroplating, then spin coating, spray pyrolysis, and the dip coating techniques.

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Gas phase deposition techniques:

Physical vapour deposition:
The word 'Physical' distinct from 'Chemical' is intended to indicate the absence of any chemical reactions in the formation of the films. Generally, it is abbreviated as PVD.

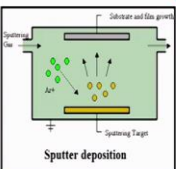


Advantages:

- Excellent process control.
- Low deposition temperature.
- Dense, adherent coatings.

Disadvantages:

- Vacuum processes with high capital cost.
- Limited component size treatable.
- Relatively low coating rates



Sputter deposition

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Now, in a single or may be brief manner I am going to discuss about the gas phase deposition techniques which is the first one is called the physical vapour depositions. The word physical distinct from chemical is intended to indicate the absence of any chemical reactions in the formation of the films; generally it is abbreviated as PVD. Simple we are having the (Refer Time: 09:47) we have hitting that material, we are making any kind of gas or molecules, and then directly the gas and molecules are coming on to the substrate there is no chemical reactions in between that coatings and the substrate. So, that is in general says call the psychical vapour deposition technique.

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➤ **Chemical Vapour deposition (CVD):**

CVD supports the formation of a non-volatile solid film on a substrate by the reaction of vapour phase chemicals (reactants) which consists of required constituents.

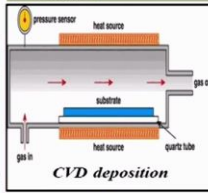
PVD	CVD
<ul style="list-style-type: none"> Evaporation is limited to certain materials. Sputter yield problem 	This method is preferred for Poly-silicon layers and Silicon nitride
Generally no hazardous by-products	Hazardous by-products
Low working temperature	Often requires high temperature (500 - 850 °C)
Highly directional	Poor directionality

Advantages:

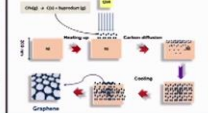
- High coating hardness.
- Good adhesion.

Disadvantages:

- High temperature process.
- Toxic gases.



CVD deposition



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Next the chemical vapour deposition technique also discuss in our earlier slides. So, the chemical vapour deposition is that the same thing like that we are introduced some kind of molecules, ions, some kind plasmas, but those materials can react with substrate they can form new pieces and like this they can do the coating on to the substrate material.

So, here the difference between the PVD and CVD we have shown over there. Then some cases we are getting some good properties some cases we are getting the some bad properties on may be the greater than the PVD methods. So, is actually depends on what kind of substrate you are going to use depending upon that we have to choose that whether you go for the PVD method or may be go for the CVD methods.

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Liquid phase deposition:

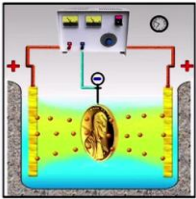
a) **Electroplating:**
An electrochemical process where metal ions are transferred from a solution and are deposited as a thin layer onto surface of a cathode.

Advantages:

- Low temperature treatment.
- Applicable to metal substrate.

Disadvantages:

- Not applicable to insulating materials.
- Poor thickness uniformity.



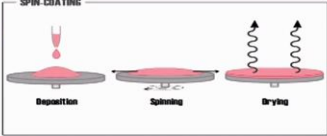
b) **Spin coating:**
In this process, liquid precursor is deposited onto a smooth and flat substrate which is subsequently spun at a high speed to centrifugally spread the solution over the substrate.

Advantages:

- Production of uniform film.
- Low temperature deposition.

Disadvantages:

- Difficulty with large area.



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So, now we are going to discuss in details about the liquid phase deposition techniques. So, first one is call the electro plating, so an electro chemical process were metal ions are transform for the solution and deposited as the thin layer on to surface of a cathode. So, from this particular figure you can understand that we are having one cathode, we are having one anode. And then we are using certain kind of potential different in between that so that metal ions are coming, we are using some kind of electrolyze solution over there. Then some kind of pleating is taking place electronically.

So, what are the advantages? Low temperature treatment; applicable to metal substrate; disadvantages: not applicable to insulating materials, poor thickness uniformity. That means that we need some kind of conducting materials for doing this kind of modifications.

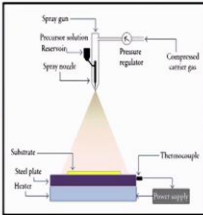
Next one is called the spin coatings process. So, in this process liquid precursor is deposited onto a smooth and flat substrate which is subsequently spanned at a high speed to centrifugally spread the solution over the substrate. So, here is the positions by the drop casting methods we have putting a droplight onto that particular surface, then we are rotating the disk in a very high rpm and due to the centrifugal force this material is spared all over around this disk, then we are trying that material and we are taking out that the material and that is known as a thin film deposition by the spin coating process.

So, what are the advantages? Production of uniform film, low temperature deposition; disadvantages: difficulty with the large area because we have putting some kind of droplets sometimes it cannot cover the whole disk area at a time.

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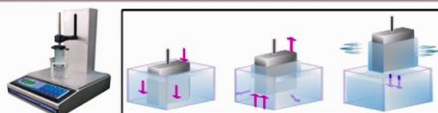
c) Spray pyrolysis deposition:
 It is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound.

Advantages:	Major disadvantage:
<ul style="list-style-type: none"> • Coating of metals & insulators • Cost effectiveness. • Deposition of large area. 	<ul style="list-style-type: none"> • Difficulties with growth temperature determination.



d) Dip coating:
 It is a process where the substrate to be coated is immersed in a liquid and then withdrawn with speed under controlled temperature and atmospheric conditions.

Advantages:	Disadvantages:
<ul style="list-style-type: none"> • Low cost. • Low processing temperature. 	<ul style="list-style-type: none"> • Poor adhesion.



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Then next one we are discussing about the spray pyrolysis deposition. Here it is nothing, it is a simple like the paint when we are doing on to our automatic parts or may be the wall are some kind of spray painting we are doing. So, it is the process in which a thin film is deposited by spraying a solution on a heated surface where the constituents react to form a chemical compound. So, what are the advantages? Coating of metals and insulates, cost effectiveness deposition of large area. Major disadvantages: difficulties with growth temperature determination.


So, from this particular figure you can understand that we have some kind of spray gun. So, directly some kind of carrier gas it is coming over there, we can regulate this pressure of this particular gas. Then we are having some reservoir; that means which material we have going to coat on to that materials that reserve we putting over there. Then we having a spry nozzle or may be some kind we can calling it has gun; in that gun we having that facility that this precursor materials and this compares air can be mixed properly, and then that can be thrown on to the substrate itself. And the substrate is kept on some heater so that we can increase or decrease the temperature of that particular substrate. So, we have to heat that substrate so that when that precursor with the gas





molecule it is directly come into the contact with the substrate they will make certain kind of chemical bounding and the material will be agitated and they will be form a new material, so that we can get a film on to the stop of the substrate.

Next is called as the dip coating; it is a process were the substrate to be coated immersed in a liquid and then withdrawn with speed under controlled temperature and atmospheric conditions. So, simple we are depending that material into the solutions and then we are taking in out. So, what are the advantages? It is very low cost, low processing temperature but it is the poor addition, because we are not using any kind of temperature over there simply we are dipping our substrate materials into solution and we are taking it out and then we are drawing and we are using those materials.

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Applications of Thin Film Technology:
Engineering/Processing :



			
Hard coatings for cutting tools.	Protection against high temperature corrosion.	Catalyzing coatings.	Tribological Applications: Protective coatings to reduce wear, corrosion and erosion.

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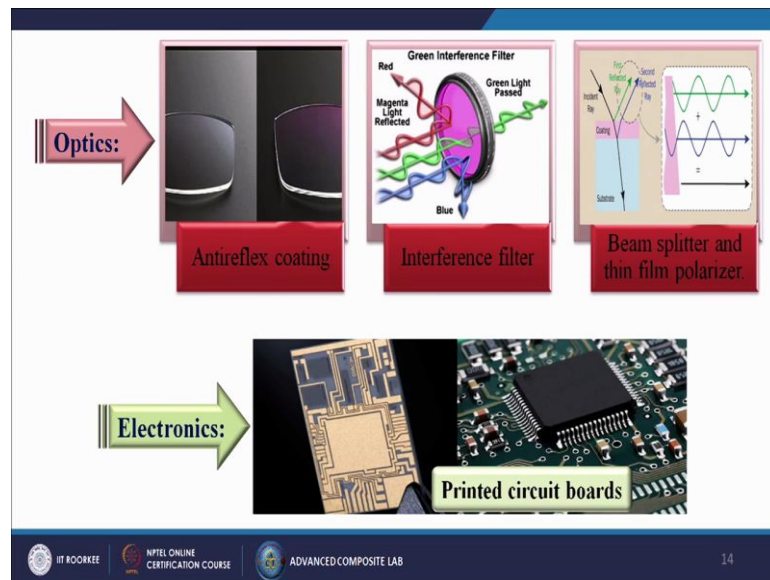
So, what at the applications of that thin film technology, engineering processing? Generally we are using for this materials for the hard coatings for cutting tools. So, generally we can do the coatings only the cutting regions so that the tool will be in expensive. Not only that sometimes we can change the carting geometric of this particular tool by using different types of inserts, that inserts can be made by different types of coating techniques.

Then protection against high temperature corrosion; generally for the chimney or may be some kind of exhorts pipe we can use this kind of coatings where they flew gases is

directly coming it is getting the contact with material or may be the substrate it can harm that material so that we are doing the certain kind of coating so that the flue gases or may be the toxic gases not directly come with the contact with that particular material.

Then we are using this materials for the catalyzing coatings, for some decorative thing, then some tribological applications protective coatings to reduce wear corrosion and erosion any kind of vehicles or may be some kind of airplanes or may be the any kind of submarine, ships where that materials is going into the water or may be that materials is going to the sky so that there will not be corrosions there not be any scratch on that particular material.

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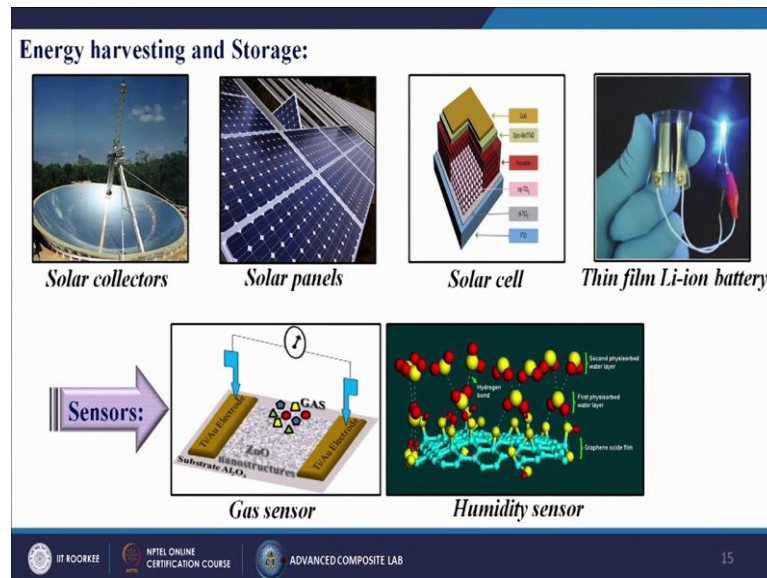


So, for optics also we are using kind of coatings for the anti reflection coatings, so right side is the antireflection coatings you can see the changing in to color itself, but both are the transparent but the difference in between that the light can passed through by this lenses, but here the light will be reflected; that is a very good for using this kind of glass while we are using some kind of computers while we are driving our cars so that the opposite side head light not directly come in to our eyes.

Some interference filter also, so we can use that certain and materials or may that certain light it can pass through this material and certain lights can be reflected by this materials, so that we can segregates the different frequency of that particular light. Then we can use

it for the beam splitter and thin film polarizer materials and the best application is that we can use this kind of coatings or may be the thin film technology for the electronic (Refer Time: 17:06) for the printed circuits boards. So, nowadays we are using this type of materials for our tablets for our mobiles or may be for our computers or may be the laptops.

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Then we are using this kind of thin films for the solar connectors, solar panels, solar cells; here you can see that there are several layers by which we are making the solar cells to increase the efficiency of that particular material. We are using this kind of materials for the lithium ion battery. Not only that we are using this kind of materials for the gas seniors and the humidity sensor which can detect the humidity of that particular room, which can be detect the toxic gas are present in the particular room or that particular area or not. And not only that we can use this materials for the energy harvesting applications, we can use this materials for the energy storage application so there are lots of applications where we can use this kind of thin film technology.

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Summary:

- Discussed various stages in thin film development from historical perspective.
- There are various thin film fabrication techniques including PVD, CVD, spin coating, electro spinning and so on.
- Thin films have been extensively recognized for wide range of potential applications such as electronic, optical, sensors, solar cell and battery etc.

Potential of thin films for future usage:

- Developing molecules out of organic compounds like carbon and hydrogen.
- Super thin film about 100 nm thick, can be applied as paint.
- Replace heavy metals currently being used in cells, creates biodegradable, natural cell.

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So, now in summary we are going to discuss that what we have learn from this particular lecture. So, discuss various stages in thin films development from historical prospective. There are various thin film fabrication techniques including PVD, CVD, spin coating, electro spinning and so on. We have already discussed all those things in details in our earlier slides. Thin films have been extendibility recognized for while range of potential applications such as electronic, optical, sensors, solar cell and battery. But again I am telling the same thing these applications are very few, there are numerous application which where we can use this kind of thin film technology.

So, potential of thin films are feature usage: developing molecules out of organic compounds like carbon and hydrogen. Super thin film about 100 nanometer thin can be applied as paint. Replace heavy metals currently being used in cells create bio degradable natural cell. So, these all are the future application of the thin films. Still the scientist and researchers all over the world they are working for preparing different type of thin films for numerous applications.

Thank you.