Non - Metallic Materials
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Module - 08
Thin film growth and fabrication of devices
Lecture - 40
Fundamental of thin film growth, growth mechanism and kinetics

Welcome to my course Non Metallic Materials and today we are in module number 8 - Thin film growth and fabrication of devices. This is lecture number 40 and I will be discussing the Fundamentals of thin film growth and it is growth mechanism followed by kinetics.

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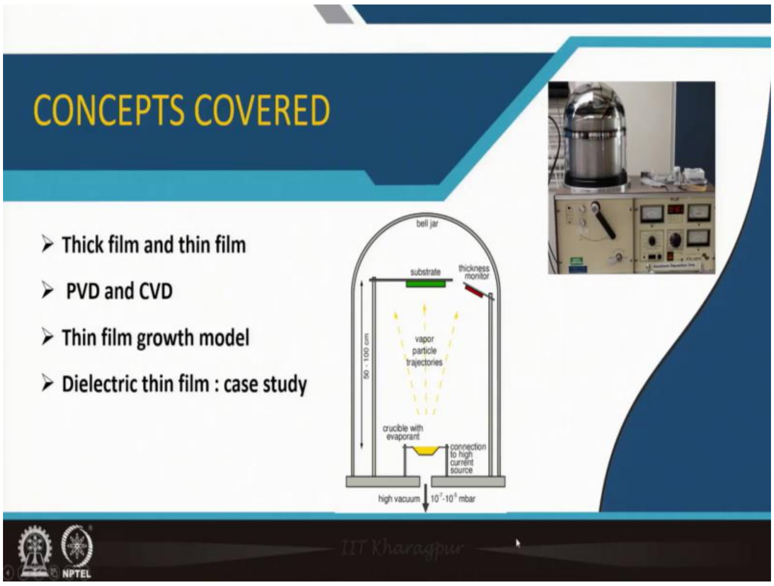

CONCEPTS COVERED

- Thick film and thin film
- PVD and CVD
- Thin film growth model
- Dielectric thin film : case study

Now, first I will introduce that what is the difference between a Thick film and a thin film, then these films can be deposited either by physical vapor deposition or by chemical vapor deposition routes. So, we will talk about the thin film growth model in a generalized form taking into example of the well known thermal evaporation technique. And as a case study we will be talking about dielectric thin film growth.

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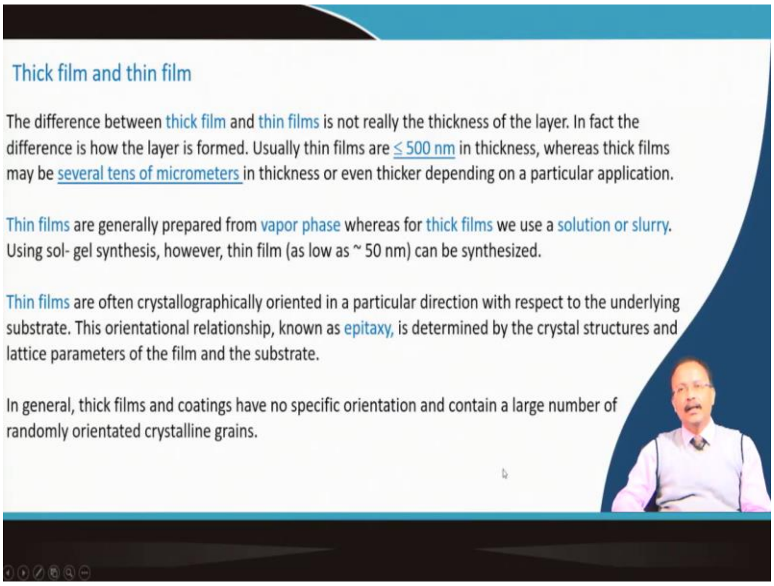

Thick film and thin film

The difference between thick film and thin films is not really the thickness of the layer. In fact the difference is how the layer is formed. Usually thin films are ≤ 500 nm in thickness, whereas thick films may be several tens of micrometers in thickness or even thicker depending on a particular application.

Thin films are generally prepared from vapor phase whereas for thick films we use a solution or slurry. Using sol- gel synthesis, however, thin film (as low as ~ 50 nm) can be synthesized.

Thin films are often crystallographically oriented in a particular direction with respect to the underlying substrate. This orientational relationship, known as epitaxy, is determined by the crystal structures and lattice parameters of the film and the substrate.

In general, thick films and coatings have no specific orientation and contain a large number of randomly orientated crystalline grains.

Now, it is really difficult to differentiate between a thin film and thick film and the difference that is not really only on thickness, difference in fact is the way this layers are formed. But, usually when the film thickness is less than about 0.5 micron 500 nanometer, then we call this is a thin film.

Whereas, several 10 of micrometers thicker layer we call this is a thick film and whether you go for a thin film or thick film that certainly will depend on the type of application that you are looking at. So, usually in vapor phase the thin films are deposited and we call this is a physical vapor deposited film and when a thicker film is required usually we use either precursor solution or the slurry.

Although sol gel technique you know that we discussed about it earlier, in sol-gel-technique very thin film can be deposited as low as 50 nanometer films can be deposited. Now, sometimes this film is having a very definite relationship with the underlying substrate and depending on the actually the direction is direction of growth of a thin film is directly influenced by the substrate.

So, depending on that we can end up with a textured thin film or an epitaxial quality film and particularly in this type of film the structure of the substrate and the film they are actually well matched. So, we will be just talking about very briefly about this kind of growth. But in case of thick film this definitive relationship between the substrate and the film is lost and basically it is a large number of very randomly oriented crystalline grain that is there in case of the so called thick film.

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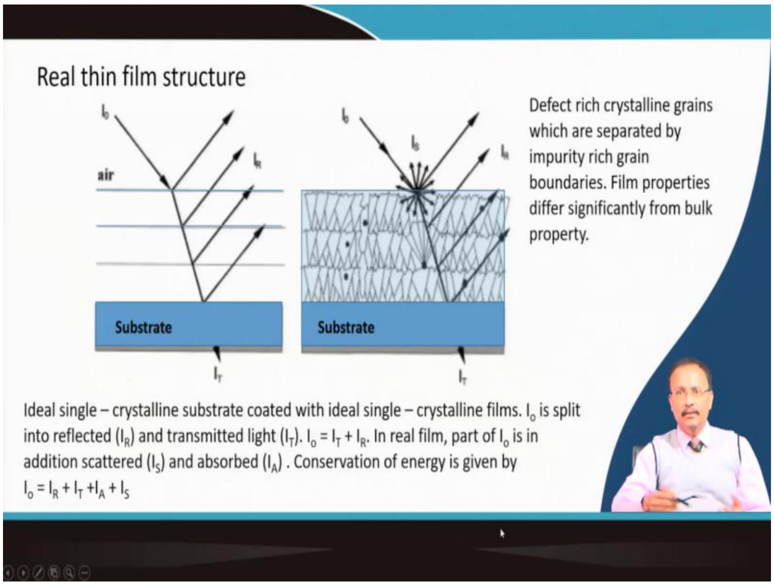

Real thin film structure

Defect rich crystalline grains which are separated by impurity rich grain boundaries. Film properties differ significantly from bulk property.

Ideal single – crystalline substrate coated with ideal single – crystalline films. I_o is split into reflected (I_R) and transmitted light (I_T). $I_o = I_T + I_R$. In real film, part of I_o is in addition scattered (I_S) and absorbed (I_A) . Conservation of energy is given by $I_o = I_R + I_T + I_A + I_S$

So, here you know that if you are talking about a thin film which is deposited on a particular substrate and which is single crystalline in nature, then the light wave part of it will get reflected from the crystalline plane in the film. And most of it will get transmitted if it is a insulating film which are having very large band cap.

But if you are talking about a metallic film then certainly this kind of transmission is not possible mostly it will get reflected. But once you talk about a real thin film structure then it is certainly not single crystalline. So, it is having lot of grain along with the grain boundary certain defects are also embedded in the thin film.

So, there the light will certainly be transmitted if it is an insulating film, but part of the light that is also scattered and part of the light is also absorbed in the material. So, if you consider a ideal single crystalline substrate coat it with a ideal single crystalline film, then you have only the transmittance and the reflectance. But actually in actual thin film you have all these 4 components reflection, transmission then absorption and scattering so all are applicable.

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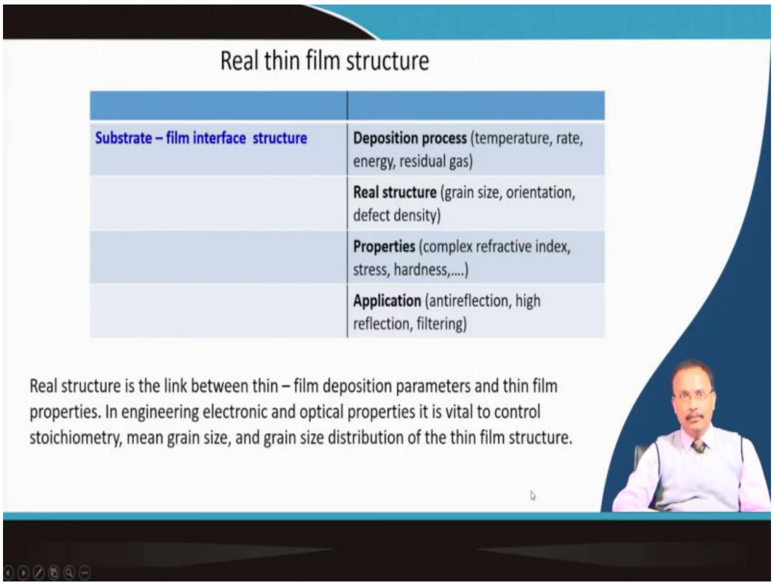

Real thin film structure

Substrate – film interface structure	**Deposition process** (temperature, rate, energy, residual gas)
	Real structure (grain size, orientation, defect density)
	Properties (complex refractive index, stress, hardness,....)
	Application (antireflection, high reflection, filtering)

Real structure is the link between thin – film deposition parameters and thin film properties. In engineering electronic and optical properties it is vital to control stoichiometry, mean grain size, and grain size distribution of the thin film structure.

Now, in real thin film structure there is substrate and thin film interface that is important and the thin film is basically dependent on the deposition process. So, what is the temperature of the substrate? What is the rate of so called evaporation then whether any residual gas is present in the chamber? So, the deposition process will control this film surface film and substrate interface.

Then as I said the microstructure of the film including grain size, grain diameter defect density in the grain, that will also affect the properties as well as the interface. The property like refractive index the stress in the thin film hardness of the film they are also affected.

So, this and suddenly application films are grown for anti-reflection coating or optical filtering there are also these deposition parameters they are of vital importance. And they basically this deposition parameters they control the stoichiometry of the grain, the size of the grain, grain size distribution. So, they are affected by the so called deposition parameter.

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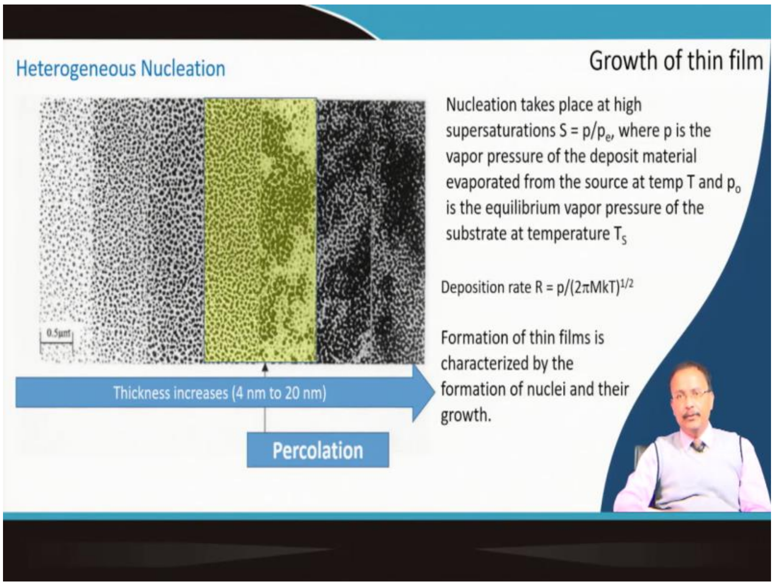

Growth of thin film

Heterogeneous Nucleation

Nucleation takes place at high supersaturations $S = p/p_e$, where p is the vapor pressure of the deposit material evaporated from the source at temp T and p_o is the equilibrium vapor pressure of the substrate at temperature T_S

Deposition rate $R = p/(2\pi MkT)^{1/2}$

Formation of thin films is characterized by the formation of nuclei and their growth.

So, when we start this thin film deposition it starts with a Heterogeneous nucleation, because the vaporized atom in case of a thermal evaporation route, that vaporized atom they are actually getting nucleated on a heterogeneous substrate surface, so that is of prime importance.

So where you can see that how with the change in thickness, because this microstructure grows with the thickness of the film as well, so as the thickness increases progressively to about 4 nanometer to about 20 nanometer, then there is a series of change of microstructure.

So, when this adatom I mean the vaporized atom is having a super saturation, then actually it will try to deposit from this vapor state on the relatively cold substrate surface at a particular temperature T. And the deposition rate that can be approximated by this simple relation, where this small p is the vapor pressure of the material that is evaporated and M is it is molecular weight Boltzmann constant and the temperature of operation.

So, this is characterized the thin film formation is characterized by the formation of small nuclei and subsequently they start to grow and during the growth process as you can see at some particular thickness. And this is very particular for the film, so this is a metallic film has been taken into account. Then it percolates and it forms a continuous channel and basically this channel grows.

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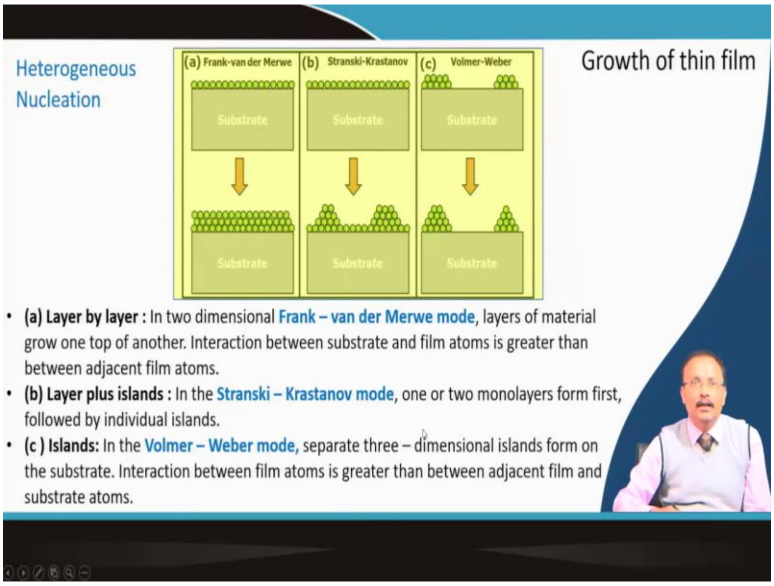

Growth of thin film

Heterogeneous Nucleation

- **(a) Layer by layer :** In two dimensional **Frank – van der Merwe mode**, layers of material grow one top of another. Interaction between substrate and film atoms is greater than between adjacent film atoms.
- **(b) Layer plus islands :** In the **Stranski – Krastanov mode**, one or two monolayers form first, followed by individual islands.
- **(c) Islands:** In the **Volmer – Weber mode,** separate three – dimensional islands form on the substrate. Interaction between film atoms is greater than between adjacent film and substrate atoms.

So, basically three types of this growth model is available the first one is a layer by layer model, as you can see first the monolayer forms and then subsequently the other layers form on top of it and this two dimensional growth mechanism is known as Frank van der Merwe model.

So, interaction between the substrate and film matters is greater between the adjacent film atoms so therefore it grows layer by layer. Sometimes it forms a layer and then it forms a island kind of growth and this is called Stranski Krastanov of mode. So, one or two monolayer initially forms and then individual islands form and sometimes only island forms, so that is called Volmer Weber growth.

So, separate three dimensional ions form on the substrate. So, in this case interaction between the atoms that is much larger as compared to adjacent film and substrate atom. So, depending on which type of kinetics is dominating we have three different types of model.

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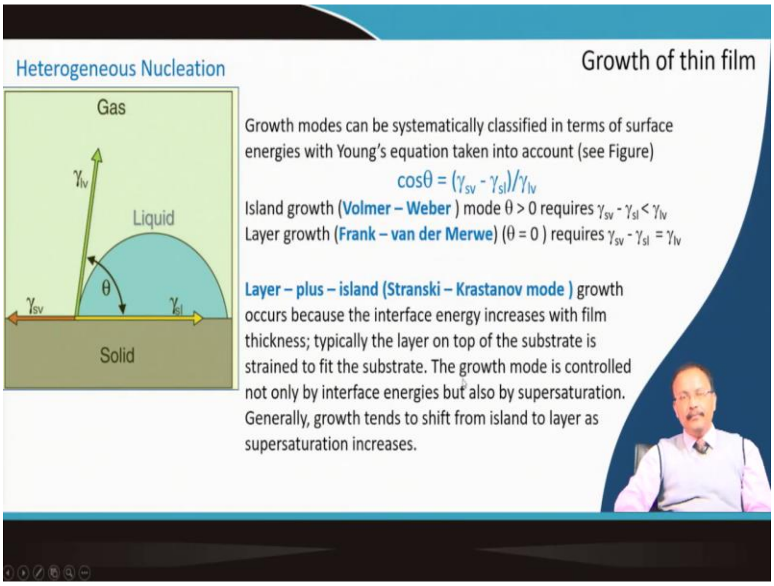

Heterogeneous Nucleation

Growth of thin film

Growth modes can be systematically classified in terms of surface energies with Young's equation taken into account (see Figure)

$$\cos\theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv}$$

Island growth (**Volmer – Weber**) mode $\theta > 0$ requires $\gamma_{sv} - \gamma_{sl} < \gamma_{lv}$

Layer growth (**Frank – van der Merwe**) ($\theta = 0$) requires $\gamma_{sv} - \gamma_{sl} = \gamma_{lv}$

Layer – plus – island (Stranski – Krastanov mode) growth occurs because the interface energy increases with film thickness; typically the layer on top of the substrate is strained to fit the substrate. The growth mode is controlled not only by interface energies but also by supersaturation. Generally, growth tends to shift from island to layer as supersaturation increases.

Now, this kind of film growth is very closely related with the Young's equation that already I have described in my earlier lecture. So, this can be very systematically classified in terms of the surface energy that you know that this weighting angle that depends on solid vapor surface energy as well as solid liquid and liquid vapor surface energy.

So, in case of island growth certainly this weighting angle theta should be more than 0 degree and from this kinetics this numerator that should be less than the denominator to satisfy that. And in case of layer growth that is Frank van der Merwe type of growth, so theta should be 0.

So, it should completely wet and that requires the numerator is roughly equal to be the denominator. In case of this layer plus Island this Stranski Krastanov type of growth, this basically occurs because the interface energy increases as the film is grown in z direction.

So, typically layer on the top of the surface is strained to fit the surface fit the substrate. In fact so the growth model is basically controlled not only by the interface energy, but also the super saturation of the vapor phase. And in general this growth tends to shift from island type to layer type as the super saturation increases. So, that is generally observed through a lot of experimental data.

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Coalescence

Growth of thin film

- The next stage of three – dimensional film formation is the growth of islands until they touch one another to form a continuous network. This is so called **coalescence process.**
- After solidlike coalescence of two islands there may remain a grain boundary between them, or they may fuse together in liquidlike fashion to form a new larger, and boundary free island.
- Surface energies and supersaturation are the factors that control these processes through material transport by surface and bulk diffusion.
- The transition from isolated islands to a continuous macroscopic network can be characterized by **a percolation threshold thickness.**
- For metallic thin films, at percolation thickness, coalescence creates a continuous path for electrons through the network and conductivity rises steeply by several orders of magnitude.

So, after it nucleates the next stage is coalescence. So, for three-dimensional film formation takes place and in earlier slide you have seen it that it start to percolate and then it forms the island forms until they touch to each other and form a continuous type of network and this particular process is known as coalescence process.

So, it could be solid like coalescence between two islands with a grain boundary in between or they may be fused together. So, in a liquid light fashion also they can grow. So, the surface energies and super saturations they are the two prominent factor they control the process and this is actually controlled by material transport and both surface and bulk diffusion which earlier I have covered in my course so that is operative here.

So, this transition from a isolated island to a continuous microscopic network as you can see here, so that actually is characterized by a percolation threshold. So, a threshold thickness that controls this kind of percolation. So, for metallic thin film the percolation thickness coalescence create a continuous path of electrons. So, initially when the islands are there if you measure it is resistivity it is quite limited.

But suddenly when a particular thickness is achieved and it percolates and you measure it is conductivity or resistance between this 2 portion you will see there is a sudden jump several order of magnitude change that will occur. So, that will characterize the threshold thickness of this percolation limit.

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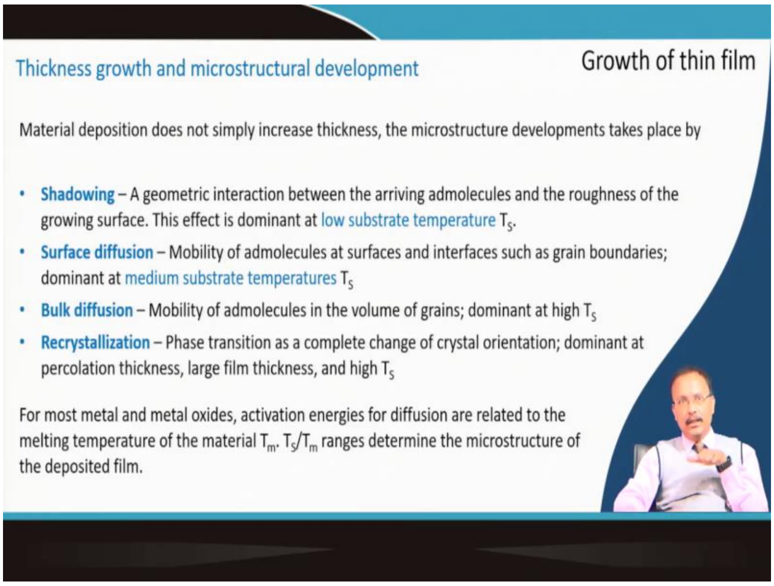

Thickness growth and microstructural development

Growth of thin film

Material deposition does not simply increase thickness, the microstructure developments takes place by

- **Shadowing** – A geometric interaction between the arriving admolecules and the roughness of the growing surface. This effect is dominant at low substrate temperature T_S.
- **Surface diffusion** – Mobility of admolecules at surfaces and interfaces such as grain boundaries; dominant at medium substrate temperatures T_S
- **Bulk diffusion** – Mobility of admolecules in the volume of grains; dominant at high T_S
- **Recrystallization** – Phase transition as a complete change of crystal orientation; dominant at percolation thickness, large film thickness, and high T_S

For most metal and metal oxides, activation energies for diffusion are related to the melting temperature of the material T_m. T_S/T_m ranges determine the microstructure of the deposited film.

So, the material that you are depositing in thin film form so, that one criteria is that with time the thickness will grow and microstructure also will change of this thicker layer. So, 4 different types of process can be identified. So, first is what is called Shadowing. So, it is a geometric interaction between the arriving vapor molecules and the roughness of the growing surface, because it grows initially smooth.

But, depending on the type of growth the surface is undulated and low at low temperature this kind of shadowing takes place, so that is the interaction between the deposited atom and the roughness of the surface that is grown. Then surface diffusion takes place. So, this adatoms they are actually mobile in nature and at the surface and interface of the grain boundaries it the surface diffusion takes place.

So, it is dependent on the substrate temperature and then bulk diffusion takes place. So, the adatom which is deposited on the substrate that tries to diffuse through the volume of the grain and relatively higher substrate temperature that will give this kind of bulk diffusion.

So, in many of the thin film process the substrate is also simultaneously heated during deposition, so that will lead to this bulk diffusion. So, all this process the shadowing after this surface diffusion and bulk diffusion the material is still amorphous in nature. So, at a certain temperature substrate temperature there is a phase transformation takes place when this amorphous phase is basically converted into a crystalline phase.

And this is dominant at the percolation thickness when the percolation takes place in the thin film structure. So, the film should be sufficiently thick, so that it is actually go to the crystalline state. So, activation energy of this diffusion are related to the melting temperature. In fact, the substrate temperature and melting temperature ratio that basically determines the microstructure of the film in question.

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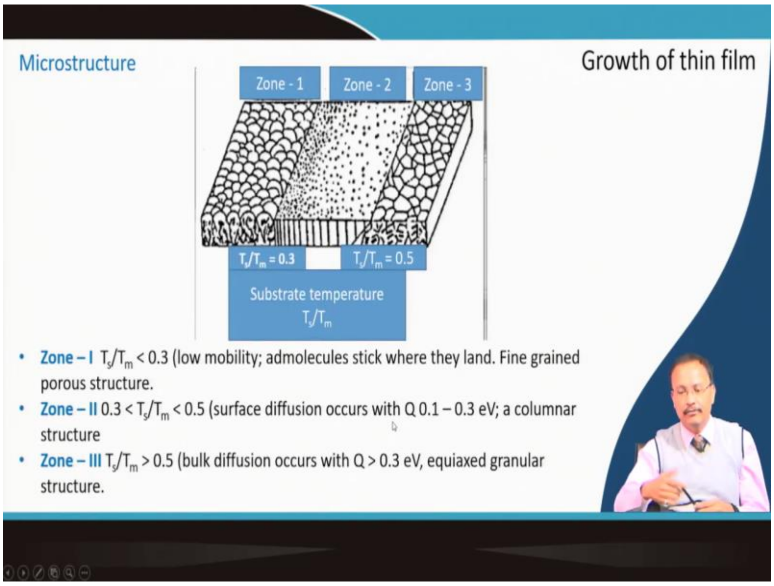

Microstructure

Growth of thin film

- **Zone – I** $T_s/T_m < 0.3$ (low mobility; admolecules stick where they land. Fine grained porous structure.
- **Zone – II** $0.3 < T_s/T_m < 0.5$ (surface diffusion occurs with Q 0.1 – 0.3 eV; a columnar structure
- **Zone – III** $T_s/T_m > 0.5$ (bulk diffusion occurs with Q > 0.3 eV, equiaxed granular structure.

So, we can now differentiate three types of zone in a grown film, the zone 1 here you can see that the substrate temperature and melting temperature ratio is about 0.3 and we call this is a low temperature zone and here they just the adatom starts to stick and they are fine grain structure and after that after you increase this temperature regime then this is zone 2 where columnar kind of growth takes place.

So, you can see from the substrate surface the columns grow and finally at zone 3 when bulk diffusion is operative in this case surface diffusion is operative. So, when the bulk diffusion is operative with a typical activation energy about 0.3 electron volt, then you have equiax grain and a typical poly crystalline structure of the film.

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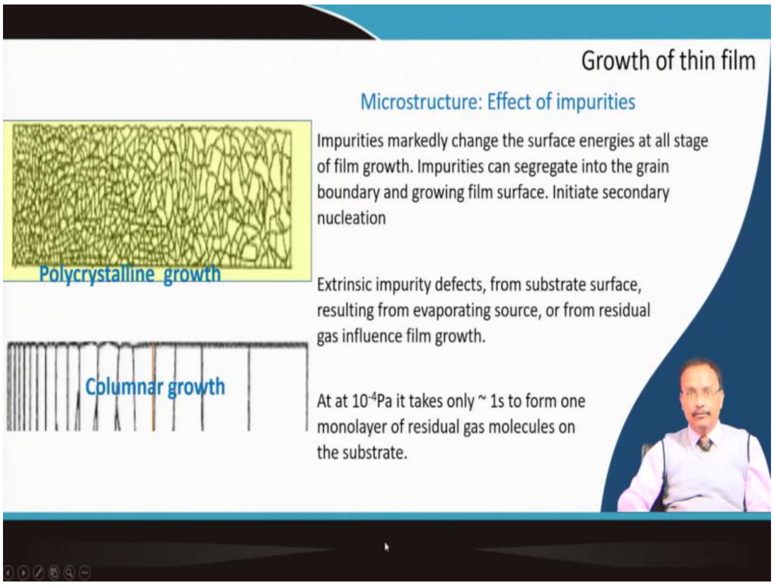

Growth of thin film

Microstructure: Effect of impurities

Impurities markedly change the surface energies at all stage of film growth. Impurities can segregate into the grain boundary and growing film surface. Initiate secondary nucleation

Extrinsic impurity defects, from substrate surface, resulting from evaporating source, or from residual gas influence film growth.

At at 10^{-4}Pa it takes only ~ 1s to form one monolayer of residual gas molecules on the substrate.

So, impurities they are adhered to the film surface, because it is not only the gaseous atom the depending on what type of vacuum is there you have other atom like moisture or gaseous atoms they are there. So, they markedly change the microstructure at all this stage zone 1 zone 2 and zone 3.

So, this extrinsic impurity defects from the substrate surface or from the evaporating source form or from the residual gas they interact with the film and they also control this types of adatom inclusion that also control the microstructure of the thin film. Usually when the vacuum level is low then you have other atoms present and they also can form a monolayer along with your film material.

So, they really interact with the columnar growth type of microstructure and eventually it leads to a polycrystalline surface where all the defects are basically segregated at the grain boundary. So, this poly crystalline growth is shown here and defects plays a major role to control this types of defect.

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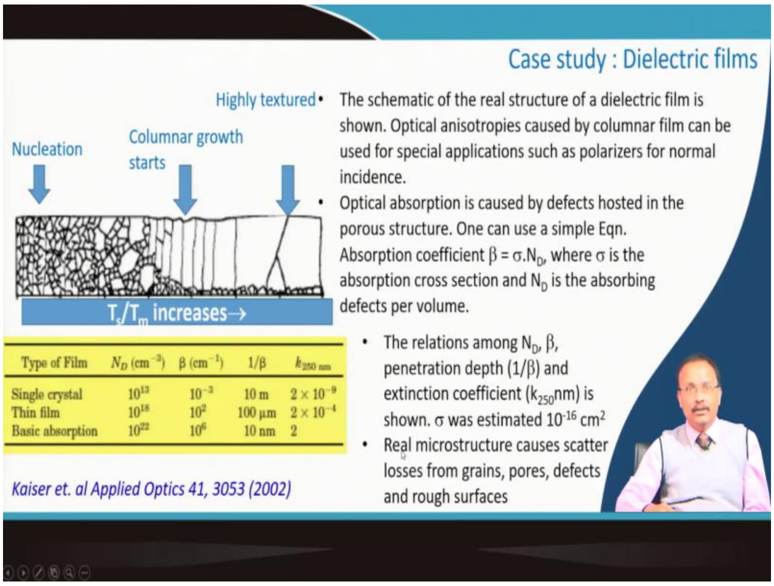

Case study : Dielectric films

- The schematic of the real structure of a dielectric film is shown. Optical anisotropies caused by columnar film can be used for special applications such as polarizers for normal incidence.
- Optical absorption is caused by defects hosted in the porous structure. One can use a simple Eqn. Absorption coefficient $\beta = \sigma . N_D$, where σ is the absorption cross section and N_D is the absorbing defects per volume.
- The relations among N_D, β, penetration depth $(1/\beta)$ and extinction coefficient (k_{250}nm) is shown. σ was estimated 10^{-16} cm^2
- Real microstructure causes scatter losses from grains, pores, defects and rough surfaces

Type of Film	N_D (cm^{-3})	β (cm^{-1})	$1/\beta$	$k_{250\ nm}$
Single crystal	10^{13}	10^{-3}	10 m	2×10^{-9}
Thin film	10^{18}	10^{2}	100 µm	2×10^{-4}
Basic absorption	10^{22}	10^{6}	10 nm	2

Kaiser et. al Applied Optics 41, 3053 (2002)

So, this is a case study of a real dielectric film and for optical purpose we usually use it, various dielectric film starting from may be titanium oxide or zirconium oxide, aluminum oxide you can grow some of the film material that cuts the UV radiation. So, for the spectacles etcetera this kind of coatings are given, so there is a very sharp absorption edge.

So, UV is filtered out so UV protective coating they are grown. And here you can see that the stages of the microstructure evaluation that whatever I just showed you. So, initially the nucleation takes place here and then when the substrate temperature is increased progressively, then there is a possibility to get a columnar growth and a single crystal in film.

But not always it is possible because of the defect inclusion and it leads to a poly crystalline structure. So, optical anisotropy can happen because of this columnar growth and you need to control this kind of columnar growth to take care of the optical anisotropy of certain material.

And as I said the when the defects are included hosted in this film structure. So, it forms a relatively porous structure and one can use this simple relation that this absorption coefficient that is dependent on the absorption cross section which is sigma and the defect density per volume. So, defect density is related with the absorption coefficient through this simple relation.

So, basically the relation among the defect density the beta parameter. So, when it is inverse of beta we call this is a penetration depth and also the extinction coefficient extinction coefficient that is shown in this particular table. So, when in case of a single crystalline film as you can see the defect density is much lower as compared to the polycrystalline thin film structure.

And accordingly you can see that this consider if you consider this 2 value sigma and N D or from knowing this to value you can estimate the absorption cross section. And this absorption cross section for a certain case in single crystalline it can be estimated about 10 to the power minus16 centimeter square.

And due to the defect adaptation inside the film structure this microstructure of the film they cause scattering of the grain. So, the different types of pores that is present in the material or the defects that basically lead to a very rough surface and for certain optical application you need to control this defect density to have a relatively smoother surface.

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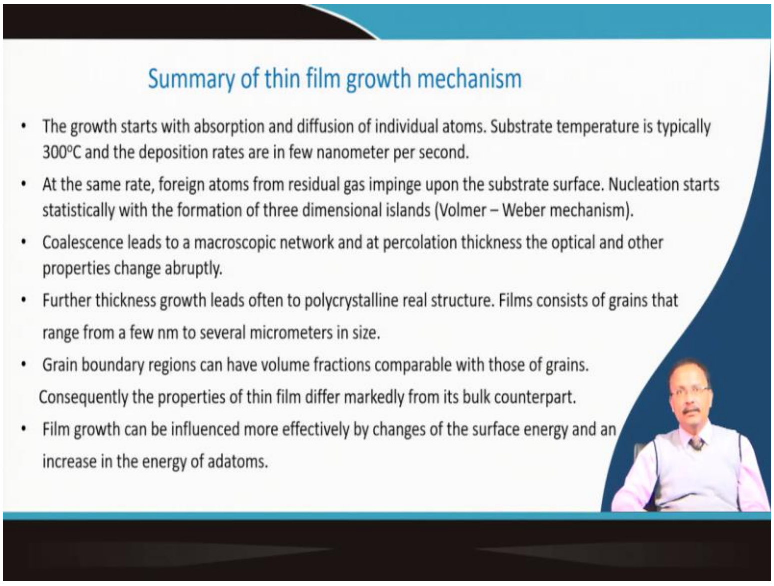

Summary of thin film growth mechanism

- The growth starts with absorption and diffusion of individual atoms. Substrate temperature is typically 300°C and the deposition rates are in few nanometer per second.
- At the same rate, foreign atoms from residual gas impinge upon the substrate surface. Nucleation starts statistically with the formation of three dimensional islands (Volmer – Weber mechanism).
- Coalescence leads to a macroscopic network and at percolation thickness the optical and other properties change abruptly.
- Further thickness growth leads often to polycrystalline real structure. Films consists of grains that range from a few nm to several micrometers in size.
- Grain boundary regions can have volume fractions comparable with those of grains. Consequently the properties of thin film differ markedly from its bulk counterpart.
- Film growth can be influenced more effectively by changes of the surface energy and an increase in the energy of adatoms.

So, I can summarize the thin film growth mechanism. So, the growth you basically start with the absorption of this vaporized atom and then the diffusion starts. First the surface diffusion followed by the bulk diffusion and substrate temperature is usually kept 300 degree Celsius and the deposition rate is very typical in case of the PVD techniques that is few nanometer per second.

At the same rate foreign atoms from the residual gas they also impinge upon the substrate surface and nucleation starts in fact in a statistical way. And various three dimensional structure forms and prominent among this structure is Volmer Weber type of islands growth. Then coalescence start leads to the formation of a microscopic network and percolation thickness can be defined where this kind of coalescence starts.

So, at that stage film consists of grain this nuclei they forms grain that range from a few nanometer to several micrometer in size. Grain boundary regions can have volume fraction comparable with those of the grains. So, as you can understand if the grain size is very small then the grain boundary concentration is also appreciable. So, that can be have this fraction can be quite large this grain boundary fraction.

So, due to this fact the same material if you measure it is various property in it is bulk form and in thin film form you will find it very different. In fact, the properties are also changes because of the microstructure change and film growth that can be influenced more effectively by change of the surface energy of the substrate.

So, substrate plays a major role to control the type of the growth. Whether it will be a textured type or it will be epitaxial type or it will be polycrystalline type or also it will remain amorphous in nature. As it is during the thin film deposition initiation of thin film deposition.

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REFERENCES

- **N. Kaiser** Review of the fundamentals of thin – film growth Applied Optics 41, pp 3053 – 3060 (2002) (Study materials)
- **C. Barry Carter, M.G. Norton** Ceramic Materials Science and Engineering, Chapter – 26, Processing glass and glass – ceramics, page 463 – 480 , Springer , 2007 (Study material)
- **K.L. Chopra** Thin film device applications, Springer, 1983

So, this is a nice paper by Kaiser he has reviewed all the fundamental models which I have covered in my lecture. So, that is basically the study material and along with that the book chapter, chapter number 26 of the book by Barry Carter and M.G Norton that also will be used may be used as a study material. And a fundamental book by professor k l Chopra thin film device and application that also can be used as a reference material.

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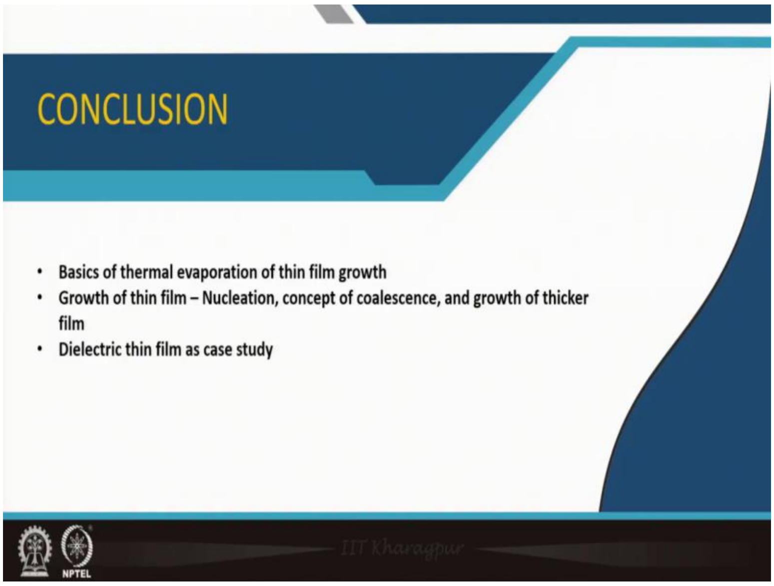

CONCLUSION

- Basics of thermal evaporation of thin film growth
- Growth of thin film – Nucleation, concept of coalescence, and growth of thicker film
- Dielectric thin film as case study

So, in this particular lecture I have covered the basics of thermal evaporation of thin film growth it is basically PVD technique and very simple PVD technique I have taken into consideration which is thermal evaporation. The details of it I will cover in my next lecture and not only thermal evaporation, but the other techniques also will be covered.

Then we talked about the growth of the thin film nucleation concept of coalescence, then the percolation thickness correspond to the percolation of this small structure to grow the thicker film and then a typical dielectric thin film as a case study we have covered.

Thank you for your attention.