Materials Chemistry
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Module - 2
Lecture - 2
Pulsed Laser Deposition Oxide Thin Films

In this module on chemical fabrication, in the last lecture we looked at one of the most sophisticated approach to make thin films, that too to confine in monolayer thicknesses, that is in atomic scale, which we call it as molecular beam epitaxy.

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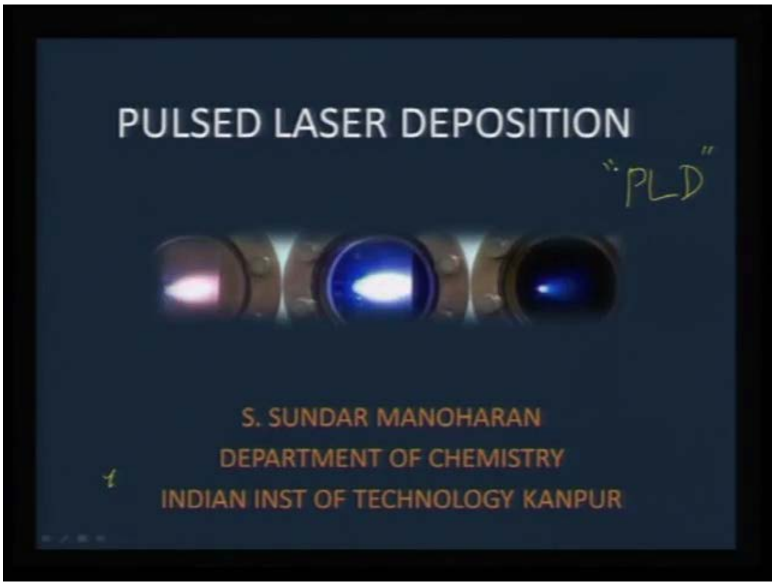

PULSED LASER DEPOSITION

"PLD"

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Molecular beam epitaxy is the one of the most refined thin film fabrication unit, that is available both for the industry as well as for basic research. As we see saw in the last lecture, the conditions that are used in MBE is not something that we can used practically this research conditions, because we work with very ultra high vacuum. But normally for us to evaluate any system and to look for new possibilities, new avenues, it is very difficult to maintain a MBE chamber and to conduct a research and specially in our country.

So, the best way to look for opportunities in research is to go for much more faster and more friendly techniques; one of the technique is pulse laser deposition, it is actually abbreviated or people popularly refer to as PLD technique. PLD technique is one of the most used throughout the world for making thin films of any material that is kind of interest. In this talk, I am going to tell you about what this PLD is all about, and as you would see, it is interaction of laser with matter and that will actually ablate a material and will help us in making films with a proper substrates.

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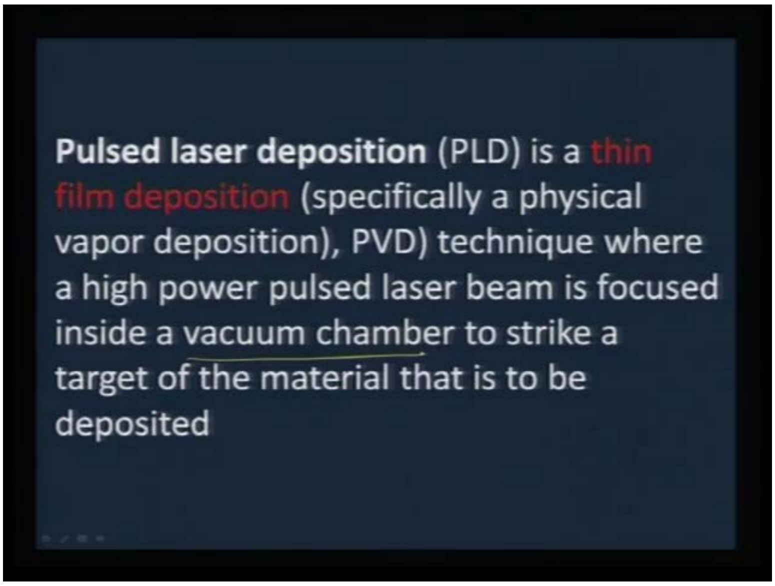

Pulsed laser deposition (PLD) is a thin film deposition (specifically a physical vapor deposition), PVD) technique where a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited

So, in terms of that a definition, pulsed laser deposition is a thin film deposition, specifically a physical vapor deposition, because there is not much chemistry involved and it is also called PVD, because a complementary chemical technique called CVD is a chemical vapor. So, this is a complementary technique to CVD technique, where a high power pulsed laser beam is focused, inside a vacuum chamber to strike a target of the material that is to be deposited. So, this is a high vacuum chamber, usually for normal practices, we use 10 power minus 7, but you can also use 10 power minus 11, that is ultra high vacuum chambers.

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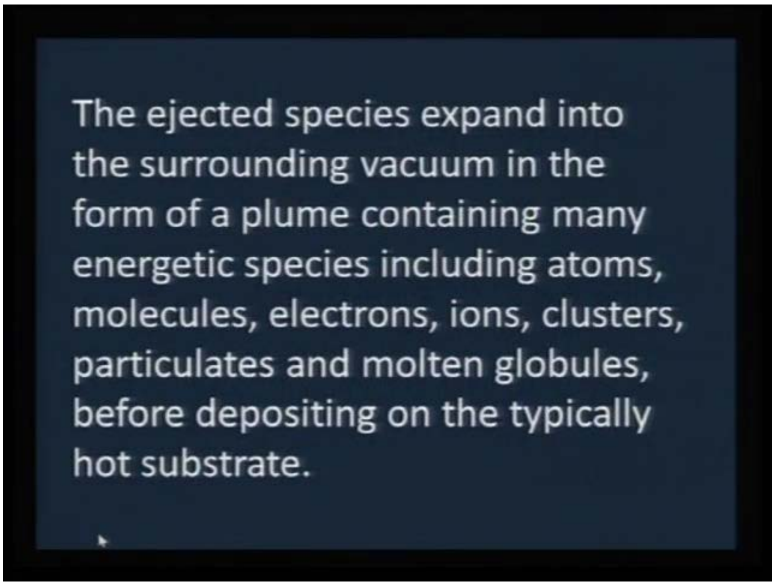

The ejected species expand into the surrounding vacuum in the form of a plume containing many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten globules, before depositing on the typically hot substrate.

So, in this pole episode of the deposition using pulsed laser, the ejected species, they expand into the surrounding vacuum and in the form of a plume, which we call it as laser plume. and this will actually bring about energetic species, which carries, atoms, molecules, fragmented molecular species, electrons, ions, clusters all this are they come in essence and reach the surface of the substrate. And at the substrate, there is another reaction that is going on, which will decide whether you are getting the required film or not. So, this is the simple dynamics of a pulse raised at the portion, we will see some animation of it in the next few slides.

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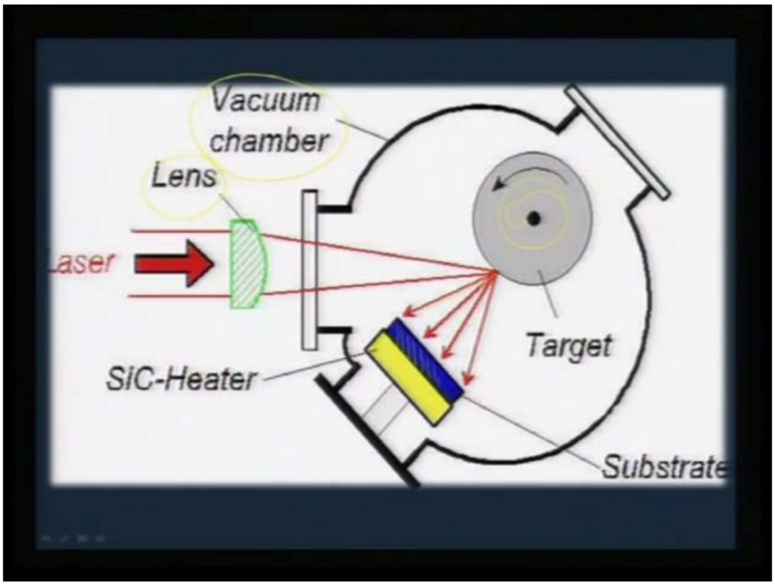

Just to tell you, what a how simple this could be, you shine a laser and through optics you try to converge, it usual usually, this laser is incident to 45 degrees to a rotating target. This target is actually keeps rotating and as it rotates laser comes and strikes and this is kept curve particular, the substrate is kept curve particular to the rotating target. So, whatever that is removed from the surface of the target is now going to come and reach the surface of the substrate. So, once the substrate is kept at high temperature, then you can actually make the desired film what you want, so this is the simple protocol, what it involves is a vacuum chamber and some optics and then whatever is happening inside is to do with the vacuum chamber. So, it is a very a simple protocol, compared to molecular beam epitaxy, in terms of achieving vacuum and in terms of handling the instrument also.

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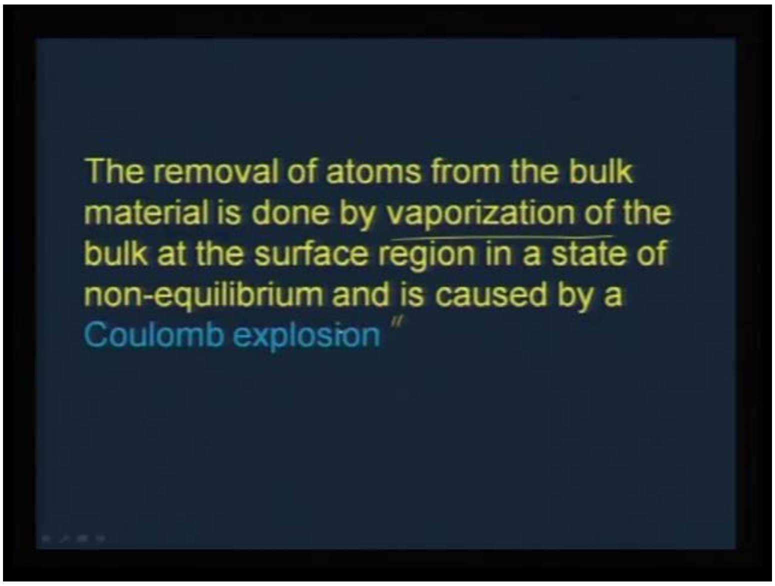

The removal of atoms from the bulk material is done by vaporization of the bulk at the surface region in a state of non-equilibrium and is caused by a Coulomb explosion "

The removal of atoms from the bulk material is done by vaporization of the bulk, at the surface region, in a state of non-equilibrium and is caused by a coulomb explosion. So, we will look into some of the requirements of what really happens at this plume and target surface. So, what exactly comes out, in the form of ions and electrons and molecular species as a laser plume this is nothing but a coulomb explosion.

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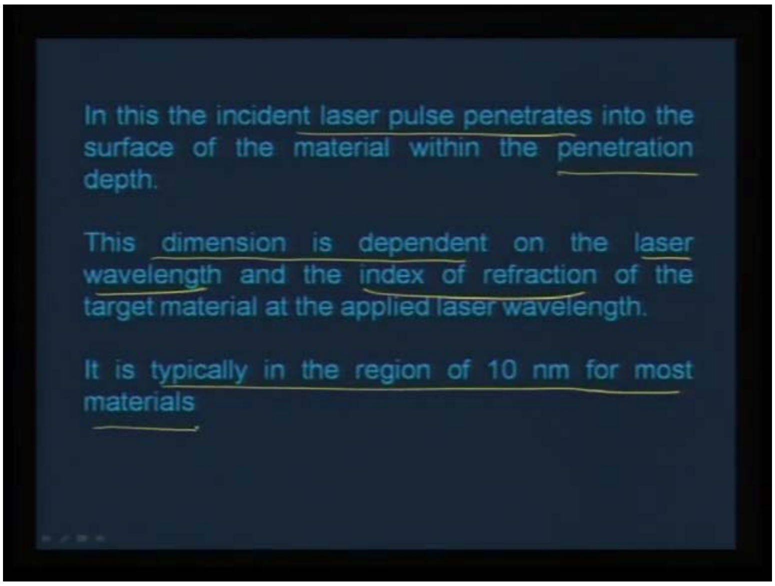

In this the incident laser pulse penetrates into the surface of the material within the penetration depth.

This dimension is dependent on the laser wavelength and the index of refraction of the target material at the applied laser wavelength.

It is typically in the region of 10 nm for most materials

In this the incident laser pulse, actually penetrates into the surface of the material within the penetration depth. So, well it is the interaction of a laser plume or a optical beam with the solid material, therefore how much of this light or the photon, can enter into the solid, determines what will come out. So, if it does not penetrate high enough then you would hardly see anything coming out, but if the penetration depth is quite deep then you will get almost all the species that is required, out from the surface of the target.

So, this dimension is actually dependent, the dimension meaning, the penetration depth is dependent on the laser wave length and the index of refraction and refraction of the target material at the applied laser wavelength. So, in this caution to be taken that, it should be a material, which will absorb your, if it does not absorb your laser light, then it will not emit therefore, your optical coefficient of your material is important, in essence you cannot oblate insulator that easily as much as, you oblate a metallic material.

So, this becomes a inherent problem specially because the penetration of the laser light is the governing factor here. So, therefore, it put some quantum restrictions on to that sort of materials, that you can use with these, so it is typically, in the region of 10 nanometer for most materials, being that penetration depth. So, if you can achieve this much then you can actually bring about the surface of the material, in the form of a plum.

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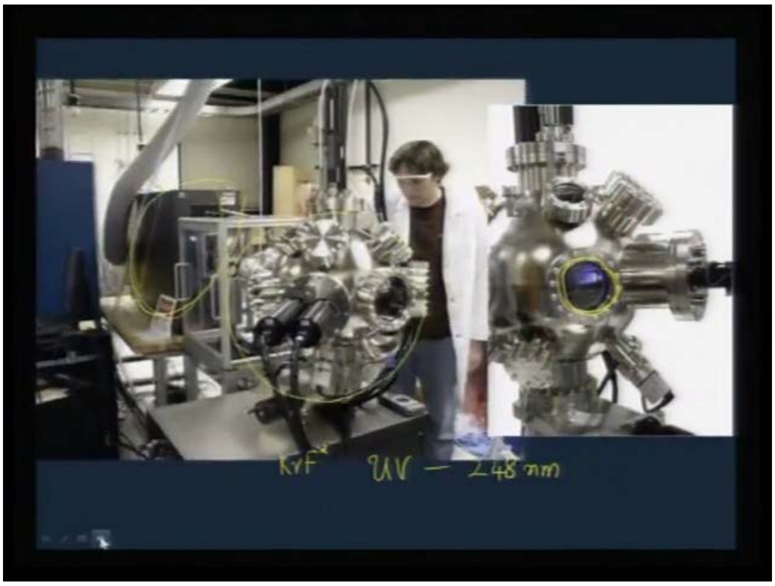

Typically, this is how laser PLD will look like, this is the vacuum chamber, as you see here and at the rear side, you see excimer laser, that is housed and in between you see this glass windows, mainly to shield from the radiation, because what you are pumping is actually u v radiation from excited krypton fluoride. And this is actually giving a u v radiation of 248 nanometer wavelength, because you are using a ultra violet radiation, it is important, that you shield it therefore, this is not a very friendly one and care should be taken, because you would not see, this u v radiation coming out of the laser.

Therefore, out of curiosity one should not even peep into the path way, because that can easily burn your eye and the person can even go blind, if he takes the one shot of this u v light, because it is monochromatic and high power laser. Therefore, it is always important to have some protocol where, this radiation effects are minimized handling becomes easy. So, this is typically PLD set up in any PLD lab, you would see the vacuum system, then the optical arrangement bringing the laser light into the vacuum chamber and then of course, be laser.

Typically, when you are trying to do reaction, what you would see during the PLD deposition is some sort of the flash like, this which means the plume is actually coming with very high intense colors. And color can actually, tell you whether you are really depositing the right material and right conditions or not, so it can be as friendly as it would be, if you get use to the laser plume. So, typically during the process, you would see some sort of flashes like this.

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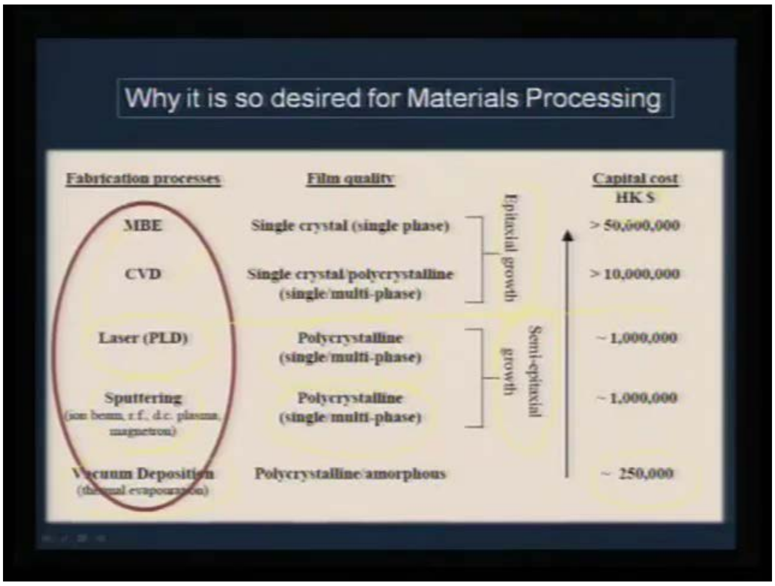

Why it is so desired for Materials Processing

Fabrication processes	Film quality		Capital cost HK $
MBE	Single crystal (single phase)	Epitaxial growth	> 50,000,000
CVD	Single crystal/polycrystalline (single/multi-phase)		> 10,000,000
Laser (PLD)	Polycrystalline (single/multi-phase)	Semi-epitaxial growth	~ 1,000,000
Sputtering (ion beam, r.f., d.c. plasma, magnetron)	Polycrystalline (single/multi-phase)		~ 1,000,000
Vacuum Deposition (thermal evapouration)	Polycrystalline/amorphous		~ 250,000

That’s how it goes now the next question is why we need to take PLD, so seriously, when you have a more refined set up like M B E, but we should also know, that research is not just limited to the efficiency but also to the economic considerations. Any lab can easily afford vacuum deposition chambers, here you can make polycrystalline and amorphous materials. If you look at the cost, this is actually in Hong Kong dollars, but nevertheless it just gives you, how simple a vacuum system can be, which involves thermal evaporation whereas, if you go for sputtering it is almost 4 times costlier than a thermal evaporation technique, but again you can play around with polycrystalline films.

The next to transient is laser PLD laser, PLD is almost of the same sputtering cost, but then you can actually play around with single and multiphase compounds or chemicals. But, there is a difference here beyond this whatever you see, those are very, very costly equipments C V D for example, chemical vapors deposition and molecular epitaxy, there of a higher value, but they usually guarantee epitaxial growths. Meaning the film will be always single crystalline, you would not see any polycrystalline phases, therefore to get a single or a multiphase product, you need to choose what sort of the position technique that you would look for. For depositions involving very high areas, large areas, usually we go for C V D, that is one of the reason, why chemical vapour deposition method still stands as a special case, I mixed all the other physical vapour deposition techniques. So, what really brings the device is not just the cost, it is also the sort of final product that you are looking for, either it is a semi epitaxial growth or an epitaxial growth. So, epitaxy is the underlined word, therefore certainly this is different from MBE.

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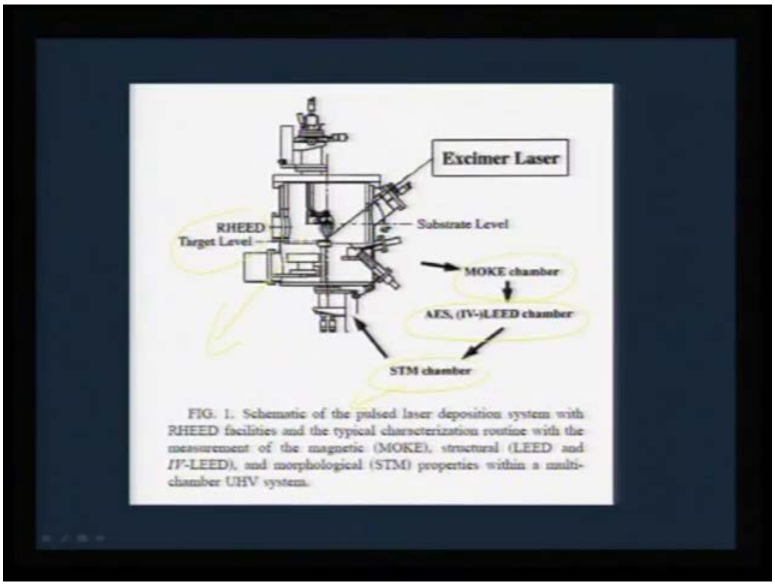

FIG. 1. Schematic of the pulsed laser deposition system with RHEED facilities and the typical characterization routine with the measurement of the magnetic (MOKE), structural (LEED and *IV*-LEED), and morphological (STM) properties within a multi-chamber UHV system.

As I told you in a M B E chamber, in the last lecture M B E chamber is usually tagged to other characterization techniques like RHEED magneto optical care effect LEED and atomic energy spectroscopy and also to a S T M. But, PLD instrument is not necessarily interface with all these other techniques, in the sense you can have the luxury of breaking the vacuum and taking the material out for characterization. So, that way it is more friendly, you can play around with a variety of materials, but in M B E, you never get to break the vacuum. So, it is always inside the vacuum chamber therefore, you need to circulate your chamber from the processing chamber to characterization chambers again you clean the crystal again you go into this. So, it is a loop, but in PLD you can actually after this, you can come out and do exito measurement in A F O model S T M chamber, you can do exito measurement on a LEED chamber. So, this gives a to play around with different systems.

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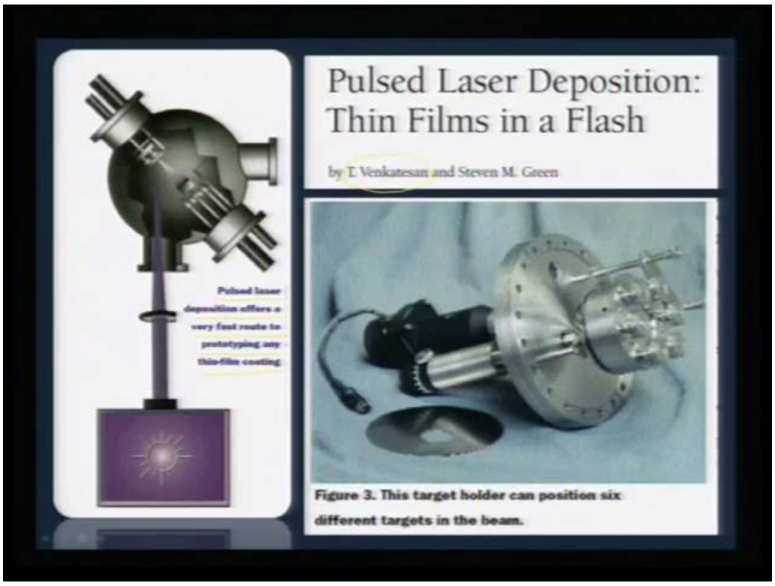

Pulsed Laser Deposition: Thin Films in a Flash

by T. Venkatesan and Steven M. Green

Pulsed laser deposition offers a very fast route to prototyping any thin-film coating

Figure 3. This target holder can position six different targets in the beam.

One of the pioneers in this field is professor Venkatesan, who actually started the application of oxide thin films, using PLD specially, he was the first one to demonstrate how a high temperature superconductor like, yttrium barium copper can be made as a thin film, for device applications, using PLD as a convenient route. Therefore, I just wanted to show the this set up and this is a good article, that has come out in a p s magazine. So, pulse laser deposition offers a very fast route to prototyping anything from coating, so if you want a quick study on any complex material, in the first thing to adopt is PLD.

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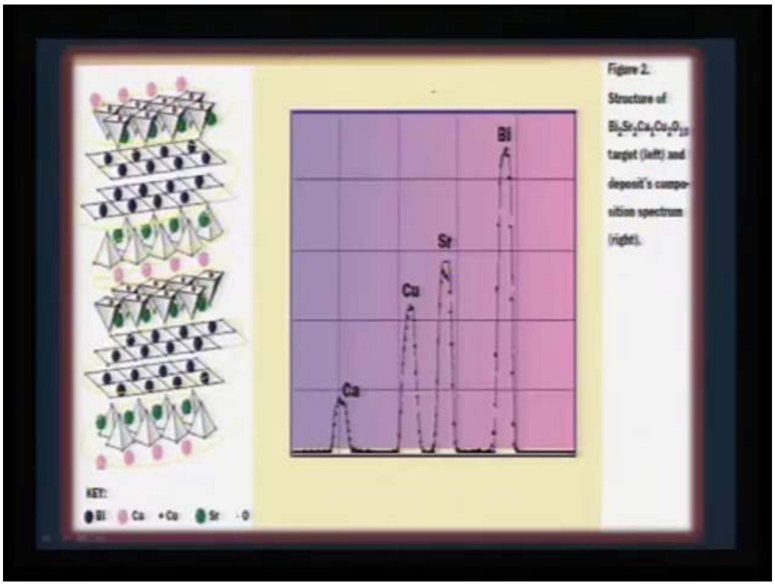

Figure 2. Structure of $Bi_2Sr_2Ca_2Cu_3O_{10}$ target (left) and deposit's composition spectrum (right).

So, just to give a clue, why you can be a versatile is that, this is a bismuth strontium calcium cuprate and this is a material, which shows high temperature super conductivity above 130 Kelvin. And if you look at a crystal structure, you would see the copper oxygen sheets and then the barium bismuth and strontium oxide layers, which are sandwiched by copper oxygen plates. So, this is the one single unit cell of this bismuth copper oxide cuprate, this is one unit cell with, so many layers and it can be effectively fabricated using pulse laser deposition. So, a complex a unit cell, but PLD will exactly bring about the same arrangement, so therefore, PLD has lot of attraction.

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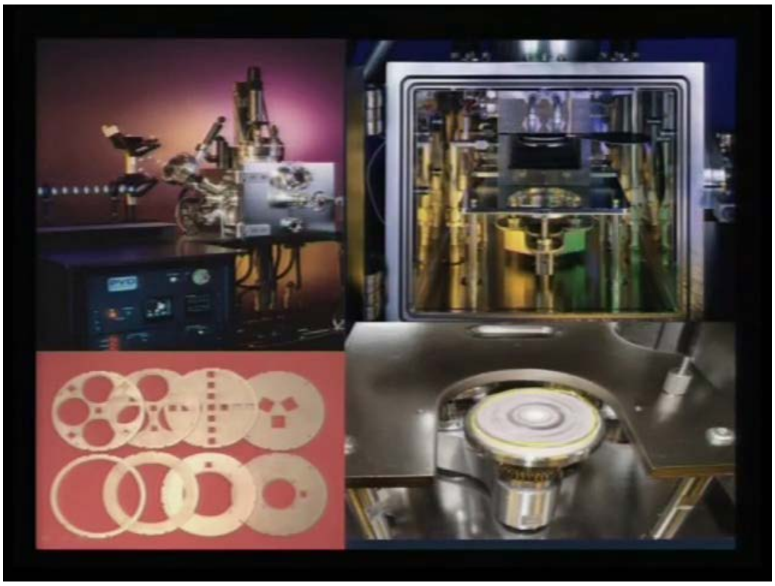

Other commercial instruments like P V D is one company, which brings about and this is one of the PLD chamber that they mark it, you can see the complexity of this. And typically, the targets, the target of the material, which you would like to deposit as a thin film is mounted on a sample folder like this. What you see here is nothing but a used target of a particular material, which has gone through several depositions, so you would see the imprints of the laser beam interrupting with a material and several times, it has been used for oblation, but not only that, you can also use multi target holder.

So, if you want to make a complex material like, what I showed in the previous slide, bismuth strontium copper oxide, you can even start with individual oxides and try to judiciously make such a layer compound. And that is why you have different target holders of with different fashion, so you can actually mount more than 6 or 7 at a time and with computer monitoring, you can switch between these targets and try to make complex oxides or these are possible in a PLD chamber. So, the inside part of the chamber, essentially will look like this, you can see here these are the rotating wheels depending on, the choice material it you can keep switching between 2 targets and therefore, this is how the deposition chamber a will look like.

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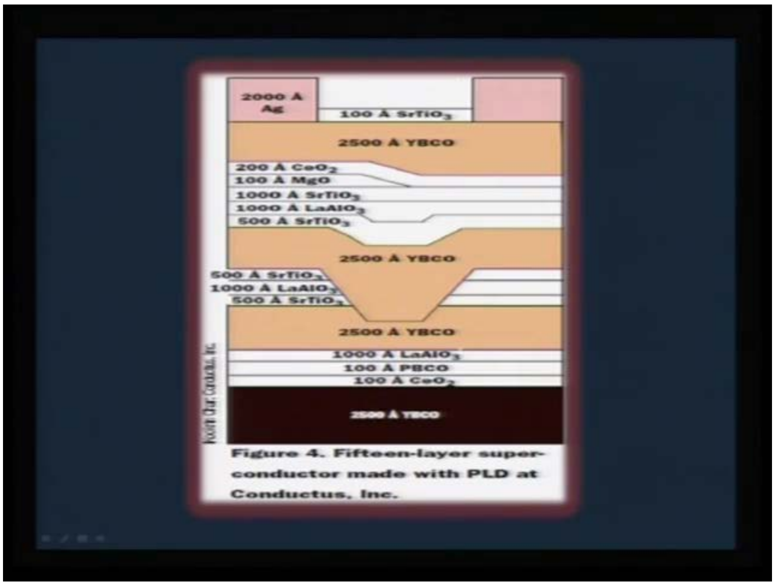

Figure 4. Fifteen-layer superconductor made with PLD at Conductus, Inc.

This is another example of how PLD can be made can be used for a superconductor and you can see here several stakings of this superconductors can be made, this is ybco, which is coated and then capped with the C B R, then presidium cuprate and then L A L O 3 as substrate. So, this is a device configuration, all this can be achieved with the same chamber with different target carousal, so if you have 6 or 7 targets mounted, you can realize such a complicated device staking.

So, in terms of versatility of PLD, they have nonvolatile targets and multi component targets are possible and multi targets for multilayer or alloy films, we can try to achieve using, PLD and this is also operated under any ambient gas. For example, you can use argon, you can use oxygen, you can use nitrogen, you can use any other helium for that matter, any gas can be used depending on the sort of system that, you are going to use. And another thing with the number of pulses that, you are generating, you can try to control the thickness of that chemical and we can also control the substrate temperature.

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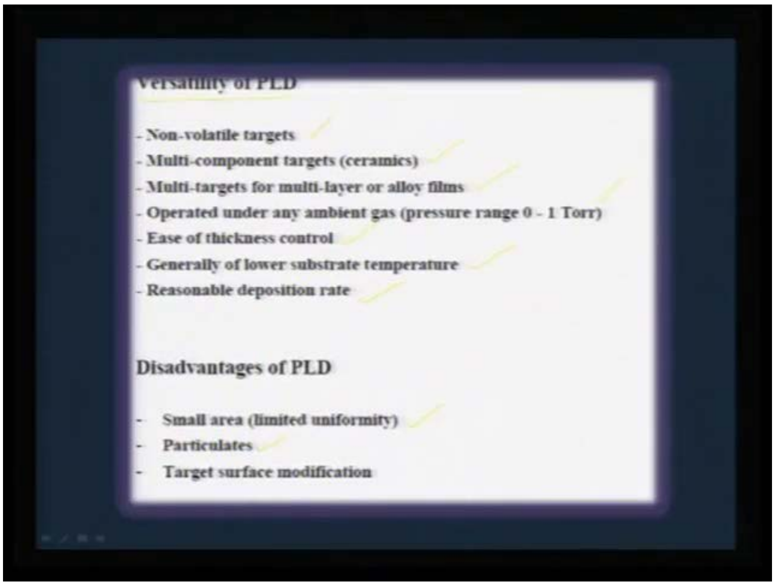

Versatility of PLD

- Non-volatile targets
- Multi-component targets (ceramics)
- Multi-targets for multi-layer or alloy films
- Operated under any ambient gas (pressure range 0 - 1 Torr)
- Ease of thickness control
- Generally of lower substrate temperature
- Reasonable deposition rate

Disadvantages of PLD

- Small area (limited uniformity)
- Particulates
- Target surface modification

For example, if you want to prepare polymer films, then you can prepare at room temperature, if you want oxide films, you can prepare at 800 degree C. So, you have flexibility to play around with the substrate temperature and deposition rate can also be fine tuned, disadvantages are, if you are trying to transient this to larger levels, for large area depositions it is not possible.

So, even to make a 6 inch wave, it is very difficult, but people are aiming at such large area depositions, because of the energetic that is involved in this reaction, usually you end up with some sort of particulates sticking meaning, some chunks of material can also be thrown out along with a very good layer growth. Therefore, this can become a problem for this half axis, PLD has been suggested and target surface modification can happen, specially when your laser is hitting the target with such a very high energy, there may be congruent melting at the surface region. Therefore, if your material is not sensitive or if it is very sensitive then it can go into a liquidous phase and it can change the property. So, such problems are inherent.

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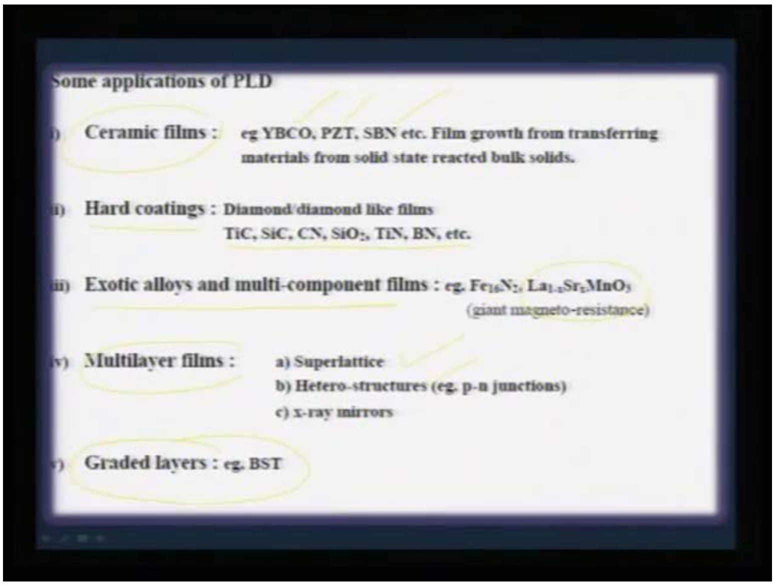

Some applications of PLD

) **Ceramic films :** eg YBCO, PZT, SBN etc. Film growth from transferring materials from solid state reacted bulk solids.

i) **Hard coatings :** Diamond/diamond like films
TiC, SiC, CN, SiO_2, TiN, BN, etc.

ii) **Exotic alloys and multi-component films :** eg. $Fe_{16}N_2$, $La_{1-x}Sr_xMnO_3$
(giant magneto-resistance)

v) **Multilayer films :**
a) Superlattice
b) Hetero-structures (eg. p-n junctions)
c) x-ray mirrors

) **Graded layers :** eg. BST

When using this some applications, we can make ceramic films, when I say ceramic films it is not about a clay and pottery, we mean the superconductor as a ceramic, we can make piezoelectric as a ceramic, nitrates as ceramic. So, several electronic materials termed as ceramics can be made, hard coatings like diamond like films, carbides, nitrites, can be made alloys and multi component systems can be made including manganese for magnetic application. Multi layers can be made super lattices or a hetero junctions can be made using this and graded layers can be also be achieved, by this way, you are almost covering entire spectrum of compounds, whatever you want, you can actually translate this into a thin film.

So, that way it is a very friendly technique one can look at, coming to the energetic and what exactly happens inside the vacuum chamber, there are 3 regimes that we need to take into consideration and each one is a dynamic in itself. Therefore, to handle this dynamics is the proficiency that is required. So, if we start as a beginner, we need to understand that, we should become more friendly with, all these 3 regimes and 1 should have a feel for, what this regime 1 will do on regime 2 and then will effect on regime 3.

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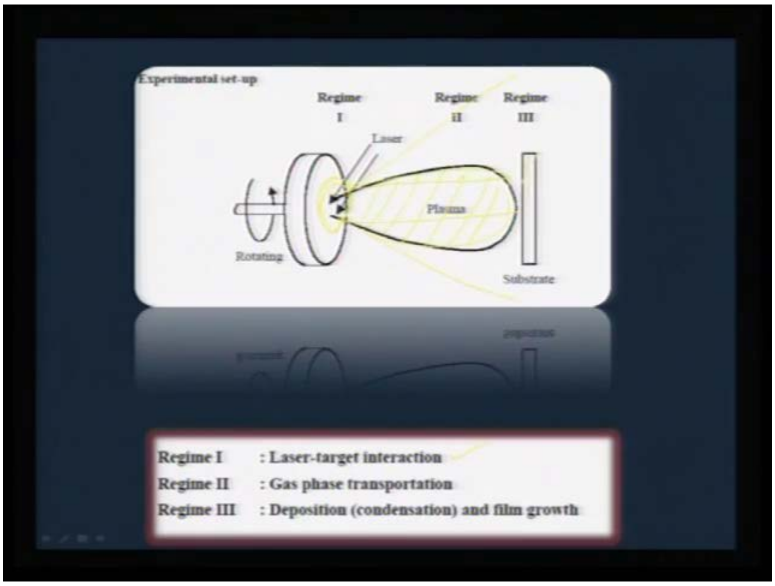

Experimental set-up

Regime I : Laser-target interaction
Regime II : Gas phase transportation
Regime III : Deposition (condensation) and film growth

So, a comprehensive understanding of, what is this dynamics, is what is needed to exploit this, deposition process, regime 1 is laser target interaction. So, laser is coming interacting with the target, what are all the things that, we need to know regime 2 gas phase transformation. So, this is nothing but the plume dynamics, so what really happens with the plume what happens, suppose the plume is going like this, what will happen if the plume is actually narrowed down like this like a bullet. So, the way the shape of the plume and the color of the plume also will control the fine stoichiometry, regime 3 is deposition and film growth. Now, something is coming from the plume and I am depositing it, what should be the control, how I can get the best film that I want.

So, all this 3 are important, in the PLD process, specially when we talk about laser target interaction, there are 2 things that, we need to understand the thermal process and the non-thermal process. Thermal process where, you have the energy of your laser light, that is E h nu, the energy is less than the binding energy of your substrate material, for example you are actually trying to break the bond and bring out the solid material in form of ion molecule or atom or as electron.

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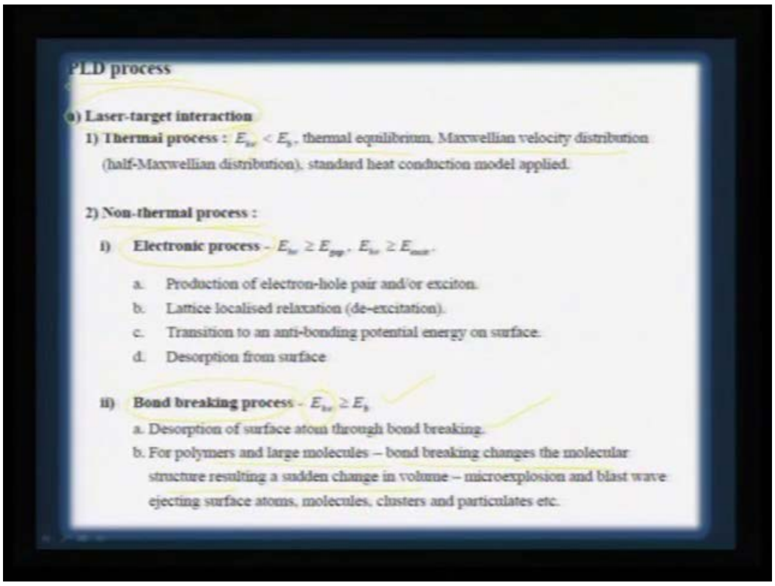

PLD process

a) Laser-target interaction

1) Thermal process : $E_{h\nu} < E_b$, thermal equilibrium, Maxwellian velocity distribution (half-Maxwellian distribution), standard heat conduction model applied.

2) Non-thermal process :

i) **Electronic process** - $E_{h\nu} \geq E_{gap}$, $E_{h\nu} \geq E_{excit}$.

a. Production of electron-hole pair and/or exciton.
b. Lattice localised relaxation (de-excitation).
c. Transition to an anti-bonding potential energy on surface.
d. Desorption from surface

ii) **Bond breaking process** - $E_{h\nu} \geq E_b$

a. Desorption of surface atom through bond breaking.
b. For polymers and large molecules – bond breaking changes the molecular structure resulting a sudden change in volume – microexplosion and blast wave ejecting surface atoms, molecules, clusters and particulates etc.

So, many things are actually going to come out, in the form of a plume and when it is happening, we need to know whether the E h nu, that is the laser light is sufficient enough to overcome the binding energy, if it is not then if it less than E b then whereas, thermal equilibrium and there will be a maxwellian velocity distribution and that is that case the whole growth process can be very difficult.

The other form is non-thermal process in non-thermal process, you actually have 2 situations, one is a electronic process and another one is a bond breaking process. Usually in the material science, we give more attention to a bond breaking process, because you know the material and you know whether, it is a ceramic, whether it is a polymer or whether it is a metallic material.

So, you know how much of the binding energy each material is associated with therefore, you can try to transcend that, by increasing their laser energy. So, it your laser light is E h nu, which is going to be far greater than or equal to E b, then you can think of these option of surface atom through bond breaking, for polymers and large molecules bond breaking changes the molecular structure resulting in a sudden change in volume or micro explosion and blast may ejecting surface atoms. So, you need to have some amount of idea, about the binding energy of the atoms and molecules in the target, so that you can essentially maneuver or you can alter the laser light.

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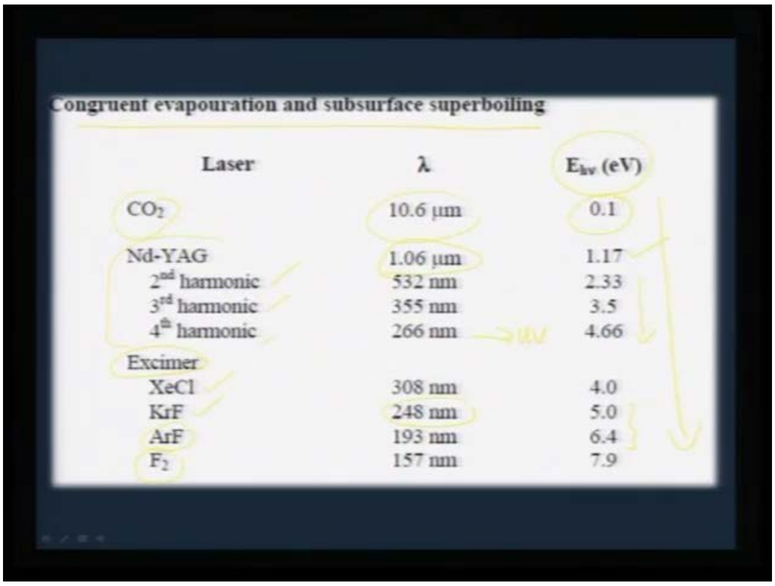

ongruent evapouration and subsurface superboiling

Laser	λ	$E_{h\nu}$ (eV)
CO_2	10.6 μm	0.1
Nd-YAG	1.06 μm	1.17
2nd harmonic	532 nm	2.33
3rd harmonic	355 nm	3.5
4th harmonic	266 nm → UV	4.66
Excimer		
XeCl	308 nm	4.0
KrF	248 nm	5.0
ArF	193 nm	6.4
F_2	157 nm	7.9

So, congruent evaporation and subsurface super boiling, these are parameters that, we need to keep in mind, because your laser light essentially will bring about knocking of this material. And because of the continuous hitting on the target material, there will be some amount of melting and boiling that will be happening at the junction. So, we need to know what sort of energy that is coming out, when laser light is interacting with your surface, for example, if we use carbon dioxide laser, the wave length, actually will generate only 0.1 e V and that is not good enough for updating any of your inorganic material.

So, what you do, you try to use N d YAG, N d YAG is another laser material and it actually gives in more than 1000 nanometer wave length and corresponding to 1.17 e V, but you can actually use fill test to generate second third or fourth harmonic, once thereby you can increase the energy of your laser light. So, that way you can go up to 4.66 and this goes into u v, so when you are using 4th harmonic, you are actually getting a u v light from N d YAG.

So, this is a high power laser, when you are operating at 266 nanometer and then you have excimer lasers, excimer lasers xenon chloride is well known, but mostly it is a krypton fluoride, which is used, which is 248 nanometer. And then you can also use argon fluoride and fluorine, but fluorine because of the handling hazard, it is not usually recommended in the commercial lasers. But, argon fluoride and krypton fluoride are used where you can see very high a power laser efficiency searching.

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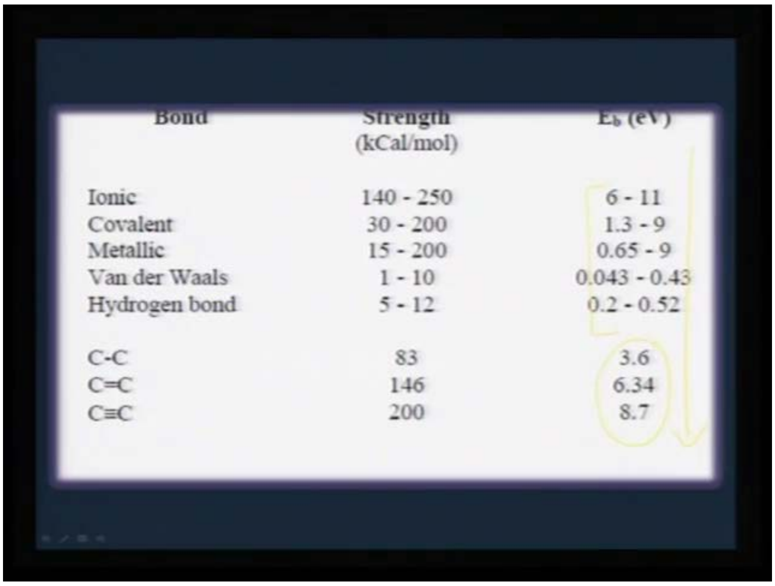

Bond	Strength (kCal/mol)	E_b (eV)
Ionic	140 - 250	6 - 11
Covalent	30 - 200	1.3 - 9
Metallic	15 - 200	0.65 - 9
Van der Waals	1 - 10	0.043 - 0.43
Hydrogen bond	5 - 12	0.2 - 0.52
C-C	83	3.6
C=C	146	6.34
C≡C	200	8.7

So, if this is the energy, that I get from the laser source, then I should also know, what is the e V governing this material, which I am planning to oblate, for example, if it is a organic material involving carbon carbon single bond, triple bond, double bond, the those are actually pretty strong. The binding energy or e V is of the order of 8.7 for carbon carbon triple bond and carbon carbon double bond, it is 6.34 e V.

So, to break this bond and bring it out, you need sufficient energy, so you need to have this idea and also you would find out, that it is the binding energy is more for ionic materials than covalent, than even metallic materials. But, those which are governed by Vander Waals force and hydrogen bond those can be easily broken. So, from this numbers, we can see that depending on the choice of the laser, you can actually try to extend the oblation of material from ionic material down to organic, depending on the choice of the laser source.

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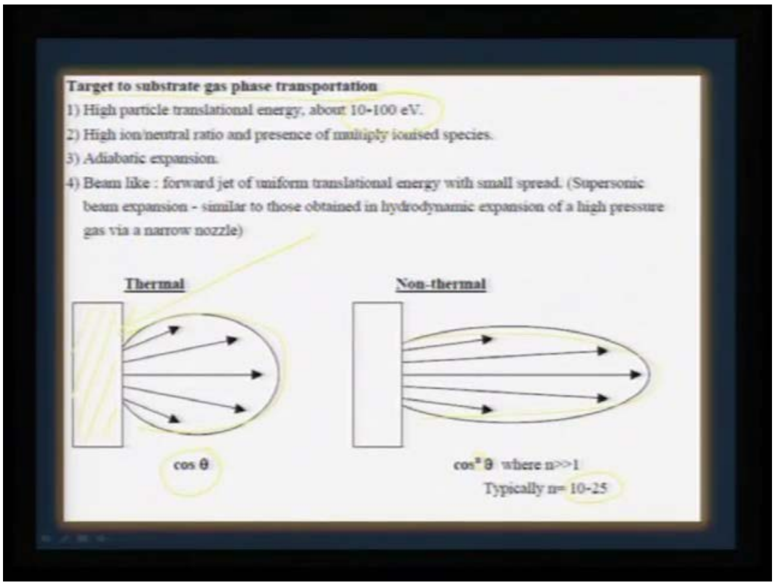

Target to substrate gas phase transportation

1) High particle translational energy, about 10-100 eV.
2) High ion/neutral ratio and presence of multiply ionised species.
3) Adiabatic expansion.
4) Beam like : forward jet of uniform translational energy with small spread. (Supersonic beam expansion - similar to those obtained in hydrodynamic expansion of a high pressure gas via a narrow nozzle)

So, when you are thinking about a target to substrate, there is a gas phase transportation, here is your target material like laser has come it has hit, now everything is going into a gas phase transportation. So, everything is being moved and typically the translational energy is of the order of 10 to 100 electron volt and that is what makes this whole process very, very rich, because the ions and the molecules and electrons atoms everything is carrying very high kinetic energy as they are rushing to the substrate.

So, in this there are 2 different conditions, one is thermal and non-thermal conditions where, you can see the gas phase transportation can actually vary quite a bit, look at the shape of this plume and look at the shape of this plume. So, depending on the shape the energetics of this transportation will change remarkably, so in the thermal case, it is actually a cos theta dependent whereas, in the non-thermal case, you see it is a power factor is associated with it.

It is cos n cos to the power n theta where n is always greater than 1, so in typically, it is of the order of 10 to 25 therefore, depending on the plume, you can actually modify the whole growth process. So, one should have an idea just by looking at it, whether your plume is really good or not otherwise you are heating somewhere and nothing is arriving at this substrate. So, you have to have an idea, how to maneuver this gas phase transportation.

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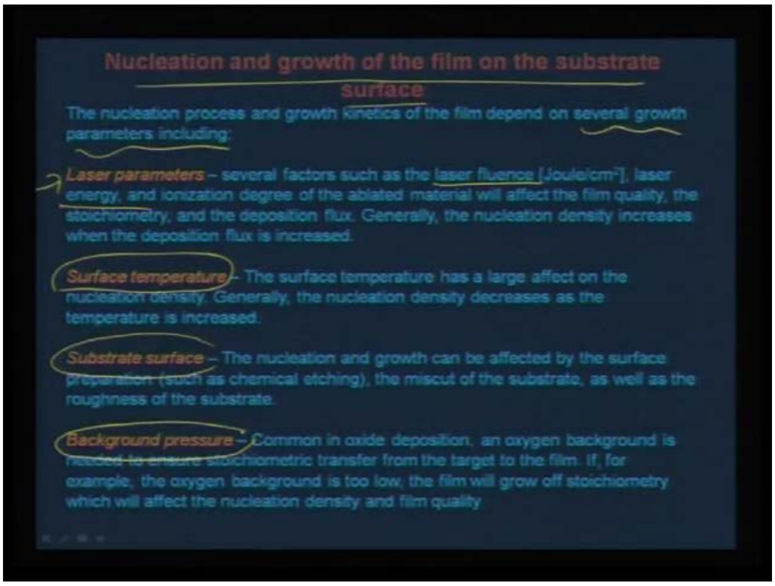

Nucleation and growth of the film on the substrate surface

The nucleation process and growth kinetics of the film depend on several growth parameters including:

Laser parameters – several factors such as the laser fluence [Joule/cm^2], laser energy, and ionization degree of the ablated material will affect the film quality, the stoichiometry, and the deposition flux. Generally, the nucleation density increases when the deposition flux is increased.

Surface temperature – The surface temperature has a large affect on the nucleation density. Generally, the nucleation density decreases as the temperature is increased.

Substrate surface – The nucleation and growth can be affected by the surface preparation (such as chemical etching), the miscut of the substrate, as well as the roughness of the substrate.

Background pressure – Common in oxide deposition, an oxygen background is needed to ensure stoichiometric transfer from the target to the film. If, for example, the oxygen background is too low, the film will grow off stoichiometry which will affect the nucleation density and film quality

So, once this plume is directed and it is reaching the substrate, then the next thing that, we need to understand is the nucleation and growth of the film on the substrate surface. The nucleation process and growth kinetics depends on several parameters, growth parameters 1, laser parameter, I have touched upon it the laser flounce or the laser energy is very important therefore, you need to know, what is the optimum laser energy that you need to use.

In fact, as a there is a celebrants, which can be used a calibrating instrument, which will tell whether you are getting the required laser energy, before every deposition, because continuously since the coating is done the optics can also take this oblation and it can filter the laser light from reaching the source to the fullest extent therefore, it has to be calibrated. Then surface temperature, suppose you are making a high temperature superconductor film, the substrate also has to be elevated to a particular temperature for the film to grow and show a crystalline phase.

Otherwise it will be a amorphous phase and it may not show even superconductor conductivity and the substrate surface also is very important, we cannot simply mount anything. Even, if you are making a mounting a silicon or any other single crystal pretreatment has to be made it should be highly uniform and it should be treated properly, before the deposition is made. And the background pressure as I told, you the plume dynamics, depends on the pressure, suppose I am using oxygen, whether I use this deposition at 10 millitorr or 100 millitorr or 400 millitorr oxygen pressure, that will decide whether it the film is going to be fully stoichiometric or not, if you are aiming for a oxide film.

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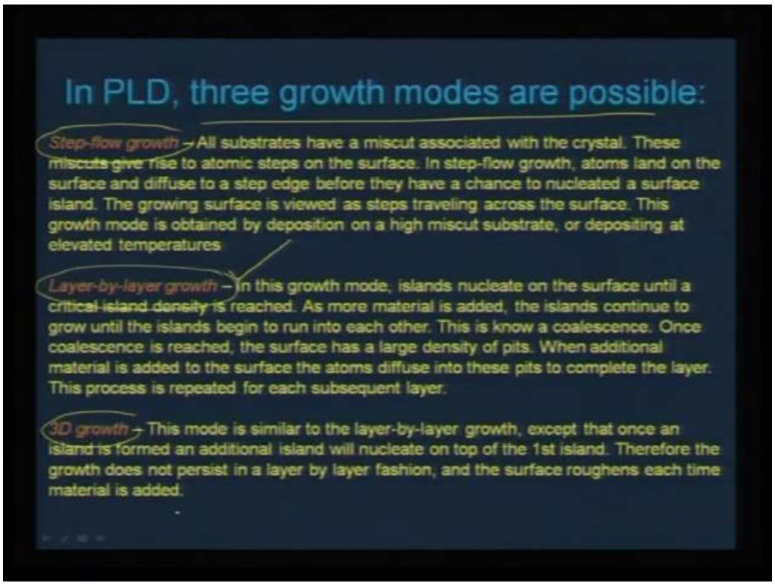

In PLD, three growth modes are possible:

Step-flow growth – All substrates have a miscut associated with the crystal. These miscuts give rise to atomic steps on the surface. In step-flow growth, atoms land on the surface and diffuse to a step edge before they have a chance to nucleated a surface island. The growing surface is viewed as steps traveling across the surface. This growth mode is obtained by deposition on a high miscut substrate, or depositing at elevated temperatures

Layer-by-layer growth – In this growth mode, islands nucleate on the surface until a critical island density is reached. As more material is added, the islands continue to grow until the islands begin to run into each other. This is know a coalescence. Once coalescence is reached, the surface has a large density of pits. When additional material is added to the surface the atoms diffuse into these pits to complete the layer. This process is repeated for each subsequent layer.

3D growth – This mode is similar to the layer-by-layer growth, except that once an island is formed an additional island will nucleate on top of the 1st island. Therefore the growth does not persist in a layer by layer fashion, and the surface roughens each time material is added.

So, background pressure is also important in PLD just like the way, I emphasize in the earlier lecture on M B E, the growth mode also proceeds similar to molecular beam epitaxy, that it can be a step flow method, it can be a layer by layer growth or it can be three dimensional growth. As I told you pulse laser deposition, because of that high kinetic energy, that is involved in these plume dynamics. Usually you get the layer by layer growth, which is the most favored deposition growth mode. But, 3 D growth mode brings about lot of roughness in the film and therefore, that is not decide, so we need to have a idea about, how to grow a layer by layer growth.

The next animation slide, you can see, we can monitor the film growth using retaliation and as you would see here, every maxima in the RHEED oscillation corresponds to one from coverage of the layer and every minima corresponds to almost half the coverage of the thin film. So, this is what we mean by layer by layer coverage, therefore, if you aim for such a deposition, then you get a flat terrace and that is more decided for making even hetero structures.

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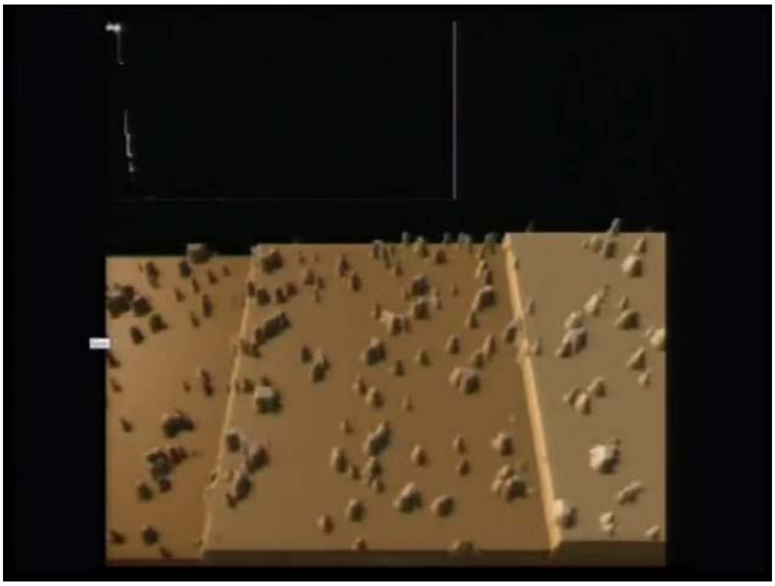

So, one should always look for a situation where, you can actually get this maximas corresponding to coverages. Typically, you would not expect, this sort of a coverages, but what could happen is sometimes in the initial phase there could be a 3 dimensional growth and then you can proceed to a 2 dimensional coverage. Therefore we need to have some optimization, before we try to go for several layer of staking.

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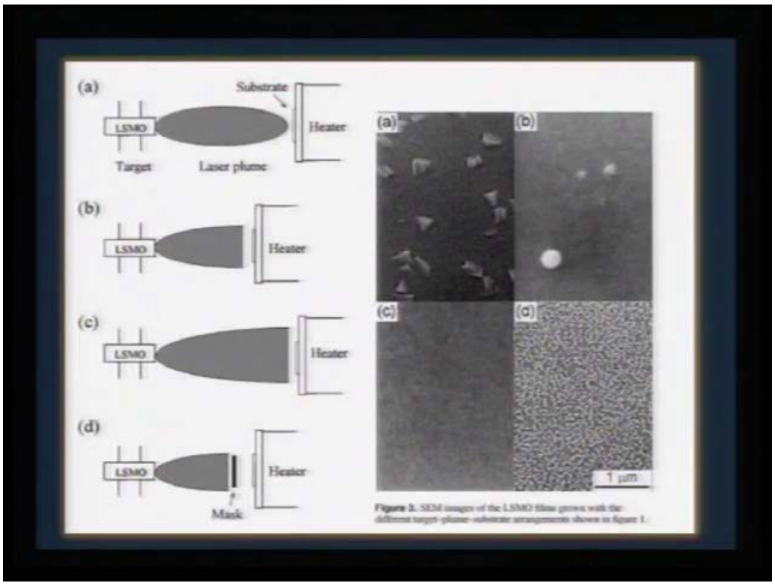

Figure 3. SEM images of the LSMO films grown with the different target–plume–substrate arrangements shown in figure 1.

So, we need to do a individual calibration, if we are going for a several a multi target systems, so in such cases some calibration is needed as to evaluate whether 2 dimensional growth is happening. This is another view graph, which tells us the distance between the target and the substrate can also play a important role, in getting the right type of material.

For example, if you allow the laser plume to converge like this and then it hits the substrate then you would see, if we adjust this distance between the target and the heater where, the substrate is mounted. You would see that the microstructure of the films changes systematically and the microstructure of the film, can be greatly influenced if you are going to introduce a mask, between the plume and the substrate.

So, the distance between target and the substrate can also play a important role, because in this case you are actually cutting half the plume. In this case nearly 3 quarter the plume, in this case you do not cut it at all in this case, you cut it half, but then let only the mask do the job, therefore the microstructure of the film can be maneuver by this distance.

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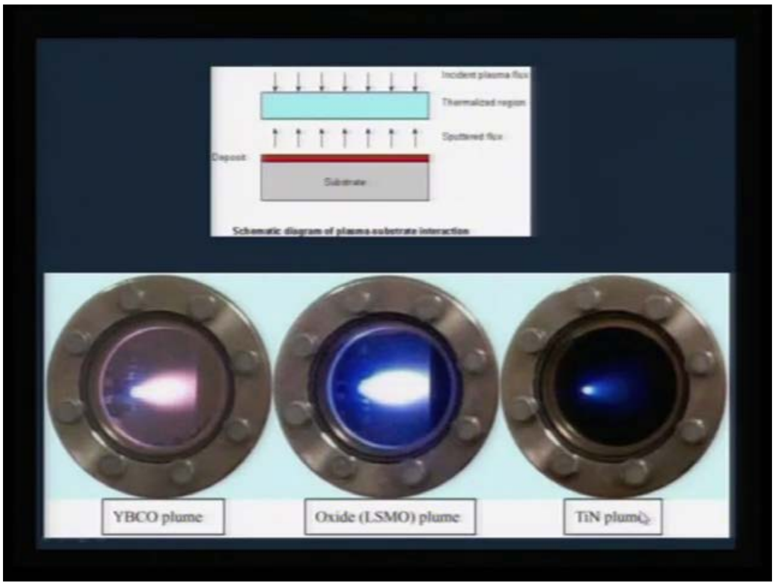

Schematic diagram of plasma-substrate interaction

YBCO plume

Oxide (LSMO) plume

TiN plume

So, it is very sensitive that way and we should also understand, when the plume has reached the substrate again the sputtered flux will go back and it will also create a thermalised region in between. So, the incoming plasma will be actually encountering a thermalised region. So, the gas pressure that you use, during the deposition will actually try to clear up this thermalised region, therefore care should be taken to get the right type of plume, that you desired.

In fact, those who are familiar with this art will easily make out whether, you are really doing the right deposition, for example the oxide plume for magnetite has to be bloom, whereas, for high temperature superconductor, it has to have a crimson red tinge to it. And if you are looking for titanium nitrite, then it has to have a bluish tinge, so just by looking at the plume itself, one can decide whether you are doing the right deposition with a right parameters or not. So, it can become that friendly provided, we know how to control the plume dynamics.

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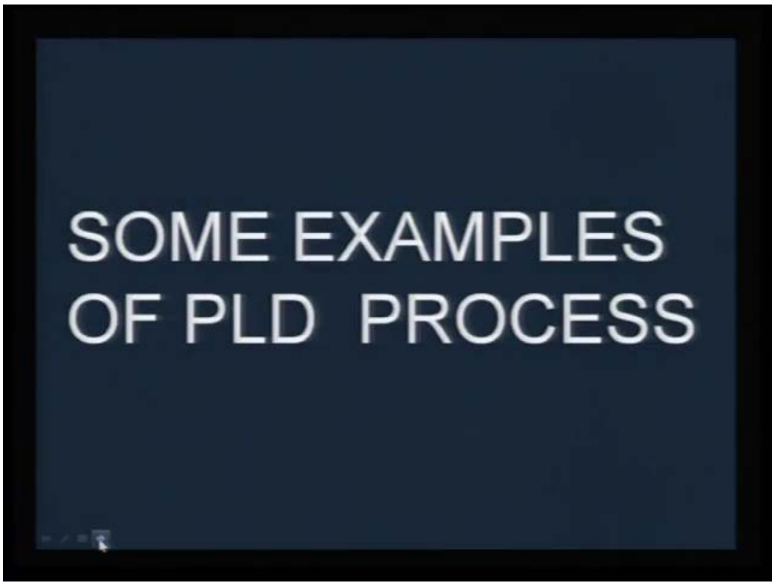

SOME EXAMPLES OF PLD PROCESS

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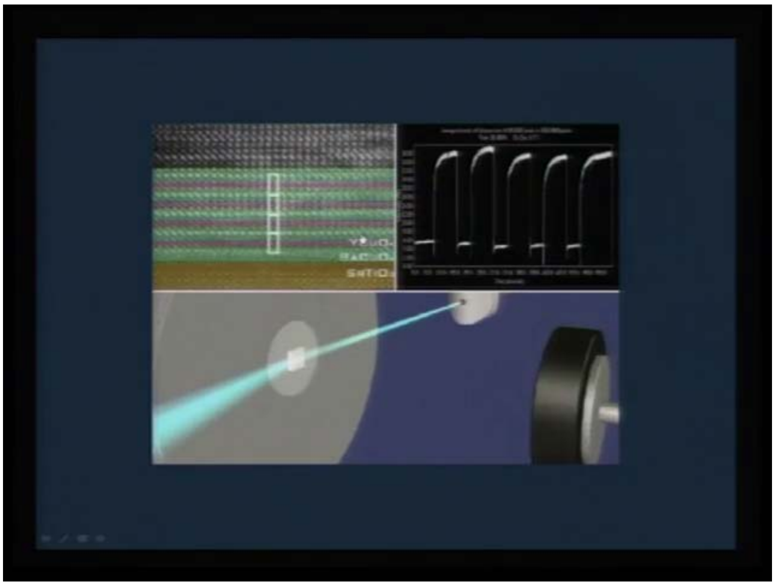

Now, I will take, you through some examples briefly, if possible on a greater detail in the subsequent lectures, first let me start with the animation of…How various layers can be coated using PLD, you can see here we are actually switching between 2 targets and this can be done and what you see as a laser light is nothing but the RHEED incident beam, which is going to monitor whether you are heating it right. So, this RHEED oscillations, as you can see in the in this cartoon, the RHEED diffraction spots are there and those spots will tell you whether you are really doing a layer by layer oscillation. As a result you can see here, this sort of oscillations are coming depending on, the way you are trying to coat the material.

So, you can make this stakings alternatively using RHEED oscillation and that way you can control and make a periodic deposition of superconductor. In this case, this your S R T A O 3 then you can put this green patch is nothing but your barium cuprate and then you can put yttrium cuprate and barium cuprate you are essentially, imitating a unit cell. And you can do that by taking a separate target of B A C O 2 and a separate target of yttrium C O 2 and keep on making this repeat deposition. And this can be monitored using the RHEED oscillations, such sophistications are already available, in today's commercial PLD instrument.

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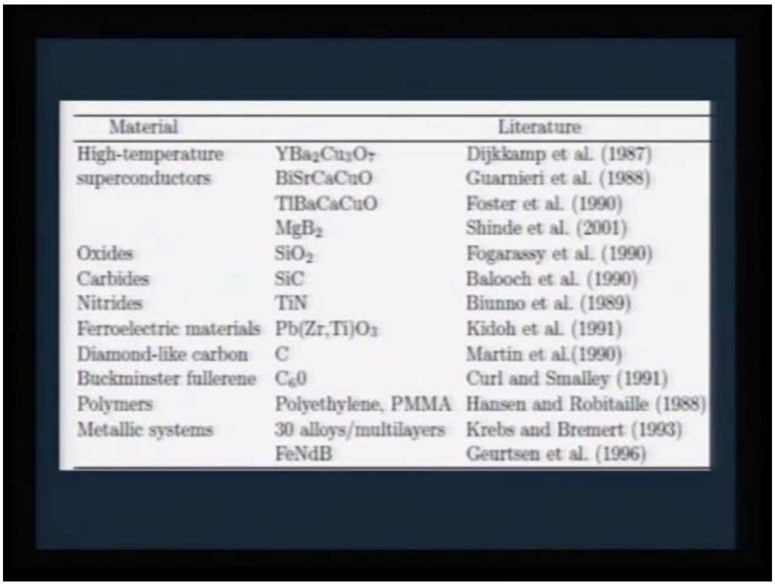

Material		Literature
High-temperature superconductors	$YBa_2Cu_3O_7$	Dijkkamp et al. (1987)
	BiSrCaCuO	Guarnieri et al. (1988)
	TlBaCaCuO	Foster et al. (1990)
	MgB_2	Shinde et al. (2001)
Oxides	SiO_2	Fogarassy et al. (1990)
Carbides	SiC	Balooch et al. (1990)
Nitrides	TiN	Biunno et al. (1989)
Ferroelectric materials	$Pb(Zr,Ti)O_3$	Kidoh et al. (1991)
Diamond-like carbon	C	Martin et al.(1990)
Buckminster fullerene	C_60	Curl and Smalley (1991)
Polymers	Polyethylene, PMMA	Hansen and Robitaille (1988)
Metallic systems	30 alloys/multilayers	Krebs and Bremert (1993)
	FeNdB	Geurtsen et al. (1996)

Now, if you look at the range of materials that you can make out of this deposition process, you have yttrium barium copper, these are all the superconductors, people have used as early as 1987. So, PLD became very prominent only, after the discovery of the superconductor, then you have the oxide silica can be made carbides nitrides, even carbon and C 60 can be made, diamond like carbons can be made, polymers like polyethylene P M M A can be made, metallic systems alloys, multi layers borides can be made of a risk. So, if you look at the spectrum almost you can achieve any sort of material.

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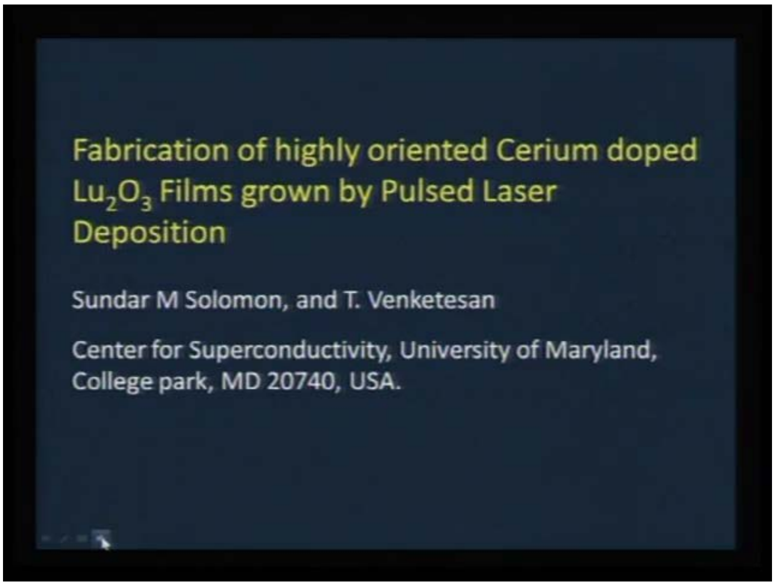

Fabrication of highly oriented Cerium doped Lu_2O_3 Films grown by Pulsed Laser Deposition

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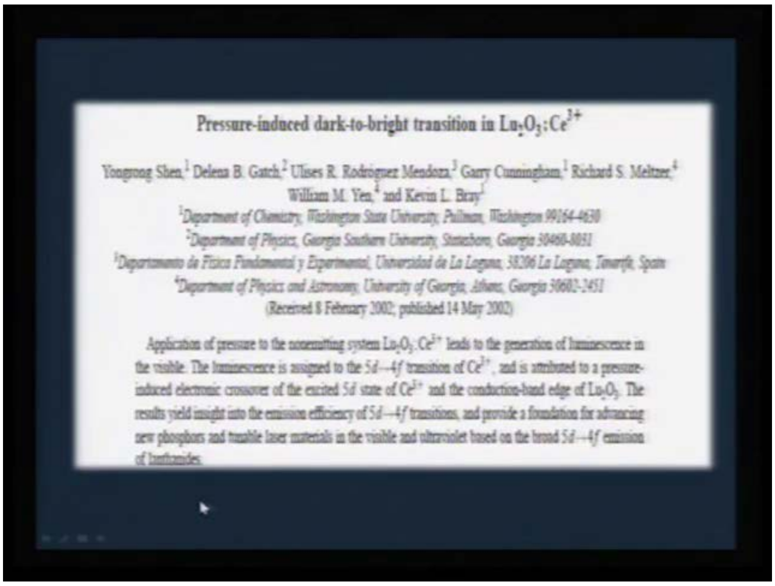

Pressure-induced dark-to-bright transition in Lu_2O_3:Ce^{3+}

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Application of pressure to the nonemitting system Lu_2O_3:Ce^{3+} leads to the generation of luminescence in the visible. The luminescence is assigned to the $5d \rightarrow 4f$ transition of Ce^{3+}, and is attributed to a pressure-induced electronic crossover of the excited $5d$ state of Ce^{3+} and the conduction-band edge of Lu_2O_3. The results yield insight into the emission efficiency of $5d \rightarrow 4f$ transitions, and provide a foundation for advancing new phosphors and tunable laser materials in the visible and ultraviolet based on the broad $5d \rightarrow 4f$ emission of lanthanides.

As a thin film, one of the example that I want to show here is L u 2 O 3, which is done in around group L u 2 O 3 grown on several substrates, why L u 2 O 3, because this is a very a important molecule. For tunable laser materials, if you can dope with for example cerium, then this can be used for tunable as a tunable laser material or as new phosphorous. So, there is lot of challenging work going on in L u 2 O 3, but the point is to make a single crystalline film, it is very, very difficult.

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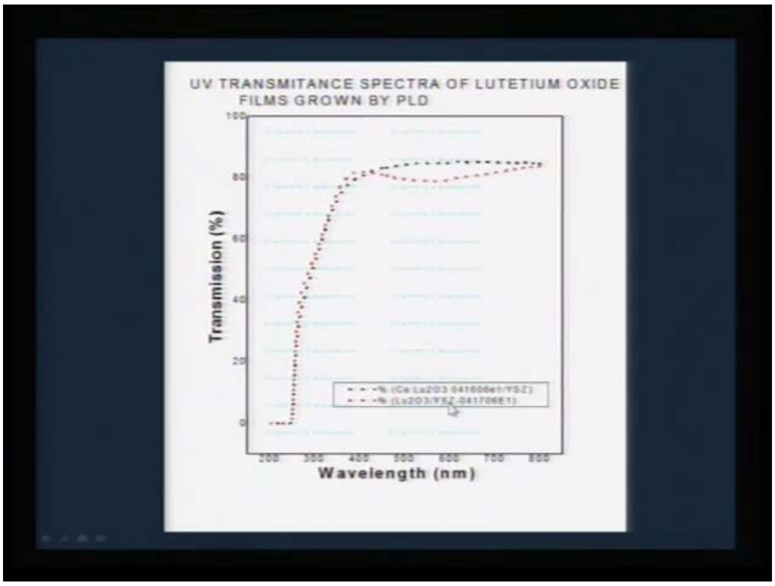

UV TRANSMITANCE SPECTRA OF LUTETIUM OXIDE FILMS GROWN BY PLD

And as you see here, using PLD, we can make a single crystalline film of lutetium oxide and this is the optical measurement in transmittance mode. And if you see here, you can make a very nice quality L u 2 O 3 film and look at the transmittance level, it is nearly a 90 percent transmittance, which means it is almost a transparent electrode sort of thing. So, you can make such clean material on variety of substrates for example, here we have used yttrium stabilized zirconia, why we used yttrium stabilized zirconia, because the lutetium oxide cell constant is exactly twice that of yttrium yttria stipulated zirconia, which is a cubic material.

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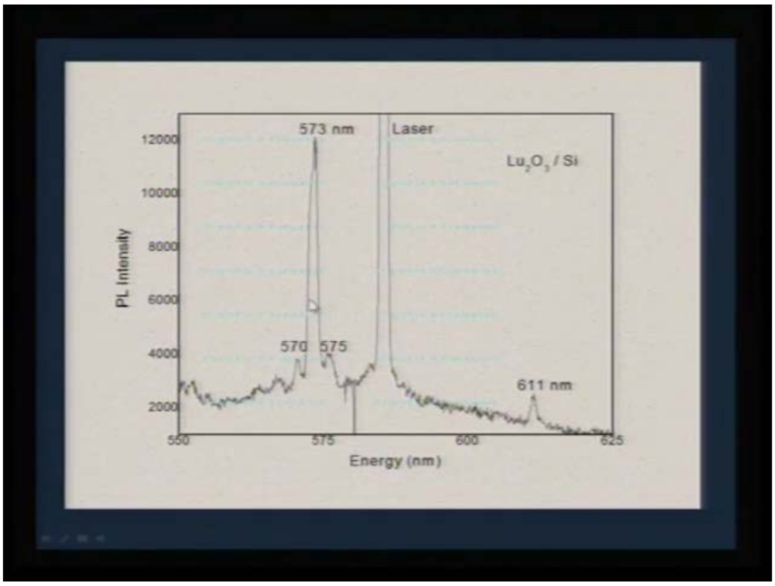

In the next slide, I will show you, how we how good quality film, we can make, but it is also surprising, that you could see lutetium oxide grown on silicon showing such high laser action. This is the laser, that is incident on the film and this is the lasing light, that is coming out of L u 2 O 3, which is grown by PLD incidentally, the full width at half maxima of this emission peak is only 1.2 nanometer, so if it is showing such sharp emission, then you can see the lasing action of such emitting stuff, this can be made out of PLD.

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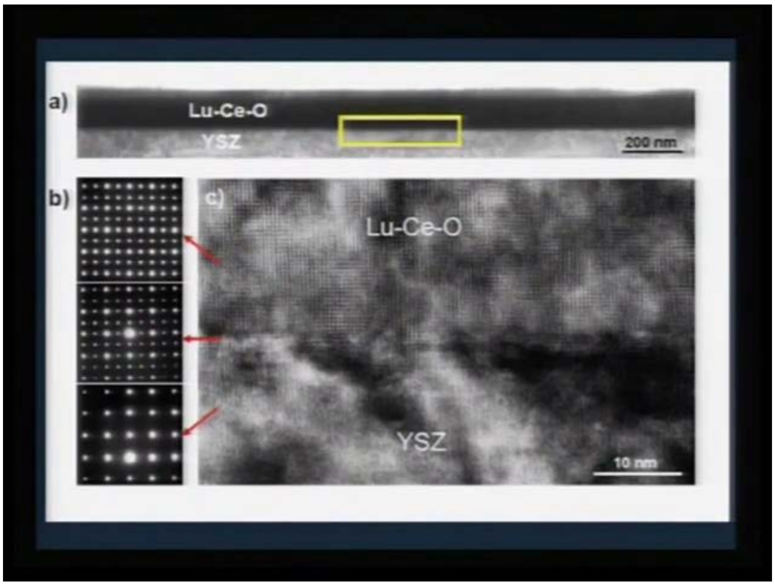

And this is a good t m image, that tells how PLD can clearly help you in growing epitaxial films for example, if you see the electron diffraction pattern of Y S Z, this is the substrate region and this is the interface region, along this line. And this is the L u 2 O 3, which is cerium doped and these are the lattice fringes, what you see as strips are the lattice fringes in other words, those are the atoms.

So, if you look at the interface here, these is no distortion between this lattice and this lattice, in other words, if you look at the diffraction spots between 2 diffraction spots, you see repeats. So, they are exactly matching and therefore, you can easily grow L u 2 O 3 on yttria stabilizer zirconia, because they have exact lattice matching, one lattice plane is equal to half of the lattice plane of Y S G therefore, it is exactly able to sit on Y S G and grow as a epitaxial layer.

So, this is one convenient way, where you can realize highly oriented epitaxial films of such complex oxides.

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Manganite thin films

Another example is that of magnetite thin films, I have discussed about this manganese extensively in the next module.

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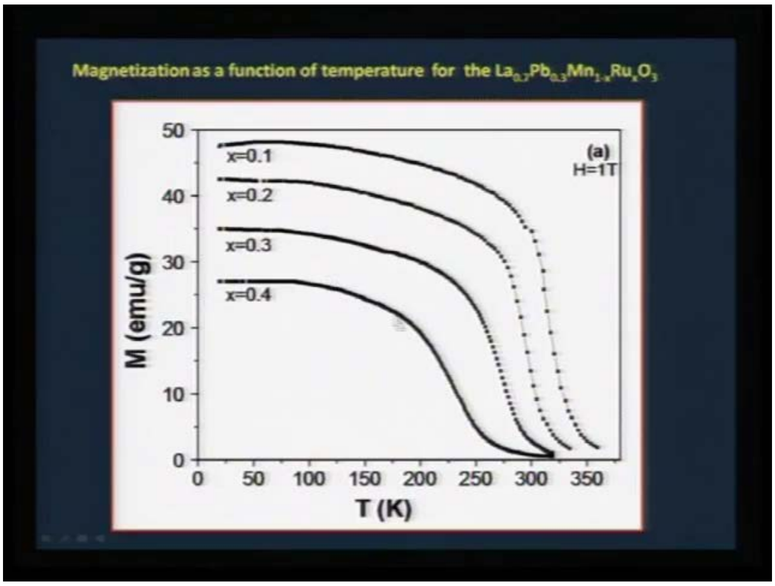

Magnetization as a function of temperature for the $La_{0.7}Pb_{0.3}Mn_{1-x}Ru_xO_3$

But, I will show you only the study related to thin films, as you see here, if you keep on doping ruthenium in this L a P b M n O 3 a strong ferromagnetic loop is shown with 10 percent ruthenium, 20 percent ruthenium, 30 percent and 40 percent, still you can see a very strong ferromagnetic signal.

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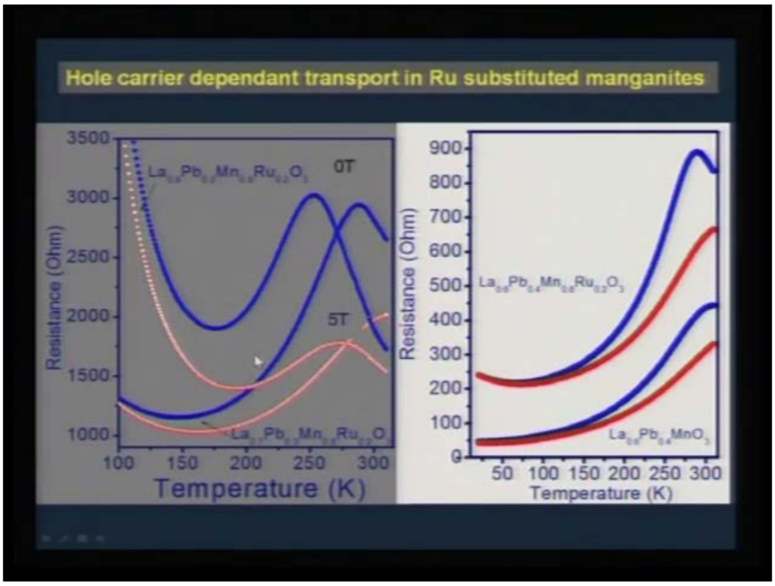

Hole carrier dependant transport in Ru substituted manganites

However, if you look at, the conductivity data as you increase the ruthenium concentration, you can see there is a upward in resistivity, that we do not know whether it comes from the bulk phenomena or whether it is due to, the anti ferromagnetic interactions, that are competing in this set of molecules. So, there is no way, you can clear this doubt, other than making thin films, because in thin films, you do not bring in the grain boundary issue. Therefore, if there is any upturn in resistivity, you can directly correlate that to magnetic phenomena. So, that way, if you are only studying bulk, then you cannot resolve some of the issues for which PLD can be a very good system to, work with you can make films of a very high quality.

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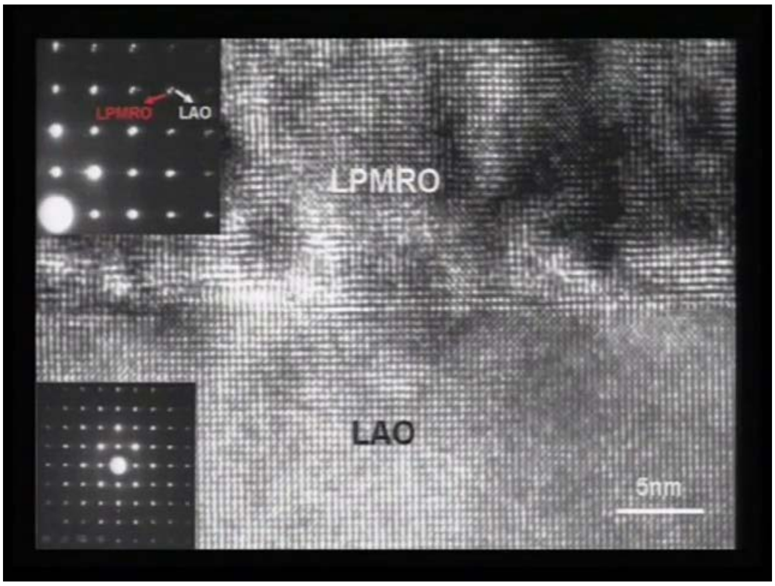

And this is again H R T E M image high resolution transmission electron microscopy, which gives you idea about the interface, as you see here every dot here is nothing but a unit cell or the atomic position of lanthanum oxide. This is the lanthanum oxide picture and this is the magnetite film that is grown on the substrate. As you can see here very clearly, there are no 2 different spots, if there are 2 different spots, then that would correspond, that it is not growing epitaxially, but if you magnify these spots.

And see here, you can see 2 spots together in each spot, whatever you see here is nothing but 2 spots and that one coming from L A O and one coming from manganite film, what it means is they have very close matching and therefore, there are epitaxially able to grow. And if you look at the interface here, this region seems to have little bit of interfacial problem roughness, but you can see here, there is no change in the interface ordering, because of the lattice match, they are able to grow epitaxially. So, highly oriented manganese film can be made using PLD and this is another example.

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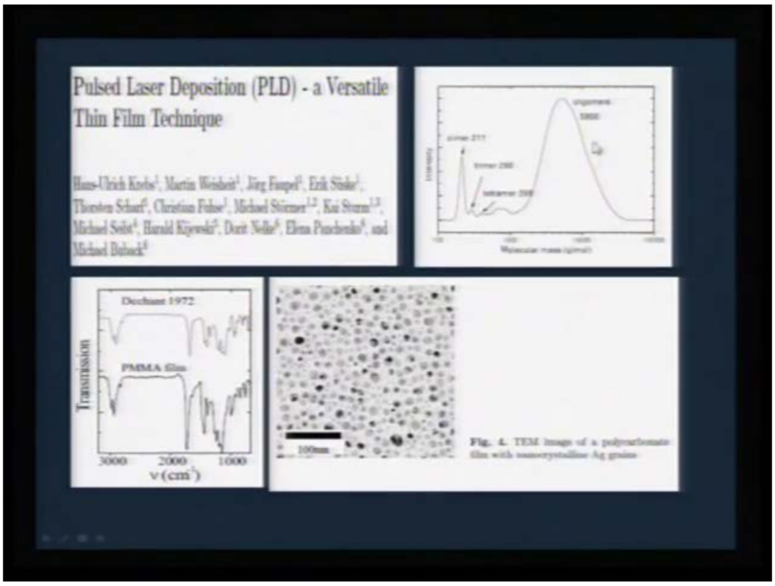

Pulsed Laser Deposition (PLD) - a Versatile Thin Film Technique

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Fig. 4. TEM image of a polycarbonate film with nanocrystalline Ag grains

By krebs crew in germany where, they have used, PLD for a thin film deposition of P M M A, this is polymethyl methacrylate as you can see their is matching T M of a polycarbonate film can also be made, embedding nano crystalline silver grains. And you can also see, that you can get predominantly oligomer based P M M A, using this PLD you can extend this to other.

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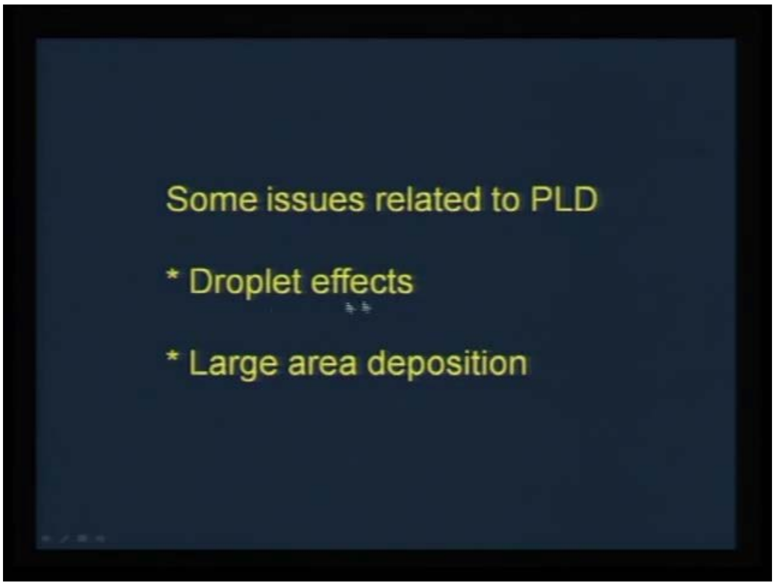

Some issues related to PLD

* Droplet effects

* Large area deposition

But, there are some issues, that we can try to address, as we use this process extensively one is droplet effect another one is the issue of large area deposition. There are several refinements, that have come on the way, just to help us to increase the utilization of this method.

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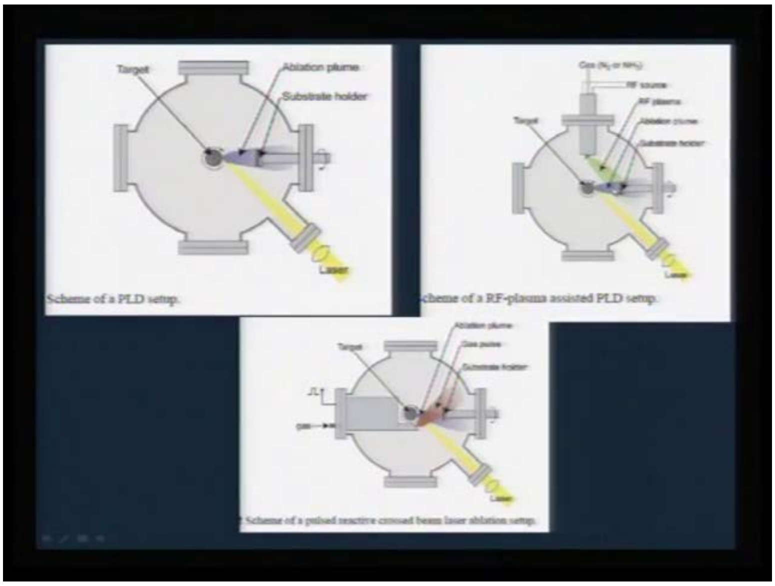

Scheme of a PLD setup.

cheme of a RF-plasma assisted PLD setup.

Scheme of a pulsed reactive crossed beam laser ablation setup.

For example to avoid the droplet effect or to minimize on the grain boundary issue or roughness, there are several schemes, that are proposed, one is you can use the this is the typical set up where laser comes oblation. And then that goes and deposits on the substrate, but there are some refinements made for example, we can have a gas pulse, which is actually crossing the oblate plume, which can bring down on the heavier atoms or chance arriving at the substrate, therefore you can reduce on the roughness of the film. There is another way to do that, you can use R F plasma here. So, one can use R F plasma, which will also interfere with your laser plume as a result, you can try to minimize on the roughness.

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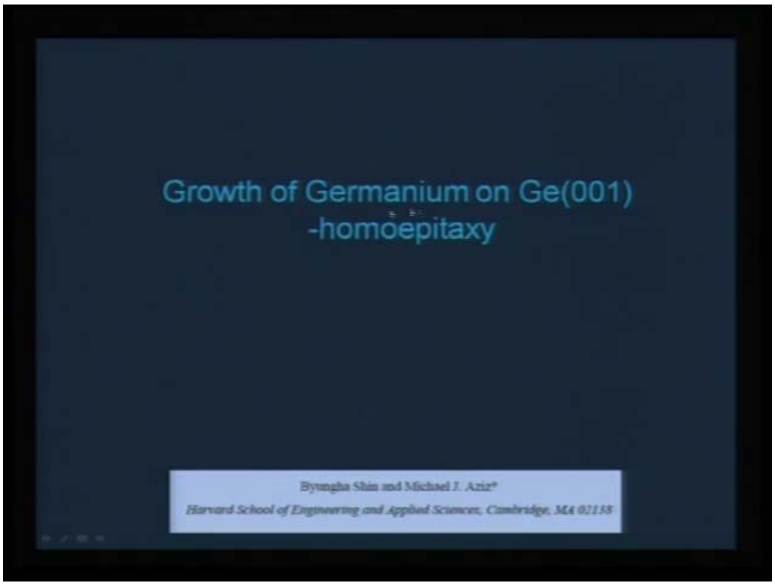

Growth of Germanium on Ge(001)
-homoepitaxy

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So, this sort of refinements can be made and there is another way one can do it, for example, look at the growth of germanium on germanium 0 0 1 Aziz group, in Cambridge have attempted this. This we call it as homo epitaxy, because you are growing the same material on the same single crystal therefore, it is called homo epitaxy and look at the dynamics here.

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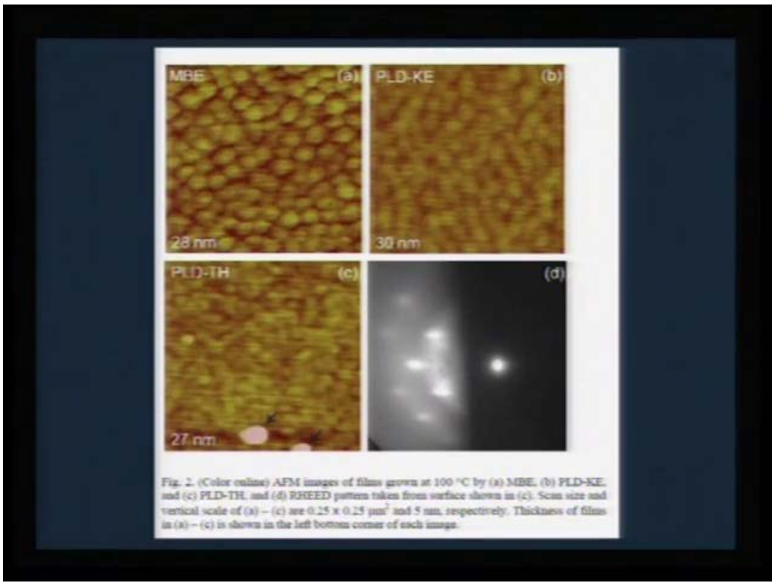

Fig. 2. (Color online) AFM images of films grown at 100 °C by (a) MBE, (b) PLD-KE, and (c) PLD-TH, and (d) RHEED pattern taken from surface shown in (c). Scan size and vertical scale of (a) – (c) are 0.25 x 0.25 μm^2 and 5 nm, respectively. Thickness of films in (a) – (c) is shown in the left bottom corner of each image.

If I use M B E, if I use PLD with the high kinetic energy, that is 300 electron volt and if I use PLD, but with a very less energy, then you can see the, these are the thickness of the films 20 nanometer, 30 nanometer, 27 nanometer almost same thickness, but you can see the microstructure vividly changing. What does it mean, this can greatly affect the epitaxial growth of your film.

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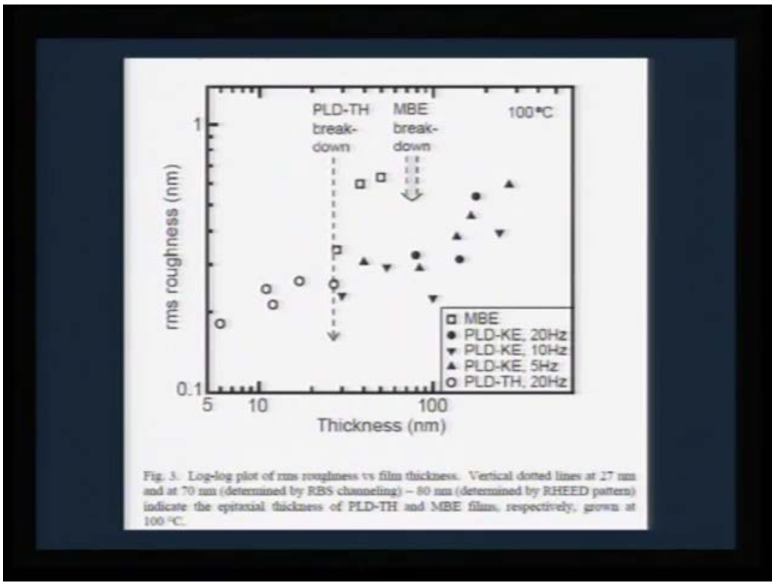

Fig. 3. Log-log plot of rms roughness vs film thickness. Vertical dotted lines at 27 nm and at 70 nm (determined by RBS channeling) – 80 nm (determined by RHEED pattern) indicate the epitaxial thickness of PLD-TH and MBE films, respectively, grown at 100 °C.

And this cartoon tells us that PLD with load threshold or with very less kinetic energy comparable to thermal evaporation. The epitaxy actually breaks down, even with just 20 nanometer thick film whereas, the next one to break down is molecular beam M B E based film whereas, the PLD with very high kinetic energy can show a very high epitaxy, even up to 100 nanometers.

So, that is the advantage of the PLD process and another refinement has come, this is called as aurora PLD method, what they are doing here, is they are trying this is the typical PLD process. But, what they have inserted here is, near to the substrate they have placed a magnet and you can see once you do that, the zinc oxide plume, that is reaching the substrate, the plume dynamic changes here.

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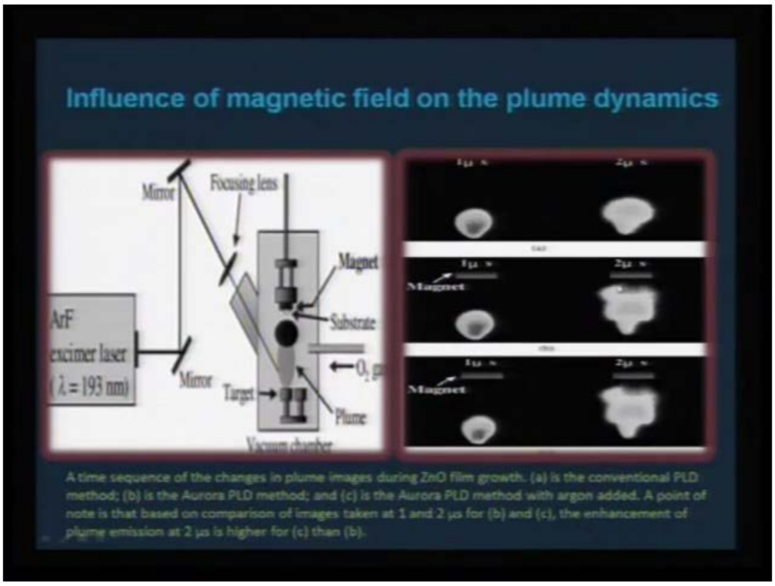
Influence of magnetic field on the plume dynamics

A time sequence of the changes in plume images during ZnO film growth. (a) is the conventional PLD method; (b) is the Aurora PLD method; and (c) is the Aurora PLD method with argon added. A point of note is that based on comparison of images taken at 1 and 2 μs for (b) and (c), the enhancement of plume emission at 2 μs is higher for (c) than (b).

You can see plume is actually travelling, but it is not clearly reaching the substrate here, whereas in the case of the aurora method where, they have kept this magnet, near to the substrate the plume is actually reaching up to the substrate, therefore the plume dynamics changes. So, in effect this magnet is actually kept like a reflecting mirror, so the electrons, which are also going, they get reflected and they transfer the kinetic energy to the atoms and species as a result you have activated a deposition process.

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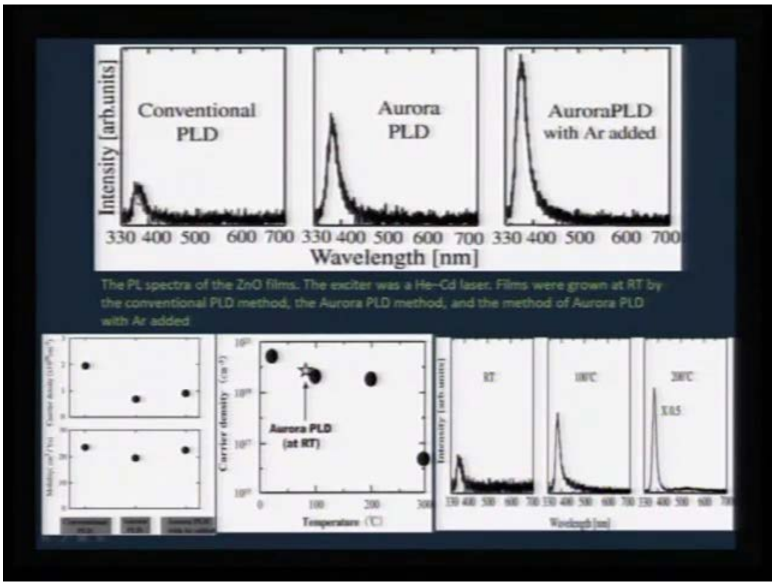

The PL spectra of the ZnO films. The exciter was a He–Cd laser. Films were grown at RT by the conventional PLD method, the Aurora PLD method, and the method of Aurora PLD with Ar added

So, if you actually look at the quality of films from a conventional PLD where, you have the P L efficiency is noted here, it is twice the P L efficiency for a aurora PLD approach. And if it is done in argon, you still feel 3 to 4 times enhancement in the P L intensity as you know the band to band emission of zinc oxide, actually is pronounced with a 380 peak. And so even though, you are getting a good quality film, yet the P L efficiencies suffers, when you are using a conventional PLD. So, you can bring about lot of modifications and that is also reflected in the carrier density and mobility, therefore we can try to fine tune on those issues also.

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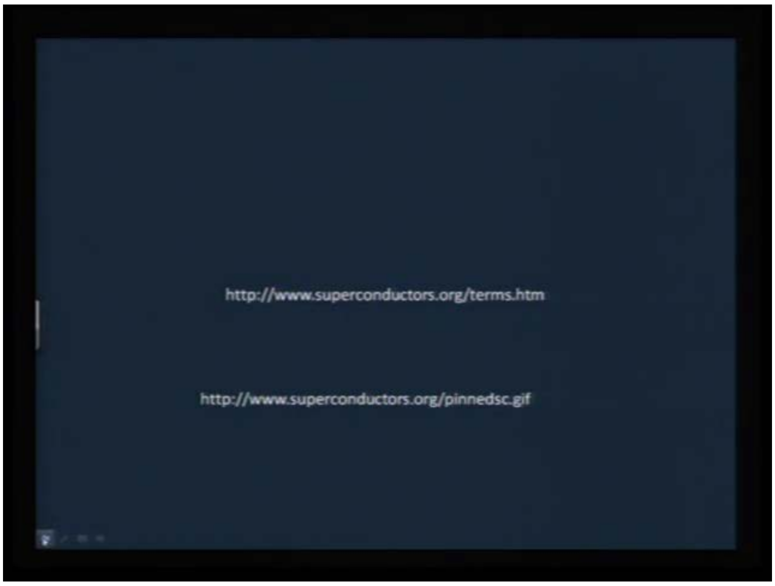

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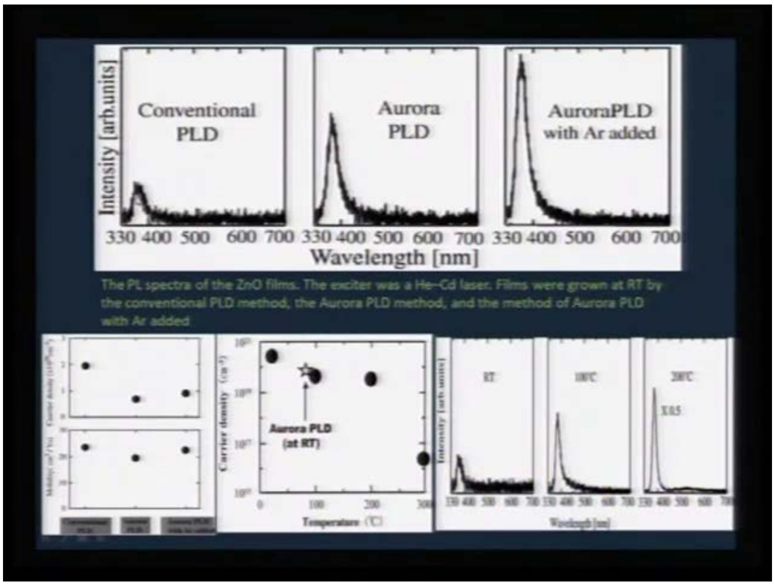

The PL spectra of the ZnO films. The exciter was a He-Cd laser. Films were grown at RT by the conventional PLD method, the Aurora PLD method, and the method of Aurora PLD with Ar added

There are some links, which can give you more idea. On the application of PLD, but I stop here and we will try to give you some more examples in the bibliography. So, that you can refer to other processing parameters which can be taken into account, to get a improved film growth and also, to extend this process to variety of other materials.