Materials Chemistry
Prof. Sundar Manoharan
Department of Chemistry
Indian Institute of Technology, Kanpur

Module - 2
Lecture - 3
Pulsed Electron Deposition From Oxides to Polymeric Films and Devices

Today’s lecture is in continuation to the previous one where we looked at the importance of very useful technique called pulsed laser deposition. And this has been one of the path breaking event in the area of thin film technology where you can translate most of the studies of bulk materials into thin films. And not only to study in lower dimensions, but also to bring about lot of device applications into perspective, PLD has been a very decisive method.

And we have looked at, some of the constraints how sensitive this process can be and we also try to understand the dynamics, especially the plume dynamics, how it affects the growth quality of these materials. Today I am going to concentrate on another equally competing thin film deposition technique, which is called pulsed electron deposition, the fact that we are replacing the word laser with electron suggest that the source of deposition is going to be different.

So, instead of using a pulsed laser beam, we are going to use pulsed electron beam and we can see why PED is more important that way and what are the advantages and disadvantages of PED over PLD. So, in this PED disposition, which is fairly a new technique compared to PLD, we will look at how we can make thin film structures, nano structures and how this can be used for device applications.

So, let us start with understanding, what PED is pulsed electron deposition is a process, in which 100 nanosecond high power electron beam, which is approximately of the order of 1000 angstrom at 15 Kilo electron volt. Penetrates of about 1 micron deep into the target and as a result there is a rapid evaporation of the target material and this transforms into a plasma. So, once it is plasma, it gets deposited on the desired substrate, which is actually a non-equilibrium extraction of the target material. And therefore, because of this nature of transporting the ions and the atoms, you can ensure a fully stoichiometric composition of the plasma and that way we can make a single crystalline film.

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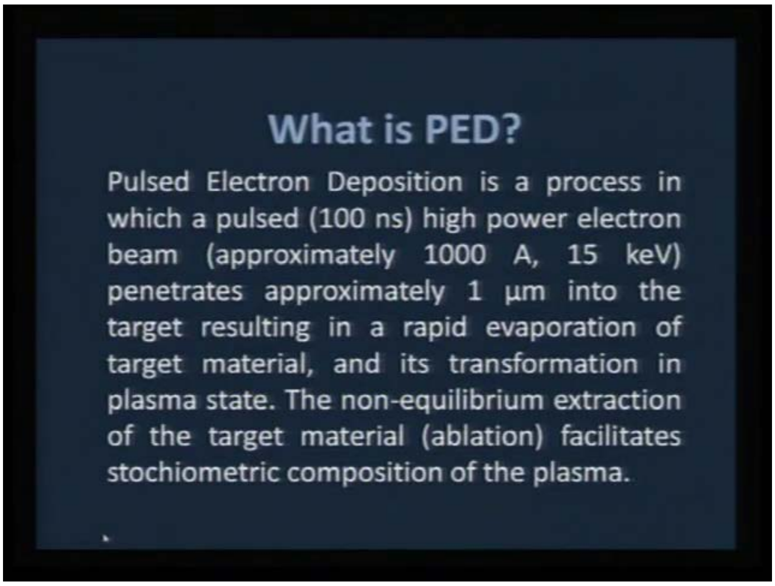

What is PED?

Pulsed Electron Deposition is a process in which a pulsed (100 ns) high power electron beam (approximately 1000 A, 15 keV) penetrates approximately 1 μm into the target resulting in a rapid evaporation of target material, and its transformation in plasma state. The non-equilibrium extraction of the target material (ablation) facilitates stochiometric composition of the plasma.

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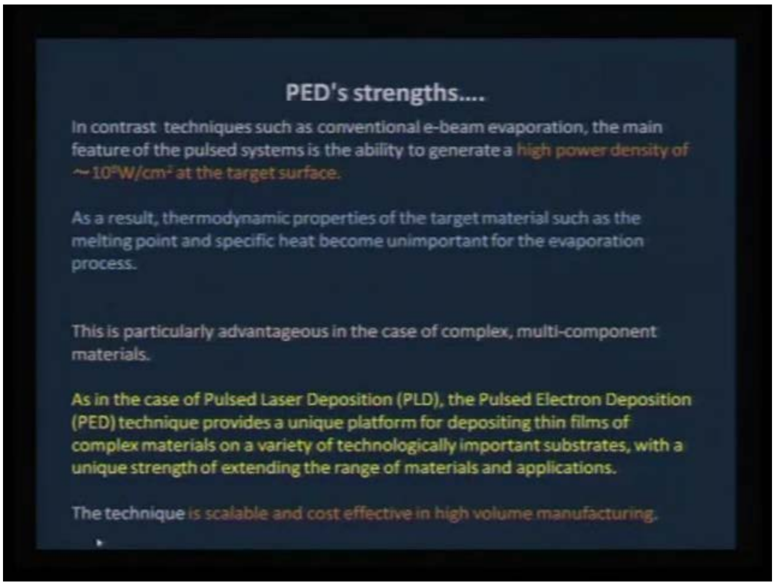

PED's strengths....

In contrast techniques such as conventional e-beam evaporation, the main feature of the pulsed systems is the ability to generate a high power density of $\sim 10^8 W/cm^2$ at the target surface.

As a result, thermodynamic properties of the target material such as the melting point and specific heat become unimportant for the evaporation process.

This is particularly advantageous in the case of complex, multi-component materials.

As in the case of Pulsed Laser Deposition (PLD), the Pulsed Electron Deposition (PED) technique provides a unique platform for depositing thin films of complex materials on a variety of technologically important substrates, with a unique strength of extending the range of materials and applications.

The technique is scalable and cost effective in high volume manufacturing.

There are some issues, which act as strength for PED compared to PLD, therefore it is better, if we familiarize, why PED stands out in many ways compared to the most established PLD technique. In contrast to other techniques, such as conventional electron beam evaporation, the main feature of this pulsed system is the ability to generate a high power density of 10 power 8 watt per centimeter square at the target surface. So, you are actually focusing this highly intense electron beam on the target and as a result a thermodynamic properties of the target material, such as melting point and specific heat becomes unimportant. Because, you are over coming all these issues by a high energy pulse and as a result, you can evaporate any sort of material that, you want.

So, this is particularly advantageous in the case of complex and multi component materials where, you have more than 2 or 3 metals, then you do not know, how these materials would respond to a pulsed laser to or a pulsed electron beam, you would see they behave in a more friendly way with PED technique. As in the case of PLD, PED provides a unique platform for depositing thin films of complex materials and therefore, it is very viable, for applications and mass production. And as a result, this is one of the scalable and cost effective high volume manufacturing process, we will look at several examples and understand where, it has a edge over PLD.

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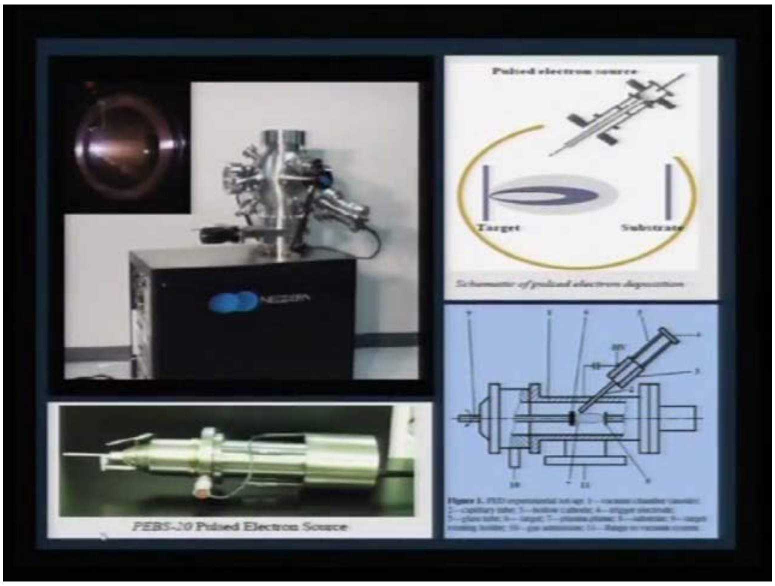

If you recap the previous lecture on PLD, you would see, that the instrument itself is quite big, because you need to bring the laser plume into the vacuum zone. And as a result several optics is required and then you also have the big lesser system, which is going to occupy. So, comparatively PED technique is a very, very amiable process, because even in lesser space, you can try to install this system.

As you would see here, this is how the dimension of a PED and what is important in this deposition technique, is the pulsed electron source, which is called PEBS source and this is the core of the PED technique where, the pulsed electron beam comes from this. But, for that the vacuum chamber and all the energetic are nearly the same like a PLD, so what you do, you avoid the complex problem of maintaining a gas source, for laser and then the cooling systems, plus the optics to guide the laser light into the vacuum chamber, all these are avoided by just using a laser electron source.

So, this is a typical way, that you can energize a material by shooting pulsed electron beam and the target is now ablated and it causes this plume and then this plume travels to the substrate. Although the pulsed electron beam looks very fancy and simple, but to take a closer look, these are the elements that are involved, you have a hollow cathode and this is focused on to the vacuum chamber, this is the vacuum chamber. And this is your PEBS source, you have this capillary tube, which is usually a ceramic and then the hollow cathode here and this is focused on the target. So, critically although it is simple, but the making of the PEBS source is a tricky stuff, which is the most important element of a PED chamber.

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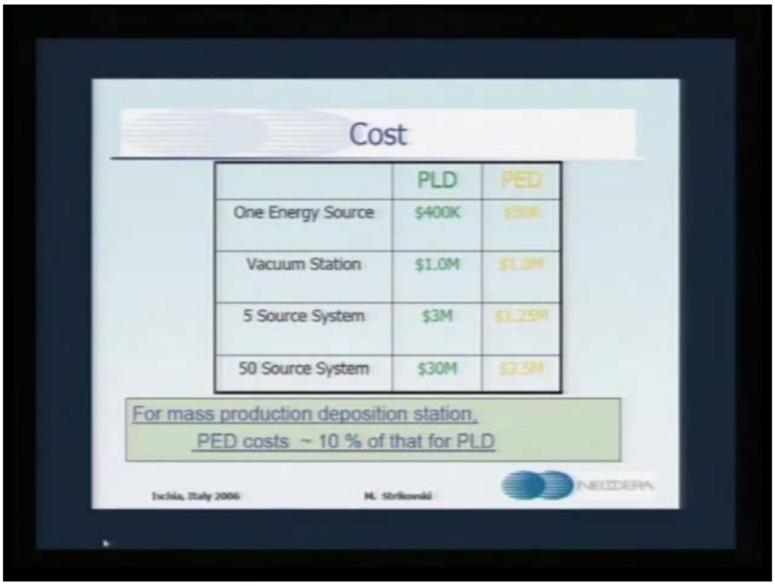

Cost

	PLD	PED
One Energy Source	$400K	$50K
Vacuum Station	$1.0M	$1.0M
5 Source System	$3M	$1.25M
50 Source System	$30M	$3.5M

For mass production deposition station,
PED costs ~ 10 % of that for PLD

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Now to get a quick look at the cost effectiveness between PLD and PED, before you look at the examples of how the PLD and PED grown films look like, you can clearly see the standout, because it is almost 1 8 of the cost, that is required. So, if you are looking for a one energy source of a PLD, you may have to sell out nearly 400 K of U S dollars whereas, PED is just 50 K. So, therefore you can actually, get more than 6 PED chambers, for installing 1 PLD chamber. So, cost wise its very effective and therefore, it is very useful for mass production deposition station, so PED cost just 10 percent, that of PLD.

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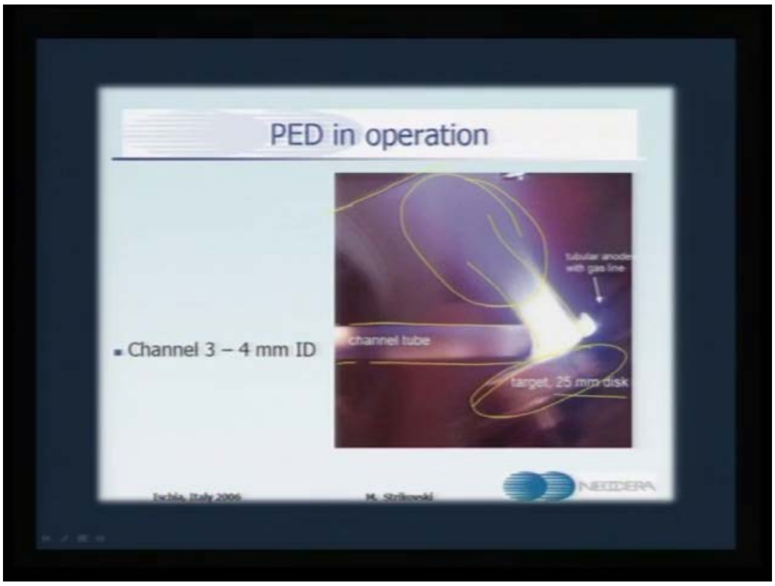

PED in operation

- Channel 3 – 4 mm ID

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If you quickly want to look at the dynamics, where PED is different, when PED is in operation, you would see a channel tube, which is also flashing or eliminating during, the process. And this is nothing but the ceramic tube, which is actually guiding the electron beam and this electron beam actually, falls on this target, this is the target, which is of typical 25 m m disk target. So, when the PED strikes, then you can see this plume is coming out, so this is typical photograph, during the operation process. So, the control of this plume and what is happening, the composition and the target, which is mounted here perpendicular to the plume, all this governs the dynamics of PED process, either it can make, it more novel or more detrimental to the film that is grown. So, this is all we are going to understand, in the next few slides as to, what are the critical parameters that govern this issue.

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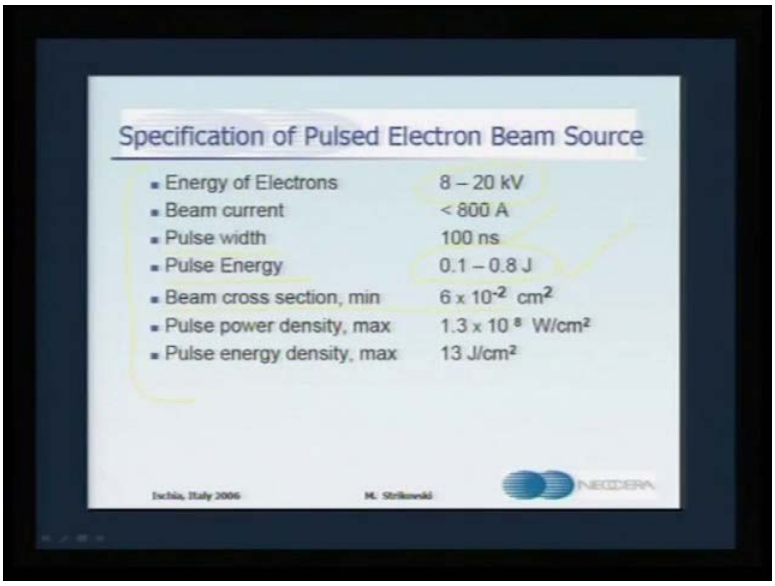

Specification of Pulsed Electron Beam Source

Energy of Electrons	8 – 20 kV
Beam current	< 800 A
Pulse width	100 ns
Pulse Energy	0.1 – 0.8 J
Beam cross section, min	6×10^{-2} cm^2
Pulse power density, max	1.3×10^{8} W/cm^2
Pulse energy density, max	13 J/cm^2

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When, we talk about the specification of pulsed electron beam source, we need to understand, the critical advantage is that, you have a pulsed width of 100 nanoseconds, which is comparably different to the pulsed width of your PLD process. And then the pulsed energy range, that you have is quite tunable, you can go from 0.1 to 0.8 joules. So, you can actually vary the strength of your pulse by operating with different measure of the energy of electron beam.

So, when you talk about electron beam, you are going to operate from 8 k V to 20 k V, so you can change 8 10 12 14 16, so with this, the pulse energy also will be affected, but the pulse width will remain the same. So, you can actually tune this for a variety of substance, including biomaterials to ceramics to metallic materials to insulators, you can play around with the energy of your electron beam and the pulsed energy, therefore you can make a judicious choice to bring the right mixture. So, these are some of the specific numbers, that govern the PEBS source and you can also see the beam cross section is pretty sharp, which is 10 into 6 into 10 power minus 2 centimeter square. So, you can really spot on a very small area, which means even with the 10 m m target, you may be able to do PED deposition.

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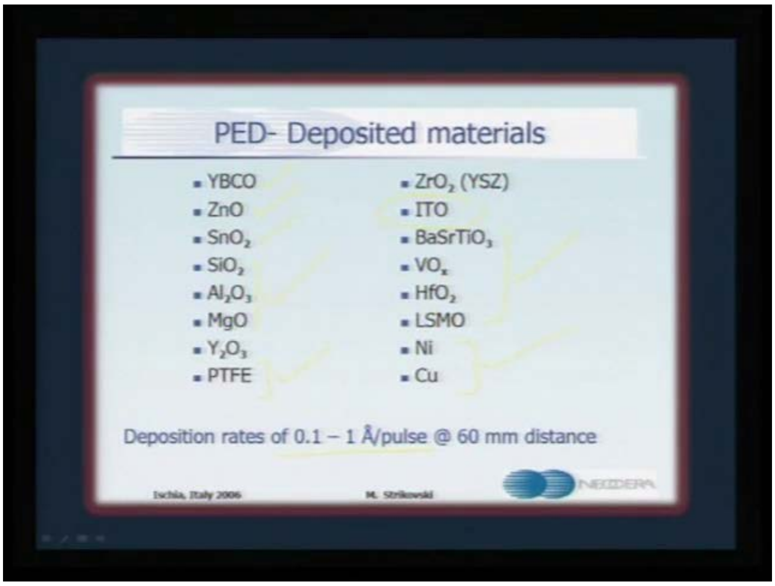

PED- Deposited materials

- YBCO
- ZnO
- SnO_2
- SiO_2
- Al_2O_3
- MgO
- Y_2O_3
- PTFE

- ZrO_2 (YSZ)
- ITO
- $BaSrTiO_3$
- VO_x
- HfO_2
- LSMO
- Ni
- Cu

Deposition rates of 0.1 – 1 Å/pulse @ 60 mm distance

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What sort of materials that, we can coat, using PED as a thin film, the spectrum is quite large now and you can see starting from a superconductor to a photonic material like zinc oxide, to a photonic material again tin oxide or to all these insulators or to polymeric substance to ferroelectric and magnetic substances or metallic substances. You see a wide range of components, that can be used, I T O of course, you know is the best material for any photonic applications.

So, if you look at the spectrum of materials, that you have you can actually play around with almost any material, that is possible through PED. And what is the control, you can actually go for a deposition rate of 0.1 to one angstrom per pulse, which is a very good choice. So, if you want a slow growth, you can effect a slow grow process, if you want a rapid deposition, you can do that at a optimum distance between the target and the plume of say 6 centimeter, you can actually vary the deposition rate considerably.

Now, in the parameters that control, the film growth has some numbers in it, so when you are actually having a substrate, which is your single crystal here and you have mounted this substrate perpendicular to the plasma. Now, then energy of the arriving atoms here, which is in the end of the plume and the number of arriving atoms, which together, these are N into E 1, they depend on the plasma energy balance. And the electron beam intensity, which is actually given as J in ampere volt in kilovolt and time in seconds.

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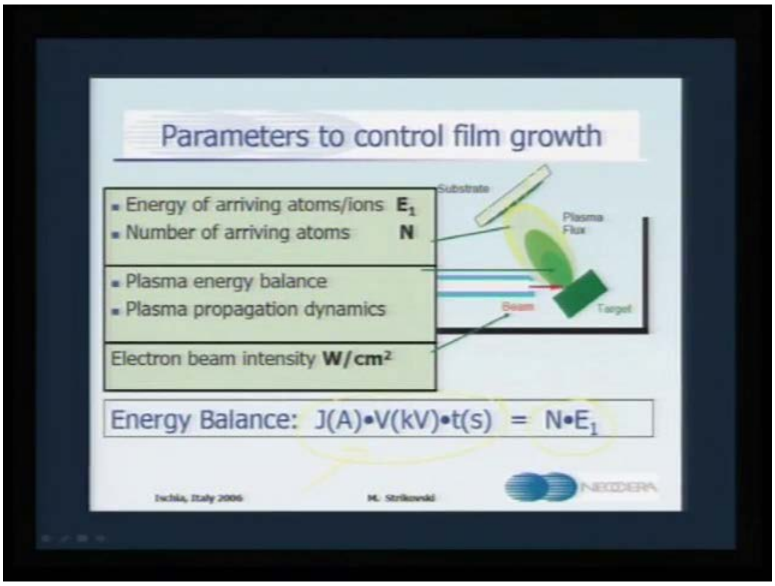

Parameters to control film growth

- Energy of arriving atoms/ions **E_1**
- Number of arriving atoms **N**

- Plasma energy balance
- Plasma propagation dynamics

Electron beam intensity **W/cm²**

Energy Balance: $J(A)\bullet V(kV)\bullet t(s) = N\bullet E_1$

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So, these 3 parameters govern, what sort of energy with, which the atoms arrive at the substrate and the number of arriving atoms. So, this is all it takes to control, therefore for every given material, you need to make sure, that you have a proper energy balance, because the way you try to evaporate zinc oxide will be quite different from the way, you evaporate nickel for example, a metallic material, if you want to ablate aluminum oxide, then you need to have a proper energy balance. So, depending on the band gap of the target material and the energy balance, that you chose, you can optimize the plume or the plasma flux.

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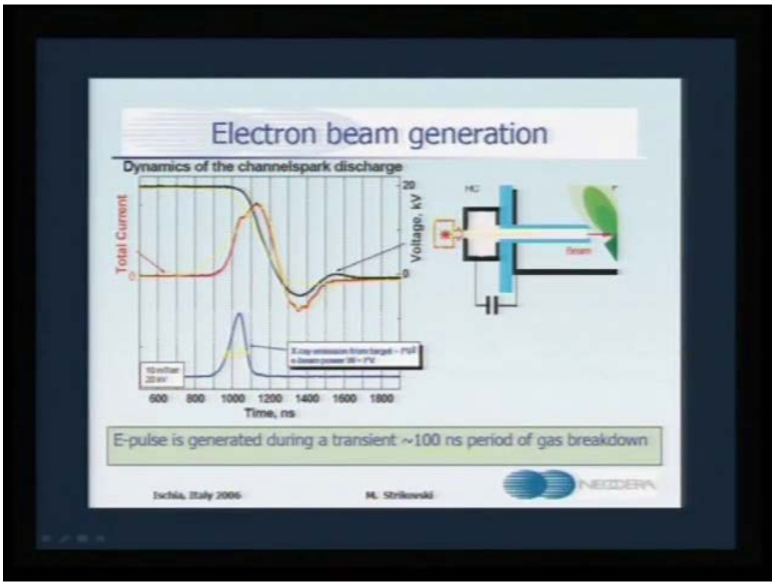

Electron beam generation

E-pulse is generated during a transient ~100 ns period of gas breakdown

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If you look at the electron beam generation, which is actually coming from a trigger and you trigger, it through a hollow cathode and it is actually coming to the vacuum chamber, which is your anode. You would see for a 20 k V pulse for example, if you provide a channels park discharge for every pulse, you would see the decay will be of this fashion, this is for the voltage and then you would see the current going through a minimum then coming down. And in this process, you would see the pulse width is actually, full width of half maxima raging to 100 nanoseconds. So, you have very narrow range where, this pulse width S of the order of 100 nanoseconds and this is the prime importance for the PED process where, you have a electron pulse, which has a very, very sharp breakdown and the pulse width is as close as 100 nanometer.

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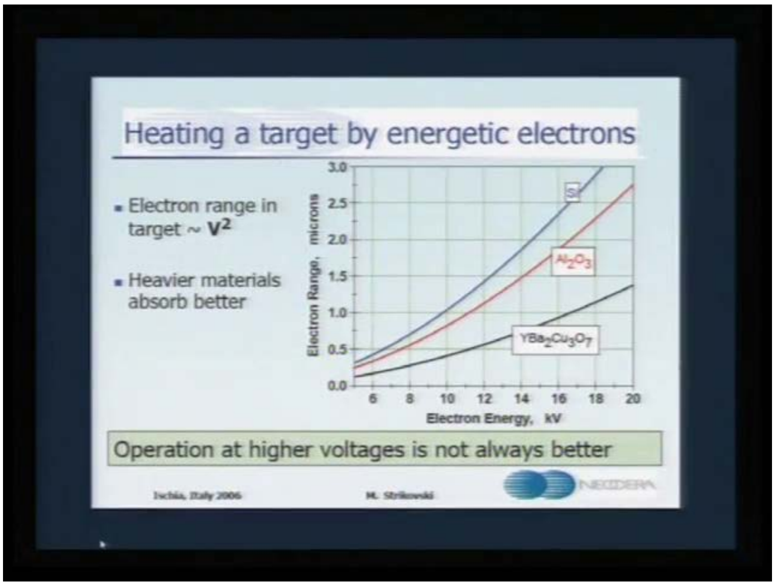

Heating a target by energetic electrons

- Electron range in target ~ V^2
- Heavier materials absorb better

Operation at higher voltages is not always better

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So, with this pulse, it is possibly to almost bring about many changes when the electron beam is actually heating on the target surface therefore, when such a high energy pulse is actually heating the target. Now, you can look at how the materials get ablated, for example, the electron range, which is actually a factor of V square electron range, if you plot as a function of the electron beam energy, you can actually keep on varying as you would see the operation are at a higher voltages are not actually favored.

So, anything beyond 14 although, it can be done, it is recommended that, we do not strain the instrument by operating at very high voltages and also, you would see that the heavier metals are ablating much better compared to oxygen. So, in case of silicon for example, the electron range is easily achievable up to 1 micron, even with 10 k V where as for alumina and yttrium barium copper, you see substantially, they are lower.

So, if you are going for 14 k V, it is easy for you to achieve a electron range of the order of 2 micron for optimum k V of 14 kilovolt, that target heating is actually more dependent on the electron range. And if we have a proper calibration for different materials, then it is very easy for us to choice depending on the target to the plume distance with this electron range.

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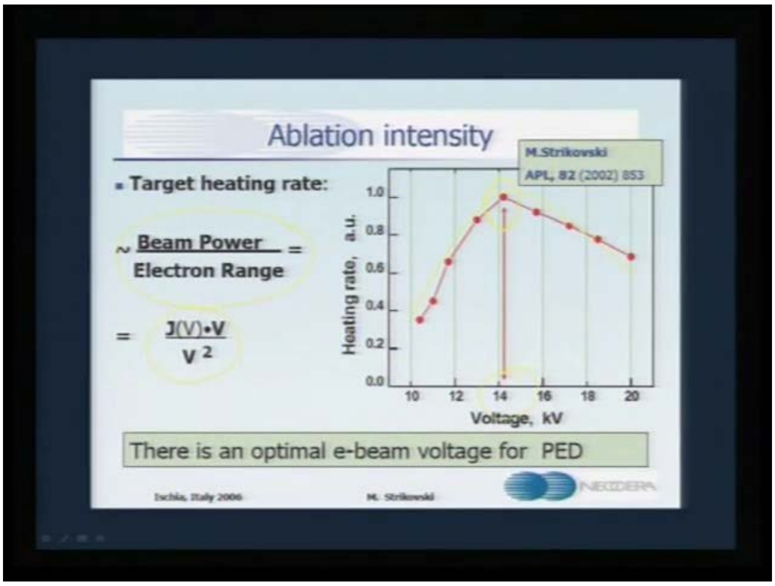

Ablation intensity

- Target heating rate:

$$\sim \frac{\text{Beam Power}}{\text{Electron Range}} = $$

$$= \frac{J(V)\cdot V}{V^2}$$

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APL, 82 (2002) 853

There is an optimal e-beam voltage for PED

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It is possible for us to determine, that target heating, because continuously this nanosecond pulse is heating and this target heating range is nothing but a beam power over electron range. So, if you know the beam power and you know the electron range, it is possible for you to measure, what is the target heating rate. So, depending on that, if you make a plot, you would see, that it is not linearly varying rather, it is actually going through a maxima.

So, maximum heating can be achieved at 14 k V, which is a very useful information, so instead of struggling at very high voltages, if you can optimize for this numbers, then it will be more efficient for you to do the oblation. We another words for this beam power and electron range, if at 14 k V, you achieve maximum heating, then we can try to bring down the other parameters like, target substrate distance is closer. So, that we can work at this efficiency, there is an optimal e beam voltage for PED and that is what, we see here.

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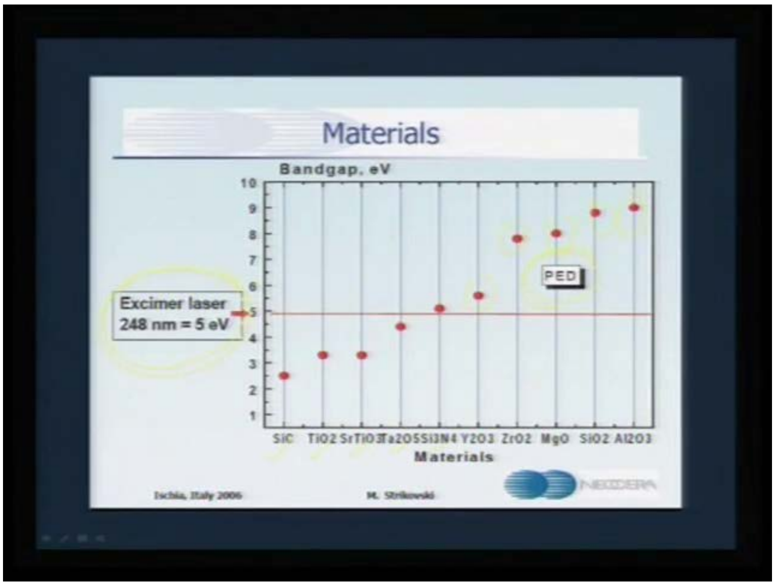

Materials

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This is another useful guideline from nocera group, which gives us some idea, why PED may be much more efficient than PLD, for example, if you take a 248 nanometer laser crypton flow rate laser and use the PLD, you would see very comfortably, we can deposit silicon carbide titania strontium titanate tantalum oxide and silicon nitrate. These are very easily deposited, using a PLD instrument whereas, when you look at the band gap of some of these materials like ytttria zirconia or magnesia, silica, alumina all these are showing a band gap above 5. And if you are excimer laser can generate only 5 electron volt, it is impossible to you to oblate with ease this high band gap materials, therefore this is where PED comes into picture. So, with PED you can actually deposit any of the insulating compounds or compounds with very high band gap, so that is one of the reasons why PED is still stands out.

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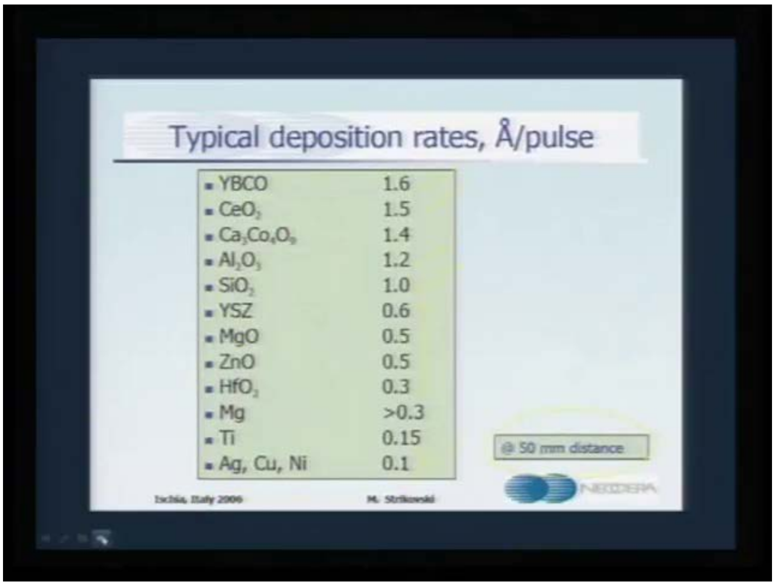

Typical deposition rates, Å/pulse

YBCO	1.6
CeO_2	1.5
$Ca_3Co_4O_9$	1.4
Al_2O_3	1.2
SiO_2	1.0
YSZ	0.6
MgO	0.5
ZnO	0.5
HfO_2	0.3
Mg	>0.3
Ti	0.15
Ag, Cu, Ni	0.1

@ 50 mm distance

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As a more prolific deposition technique with this in mind at a distance between the target and the substrate of 5 centimeters, you can anticipate typical deposition rates of the order of 1.6 angstrom per pulse, if you are going to deposit yttrium barium copper oxide, which is a superconductor. If you go for ceria, you can easily oblate, that calcium cobaltite alumina silica all these insulating materials, you can easily oblate with a very high deposition rate.

And you can also see that, the photonic materials, you can update oblate with fair amount of ease. And these are the metallic materials although, they oblation rate is nearly 10 times lower, yet it is possible for you to oblate the metallic materials also. So, the type of the materials, that you have and the electron beam energy, that you use with the fixed target to plume distance, you can actually achieve this sort of deposition rates. So, one should not think that anything and everything, operated with PLD will have the same deposition rates.

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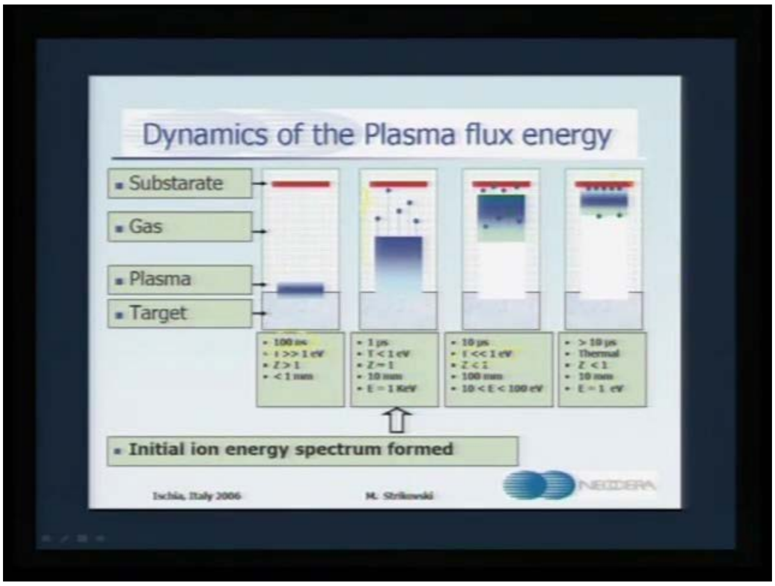

Dynamics of the Plasma flux energy

- Substarate
- Gas
- Plasma
- Target

- 100 ns
- $T \gg 1$ eV
- $Z > 1$
- < 1 mm

- 1 μs
- $T < 1$ eV
- $Z \sim 1$
- 10 mm
- $E \sim 1$ KeV

- 10 μs
- $T \ll 1$ eV
- $Z < 1$
- 100 mm
- $10 < E < 100$ eV

- > 10 μs
- Thermal
- $Z < 1$
- 10 mm
- $E \sim 1$ eV

- **Initial ion energy spectrum formed**

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So, it varies with the system and how it takes up the electron beam as you would see here, if this is your substrate and this is your gas zone and this is your plasma, which is generated at the interface with the target. You would see at 100 nanosecond, this is where the plasma is and the kinetic energy of your plasma or the ions that are generated is much much higher than 1 electron volt. But, as the plasma progresses towards the substrate, you would see in 1 microsecond the kinetic energy is falling down and it is falling down much much lower and then it becomes a thermally activated deposition. So, we should understand, how the plume propagates and therefore, depending on the material, it is possible for us, to fine tune the system.

The flux dynamics is almost similar to PLD as you would see here, in the first 100 nanoseconds when, they when the pictures are taken, this is your target location and the way the plume propagates, this way towards the substrate, you can see the plume is actually getting discharge or it decelerates in gas. So, over a period of the decay time, so at 100 nanosecond is just about to flash and then as you go down to 700 nanoseconds you can see, how the plasma decelerates, in a particular gaseous environment. And you would have also see this white region is the region where, maximum kinetic energy is there and it is still sustaining at 700 nanoseconds. So, with every pulse short, the pulse actually propagates in this fashion from here to here and then it goes and strikes on the substrate to form the thin film.

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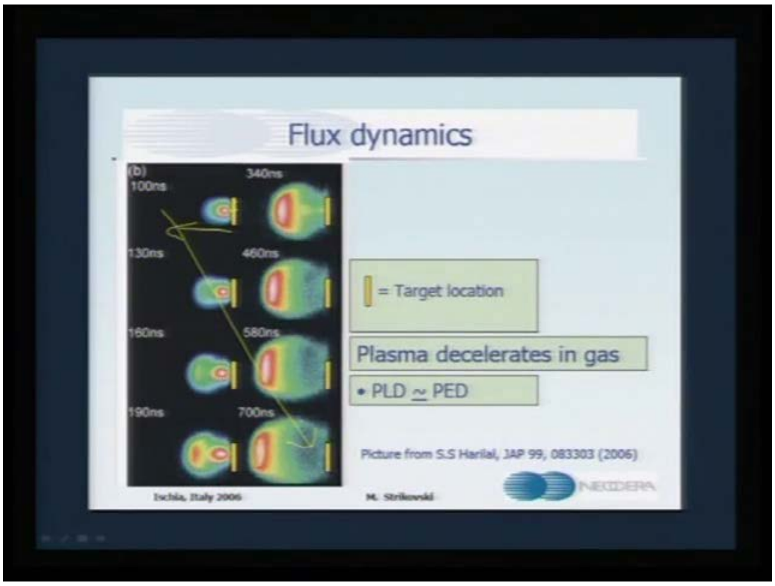

Flux dynamics

= Target location

Plasma decelerates in gas

- PLD ~ PED

Picture from S.S Harilal, JAP 99, 083303 (2006)

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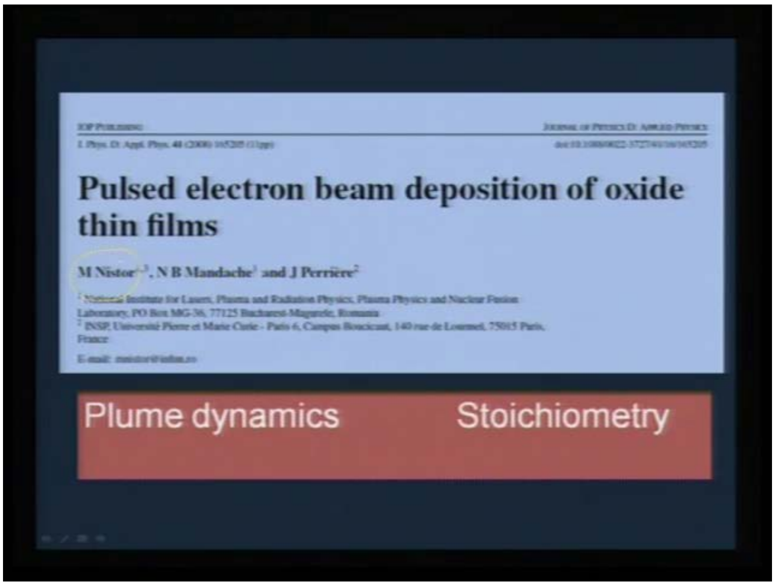

Pulsed electron beam deposition of oxide thin films

M Nistor[1,3], N B Mandache[1] and J Perrière[2]

Plume dynamics

Stoichiometry

Now go to some specific some examples, show you some thin films and also draw some conclusion on plume dynamics and stoichiometry, which might help us understand the dynamic of PED process. Some of the examples are taken, from the literature one is from nistor and coworkers who have worked on a variety of oxides film and they have made a quite a good amount of calibration. So, I want to touch on few examples nistor's group.

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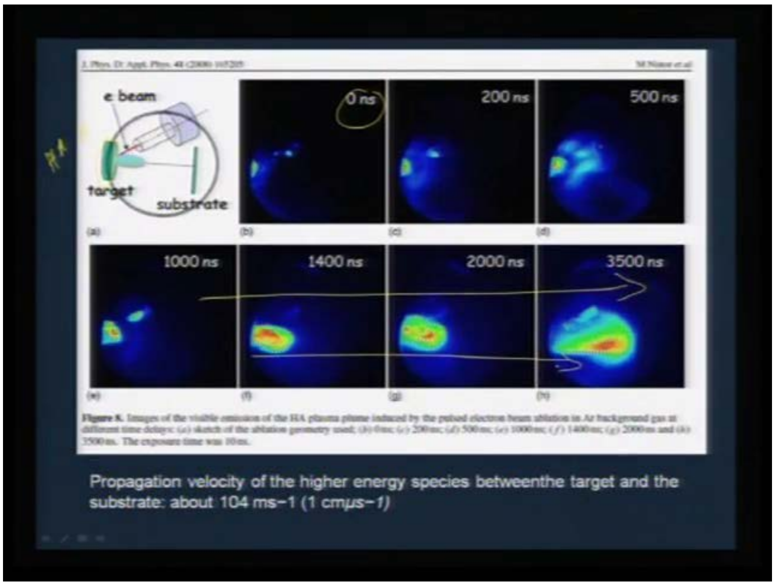

Propagation velocity of the higher energy species betweenthe target and the substrate: about 104 ms−1 (1 cmμs−1)

This is nice image of the visible emission of hydroxyl apatite, which is a bone material and you can actually translate this hydroxy apatite into a thin film form, not necessary a bulk form. And you can try to look at the strength of these hydroxy apatite films and if we have a way to deposit as a thin film form, then we can try to do it on variety of substrates.

So, here is the situation where you have this target is nothing but your hydroxy apatite hydroxy apatite and then you have the substrate, you are ablating using electron beam look at the progression of the plume. And this is actually a lumine scencing plume, because all the ions in your hydroxy apatite, usually calcium phosphorous all these are actually fluorescing. And once you trigger the pulse at 0 nanosecond, this is the how it is, but they specially grow with time and that is what you see here, over a period of 3500 nanoseconds, it has actually spatially grown.

And you can see the zone the temperature zone and how the species are still lumine scencing over, this transient period and during this period, we also understand that the heavier particles and the lighter particles, they take their share to reach the substrate surface and as a result, we can have knowledge of how complex materials can be grown. The mapping of these flashes gives us idea, about the stoichiometry and how the plume dynamics can control the n stoichiometry of the film.

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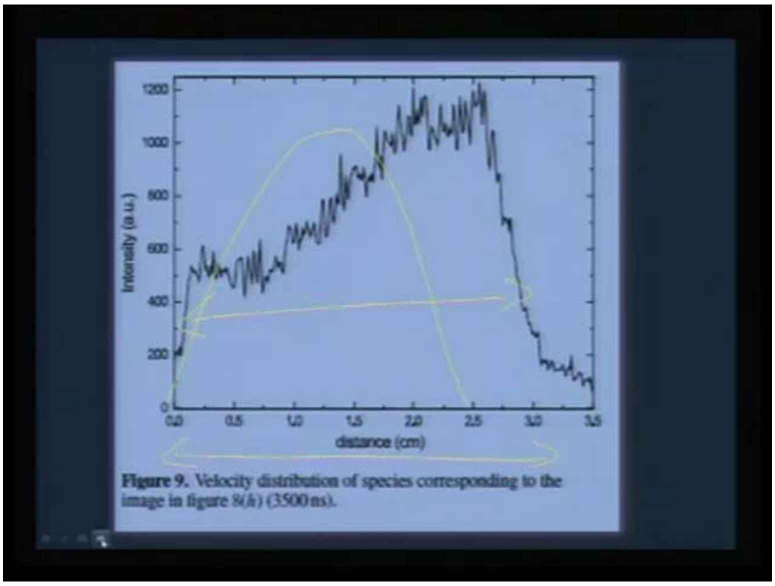

Figure 9. Velocity distribution of species corresponding to the image in figure 8(h) (3500 ns).

This figure gives us the velocity distribution of the species corresponding to the image taken from the previous example hydroxy apatite, as you would see here the velocity distribution ranges from 0 to 3 centimeter, which means you have both the high energy particles as well as low energy particles travelling together. And the spectrum is quite large and this is the one, which really makes the difference between PLD and PED, in PLD typically, you would see the spectrum like this, which means you do not have edge for high for heavier species to travel.

And because you have the velocity distribution of the specie is quite large, it makes it more versatile for you to prepare films with less particulates. Otherwise you will end up with the thin film with a lot of particle chunks, also coming into picture, because of this velocity distribution, you get a much finer film compared to PLD and I will show you some example of how it can go through.

In this example, you will see zinc oxide, for example, if you operate with the discharge voltage of 16 k V and external capacitor of say 26 nano farads, then what you see here is stoichiometric film. But, many particulates are there lot of small solids are seen on the S E M surface, but if you are going to change the discharge voltage and external capacitor, you would see for 14 26 combination, stoichiometric film is there and it is smooth and very low number of particulates are there.

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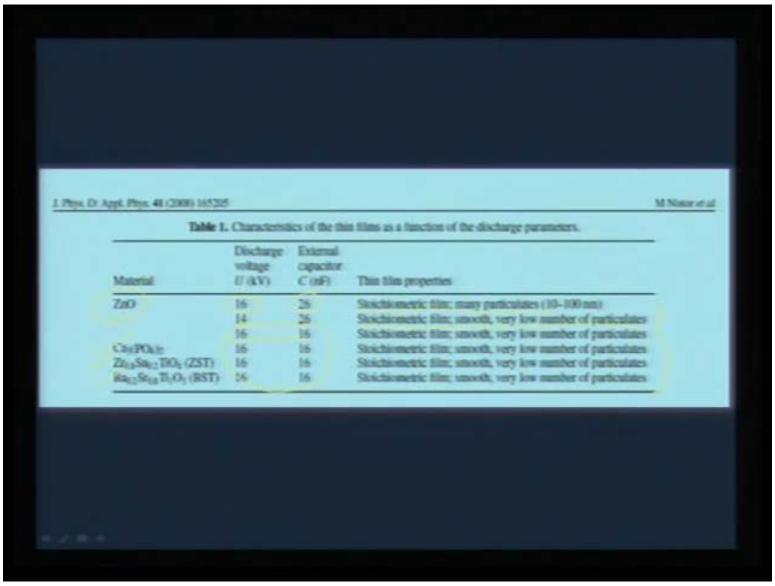

J. Phys. D: Appl. Phys. 41 (2008) 165205 M Nistor et al

Table 1. Characteristics of the thin films as a function of the discharge parameters.

Material	Discharge voltage U (kV)	External capacitor C (nF)	Thin film properties
ZnO	16	26	Stoichiometric film; many particulates (10–100 nm)
	14	26	Stoichiometric film; smooth, very low number of particulates
	16	16	Stoichiometric film; smooth, very low number of particulates
$Ca_3(PO_4)_2$	16	16	Stoichiometric film; smooth, very low number of particulates
$Zr_{0.8}Sn_{0.2}TiO_4$ (ZST)	16	16	Stoichiometric film; smooth, very low number of particulates
$Ba_{0.5}Sr_{0.5}TiO_3$ (BST)	16	16	Stoichiometric film; smooth, very low number of particulates

And you can also see the same combination works out for calcium phosphate zirconium tin, titanate barium strontium titanate in all these cases with a proper combination of your discharge voltage and capacitor external capacitor. You can actually have very smooth film coming out, this cartoon tells us what is the gambled with the stoichiometry. So, in such conditions, what is the stoichiometry of the final plume for example.

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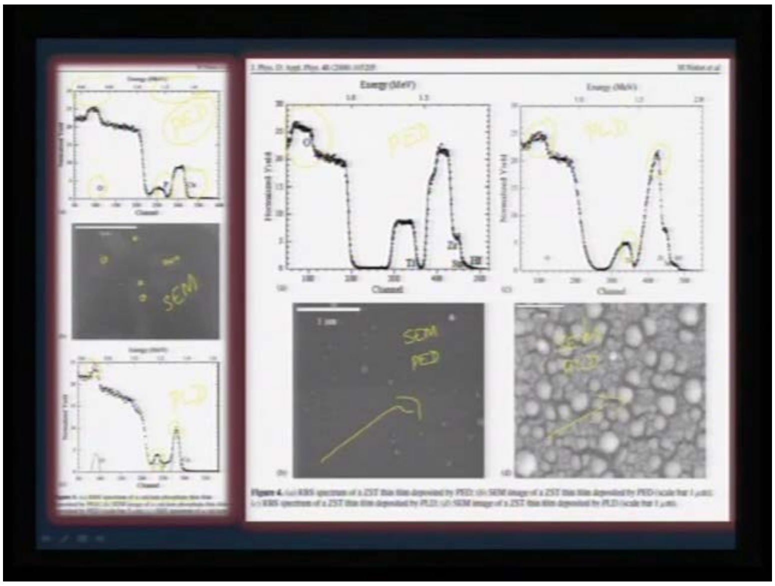

Figure 4. (a) RBS spectrum of a ZST thin film deposited by PED; (b) SEM image of a ZST thin film deposited by PED (scale bar 1 µm); (c) RBS spectrum of a ZST thin film deposited by PLD; (d) SEM image of a ZST thin film deposited by PLD (scale bar 1 µm).

In this case, this is a R B S Rutherford backscattering spectra of your calcium phosphate, which will actually estimate, how much of calcium is there, how much of phosphorus is there and how much of oxygen is there. So, you can technically evaluate your final composition based on the R B S channeling studies, that is the advantage and as you would see the solid line here is nothing but your theoretical prediction and your dotted line is nothing but your experimental plot. In the case of PED film, you would see that, there is a very good match and a both in the high energy region as well as in the low energy region.

But, notably you would see for a PLD film, there is a problem of mismatch for phosphorus even for calcium here and also there is a tailing, in the low energy spectrum, that is for oxygen. What does it mean compared to PLD PED seems to give a very good film, stoichiometrically and that you can see from the S E M micrograph also, these are the small particulates that, I was mentioning in the previous slide.

So, this sort of small particulates are there, but very minimum compared to PLD process and therefore, for complex materials PED seems to be doing a better role. And similarly, if you look at zirconium tin titanate Z S T, the R B S spectrum is given for both PED deposited and PLD deposited film, as you can see here. In this case there is some problem with the oxygen stoichiometry here, but titanium and zirconium seems to be doing pretty well and if you look at the PED oxygen stoichiometry is actually guaranteed.

There is no problem here as a result, if you look at the S C M micrograph of the PED deposited film here and the S E M micrograph of the PLD deposited film, you can see how the grain structure differs. In other words, this surface seems to be relatively much more finer and smoother than, the discontinuous grain growth in the PLD structure. Therefore there are lot of advantages, when we specially play around with a complex materials PLD, because of the energetic, that is involved it seems to have an edge over the PLD process.

In the case of PED the mechanism of interaction with the target is governed by electrons and not by photons, which is the main difference and thus the energy transfer to the target material is much much more effective in a PED process compared to PLD. So, wide gap band gap or highly reflective materials can be ablated with PED and this is one of the reason, why polymers can also be easily ablated using PED method. In the case of wide band gap material, such as calcium phosphate, it is also shown, that the surface morphology of the films grown by PLD strongly depends on the target optical properties.

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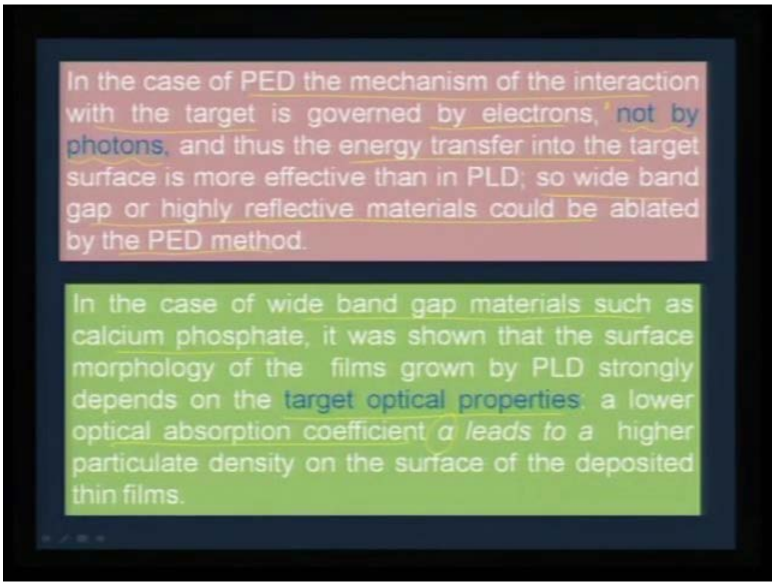

In the case of PED the mechanism of the interaction with the target is governed by electrons, not by photons, and thus the energy transfer into the target surface is more effective than in PLD; so wide band gap or highly reflective materials could be ablated by the PED method.

In the case of wide band gap materials such as calcium phosphate, it was shown that the surface morphology of the films grown by PLD strongly depends on the target optical properties: a lower optical absorption coefficient *α leads to a* higher particulate density on the surface of the deposited thin films.

So, any optically sensitive material, they will actually depend on the optical absorption coefficient say alpha and if this alpha is not comparable, then the material might throw some plume, but it is not actually ablating. So, you do not have this problem, in the case of PED, because it does not depend, the target does not depend on the optical absorption coefficient. Just depends on the beam current and as a result beam energy, therefore it is very easy to deposit optically active or materials, which are optical materials.

So, this is one of a reason, why PLD is more favored, I would like to give another example of zinc oxide, that can be deposited with PED, deposition of zinc oxide is actually favored in substrates like alumina, because aluminum oxide in this case is actually sapphire, we call it as a A l 2 O 3. So, you can deposit zinc oxide on alumina reason, the zinc oxide is also H D P and it can easily grow on sapphire, which is also H C P. And if you look at the growth, you would see only the 0 0 2 or 0 0 4 reflections of zinc oxide, which means it is a C axis oriented growth.

(Refer Slide Time: 33:02)

ZnO films deposited with PED

- Narrow (002) X-ray
- Strong band edge emission

H.L. Porter, J. Muth et al,
Mat. Sci. Eng., **B119** (2005) 210

Ischia, Italy 2006

M. Strikovski

So, zinc oxide is actually growing on the C plane of your sapphire substrate therefore, you would see only the reflections of that and the way you see the intensity of your C axis grown zinc oxide, it clearly shows that, they are very highly oriented thin films and you can make epitaxial films out of it. If you look at the cathode luminescence, that means, you are trying to excite this zinc oxide film, using a cathode, then you can see this emission, which is very typical of zinc oxide, which approximately comes around 380 nanometers corresponds to 3.27 electron volt is clearly seen.

And this is a very useful input, you get a very sharp emission, although there is camel back here, which is approximately of the order of 550 nanometer. And this camel back is usually due to the oxygen non-stoichiometry, never the less the band edge emission is very clearly seen using zinc oxide. So, you can make very good highly oriented zinc oxide films using PED.

As I told you in the previous slide, this zinc oxide can be easily made with very high degree of orientation, there are factors that, we need to bear in mind, when we deposit zinc oxide. For example, the beam energy parameter is actually given by this relationship and it goes as E is equal to C U square by 2 where, C is your capacitor and U is your discharge voltage. So, for a capacitor external capacitor of 26 nano farad and beam voltage of 16 k V, you would end up with the beam energy of 3.33 joules.

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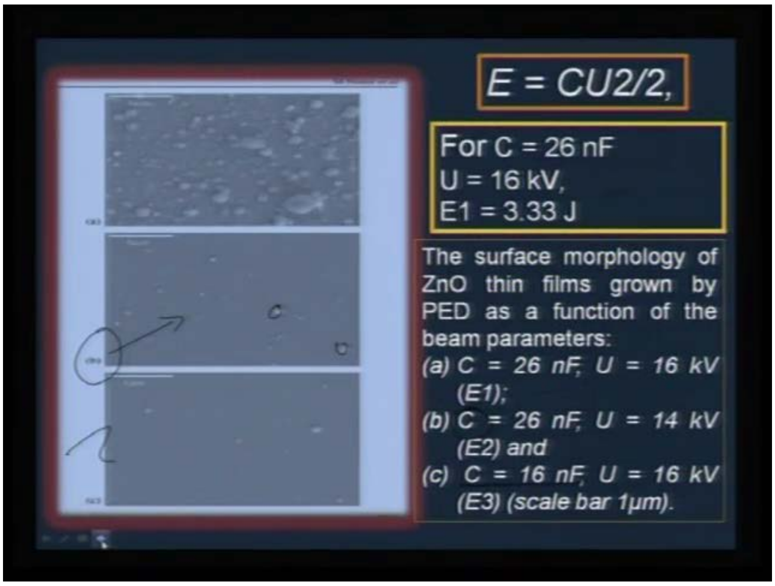

E = CU2/2,

For C = 26 nF
U = 16 kV,
E1 = 3.33 J

The surface morphology of ZnO thin films grown by PED as a function of the beam parameters:

(a) C = 26 nF, U = 16 kV (E1);
(b) C = 26 nF, U = 14 kV (E2) and
(c) C = 16 nF, U = 16 kV (E3) (scale bar 1μm).

So, if this were the case, then the you see several particulates are there, in this film and this is not a smooth film therefore, this is not good for sensing properties. So, what you do you try to play around with the capacitor numbers and the discharge voltage, suppose I reduced the discharge voltage from 16 to 14, then E 2 will be just 70 percent of your E 1. So, considerably you can bring down the beam energy from 3.3 to roughly around 2.9 joules and once you do that, you can clearly see the smoothness of the film changes quite a bit, you can see here in b, all the particulates are now vanishing and very few particulates are there. So, what you finally, do you again try to bring down, the external capacitor to 16 nano farads and for this combination, you see almost most of the particulates are avoided in zinc oxide film. Therefore, the beam parameter is very important, you need to play around with this numbers to get the right response.

So, the film roughness is very critical to the electron beam energy, that you are choosing and based on this you can see, how the profile changes, if you are looking at a polycrystalline film for Z n o for example, the target to substrate distance place a important role. If you are going to keep the distance at say 2 centimeter, then you are seeing this 3 peak, which is characteristic of zinc oxide to be more broader, in other words it is more amorphous.

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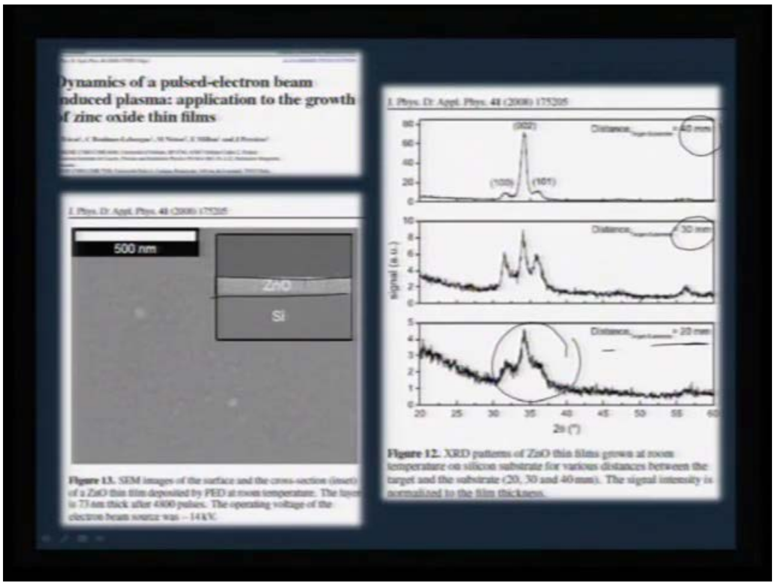

ynamics of a pulsed-electron beam nduced plasma: application to the growth f zinc oxide thin films

J. Phys. D: Appl. Phys. 41 (2008) 175205

Figure 13. SEM images of the surface and the cross-section (inset) of a ZnO thin film deposited by PED at room temperature. The layer is 73 nm thick after 4500 pulses. The operating voltage of the electron beam source was ~14 kV.

Figure 12. XRD patterns of ZnO thin films grown at room temperature on silicon substrate for various distances between the target and the substrate (20, 30 and 40 mm). The signal intensity is normalized to the film thickness.

If you are going to keep it at 3 meter distance, then the crystallinity improves and the best samples are made when, the critical distance is at 4 centimeter. Therefore, each system has its own sensitivity, we need to optimize that distance, this is a S C M image of zinc oxide, that is grown on silicon. You can see how sharp interface, you can built using pulsed electron deposition, you can either make a polycrystalline zinc oxide film or single crystalline zinc oxide film, depending on the substrate, that you are choosing.

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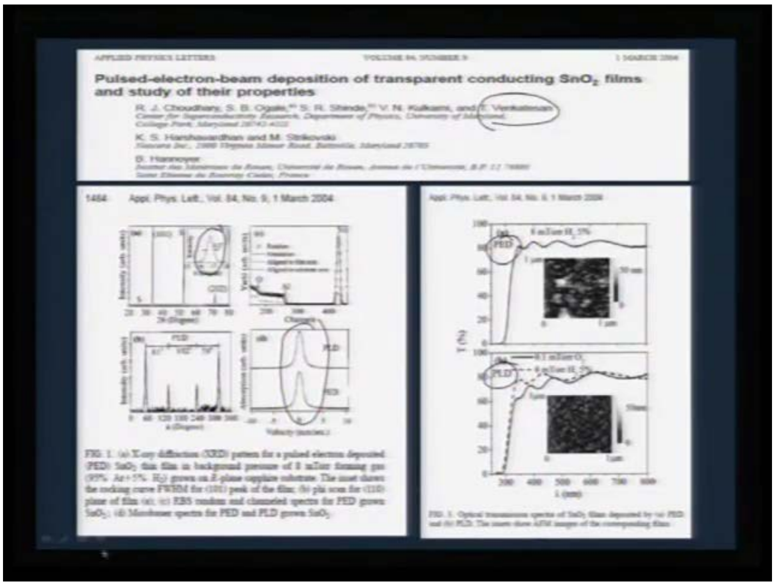

APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 9 1 MARCH 2004

Pulsed-electron-beam deposition of transparent conducting SnO_2 films and study of their properties

1484 Appl. Phys. Lett., Vol. 84, No. 9, 1 March 2004

Appl. Phys. Lett., Vol. 84, No. 9, 1 March 2004

FIG. 1. (a) X-ray diffraction (XRD) pattern for a pulsed electron deposited (PED) SnO_2 thin film in background pressure of 8 mTorr forming gas (95% Ar+5% H_2) grown on R-plane sapphire substrate. The inset shows the rocking curve FWHM for (101) peak of the film; (b) phi scan for (110) plane of film (a); (c) EBS random and channeled spectra for PED grown SnO_2; (d) Mössbauer spectra for PED and PLD grown SnO_2.

FIG. 3. Optical transmission spectra of SnO_2 films deposited by (a) PED and (b) PLD. The insets show AFM images of the corresponding films.

And this is another example by Venkatesan’s group at Maryland where, they made transparent conducting tin oxide films, why are they used, because for photonic applications. You can now use a transparent electrode, anode rather, which can replace indium tin oxide, because of the cost, that is involved tin oxide films are preferred. And you can see here PED grown films show nearly 80 to 85 percent of optical transformation, in other words, it is almost a clean transparent electrode.

So, you can get a very good transmission, out of a PED deposited one, as comparable to PLD and here also you look at the mapping of your tin oxide using mass bar, the isomer shift is exactly the same between PED and PLD that means, you can get a very good oriented film. And here again in b, you can see the phi scan of all the reflection of zinc oxide and the rocking curve shows that, the rocking curve full with half maxima is less than 1 degree, that means, it is a very, very nicely grown film, using PED method.

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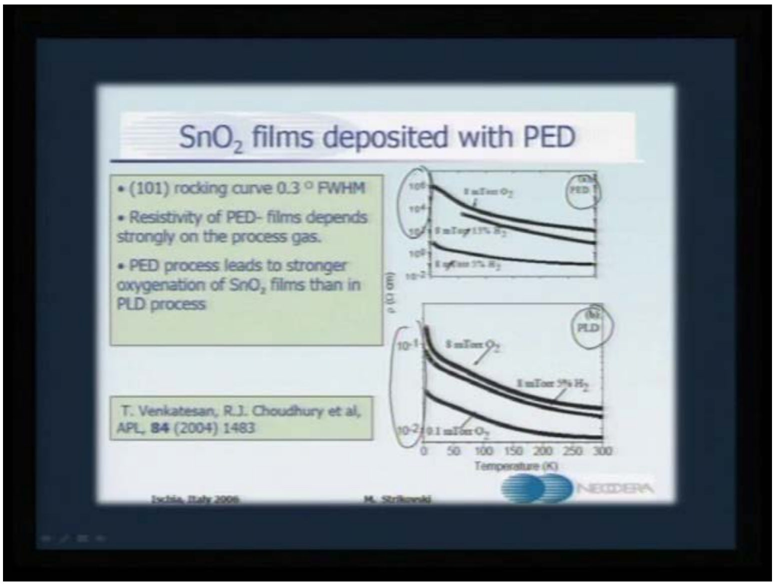

SnO_2 films deposited with PED

- (101) rocking curve 0.3 ° FWHM
- Resistivity of PED- films depends strongly on the process gas.
- PED process leads to stronger oxygenation of SnO_2 films than in PLD process

T. Venkatesan, R.J. Choudhury et al, APL, **84** (2004) 1483

And you would also see, how PED is very critical to the processing gas for example, this is a compression made between PED and PLD, for 8 meter oxygen pressure with combination with hydrogen. You can see the resistivity of your tin oxide, it is fairly low it is nearly metallic with the PLD, but for the same 8 millitorr with P A PED, you can see the resistance is of the order of 10 power 6, therefore the purging gas or the atmosphere, that we use is very sensitive. So, you need to have a optimum for PED process.

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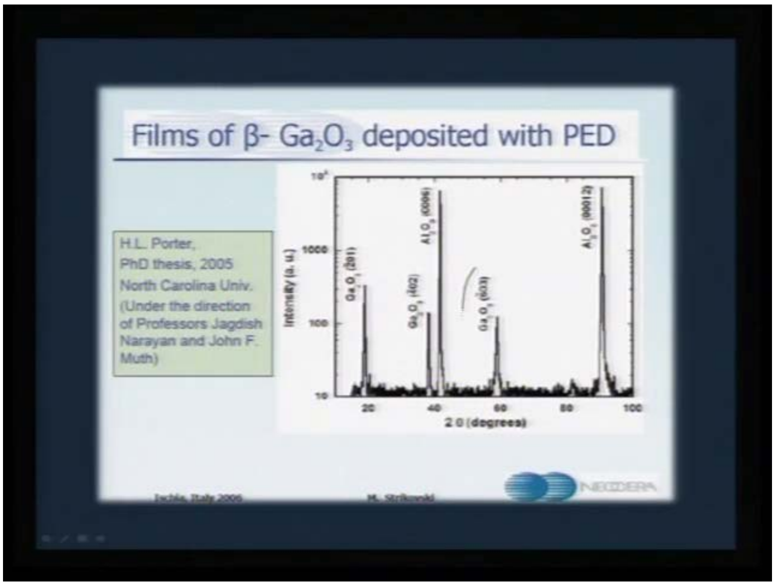

Films of β- Ga_2O_3 deposited with PED

H.L. Porter,
PhD thesis, 2005
North Carolina Univ.
(Under the direction of Professors Jagdish Narayan and John F. Muth)

Ischia, Italy 2006

M. Strikovski

And similarly one can make very nicely grown film of Gallia, which is also useful for optoelectronic applications, as you can see here, this is not exactly a singular crystalline film, this is a polycrystalline film grown on sapphire surface.

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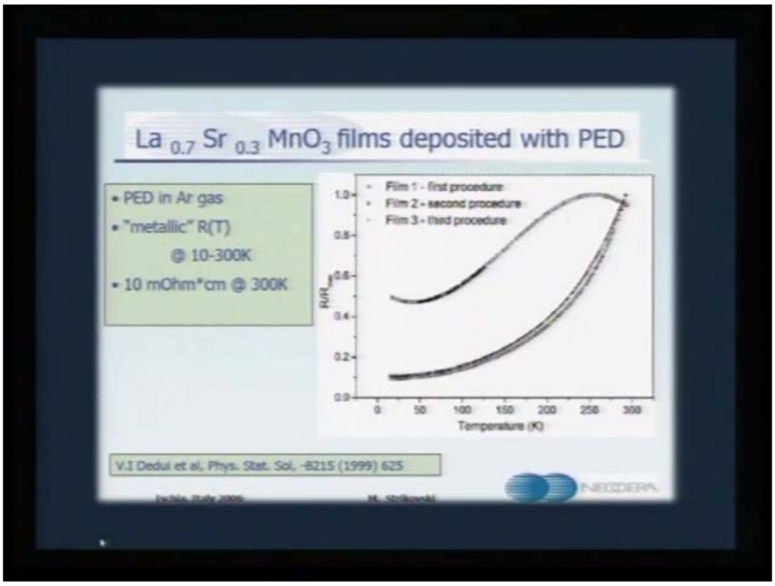

La $_{0.7}$ Sr $_{0.3}$ MnO_3 films deposited with PED

- PED in Ar gas
- "metallic" R(T) @ 10-300K
- 10 mOhm*cm @ 300K

V.I Dedui et al, Phys. Stat. Sol, -B215 (1999) 625

Ischia, Italy 2006

M. Strikovski

And L a S r M n o 3 in the last lecture, I mentioned how manganite films can be nicely grown and they show that critical metal insulated transition, same is the case, but again gives you an idea, how the transition metal insulated transition can change with the gas that you use. In this case PED in argon gas gives you a metal insulated transition, which is shifted by nearly 50 Kelvin whereas if you deposit this in gas in oxygen atmosphere, you get a room temperature metallic film.

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PULSED ELECTRON DEPOSITION (PED) at IIT Kanpur

So, we can make even manganite films with ease and this is the deposition chamber that we have at I I T, this facility is there and we can try to grow films of a verity on a verity of substrates. So, this is the processing chamber and this is the 6 target carousel, that we have and the whole thing is actually triggered using a computer, you can trigger the electron beam source.

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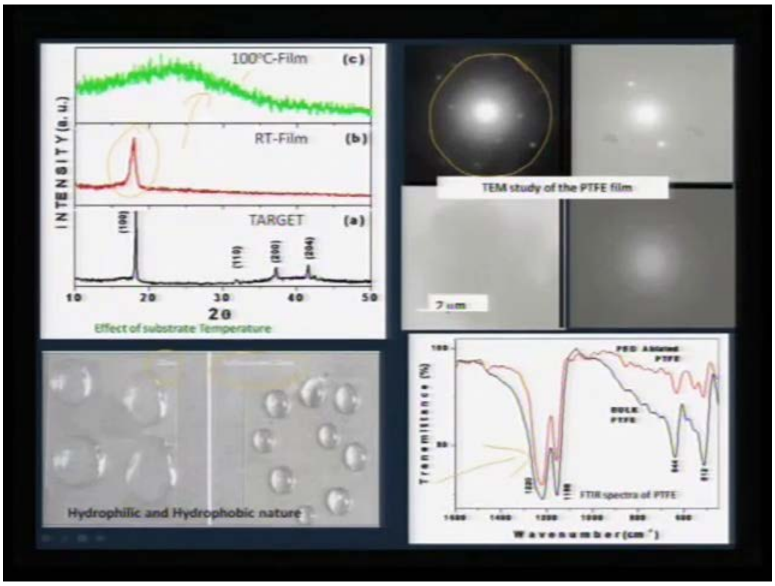

And this is one of the pictures taken at I I T kanpur where, you are ablating manganite films and this is typical plasma, that is generated during the process. I will give you an example of how a polymer can be deposited PTFE is a well known polymer, which is called teflon and to ablate material like, that is impossible using PLD, because of the optical absorption coefficient, which is quite different, as a result it is not possible to ablate, that easily using PLD process. But you can see in PED, you can deposit such a film and room temperature grown film shows the x-ray pattern, which is typical of the target and suppose, you grow the same film at 100 degree C, you see a amorphous state.

And that is what you see from the T E M also have crystalline film pattern emerging, how do I know, because you are controlling in nano size, it is very difficult to know whether you deposited any film or not. If you are going to deposit on a teflon coated glass, this is the teflon coated glass and this is on water droplets on glass, you can clearly see that the contact angle changes in the teflon coated glass meaning, you have made a very effective coating of teflon on the glass. So, you can also see the I R very clearly, that showing that P T F E can be made using PED.

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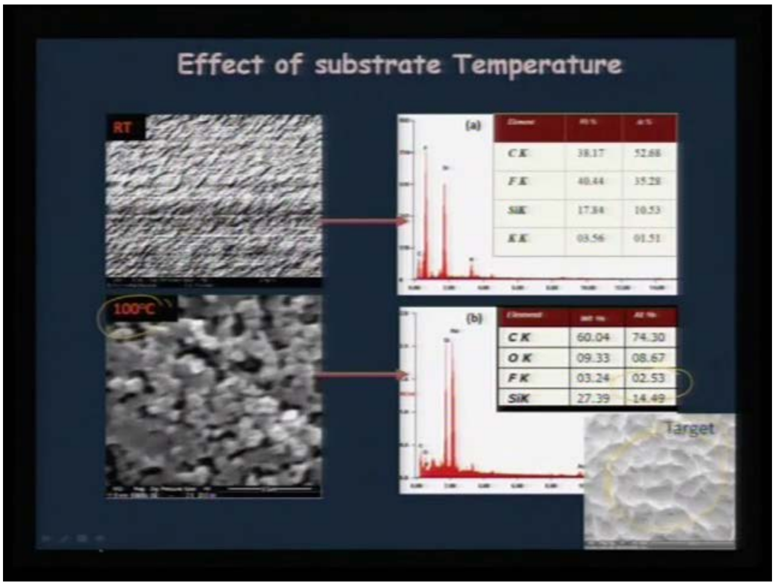

Effect of substrate Temperature

(a)

Element	Wt%	At%
C K	38.17	52.68
F K	40.44	35.28
SiK	17.34	10.53
K K	03.56	01.51

(b)

Element	wt %	At %
C K	60.04	74.30
O K	09.33	08.67
F K	03.24	02.53
SiK	27.39	14.49

And in room temperature, it gives a SEM feature like this, but when it going to 100 degree C, you can see a considerable loss in the fluorine contents, therefore it is not really a teflon. But, it is actually a non-stoichiometric polymer film and this is the SEM of the target, you can see a very nicely cut solid surface of a polymer and the microstructure changes when you try to deposit.

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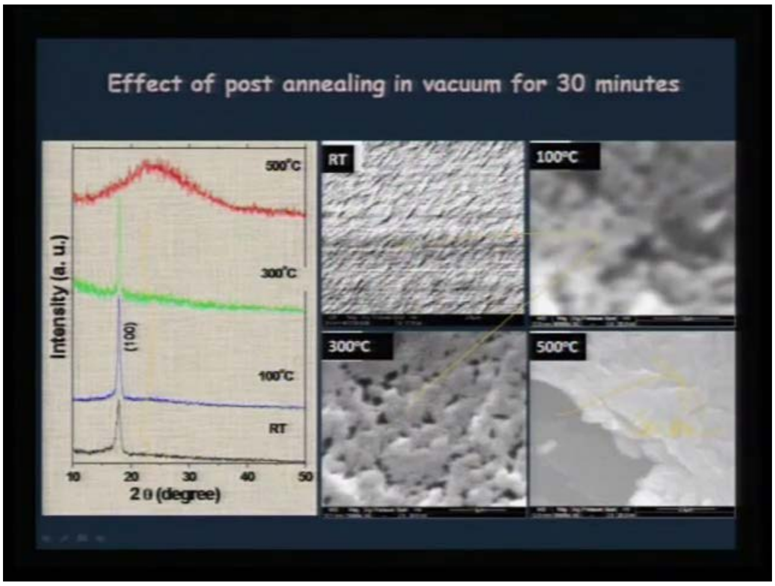

Effect of post annealing in vacuum for 30 minutes

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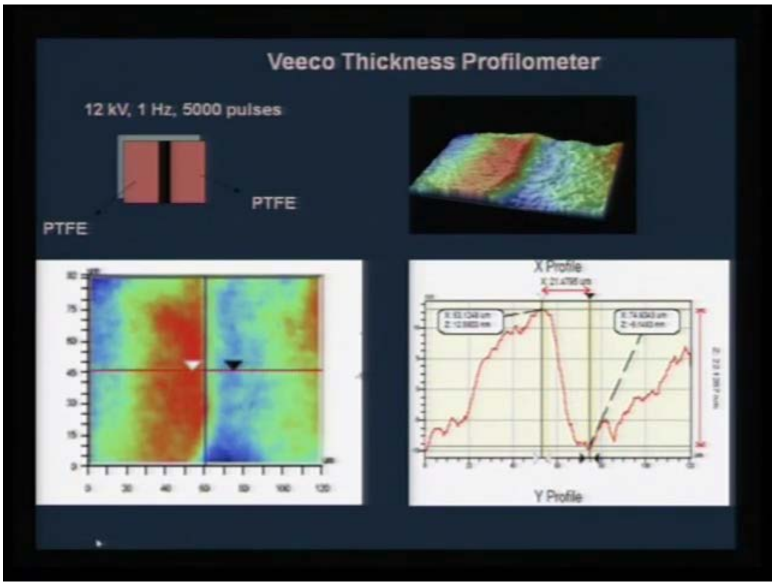

Veeco Thickness Profilometer

12 kV, 1 Hz, 5000 pulses

This film with different temperatures and this is another example of how the crystallinity of the polymer varies, from room temperature to 100 to 300 and to 500. Although the x ray remains the same, it is very tempting to conclude that I am making a P T F E film, but as you see here, you go a down this S E M features, you can clearly see the microstructure changes, which means when you deposit or when you post anneal these films at high temperature, you are actually loosing quite amount of fluorine.

So, care should be taken to optimize the condition and if you go to 500 actually the compound has transformed into mere carbon. So, what you see here is nothing but carbon, so we need to understand this dynamics closely when you deposited PED. And it is also possible for us to gauge, what is the thickness of this film, that you are making and using a profilometer is possible to measure exactly the thickness of your P T F E layers.

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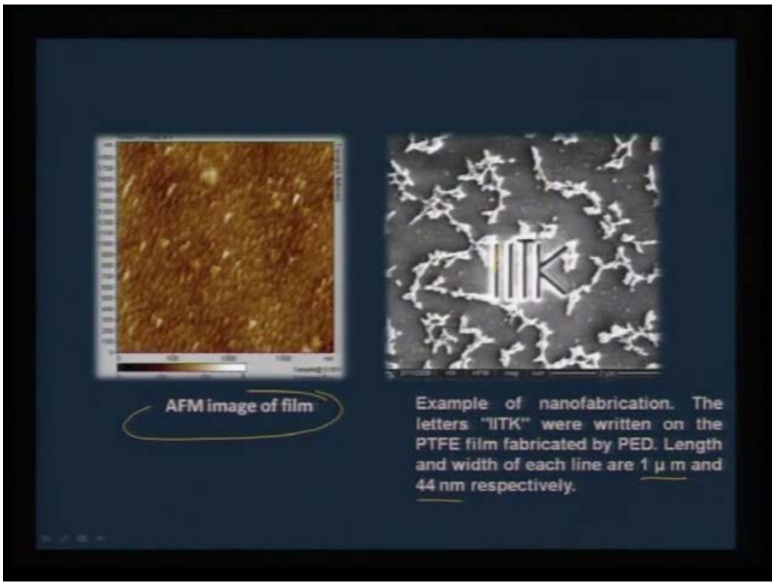

AFM image of film

Example of nanofabrication. The letters "IITK" were written on the PTFE film fabricated by PED. Length and width of each line are 1 μ m and 44 nm respectively.

This is a typical A F M image of the film and we can also do some nano structuring, you can write I I T kanpur as a nano structure and length and width of each line is 1 micron and 44 nanometer. So, you can actually do this sort of writing some polymer films, its possible once, you write using electron beam, you can try to cap this with any sort of dopants. So, you can actually try to fabricate any device by nano structuring, this polymeric surfaces.

And this is another effect where, you can use PED to make devices, I want to make spintronics device then I can actually go through this protocol, I first take a glass electrode like this 5 mm by 5 mm and I can put a stripe. The first black stripe, what you see here is nothing but ion stripe and on the ion stripe, I can actually put P T F E square layer and then on the top of the P T F E layer, I can put another ion stripe. So, this is ion electrode and ion electrode and P T F E is sandwiched between 2 ion electrodes.

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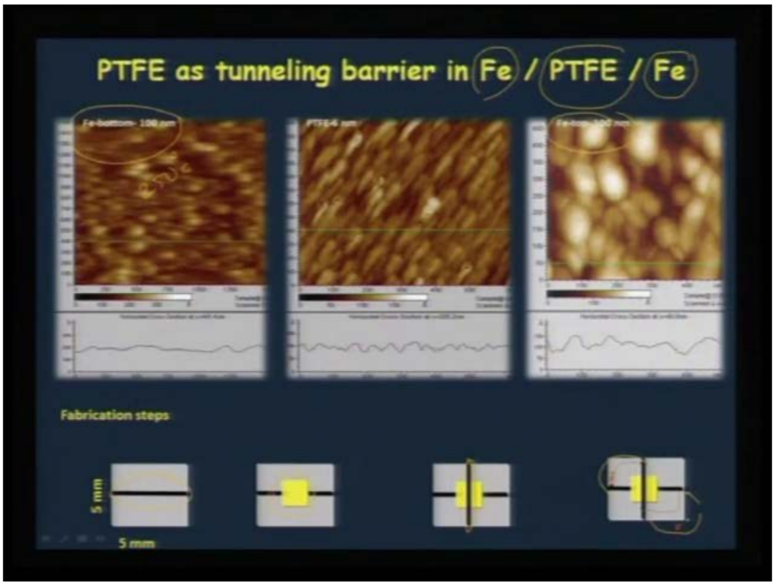

PTFE as tunneling barrier in Fe / PTFE / Fe

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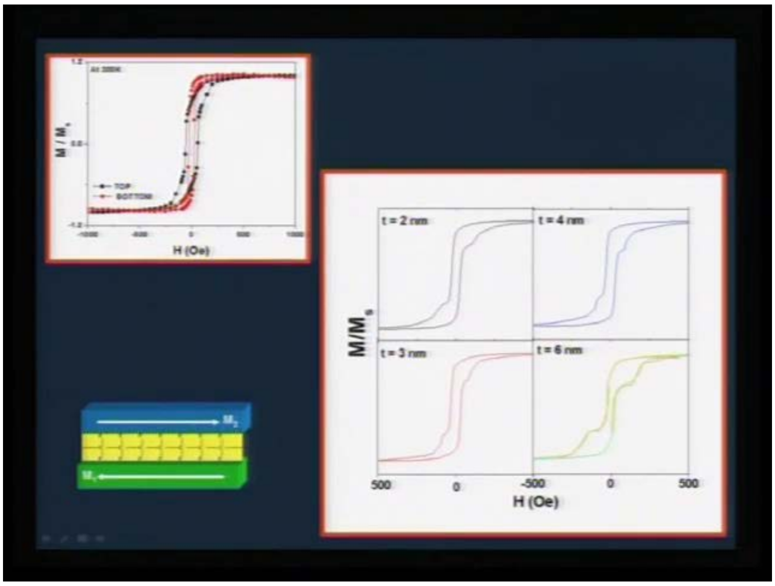

So, the A F M of each this layer is shown on the top, you can see the microstructure is varying the microstructure of top electrode is quite different from bottom electrode, because you are heating this sample during deposition at 250 degree C, therefore you get a fine grained structure, compared to amorphous room temperature grown film. So, once you make these film, you can actually measure the resistance by applying voltage across these 2 ends and you can measure, the you can apply current across this and measure the voltage across these 2 leads.

So, this way you can make a plot of resistivity and before that, if you take a look at the individual layers, you can see the bottom and the top layers do show different coercivity and in a device they typically show this 2 step loop. And this 2 step loop is very critical or characteristic, that are devices made meaning, the electrons are now tunneling through the polymeric layer and only then you will see this sort of a 2 loop situation.

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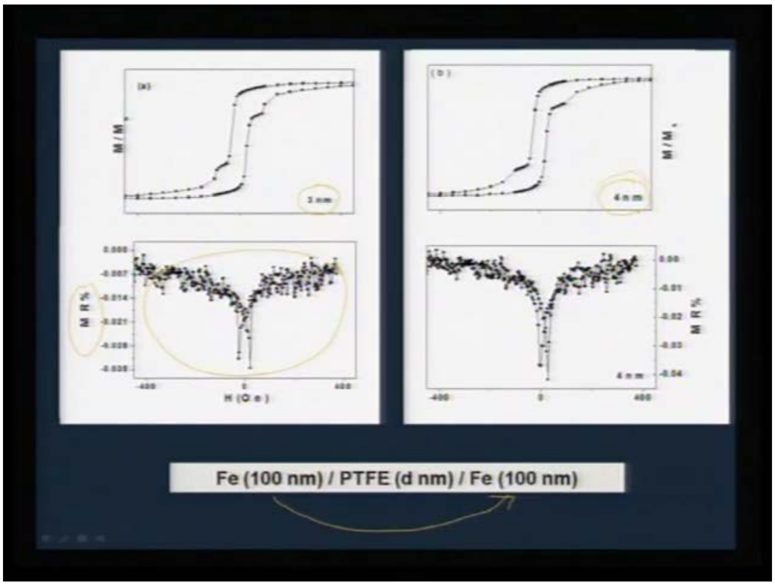

Fe (100 nm) / PTFE (d nm) / Fe (100 nm)

But, if you actually measure for the that device with the polymer thickness varying from 3 nanometer to 4 nanometer, what you really see is pin holes, which are short circuiting the top and the bottom electrode, as a result, you get a magneto resistance, which is negative in nature. If it is negative that means, there is a short circuiting between this electrode and this electrode via pin holes, which are formed by P T F E therefore, this is not the desirable one therefore, what I can do is I can increase this layer thickness of P T F E, which is in the middle.

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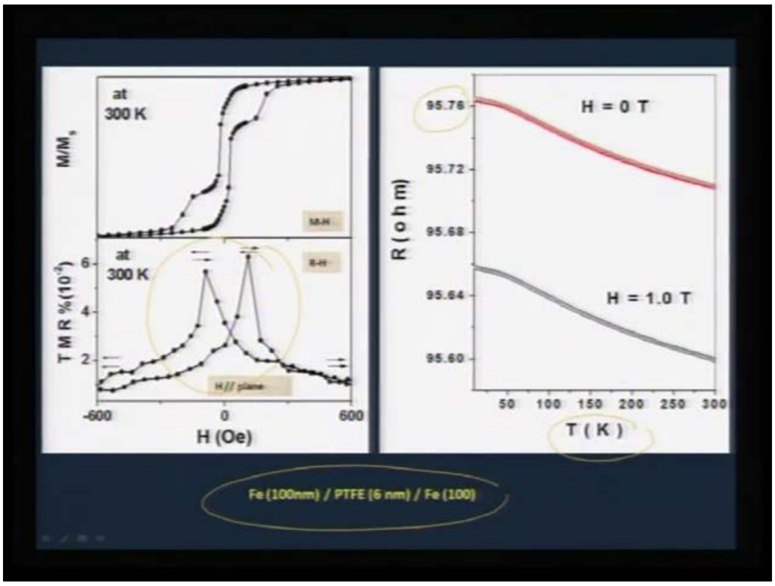

Fe (100nm) / PTFE (6 nm) / Fe (100)

And if I increase it to say 6 nano meter, then I immediately you see the magneto resistance switches to positive in nature, which means the device is actually operating. So, this is a very useful information to understand how PED can be used for making critical devices, it is not just making films, you can make devices and how do I know that, I have made a device. If you actually do r versus t plot, typical values of your resistance has to be something like this say 95 ohms.

What does it mean the ion electrodes are actually delinked therefore, resistance has gone up, if through the pin hole, they are short circuited the resistance will be less than a ohm, it will be in milliohm that means, both the electrode are in contact with each other. Therefore resistance will give you a useful map, whether your device is really flat and it is working or not. So, PED can helps us make films like this and this is incidentally one of the good examples of a tunneling magneto resistance curve. Lastly I would like to show some example of yttrium barium copper, which is superconductor and how this can be deposited. And christen group have reported, how this can be made not just as a film, but as a tape, because for practical applications, you need to use it as a tape.

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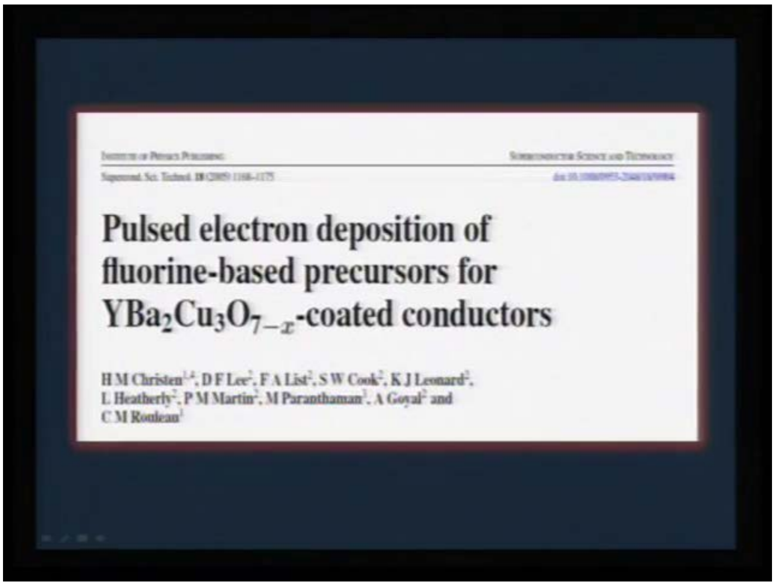

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Superconductor Science and Technology

Supercond. Sci. Technol. 18 (2005) 1168–1175

Pulsed electron deposition of fluorine-based precursors for $YBa_2Cu_3O_{7-x}$-coated conductors

H M Christen[1,4], D F Lee[2], F A List[2], S W Cook[2], K J Leonard[2],
L Heatherly[2], P M Martin[2], M Paranthaman[3], A Goyal[2] and
C M Rouleau[1]

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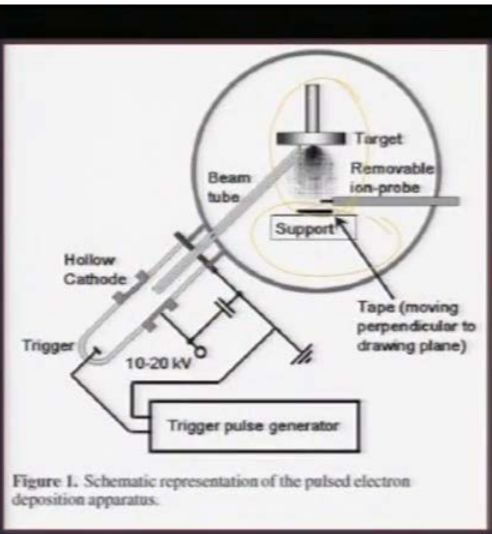

Figure 1. Schematic representation of the pulsed electron deposition apparatus.

And this is the profile where they have used it, as you can see, this is not just a substrate, but this is a polymer tape material called a rabbit. So, rabbit tapes are nickel tungsten tape, which can be rotated like a reel and as the reel is rotated, you can try to deposit yttrium barium copper on the substrate and therefore, you can do a reel to reel disposition, which is one of the biggest advantages with PED process, this cannot be done with ease with the PLD instrument. So, that that way you can actually make a substantially good application oriented depositions using PED.

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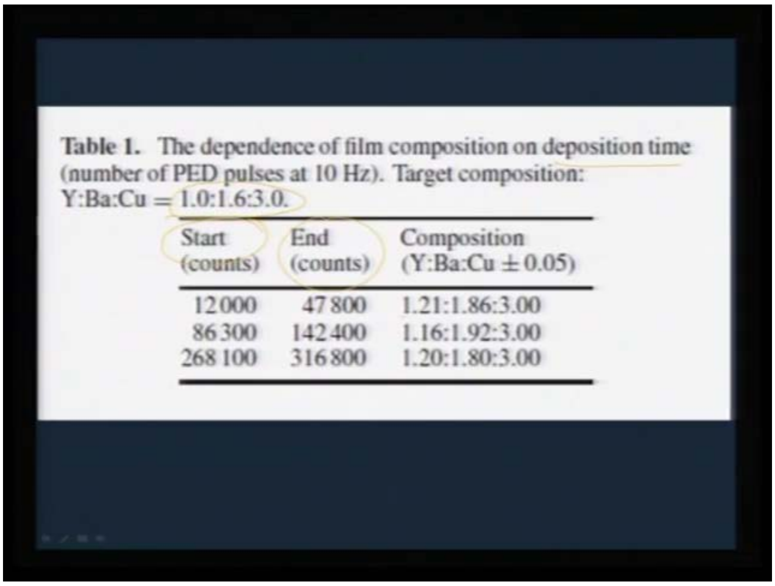

Table 1. The dependence of film composition on deposition time (number of PED pulses at 10 Hz). Target composition: Y:Ba:Cu = 1.0:1.6:3.0.

Start (counts)	End (counts)	Composition (Y:Ba:Cu ± 0.05)
12 000	47 800	1.21:1.86:3.00
86 300	142 400	1.16:1.92:3.00
268 100	316 800	1.20:1.80:3.00

And you can also map depending on the pulse time, deposition time, how the composition varies, this should be your actual composition 1 is to 11.6 is to 3 for yttrium barium copper. And as you are keeping on pulsing, you can stop at some counts and C, what is the composition as you would see copper does not suffer stoichiometry, but there is a give and take between yttrium and barium as you keep on progressively depositing high T C films.

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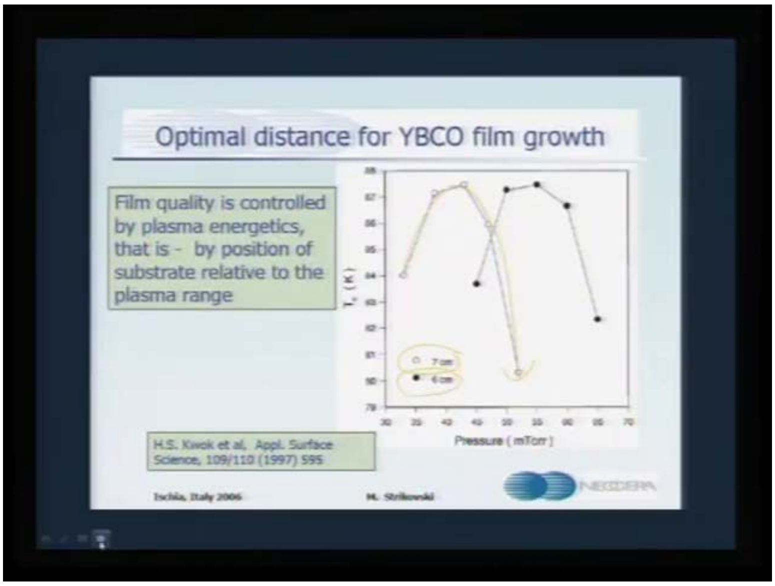

Optimal distance for YBCO film growth

Film quality is controlled by plasma energetics, that is - by position of substrate relative to the plasma range

H.S. Kwok et al, Appl. Surface Science, 109/110 (1997) 595

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So, you need to have some idea how the chemical composition can vary and also the distance between target and the substrate is if you are going to keep at 6 centimeter, you can see the T C is varying as a function of millitorr of oxygen partial pressure. If you are going to keep it at 7 then you can see, you can achieve a good stoichiometric film, even below 50 millitorr. So, all this are very sensitive and one depends on the other.

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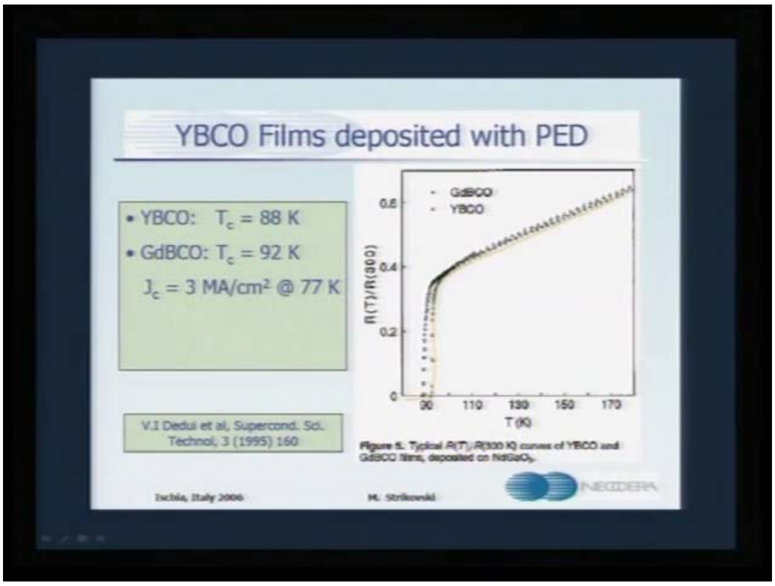

YBCO Films deposited with PED

- YBCO: $T_c = 88$ K
- GdBCO: $T_c = 92$ K
  $J_c = 3$ MA/cm^2 @ 77 K

V.I Dedui et al, Supercond. Sci. Technol, 3 (1995) 160

Figure 5. Typical $R(T)/R(300\ K)$ curves of YBCO and GdBCO films, deposited on $NdGaO_3$.

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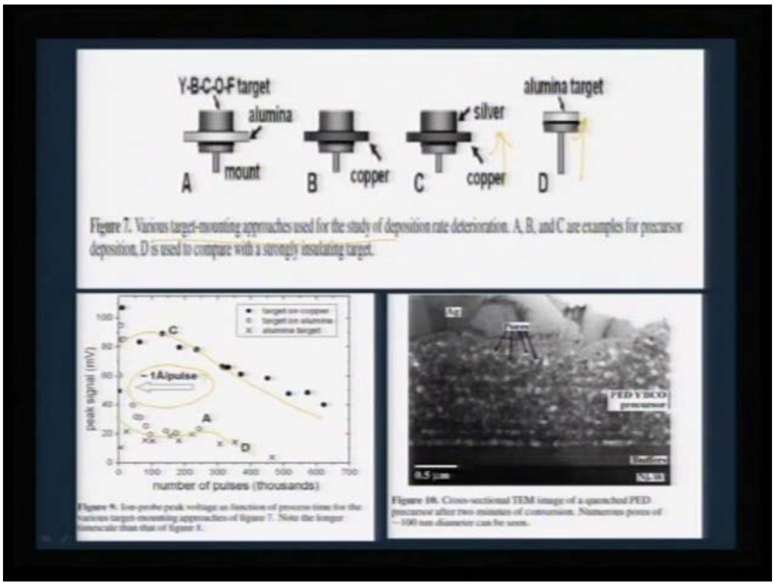

Figure 7. Various target-mounting approaches used for the study of deposition rate deterioration. A, B, and C are examples for precursor deposition, D is used to compare with a strongly insulating target.

Figure 9. Ion-probe peak voltage as function of process time for the various target-mounting approaches of figure 7. Note the longer timescale than that of figure 5.

Figure 10. Cross-sectional TEM image of a quenched PED precursor after two minutes of conversion. Numerous pores of ~100 nm diameter can be seen.

Therefore depending on the system, we need to make a compromise and these are some of the superconducting films, these are the actual plots of yttrium barium copper oxide as you see, a typical superconductor will show a metallic behavior. And then it drops down to 0 shows absolute resistivity at 90 K and such films can be easily grown with PED technique.

So, in one sense, we can sort of map to understand that, for various compositions, you need various mapping, if you are going to use aluminates target probably the distance or the target mount has to be like this, if you are going to use a copper plate, then you need to have go for a probe like this. So, different mounting approaches are also useful depending on the sort of material that we are using and also this gives some idea about, the peak signal and the number of pulses as you can see here.

You can easily do it for copper whereas, when you go for alumina targets, the ion probe peak voltages is fairly low and if you want to achieve one angstrom per pulse then you need to sufficient sufficiently go for comprise even on the target mounting approach. So, all these are very important when we try to look at PED process, so to some up, some word of comparison between PED and PLD.

PED is having its own limitations in terms of the stringent parameters that are critically linked between each other for example, target distance the amount of or the millitorr of the gas, that you are using, the nature of gas that you are using. And then the probe voltage electron beam, that is coming and how the distance is kept between the target and the substrate, all these are very sensitive, in case of PLD, this is not too critical though the partial pressure of the oxygen or argon is very critical in PLD process. So, with the fair amount of understanding, it is possible to extend PED process to a variety of useful applications and therefore, more studies will be done and specially for device applications using PED, so with this I stop.