

Plasma Physics and Applications

Guest Lecture by Prof. Anirban Mitra

Department of Physics

Indian Institute of Technology Roorkee

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Lecture 59: Laser Produced Plasma and Pulsed Laser Deposited (PLD) Thin Film

Good morning. So, I am Dr. Anirban Mitra from Physics Department of IIT Roorkee. So, today I will talk about the laser produced plasma and pass laser deposited thin films. This plasma is also almost become synonymous with the lasers after the discovery of lasers this plasma this field also become very much interesting because it is very easy to generate plasma with the help of laser. Laser we know that it is a light amplification by stimulated emitted radiations which is nothing, but a light and it is a type of coherent light where the phase relations between all the photons are maintained and it can produce a huge amount of energy within a very small region.

So, that is why it is very much useful for generation of plasma. Of course there are several other techniques for generation of plasma apart from the laser that is with the help of electrical discharge inside a gas. So, you can produce the gas also by sputtering we can have a RF sputtering type of equipment where you can accelerated the ions and which can bombard the a solid target and which can also generate plasma. But in those case there is some limitations sometimes you need a conducting target.

So, in case of lasers produce plasma it is very easy to vaporize any kind of materials whether it is gas solids or liquids. So, with a very huge amount of energy within a very small time you can generate the plasma. Now with the invention of this short pulse lasers like nanosecond lasers which can be generate with the help of Q switch or mode locking. So, in the nano order of 10^{-2} to 10^{-9} nanoseconds or more than that you can also generate the pico second, shaft pico second that is a femto second lasers which can also very useful for generation of plasma or laser ablating the materials and other things. Here today I will talk more about the pulse laser deposited thin film which is a very versatile useful technique by using the laser and where also the knowledge about the laser produced plasmas are also very useful.

Now I will talk about something about the historical background about the pulse laser deposition techniques. This pulse laser deposition techniques as I have told you invented after the development of the pulse laser very fast pulse laser like Q switch lasers or of the order of 2 to 10 nanoseconds and which can generate a huge amount of energy. Suppose the lasers which we have in our lab if it is a 1 joule per pulse in that fundamental wavelength that is the 1064 nanometer it is a kind of Nd:YAG lasers where this neodymium are doped in yttrium aluminium garnet which is a solid state lasers. So in that lasers we have the pulse repetition rate of 10 hertz and is the pulse width is 10 nanoseconds so if 1 joule energy is delivered within 10 nanoseconds so you can see that it is 0.1 gigawatt which is a huge amount of power can be generated within a very small time and this energy can be very useful for generation of plasmas like in solids liquids or gases.

Now this laser light if you can focus it like the common lights you can focus it with the lens so it can deliver a huge amount of energy within a very small area. So this that can be almost say 2 to 3 millimeters. So with this kind of energy the first successfully that thin film which is has been grown is the YBCO that is the yttrium barium copper oxide and it is a superconducting thin film and this pulse laser deposition technique becomes very much interesting and very much useful and it becomes attract and draws attraction among the scientist after the successful deposition of YBCO which is very difficult to deposit with other technique because you can see that it is a yttrium barium copper oxide which is a room temperature or high temperature you can say not room temperature high temperature superconductor which was invented in the year of 1987 and these films are very difficult to deposit because it has a 4th type of element like yttrium barium copper and the oxygen also. So all this material should be the stoichiometry of this elements or of this all this material should be maintained properly. So what is the advantage of pulse laser deposition is technique is that you can deposit the same material as the material of the target.

So you can maintain the stoichiometry or the composition of the material. So that is the very useful advantage of pulse laser deposition technique moreover it is much more easier to handle compared to the other deposition techniques like sputtering and other techniques also MBE that is molecular beam epitaxis chemical vapour deposition and other techniques. So here you can deposit any kind of material whether it is a metal semiconductor conductor or any kind of material. So after the successful growth of yttrium barium copper oxide the pulse laser deposition technique become very much useful and it becomes routinely used by the researcher. So now I will show a video of that pulse laser deposition techniques while we are doing the pulse laser deposition in our lab with the help of a Nd or third harmonics that is the 355 nanometer of a Nd:YAG laser that is the neodymium doped yttrium aluminium garnet actually the actual

wavelength that is the fundamental wavelength is 1064 nanometer but you can use the non-linear crystals to generate the third harmonic of this so which is the 355 nanometer so which is useful for deposition of thin films and I will explain that why this wavelength is useful and you can see that a blue light that is the blue colour plasma is generated so you can see the video so laser light is coming from this side and then it is falling on the target and then the plasma is generated and then it will this plasma is ejected from the target materials with a very high velocity and then it will this is the substrate where we will generally deposit the thin film so materials will be ejected at a very high velocity from the target materials so and then it will just deposit on the substrate and this is the your chamber and we can use the different kind of gas also inside the sometimes you can use the inert gas like argon or helium to slow down the species which are ejected from the target or you can use some reactive gases like you can use oxygen or you can use nitrogen also generally so to deposit nitride or oxide kind of films thin films here we are depositing zinc oxide and nickel oxide mainly the oxide based thin films so you can see the generation of plasma inside the lab with the help of laser.

Now I will show another video where you can see the generation of the ionization of gas or the plasma of air inside the simply in the air just by focusing the laser light so you can see the how the huge amount of energy can be focused with the help of lens within a very small region and you can generate the plasma of different materials like it can be gas solids or even liquids so here you can say see this is the lens where with the help of lens the laser beam is focused here laser beam is focused here and if the help of this lens and here you can see that a spot is which is glowing here so that is the plasma of it is that plasma of the air. So this is the another video you can see that with the help of laser light you can the generation of plasma of air or even of the solids. So now with this introduction so slowly I will go more into the details of the deposition procedure of the plasma of the laser produced plasmas and the pulse laser deposited thin films. So now what is the mechanism of pulse laser deposition? So first of all that your laser beam should be focused onto the target as I have already mentioned so a huge amount of energy should be convert or it will be focused onto a small area. Now this after the laser light interact or it will be absorbed by the materials or the solid targets so then it will heat up.

So it will use basically initially it will be just the heating the target and then when it will reach the vaporization temperature initially it will be melt and then it will vaporized and then the material will injected and when the material will injected and then it will further is energy will increase because this pulse width is very short it is of the 10 nanosecond. So initial part of the pulse mainly the energy will be used for the heating the target and next part of the pulse will used to generate the plasma and ejecting the

materials with a high velocity. So you can say that now there will be a plume which will be ablated from the material and generally it will be ablated from the just normal to the target because in that region your velocity of the materials will be very high and at the angles the velocities will be small. So you can see that plasma plume was highly directed is like a conical shape you can see in the video that the plasma shape is like a conical type so it will have an angle dependent. So in when it will the velocity will also depend upon the angles and the amount of material which will also depreciated at the angles are also vary so that is also a disadvantage of pulse laser deposition technique because you can deposit the very good uniform thin film within small areas of 2 to 3, 4 millimeter but further if you want to deposit the very large area thin film then it may not be so useful but there are other techniques of the pulse laser deposition like rastering or some by other method now a days even for industrial purpose one can generate the large area thin film and due to that now that plasma laser plasma interactions are also become very much important or very much useful.

So if the knowledge of plasma laser plasma interactions because when initially the plasma will form and then when the further in that later part of the pulse when the laser will comes and then it can absorb by the plasma which will also further heat the temperature increase the temperature of the plasma and it will also can accelerated the ions of the plasma and then it will deposit on the substrate with a very high velocity so initially you can say that this all this materials if it is a compound materials if it is not an element single element like if it is a zinc oxide copper oxide aluminum oxide magnesium oxide or some it is a barium copper oxides aluminum nitride or any other kind of material or say molybdenum oxides so in this it will decompose or it will decompose into the ions and the electrons like it can form the for zinc it can form the zinc ions and the oxygen ions and electrons so all this ions and electrons they will move with the different velocity and towards the substrate and then again it will recombines so again it will chemi absorb or fig absorbed on the substrate and then they will form again that same material on to the substrate but there are several parameters which one should maintain for the deposition of thin flames it is not that stoichiometry automatically it will maintain so sometimes there are the like in case of oxide thin flames there will be vacancies of oxygen so in that case controlling the oxygen pressure is also very important and then heating the substrate because when these atoms and all this will recombine on to the on the substrate so then it will diffusion process will takes place and to further promote the diffusion process sometimes one has to heat the substrate which will grow which will helpful in growing very good quality thin flames. So all these things also maintained and there are certain other parameter like the target to substrate distance that is also important parameter because that all this ejected species they should have sufficient velocity to reach the substrate so that also one has to maintain and then the pressure of the oxygen gas because sometimes the inert gases like helium, argons

those are using to slowing down this species plasma species which are ejecting from the target. But if you use and then so how much will be the pressure so depending if the pressure is very high then the all the ejected species may not have the sufficient amount of energy to reach the substrate. Now if the pressure is very low so in that case it can also ejected to the very high velocity and then that may damage the substrate also that may not be very useful for the good quality thin flames. So sometimes you have to optimize the background gas pressure whether it is inert gas or in case of the reactive gases like oxygens or nitrogen so then also you have to maintain the oxygen pressure to control the reactions inside the gases to get a good quality thin flames and also maintaining the exact stoichiometry of the target.

So depending upon the applications and what is the requirement so one can maintain all these things and then another parameter so there are several parameter like the oxygen gas pressure, the target to substrate distance, substrate temperature and then some laser parameter like choosing the laser wavelength. So how one can choose the laser wavelength is also important because that amount of energy which will be initially absorbed by the target that absorption coefficient should be very high for that particular wavelength. So generally use that laser wavelength of in the UV region because generally if we want to deposit the semiconductor or insulators so that band gaps are quite large so one can use the UV laser so generally either XIMO laser which are the wavelength of 248 nanometers or 193 nanometers or 308 nanometer depending upon the different gases or we use the neodymium doped yttrium aluminium garnet laser that is the India laser so which can also generate the 355 nanometer or 266 nanometer in the UV region. So we can see that there are the effect of background gases and also the energy, energy is also laser energy is also very useful so you should have first of all it should be above the threshold so that it can able to eject the ablate the above the ablation threshold so that it can be removed or ablate the material from the target and then it will be have enough energy to form the plasma and then you will have enough energy to reach to the substrate. So sometime if one use very high energy so it can deplete the material from the substrate so it can again damage the flame.

So one has to be very careful for choosing all these things parameter and generally the pulse widths are of the order of nanosecond but now a days femtosecond lasers are also available so one can use the femtosecond but the mechanisms for femtosecond lasers are completely differ very much different from the nanosecond lasers. So mainly here we will talk about the nanosecond laser produce plasmas and then so already we have discussed that first of all you will have so all that three steps you will have to perform in the pulse laser deposition technique. So it can classified into the three stages for the pulse laser deposition of thin flame first of all is the ablation of the material so that I have already mentioned that it will target will absorb the laser light and then it will heat

the target with the help of laser and slowly slowly the temperature will reach to the melting temperature and then after melting vaporization will take place and it will be ejected from the target and then the plasma will form and then this plasma will expand and there is another phenomenon where it is called that it will form a shock wave type shock waves will form from the plasma which will go with very high velocity and from the target toward the substrate and then further nucleation and growth which will be occurred on the onto the substrate. We will describe the small description about the overview of the experimental setup of that pulse laser deposition technique. So here you can see that there is a Nd-YAG laser actually I have shown you because this laser we are using in our laboratory in that physics department of IIT Roorkee.

So here we generally we use the third harmonic of the Nd-YAG laser so it is 355 nanometer but the 266 nanometers and wavelength is also useful and in 355 nanometer the energy which will use generally of the order of 200 to 300 millijoule per pulse and so this system is quite versatile and relatively it is simple compared to other deposition technique. So you can see that the laser is just coming and then it will focus with the help of a lens towards the target and this target holder it will rotate continuously so that always the fresh surface of the target should come otherwise what will happen there will be a crater will form so which will hamper the or which will obstruct the formation of the plasma. So fresh surface or the poly surface is always required so that is why sometimes we have to change the target routinely or we have to raster or rotate the target continuously and then you can have rotating substrate holder or the fixed substrate holder also. Rotating means if we want to deposit a very uniform film so in that case maybe one can rotate the substrate but it is difficult sometimes because there is a heater is attached with the substrate holder so sometimes it is difficult and there are the observation windows also available through which you can do the diagnostic. So what are the characteristics of plasma one can do just by doing the spectroscopic measurement that is the whatever the species are coming from the this target so one can analyze those species and what is the velocity of the species what is the temperature of the plasma so all these things one can monitor sometimes one can monitor in situ while depositing the thin films so most of the time we deposited we monitored this in situ this plasmas and with the help of these things one can find out the this parameters like electron temperature and velocity of the ions and densities of this ions and electrons and this information are very useful for deposition of the good quality thin film.

So you can use this knowledge further for deposition of better quality of thin film. Now as I have told you so there are the wavelengths which are available from the XMR lasers by changing the gases XMR lasers are also routinely used so because it is very useful because the wavelengths are available in the ultraviolet range or UV range so you can have by changing the gases also you can have different wavelengths like if you use

genuine chloride you can have 308 nanometer or if you use KRF krypton fluoride you will have 248 nanometer and 193 for argon fluoride if you use and similarly you have fundamental wavelength for Nd-YAG laser 1064 nanometer so generally we do not use this but 532 and also visible range it is also 532 nanometer this is also not used very much useful but more useful is 355 nanometer and 266 nanometers and the deposition chamber is generally made up with stainless steel and it is connected with a vacuum part like a diffusion or the turbo molecular pump so up to the tender minus 6 to minus 8 9 you can reach and then the target holder it should be rotate and the substrate heaters should also be there. Now initial mechanisms of laser matter interactions so when it will laser will interact with the material so generally I will discuss more about the insulator and insulators and the semiconductors so there can be different kind of transitions either it can be inter band transitions so it can go directly from the valence band that electrons which will absorb in the valence band that electrons which will absorb by the materials so this laser wavelength which is say 248 nanometer so then it will be equivalent to say around 4 point some electron volt which is much larger than the band gap of the semiconductor and insulator available generally like zinc white band gap semiconductor like zinc oxide gallium nitride they have of the band gap energy 3.4 electron volt and that laser energy in the electron volt should be larger than this band gap energy of that semiconductor so that the electrons which will have sufficient energy to jump from the valence band to the conduction band. And then when it will jump to the conduction valence band to conduction band then there can be a non radiative radiations by which through the phonon so there will be a phonon generation so by which it will comes down to another level inside the conduction band and from there it will again de-excite to the valence band and so that wavelength which will emit and which will absorb so which that emission wavelength will be higher than the absorb absorbed wavelength.

Now there can be also this is the inter band transitions so generally if we use the laser wavelength which have the energy greater than the band gap so then one can expect the inter band transition. Now if we use the so each is generally very much efficient so you will have a single photon excitation. Now if we use the wavelength say 1064 nanometer so it is around 1.7 electron volt which is much lower than the band gap so then what we required that there will be 2 photon or 3 photon or multi photon excitation. So in that case you need 2 photon to excite an electron from the valence band to conduction band.

So in that case the laser ablation process or laser vaporization process are not very useful so that is why most of the cases one can see that we use the laser switching in the UV region like either 248 nanometer, 193, 355 or 266 so all these are in the either UV or blue region so these are the mainly used. There can be other thing also sometimes even with the IR laser like 1.06 nanometer can also be useful for deposition of partially deposited thin plumes when you have some defect state. So in between the valence band

and conduction band if you have some defect state so then the laser can be absorbed and by the electrons and it can go to this defect state and then it will de-excite to the valence band. So in this process also there if we use the lower higher wavelength or with the lower photon energy so this process can also be useful.

There can be also inter band transitions within the conduction band also. So these are the different mechanism which can takes place. Generally for metals, metals are very highly reflective in either and both either IR or visible regions also and even in that UV regions also it can the conduction electrons, conduction band electrons can block the laser. So that generally the partial laser deposition process for metals are slower than the other the semiconductor or the insulators. So with this I will just complete. Thank you.