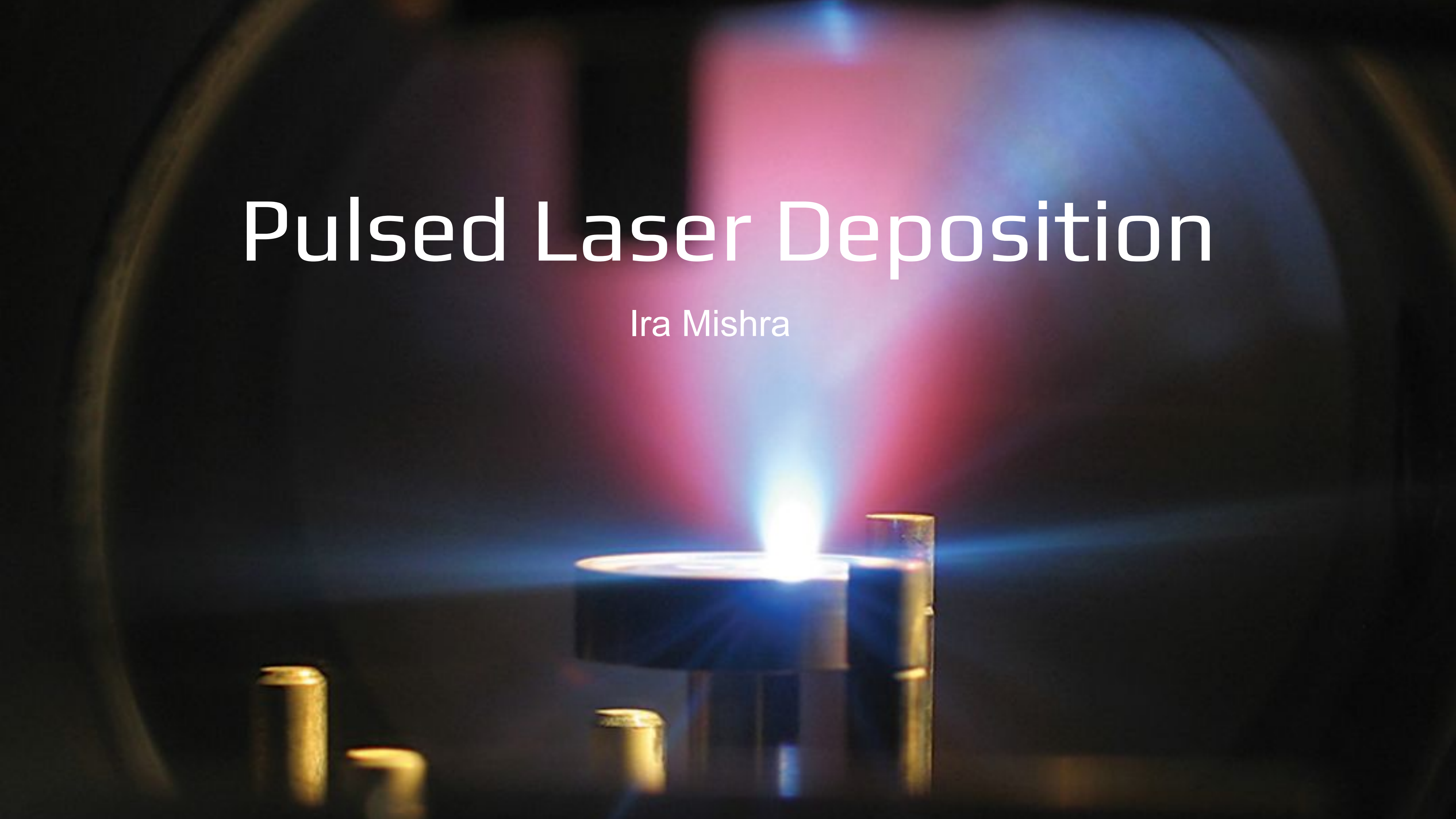
Pulsed Laser Deposition

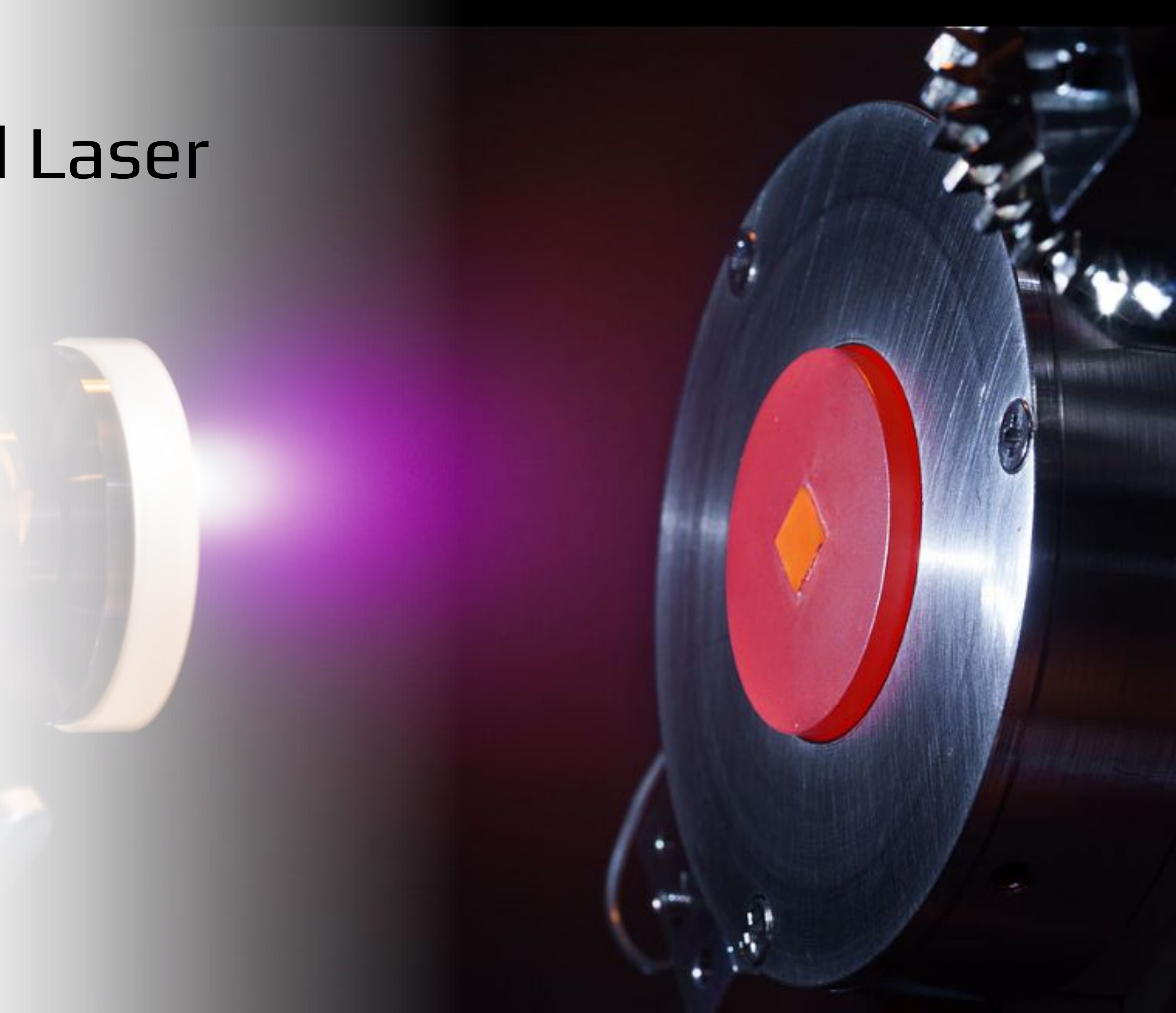
Ira Mishra

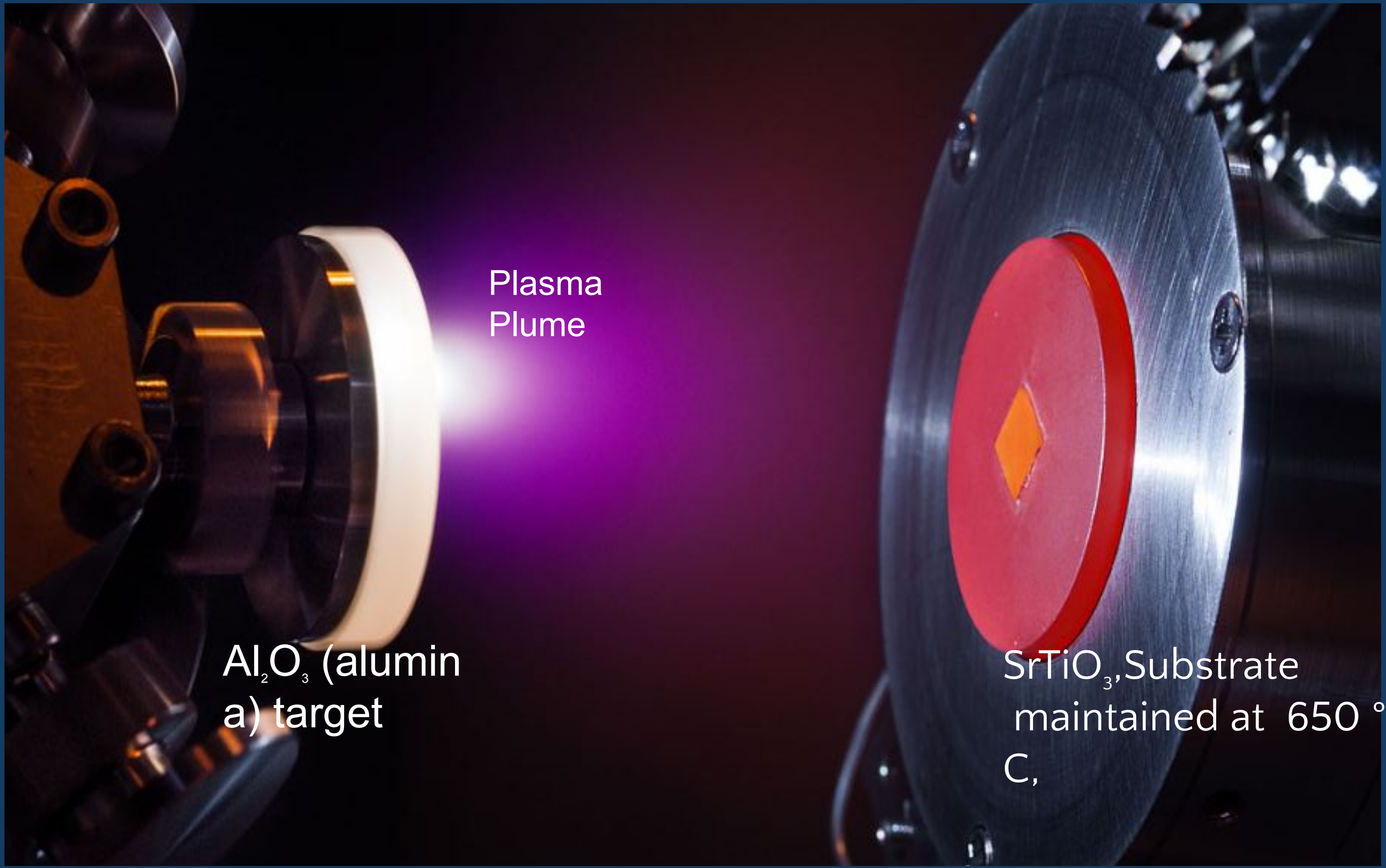


What is Pulsed Laser Depostion?

- **Pulsed laser deposition** (**PLD**) is 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.

Ref: Wikipedia



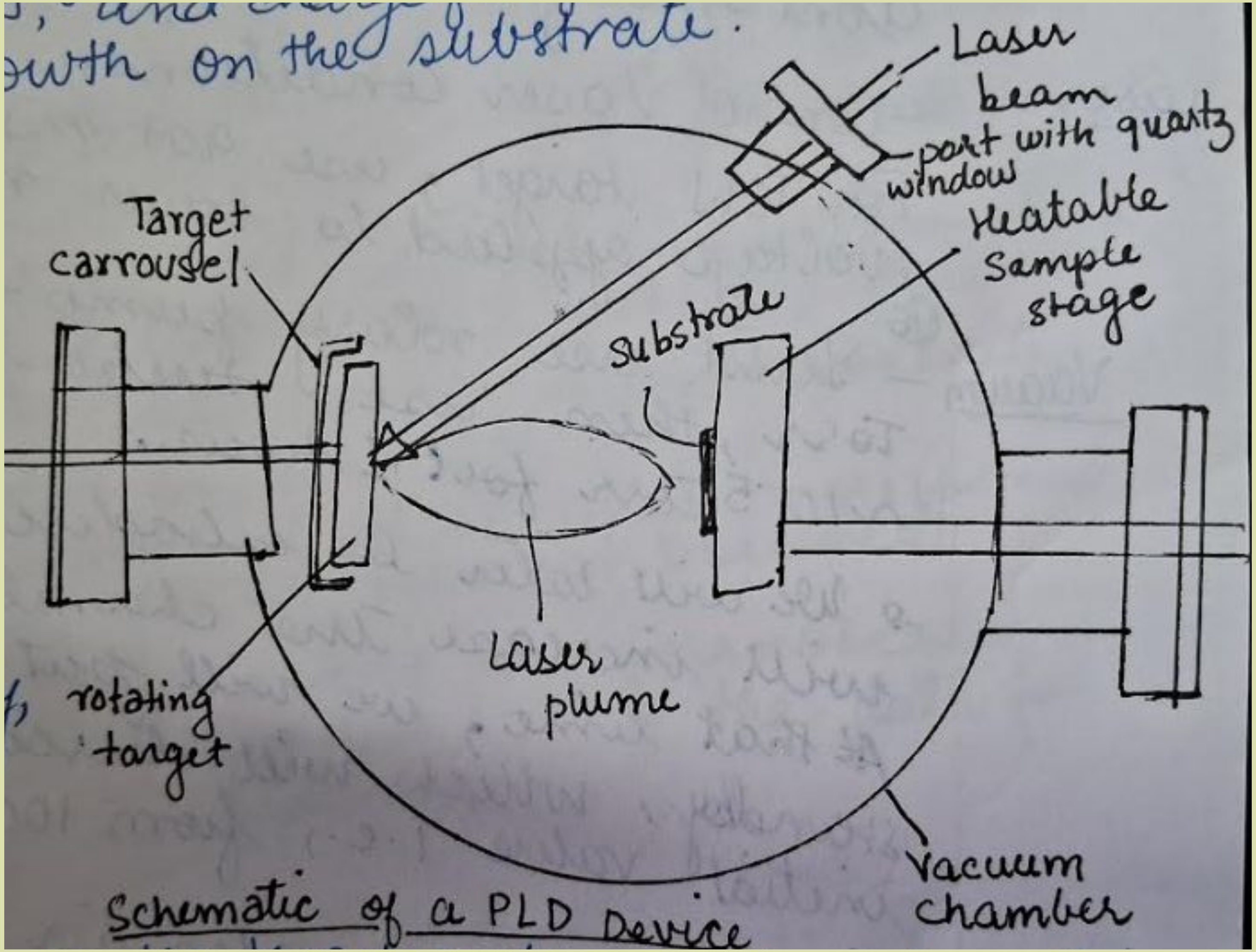


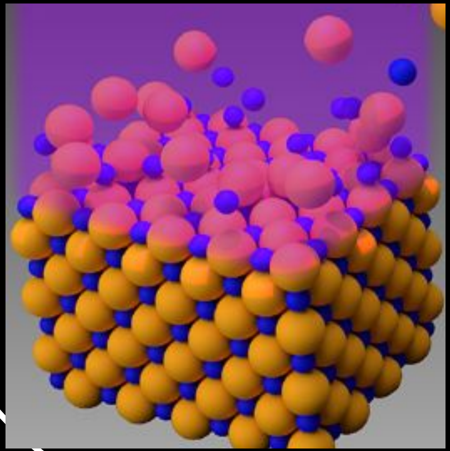
Thin films of oxides are deposited with atomic layer precision using pulsed laser deposition. In this picture, a high-intensity pulsed laser shoots a rotating white disk of Al_2O_3 (alumina).

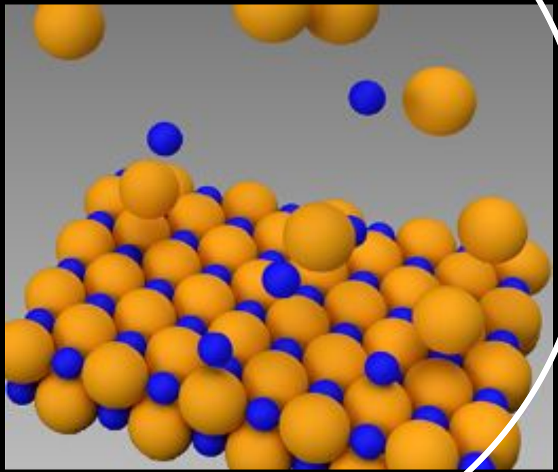
epitaxial

- Epitaxial films are defined as thin films with highly ordered atomic arrangement following their substrates, which serve as seed crystals.

Schematic Diagram







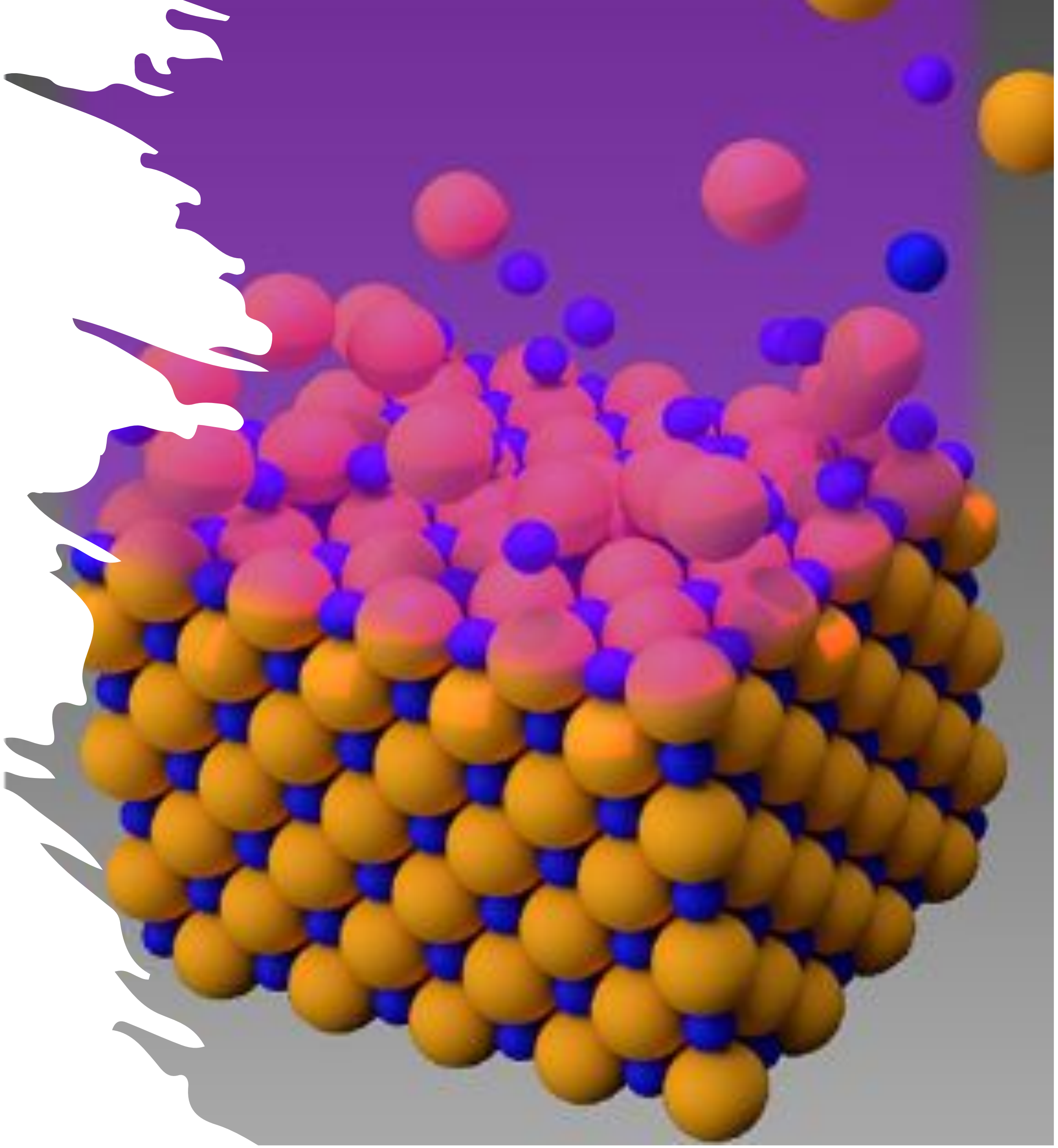
The Process and the Parameters that can be controlled

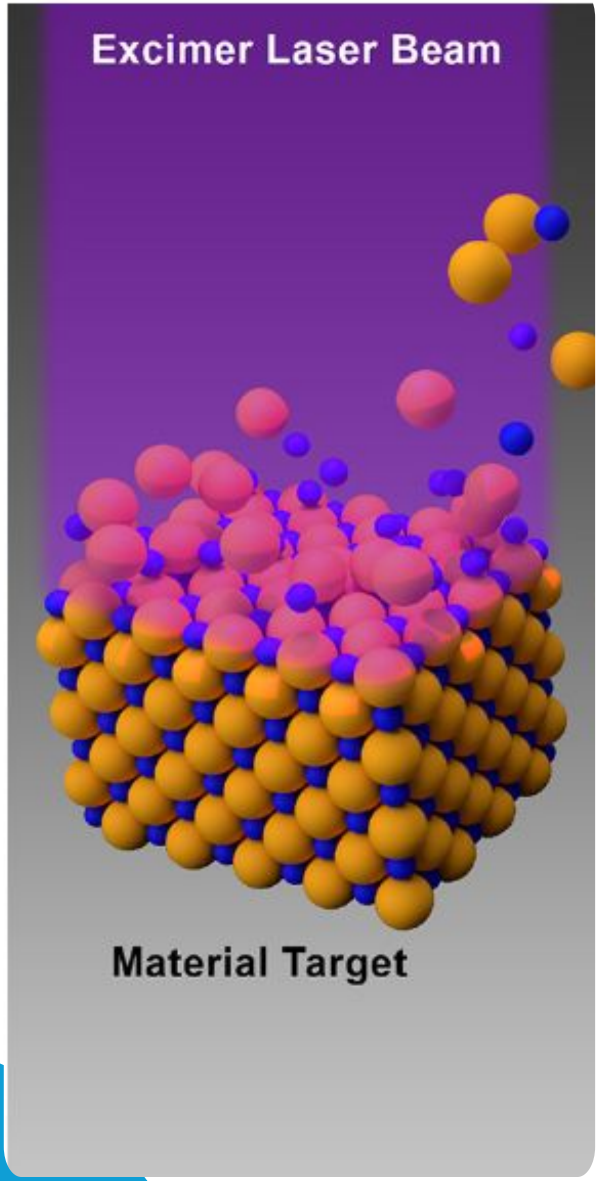
Pulsed Laser Depostion has 4 stages:

- Laser-Target Interaction
- Plasma-Plume Formation
- Deposition on the Substrate
- Nucleation and Growth

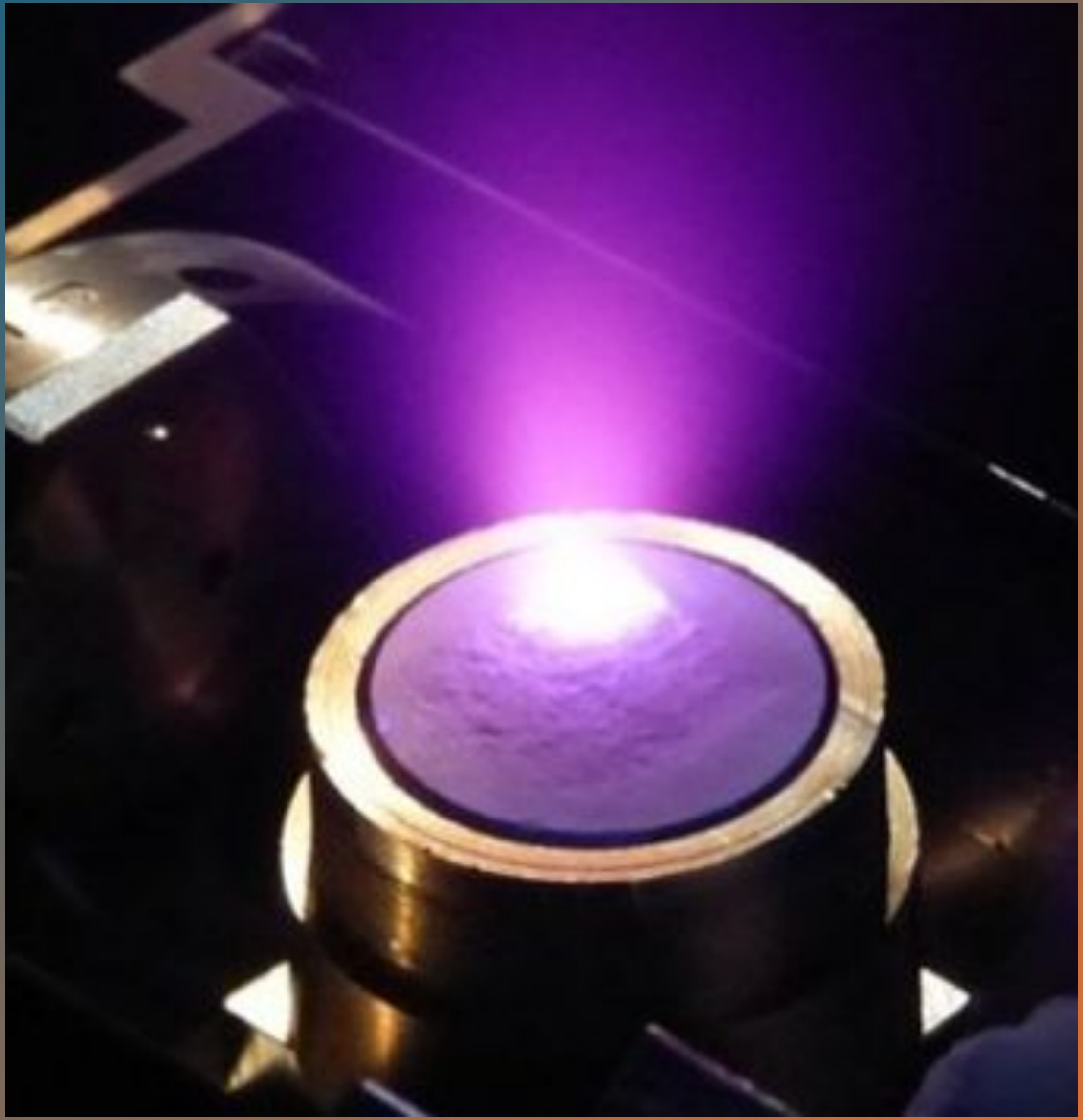
Laser ablation of the target material

- 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 and is typically in the region of 10 nm for most materials.
- The strong electrical field generated by the laser light is sufficiently strong to remove the electrons from the bulk material of the penetrated volume.





- This process occurs within 10 ps of a ns laser pulse and is caused by non-linear processes such as **multiphoton ionization which are enhanced by microscopic cracks at the surface, voids, and nodules**, which increase the electric field.
- The free electrons oscillate within the electromagnetic field of the laser light and can collide with the atoms of the bulk material thus transferring some of their energy to the lattice of the target material within the surface region. The surface of the target is then heated up and the material is vaporized.



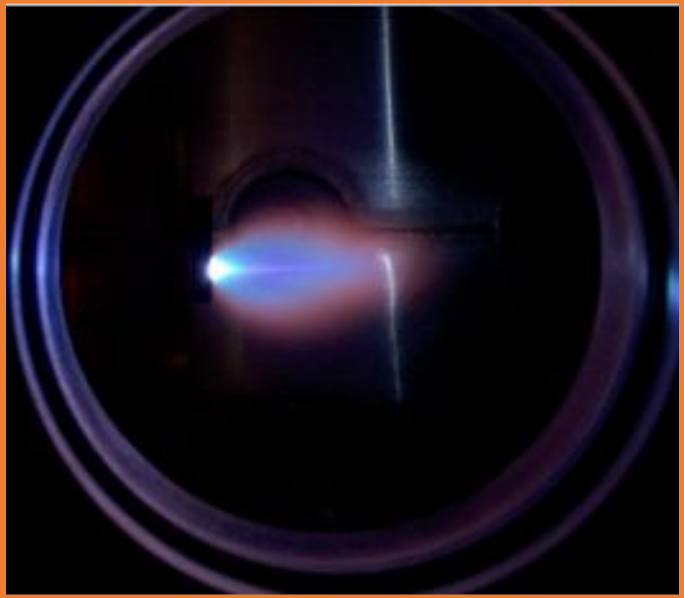
Dynamic of the plasma

- In the second stage the material expands in a plasma parallel to the normal vector of the target surface towards the substrate due to Coulomb repulsion and recoil from the target surface.
- The spatial distribution of the plume is dependent on the background pressure inside the PLD chamber.
- The density of the plume can be described by a $\cos^n(x)$ law with a shape similar to a Gaussian curve.

Effect of

1)Pressure

- The vacuum stage, where the plume is very narrow and forward directed
- The intermediate region where a splitting of the high energetic ions from the less energetic species can be observed. The time-of-flight (TOF) data can be fitted to a shock wave model; however, other models could also be possible.
- High pressure region where we find a more diffusion-like expansion of the ablated material.



vacuum

Affects:

- Plume shape
- Stoichiometry
- Specific gases for chemical reactions; example oxide deposition

Types

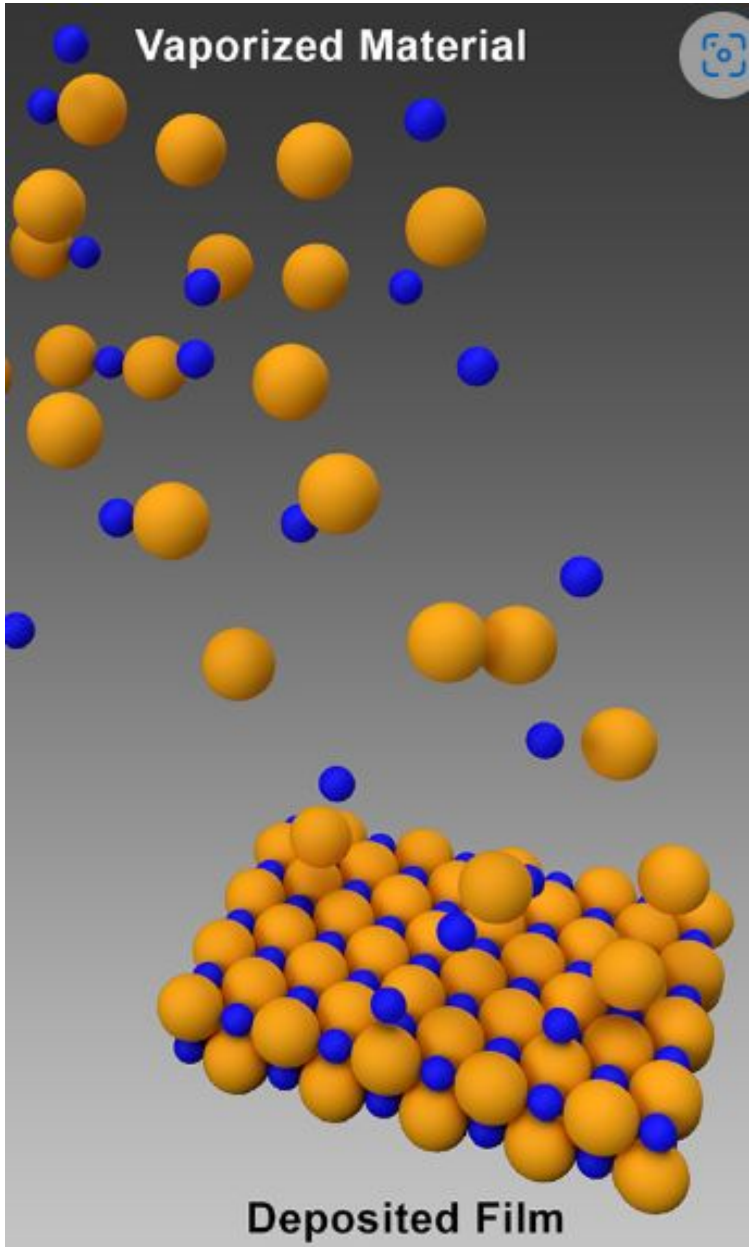
- Rough Vacuum:atm(760torr)-10^-2 (rotary pump)
- High Vacuum:10^-3 to 10^-7 torr (turbo pump)
- Ultra high vacuum

Kinetic energy

It has been shown that particles with kinetic energies around 50 eV can resputter the film already deposited on the substrate.This results in a lower deposition rate and can furthermore result in a change in the stoichiometry of the film.

Deposition of the ablation material on the substrate

- The high energetic species ablated from the target are bombarding the substrate surface and may cause damage
- collision region



Nucleation and growth of the film on the substrate surface

- The nucleation process and growth kinetics of the film depend on several growth parameters
- Epitaxial(stress/strain)

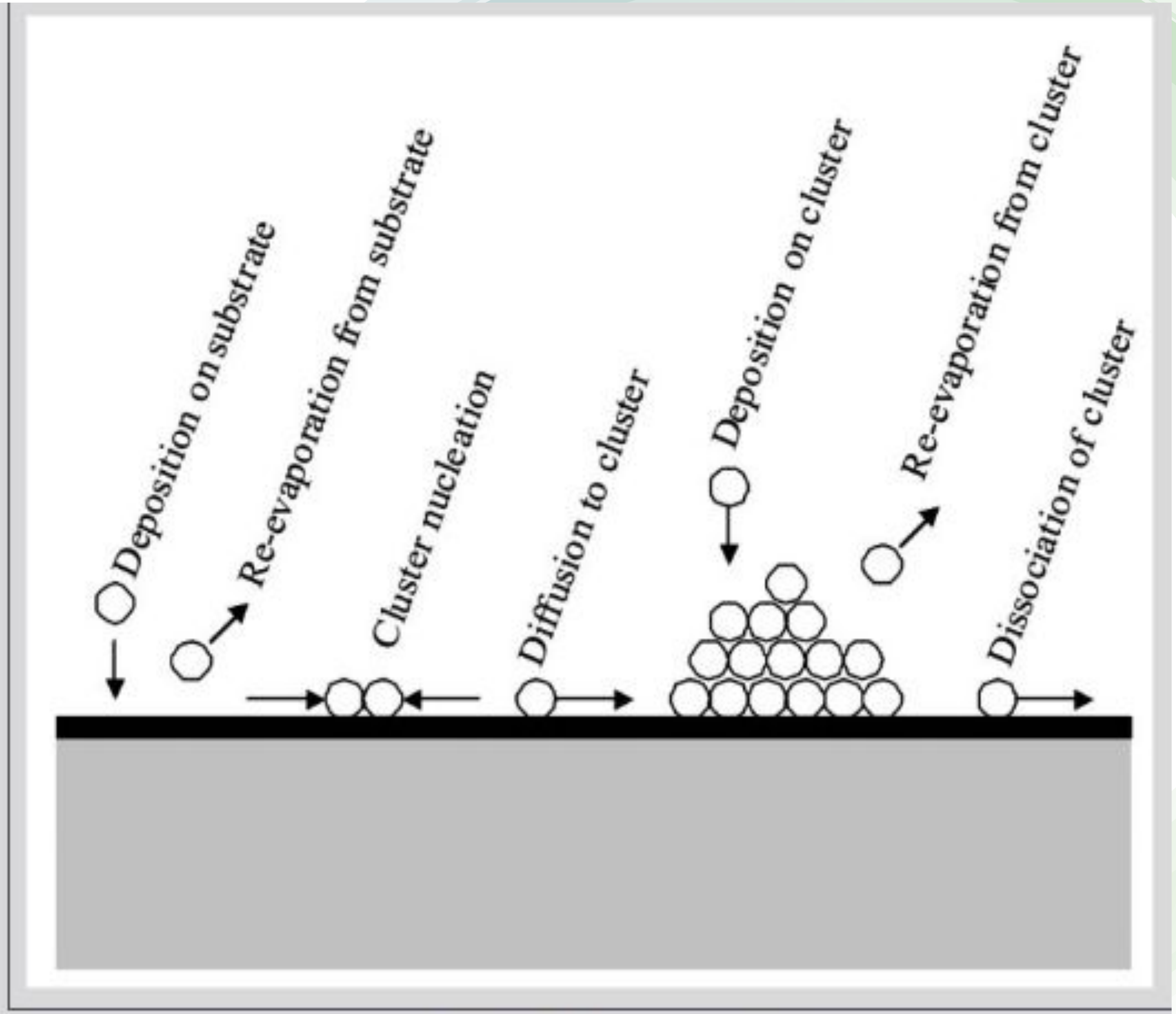
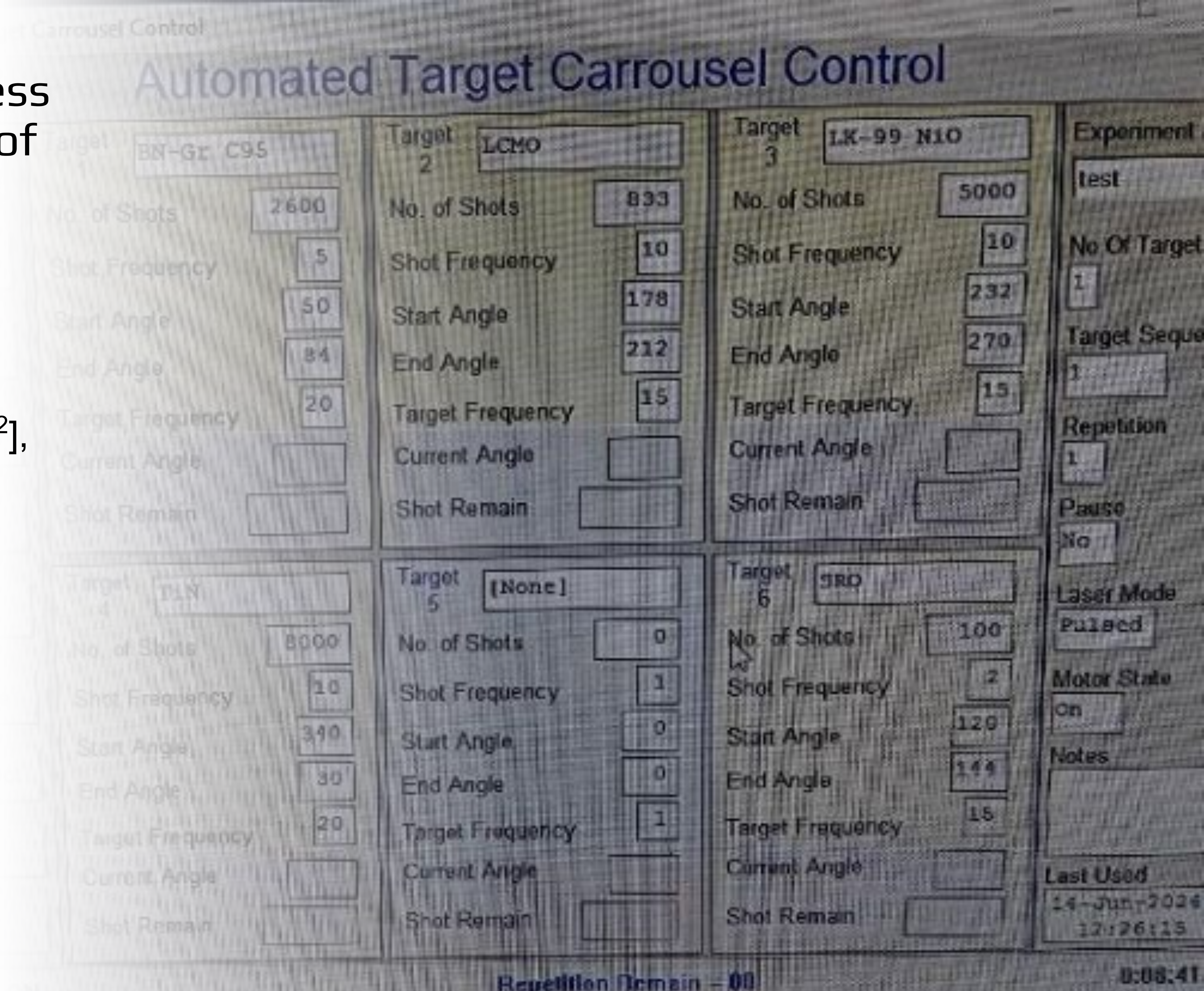


Figure 3. Thin Film Growth Steps

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

- ***Laser parameters*** –
- laser fluence [Joule/cm^2],
- laser energy,
- ionization degree of the ablated material
- , the stoichiometry,[3]
- the deposition flux.



- ***Surface temperature***
- Diffusion rate
- Chemistry
- heating plate or the use of a CO_2 laser.
- Amorphous vs crystalline structures
- the nucleation density decreases as the temperature is increased.

- ***Substrate surface* –**
- The nucleation and growth can be affected by the surface preparation (s chemical etching[6]),
- the miscut of the substrate, as well as the roughness of the substra
- CLEANING

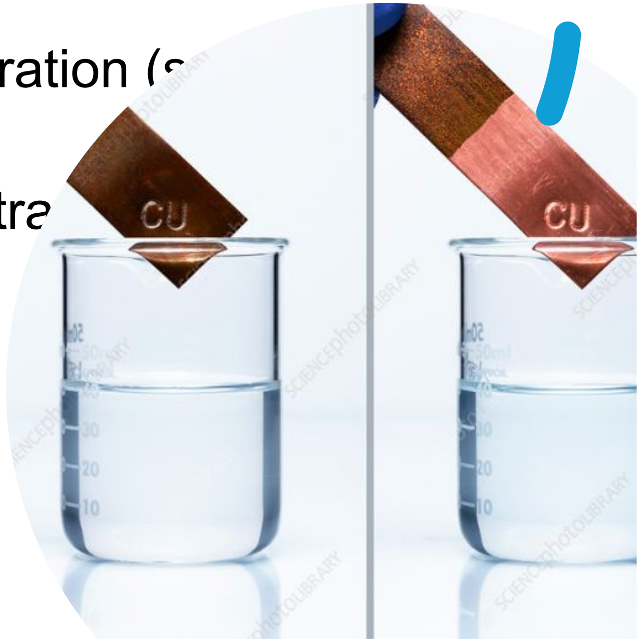
Ultrasonicator

Ethanol, acetone

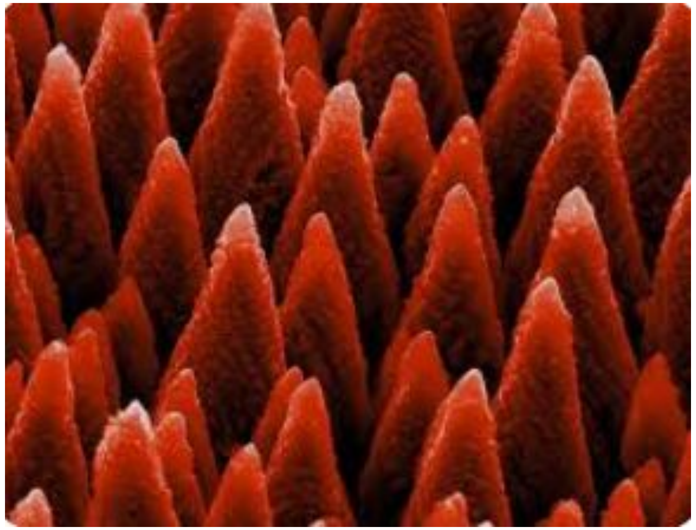
Acid Wash

Background pressure –

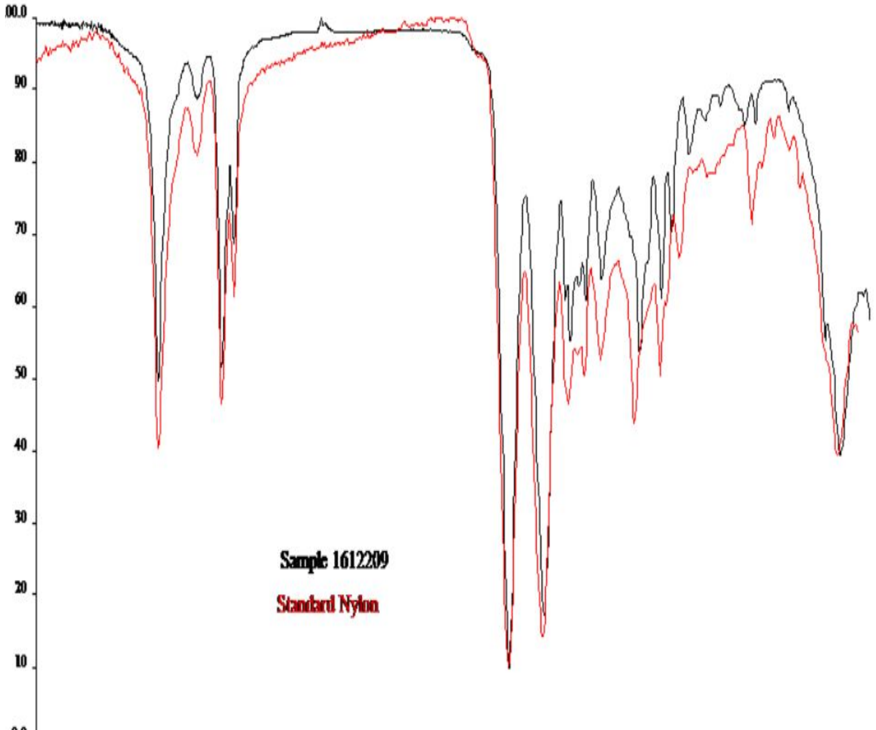
- Common in oxide deposition, an oxygen background is needed to ensure stoichiometric transfer from the target to the film. If, for example, the oxygen background is too low, the film will grow off stoichiometry which will affect the nucleation density and film quality.[7]



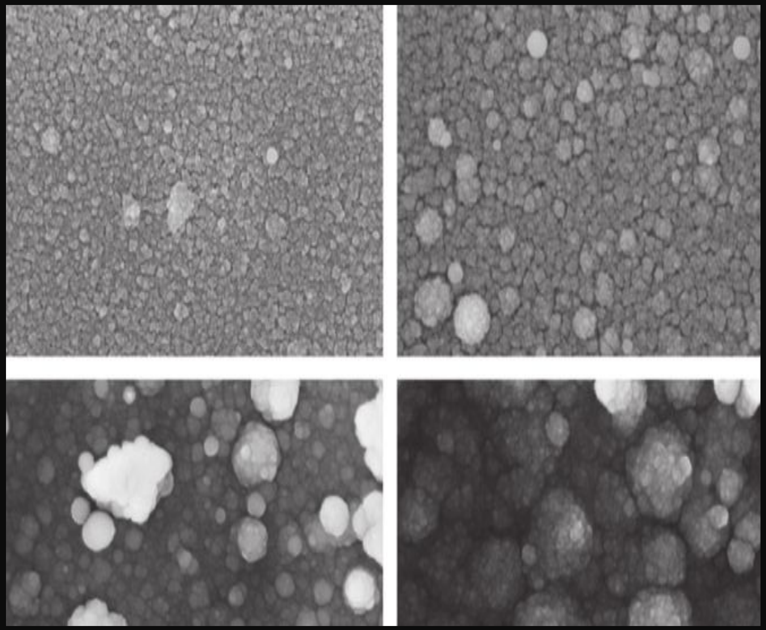
Characterization of the deposited material

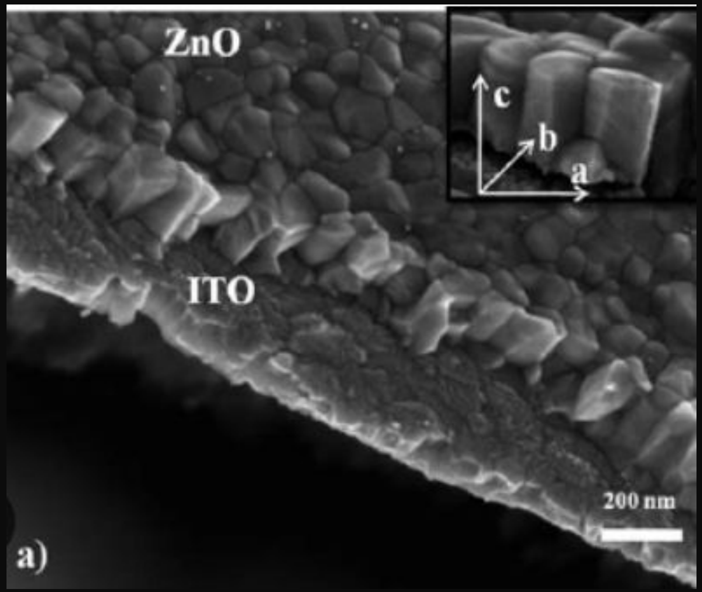


- **Atomic force microscopy** (**AFM**) or **scanning force microscopy** (**SFM**) is a very-high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit.
- **Fourier Transform Infrared Spectroscopy**, uses infrared light to scan test samples and observe chemical properties.The absorbed radiation is converted into rotational and/or vibrational energy by the sample molecules. Each molecule or chemical structure will produce a unique spectral fingerprint, making FTIR analysis a great tool for chemical identification.



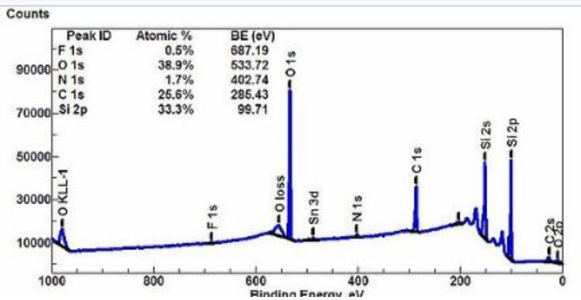
- **Scanning electron microscope** (**SEM**) Some SEMs can achieve resolutions better than 1 nanometer.
- **Transmission electron microscopy** (**TEM**) beam is transmitted through the specimen

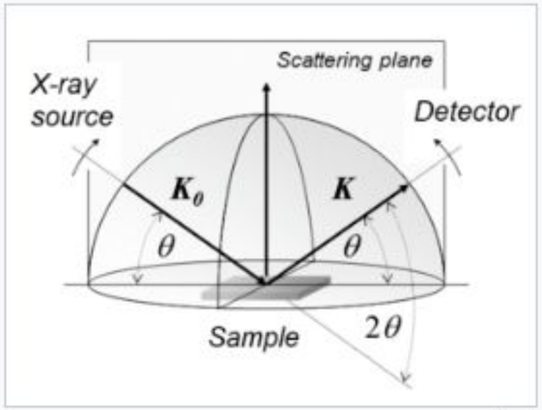




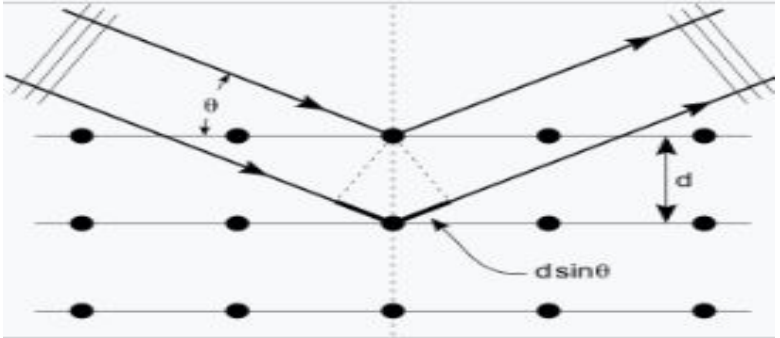
Uses?

- **X-ray photoelectron spectroscopy** (**XPS**)surface-sensitive quantitative spectroscopic technique that measures the very topmost 200 atoms, 0.01 um, 10 nm of any surface.
- X-ray diffraction
- Bragg's law,
- GIXRD
- Uv absorption spectroscopy
- Raman





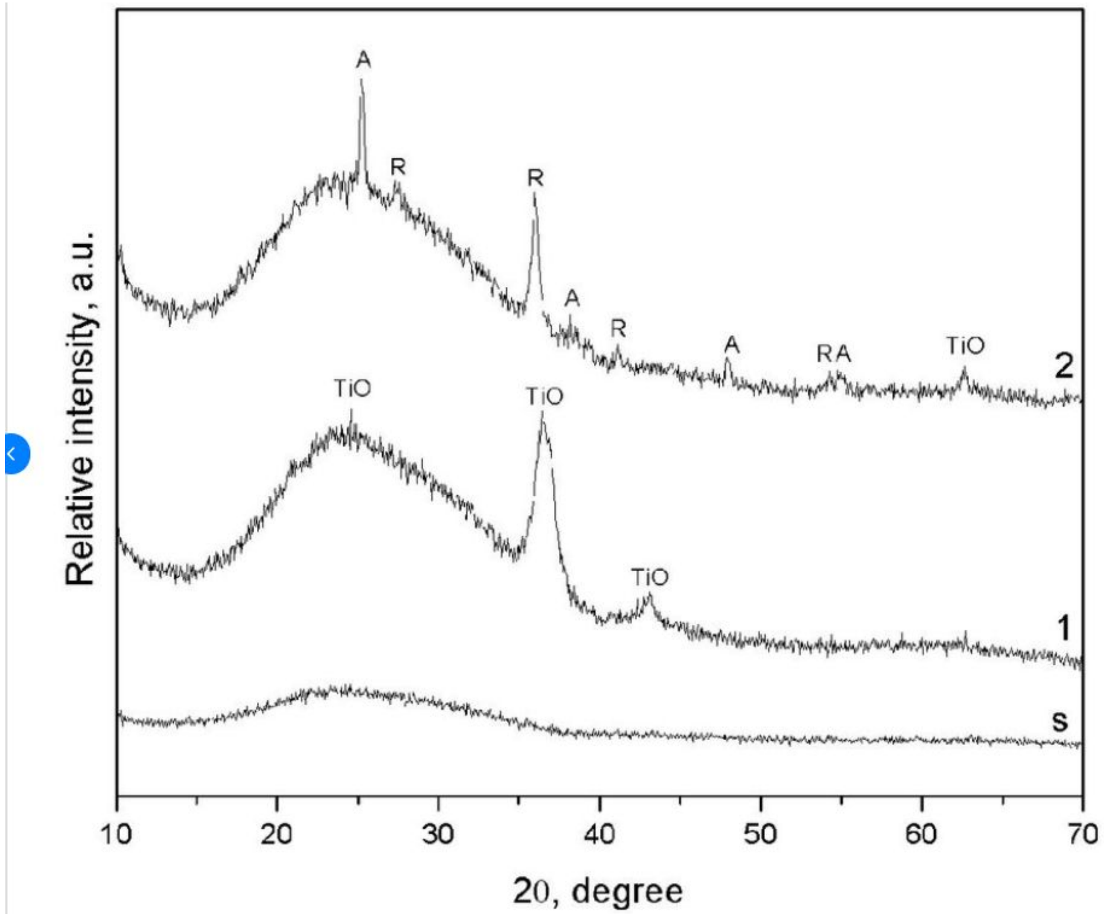
Hemisphere of Diffraction



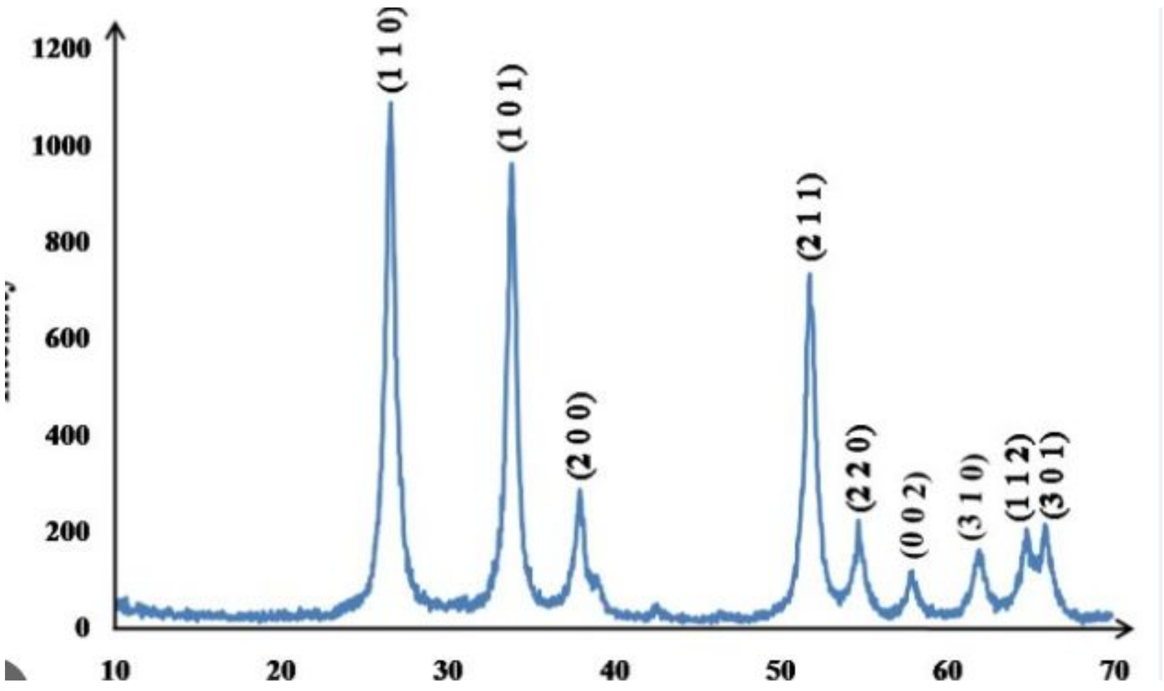
The incoming beam (coming from upper left) causes each scatterer to re-radiate a small portion of its intensity as a spherical wave. If scatterers are arranged symmetrically with a separation *d*, these spherical waves will be in sync (add constructively) only in directions where their path-length difference 2*d* sin θ equals an integer multiple of the wavelength λ. In that case, part of the incoming beam is deflected by an angle 2θ, producing a *reflection* spot in the diffraction pattern.

Ref: Wikipedia

Xrd



A
R
R
A
R
A
RA
TiO
2
TiO
TiO
TiO
1
S
Relative intensity, a.u.
10
20
30
40
50
60
70
2Θ, degree

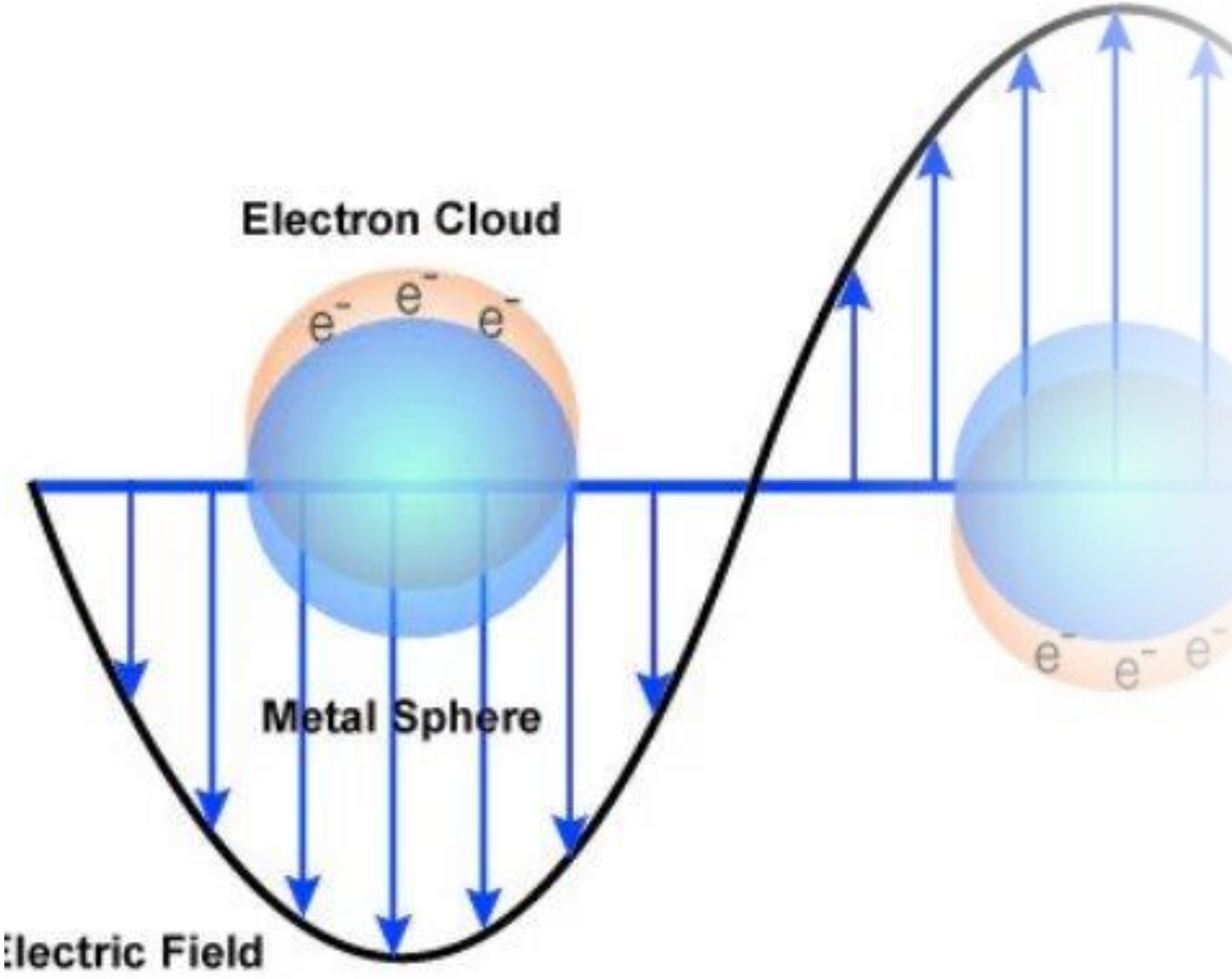


1200
1000
800
600
400
200
0
(1 1 0)
(1 0 1)
(2 0 0)
(2 1 1)
(2 2 0)
(0 0 2)
(3 1 0)
(1 1 2)
(3 0 1)
10
20
30
40
50
60
70

- Cu_2O and TiN
- Cubic lattices

• Lattice parameters	TiN	Cu_2O
a	4.25	4.24
b	4.25	4.24
c	4.25	4.24
α	90	90
β	90	90
γ	90	90

X-Ray diffractometer, G1



Applications

- Basic Science
- Plasmonic properties
- plasmonic nanoparticles exhibit interesting scattering, absorbance, and coupling properties based on their geometries and relative positions.

Ref: nanoComposix

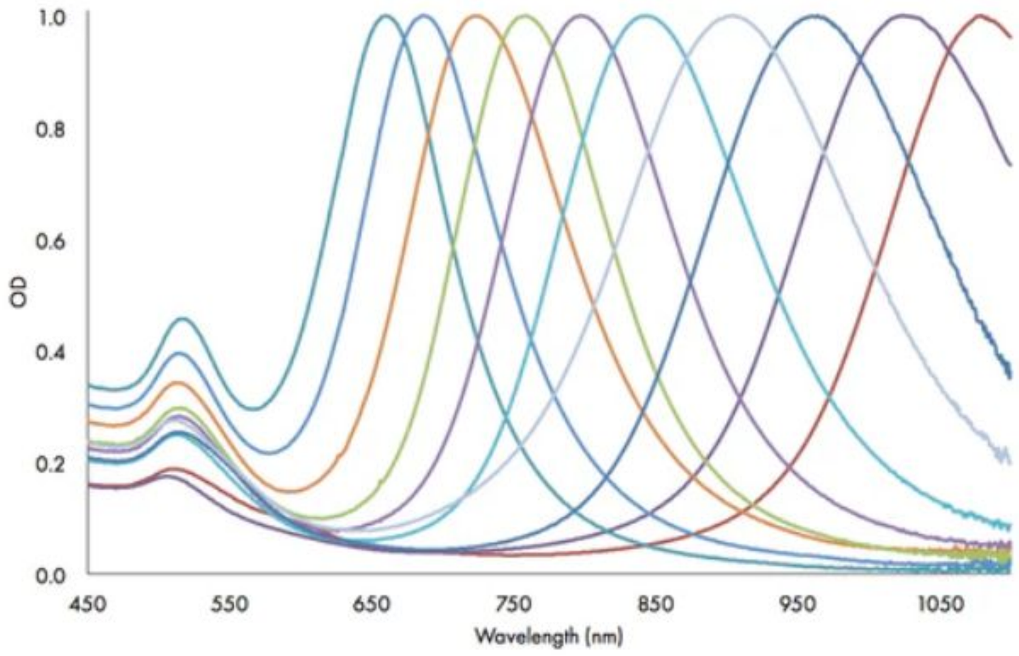
- the conduction electrons on the nanoparticle surface undergo a collective oscillation when excited by light at specific wavelengths (shown below). This oscillation, which is known as a ***surface plasmon resonance*** (SPR), results in the unusually strong scattering and absorption of light. When these resonances are excited, absorption and scattering intensities can be up to 40x higher than identically sized particles that are not plasmonic.
- For a spherical nanoparticle, the quasi-static polarizability of the nanoparticle is given by

$$\alpha = 4\pi\varepsilon_0 r^3 \frac{\varepsilon_1(\omega)-\varepsilon_2}{\varepsilon_1(\omega)+2\varepsilon_2}$$

- applications including solar cells, spectroscopy, signal enhancement for imaging, and cancer treatment.[1]
- By changing nanoparticle size, shape, and composition, the optical response can be tuned from the ultraviolet through the visible to the near-infrared regions of the electromagnetic spectrum. By shifting the absorption and scattering, the color of nanoparticle dispersions and films can also be tuned: for example, solutions of spherical gold nanoparticles are ruby red in color due to the strong scattering and absorption in the green region of the spectrum, while solutions of silver nanoparticles are yellow due to the plasmon resonance in the blue region of the spectrum (red and green light is unaffected).

1. Barnes, W. L., Dereux, A., & Ebbesen, T. W. "Surface plasmon subwavelength optics." *Nature*, *424*(6950), 824-830 (2003).

well as the dielectric function of the medium. Consequently, the nanoparticle optical properties are highly dependent on material composition, size, and the medium in which the particles are embedded. For example, increasing the aspect ratio of gold nanorods causes the plasmon resonance to shift from the visible into the NIR, as shown below.



- Catalysis: water splitting,
- Li-ion battery
- Energy, optics

PLD coated Boron nitride doped graphite used in anode – free cells

PLD: Advantages and disadvantages

Disadvantages

- Splashing or deposition of micrometer sized particulates on the film because of sub surface boiling and expulsion of liquid layer
- Narrow angular distribution of ablated species of laser
- Time consuming

Though these issues can be overcome by inserting a shadow mask to block off the large particulates, or rotating the target and substrate to produce larger uniform films such shortcomings have hindered fully utilizing PLD in the industry

Advantages:

- Retaining target stoichiometry in the the deposited film
- Ability to produce multi-layered films of different materials by sequential ablation of various targets(CeTaN3-pase vs sequential ablation)
- Controlling film thickness down to atomic monolayer by manipulating the number of pulses
- Lower substrate temperature compared to other deposition techniques

The PLD setup

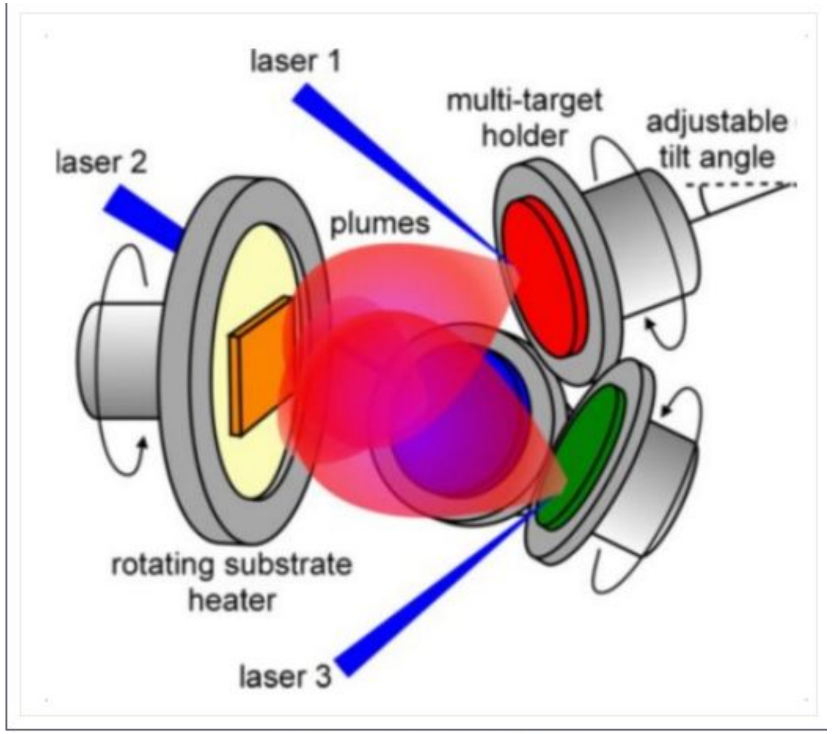


Figure 7. Multi-Beam PLD


thank you!

• References

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- NanoComposix

Disclaimer: some of the pictures and data showcasing the work done in our lab had to removed. They were discussed during the presentation.