PULSED LASER DEPOSITION OF THIN FILMS

Douglas B. Chrisey and Graham K. Hubler (1994)

Diagnostics and Characteristics of Pulsed Laser Deposition Laser Plasmas

- Success of Pulsed Laser Deposition has far outpaced understand of laser ablation process, at least in the range of laser energies used for film growth ($\sim 50 MW cm^{-2}$)

- Requires diagnostics with ~ 1nanosecond speed

- Requires in situ diagnostics to correlate gas-phase conditions with film properties

- We want to be able to measure various state variables of the plasma (Temperature, Density) as well as ionization states and behavior of the various species in the plasma

- Here we will utilize gas-phase diagnostics to attempt to characterize the formation, propagation, and properties of plasma plumes typically seen in a PLD apparatus

Diagnostics and Characteristics of Pulsed Laser Deposition Laser Plasmas

- Various diagnostic techniques are better suited for high or low density plasma plumes
- Each diagnostic may only one or two components of the plasma plume (monoatomic atoms and ions, molecules, clusters, particles, etc)
- Understanding of PLD plasma and diagnostics primarily derived from prior experimental and theoretical research in higher laser power density regimes ($> 1\ GW\, cm^{-2}$) as a result of laser fusion research (as of 1994)

Diagnostics and Characteristics of Pulsed Laser Deposition Laser Plasmas

Various major unresolved question about PLD plasma plumes (1994) include (but are not limited to)

- Role of electronic and thermal sputtering mechanisms in the ablation of material amounts necessary for film growth
- Extent and explanation of laser absorption by initial ejectants (atoms or clusters/flakes of sputtered material)
- Etching effects of laser plasma on the target
- Expansion mechanism(s) responsible for unexpected high kinetic energy of ejectants; i.e. the competition between adiabatic expansion of the plasma and space charge acceleration models

Diagnostics and Characteristics of Pulsed Laser Deposition Laser Plasmas

- Fractional ionization of the plasma plume and the extent to which it can be electromagnetically steered

- Roles of diffusion, scattering and hydrodynamics in the slowing and thermalization of the plume by background gases.
- Factors governing the optimal film growth for various materials (kinetic energy, deposition rate, etc)
- The role of chemistry with the background gas
- Would altering the target surface morphology and phase have any affect on the ejecta?

General Features of Laser Plasmas and their Characterization

Saha Equation- Describes ionization state of a plasma in local thermodynamic equilibrium (LTE)

$$\frac{(n_{i+1})n_e}{n_i} = \frac{2g_{i+1}}{\Lambda^3 g_i} e^{[\frac{\epsilon_{i+1}-\epsilon_i}{k_B T}]}$$

$$\Lambda = \sqrt{\frac{h^2}{2\pi m_e k_b T}}$$

$n_{i+1} = number\ density\ of\ the\ (i+1)\ ions\ \ (cm^{-3})$
$n_{i+1} = number\ density\ of\ the\ (i)\ ions\ \ (cm^{-3})$
$n_e = electron\ number\ density\ \ (cm^{-3})$
$g_{i+1} = degeneracy\ states\ for\ the\ (i+1)\ ions$
$gi = degeneracy\ of\ states\ for\ the\ (i)ions$
$\Lambda = Thermal\ de\ Broglie\ wavelength\ of\ the\ electrons$
$\epsilon_{i+1} = ionization\ potential\ of\ the\ (i+1)ions$
$\epsilon_i = ionization\ potential\ of\ the\ (i)ions$

$k_B = Boltzmann\ constant$
$T = Temperature\ (K)$
$m_e = \text{mass of electron}$
$h = Planck's\ constant$

General Features of Laser Plasmas and their Characterization

Simplified to

$$\frac{n_i}{n_n} = 2.4x10^{15}\frac{T^{3/2}}{n_i}e^{-U_i/kT}$$

For the ratio of singly charged ions to neutrals in a plasma, and a fractional ionization of

$$\frac{n_i}{(n_n + n_i)}$$

Example: in a plasma of 10^{14} atoms with $U_i = 7\ eV$ in an Ablation volume of

$$Av\Delta t = (0.04\ cm^2)\left(10^6\,\frac{cm}{s}\right)(50\ ns) = 0.002\ cm^3\ , n_n = 5x10^{16}\ cm^{-3}$$

The fractional ionization would be ~0.0001 for T~3000K but rises to ~0.80 at T~10000K

General Features of Laser Plasmas and their Characterization

- The heating of a gas to the these temperatures is thought to occur through the inverse-Bremsstrahlung absorption of laser light in a free-free transition of electron-ion pairs

- Basically means that photons impact and accelerate ions/electrons in plasma?

- Absorption coefficient

$$\alpha = (3.69x10^8)\frac{Z^3 n_i^2}{T^{1/2} f^3}(1 - e^{-hf/kT}) \quad (in\ cm^{-1})$$

- Significant absorption requires $n_i{\sim}10^{19}cm^{-3}$. This model also predicts better absorption at longer wavelengths.
- Example: with a KrF laser (hf=5eV), T=5000K, average charge Z=1, path length of 0.05cm, and $v\Delta t{\sim}(\frac{10^6 cm}{s})(50ns)$, a 1% absorption would require $\alpha = .2\ 1/cm$ and an average ion density of $n_i{\sim}8x10^{18}cm^{-3}$. But for 10^{15} released in a pulse of beam area $0.04\ cm^2$, this number density can only exist for distances $< 0.003\ cm$

General Features of Laser Plasmas and their Characterization

- Shows the need for dynamic modeling of combined thermal, radiative, plasma and hydrodynamic phenomena with time step sizes << 1 ns.
- Since $\alpha \propto n_i^2$, spatially non-uniform beams may introduce localized hot spots in plumes
- Photoionization and dissociation of clusters may be important absorption processes

General Features of Laser Plasmas and their Characterization

- A ~30ns PLD laser pulse in vacuum therefore produces a high pressure (~10-500 atm) bubble of hot plasma $\leq 50\mu m$ from the target.

- Expansion of this bubble modeled by fluid dynamics and hydrodynamic effects covered in Chp 3

- Expansion produces a supersonic ‘beam’ vaguely similar to a jet nozzle

- Angular distribution of the ‘beam’ is different for each species of the plasma plume

- Can lead to stoichiometry variations on the deposited film

General Features of Laser Plasmas and their Characterization

- Electrons more mobile than ions or neutrals, but cannot escape plasma
- Due to strong space-charge field generated by moving away from the ions
- Leads to space-charge acceleration model for ions in the plume
- Electric field produced by electrons at plume boundary accelerate ions according to their charge
- Time of Flight (TOF) data substantiates this model
- Multiply charged ions travel faster than singly charged ions or neutral atoms
- Fast neutral atoms can be explained by recombination of the ions with electrons and/or resonant charge exchange between fast ions and slow neutrals

General Features of Laser Plasmas and their Characterization

- Electrons in the plasma also respond quickly to internal or external potentials
- Form a “sheath” that shields the majority of the plasma from the applied field
- We can define the Debye length as a measure of this shield distance

$$\lambda_D = \left(\frac{kT_e}{4\pi n_e e^2}\right)^{1/2} = 6.9\left(\frac{T_e}{n_e}\right)^{1/2}\ \text{cm} \qquad \text{[for } T_e \text{ in K]}$$

$$740\left(\frac{kT_e}{n_e}\right)^{1/2}\ \text{cm} \qquad \text{[for kT in eV]}$$

- Even after expansion of plasma plume, shielding effect is still significant; after expanding to $n_e{\sim}10^8 cm^{-3}$ and cooling to $kT_e{\sim}0.01\ eV$, plasma will still have a $\lambda_D{\sim}25\mu m$
- Attempts to steer or strip plume with fields will only penetrate a layer of the plume ~ λ_D

$$\frac{(n_{i+1})n_e}{n_i} = \frac{2g_{i+1}}{\Lambda^3 g_i} e^{[\frac{\epsilon_{i+1}-\epsilon_i}{k_B T}]}$$

$$\frac{n_i}{n_n} = 2.4x10^{15}\frac{T^{3/2}}{n_i} e^{-U_i/kT}$$

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$$740(\frac{kT_e}{n_e})^{1/2} \text{ cm} \quad \text{[for kT in eV]}$$