PLD Sputtering Mechanisms

Pulsed Laser Deposition of Thin Films
Chrisey and Hubler, 1994
PLD Sputtering Mechanisms

- Sputtering also known as ablation or desorption
- Occurs when condensed phases (solids) are bombarded with ions, electrons or photons
- Occurs via primary and secondary mechanisms
- Primary mechanisms include collisional, thermal, electronic, exfoliational and hydrodynamic sputtering
PLD Sputtering Mechanisms

- Secondary mechanisms arise from bombardments that involving pulses of particles interact with each other.
- Lose ‘memory’ of primary mechanism and become associated with secondary mechanisms.
- Includes outflow with either reflection/recondensation or effusion with either reflection/recondensation.
- Reflection and recondensation refer to the behavior of particles reflected back towards the surface.
- Emitted particles tend to move according to laws of gas dynamics.
Thermal Sputtering

- Laser pulse bombards target to vaporize material
- Target has to be heated substantially above melting or boiling point
- Observed rate of sputtering during release time ($\tau_r$) requires sufficiently high surface temperature ($T$)
- Release time ($\tau_r$) may be shorter or longer than pulse time ($\tau$)
- $T$ cannot exceed Thermodynamic Critical Temperature ($T_{ct}$)
Thermal Sputtering

Vaporizing flux = condensing flux

\[ p(2\pi k_b T)^{-1/2} = p_0 e^{-\Delta H_v} (2\pi m k_b T)^{-1/2} \text{ atoms/m}^2\text{s} \]

- \( p \): equilibrium vapor pressure
- \( \Delta H_v \): heat of vaporization
Thermal Sputtering

Depth/pulse = $\frac{p_0}{n_c} (2\pi mk_b)^{-1/2} \int_0^\infty e^{-\Delta H_v/k_b T} T^{-1/2} dt$

$n_c$ = number density of condensed phase (target)

Depth/pulse $\sim \frac{p_{atm}(T^{-1/2})}{M^{1/2} \Delta H_v} \times 1.53 \times 10^6 \text{ nm/pulse}$

T- maximum surface temperature
M- molecular weight of vaporized species
We also assume top-hat pulse form (near uniform intensity in circular disk)
Thermal Sputtering

- Previously used expression to describe vaporization from a transiently heated target from conservation of energy (Batanov and Federov, 1973)

\[
\frac{\text{Depth}}{\text{pulse}} = \frac{I\tau}{n_c\Delta H_v}
\]

- Is actually incorrect; if \( I\tau = 2.5 \text{ J/cm}^2 \) then we would see 1 \( \mu \text{m/pulse} \) but we actually observe \( \sim 1 \text{ to } 10 \text{ nm/pulse} \)

- Due to actual loss rate being determined by kinetics, we must take into account the surface temperature \( T \)
Collisional Sputtering

- Direct beam-surface interaction
- Via momentum transfer from incident ions, electrons or photons
- Maximum Energy transfer (including relativistic effects)

\[ E_2 = \frac{2E_1^2}{m_2c^2} + \frac{4M_1M_2E_1}{(M_1+M_2)^2} \]

\[ = \frac{E_1^2}{M_2} \times 2.147 \times 10^{-9} + \frac{4M_1M_2E_1}{(M_1+M_2)^2} \text{ eV} \]
Collisional Sputtering

- Assume displacement energy threshold of 25 eV
- In this case, photons do not directly sputter atoms from lattice structure
- High enough voltage electron microscope could displace some atoms
Collisional Sputtering

- Indirect collisional effects with photons
- Plasma produced during laser-surface interaction
- Laser-plasma interaction accelerates ions in plasma (100-1000ev)
- Ions then bombard nearby surfaces
Collisional Sputtering

- Produces substrate erosion
- Particles emitted from laser bombarded target cause erosion on nearby surfaces
- Cd target bombarded by 4-10 J/cm² pulses
- Vaporize 22 nm/pulse
- Ions accelerated by laser-plasma interaction caused erosion on order of 0.02 to 0.12 nm
- Still one or two orders of magnitude smaller
Collisional Sputtering

- Cone formation - if surface undergoing bombardment is non-uniform then it will undergo cone formation due to angular dependence of sputtering
- Could also be caused by impurities, scattering off dust, etc
- Ultimately due to surface irregularities directing ions to their bases
Electronic Sputtering

- Refers to group of processes that involve excitation or ionization
- Can occur due to ion explosions, the ‘hole-pair’ mechanism, defect formation or surface plasmon interaction
- Normally confined to dielectrics and wide bandgap semiconductors except when due to plasmons
Electronic Sputtering

- Sufficiently high laser-pulse energy will cause dense electron excitation in surface
- In $\text{Al}_2\text{O}_3$, excitation can be as high as $n_e = 10^{22} \text{ cm}^{-3}$ (excited electron number density)
- Increases total Energy of each atom by $n_eE_{gap}/n_c$
- Since $E_{gap}\sim 9\text{ ev}$ and $n_c\sim 4.7x10^{22}$, the pulse increases the energy of each atom by $\sim 2\text{ eV}$
- Sufficient to increase vapor pressure by at least an order of magnitude or render lattice unbound
Electronic Sputtering

- Related to rapid energy deposition model
- Explains response of solids to incident particles such as laser pulses, fission fragments, electron pulses or small accelerated dust particles
- System makes transition from tightly bound solid to dense, repulsive gas
- Individual atoms expelled