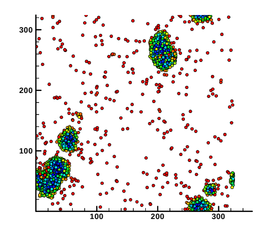

Numerical Studies of Ultra-Short Laser Interactions: Application for Nanotechnology

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Pavel R. Levashov, Konstantin V. Khishchenko

Joint Institute of High Temperatures, Moscow, Russia

Collaborations with

Laboratoire Hubert Curien, Saint-Etienne, France

Laboratoire Lasers, Plasmas et Procédés Photoniques, Marseille, France

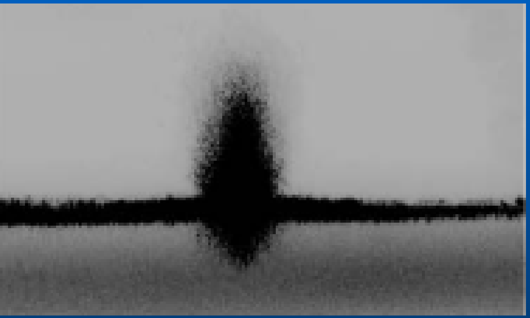
Rosnauka Kadri project, The Minister of Education and Science of the Russian Federation
Academy of Sciences - CNRS of France

Laser-Assisted Nanoparticle and Nanostructure Production

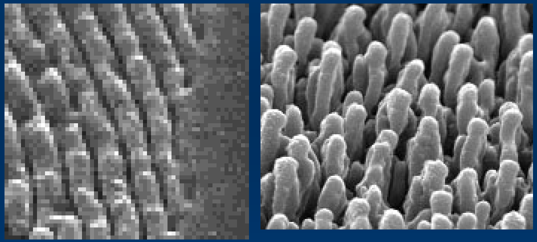
- Nanoparticles in the plume
- Deposition of nanoprticles on a substrate
- Particles can be produced on the target
- Colloidal nanoparticles
- Nanoparticles in solids (ex: sol-gel)
- Periodic and non-periodic surface structures
- Dendrides
- Nanoparticle-assisted structures (ex: nano-holes)
- Etc…

Q: Formation mechanisms ? Possibility of control ?

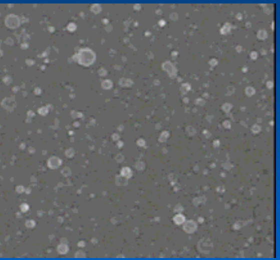
How to choose laser parameters? Ambient environment parameters ?



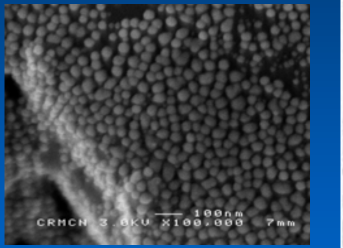
Heiroth et al. JAP 2009



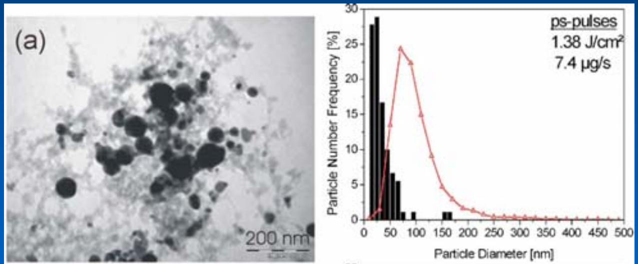
Courtesy of Torres et al., LP3



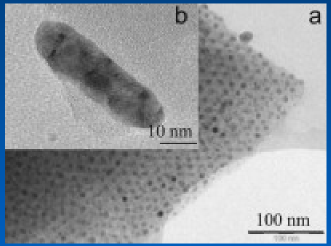
Deposited nanoparticles, Courtesy of Garrelie et al.



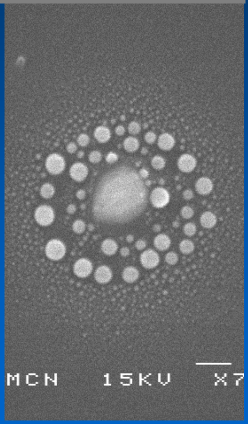
Nanoparticles produced on the target Kabashin et al.



Colloidal nanoparticles Barcikowski *et al. APL 2007*



Sol-gel nanoparticle arrays L. Bois et al. J. Sol. State Chem. 2009

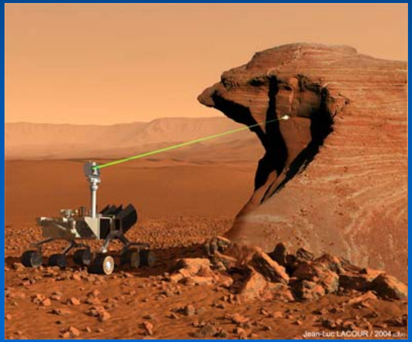


Grojo et al.

LIBS application

Industrial applications

Pharmaceutical analysis



Planetary science

Advantages	Disadvantages
•Versatile sampling of solids, gases or liquids. •Little or no sample preparation is necessary. •LIBS typically samples very small amounts of material and is non-destructive. •Permits analysis of extremely hard materials. •Possibility of simultaneous multi-elemental analysis. •Potential for direct detection in aerosols (a solid or liquid particle in a gaseous medium). •Simple and rapid analysis (ablation and excitation processes are carried out in a single step).	•Increased cost and system complexity. •Large interference effects (including matrix interference and, in the case of LIBS in aerosols, the potential interference of particle size). •Detection limits are generally not as good as established solution techniques. •Poor precision - typically 5-10%, depending on the sample homogeneity, sample matrix, and excitation properties of the laser.

Physical Processes

-absorption (Drude, interbande) for dielectrics: ionization (multi-photonic/tunnel, photo-abs, absorption on defects)

-relaxation (el-el, el-ph, STE, recombination…)

-photoemission

-structural modifications (defects, melting, densification,…)

-thermal effets (phase transitions: melting, evaporation, phase explosion)

-mechanical effects (spallation, shock waves, rarefaction, fragmentation)

-surface structuring («ripples», « spikes », «cones»)

-material ejection (formation of laser plume, nanoparticles)

$\tau <$ *relaxation time* => no e-ph ou e-i equilibrium

Laser Interactions in Vacuum

Heiroth et al. JAP 2009

- <u>**Nanosecond and longer pulses**</u>

-Evaporation

-Radiation absorption

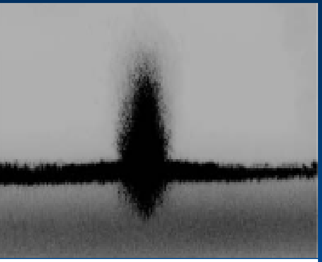
=>Plume temperature rises and mostly atoms are evaporated, then particulates are ejected et the end of the ablation process

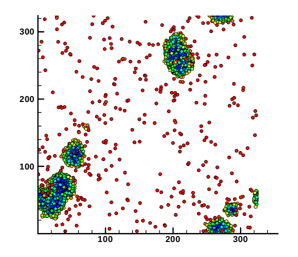
- <u>**Picosecond and shorter pulses**</u>

-Fast explosive ablation mechanisms

-No radiation absorption by the plume

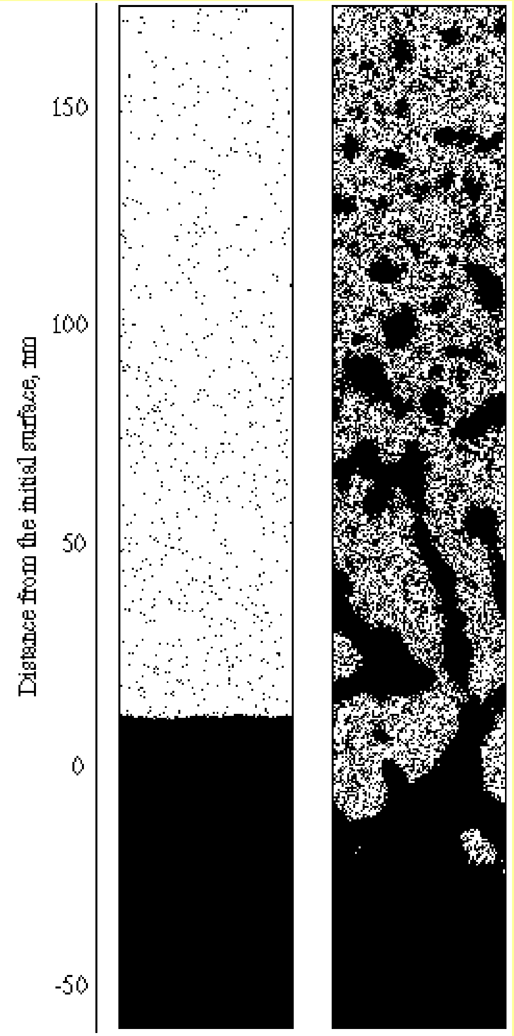
=>A mixture of monomers and clusters is ejected





Chem. Phys. Lett. , **452**,
129-132 (2008)

Molecular Dynamics Simulations



Targets: metals, molecular matrices

-Photo-thermal (phase explosion) and/or

-Photo-mechanical (spallation)

Mixture of gas and nanoparticles

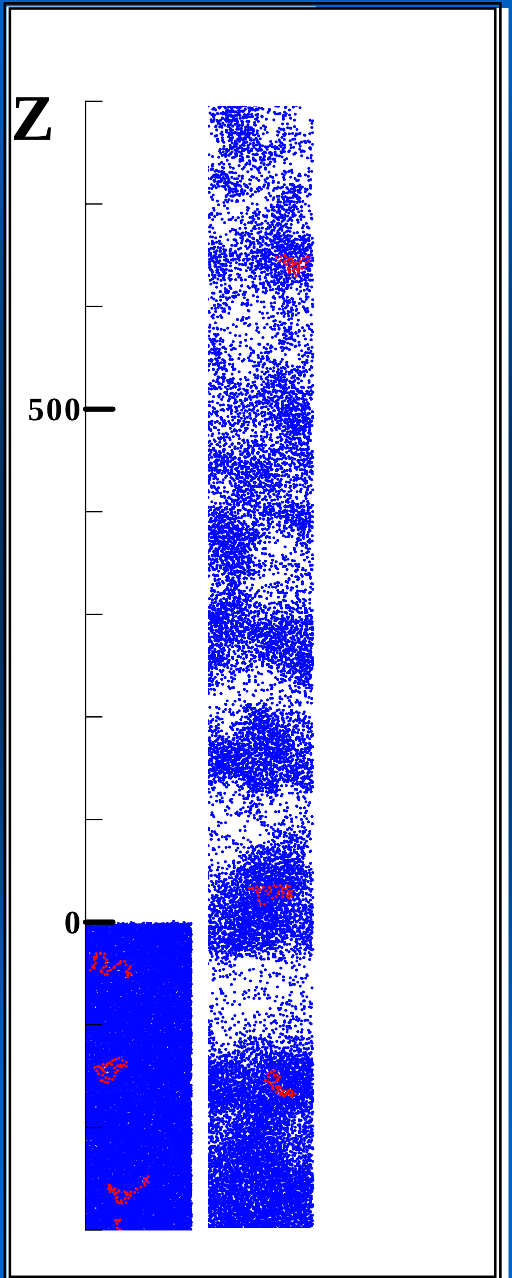
(size rises at the back side of the plume)

Non equilibrium processes

=>difficult for classical modeling

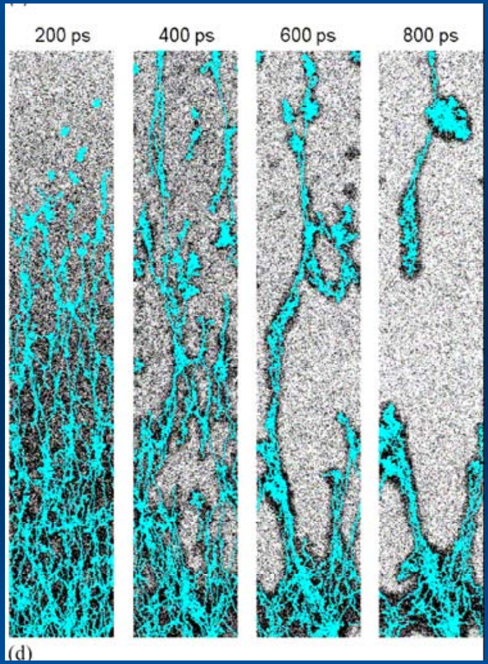
T. E. Itina, L. V. Zhigilei, B. J. Garrison, J. Phys. Chem.B , 106, 303-310 (2002)

MALDI and MAPLE Applications



Method: Molecular Dynamics

New model : « breathing spheres » - « bead-and-spring»



Demonstrated

- molecular ejection
- nanoparticles formation
- polumers are sitting in matrix clusters

For MALDI and MAPLE

Appl. Surf. Sci., 203-204, 69-71(2003)

Two-temperature multi-material Eulerian hydrodynamics

Basic equations

$$\frac{\partial f^\alpha}{\partial t} + \nabla\cdot(f^\alpha\mathbf{u}) = \frac{f^\alpha\overline{K}_S}{K_S^\alpha}\nabla\cdot\mathbf{u}$$

$$\frac{\partial(f^\alpha\rho^\alpha Z^\alpha)}{\partial t} + \nabla\cdot(f^\alpha\rho^\alpha Z^\alpha\mathbf{u}) = f^\alpha m_i^\alpha S^\alpha$$

$$\frac{\partial(f^\alpha\rho^\alpha)}{\partial t} + \nabla\cdot(f^\alpha\rho^\alpha\mathbf{u}) = 0$$

$$\frac{\partial\left(\overline{\rho}\mathbf{u}\right)}{\partial t} + \nabla\cdot(\overline{\rho}\mathbf{u}\otimes\mathbf{u}) + \nabla\overline{P} = 0$$

$$\frac{\partial}{\partial t}\left[f^\alpha\rho^\alpha\left(E_e^\alpha + \frac{|\mathbf{u}|^2}{2}\right)\right] + \nabla\cdot\left[f^\alpha\rho^\alpha\left(E_e^\alpha + \frac{|\mathbf{u}|^2}{2}\right)\mathbf{u}\right] + \frac{f^\alpha\rho^\alpha}{\overline{\rho}}\nabla\overline{P}\cdot\mathbf{u} =$$

$$-\overline{P}_e\frac{f^\alpha\overline{K}_S}{K_S^\alpha}\nabla\cdot\mathbf{u} - \boxed{f^\alpha Q_{ei}^\alpha} + \boxed{Q_L^\alpha} + \boxed{\frac{f^\alpha\rho^\alpha C_e^\alpha}{\overline{\rho}\overline{C}_e}\nabla\cdot(\overline{\kappa}_e\nabla\overline{T}_e)} + \boxed{f^\alpha Q_J^\alpha} + \boxed{f^\alpha Q_{rad}^\alpha}$$

$$\frac{\partial\left(f^\alpha\rho^\alpha E_i^\alpha\right)}{\partial t} + \nabla\cdot(f^\alpha\rho^\alpha E_i^\alpha\mathbf{u}) = -\overline{P}_i\frac{f^\alpha\overline{K}_S}{K_S^\alpha}\nabla\cdot\mathbf{u} + \boxed{f^\alpha Q_{ei}^\alpha}$$

$$\boxed{\begin{aligned} &F_i^\alpha(\rho, T_i) \Rightarrow E_i^\alpha, C_i^\alpha, P_i^\alpha, K_{iS}^\alpha \\ &F_e^\alpha(\rho, T_e) \Rightarrow E_e^\alpha, C_e^\alpha, P_e^\alpha, K_{eS}^\alpha \end{aligned}}$$

Mixture model

$$\sum_\alpha f^\alpha = 1$$

$$\overline{\rho} = \sum_\alpha f^\alpha\rho^\alpha$$

$$\overline{C}_e = \frac{1}{\overline{\rho}}\sum_\alpha(f^\alpha\rho^\alpha C_e^\alpha)$$

$$1/\overline{K}_S = \sum_\alpha(f^\alpha/K_S^\alpha)$$

$$\overline{P} = \sum_\alpha\frac{f^\alpha P^\alpha}{K_S^\alpha}\Big/\sum_\alpha\frac{f^\alpha}{K_S^\alpha}$$

$$\overline{\rho}\overline{C}_e/\overline{\kappa}_e = \sum_\alpha(f^\alpha\rho^\alpha C_e^\alpha/\kappa_e^\alpha)$$

$$\overline{T} = \sum_\alpha f^\alpha\rho^\alpha C^\alpha T^\alpha\Big/\sum_\alpha f^\alpha\rho^\alpha C^\alpha$$

Povarnitsyn et al. Phys. Rev. B , 75, 235414 (2007)

Transport properties

$$\nu = \min(\nu_{met}, \nu_{pl}, \nu_{max})$$

$$\nu_{met} = \boxed{A_1}\frac{k_B T_i}{\hbar} + \boxed{A_2}\frac{k_B T_e^2}{\hbar T_F}$$

$$\nu_{pl} = \frac{4\sqrt{2\pi} n_e Z e^4}{3\sqrt{m_e}(k_B T_e)^{3/2}}\Lambda$$

$$\nu_{max} = \frac{\sqrt{v_F^2 + k_B T_e / m_e}}{r_0}$$

$$\varepsilon = \varepsilon_{bb} + 1 - \frac{\omega_{pl}^2}{\omega_L(\omega_L + i\nu)}$$

$$\gamma_{ei} = \boxed{A_3}\frac{3 m_e n_e \nu}{m_i}$$

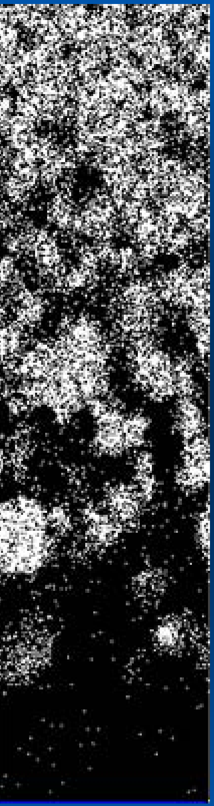
$$\chi = \boxed{A_4}\frac{k_B^2 n_e T_e}{m_e \nu}$$

Handbook of optical constants of solids, E. Palik *et al.*

	λ_L, mkm	n	k	$\varepsilon_1 = n^2 - k^2$	$\varepsilon_2 = 2nk$	R
Cu	0.83	0.260	5.26	-27.60	2.74	0.964
Cu	1.24	0.433	8.46	-71.38	7.33	0.976
Au	0.83	0.188	5.39	-29.02	2.03	0.975
Au	1.24	0.372	8.77	-76.77	6.52	0.981

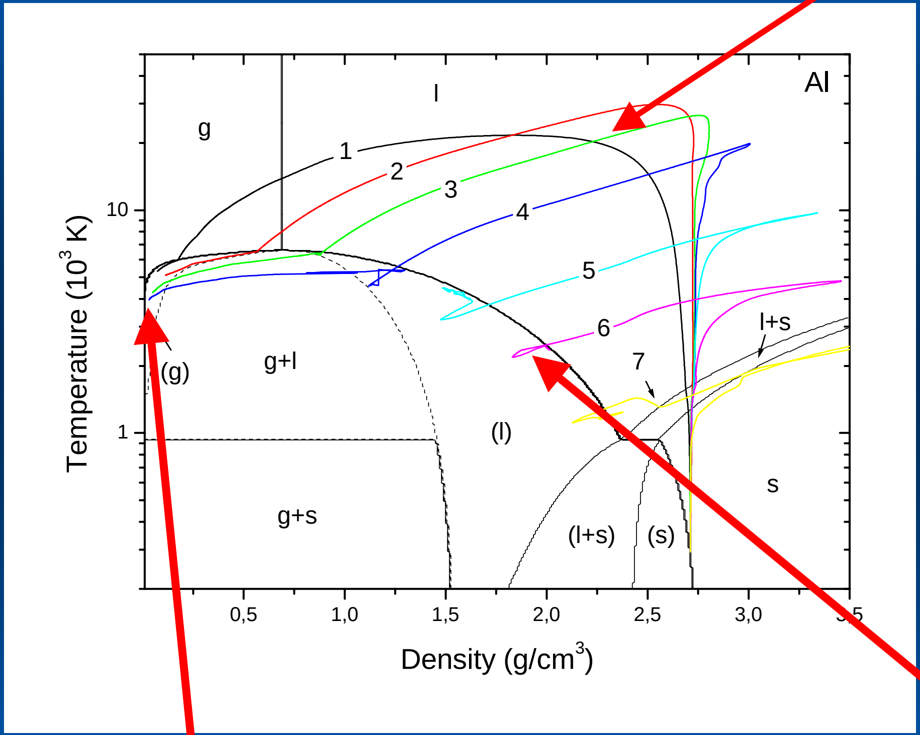
Analysis of Short-Pulse Laser Ablation

MD



L. V. Zhigilei and B. J. Garrison, *J. Appl. Phys. 88, 1281* (2000)

2T hydrodynamic model



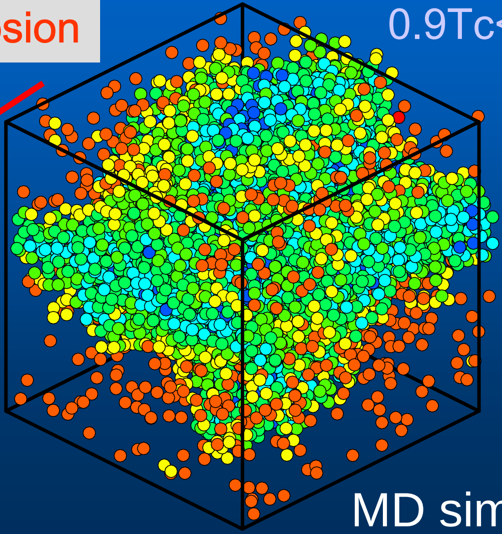
Phase explosion

Condensation

Fragmentation

M. E. Povarnitsyn et al, Phys. Rev. B , 75, 235414 (2007)

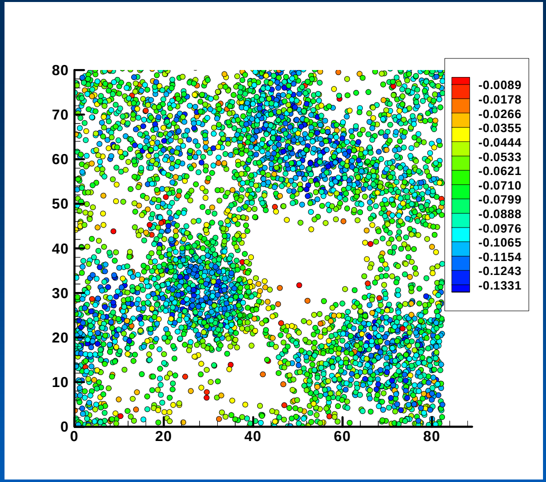
τ_L = 100 fs, λ = *800 nm,*
F = 5.0 J/cm^2



0.9Tc<T<Tc

Garrison et al, Phys. Rev. E (2003)

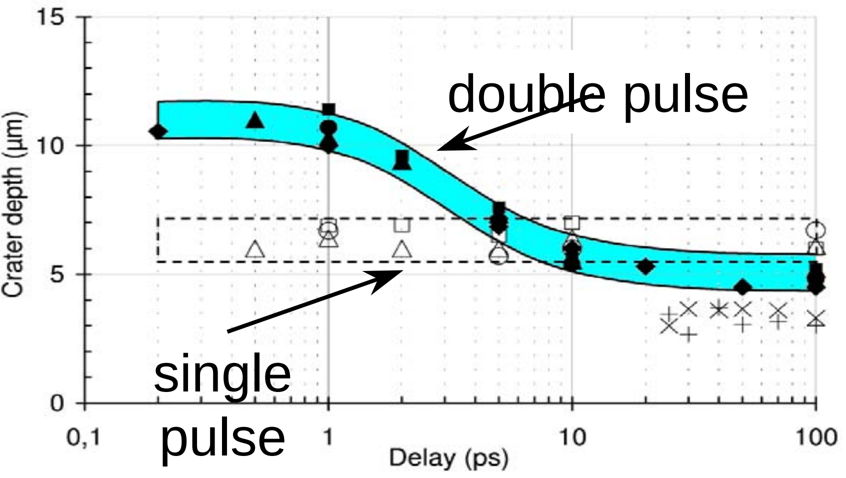
MD simulations



T. E. Itina, Chem. Phys. Lett. (2008)

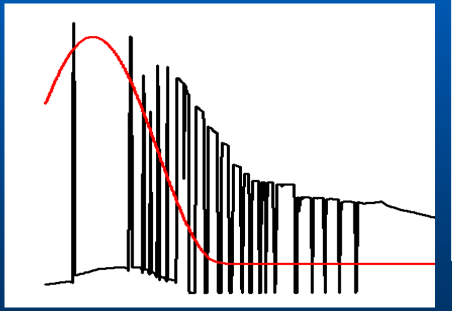
Ablation Suppression in Double Pulse Ablation

Experiment



A. Semerok et al. Thin Solid Films 453–454, 501 (2004)

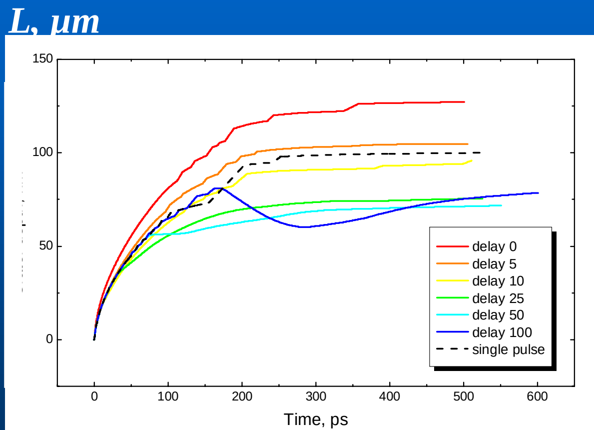
Modeling

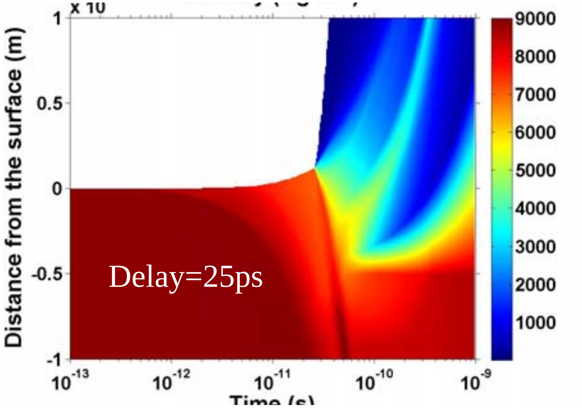


Moving material:

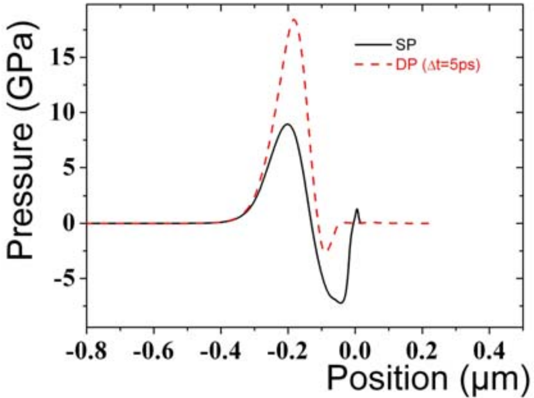
Helmholtz equation

Povarnitsyn et al. PRL 103, 195002 2009





Colombier et al.



Different cases

•<u>Very short delay</u> => Interaction with solid target, like 1 pulse with twice energy

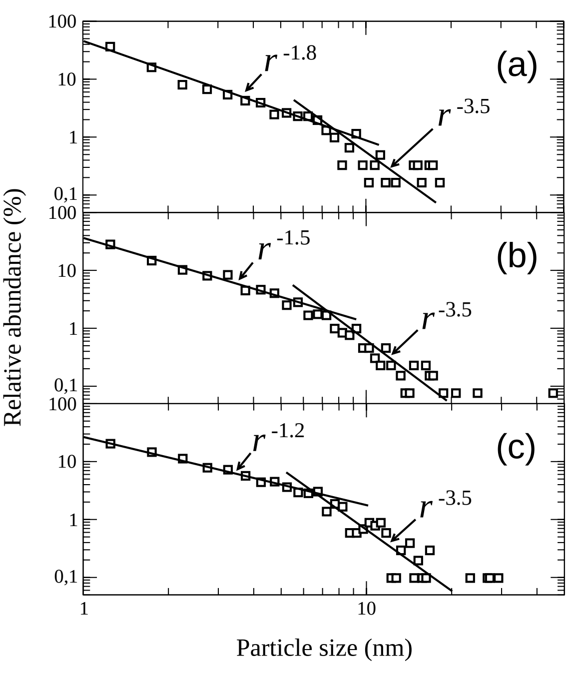
•<u>Intermediate delay</u>=> interaction with nascent ablation plume=> absorption and generation of the second shock wave that suppresses the rarefaction wave from the 1st pulse

•<u>Longer delay</u>=>back to one pulse

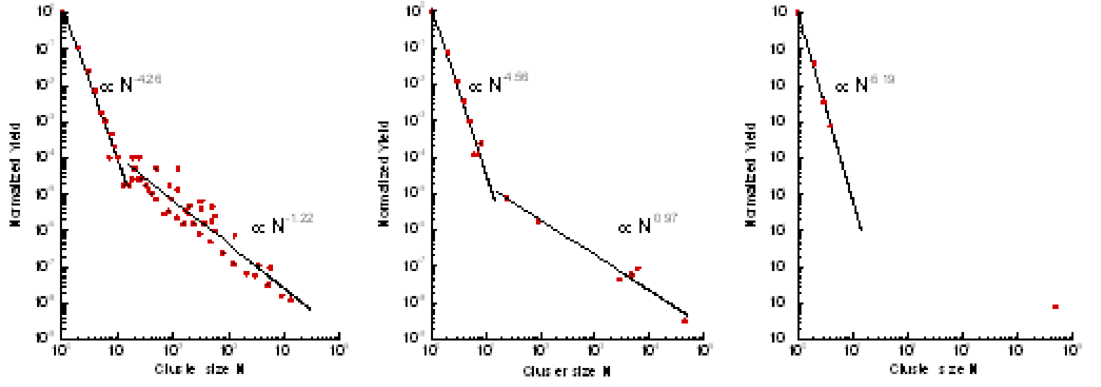
Nanoparticle Size Distribution

Expriments

100 fs F=4 J/cm2



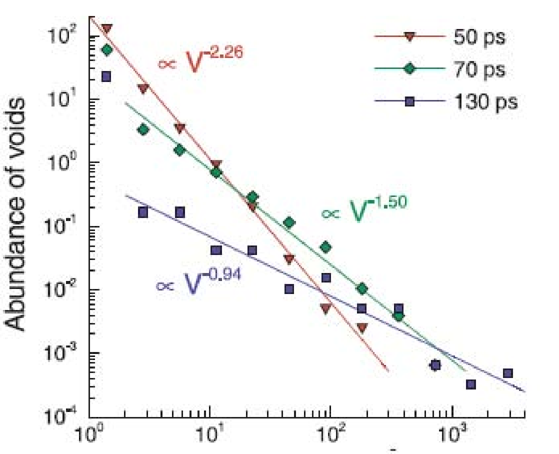
Molecular Dynamics (MD) simulations



Cluster size distribution: (t = 1 ns, τ = 15 ps), where N is the number of monomers. (a) - fluence F = 6 mJ/cm^2, (b)- F = 4 mJ/cm^2; (c) - F = 3 mJ/cm^2

Courtesy of Zhigilei et al.

Void size distribution

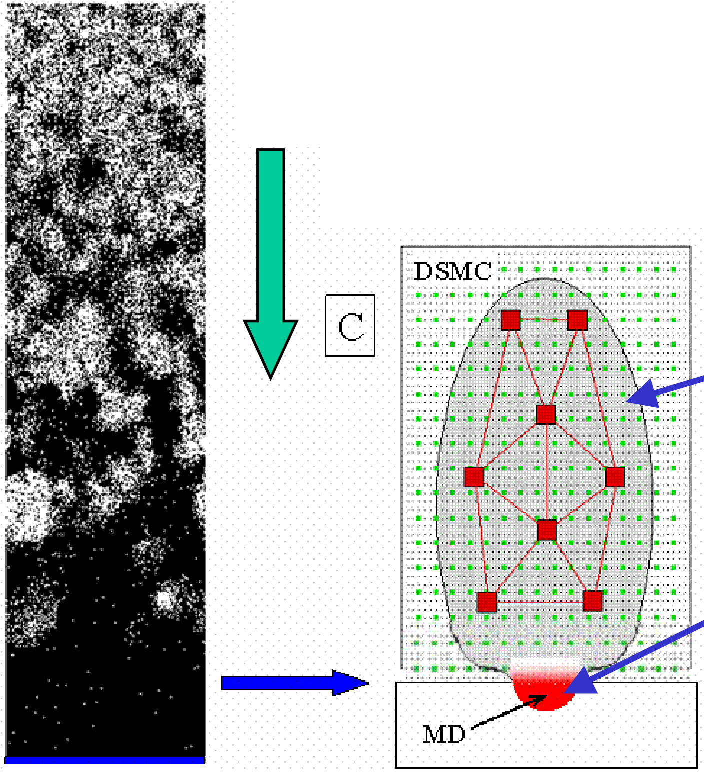


Ablation of molecular solids in vacuum

- Evaporation
- Longer scale time evolution?

Leveugle et al. Appl. Phys. A 79, 1643–1655 (2004)

Nanoparticle formation mechanisms



collaboration with

University of Virginia, USA

Coupling:

- Direct Simulation Monte Carlo
- Molecular Dynamics

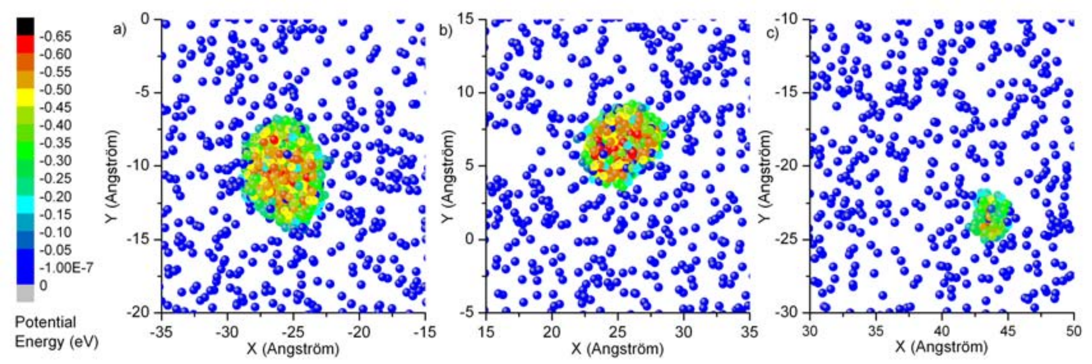
More detailed Information

- *Cluster composition*
- *Size distribution*

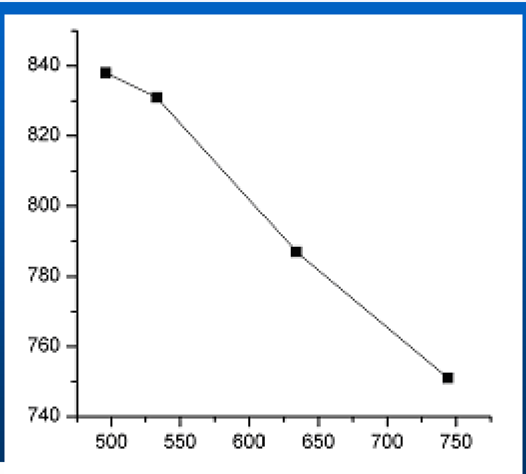
K. Gouriet, PhD (2005-2008)

Cluster Evolution

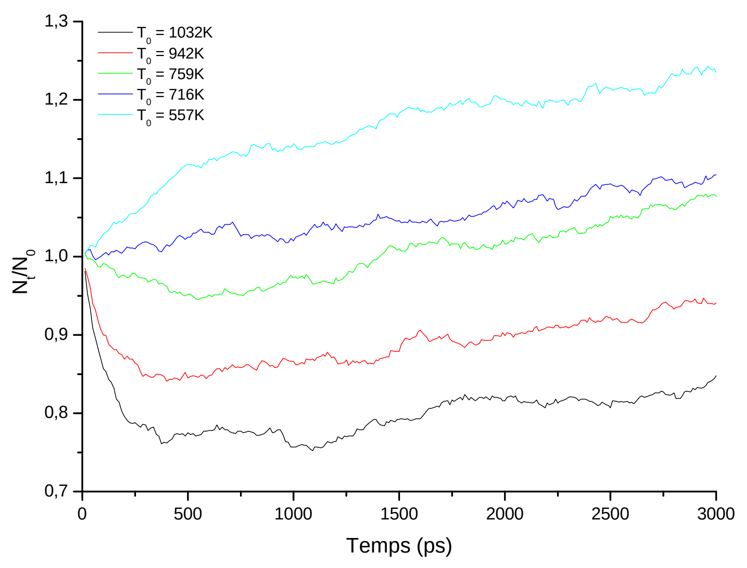
MD

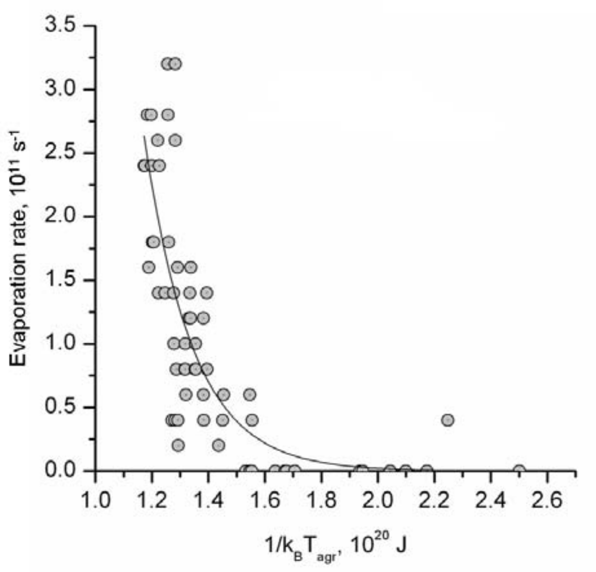


size



Tgas, K





- **Clusters (T, R)**
- **Gas/plume (T, density)**

RRK theory

$$\nu_e^{\mathrm{RRK}} = \nu_0 g_n \left[\frac{E_n - D_n}{E_n}\right]^{s_n-1}$$

Hotter particles tend to evaporate

Colder clusters tend to grow

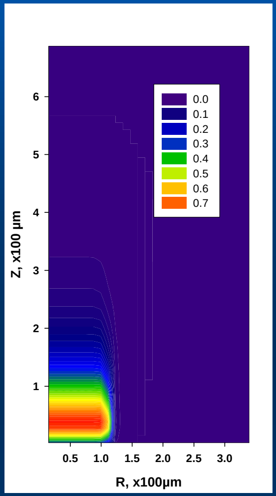
=> Evaporation of small clusters

K. Gouriet, M. Sentis, T. E. Itina, *J. Phys. Chem. C* , 113(43), 18462-18467 (2009)

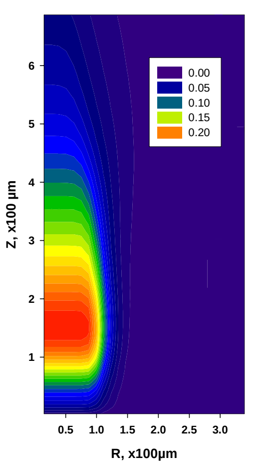
(metals and molecular solids)

Plume expansion

Hydro 1D + Hydro 2D



24 ns



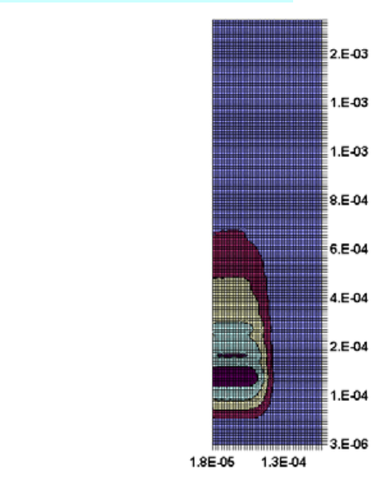
44 ns

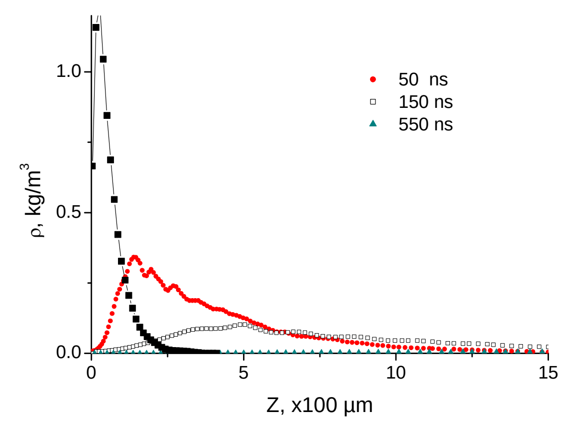
Calculated plume density pour λ = 800 nm

Laser pulse duration 100 fs, laser fluence Is 5 J /cm2, le , laser spot is 100 µm.

Rarefaction wave → plume shape

Hydro 1D +SDMC



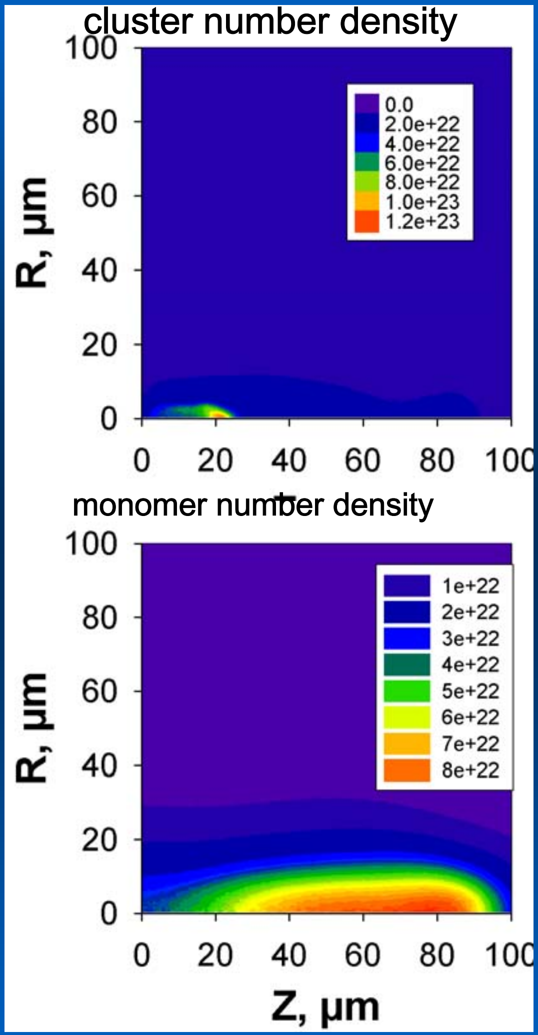


Aluminum target (a) –2D density distribution ; (b) density as a function of distance for different delayes

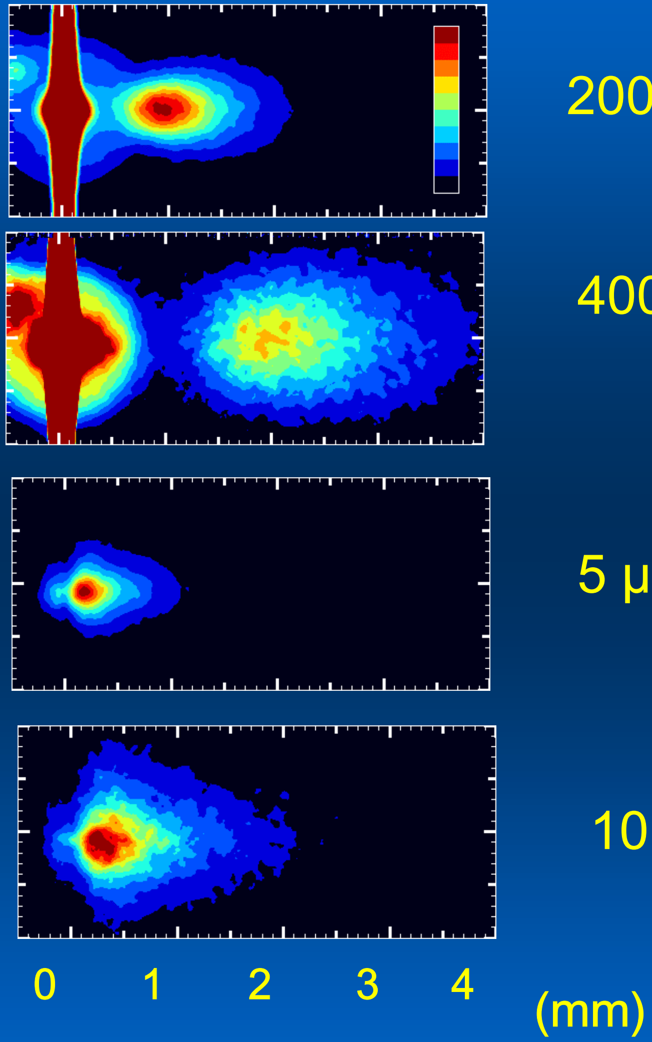
MD-DSMC

Laser

F_{las} = 4 Jcm^{-2}



Calculation results



Experimental results (J. Hermann, S.Noël)

t= 50 ns, 15 ps, F=61 J/m2, R=10 µm

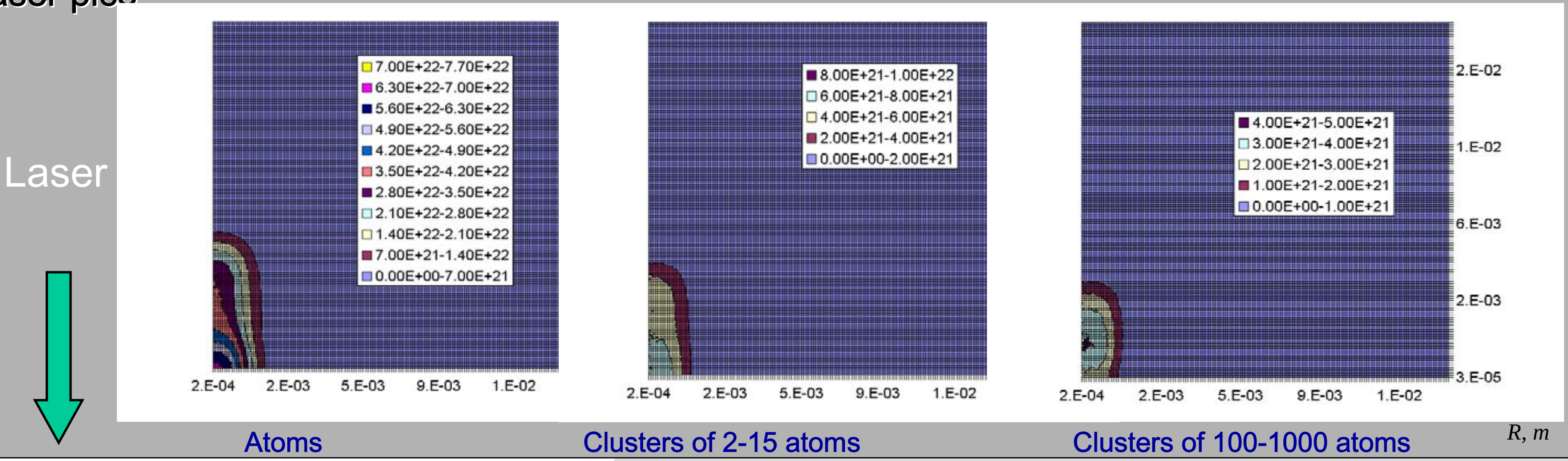
100 fs F=4 J/cm2

Appl. Surf. Sci. , 253, 7656-7661 (2007)

Courtesy of Hermann et al.

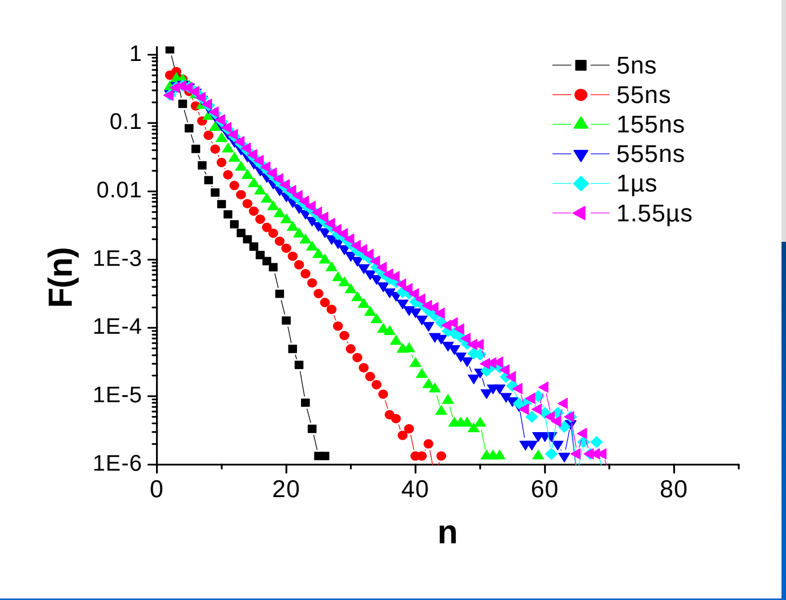
Plume Expansion in Vacuum: Monte Carlo Simulation

- Laser pico
- C



Atoms | Clusters of 2-15 atoms | Clusters of 100-1000 atoms

R, m

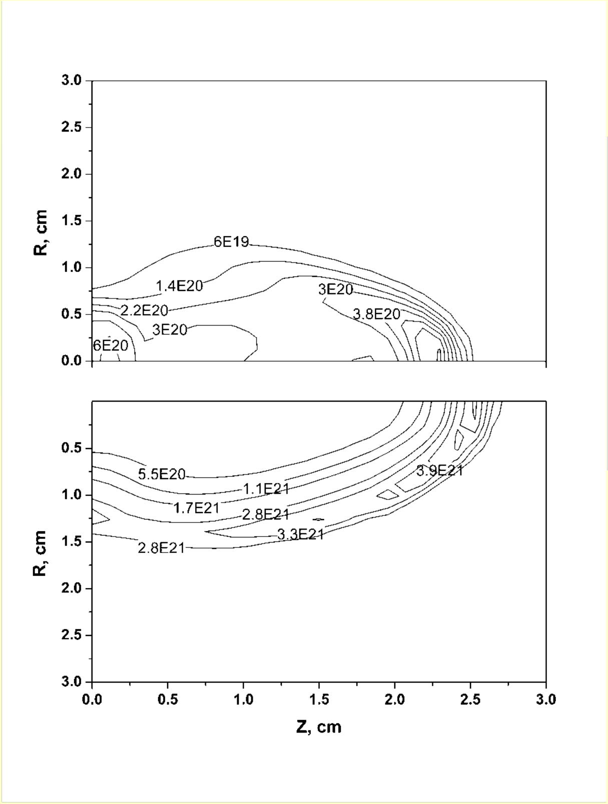


Delay t =1.55 µs
(a) – atoms (b) –small clusters (2 –10 atoms)
(c) –larger clusters (>10 atoms)
12 ps, 8.6 J/cm^2

- Here, growth is observed, but only until 1 µs (vacuum => expansion=> collisionless plume)

If plume is initially dense and not too hot
=> growth can be observed, but negligible

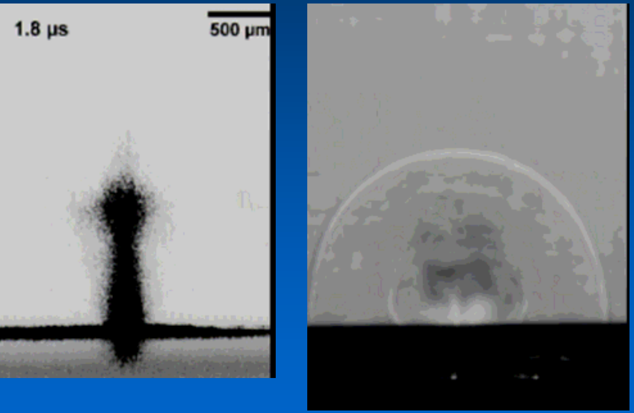
Laser Interactions in the Presence of a Gas



Plume confinement=> nucleation

Short pulses => mixture of atoms and clusters initially

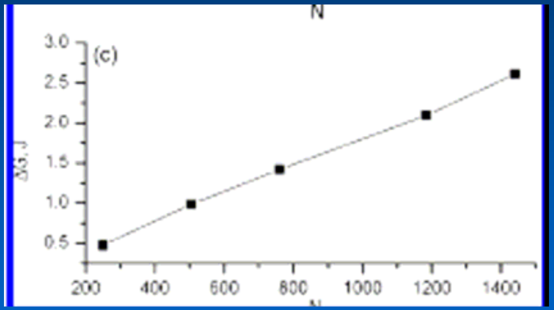
+Additional collisions with the gas => condensation/evaporation, coalescence/aggregation/fragmentation



Heiroth et al. JAP 2009

Confinement in a gas

$$R = \xi_0 \left(\frac{E_0}{\rho_0} \right)^{1/5} t^q$$



Sedov, Zel’dovich & Raizer

Nucleation

Size distribution is controlled by free energy

$$\Delta G(n,c) = -nkT\ln(c/c_0) + 4\pi a^2 n^{2/3}\sigma$$

Supersaturation ratio

$$S = c/c_0$$

The peak of the nucleation barrier corresponds to the critical cluster size
-decreases with T
-decreases with S

$$n_c = \left[\frac{8\pi a^2\sigma}{3kT\ln(c/c_0)}\right]^3$$

Rate of production of supercritical clusters
-rises with S
-rises with T

$$\rho(t) = K_c c^2 \exp\left[\frac{-\Delta G(n_c,c)}{kT}\right]$$

Cluster time-evolution=> master equation

$$\frac{dn_s}{dt} = \frac{1}{2}\sum_{i+j=s}[K(i,j)n_i n_j - F(i,j)n_s] - \sum_{j=1}^{\infty}[K(s,j)n_s n_j - F(s,j)n_{s+j}].$$

where Ks is attachment rate constant
F is fragmentation rate

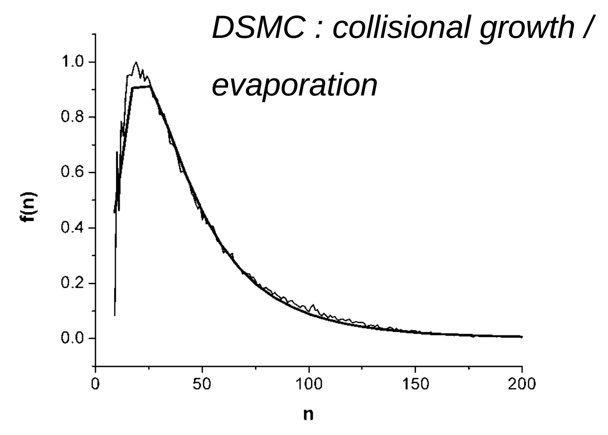
$$\frac{dN}{dt} = K_{S-1}N_1 N_{S-1} - K_S N_1 N_S \quad (s \geq 3)$$

Sintes et al. PRA 1992

J. Park, V. Privman, E. Matijevic,
J. Chem. Phys. B 105, 11603-11635 (2001)

Nucleation+Growth or Condensation ?

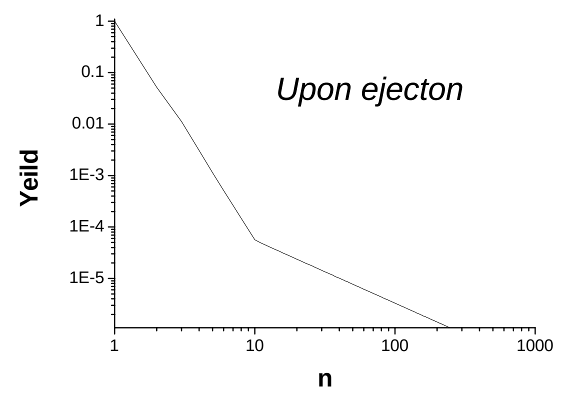
Nucleation+Growth

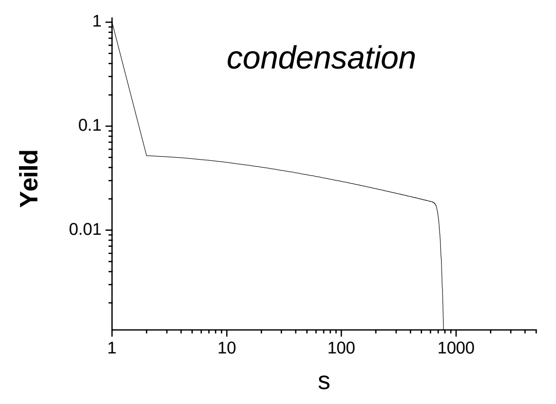


- **Typical for nanosecond ablation in a gas**
- **Log-normal distribution**

Gold ablation in water

Growth without nucleation



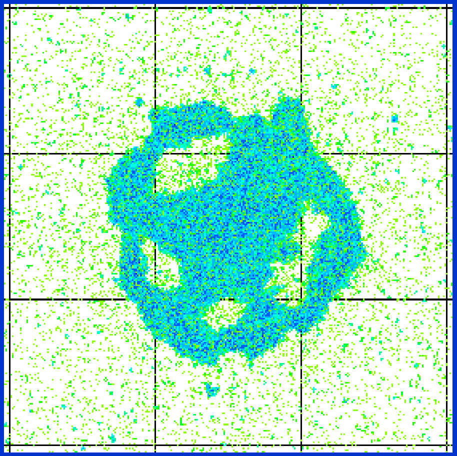


- **Typical for femtosecond and picosecond ablation in vacuum (cluster precursors are ejected)**
- **No log-normal distribution**

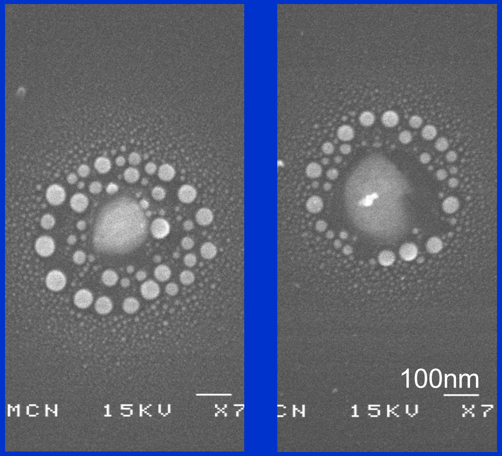
Gold in a gas

Laser – Particle Interactions

=>structure on the surface



MD model



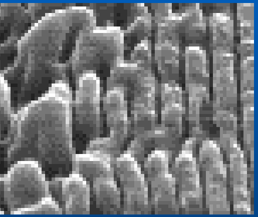
Experiments (D. Grojo, Ph. Delaporte)

Gold nanoparticle on Si surface, 400 ps
after laser irradiation

(simulation, laser picoseconde)

MEB

Periodic Structure Formation

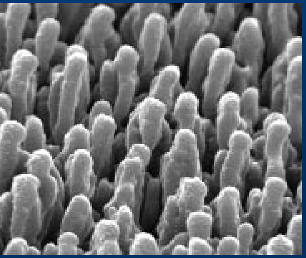


•Periodic (resonant) surface structures (« ripples »)

-Interference

-Surface plasmons - under certain conditions ? $\Re(\varepsilon) < 0$

-Surface quality (diffraction)



•Non-periodic (non-resonant) structures

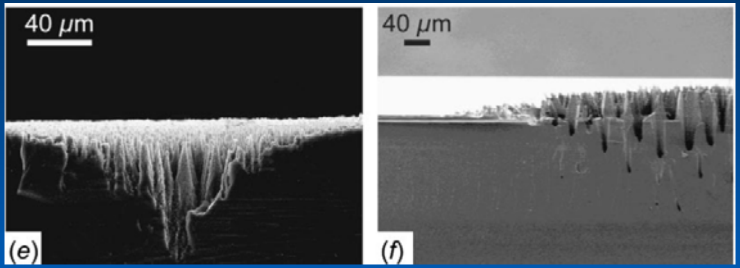
-melting

-instabilities

-defects, chemical reactions, etc

Ex: « black silicon » production for sollar cells (E. Mazur et al., Th. Sarnet et al.)

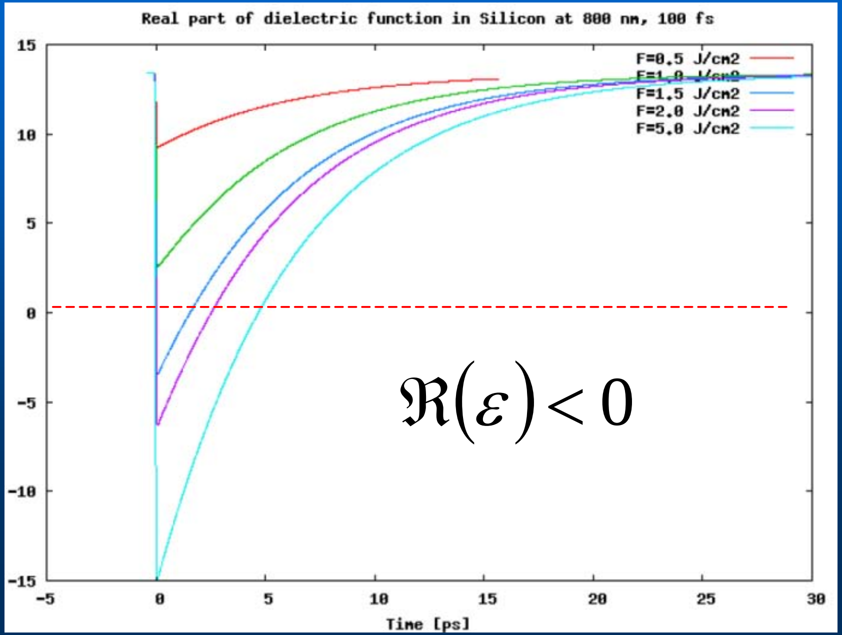
- ◆ **Femto => in depth**
- ◆ **Nano => on the surface**



CH Crouch, APL 84, 11 (2004)

Femtosecond Nanosecond

Periodic Surface Structures (Ripples) on Si

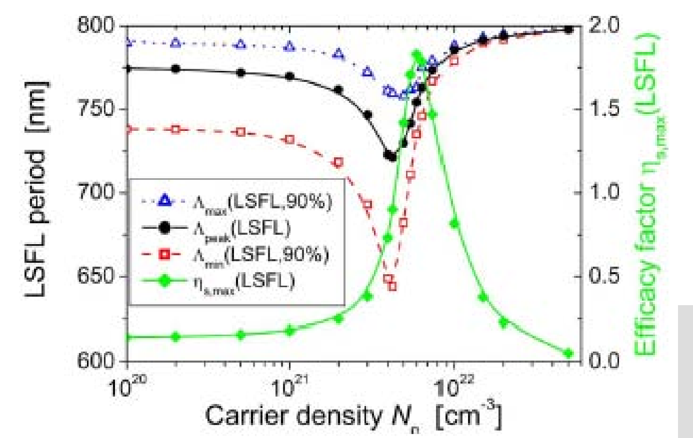


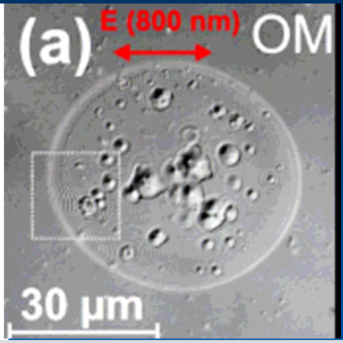
$\Re(\varepsilon) < 0$

- surface EM wave (plasmons) ?

$$\varepsilon^*(n_e) \cong 1 + (\varepsilon_g - 1)\left(1 - \frac{n_e}{n_0}\right) - \frac{n_e}{n_{cr}} \frac{1}{1 + i\frac{1}{\omega\tau}}$$

Derrien et al.





A minimum in the period of ~720 nm is observed around the critical carrier density

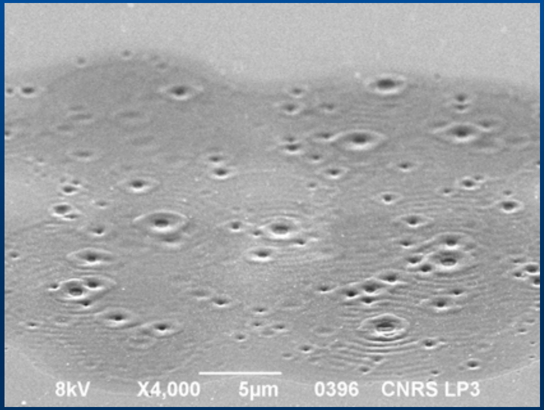
Bonse et al JAP 106, 2009

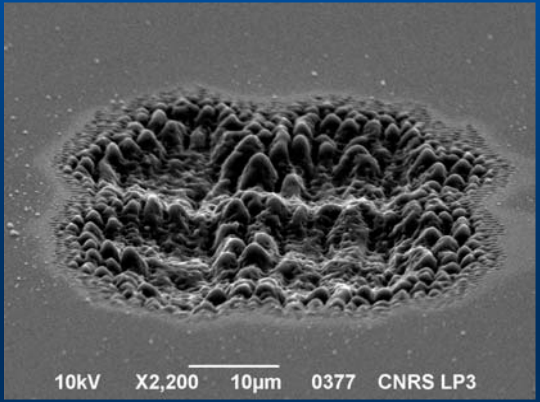
Structure Formation: Number of Pulses

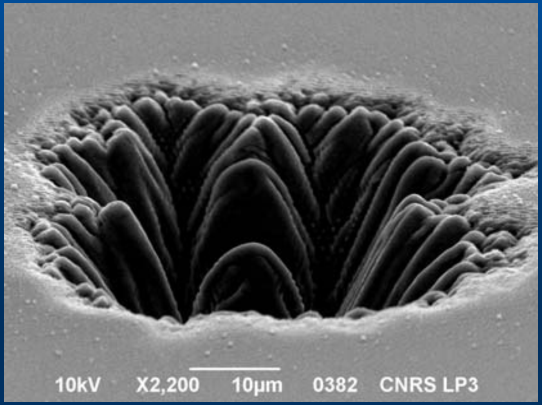
F=900 mJ/cm², τ=100 fs, λ=800 nm

Si

For different number of shots, N







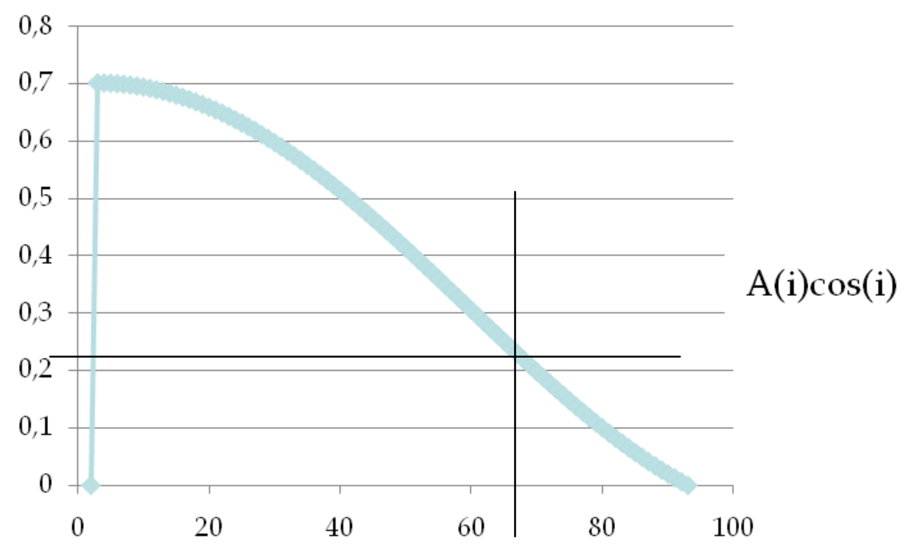
Stochastic N=2 N=5 N=1000 Large structures

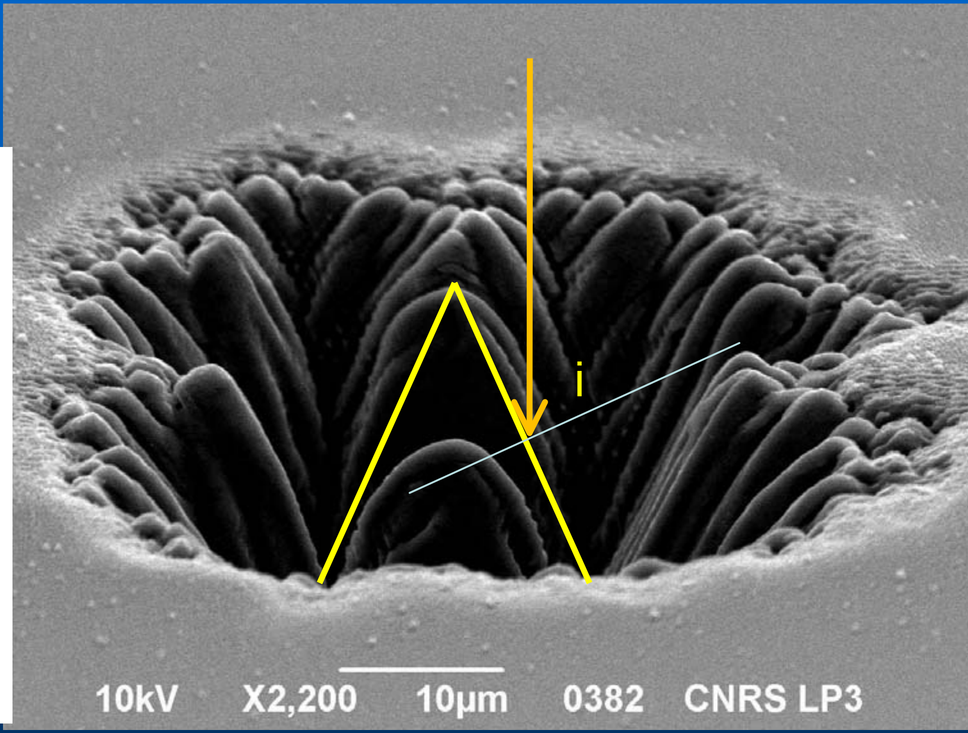
Courtesy of R. Torres,
LP3 CNRS , Marseille

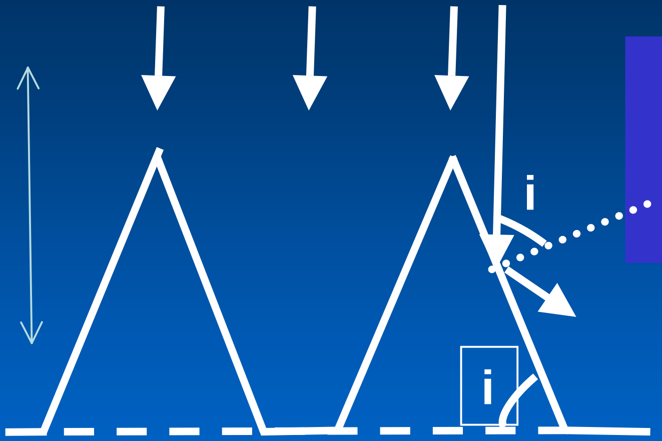
=>Ablation on randomly-distributed sites
=>Melting, instabilities, capillary waves => «beads»
=>Further ablation and re-deposition => conical structures

◆**Saturation of structures after a certain number of laser pulses**

Structure Saturation Effect







$F_a = FA(i)\cos(i) = F_{th}$

Fth=0.2 J/cm²

Fexp = 0.9 J/cm²

➔ Fth/F ~ 0.22

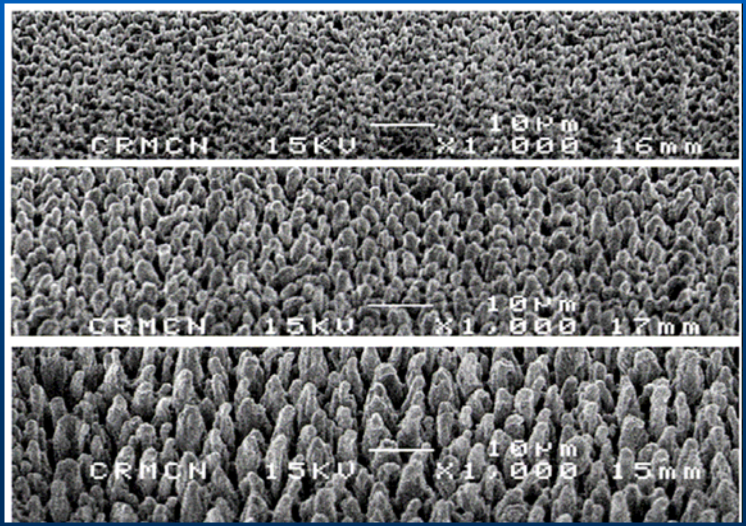
➔good agreement

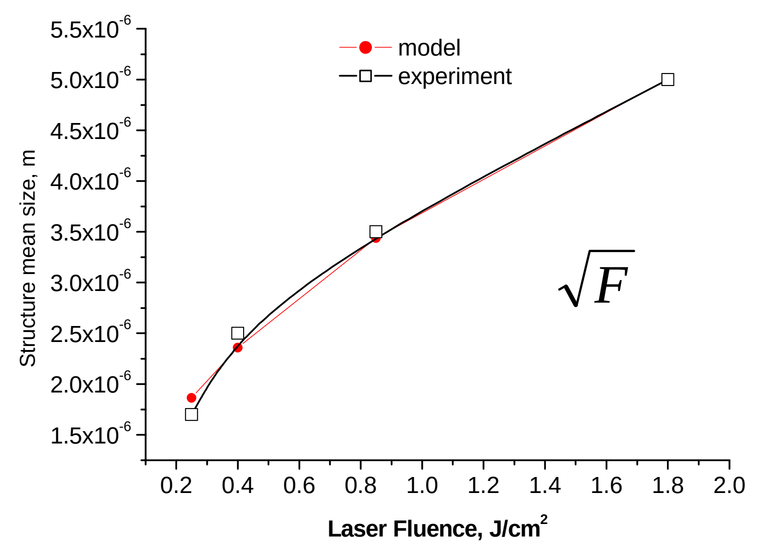
Ablation threshold depends on the angle !

Dyer et al. Appl. Phys. B 48 489 (1989)

courtesy of V. Tokarev

Structure Formation: Laser Fluence





Surface structure formation on Si by femtosecond laser pulses: SEM pictures of laser treated surfaces (tilt 50°, same magnification) and different laser fluences

(a)- 250, (b)- 400, (c)- 850 mJ/cm^2

Mean diameter of surface structures as a function of laser fluence, where black line corresponds to the experimental results and red one to

$d=3.73\ 10^{-6}\ \sqrt{F}$ [m].

Sarnet at al. SPIE Vol. 6881, 688119 (2008)

Summary

- **Modeling helps to explain**
  - nanocluster formation in laser ablation
  - parameters required for nucleation
  - role of cluster ejection, nucleation, condensation, aggregation

- **Femto regime=> no energy absorption by the plume**
- **Plume confinement is required to induce nucleation and growth**
- **Larger ablated mass, optimum temperature, and high collision rate favor nanoparticle formation**

- **Non-periodic structures have been attributed to**
  - -Surface EM waves -> periodic ripples
  - -random absorption on defects -> non-periodic structures
  - -melting
  - -ablation and re-deposition with angle-dependent ablation threshold

Thank you !

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