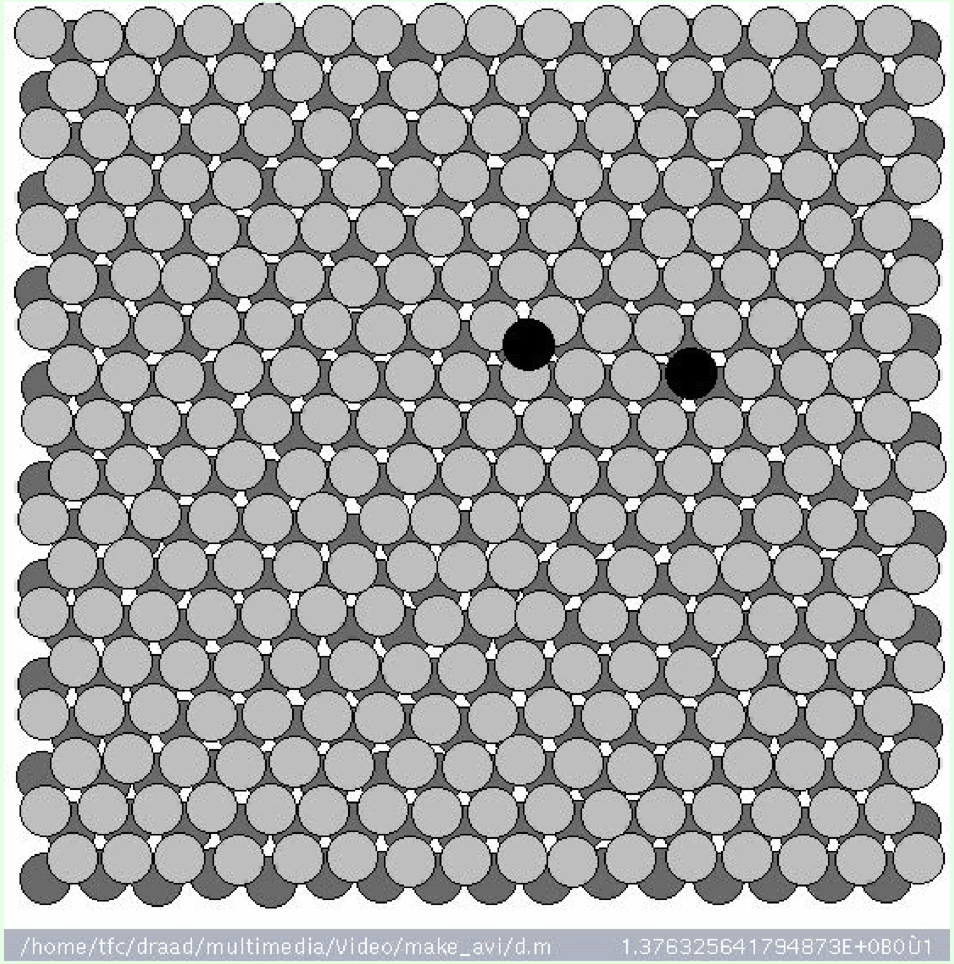
Applications of MD Simulations in Thin Film Physics

Thin Film Growth



Classical MD studies of mass transport processes

Motivation

- **Inter/intralayer mass transport** and **island morphology** are critical factors in determining the growth mode of crystals and epitaxial thin films.

- **Adatoms** and/or **vacancies**[1] play the crucial role in promoting mass transport at the rates required to achieve layer-by-layer (2D) growth.

- The **decisive criteria** in establishing and maintaining 2D growth is whether or not **critical nuclei coalesce** on top of growing islands.

-**Adatoms** deposited on top 2D islands **must descend** onto lower terrace sites before combining with other adatoms. For most systems (metals, semiconductors, ceramics) there is a barrier to passing over step edges[2].

[1] T. Michely and G. Comsa, *Surf. Sci* **256**, 217 (1991).
[2] Nostrand et. al, *PRL* **74**, 1127 (1995); Kodambak et. al. *PRL* (2005).

Studied Phenomena

- Adatom/vacancy – clusters interactions

- Small clusters diffusion

- Adatom-vacancy pairs interactions on small clusters

- Dendritic-to-compact morphological transitions

- Coalescence dynamics of small clusters

- Low-energy ion irradiation effects in thin film growth

- System studied: Pt(111) surface

- Pt → technological important material
- Large set of experimental FIM and STM studies
- 1000 K → typical growth temperature

- Results are valid for most fcc metal surfaces:

FIM measurements of adatom self-diffusion barriers are essentially identical on Pt(111)[1] (0.25±0.02 eV) and Ir(111)[2] (0.27 eV).

[1] P. F. Feibelman et. al, PRB **49**, 10548 (1994).
[2] S.C. Wang and G. Ehrlich, PRL **62**, 2297 (1989).

Method

- Pt(111) substrate, 4/9 layers of 16x18 atoms each for a total of 1152/2592 atoms

    - Embedded-atom method (EAM)[1]
    - Molecular Dynamics (MD)
    - Statistically independent starting configurations
    - T = 1000 K

- Separate runs ranging in time from 2 ps to 2 μ s
- Total simulation time ~ several μs
- Results stored in movie files with 10 fs resolution

[1] R. A: Johnson, PRB **39**, 12554 (1989).

Comparison of E_D: EAM vs experimental data

Adatom self-diffusion on Pt(111)

0.22 eV (EAM) → **Present work**

0.25 eV (FIM) → **Feibelman et. al, PRB 49, 10548 (1994)**

0.26 eV (STM) → **Hohage et. al. PRL 76, 2366 (1996)**

Cluster diffusion on (111) surfaces

Pt_6 ~ 1.22 eV (concerted motion) → **Present work**

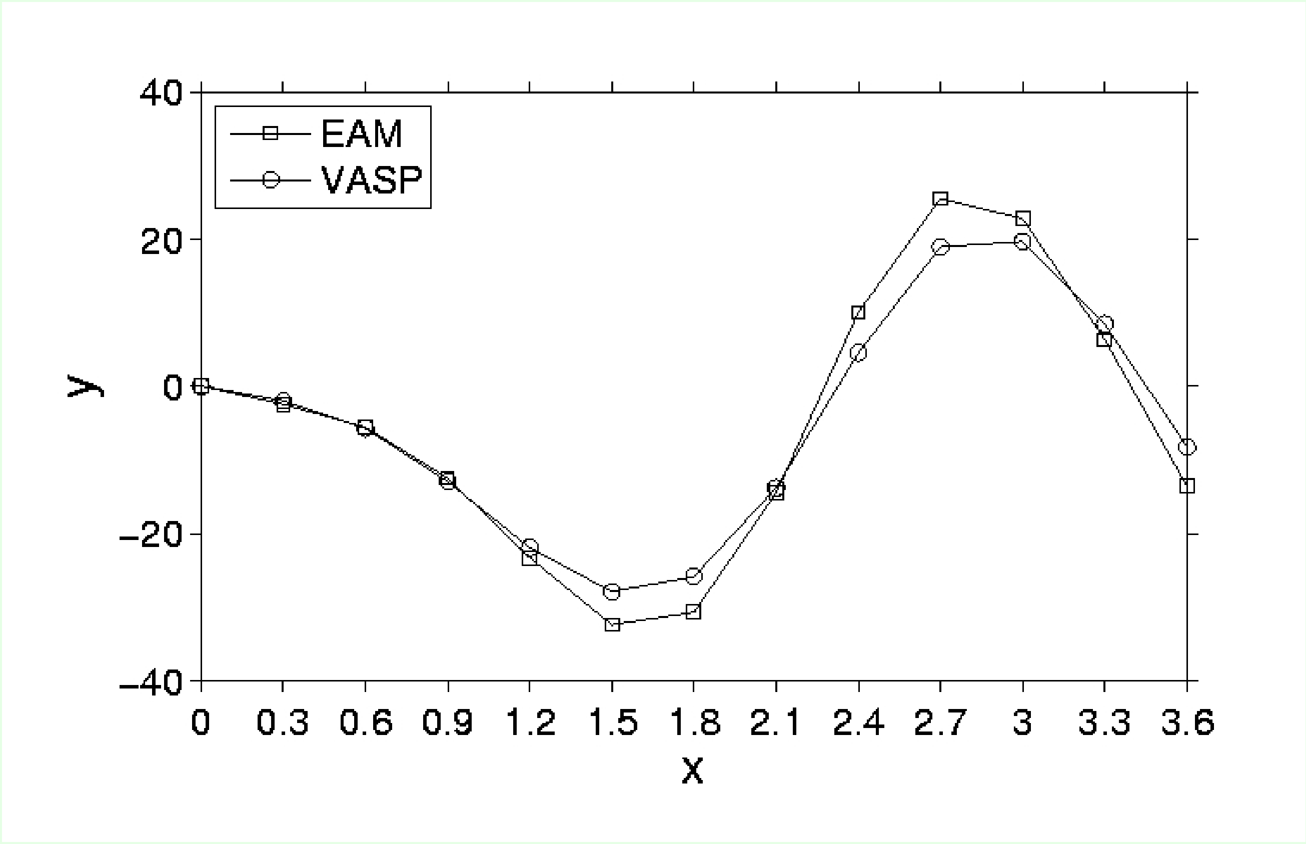
~ 0.24 eV/ additional atom (Pt_6 to Pt_{19})

Ir_6 ~ 1.00 eV (FIM)[1]

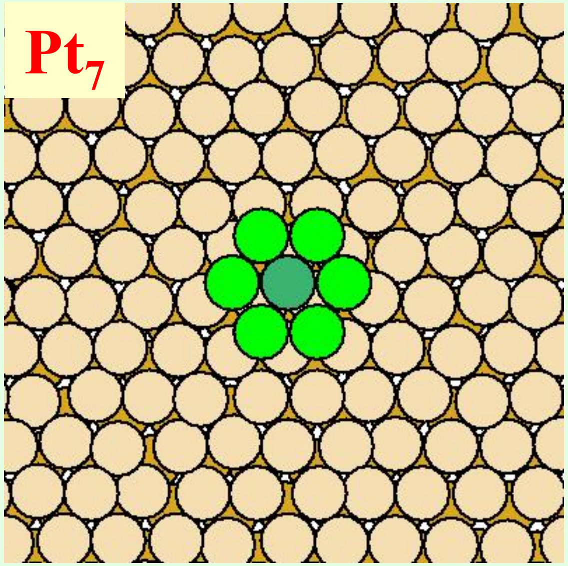
~ 0.20 eV/additional atom (FIM)[1]

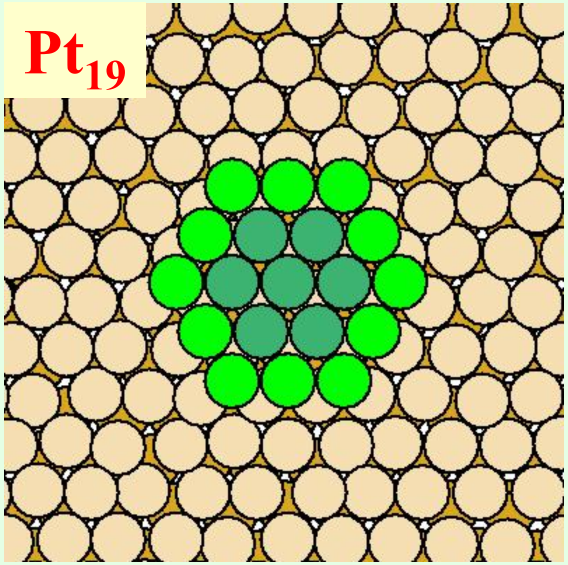
[1] Wang & Ehrlich, *Surf. Sci*. **239**, 301 (1990)

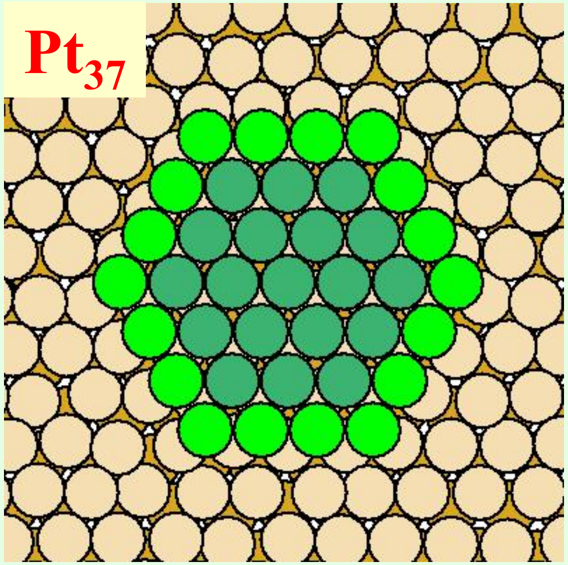
Comparison of MD forces: EAM vs Ab-initio



Typical clusters configurations



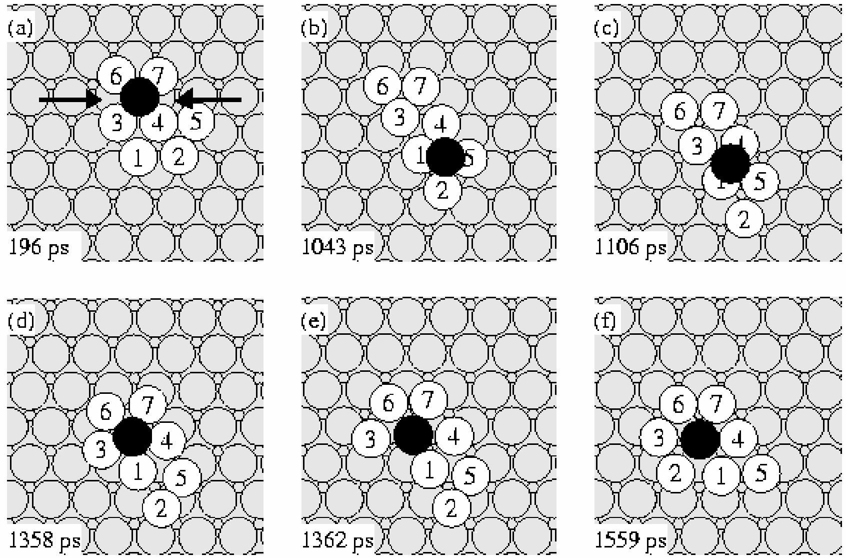


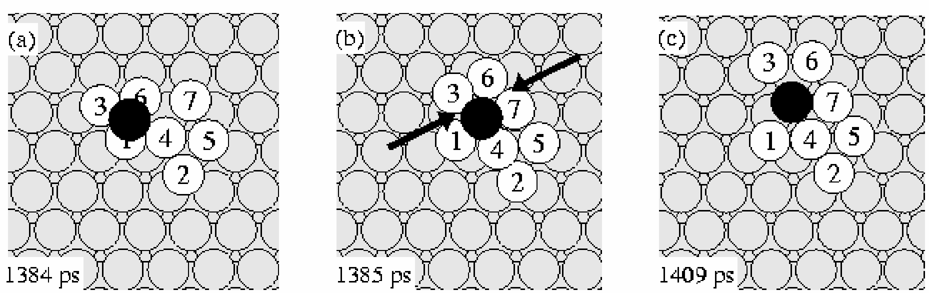


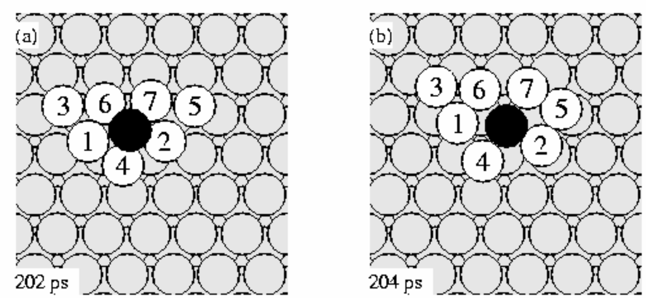
High diffusion and dissociation energy barriers

Most stable cluster configurations on (111) planes

Adatom – clusters interactions



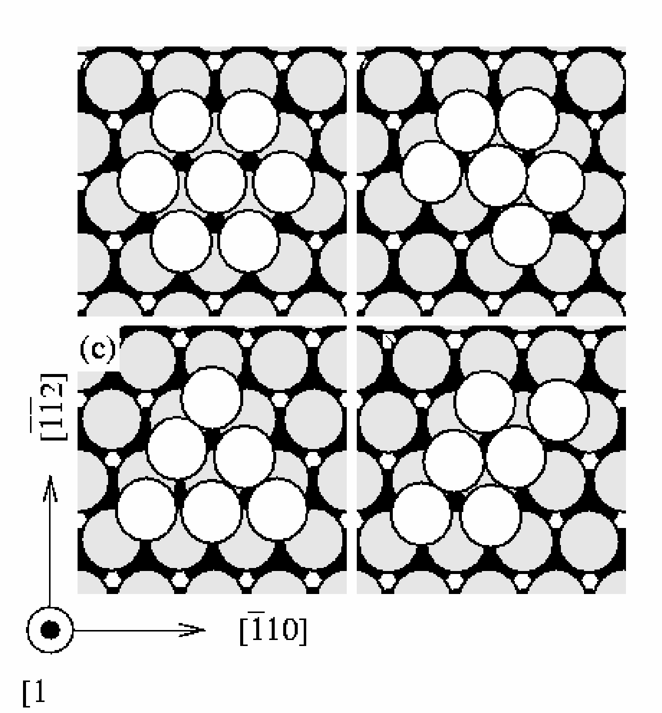


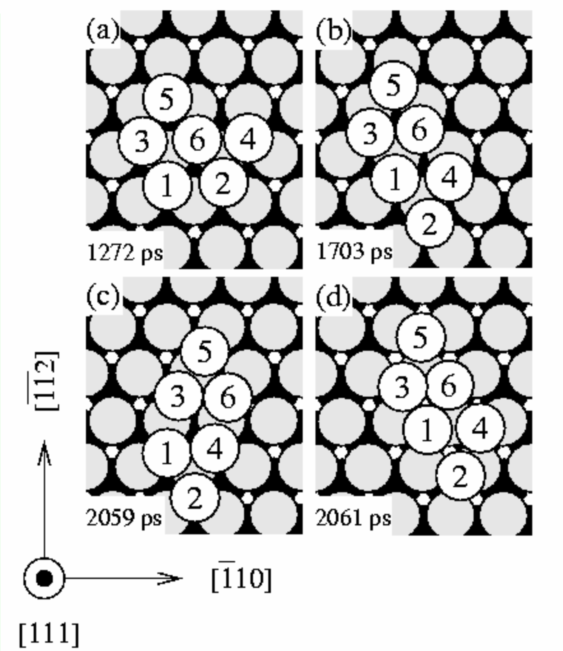


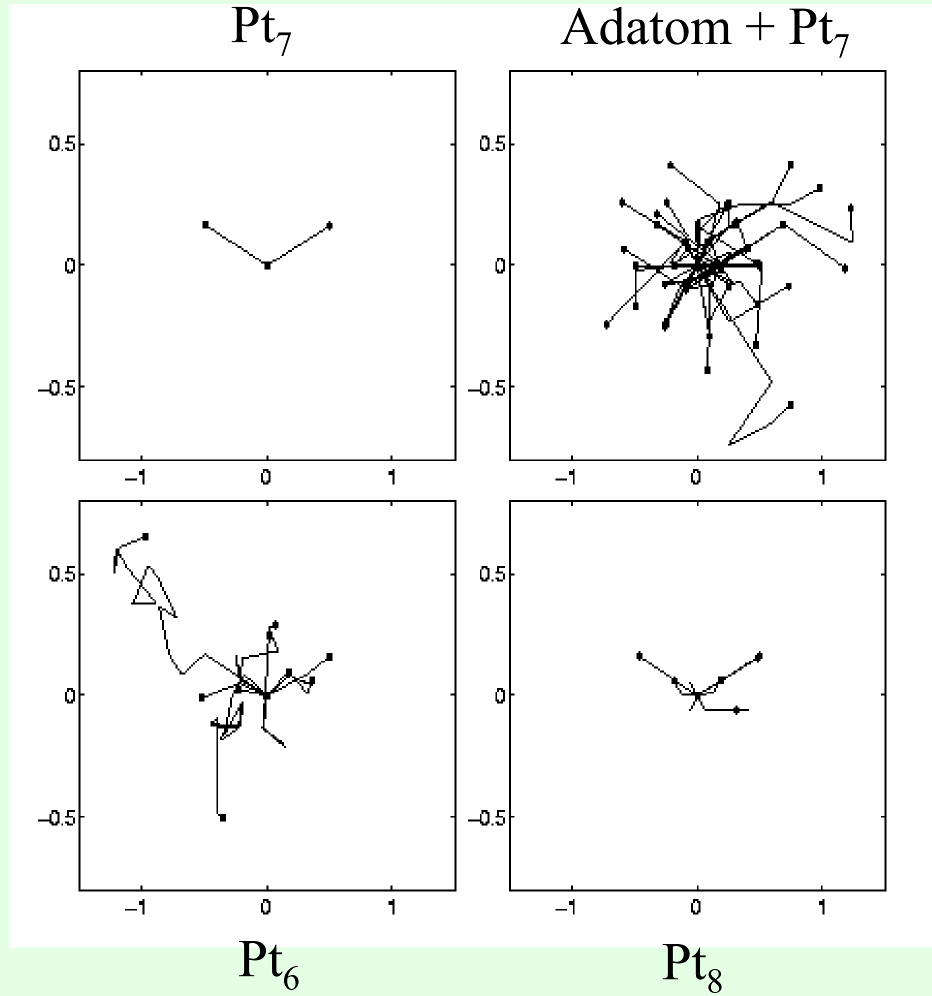
Münger et. al., *Surf. Sci.* **355**, L325 (1996)

Chirita et. al., *APL* **72**, 127 (1998)

Vacancy – clusters interactions

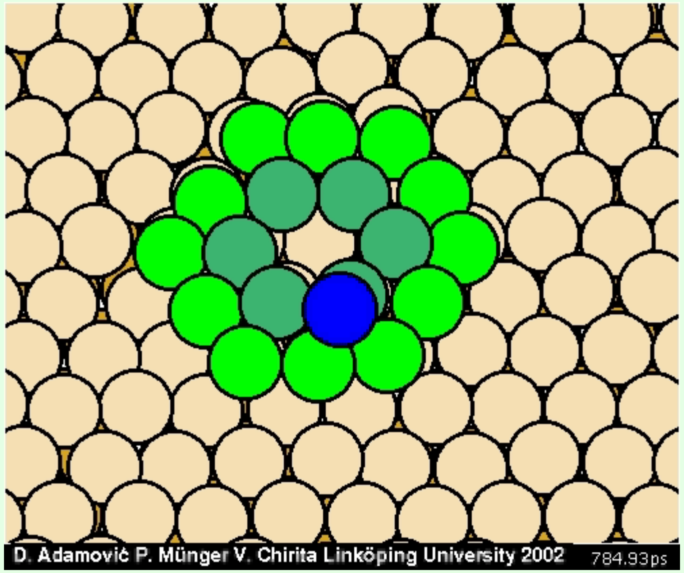


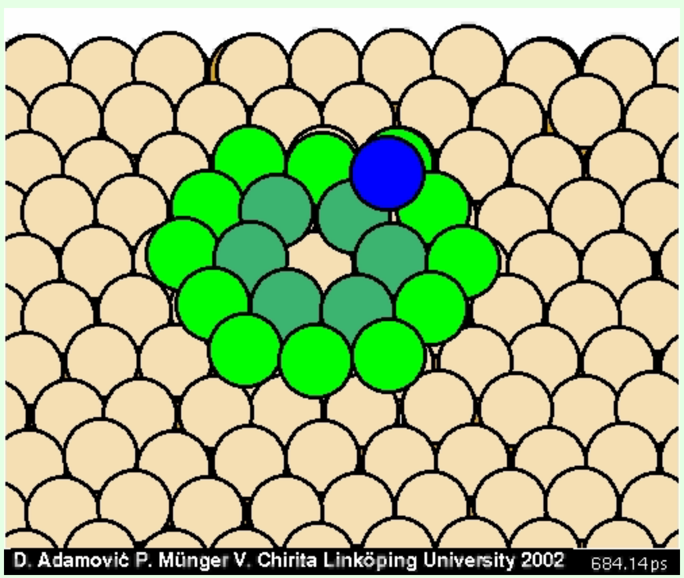


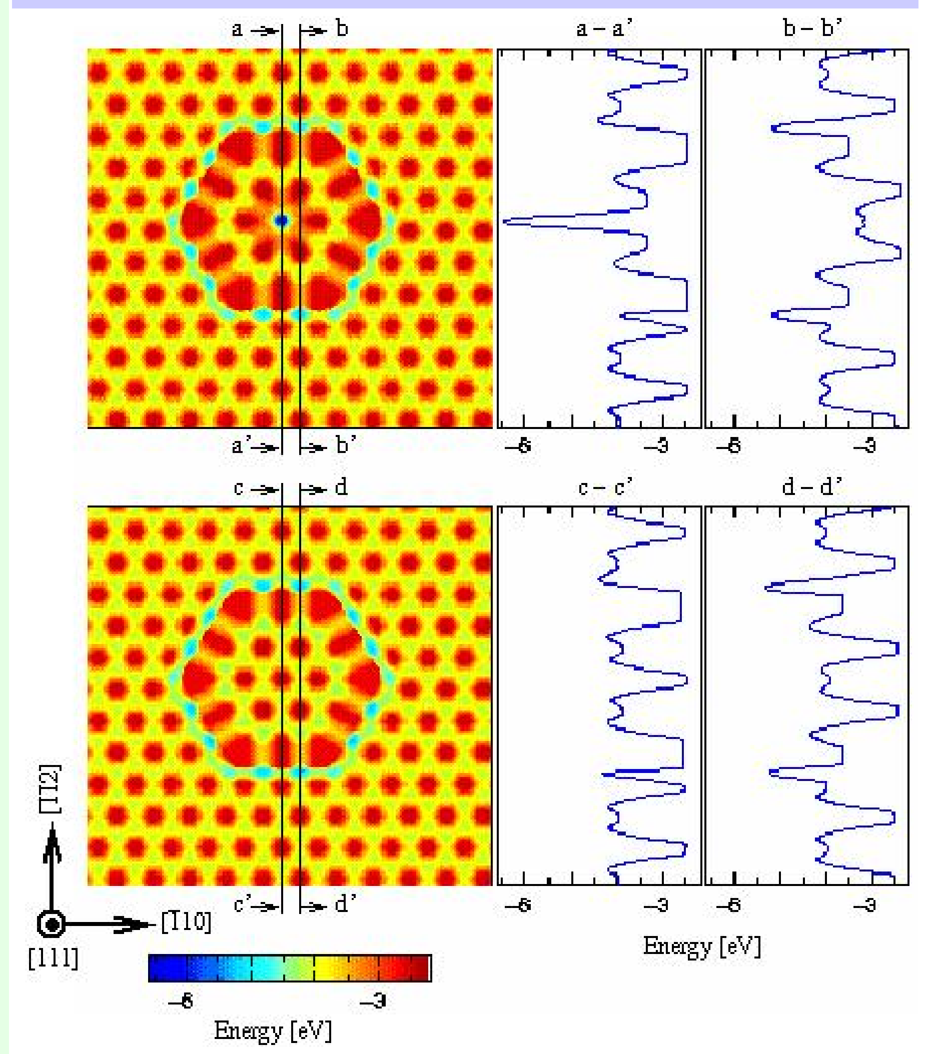


Münger et. al., *Surf. Sci.* 539, L567 (2003)

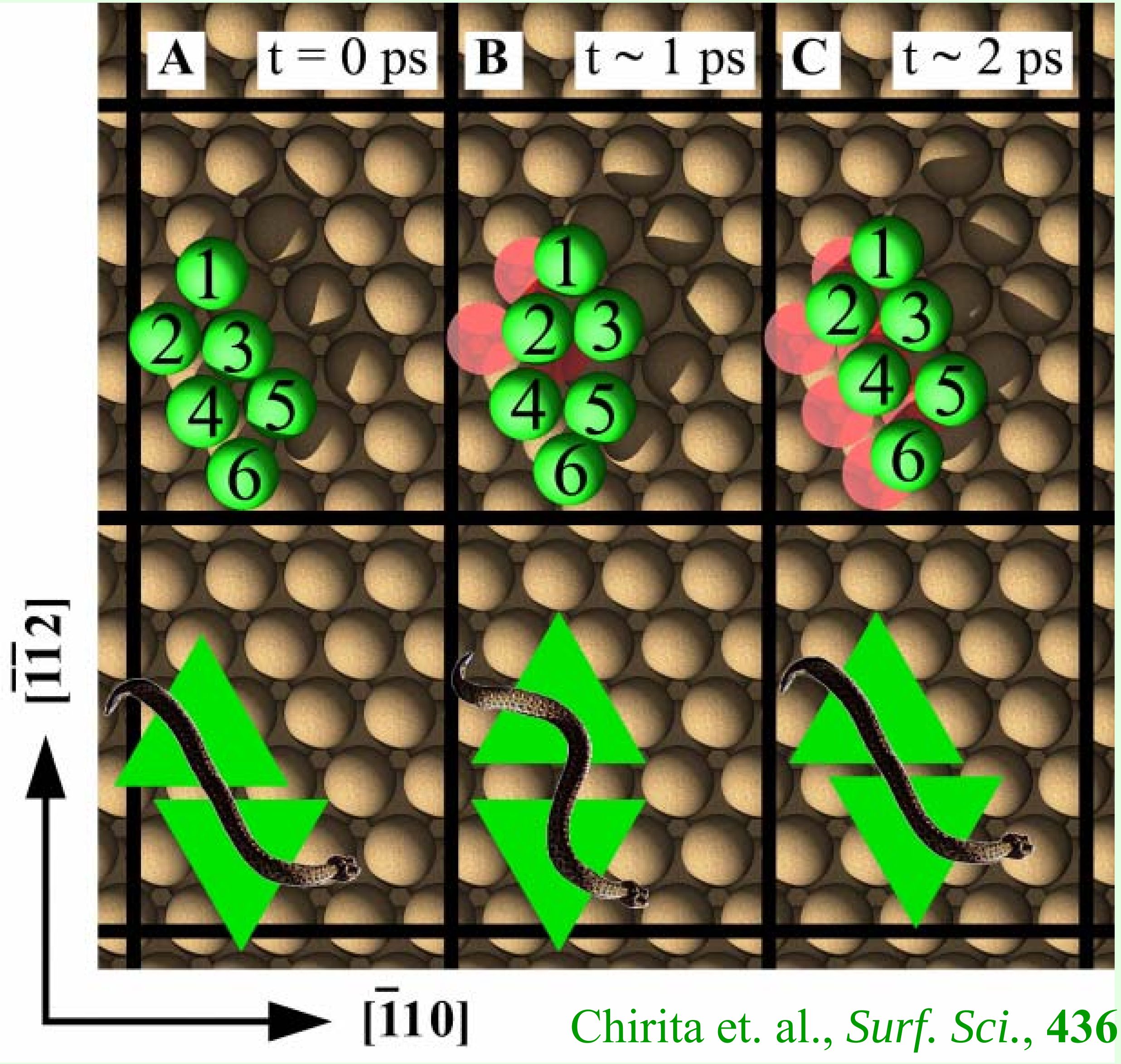
Adatom/vacancy pairs interactions on small clusters





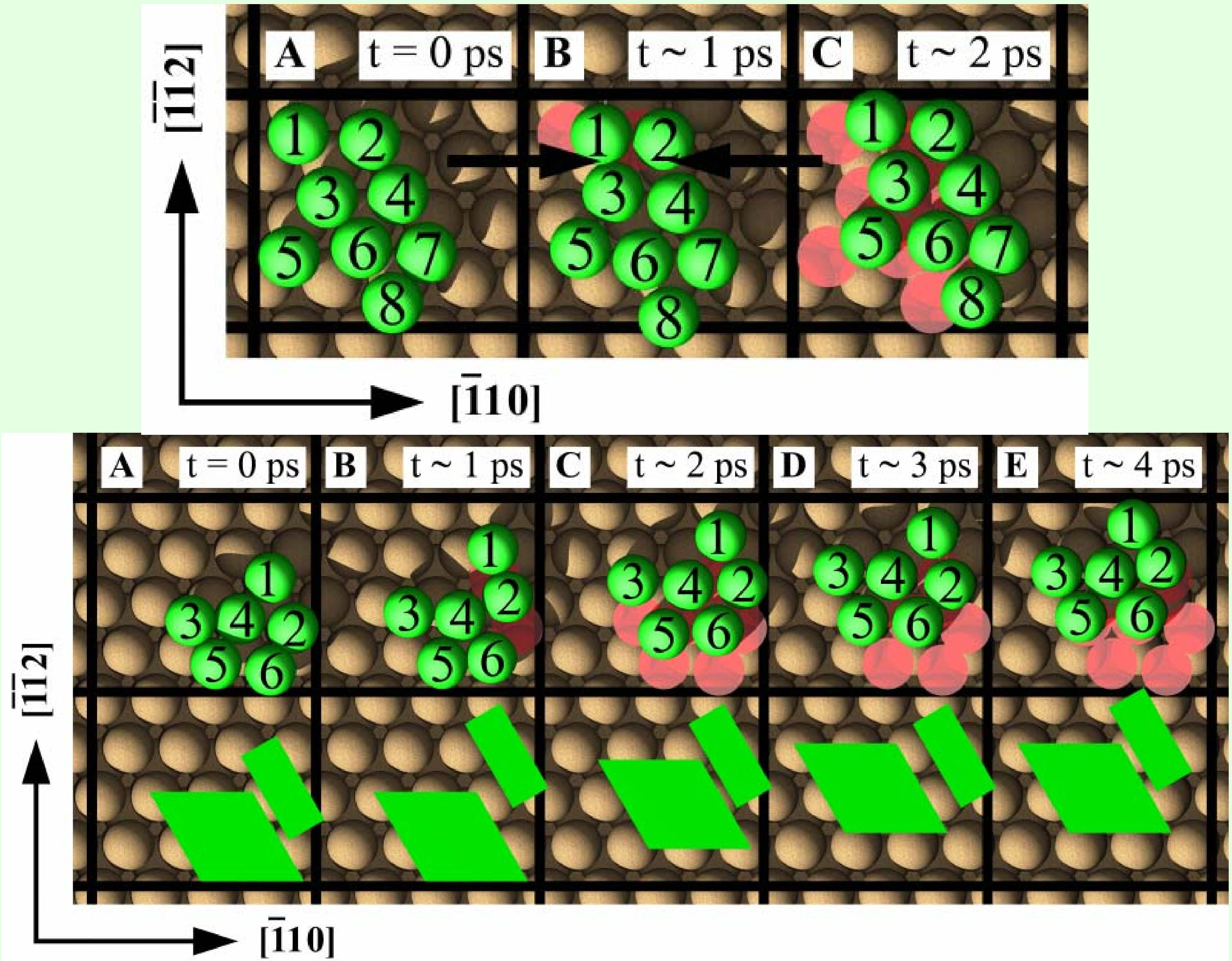


Cluster diffusion - Reptation

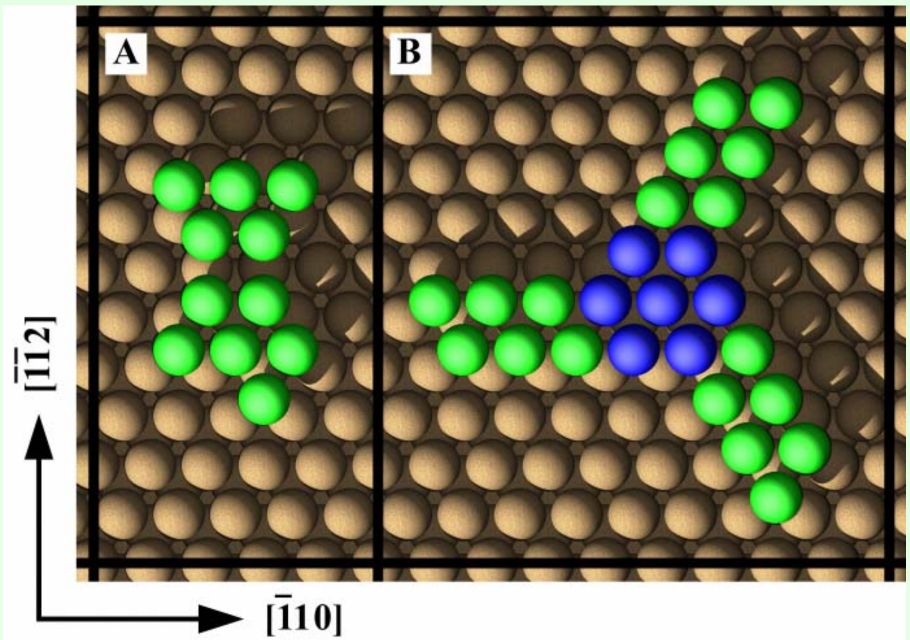


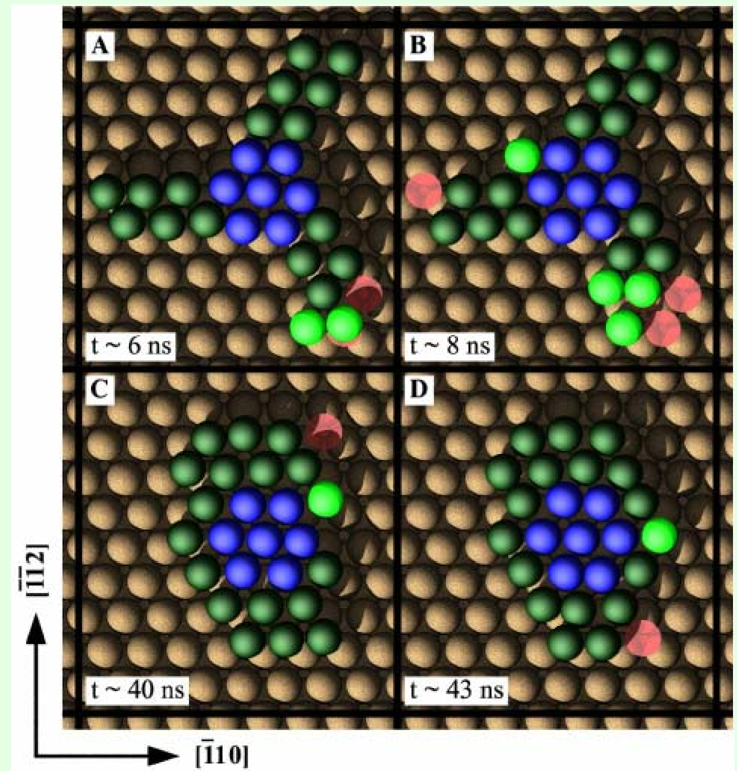
Chirita et. al., *Surf. Sci.*, **436**, L641 (1999)

Cluster Diffusion

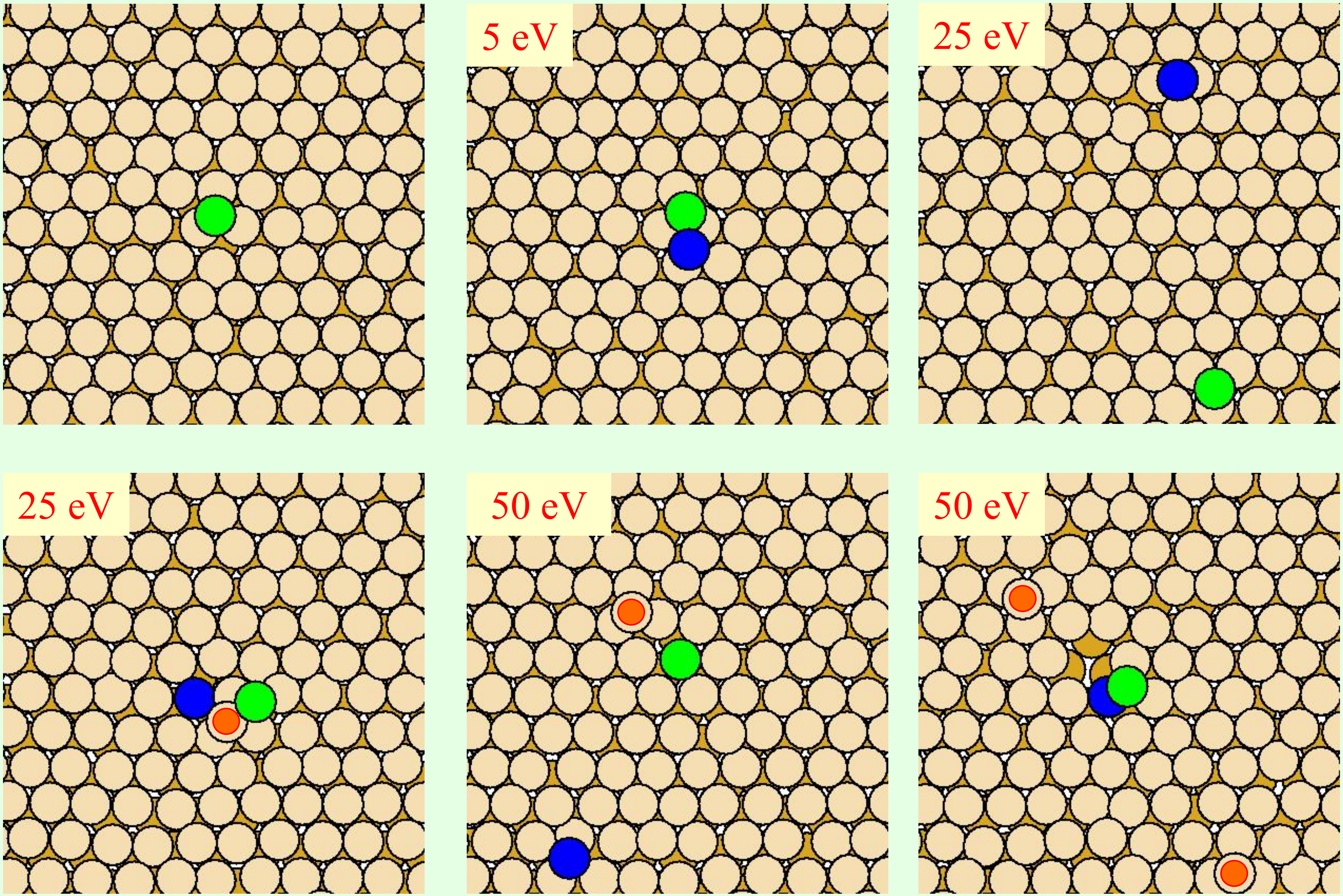


Dendritic to compact morphological transitions





Low-energy irradiation of single adatoms (monomers)

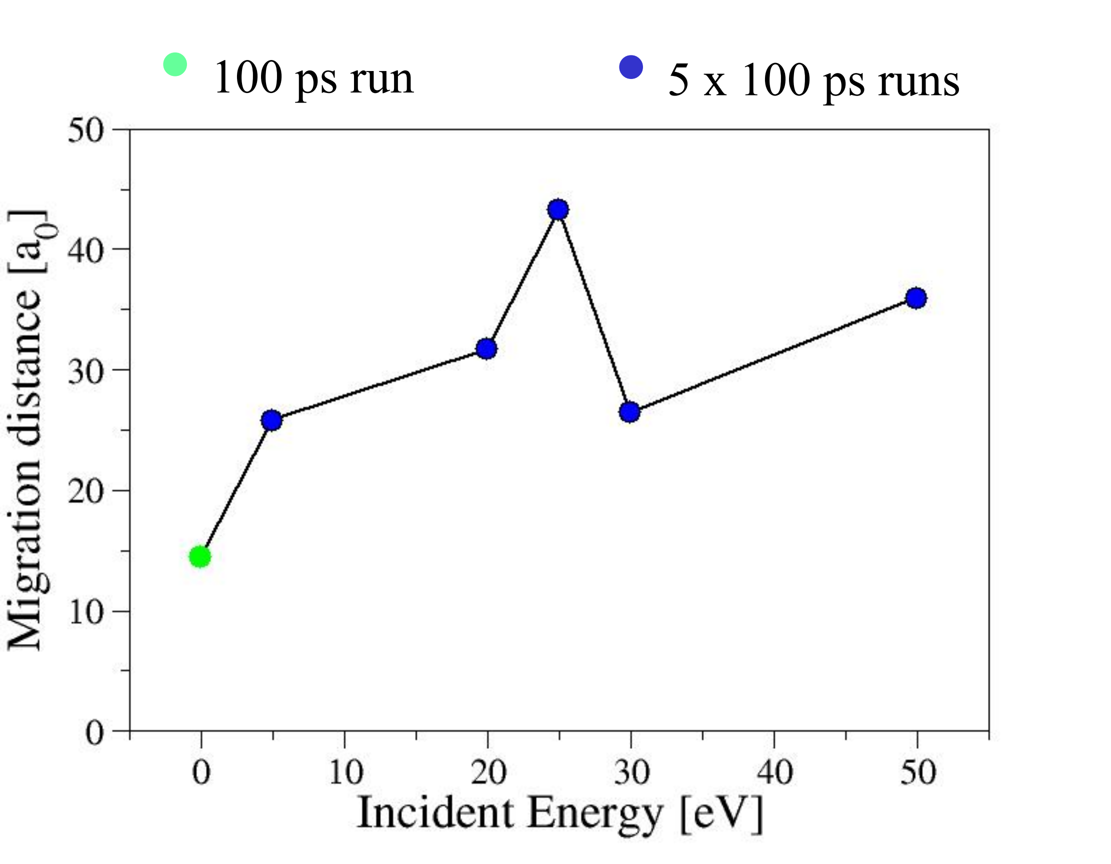


Monomer events statistics

	5 eV	20 eV	25 eV	30 eV	50 eV
Dimer formation	4	5	3	3	3
Exchange Impact/surface		2	2	4	3
Exchange Monomer/surface				2	1
Surface vacancy					2

Monomer migration rates

Enhanced monomer migration rates → ion-irradiation effect



D. Adamovic et. al., APL **86**, 211915 (2005)

Low-energy ion irradiation studies reveal the dynamics of:

- Cluster reconfiguration & reshaping

- 2D-3D cluster transitions

- Cluster disruption

- Point defects (vacancies/interstitials) formation events

- Exchange events involving energetic cluster/surface atoms

Ion-irradiation models span two decades

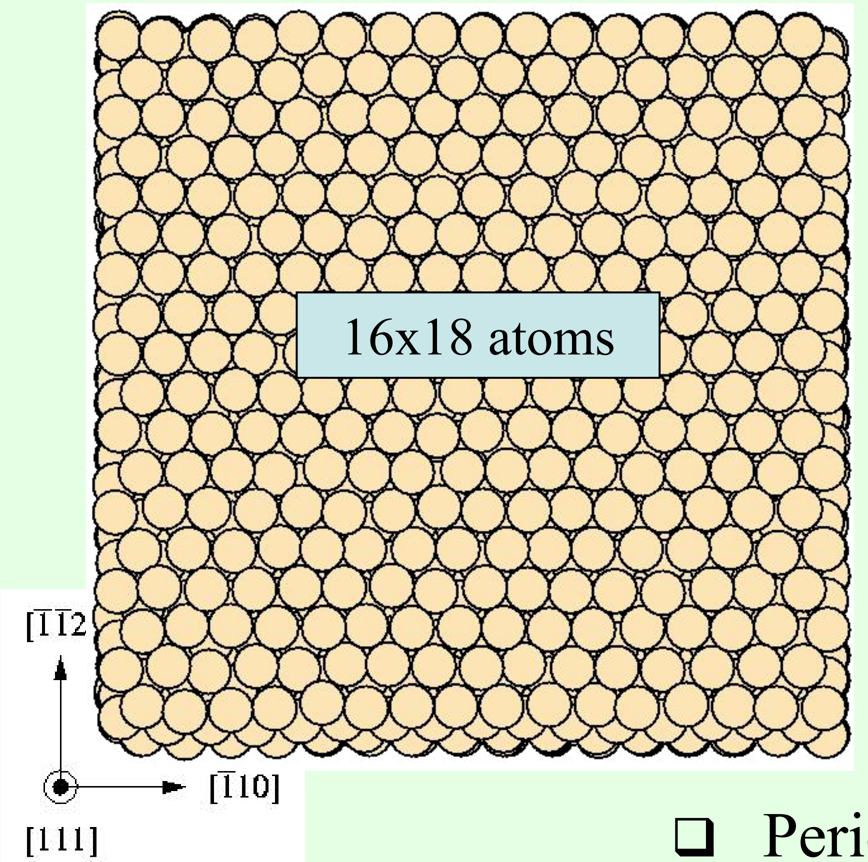
- Suppresses 3D multilayer growth.
- Enhances adatom and cluster mobilities.
- Enhances adatom and island number densities.
- General model: all effects promote layer-by-layer growth.
- No direct evidence has been given yet.

Understanding ion-irradiation processes

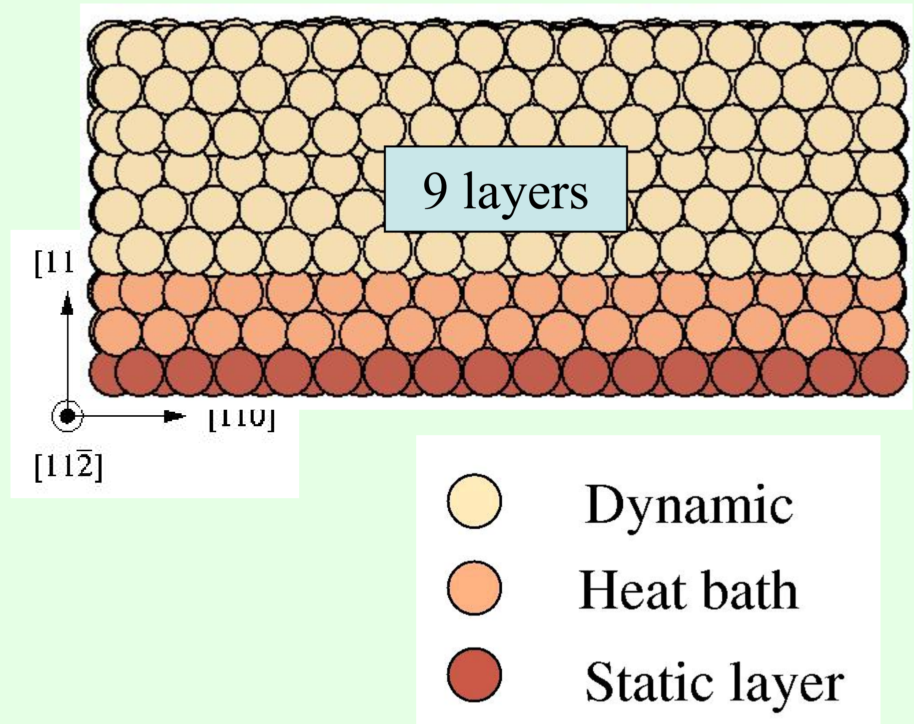
- Complex, detailed pathways and not fully known.
- Strong incentive for investigations on the atomic scale.
- Non-equilibrium, transient processes.
- Not accessible with experimental techniques – ps timescale.
- Computer simulations (molecular dynamics).

Substrate and impact geometry

Top view

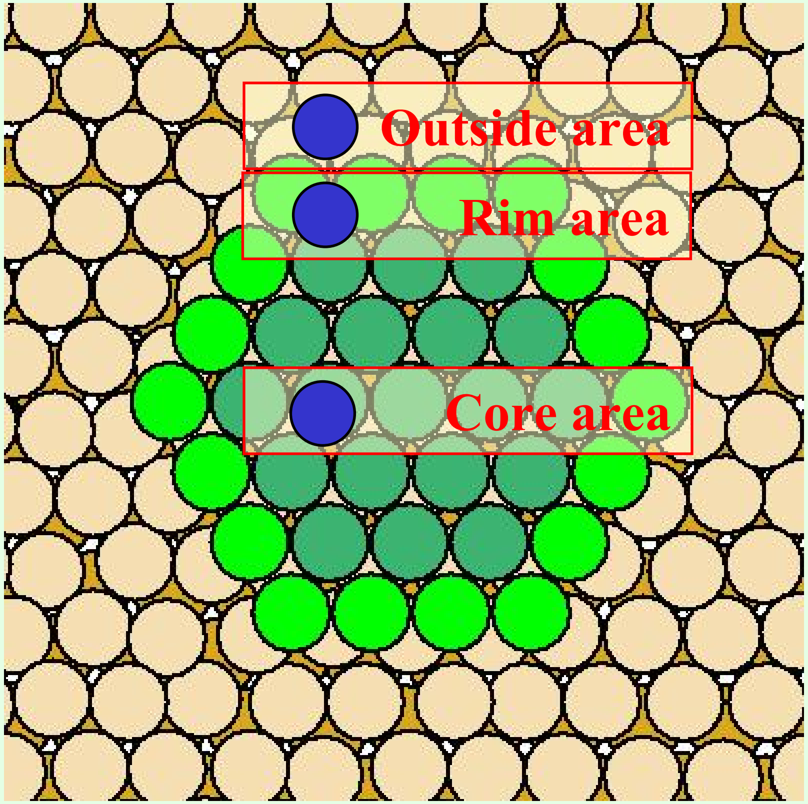


Side view

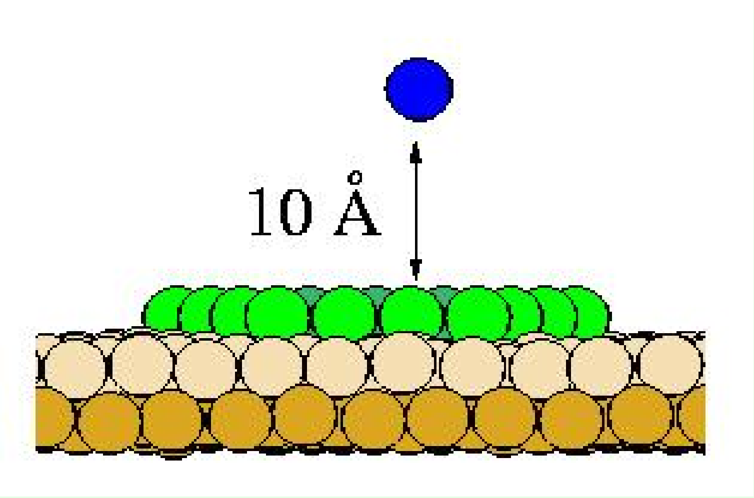


- ❑ Periodic in-plane boundary conditions
- ❑ Substrate temperature 1000 K

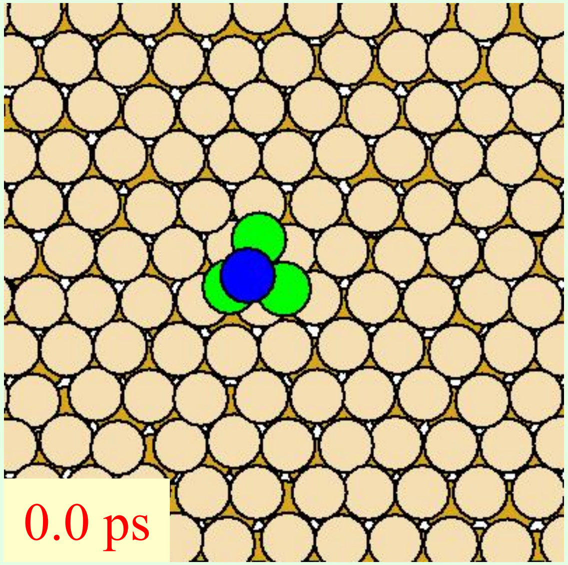
Impact areas and energies

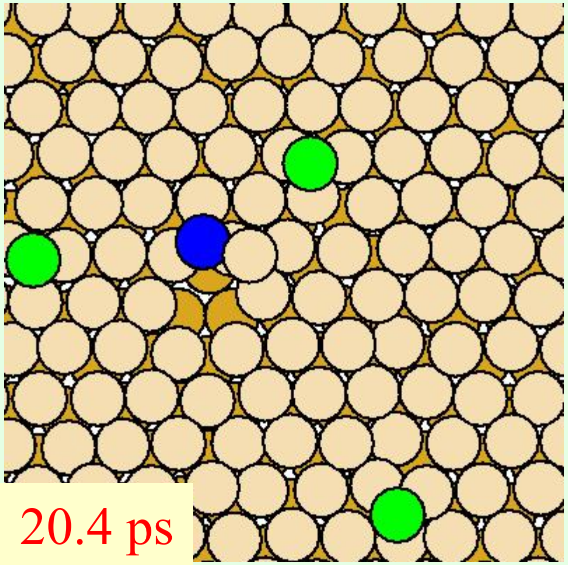


Incident energies
5 eV
20 eV
25 eV
30 eV
50 eV

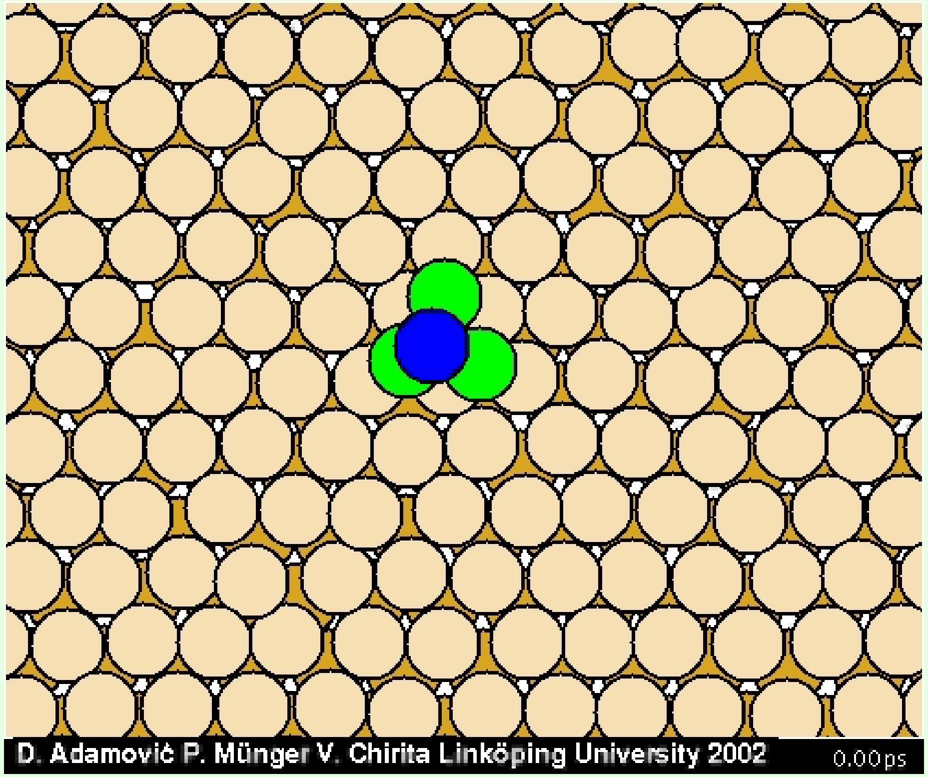


Typical vacancy formation event

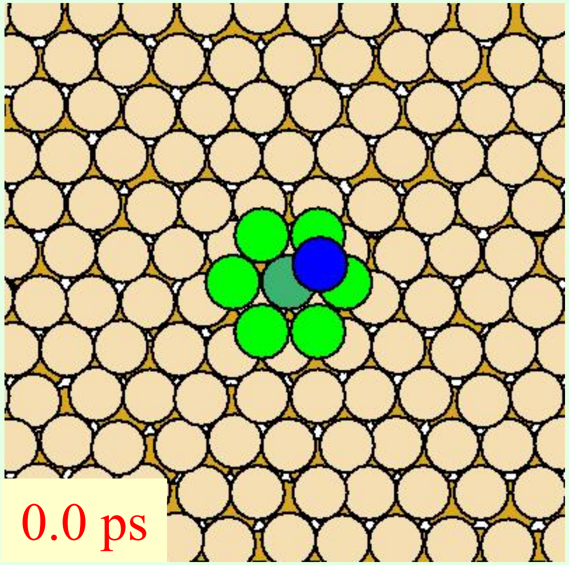




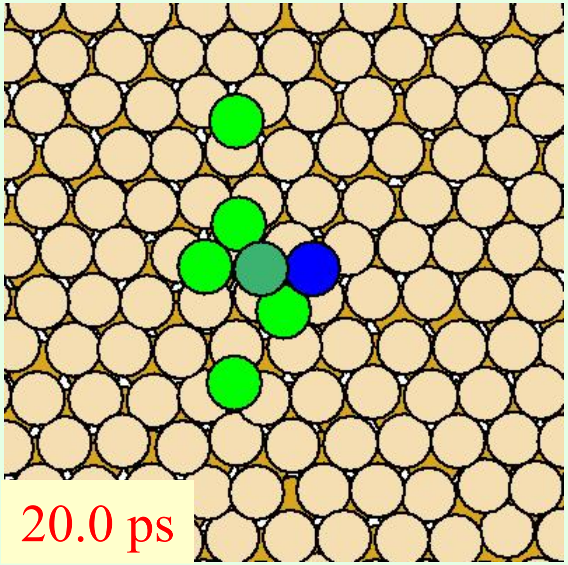
Cluster size: Pt_3
Impact energy: 50 eV
Impact area: Rim

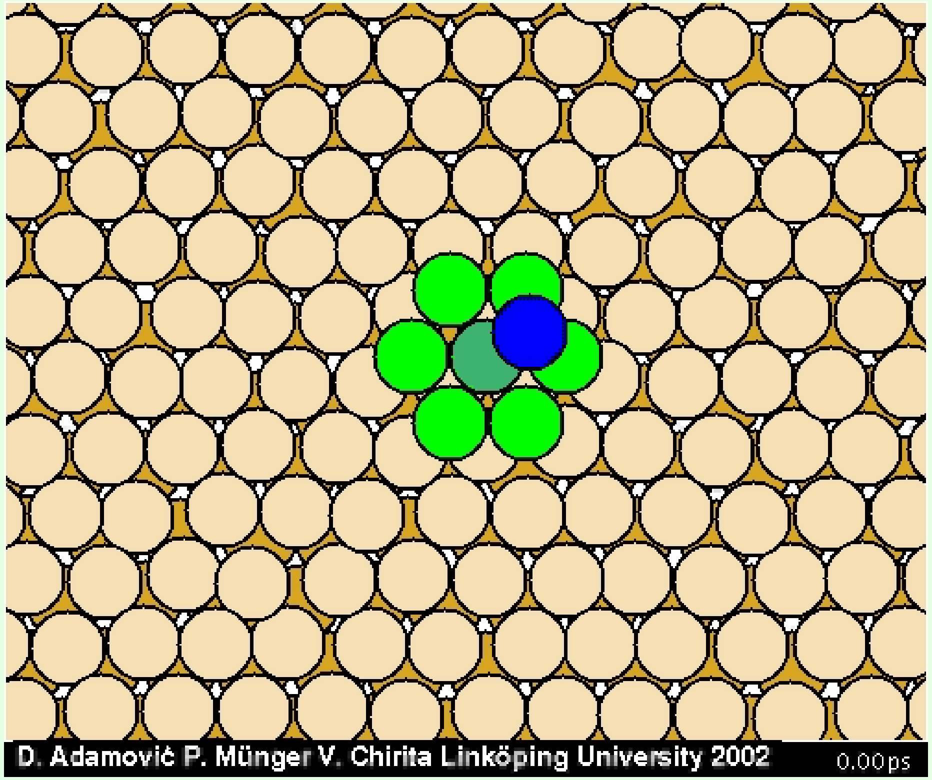


Typical cluster disruption event

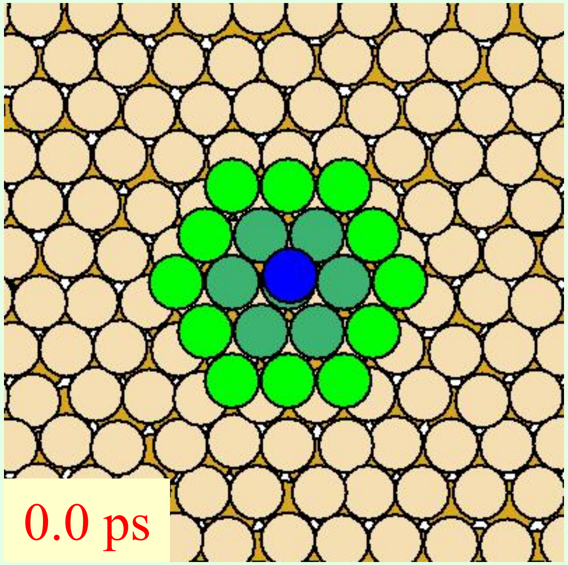


Cluster size:	**Pt_7**
Impact energy:	**50 eV**
Impact area:	**Rim**

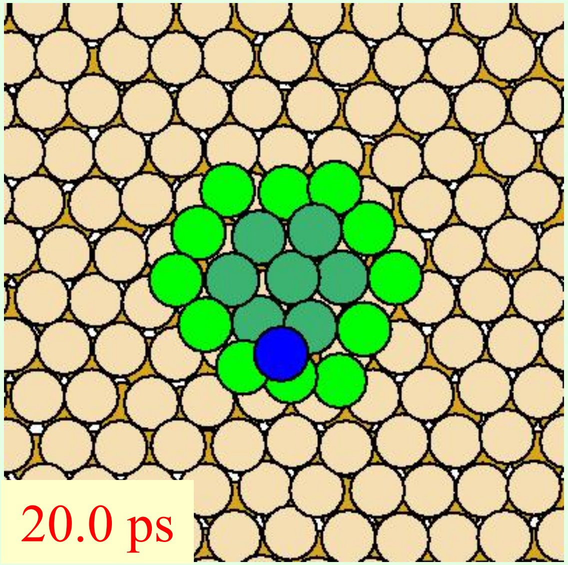


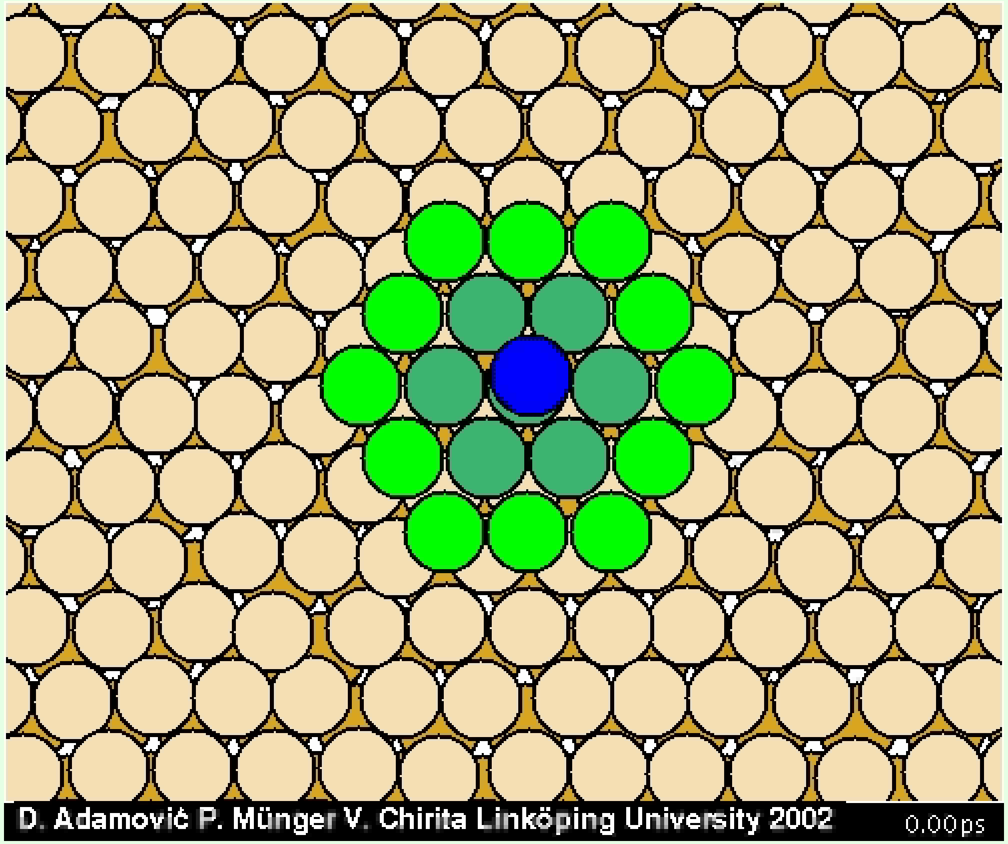


Typical cluster preservation event



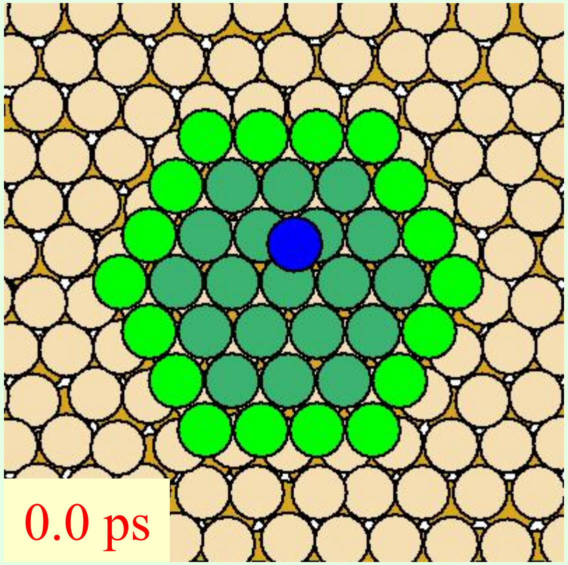
Cluster size:	**Pt_{19}**
Impact energy:	**50 eV**
Impact area:	**Core**

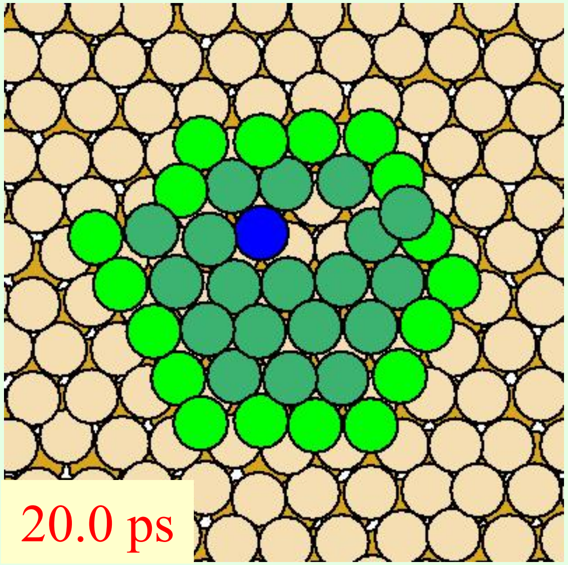


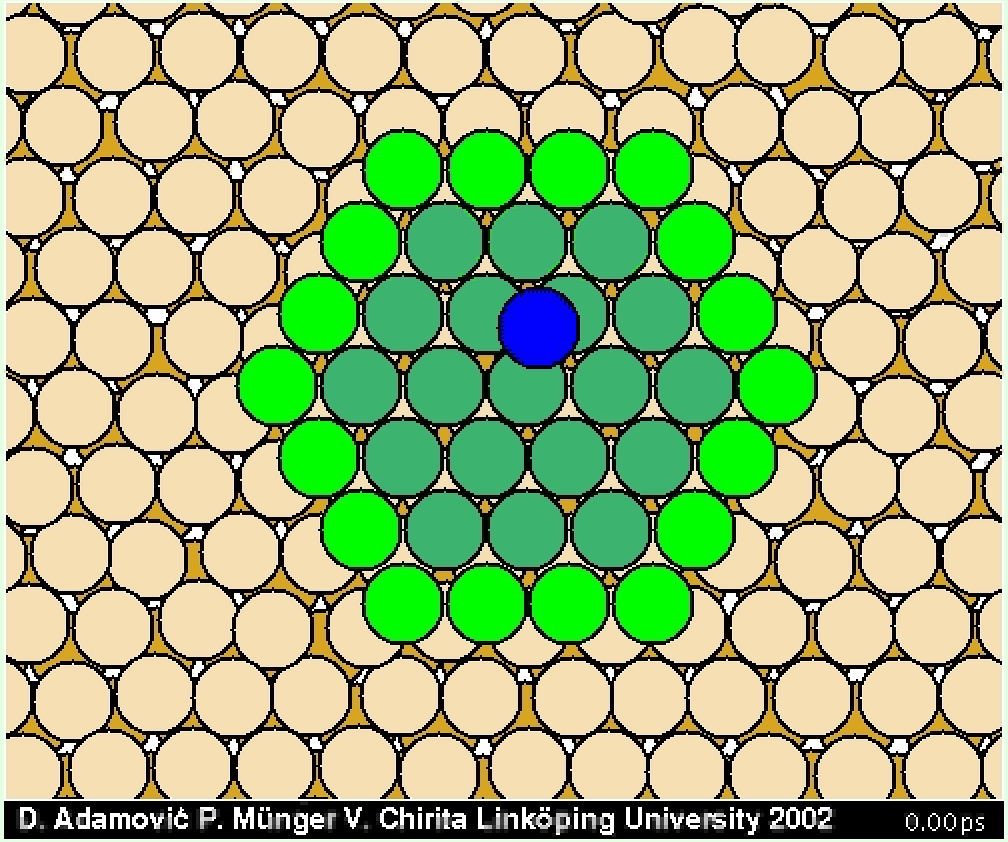


Typical 2D-3D transition event

Cluster size:	Pt_{37}
Impact energy:	30 eV
Impact area:	Core

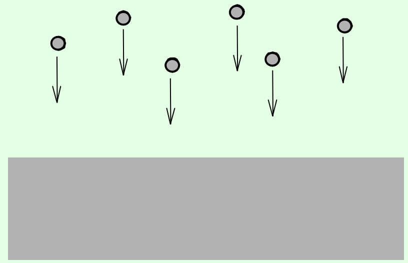




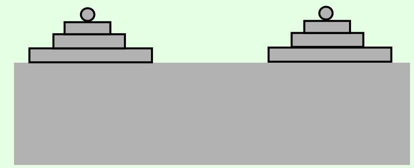


Experimental evidence

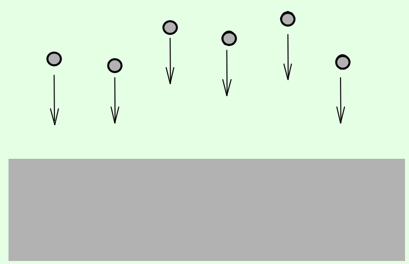
Thermal deposition
(< 1 eV)



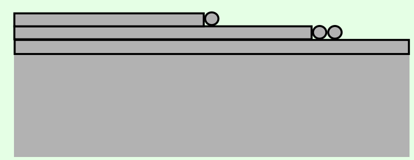
Multilayer (3D)

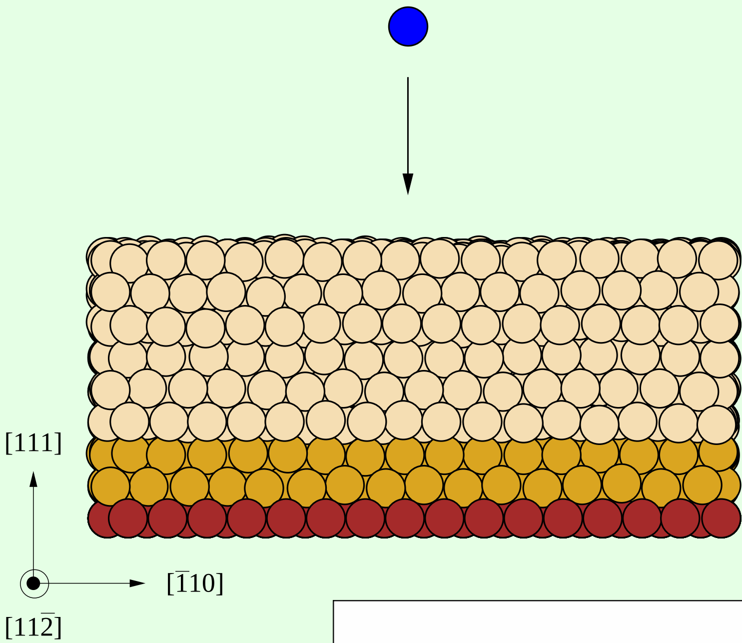


Low-energy irradiation
(< 50 eV)

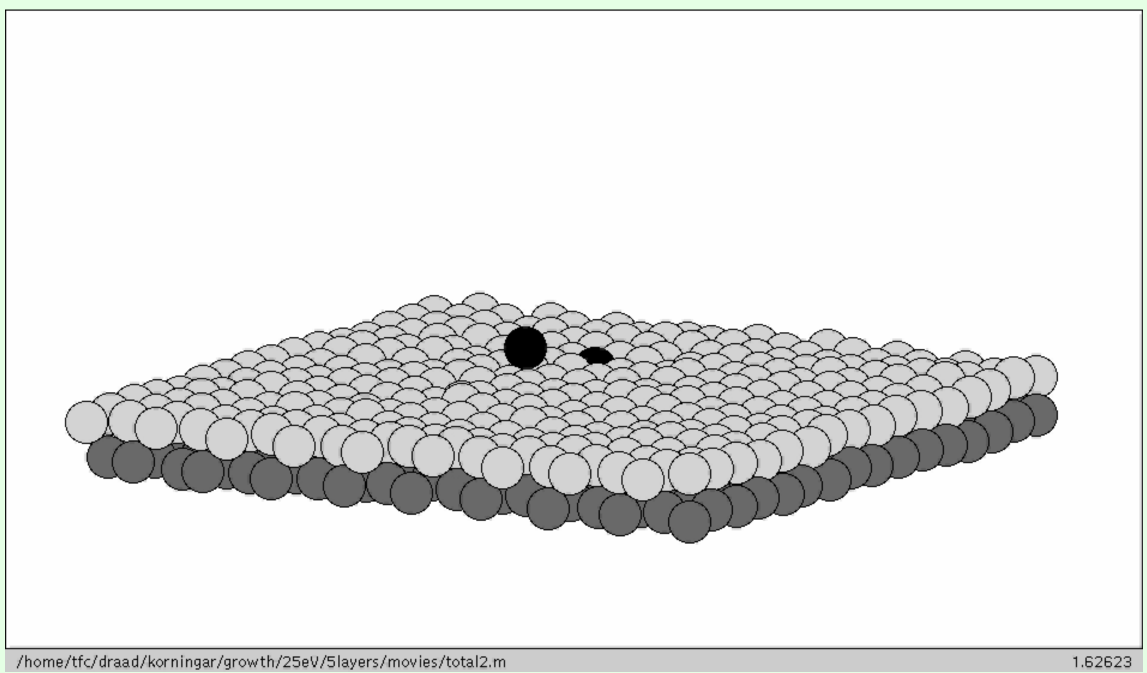


Layer-by-layer (2D)



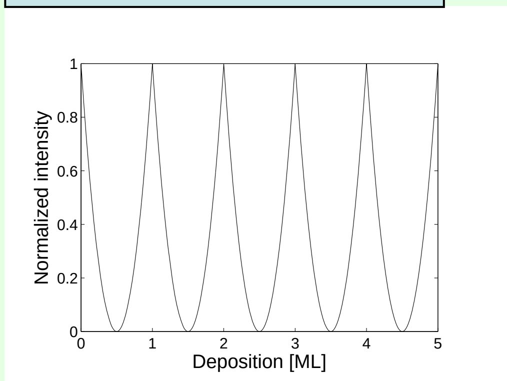


- E_{Pt} = 0.2 eV and 5-50 eV, 5 eV intervals
- We deposit 5 ML at two flux rates
- R = 10 ns^{-1}, or deposition rate of $5x10^5$ μm/min, i.e. 10^3 > EB – PVD.
- R = 1 ns^{-1}, i.e. 10^2 > EB – PVD (25 eV).

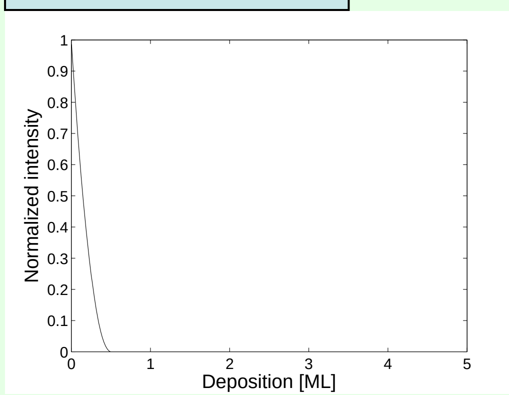


Determining growth mode

2D Layer-by-layer



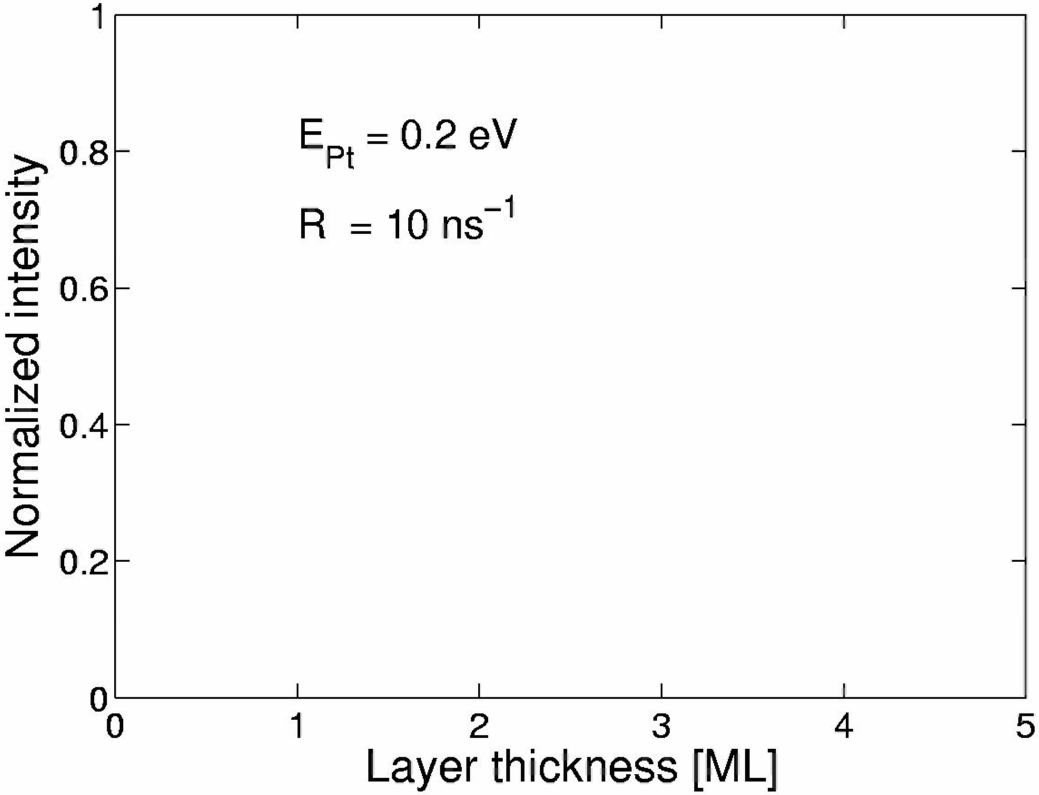
3D Multilayer

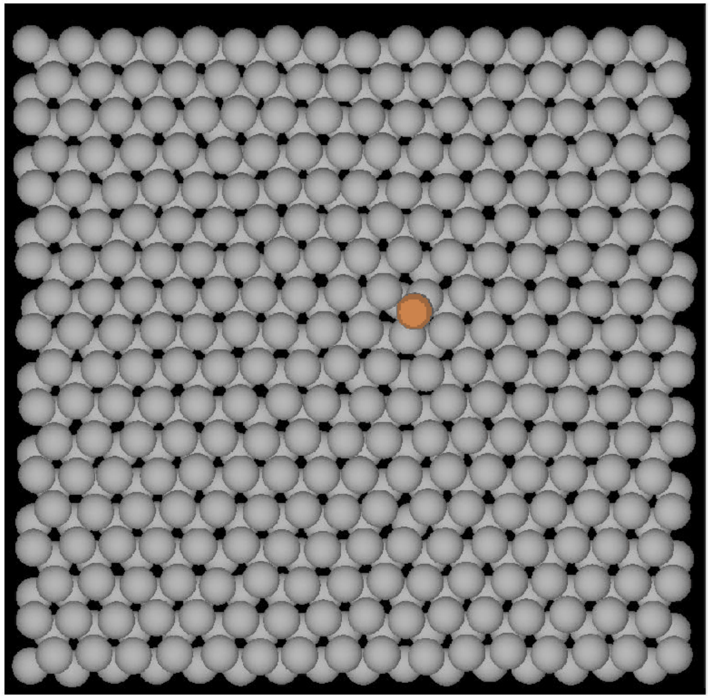


- ❑ Follow motion of all atoms individually » adatom coverages as f(t).
- ❑ Calculate antiphase diffraction intensity oscillations » growth mode.
- ❑ Periodic oscillations » layer-by-layer growth.
- ❑ Monotonic decrease » multilayer growth.

Typical 3D multilayer growth mode

Homoepitaxial Pt(111) growth from hyperthermal atoms





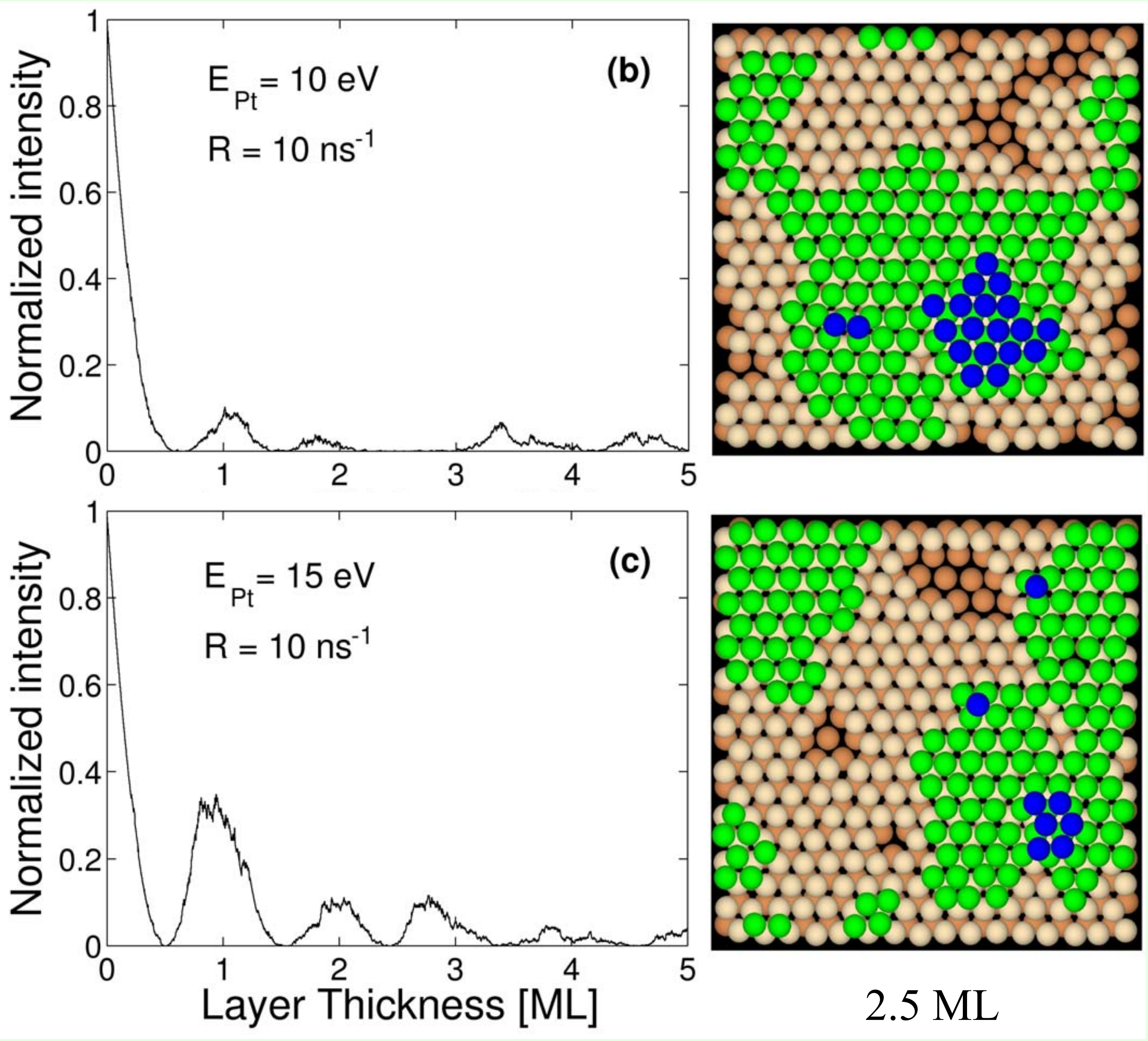
Time 0.0 ns

Dragan Adamovic, Peter Munger, Valeriu Chirita, Lars Hultman, Joe Greene

Department of Physics, Chemistry, and Biology, IFM Linkoping University, Sweden

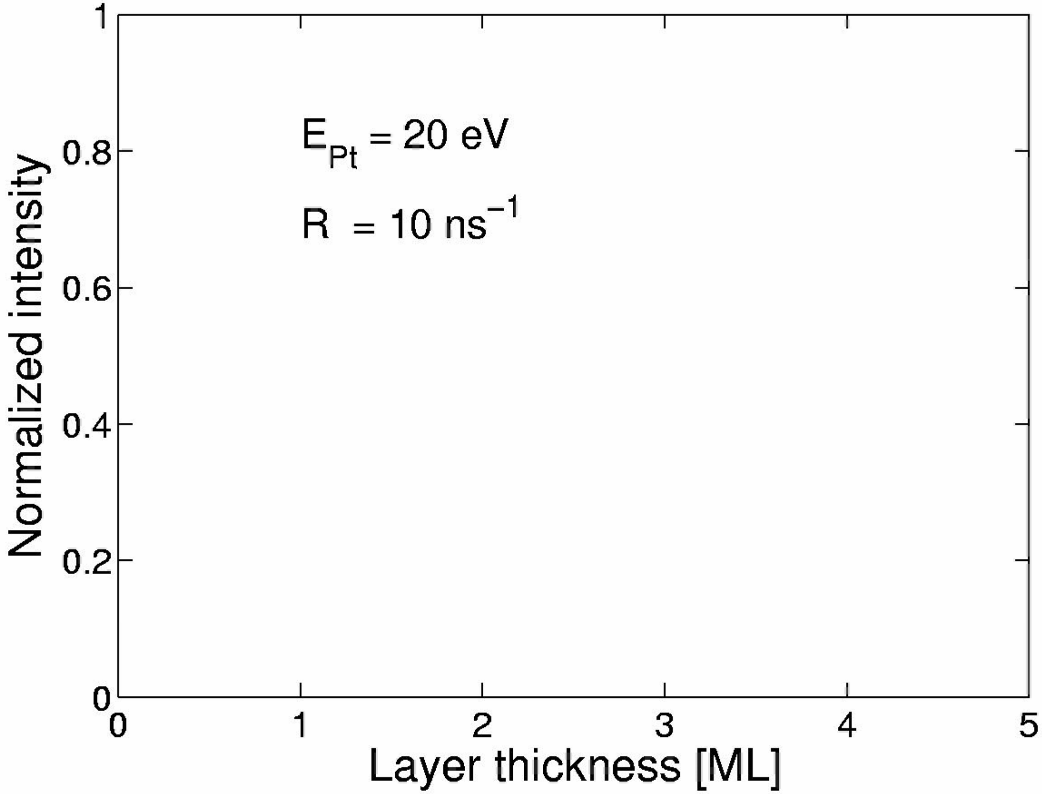
Materials Science Department and the Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, USA

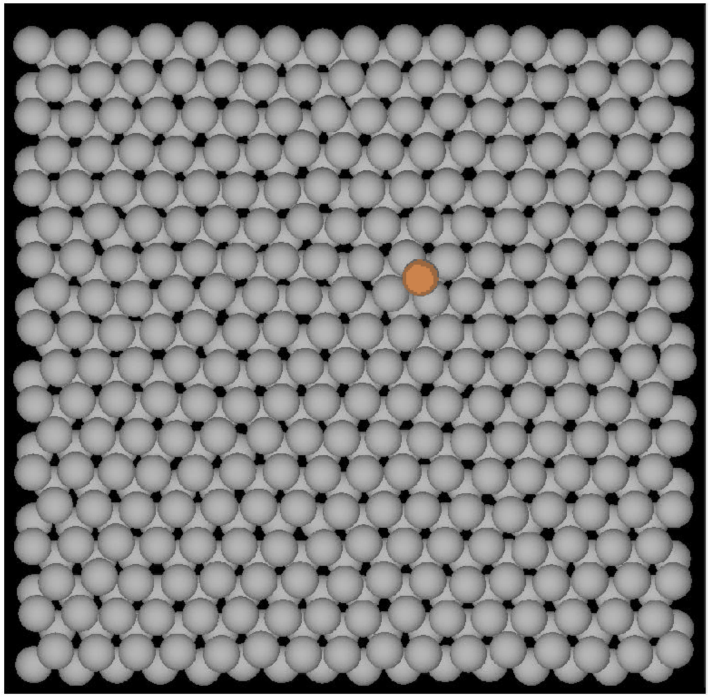
3D Multilayer Growth Mode



Typical 2D, layer-by-layer growth mode

Homoepitaxial Pt(111) growth from hyperthermal atoms





Time 0.0 ns

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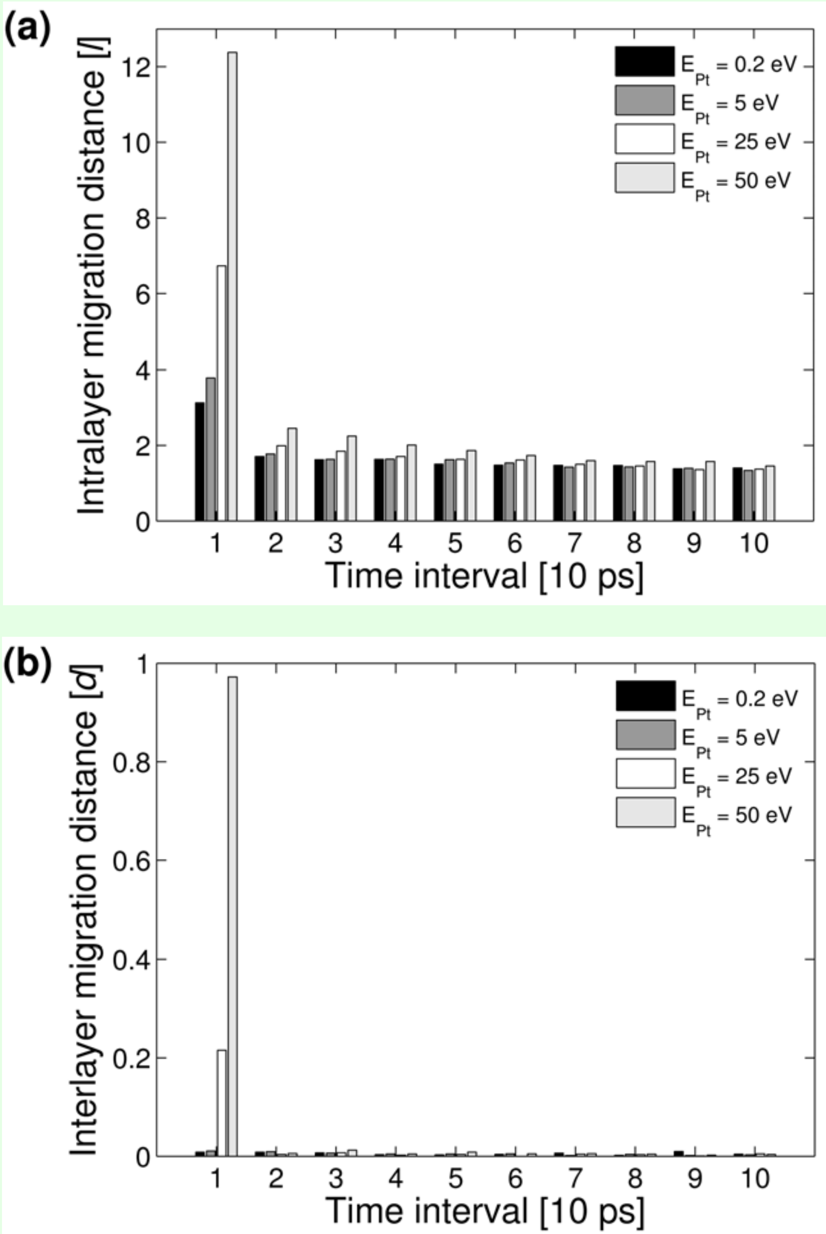
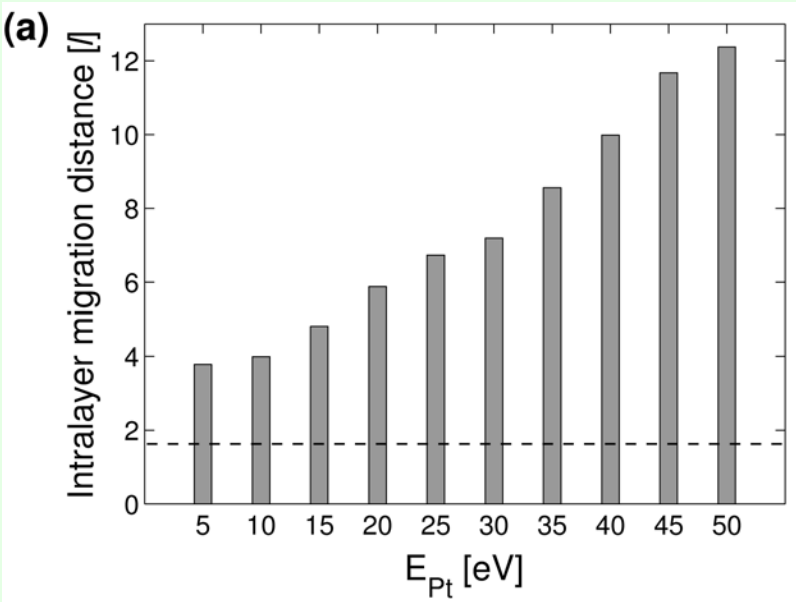
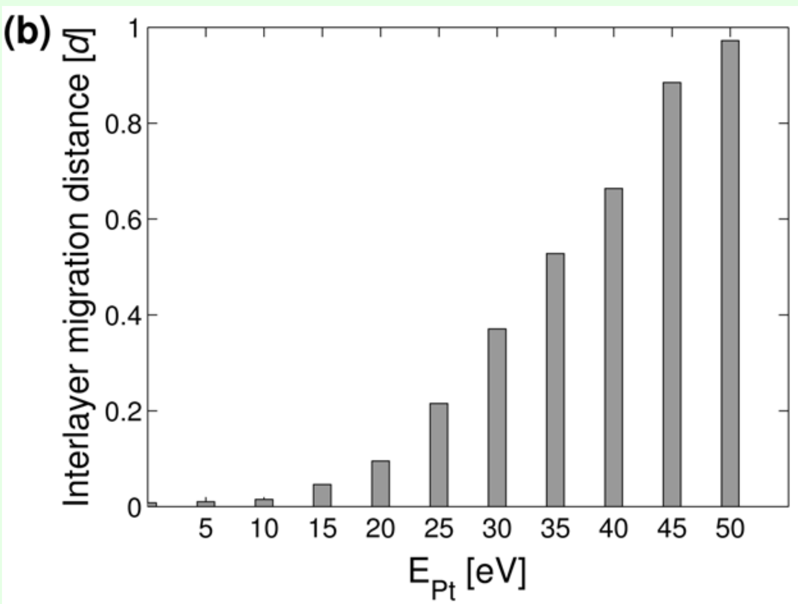


Average mass transport

- Overall mass transport dominated by events in the **first 10 ps**.
- Atomic migration in the first 10 ps interval is strongly correlated to E_{Pt}. **Irradiation interval**.
- Migration in the remaining 10 ps intervals is independent of E, rather f(T). **Thermal period**.
- Trend is observed at all energies.





The 1st 10 ps! Irradiation-induced mass transport

- Intralayer migration increases by a factor of ~ 2x, when E_{Pt} increases from 5 eV to 20 eV.
- Thermal component in the irradiation interval identified by eliminating atoms not directly involved in collisions (dotted line in Fig.a).
- Interlayer migration increases by a factor of ~ 5x, when E_{Pt} increases from 5 eV to 20 eV.

Quantification: **1^{st} 10 ps** vs. **thermal** mass transport

$$\rho = d_1/(d_2 + d_3 + \ldots + d_n)$$

$$r = d_1/\bar{d}_n ; \bar{d}_n = (d_2 + d_3 + \ldots + d_n)/n$$

d_1 – 1^{st} 10 ps interval

$d_2 \ldots d_n$ – all other 10 ps intervals

	Intralayer mass transport		Interlayer mass transport	
E_{Pt}(eV)	**ρ_{intra}**	**r_{intra}**	**ρ_{inter}**	**r_{inter}**
5	0.27	2.47	0.27	2.45
25	0.47	4.19	7.49	67.57
50	0.75	6.75	19.34	174.05

Kinetic Pathways promoting layer-by-layer growth

- Adatom scattering, surface channeling, dimer formation – all energies[1].

[1] D. Adamovic et. al., APL **86**, 211915 (2005)

[2] D. Adamovic et. al., TSF **515**, 2235 (2006)

Kinetic Pathways promoting layer-by-layer growth

- Adatom scattering, surface channeling, dimer formation – all energies[1].

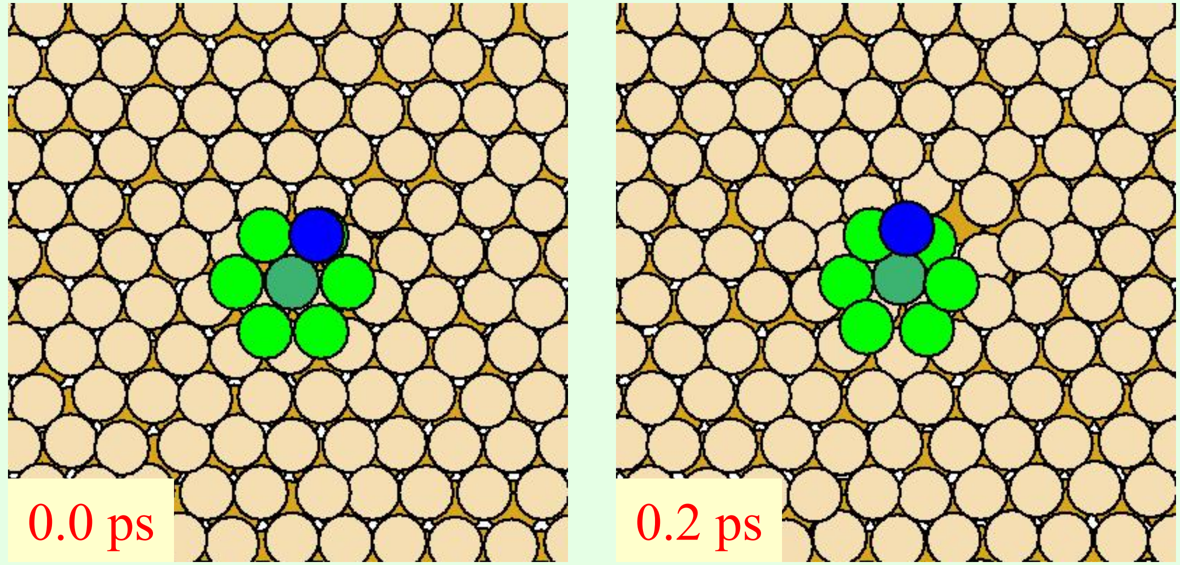
- Onset of significant interlayer migration at $E_{Pt} \geq 15$ eV[1,2].

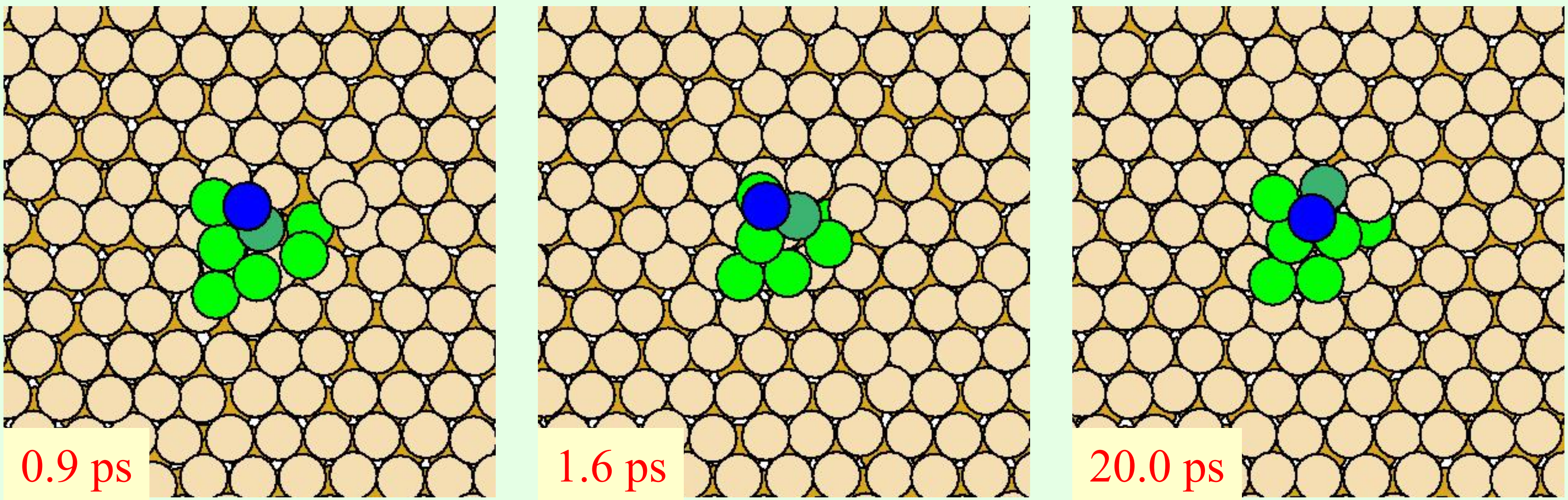
[1] D. Adamovic et. al., APL **86**, 211915 (2005)

[2] D. Adamovic et. al., TSF **515**, 2235 (2006)

Typical ion-induced exchange (interlayer) event

Cluster size: Pt_7
Impact energy: 30 eV
Impact area: Rim





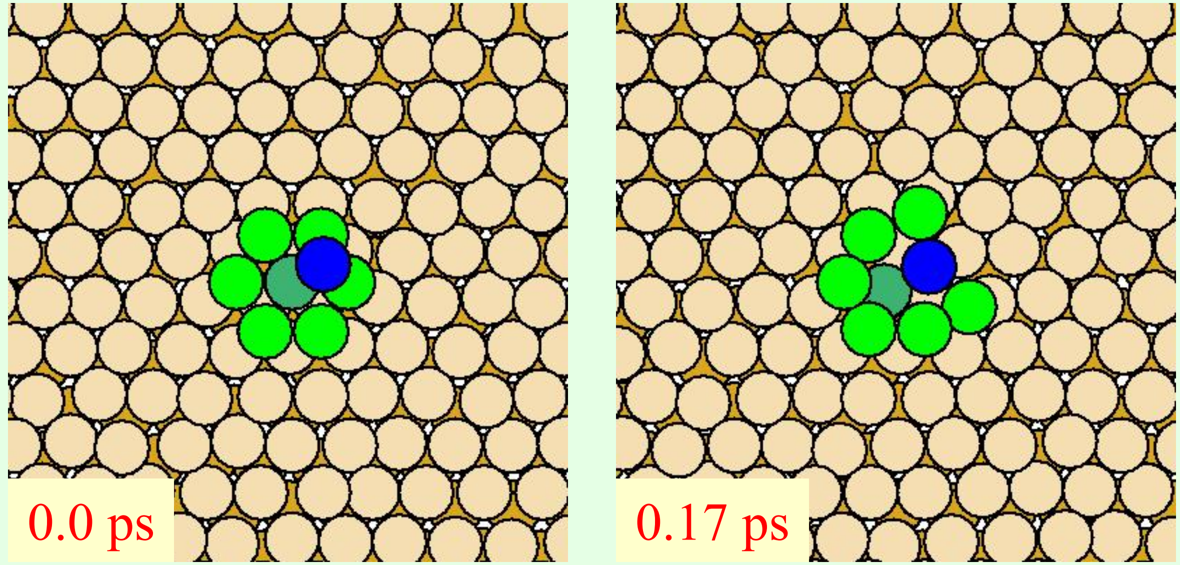
Kinetic Pathways promoting layer-by-layer growth

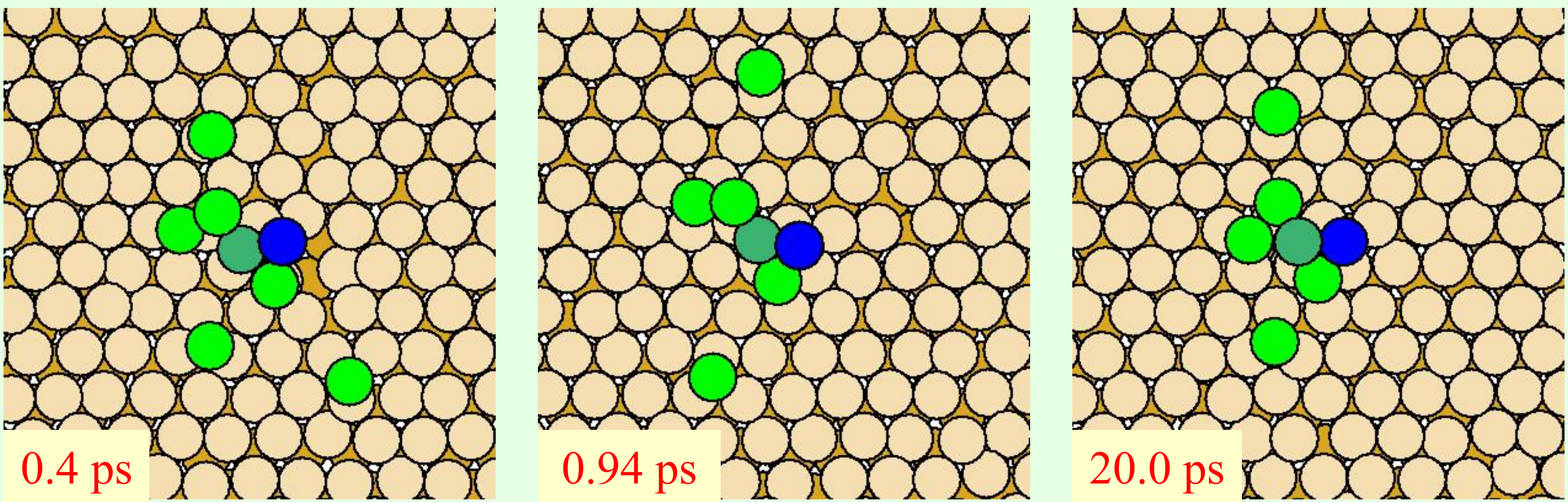
- Adatom scattering, surface channeling, dimer formation – all energies[1].
- Onset of significant interlayer migration at $E_{Pt} \geq 15$ eV[1,2].
- Cluster disruption observed from $E_{Pt} \geq 20$ eV[1,2].

[1] D. Adamovic et. al., APL **86**, 211915 (2005)
[2] D. Adamovic et. al., TSF **515**, 2235 (2006)

Typical cluster disruption event

Cluster size: Pt_7
Impact energy: 50 eV
Impact area: Rim





Kinetic Pathways promoting layer-by-layer growth

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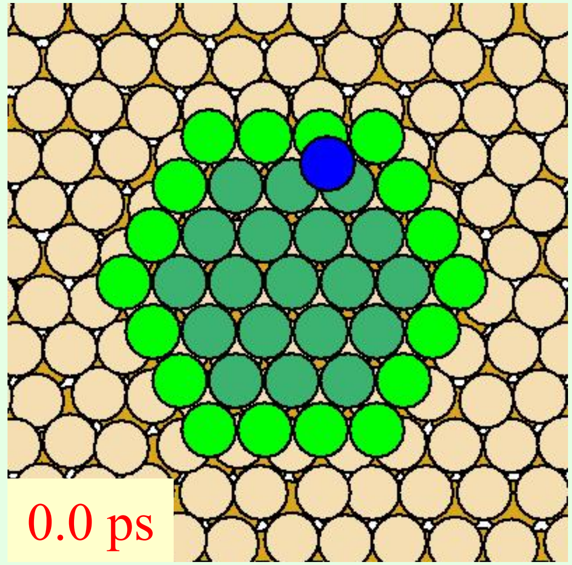
- Probability of 3D island formation decreases with increasing E_{Pt}[2].

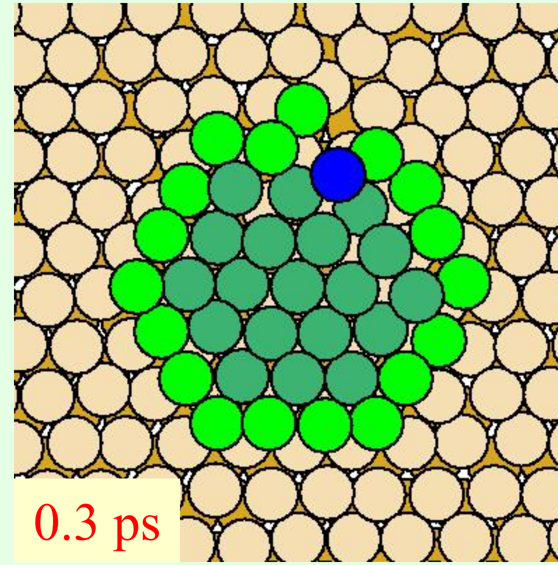
[1] D. Adamovic et. al., APL **86**, 211915 (2005)

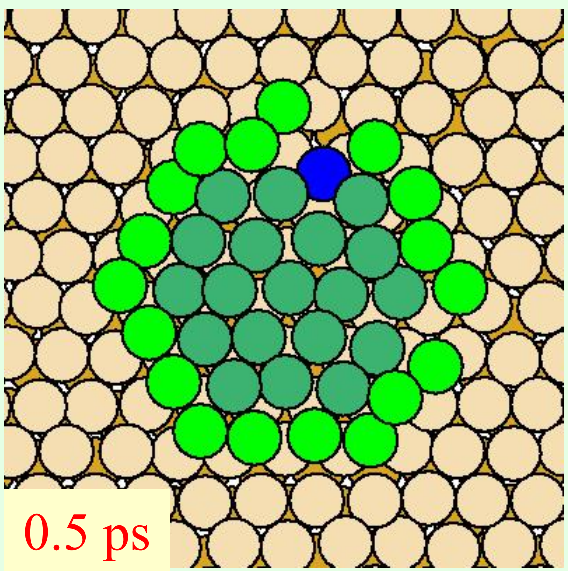
[2] D. Adamovic et. al., TSF **515**, 2235 (2006)

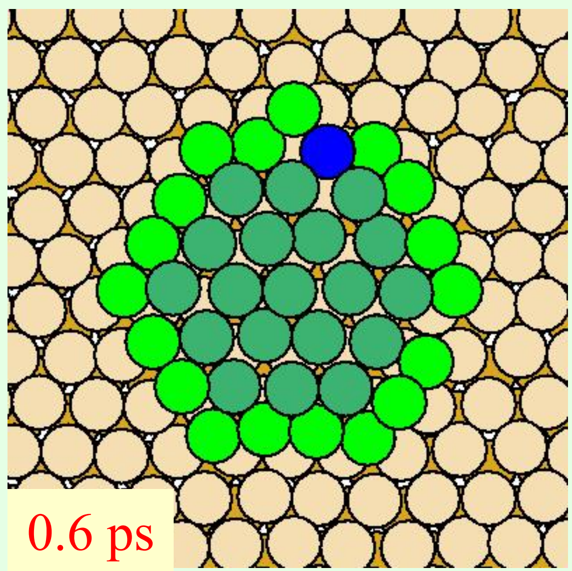
Typical adatom incorporation event

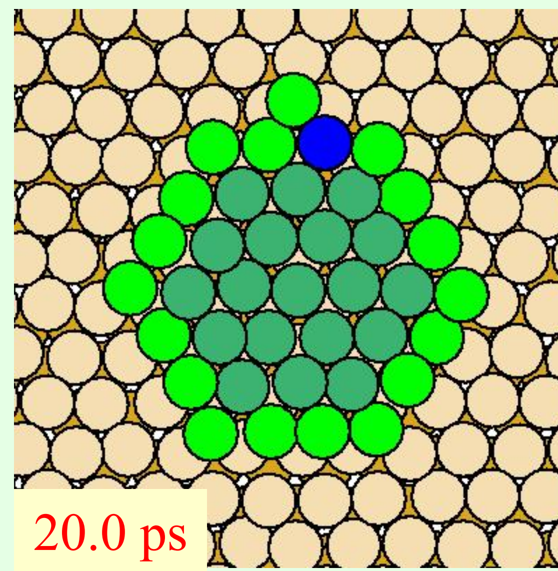
Cluster size: Pt_{37}
Impact energy: 25 eV
Impact area: Rim











Kinetic Pathways promoting layer-by-layer growth

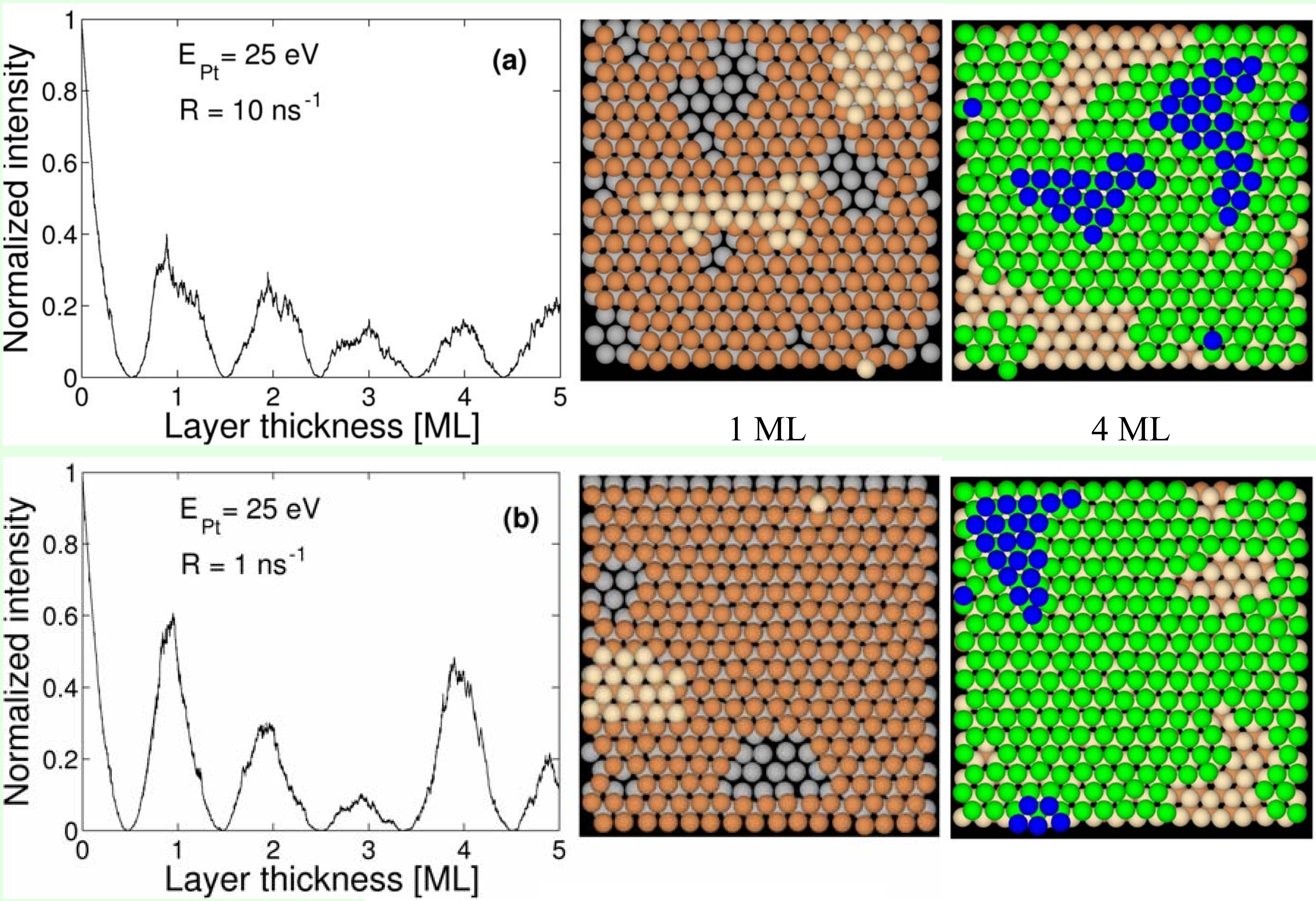
- Adatom scattering, surface channeling, dimer formation – all energies[1].
- Onset of significant interlayer migration at $E_{Pt} \geq 15$ eV[1,2].
- Cluster disruption observed from $E_{Pt} \geq 20$ eV[1,2].
- Probability of 3D island formation decreases with increasing E_{Pt}[2].
- The combination of all these irradiation-induced effects, **in the 15-20 eV energy interval,** → transition from 3D multilayer to 2D layer-by-layer growth.

[1] D. Adamovic et. al., APL **86**, 211915 (2005); TSF **515**, 2235 (2006)

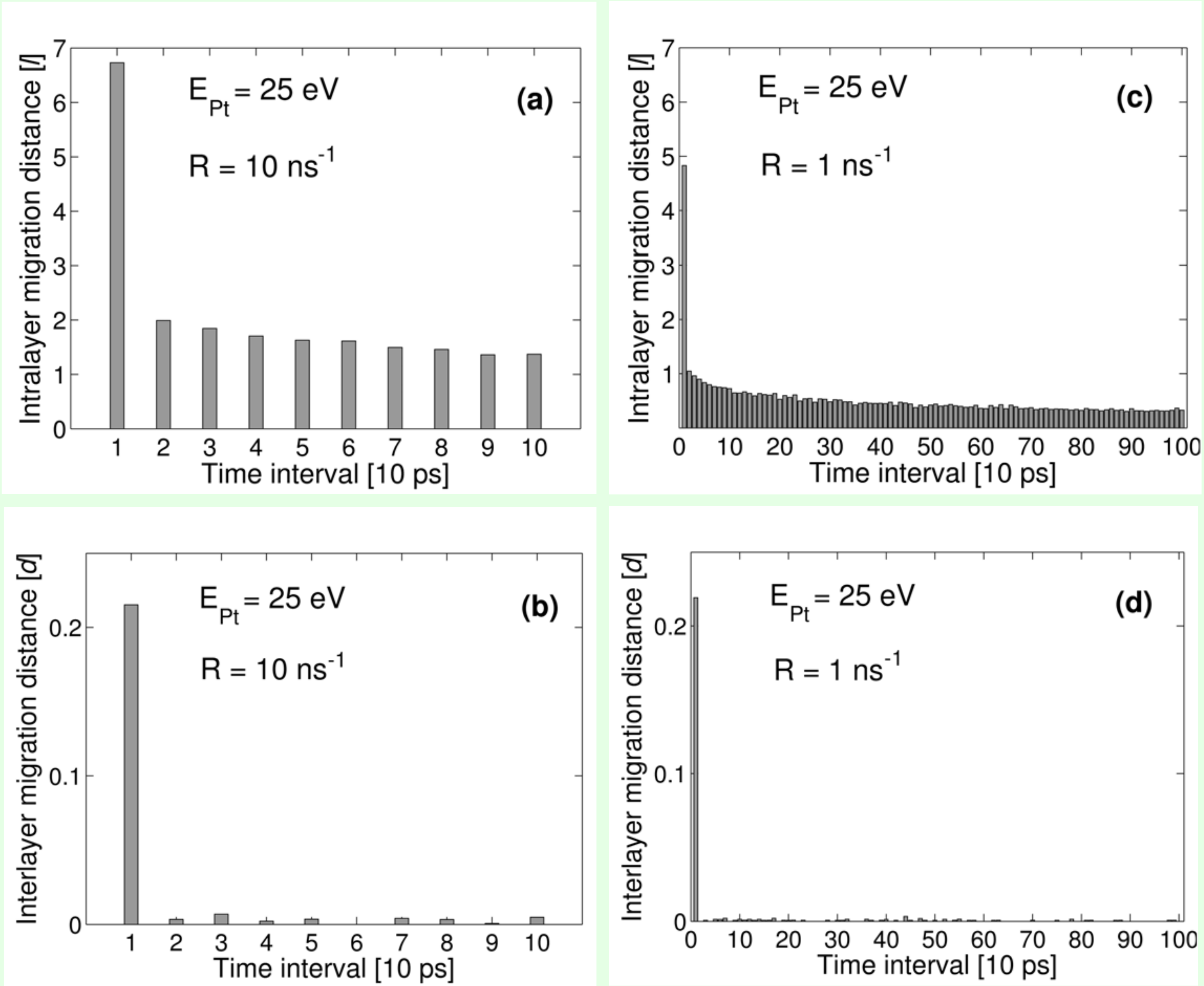
[2] D. Adamovic et. al., PRB (in press)

Test against inherent MD limitations

- Typical MD simulations of film growth use very high fluxes leading to unrealistic deposition rates (10^4 to 10^6 or more higher).
- We deposit 5 ML, at 25 eV and R = 1 ns^{-1}, flux rate only 10^2 > EB-PVD.
- Single MD run, 1.5 μs-long, spanning 1.5×10^9 time steps.
- First attempt to simulate deposition in a fully deterministic manner at deposition rates approaching experimental values.



Normalized intensity
Layer thickness [ML]
E_{Pt} = 25 eV
R = 10 ns^{-1}
(a)
E_{Pt} = 25 eV
R = 1 ns^{-1}
(b)
1 ML
4 ML



(a)
E_{Pt} = 25 eV
R = 10 ns^{-1}
Intralayer migration distance [*l*]
Time interval [10 ps]
(b)
E_{Pt} = 25 eV
R = 10 ns^{-1}
Interlayer migration distance [*d*]
Time interval [10 ps]
(c)
E_{Pt} = 25 eV
R = 1 ns^{-1}
Intralayer migration distance [*l*]
Time interval [10 ps]
(d)
E_{Pt} = 25 eV
R = 1 ns^{-1}
Interlayer migration distance [*d*]
Time interval [10 ps]

Use of realistic (lower MD) deposition rates

- Irradiation-induced mass transport unaffected as R decreases by 10x.
- Decreases by **2x** in intralayer, and **7x** in interlayer mass transport.
- Longer times for thermal accommodation:
  - significant increase in number of nucleation and coalescence events
  - fewer itinerant adatoms & fewer but larger 2D clusters
  - reduced probability for interlayer exchanges in the thermal period.
- **Mass transport is still dominated by events occurring in first 10 ps.**

Quantification: 1st 10 ps vs deposition rates

$$\rho = d_1/(d_2 + d_3 + \ldots + d_n)$$

$$r = d_1/\bar{d}_n ; \bar{d}_n = (d_2 + d_3 + \ldots + d_n)/n$$

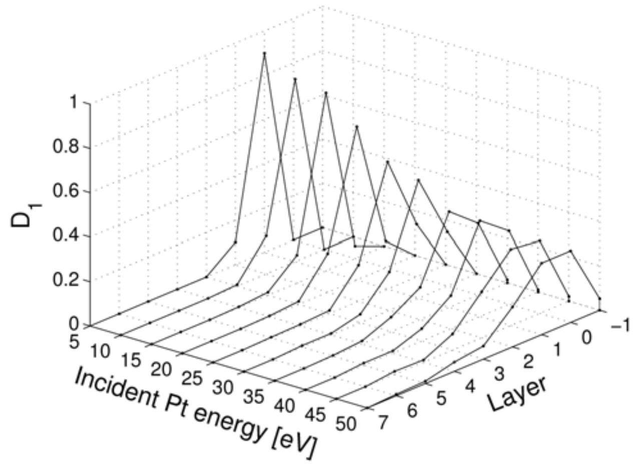
d_1 – 1st 10 ps interval

$d_2 \ldots d_n$ – all other 10 ps intervals

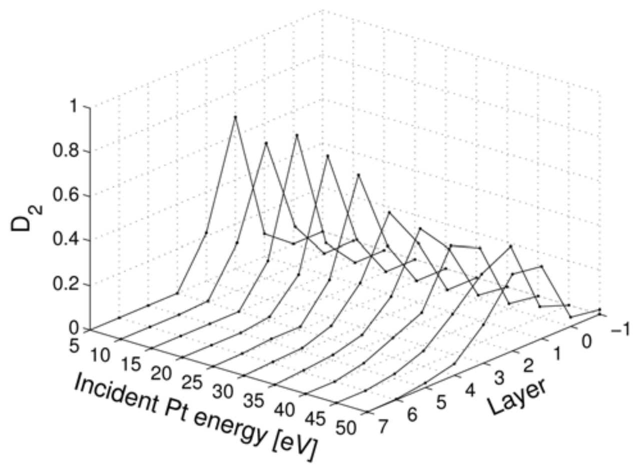
	Intralayer mass transport		Interlayer mass transport	
R (ns^{-1})	ρ_{intra}	r_{intra}	ρ_{inter}	r_{inter}
10	0.47	**4.19**	7.49	**67.57**
1	0.10	**10.39**	4.86	**481.15**

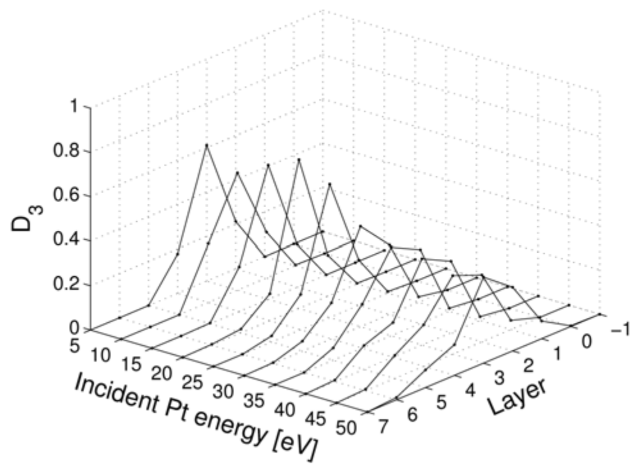
Obs: **Very significant increases in r_{intra} (~2x) and r_{inter} (~7x)!**
Still 10^2 – 10^4 off real deposition rates!!!

Atomic distribution in deposited layers

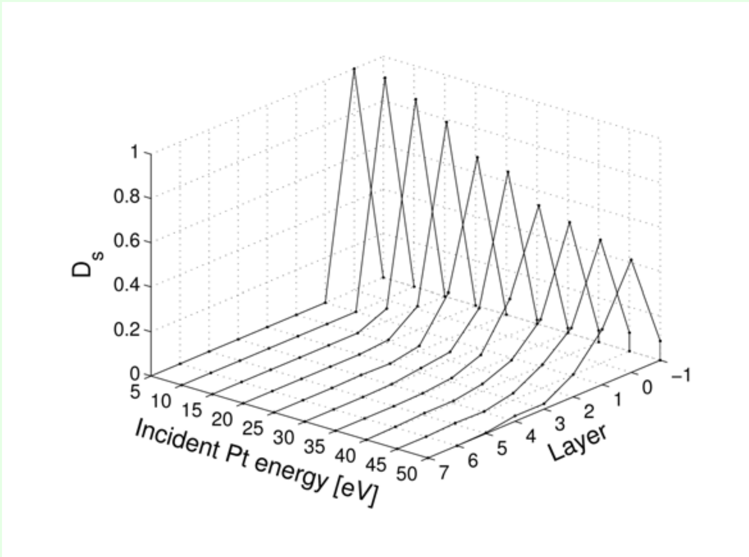


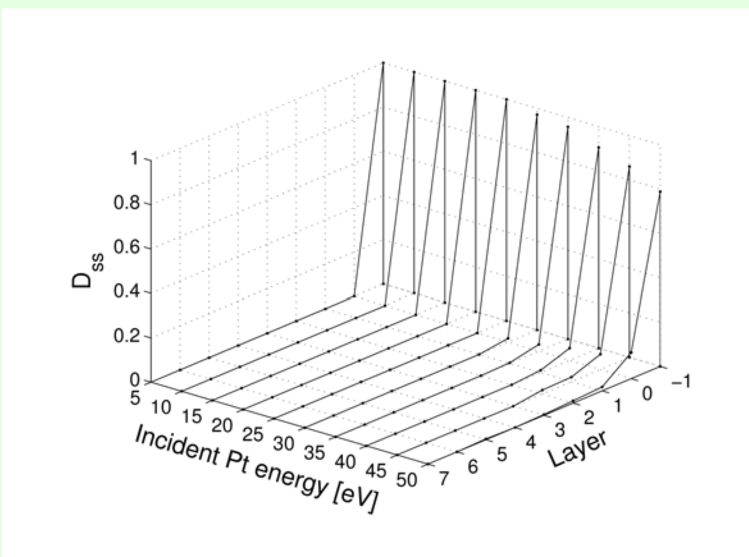
- Broader distributions and lower peacks for higher energies and sequentially deposited layers.
- Signature of mass transport leading to 2D growth





Interlayer Mass Transport

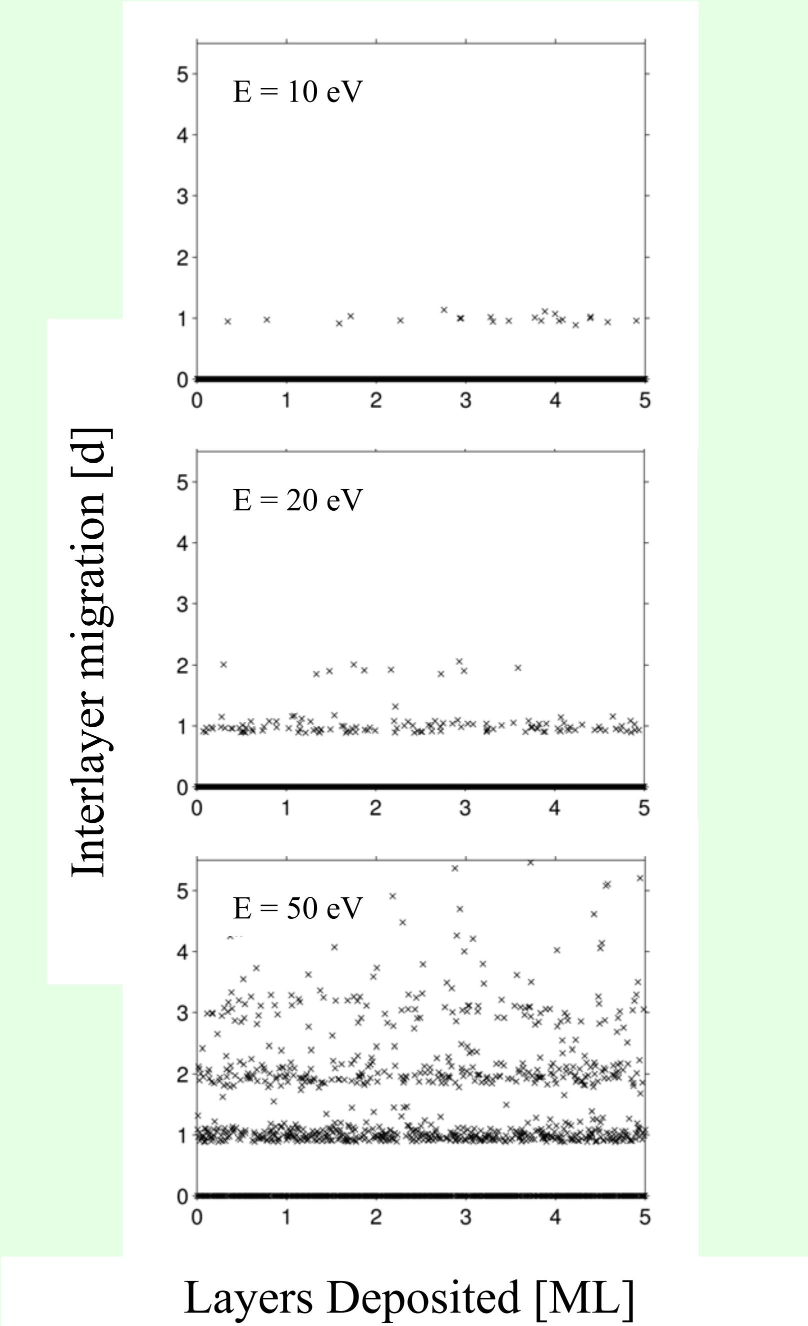




Atomic distribution in substrate

- 10 eV – No interlayer exchange with topmost substrate layer.
- 20 eV – interlayer exchanges are triggered.
- 50 eV – 50% of atoms in topmost substrate layer move upwards, up to the 5th deposited layer.
- Similar but much weaker behaviour in next substrate layer.
- 50 eV – 80% of atoms remain in their original lattice positions.

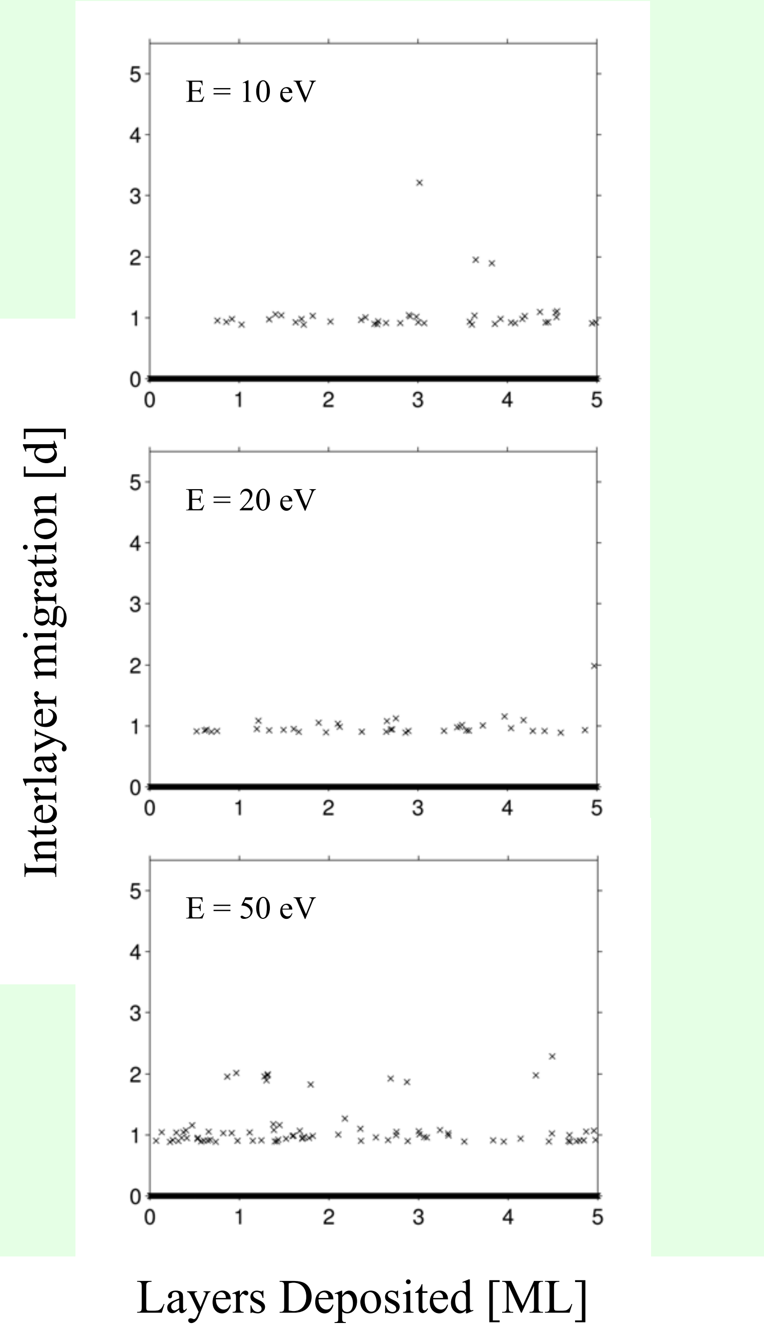
Interlayer Mass Transport



Irradiation Interval = 1st 10 ps

- Strong dependence on irradiation energy.
- 10 eV – 2% of atoms contribute to interlayer migration events.
- 20 eV – increase by a factor of 5 compared to 10 eV.
- 50 eV – 50% of atoms are involved in interlayer migration events.

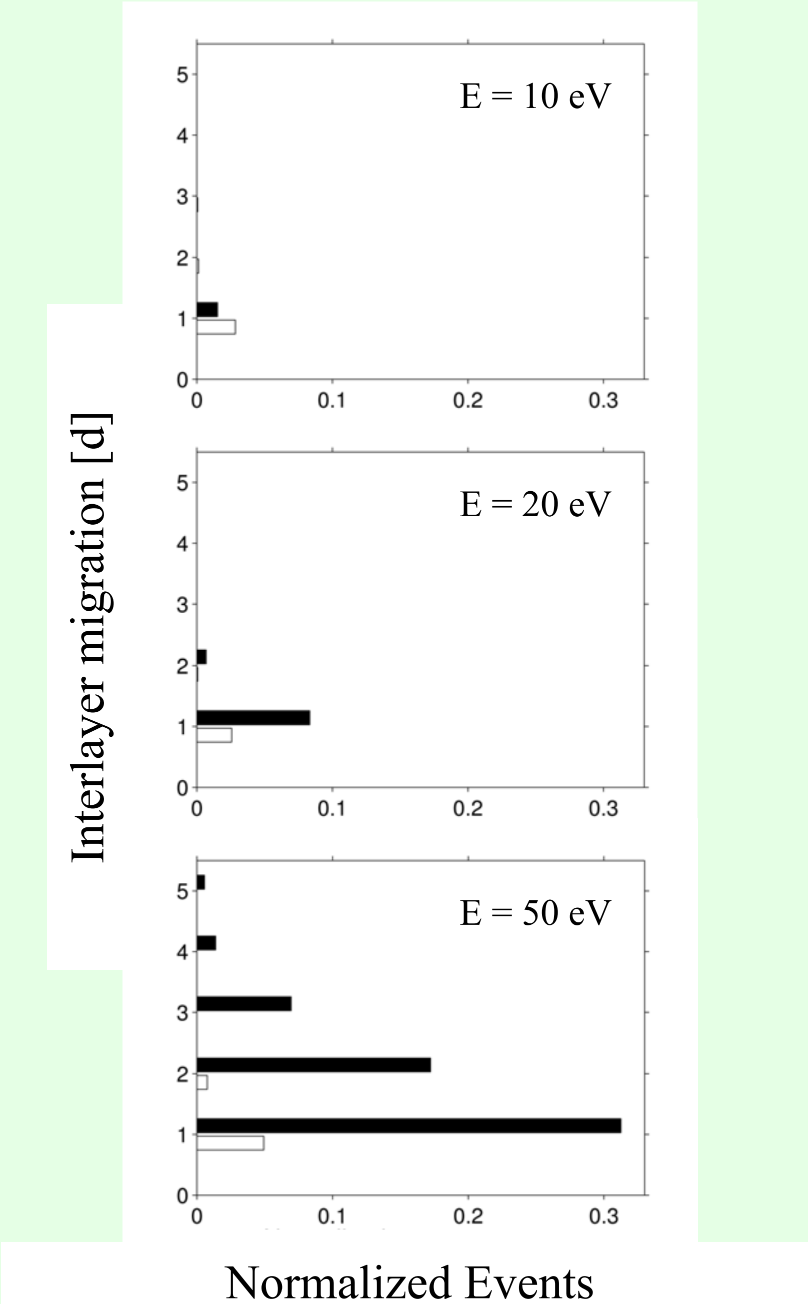
Interlayer Mass Transport



Thermal Period

- Energy dependence is considerably weaker in the 10 to 20 eV interval.
- 50 eV – increase by a factor of 3 compared to 10 or 20 eV.
- Migration over 1*d* dominates during the thermal tail.
- Most events involve the exchange between incident and surface atoms.

Interlayer Mass Transport

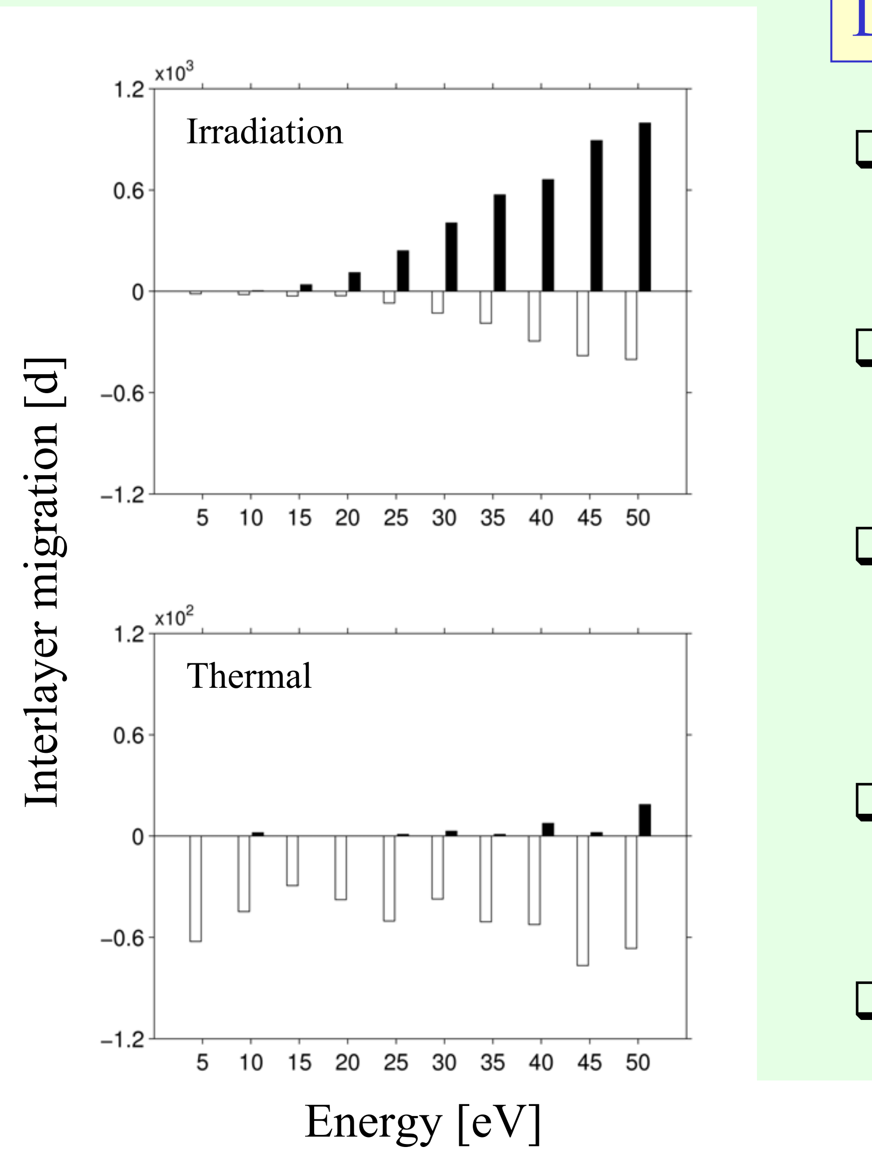


Total interlayer migration

- **Irradiation** = Black bars.
- **Thermal** = White bars.
- 10 eV – only 1*d* events.
- 50 eV – full spectrum of migrations events.
- 50 eV – irradiation induced part increases by ~ 100.

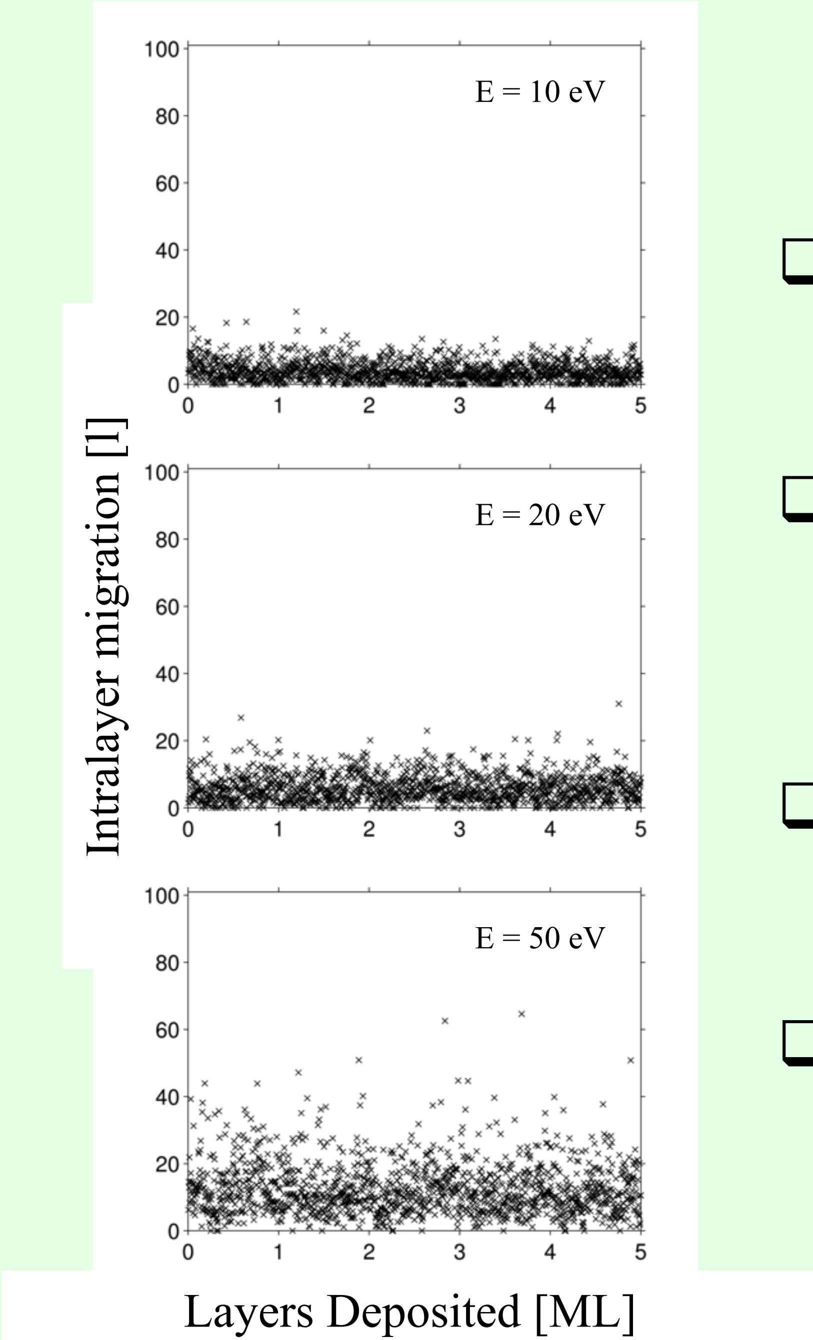
Interlayer Mass Transport

Directional interlayer migration



- Black bars = Migration in the upward direction.
- White bars = Migration in the downward direction.
- Starting from 20 eV, upward migration dominates in the irradiation interval.
- Downward migration dominates during the thermal tail.
- One order of magnitude difference between irradiation and thermal components.

Interlayer Mass Transport

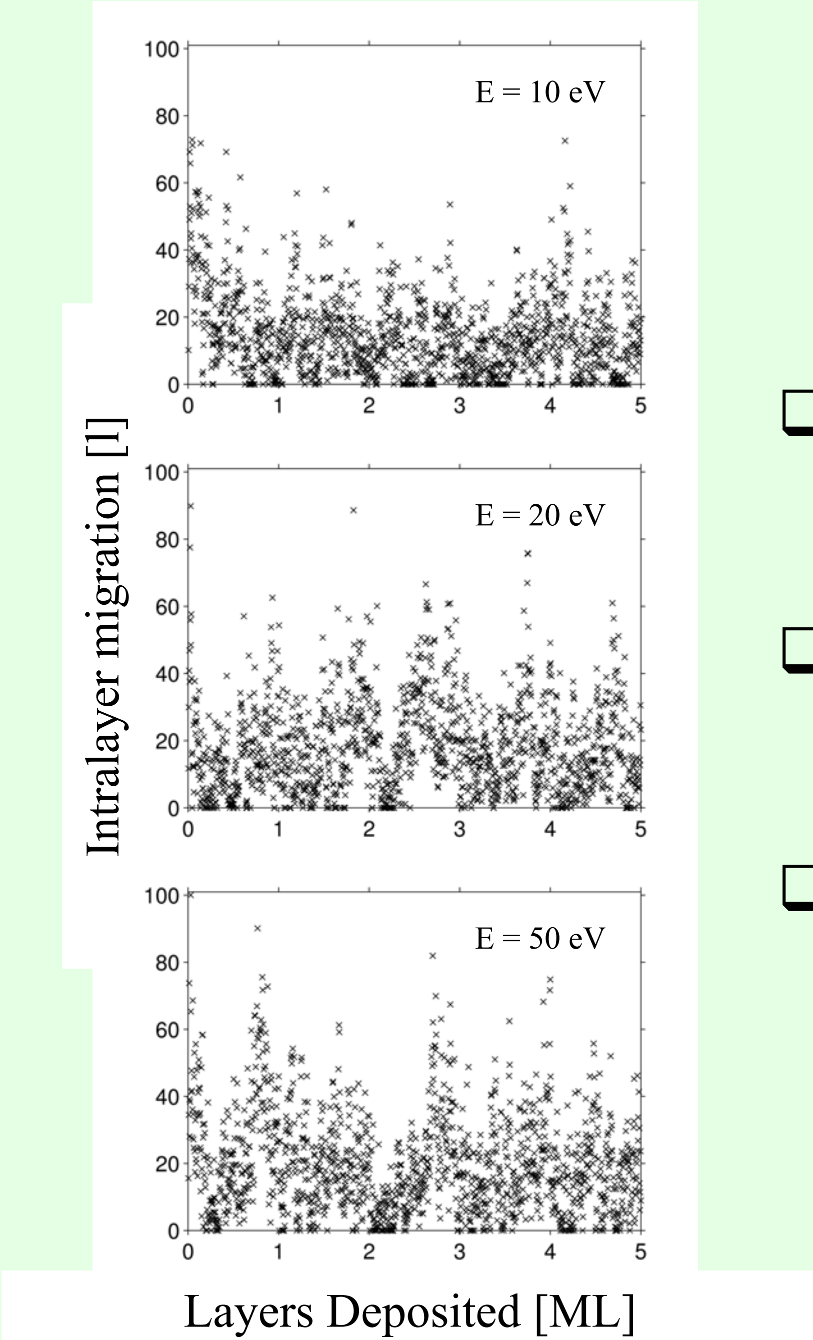


Irradiation Interval = 1st 10 ps

- 90% of atoms involved in intralayer events.
- 10 eV – most impacts result in migration with less than 10 fcc-hcp (*l*) distances.
- 20 eV – migration distance is almost double.
- 50 eV – large migration distances primarily due to scattering and cluster disruption.

Intralayer Mass Transport

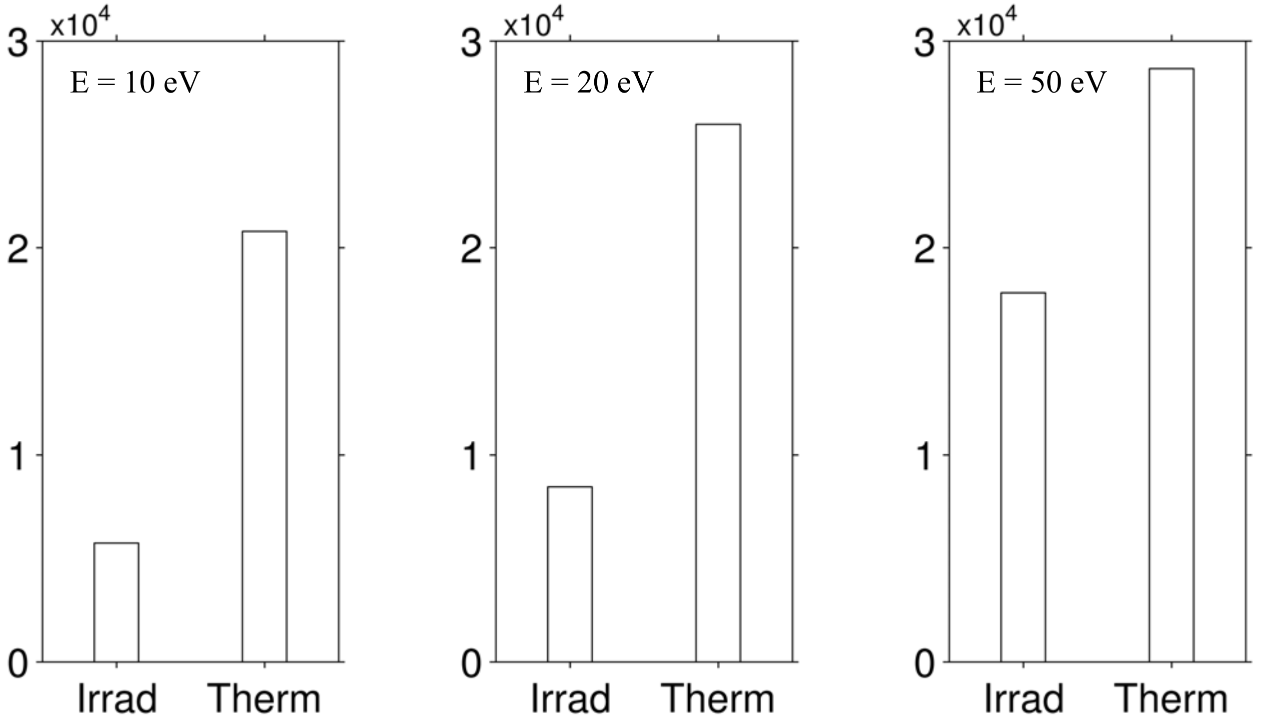
Thermal Period



- Significantly larger migration distances at all energies.
- Expected effect at the temperature chosen for the MD experiment.
- A decrease in temperature would lead to an exponential decrease in intralayer mass transport.

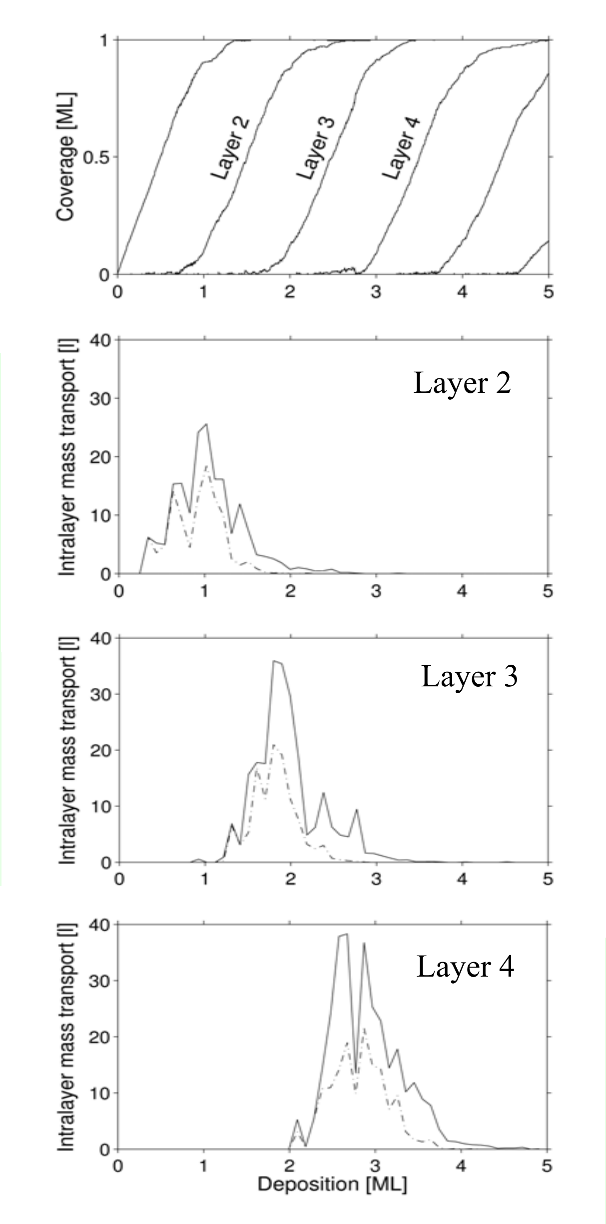
Intralayer Mass Transport

Total intralayer migration



Intralayer Mass Transport

Layer-by-layer growth at 20 eV

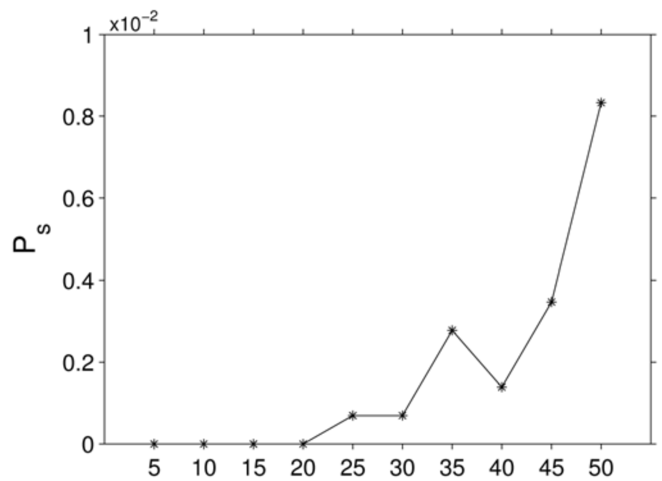


- Intralayer activity is strongly correlated to layer coverage.
- Maximum intralayer transport is observed at coverages of 0.05 ML, in agreement with experiments[1].
- Significant adatom contribution to intralayer migration – dotted lines.

[1] T. Michely, G. Comsa et. al., Surf. Sci. **365**, 187 (1996)

Intralayer Mass Transport

Sputtering Probability



- Calculated as the ratio of atoms out of interaction range after 5ML and total number of atoms deposited.
- No sputtering observed up to ~ 20 eV.
- Exponential increase up to 50 eV.
- Overall still under 1% probability.

Conclusions

- Multi-billion time step MD of homoepitaxial growth from low-energy (E_{Pt} = 5-50 eV) hyperthermal Pt atoms and thermal beams (E_{Pt} = 0.2 eV).
- Transition from 3D multilayer toward 2D layer-by-layer growth is observed at $E_{Pt} \geq 20$ eV. Layer-by-layer growth is maintained until 50 eV.
- Simulations allow to isolate with unprecedented accuracy irradiation-induced and thermally-activated effects on mass transport rates.
- **Irradiation-induced** processes occurring during **the first 10 ps** following the arrival of each hyperthemal atom are determinant in promoting 2D growth.
- Primary kinetic pathways:
  - ion-induced exchange of atoms between layers (interlayer)
  - direct incorporation of energetic atoms into clusters
  - cluster disruption

Conclusions

- Mass transport is strongly correlated to the deposition energy:
  - Interlayer migration increases by two orders of magnitude (5 – 50 eV).
  - Intralayer migration increases by a factor of 3 in same interval.
- At 20 eV, upward interlayer migration becomes the dominant process (adatom-vacancy pairs) while cluster disruption dominates intralayer migration.
- Maximum intralayer transport is observed at coverages of 0.05 ML. Single atoms play a major role in promoting 2D layer-by-layer growth.
- **Irradiation-induced** effects reported here are increasingly important at **low temperatures**, where thermal migration decays exponentially.
- These results are expected to be valid for most fcc(111) metal films.

D. Adamovic et. al., PRB **76**, 115418 (2007)