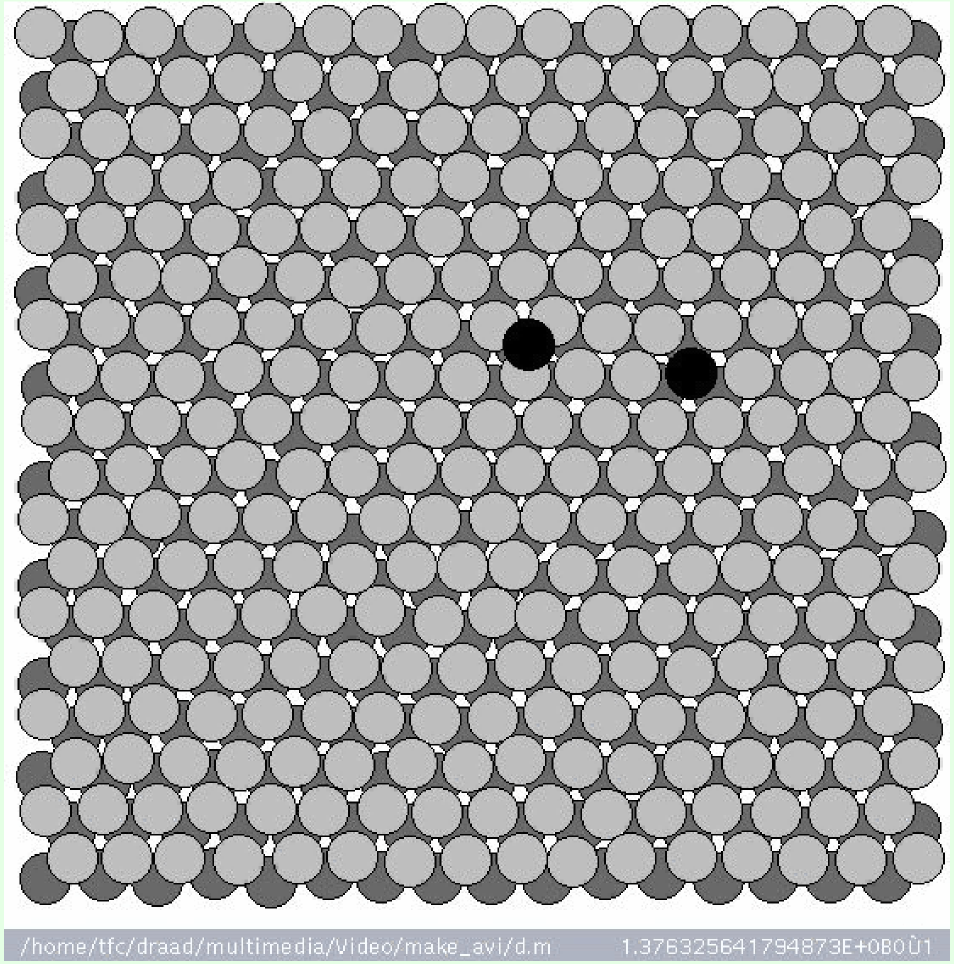
Applications of MD Simulations in Thin Film Physics

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**

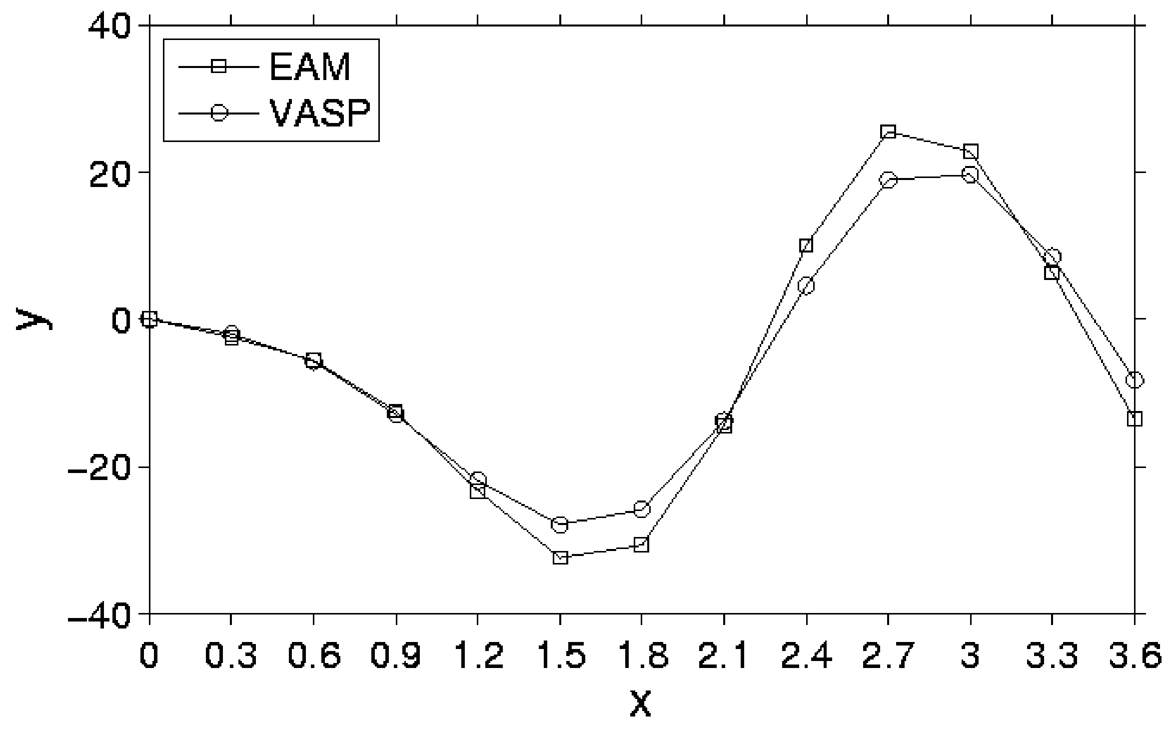
~ 0.24 eV/ additional atom (Pt_6 to Pt_{19})

Ir_6 ~ 1.00 eV (FIM)[1]

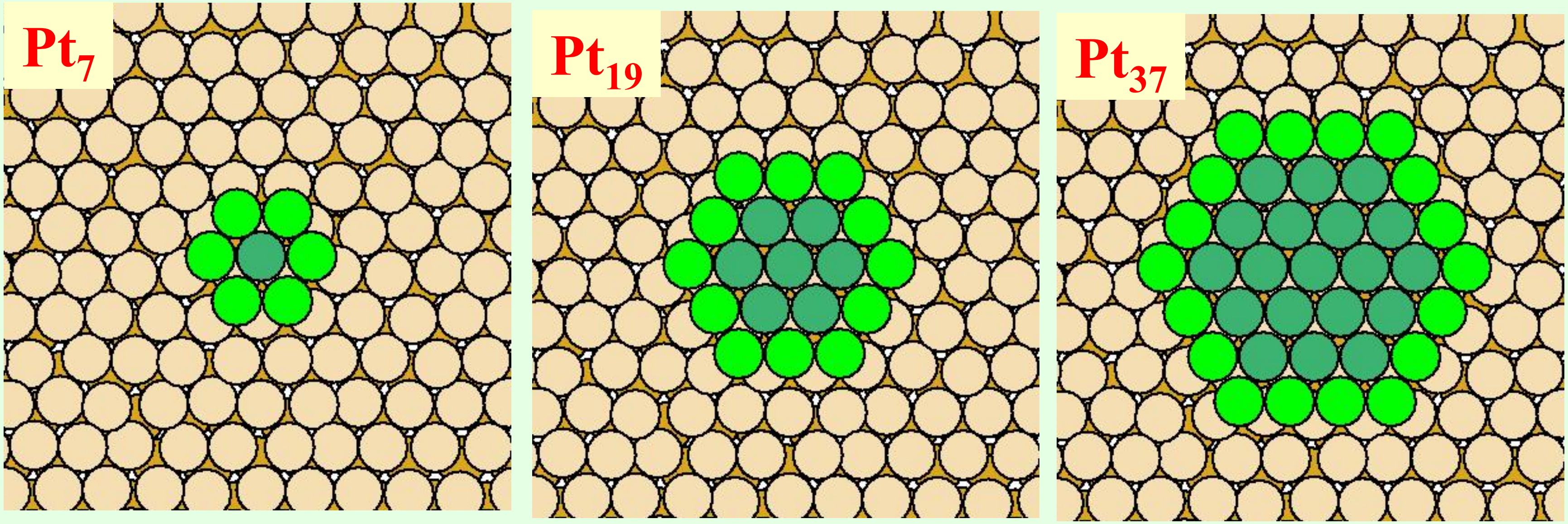
~ 0.20 eV/additional atom (FIM)[1]

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

Comparison of MD forces: EAM vs Ab-initio



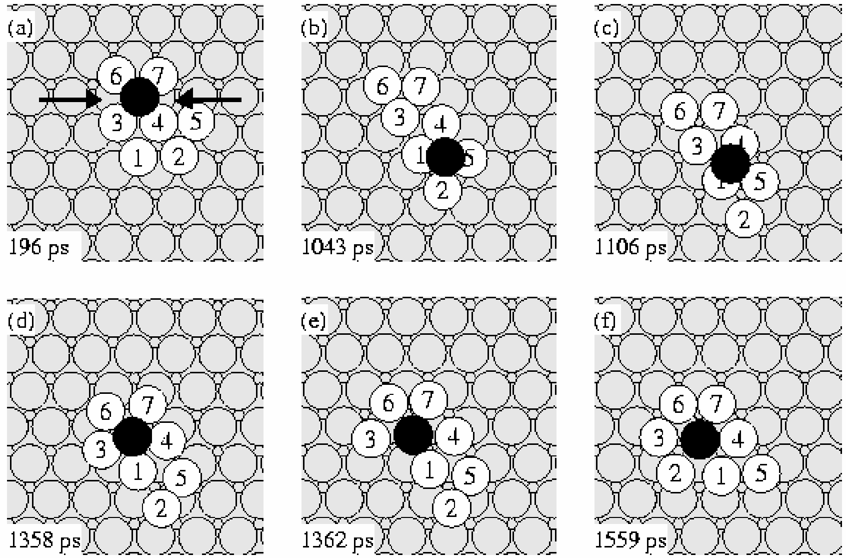
Typical clusters configurations

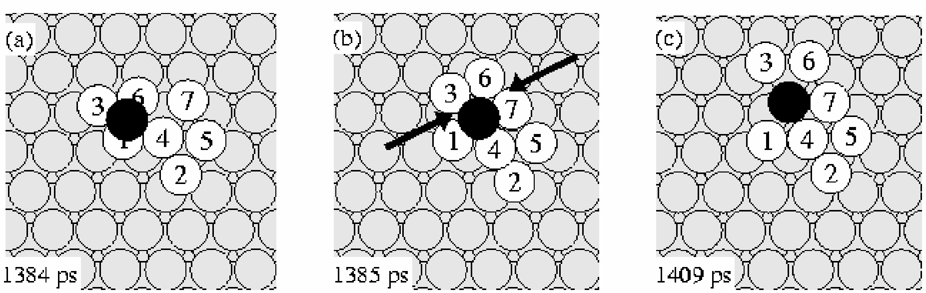


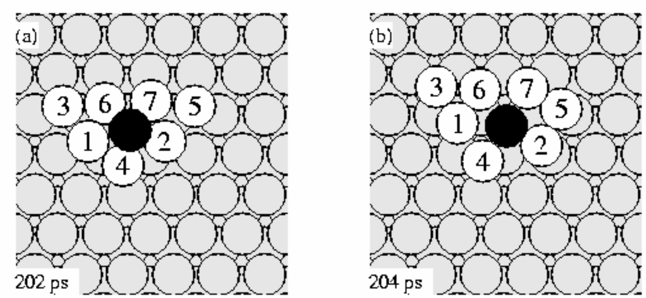
High diffusion and dissociation energy barriers

Most stable cluster configurations on (111) planes

Adatom – clusters interactions



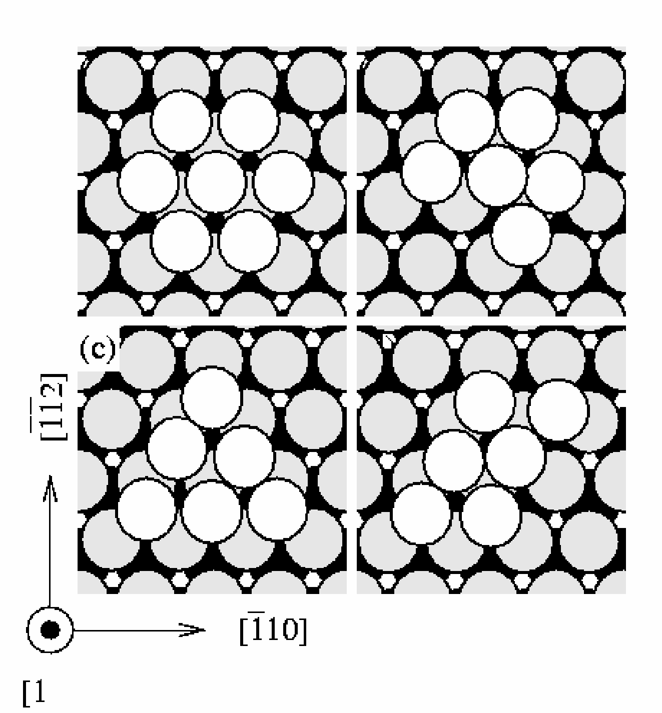


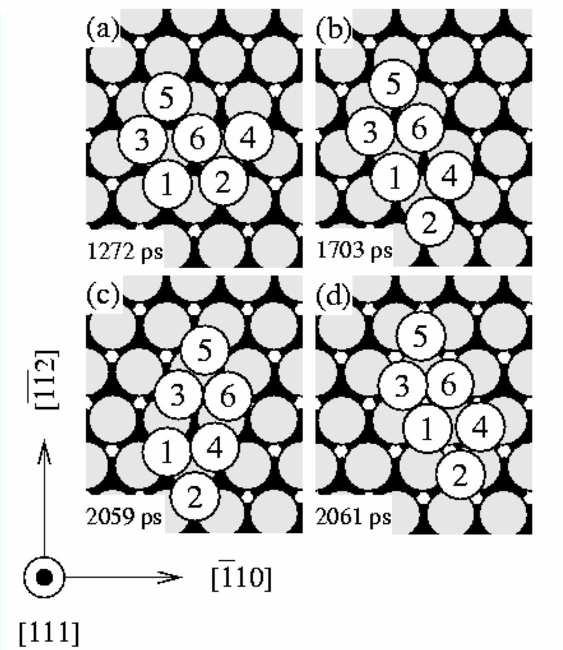


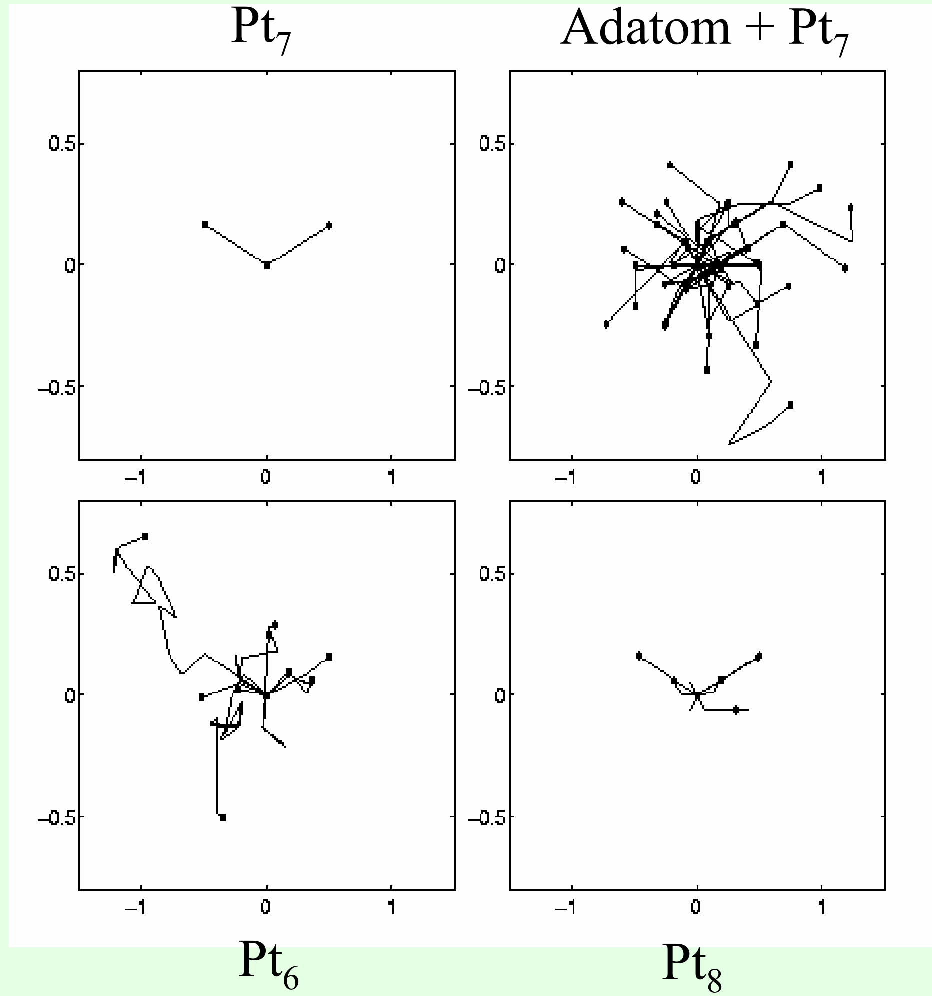
Münger et. al., *Surf. Sci.* **355**, L325 (1996)

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

Vacancy – clusters interactions

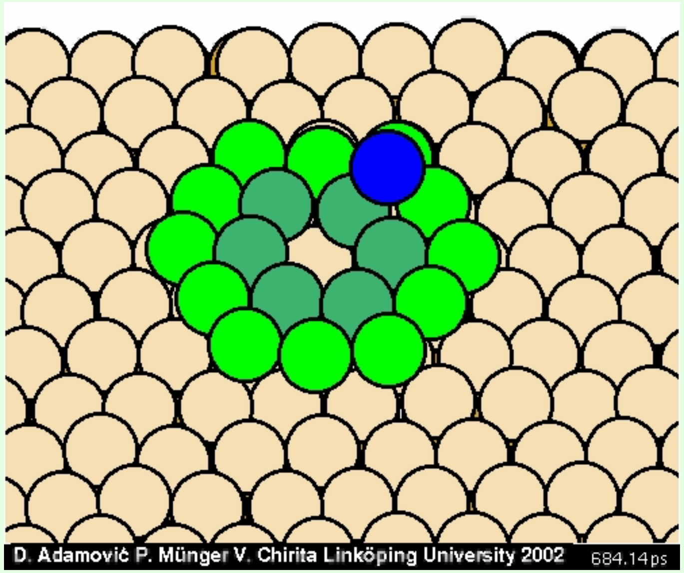


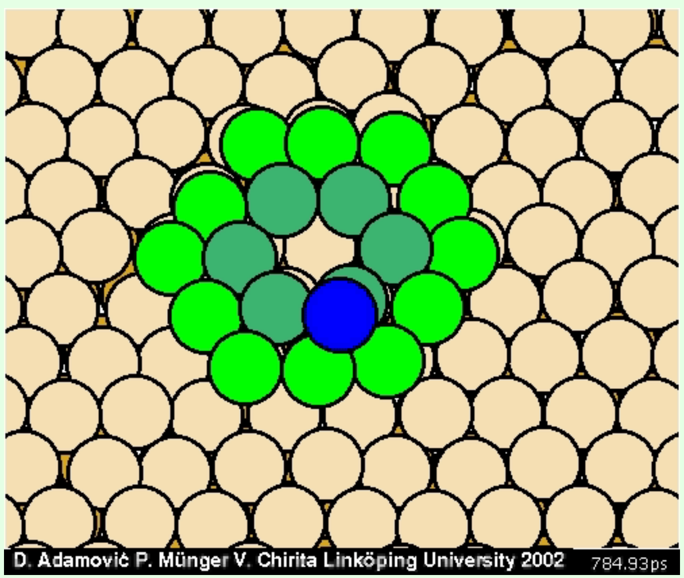


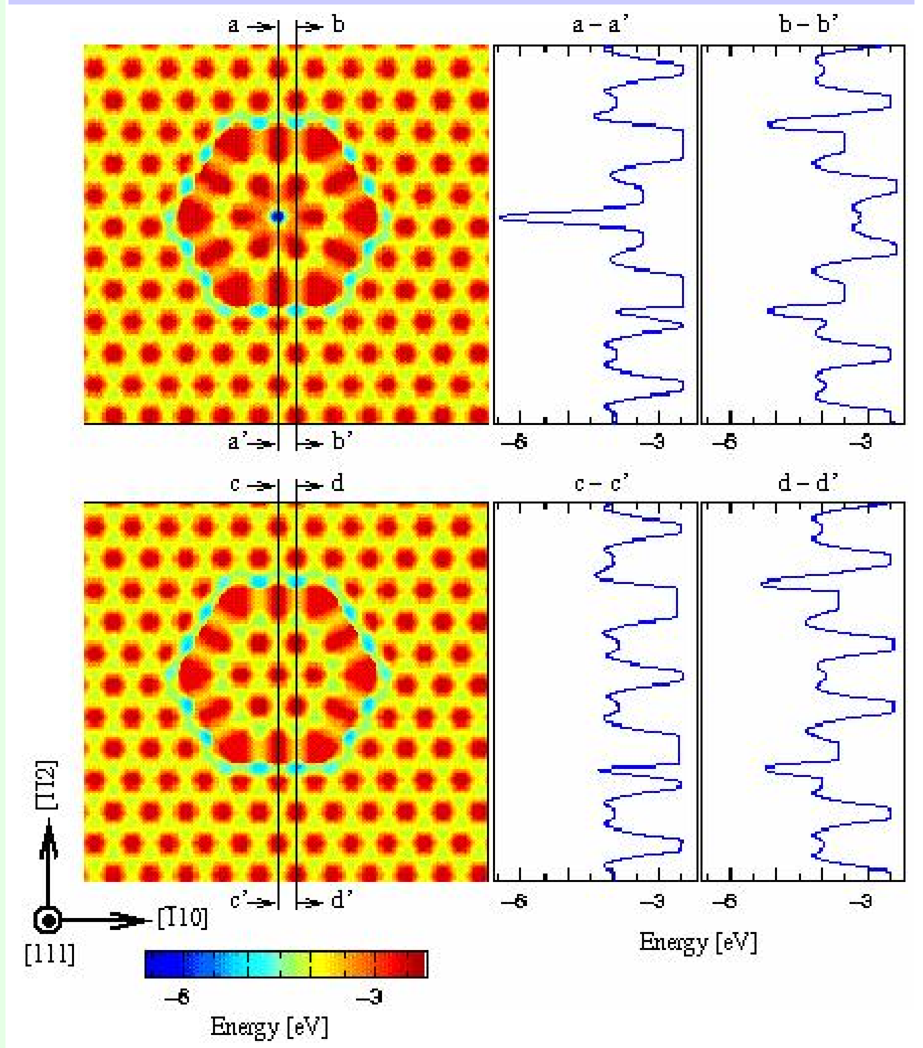


Münger et. al., *Surf. Sci.* 539, L567 (2003)

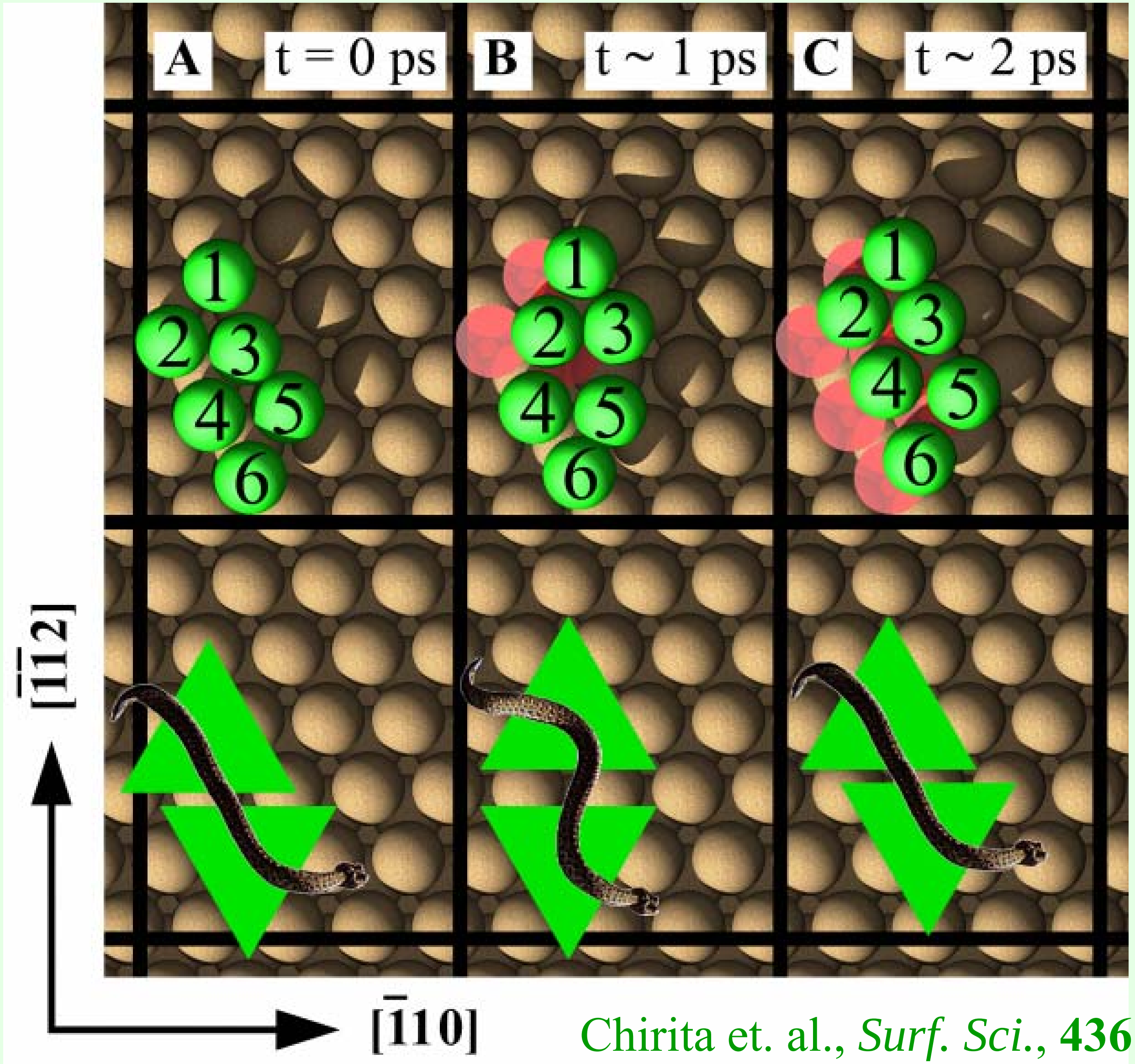
Adatom/vacancy pairs interactions on small clusters





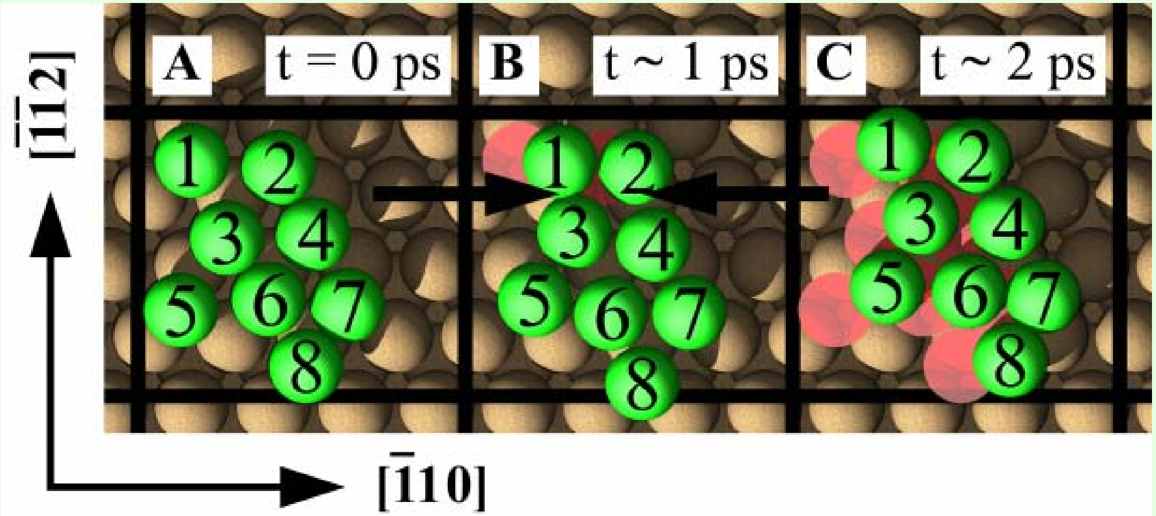


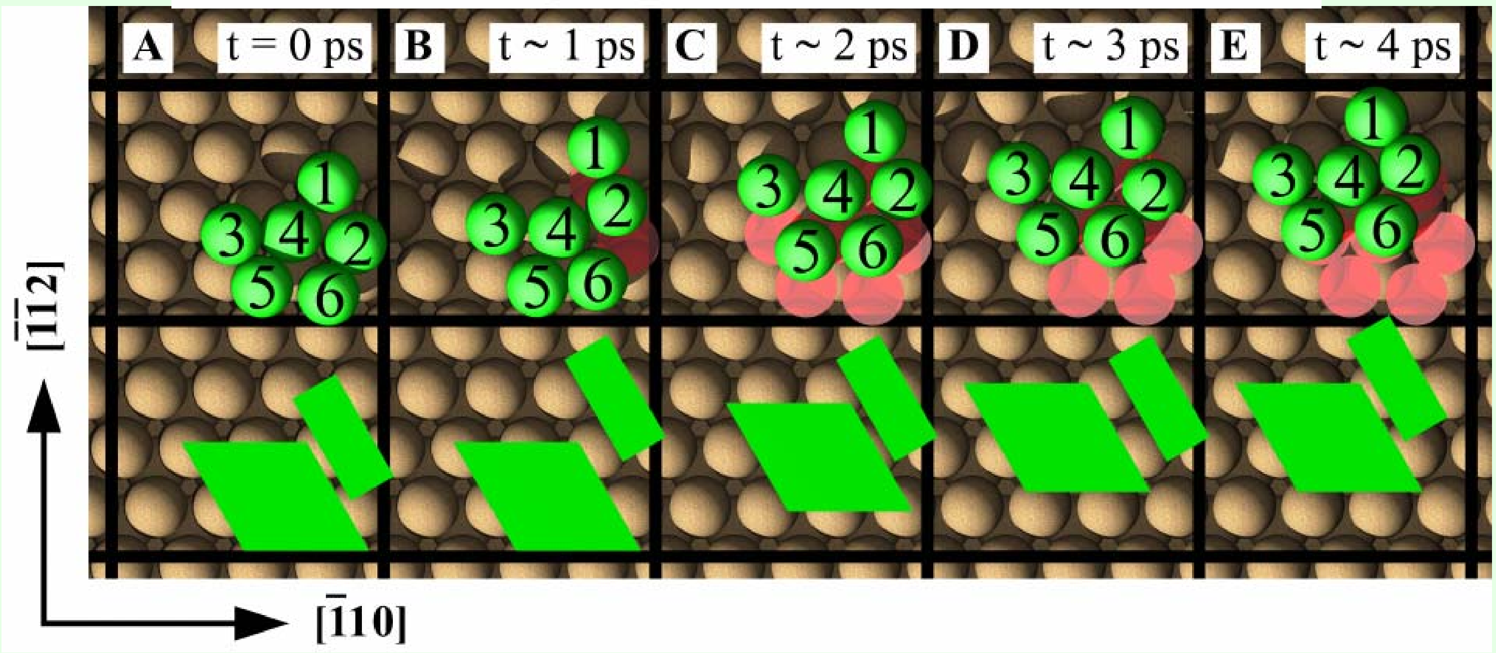
Cluster diffusion - Reptation



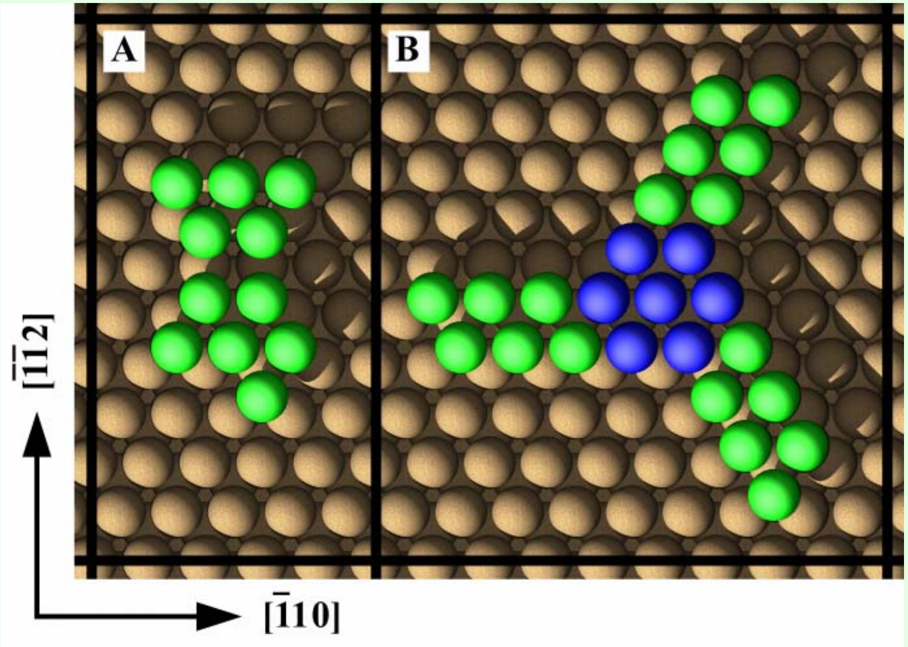
Chirita et. al., *Surf. Sci.*, **436**, L641 (1999)

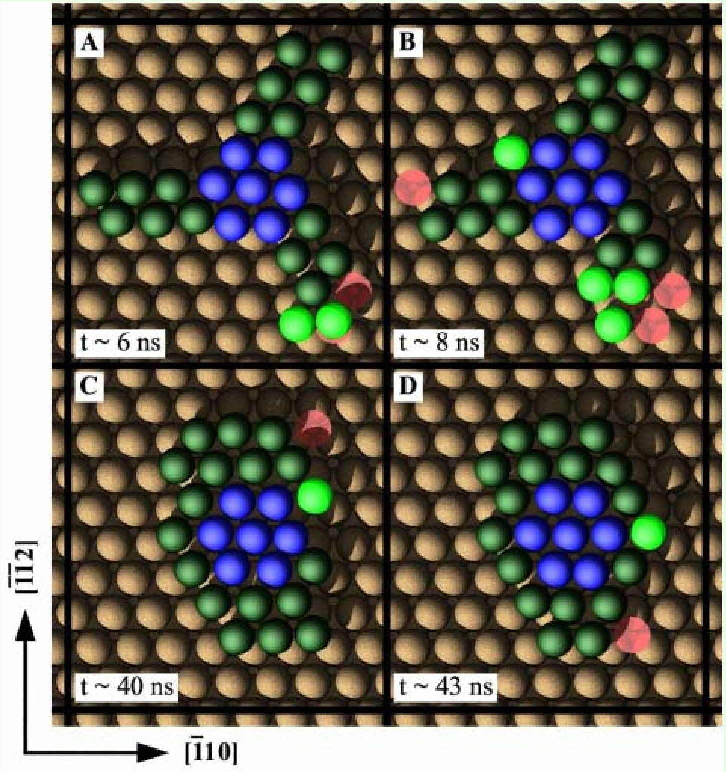
Cluster Diffusion



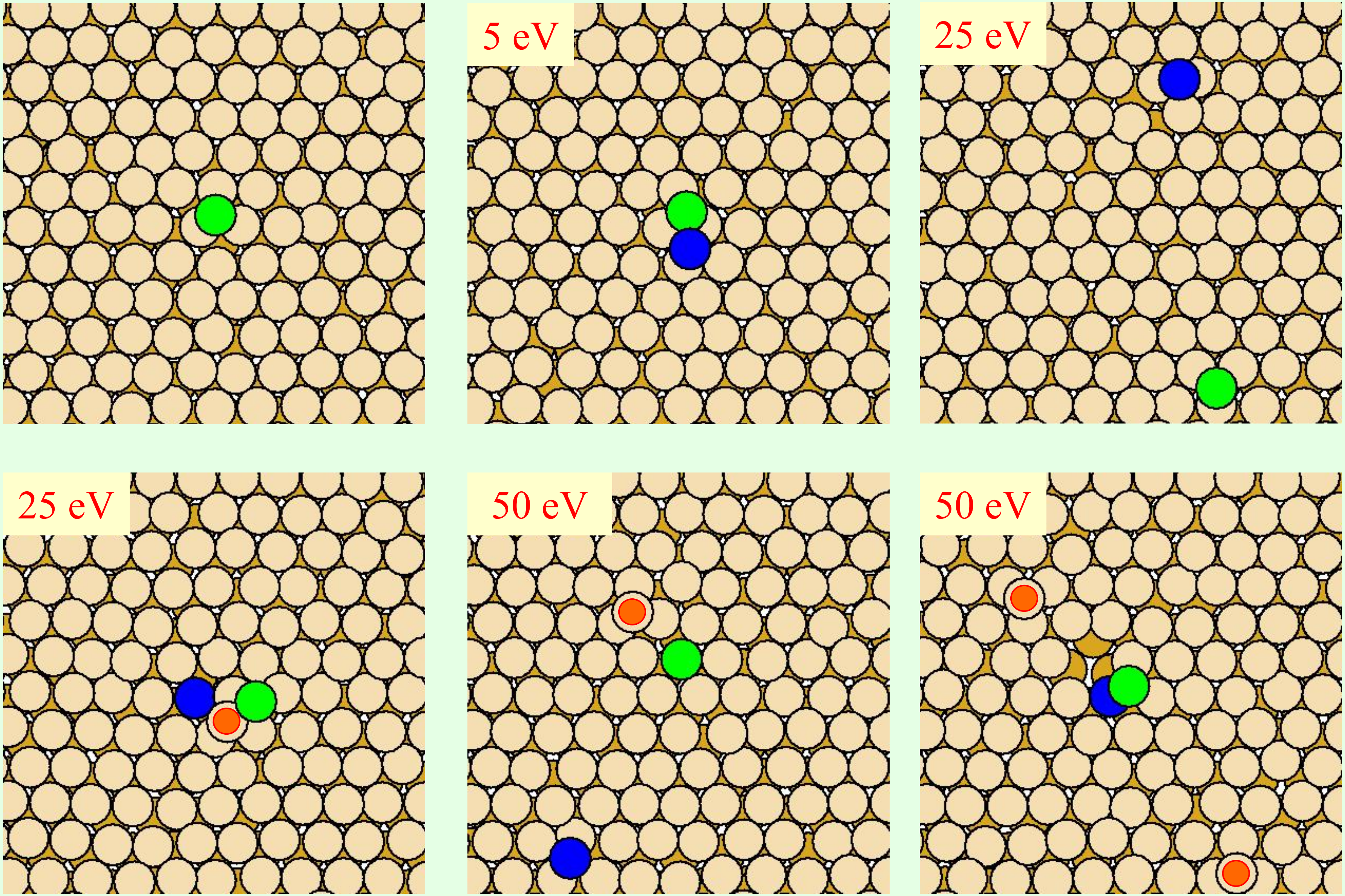


Dendritic to compact morphological transitions





Low-energy irradiation of single adatoms (monomers)

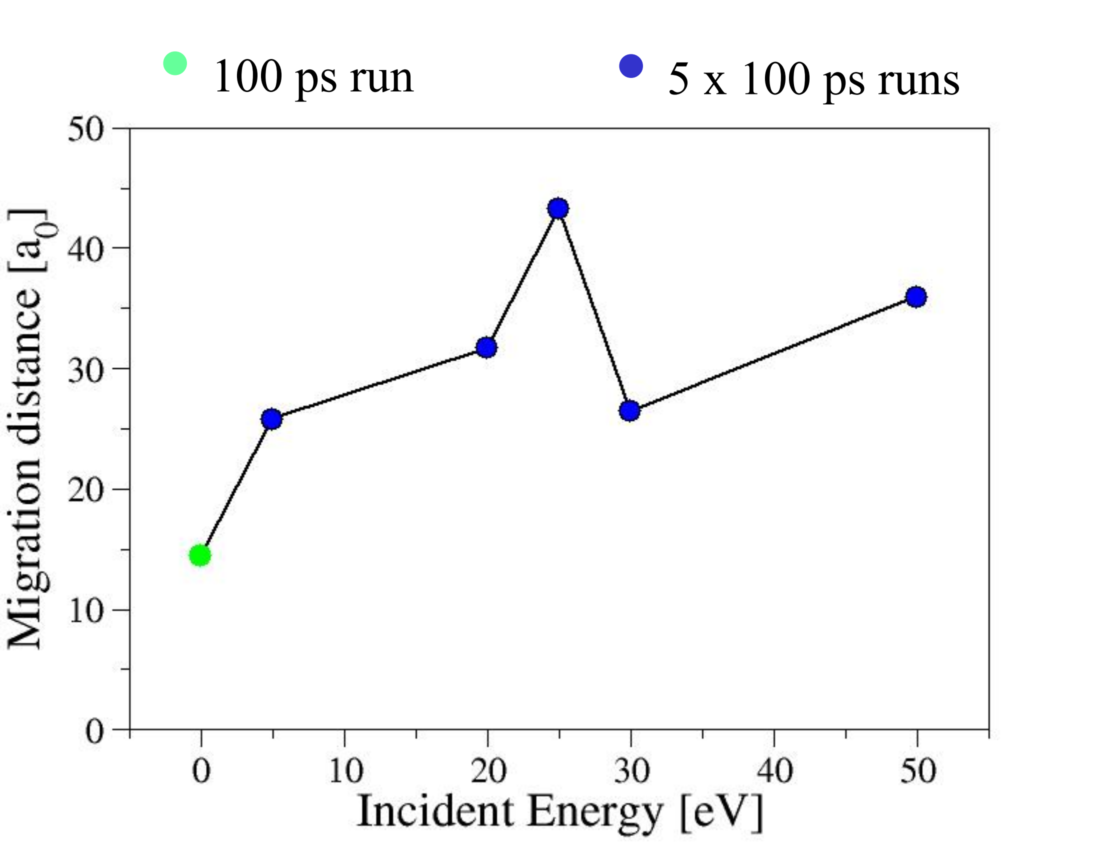


Monomer events statistics

	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

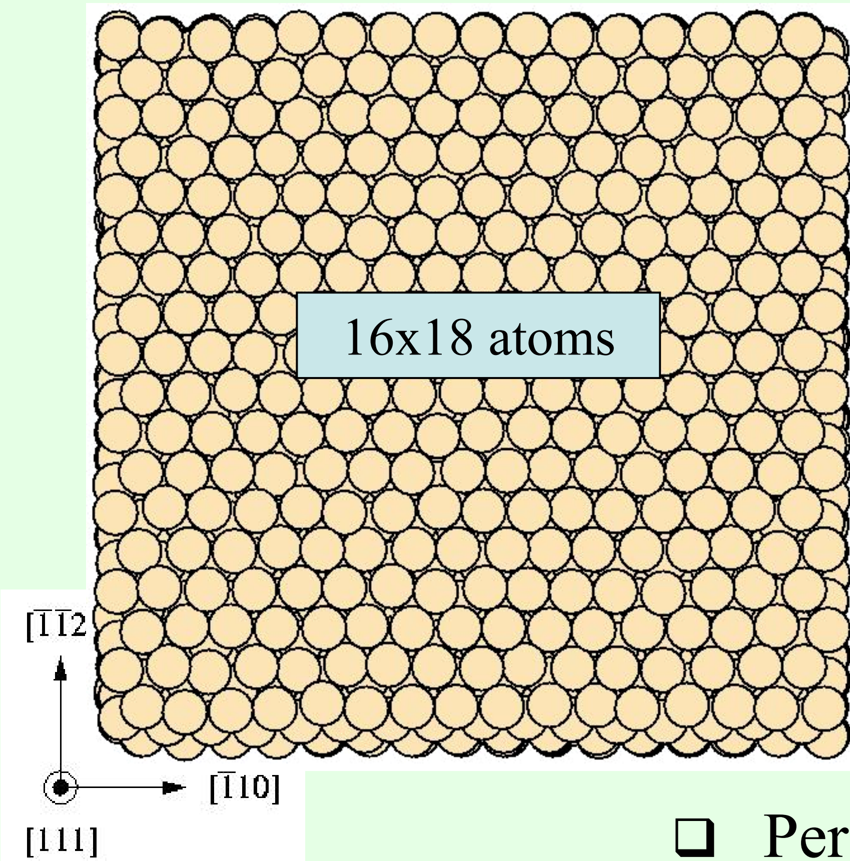
- ❑ Suppresses 3D multilayer growth.
- ❑ Enhances adatom and cluster mobilities.
- ❑ Enhances adatom and island number densities.
- ❑ General model: all effects promote layer-by-layer growth.
- ❑ No direct evidence has been given yet.

Understanding ion-irradiation processes

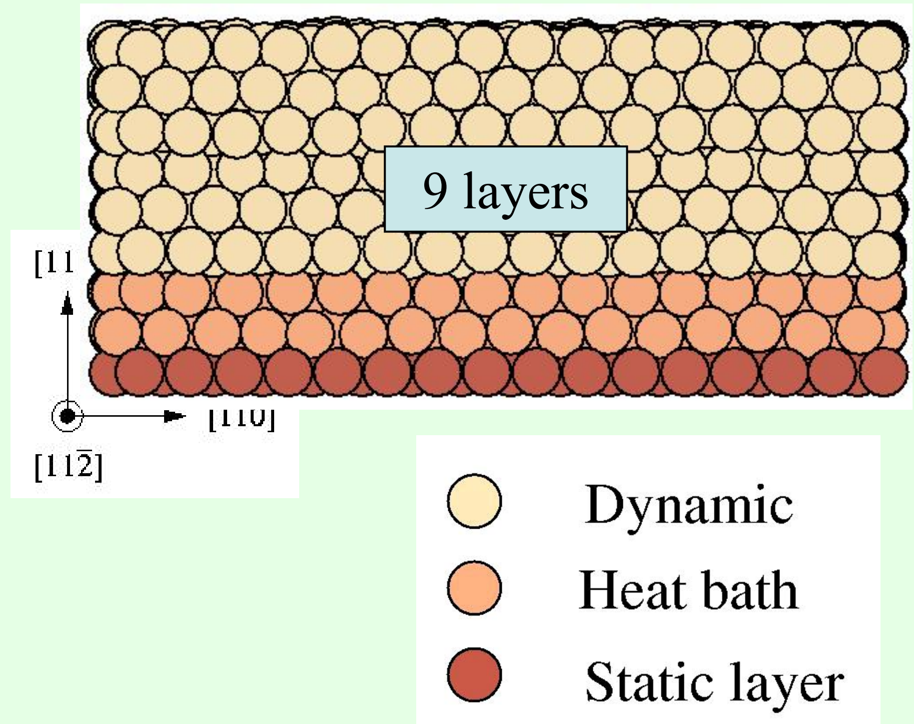
- ❑ Complex, detailed pathways and not fully known.
- ❑ Strong incentive for investigations on the atomic scale.
- ❑ Non-equilibrium, transient processes.
- ❑ Not accessible with experimental techniques – ps timescale.
- ❑ Computer simulations (molecular dynamics).

Substrate and impact geometry

Top view

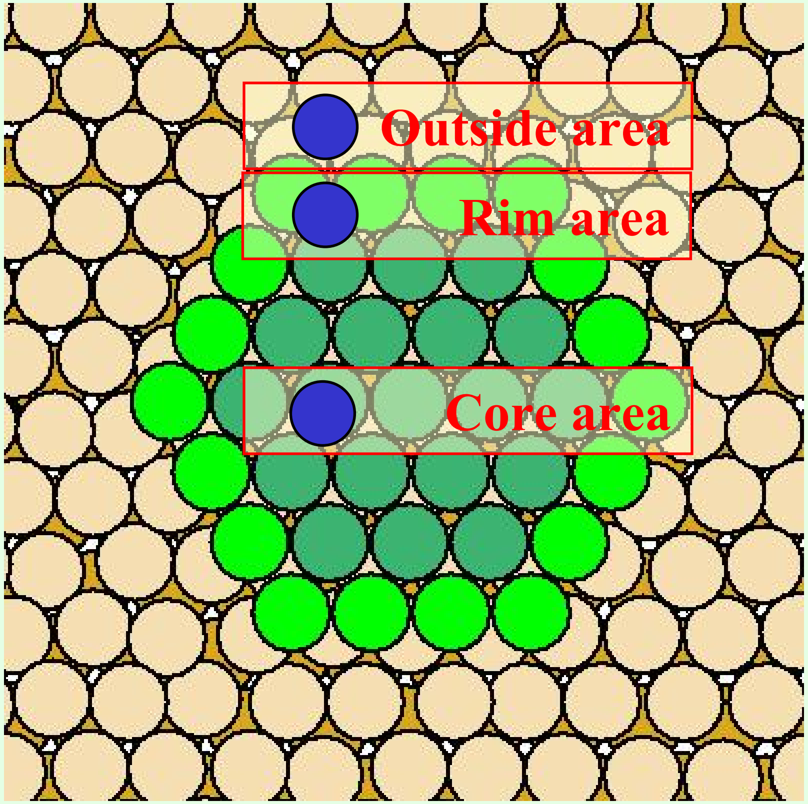


Side view

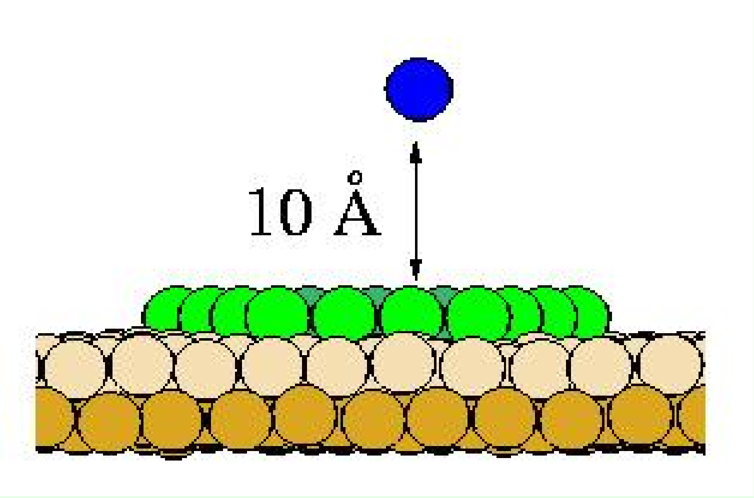


- Periodic in-plane boundary conditions
- Substrate temperature 1000 K

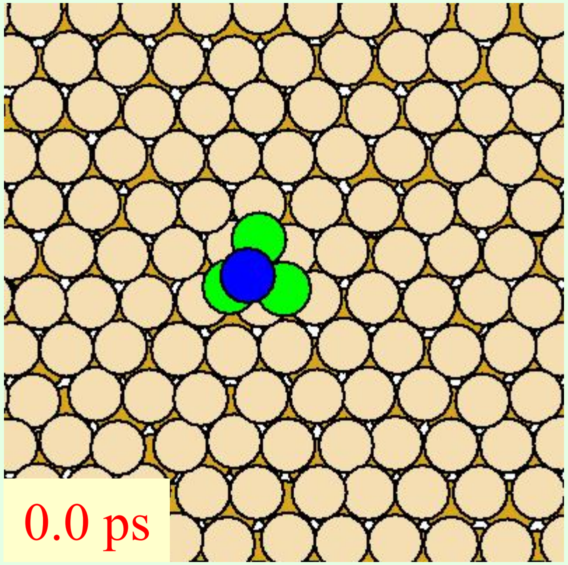
Impact areas and energies

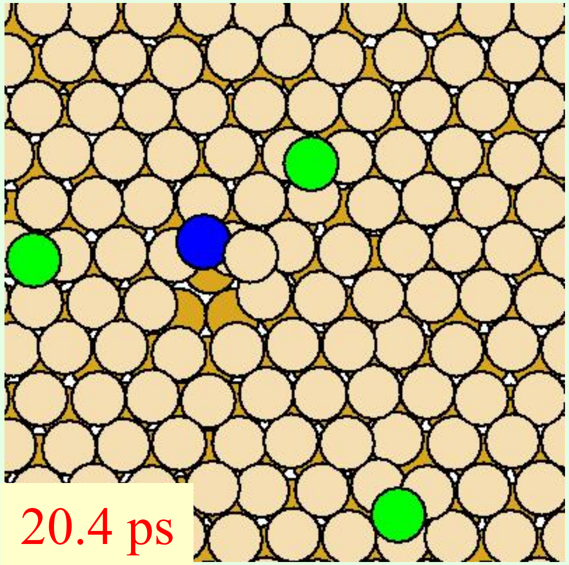


Incident energies
5 eV
20 eV
25 eV
30 eV
50 eV

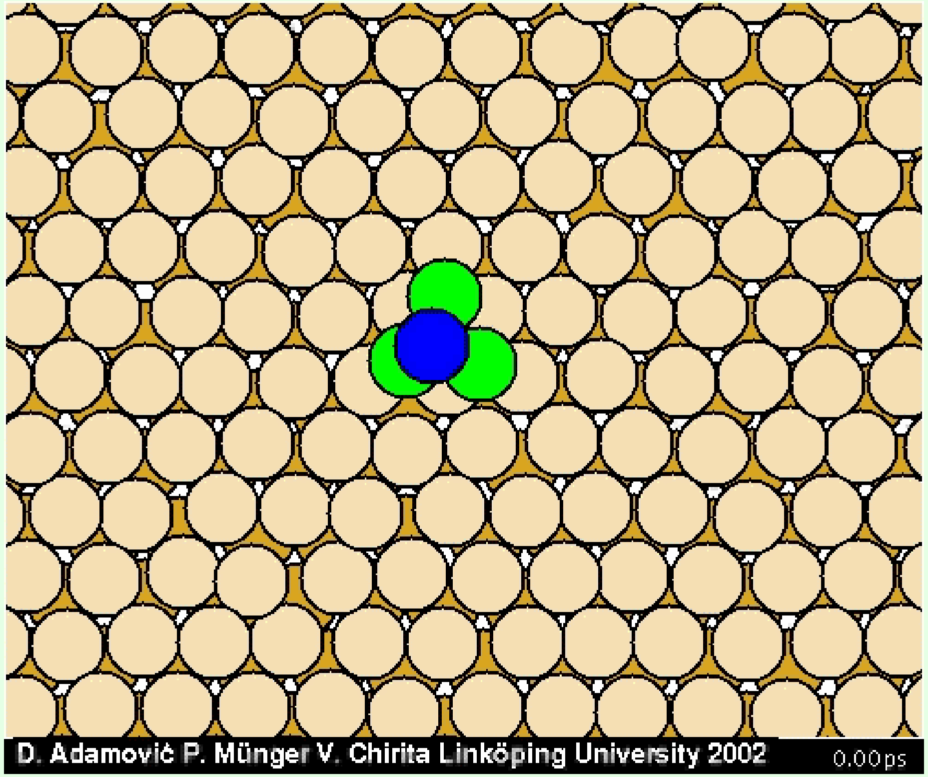


Typical vacancy formation event

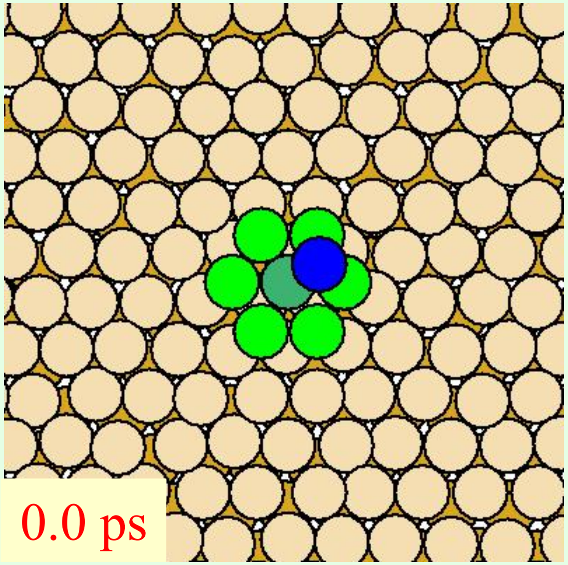


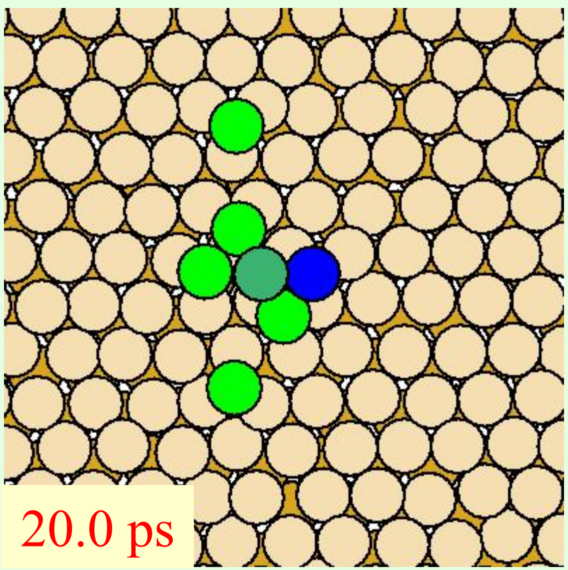


Cluster size:	**Pt_3**
Impact energy:	**50 eV**
Impact area:	**Rim**

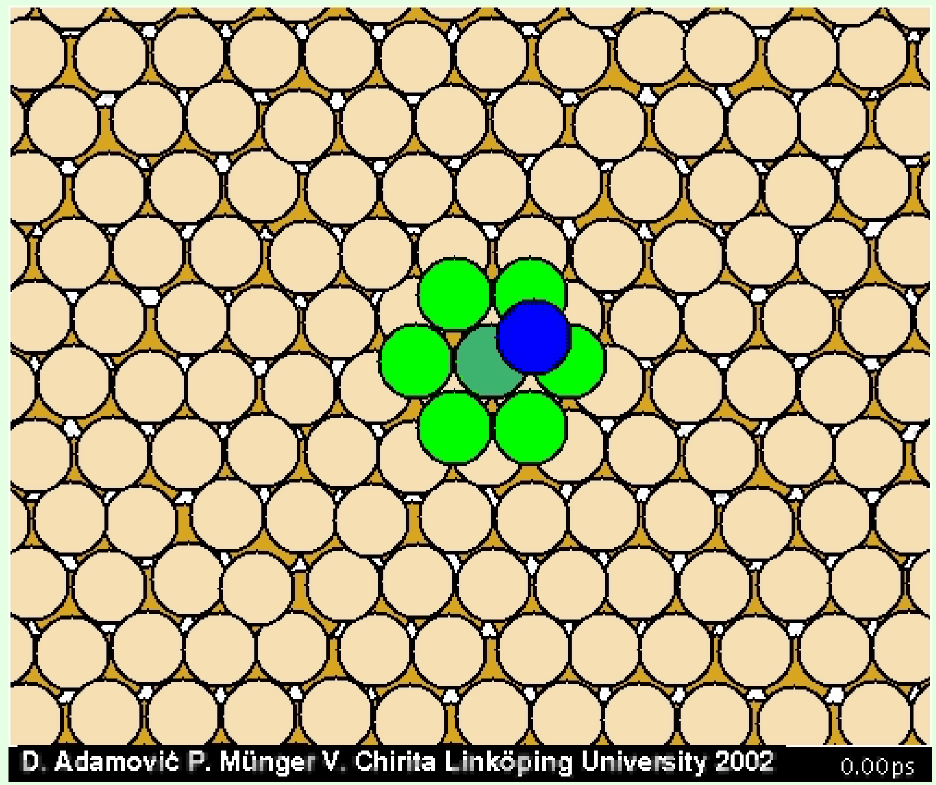


Typical cluster disruption event

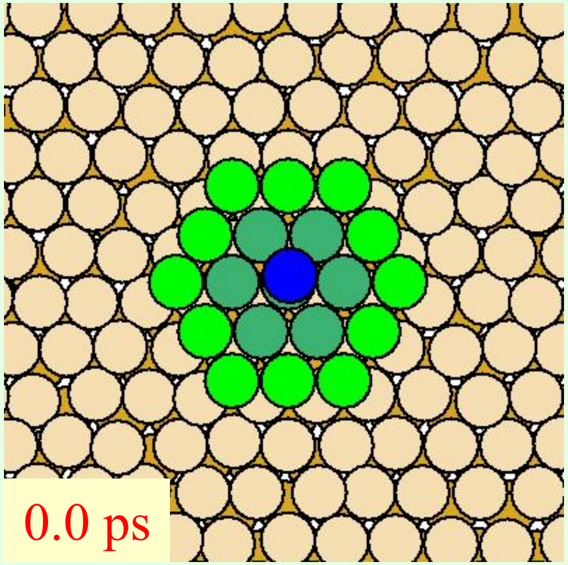




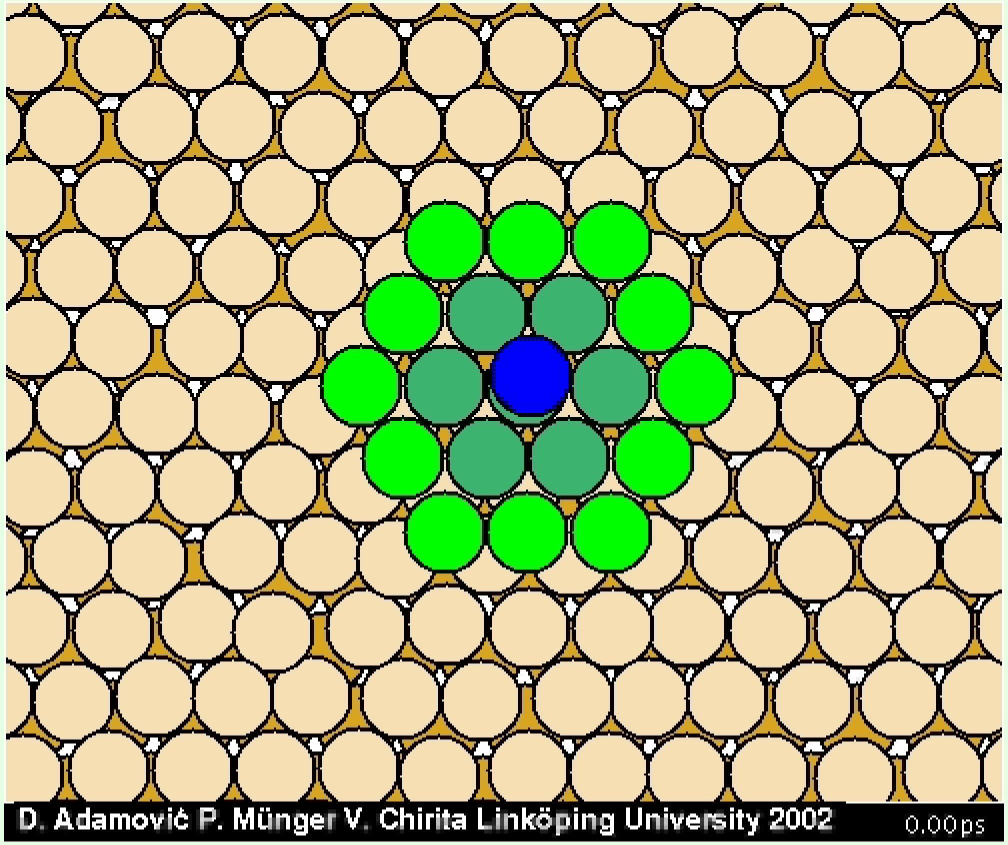
Cluster size: Pt_7
Impact energy: 50 eV
Impact area: Rim

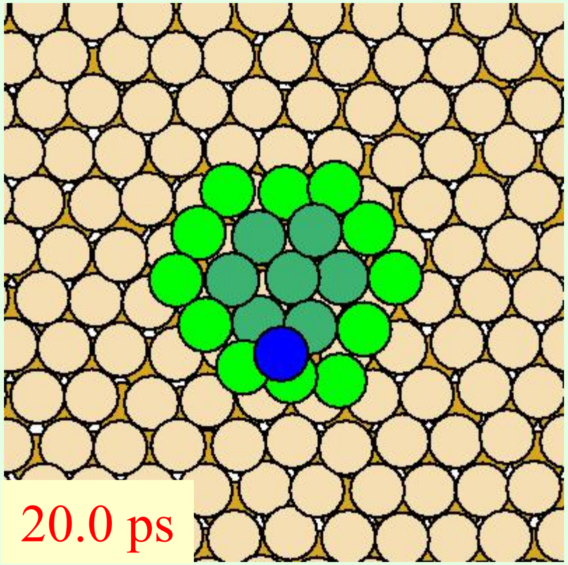


Typical cluster preservation event

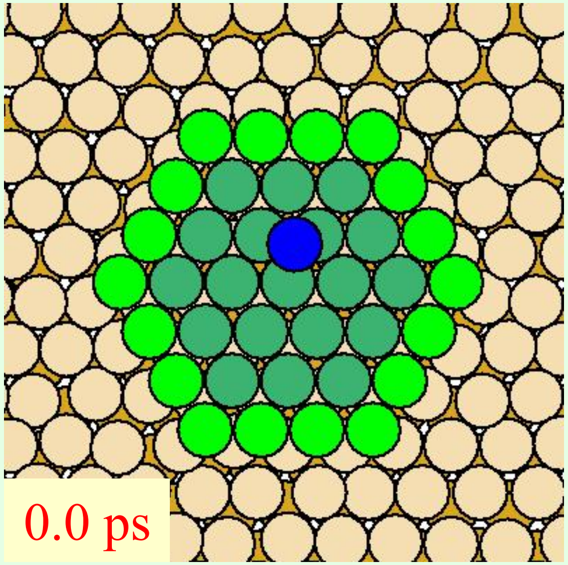


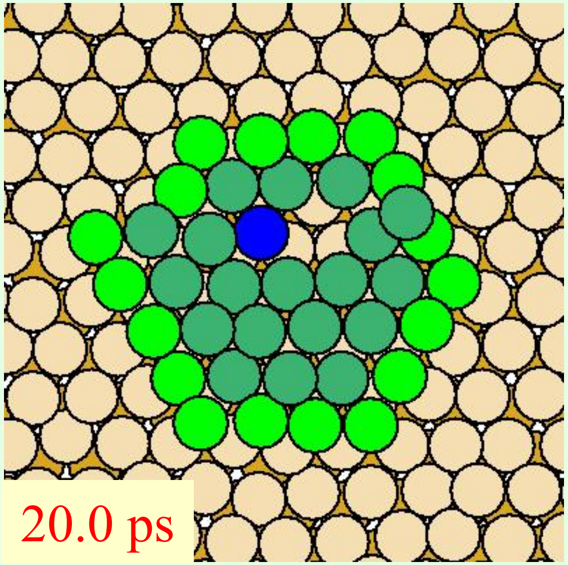
Cluster size:	Pt_{19}
Impact energy:	50 eV
Impact area:	Core



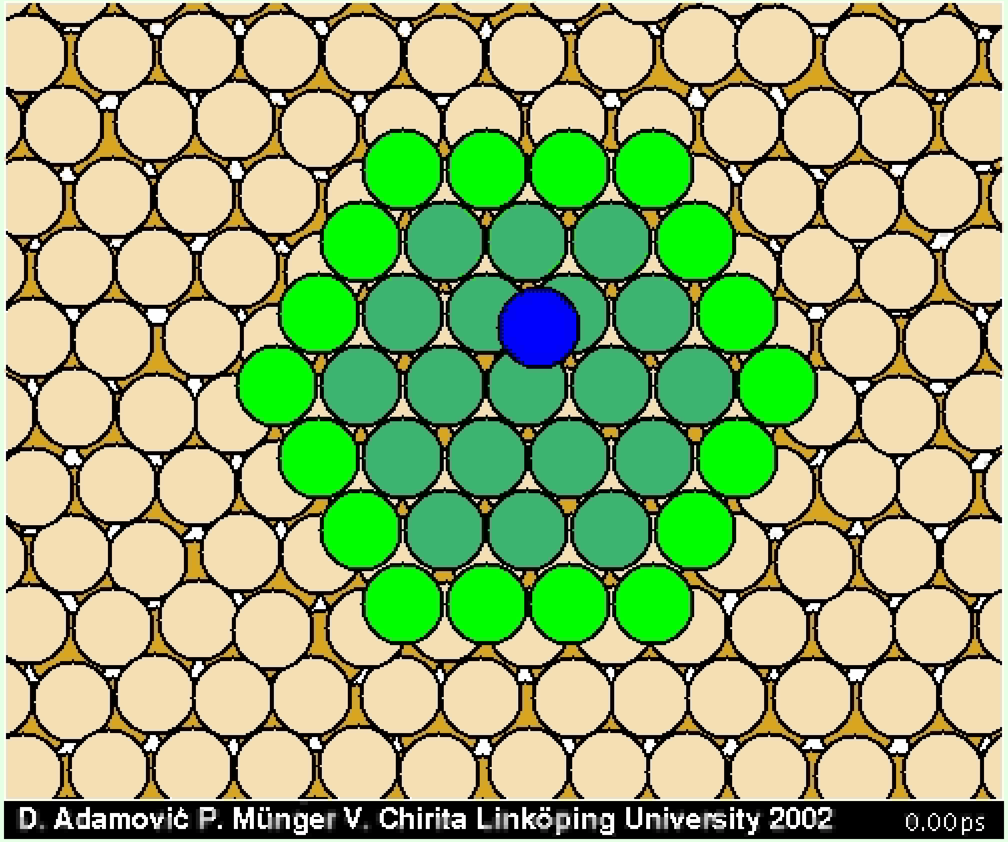


Typical 2D-3D transition event



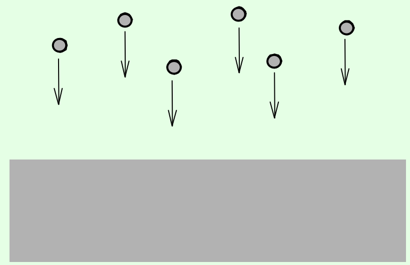


Cluster size: Pt_{37}
Impact energy: 30 eV
Impact area: Core

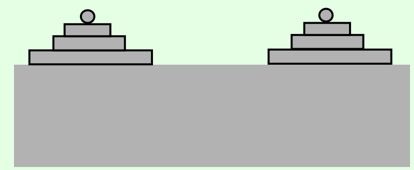


Experimental evidence

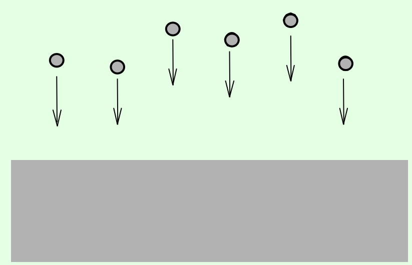
Thermal deposition
(< 1 eV)



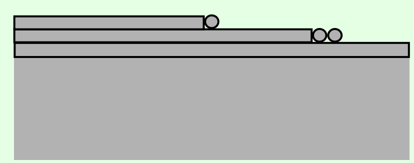
Multilayer (3D)

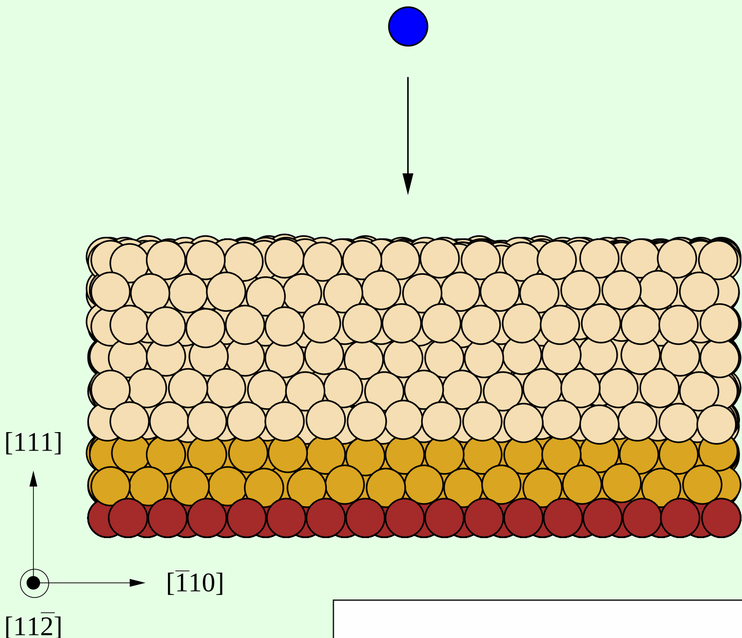


Low-energy irradiation
(< 50 eV)

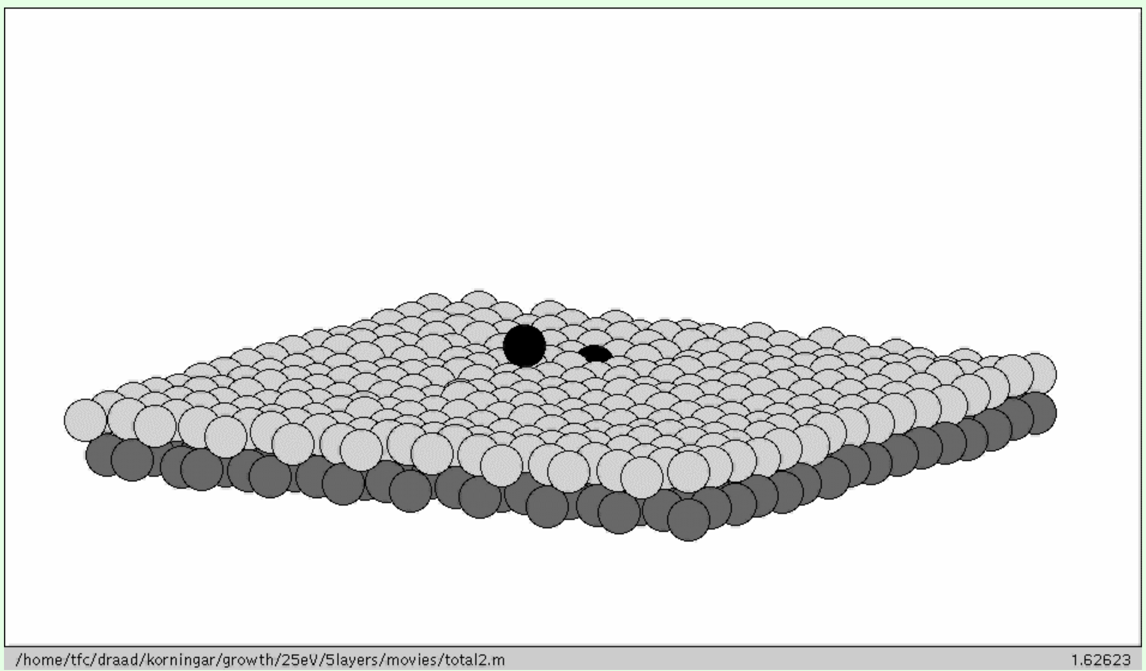


Layer-by-layer (2D)



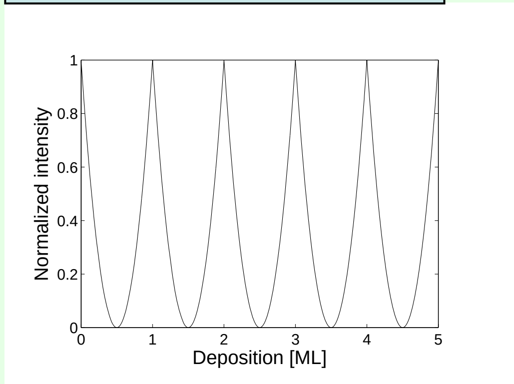


- E_{Pt} = 0.2 eV and 5-50 eV, 5 eV intervals
- We deposit 5 ML at two flux rates
- R = 10 ns^{-1}, or deposition rate of 5×10^5 μm/min, i.e. 10^3 > EB – PVD.
- R = 1 ns^{-1}, i.e. 10^2 > EB – PVD (25 eV).

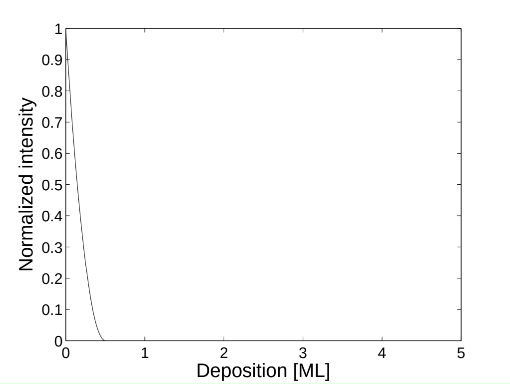


Determining growth mode

2D Layer-by-layer



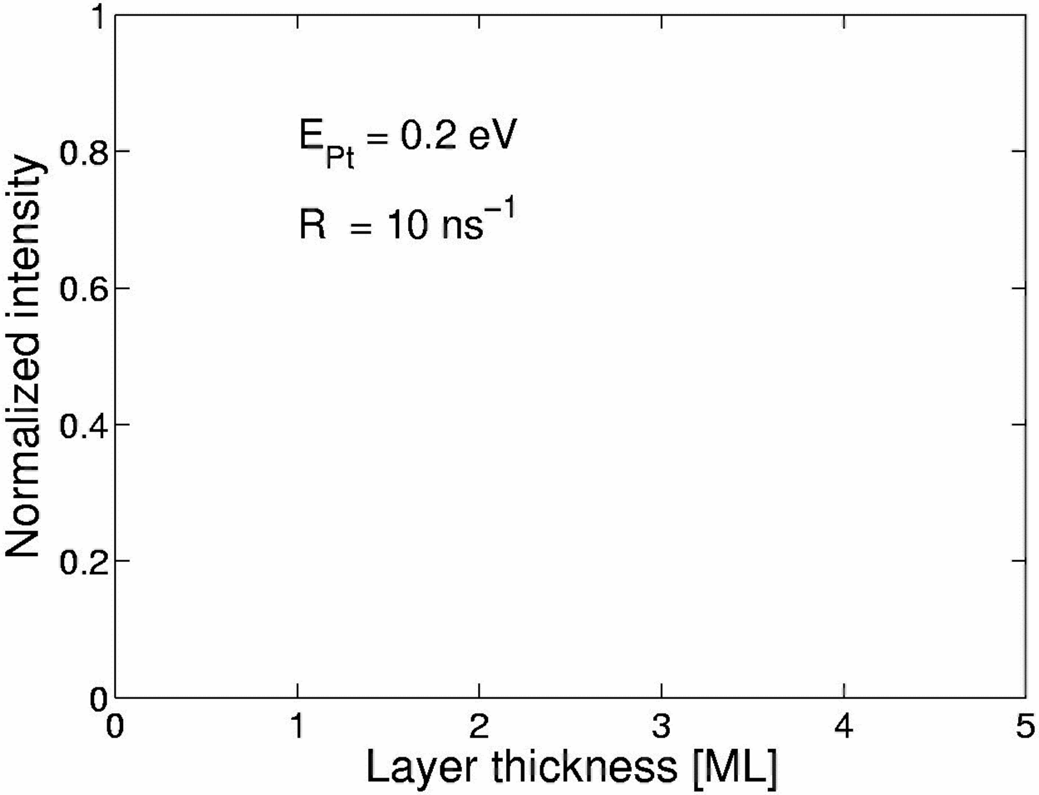
3D Multilayer

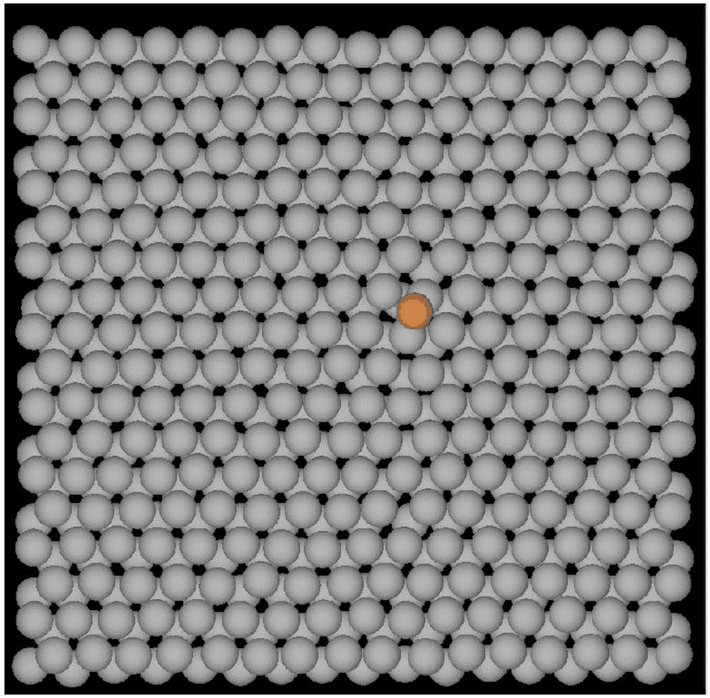


- ❑ Follow motion of all atoms individually » adatom coverages as f(t).
- ❑ Calculate antiphase diffraction intensity oscillations » growth mode.
- ❑ Periodic oscillations » layer-by-layer growth.
- ❑ Monotonic decrease » multilayer growth.

Typical 3D multilayer growth mode

Homoepitaxial Pt(111) growth from hyperthermal atoms





Time 0.0 ns

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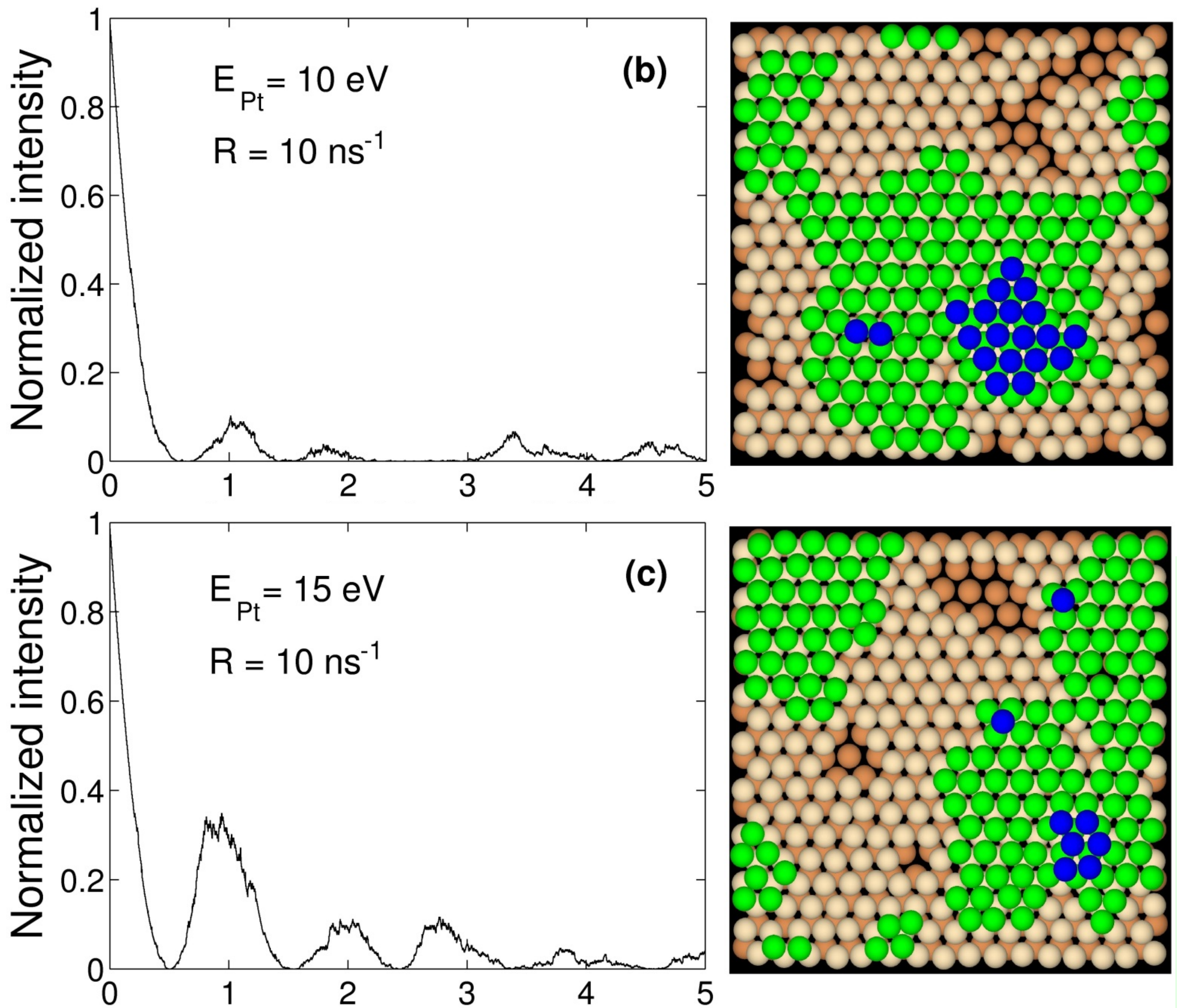
Materials Science Department and the Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, USA

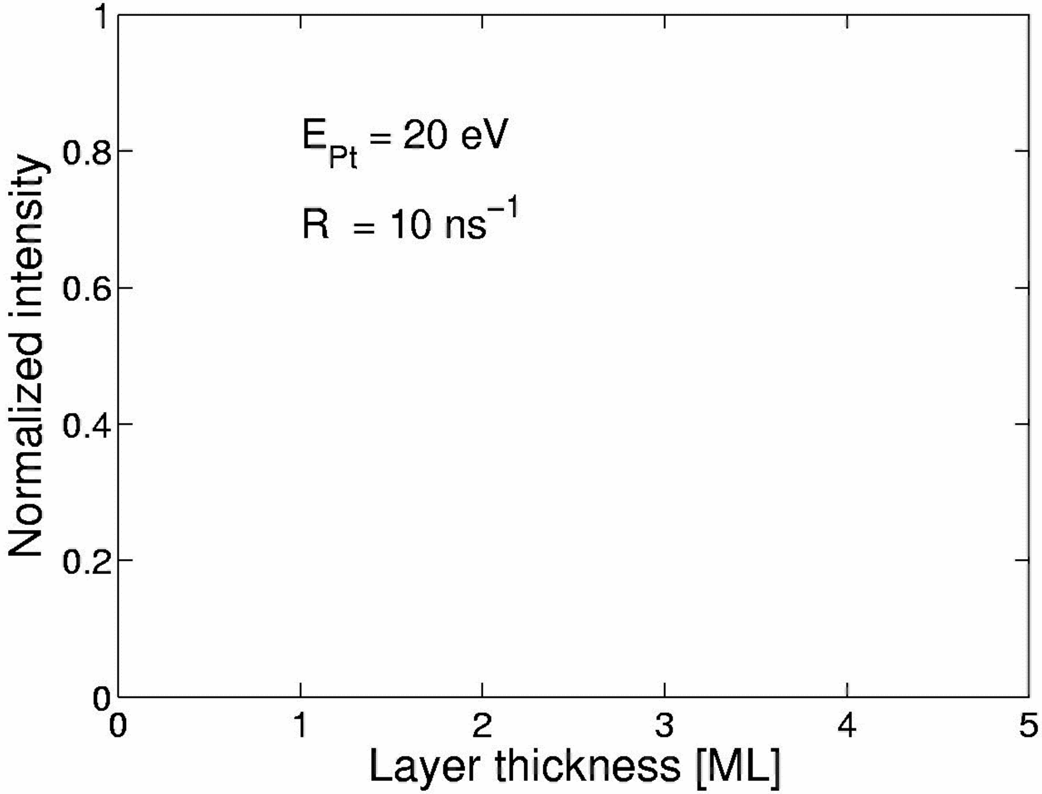
3D Multilayer Growth Mode

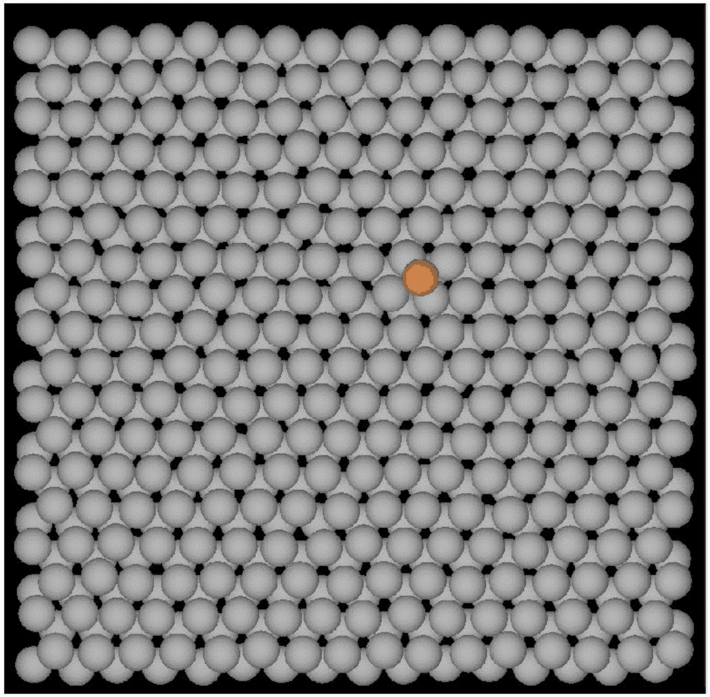


2.5 ML

Typical 2D, layer-by-layer growth mode

Homoepitaxial Pt(111) growth from hyperthermal atoms





Time 0.0 ns

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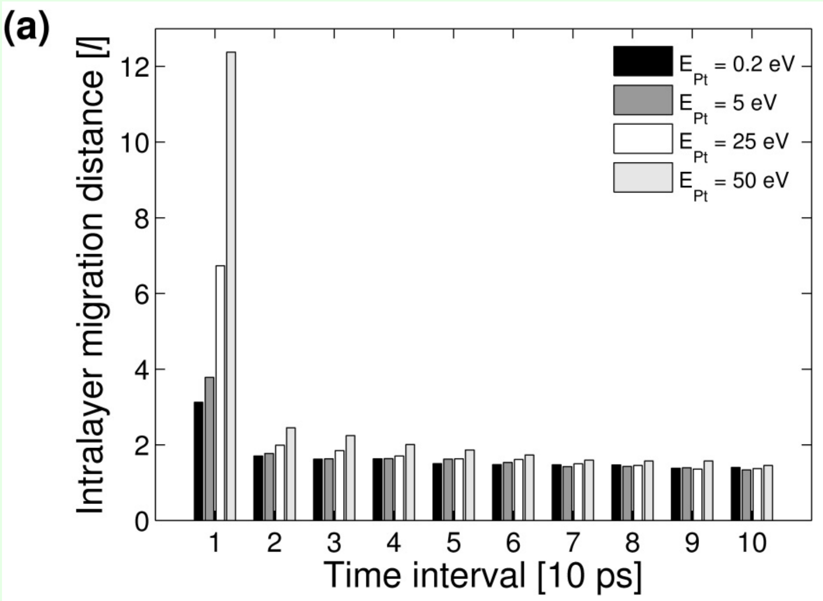
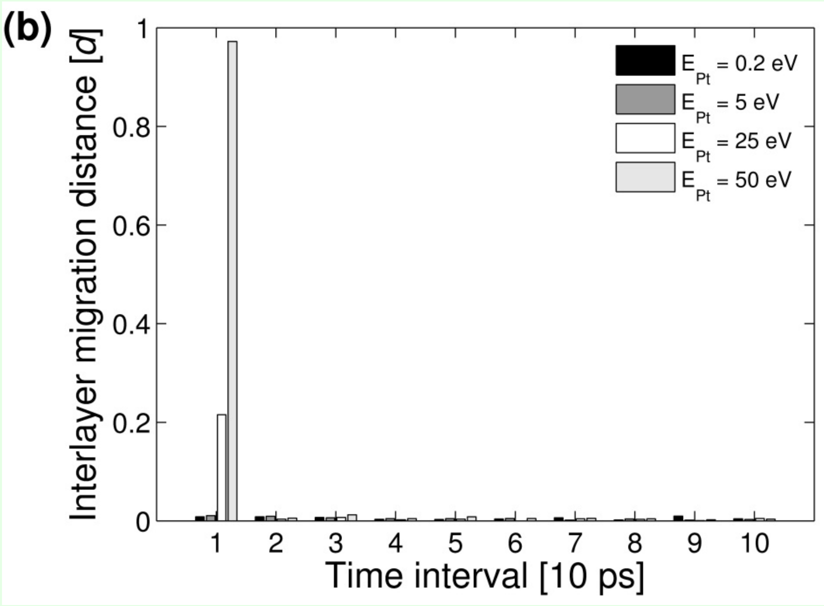
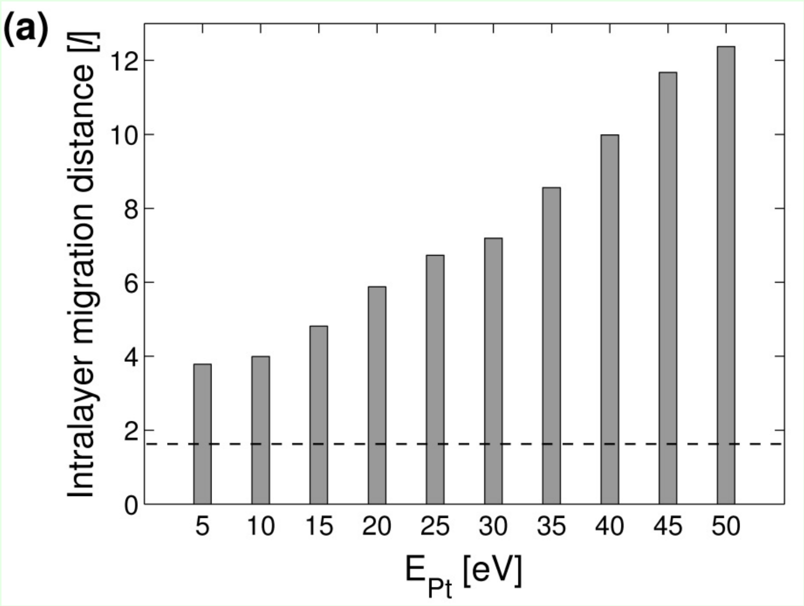
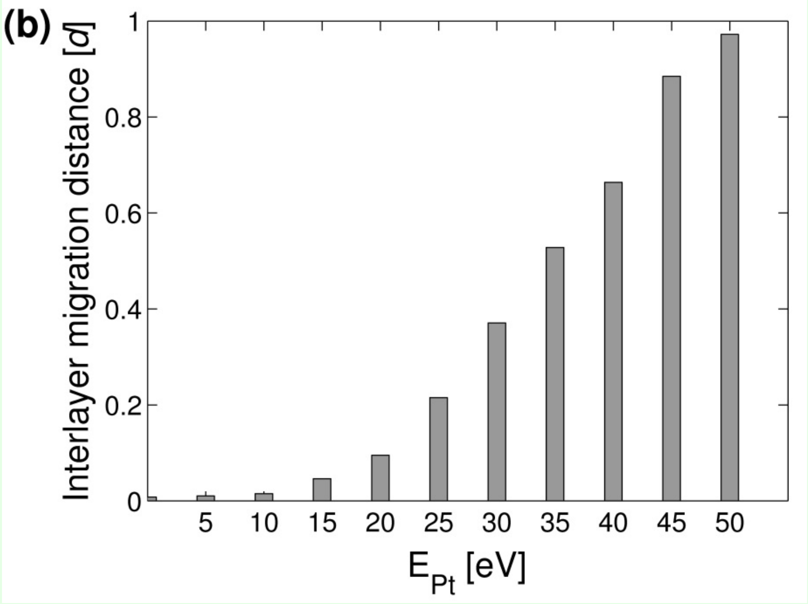




Average mass transport

- 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: **1st 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 – 1st 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].

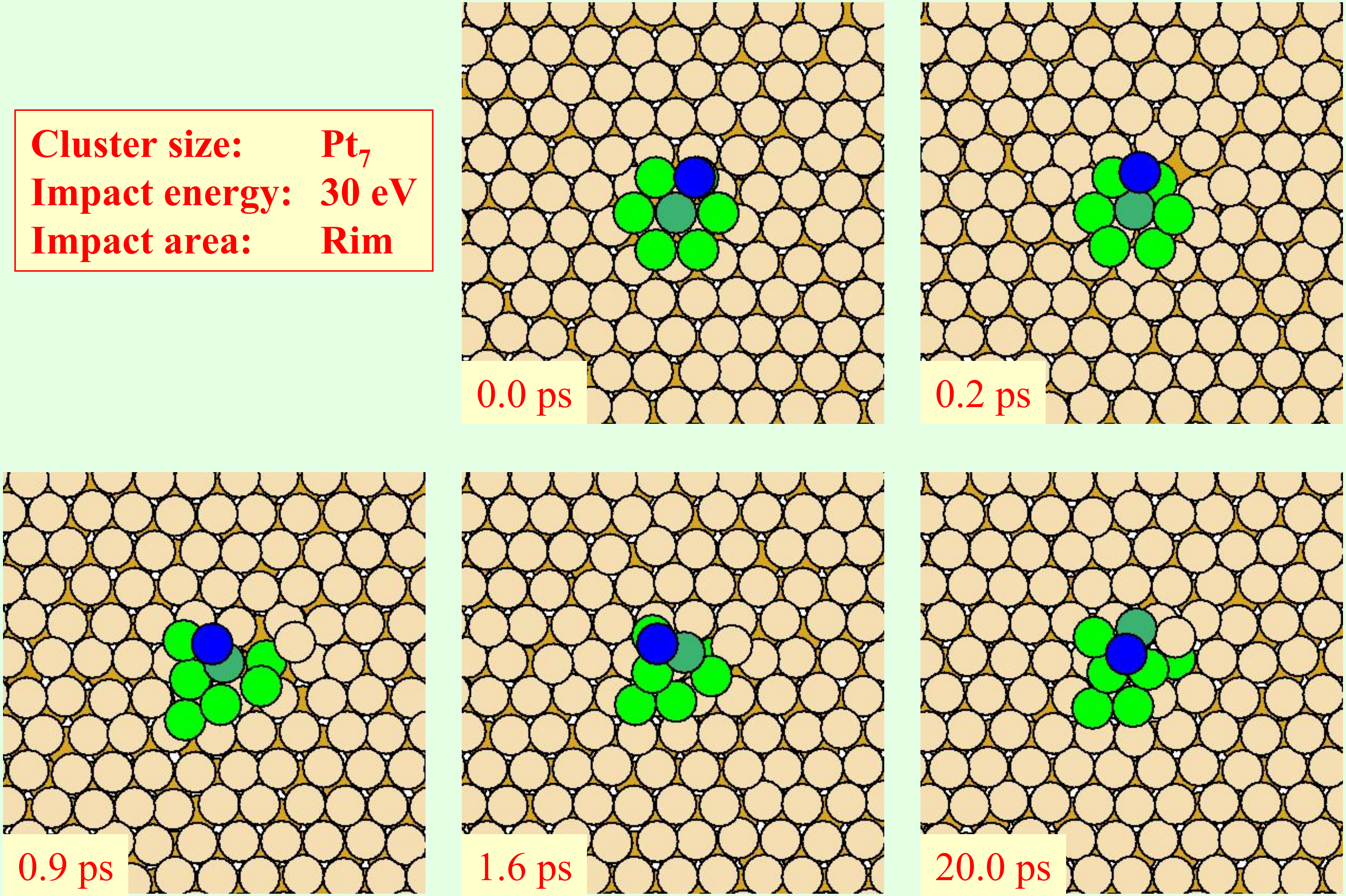
- Onset of significant interlayer migration at $E_{Pt} \geq 15$ eV[1,2].

[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

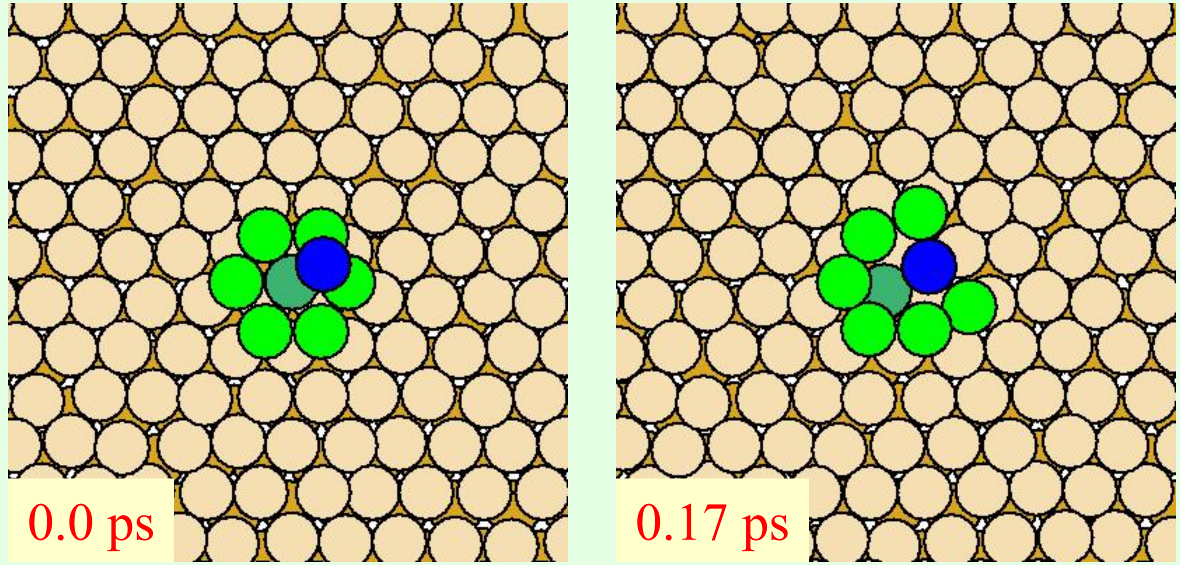
- Adatom scattering, surface channeling, dimer formation – all energies[1].
- Onset of significant interlayer migration at $E_{Pt} \geq 15$ eV[1,2].
- Cluster disruption observed from $E_{Pt} \geq 20$ eV[1,2].

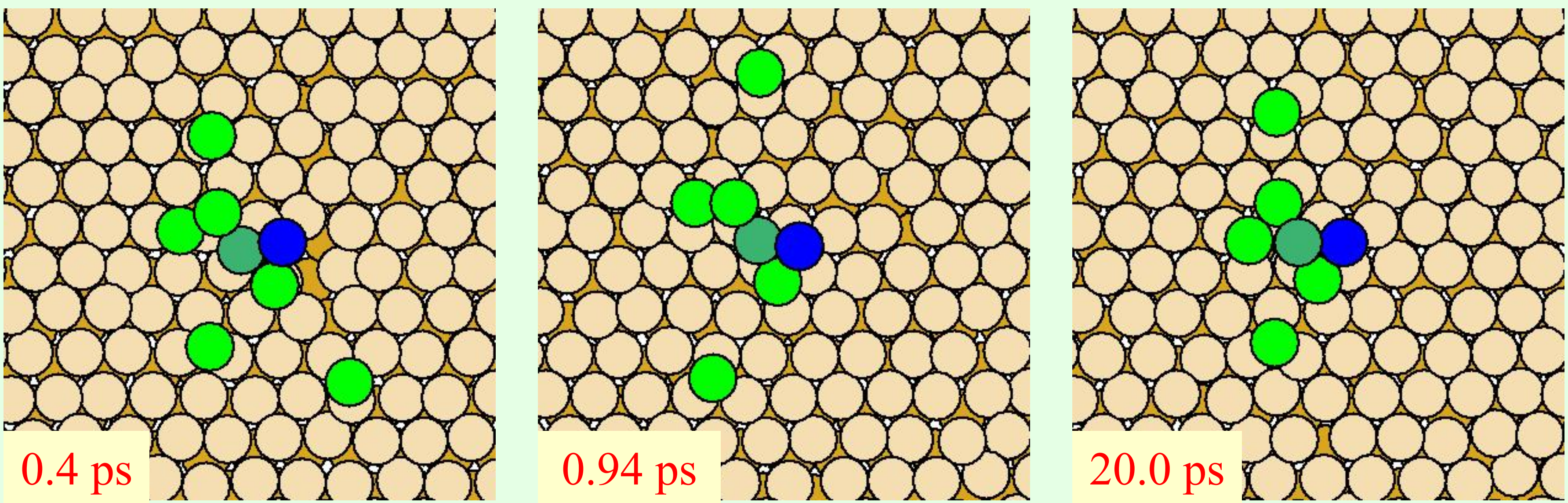
[1] D. Adamovic et. al., APL **86**, 211915 (2005)

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

Typical cluster disruption event

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





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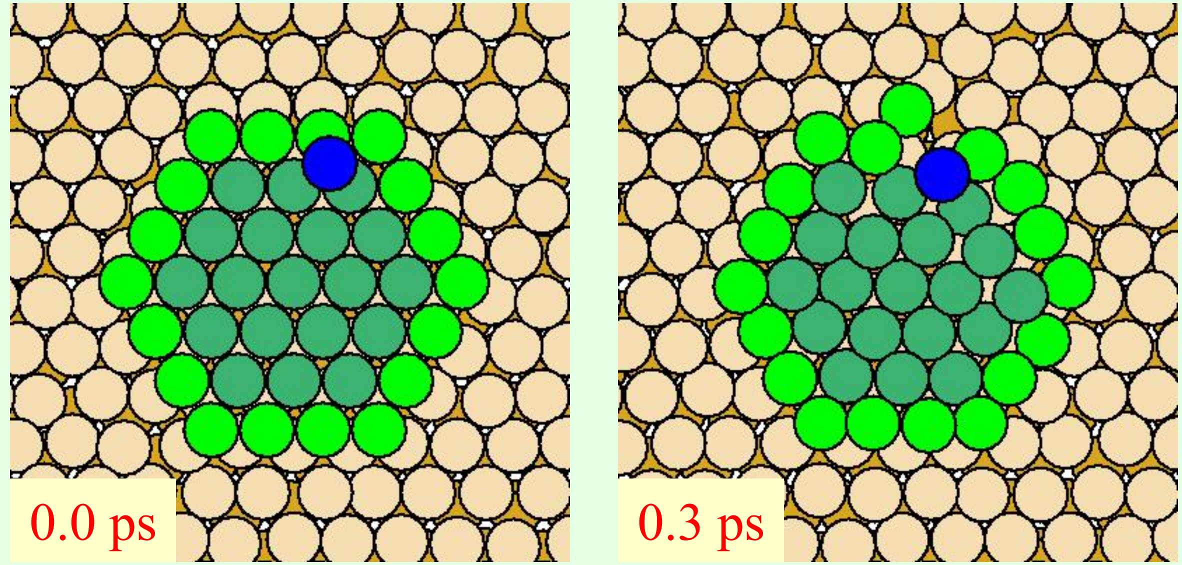
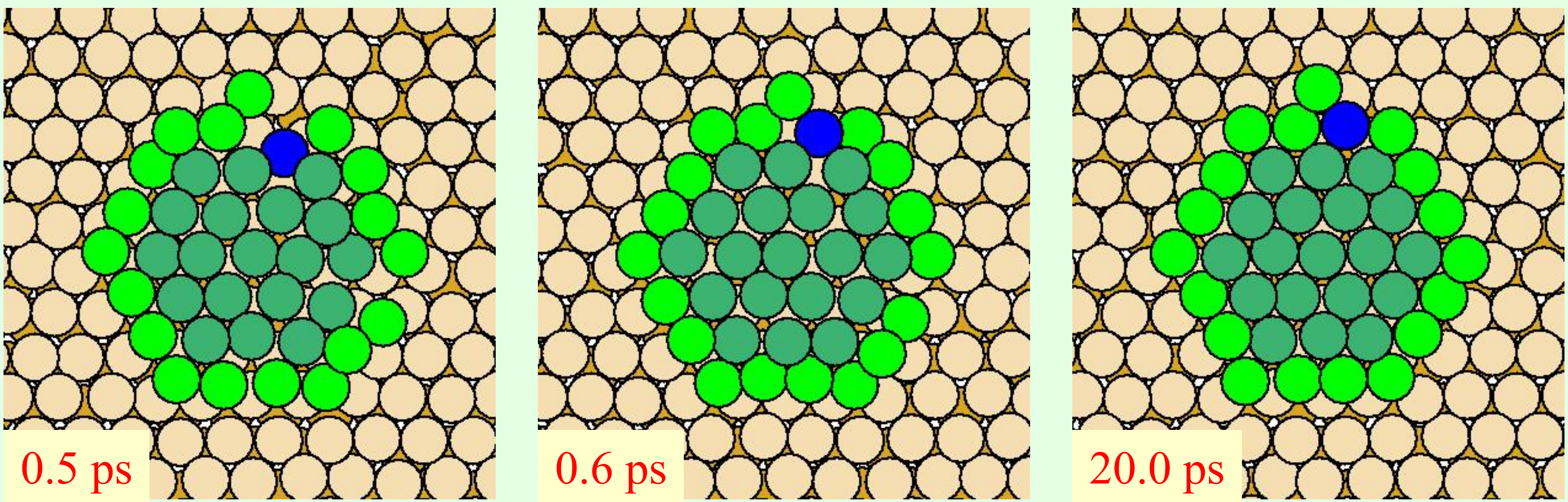
Typical adatom incorporation event

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





Kinetic Pathways promoting layer-by-layer growth

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- 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)

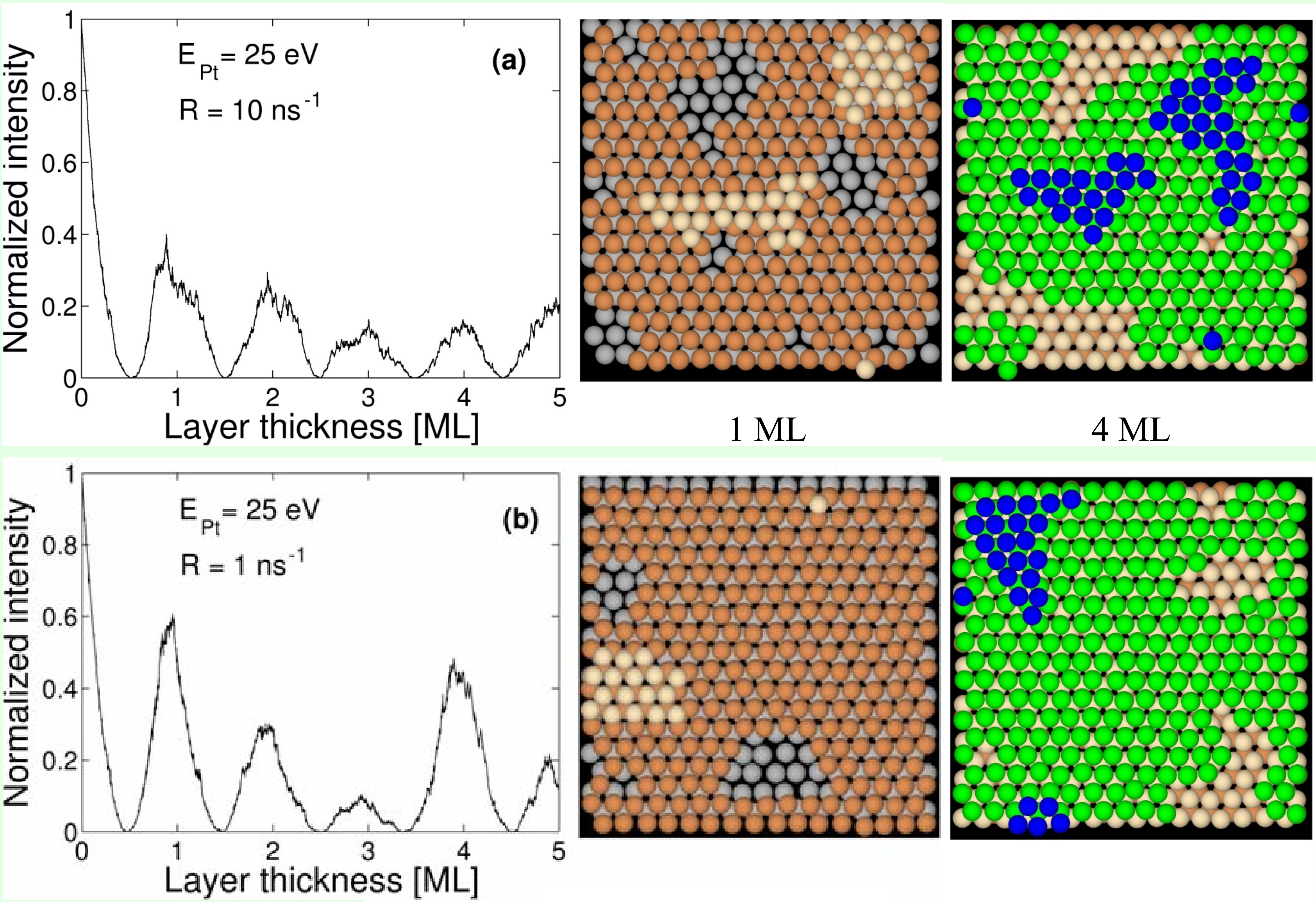
Test against inherent MD limitations

- Typical MD simulations of film growth use very high fluxes leading to unrealistic deposition rates (10^4 to 10^6 or more higher).

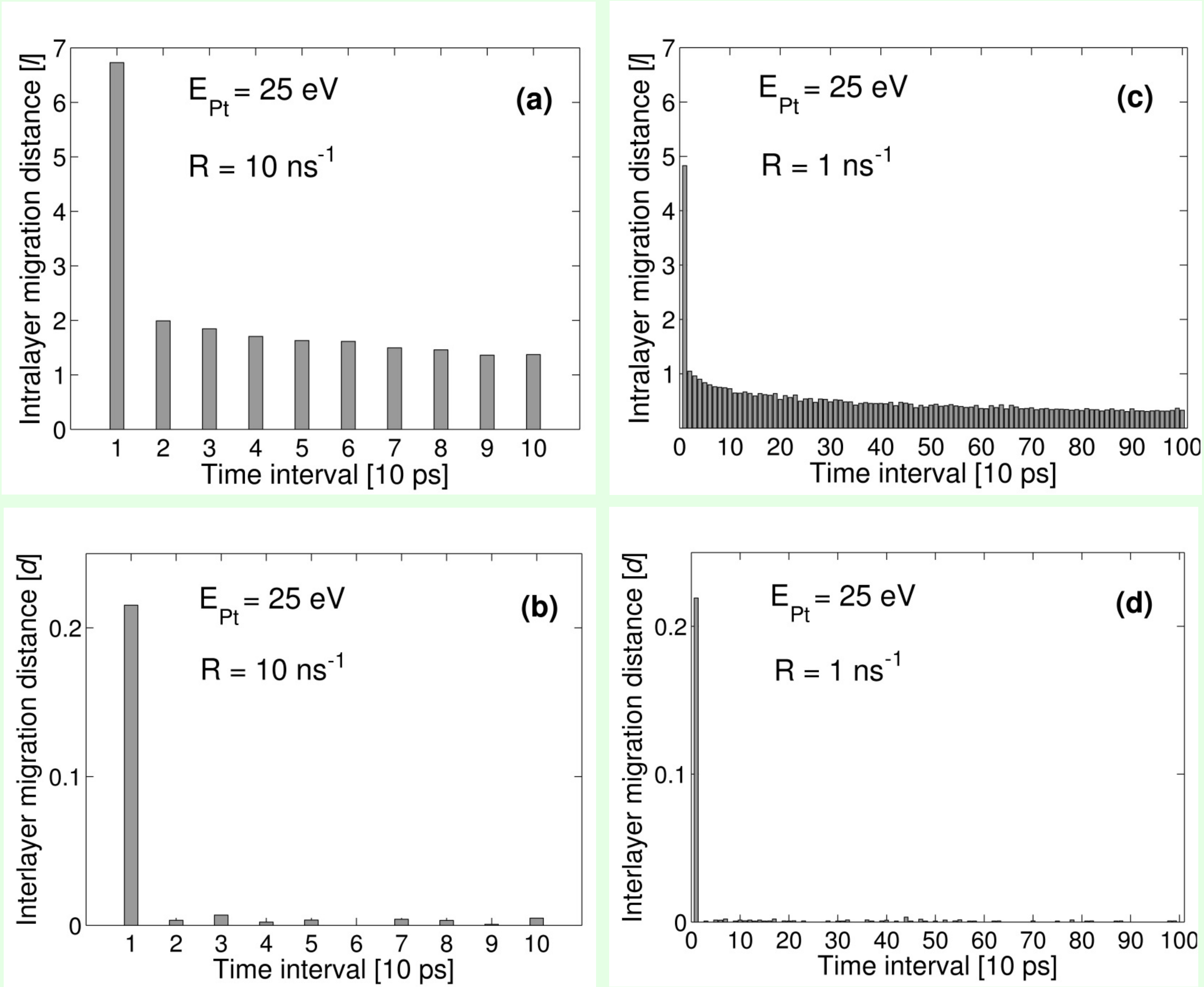
- We deposit 5 ML, at 25 eV and R = 1 ns^{-1}, flux rate only 10^2 > EB-PVD.

- 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.



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



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

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

d_1 – 1st 10 ps interval

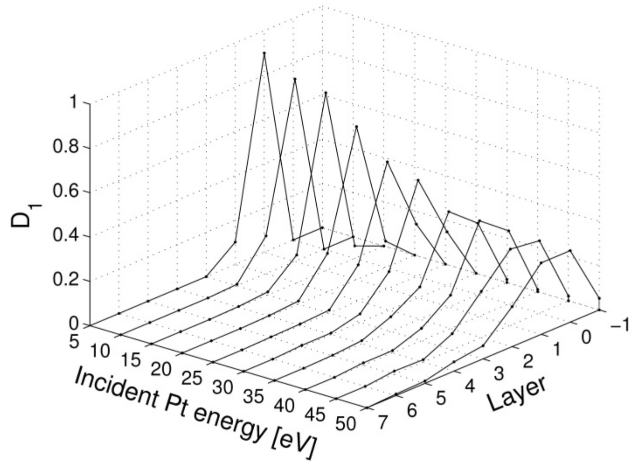
$$r = d_1/\bar{d}_n ; \bar{d}_n = (d_2 + d_3 + \ldots + d_n)/n$$

$d_2 \ldots d_n$ – 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**

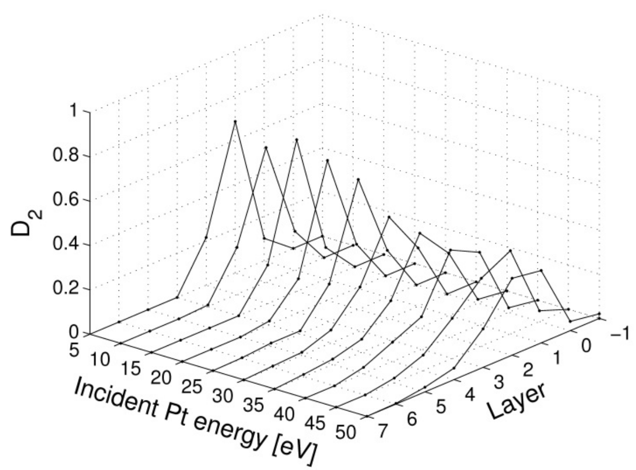
Obs: **Very significant increases in r_{intra} (~2x) and r_{inter} (~7x)!**
Still 10^2 – 10^4 off real deposition rates!!!

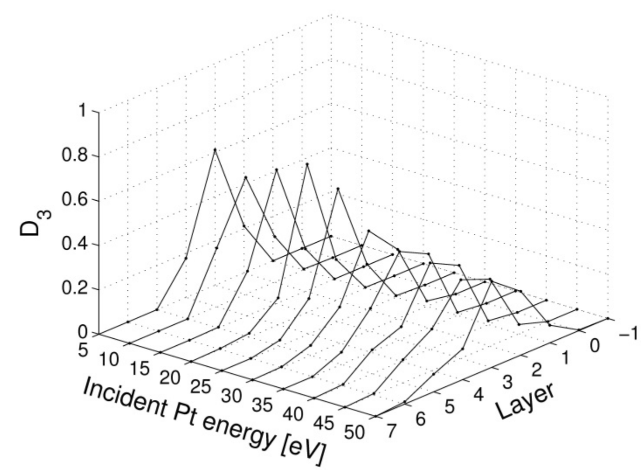
Atomic distribution in deposited layers



- Broader distributions and lower peacks for higher energies and sequentially deposited layers.

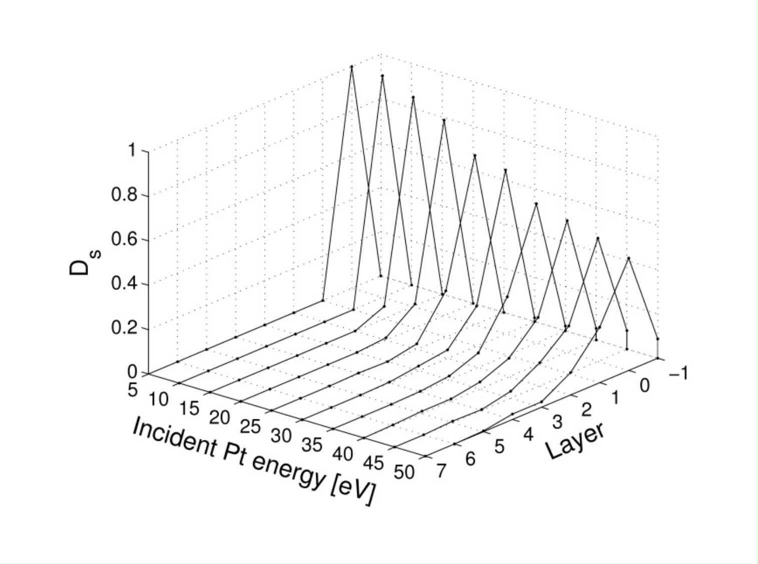
- Signature of mass transport leading to 2D growth

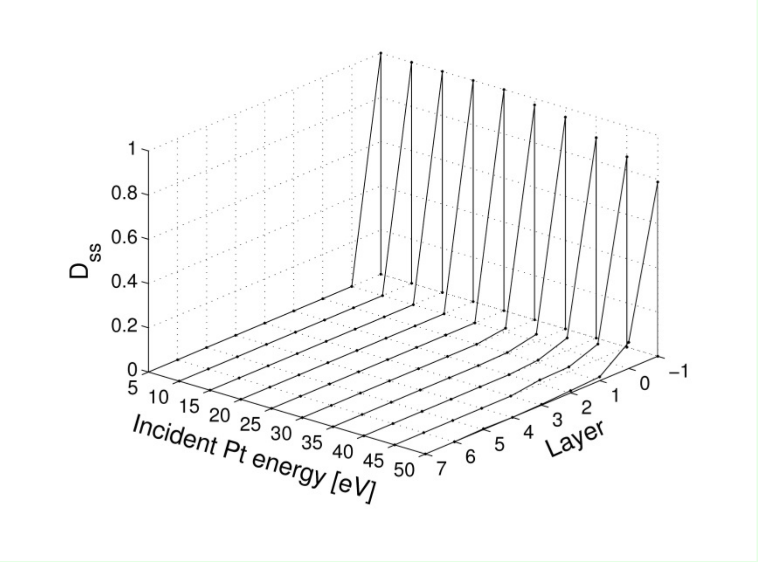




Interlayer Mass Transport

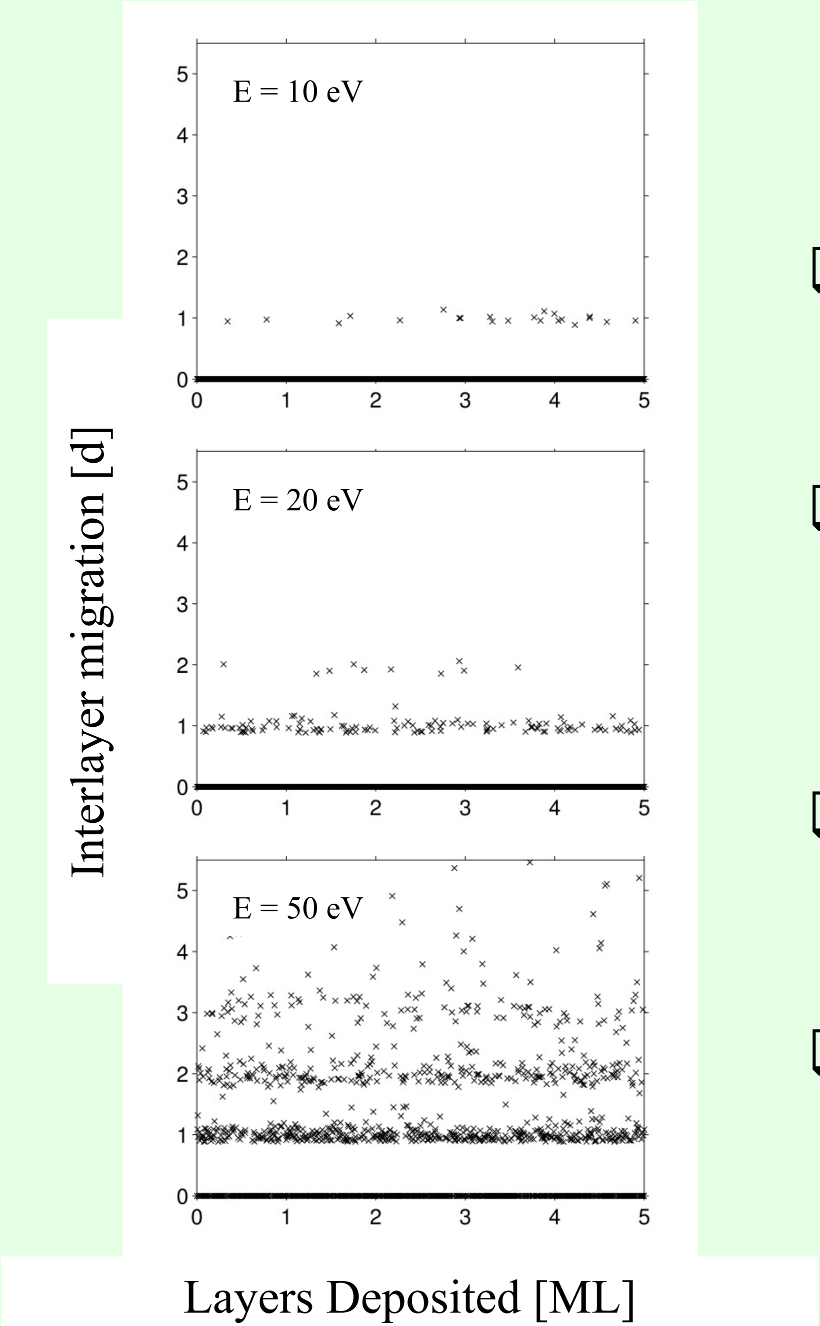
Atomic distribution in substrate





- 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.

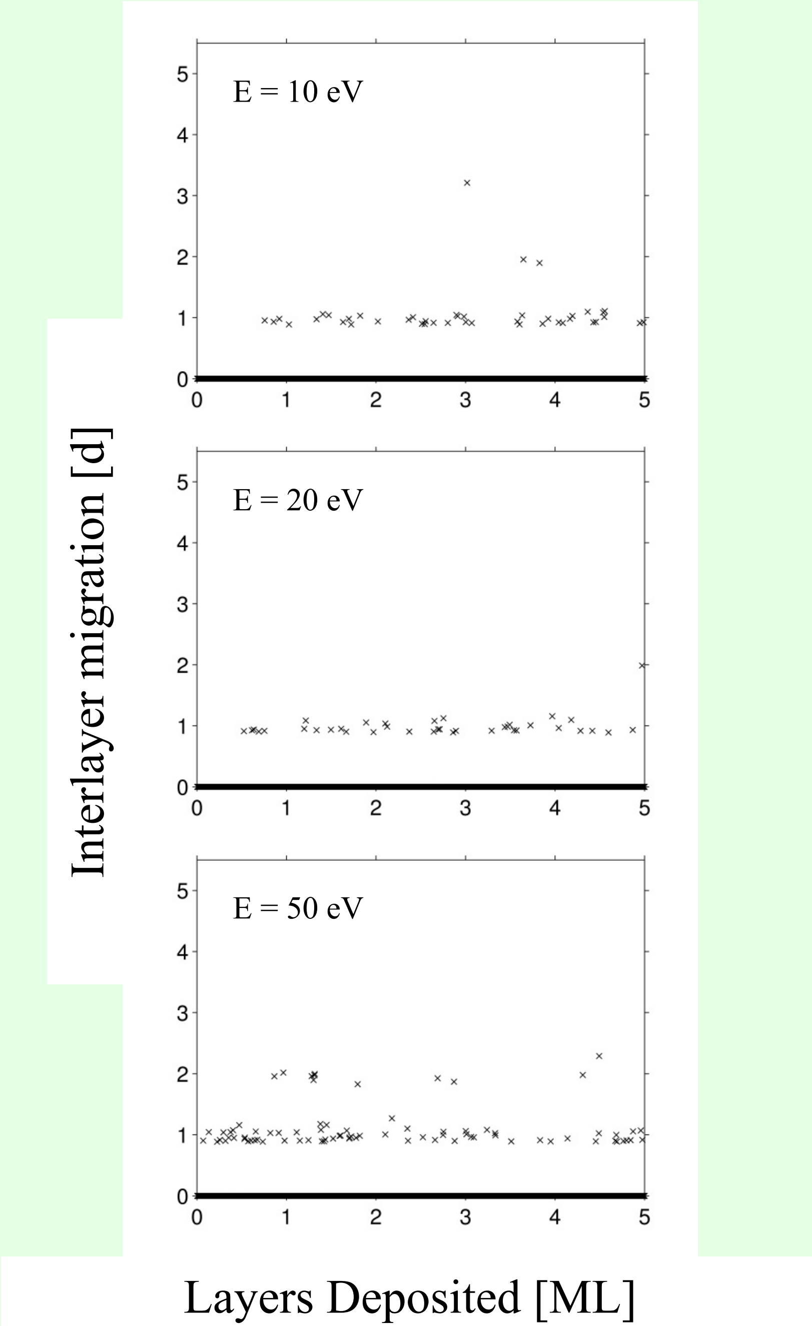
Interlayer Mass Transport



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.

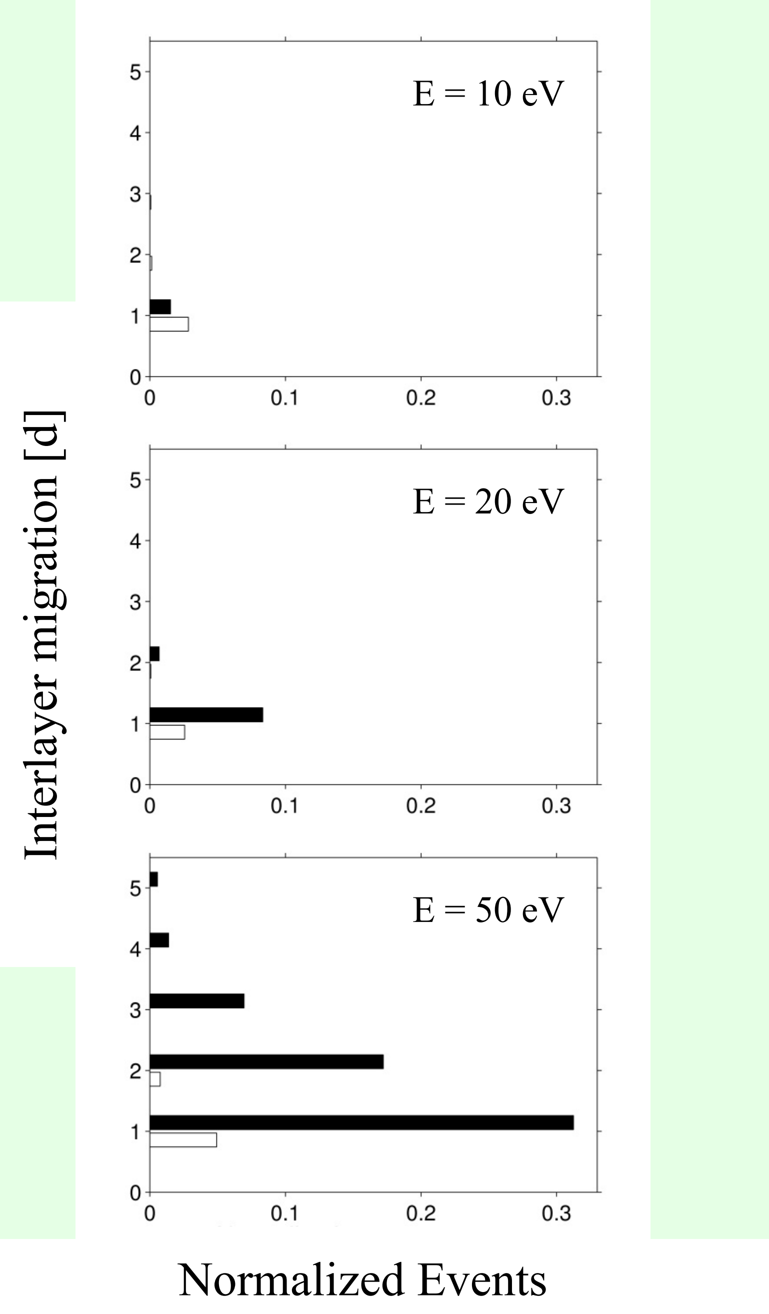
Interlayer Mass Transport



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.

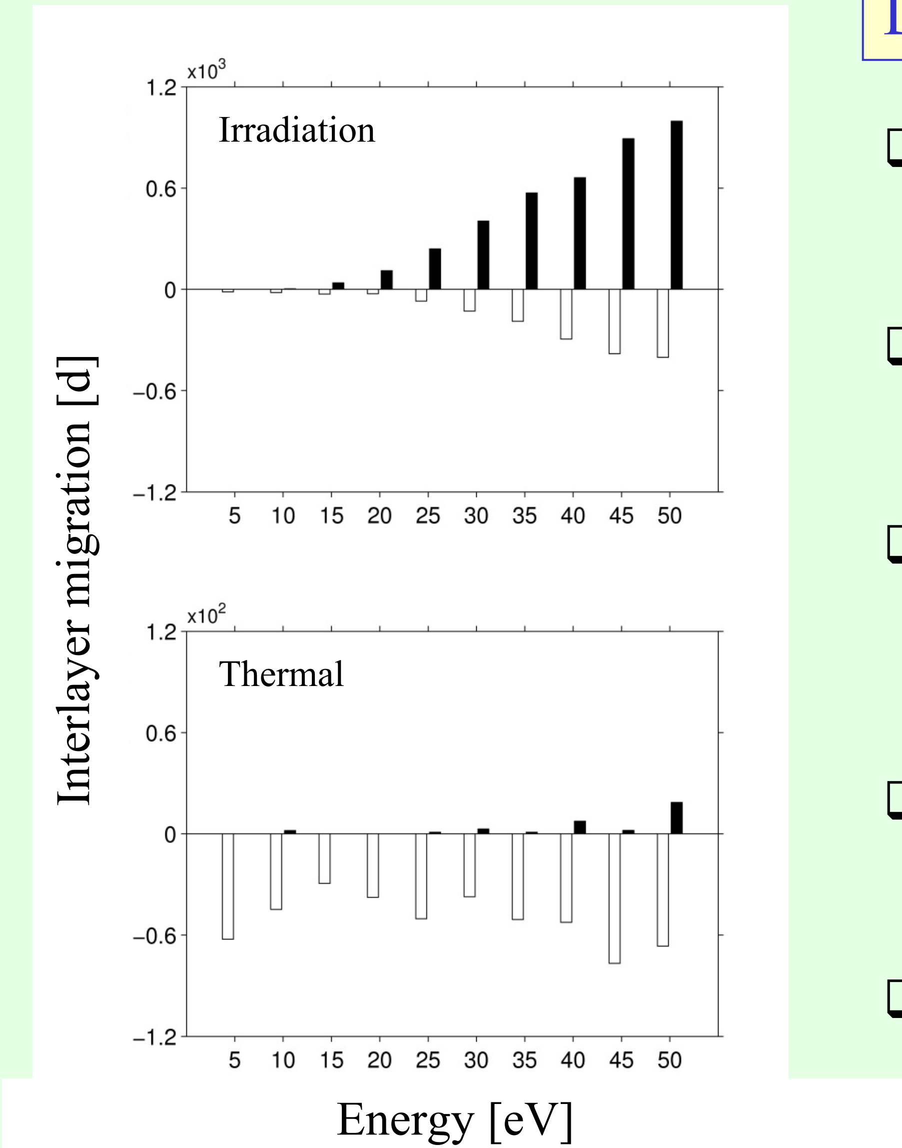
Interlayer Mass Transport



Total interlayer migration

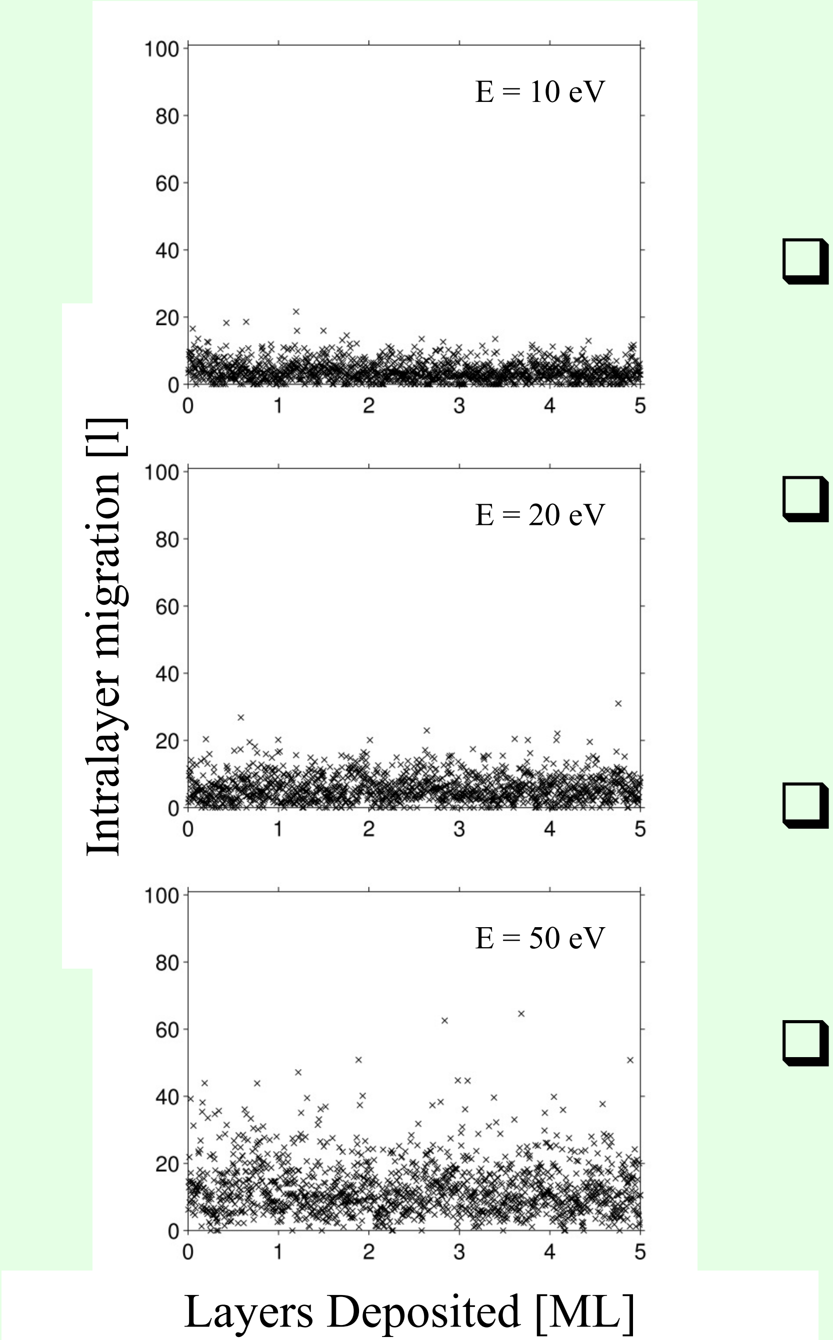
- **Irradiation** = Black bars.
- **Thermal** = White bars.
- 10 eV – only 1*d* events.
- 50 eV – full spectrum of migrations events.
- 50 eV – irradiation induced part increases by ~ 100.

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.

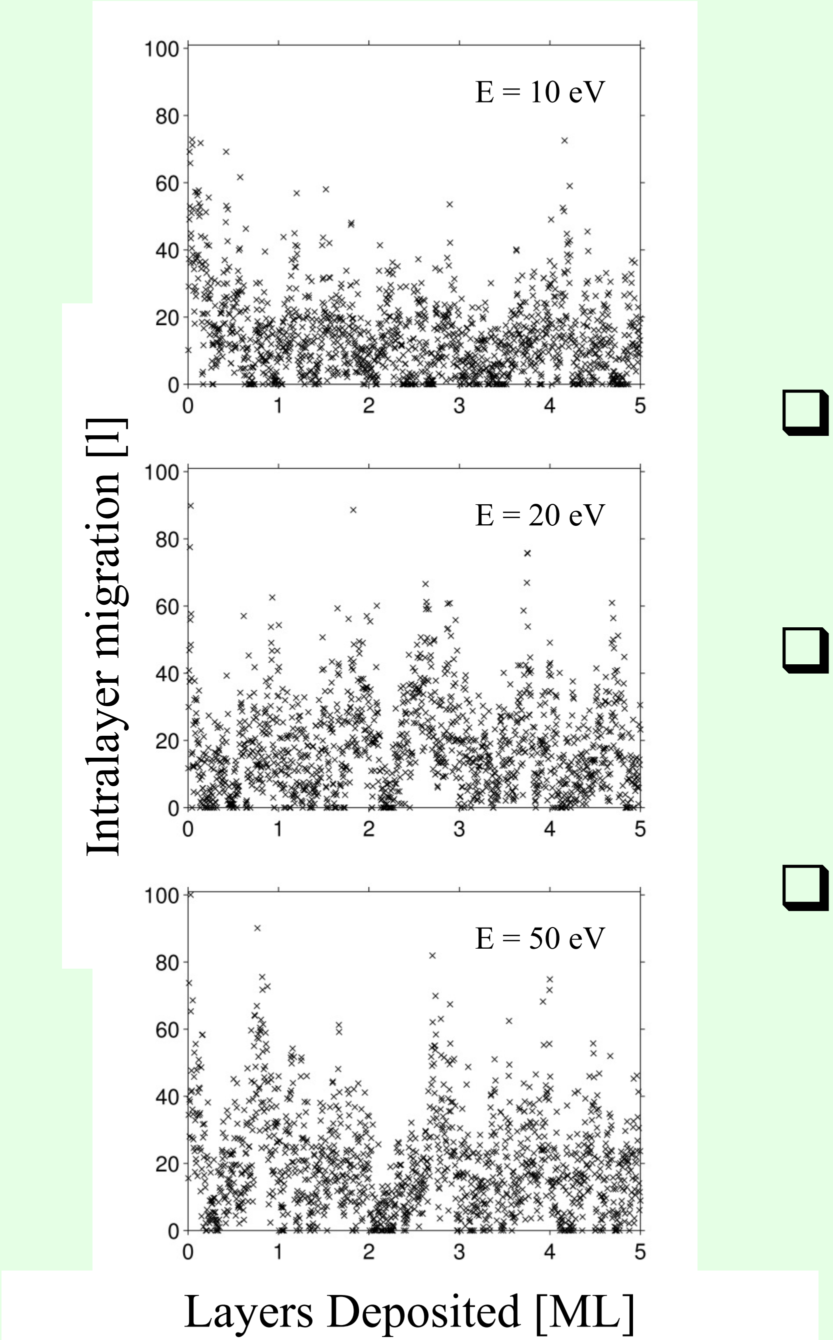


Irradiation Interval = 1st 10 ps

- 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

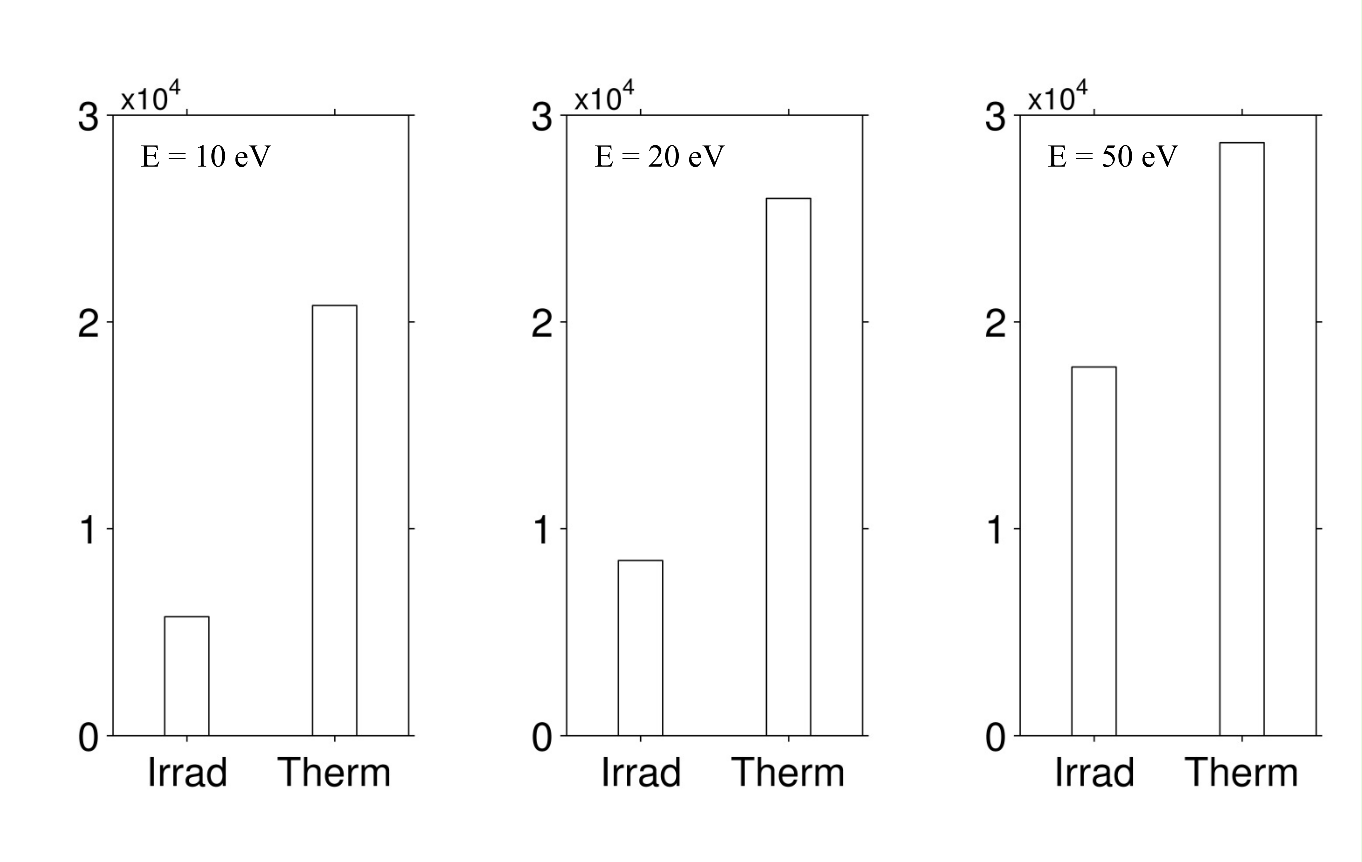
Thermal Period



- 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.

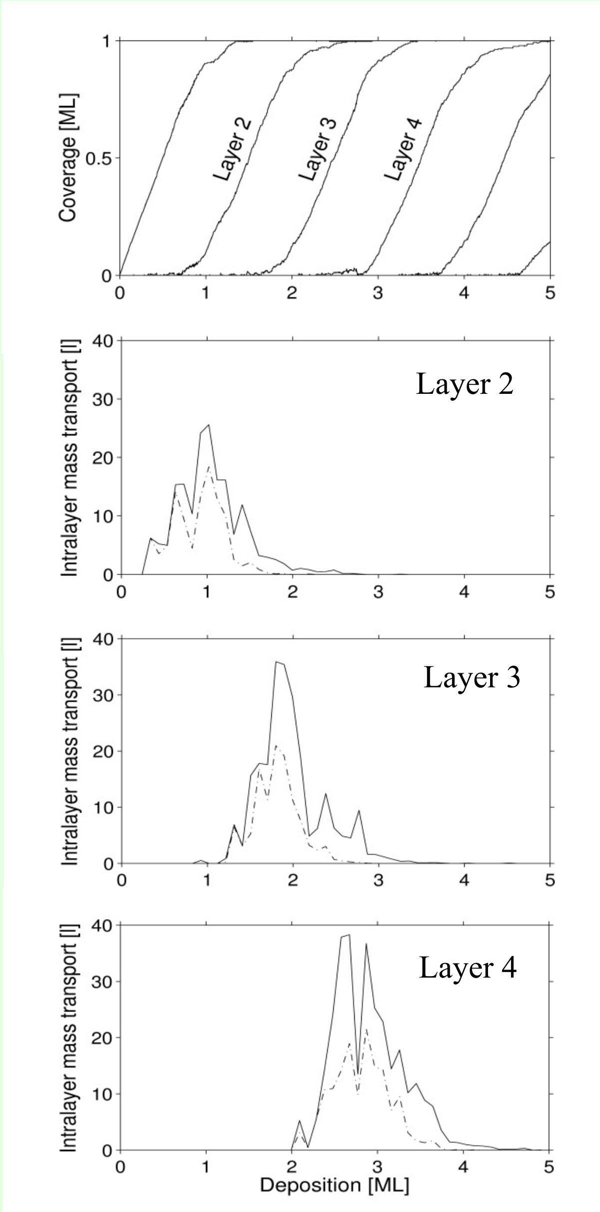
Intralayer Mass Transport

Total intralayer migration



Intralayer Mass Transport

Layer-by-layer growth at 20 eV

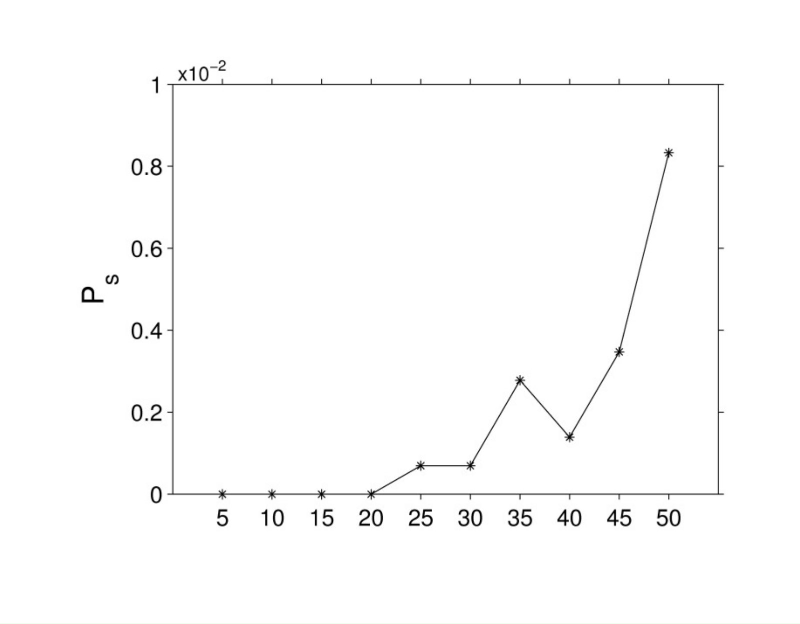


- Intralayer activity is strongly correlated to layer coverage.
- Maximum intralayer transport is observed at coverages of 0.05 ML, in agreement with experiments[1].
- Significant adatom contribution to intralayer migration – dotted lines.

[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)