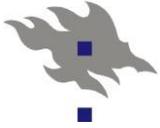




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UNIVERSITY OF HELSINKI

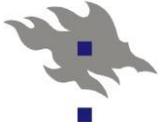
Strålnings-skador vt 2014
Säteilyvauriot kl 2014
Radiation Damage Spring term 2014

6. Long-term damage evolution



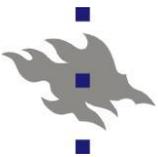
Primary damage production vs. long-term evolution

- The previous chapters described almost exclusively the primary damage production
- After the primary damage production is over, **diffusion** (*diffusion/diffuusio*) of the defects created may significantly alter the nature of damage
- The diffusive (migration) phase begins after the cascade has cooled down back to (within a few Kelvins of) the ambient temperature
 - This ends the athermal stage of the cascade
 - MD simulation and thermal diffusion calculations show this time is at about 10-100 ps depending on material



Primary damage production vs. long-term evolution

- After the system is cooled down, all further evolution of the cascade 'debris' (remaining defects) is determined by thermally activated diffusion of these defects
 - This is a near-thermodynamic equilibrium process
 - Not exactly equilibrium because defect density $\gg \gg$ equilibrium density
- ... until a next irradiation event hits in the same region of space, creating new defects
- But for typical irradiation fluxes, time between damage creation events in the same region of space is microseconds - seconds => lots of time for thermal migration in between

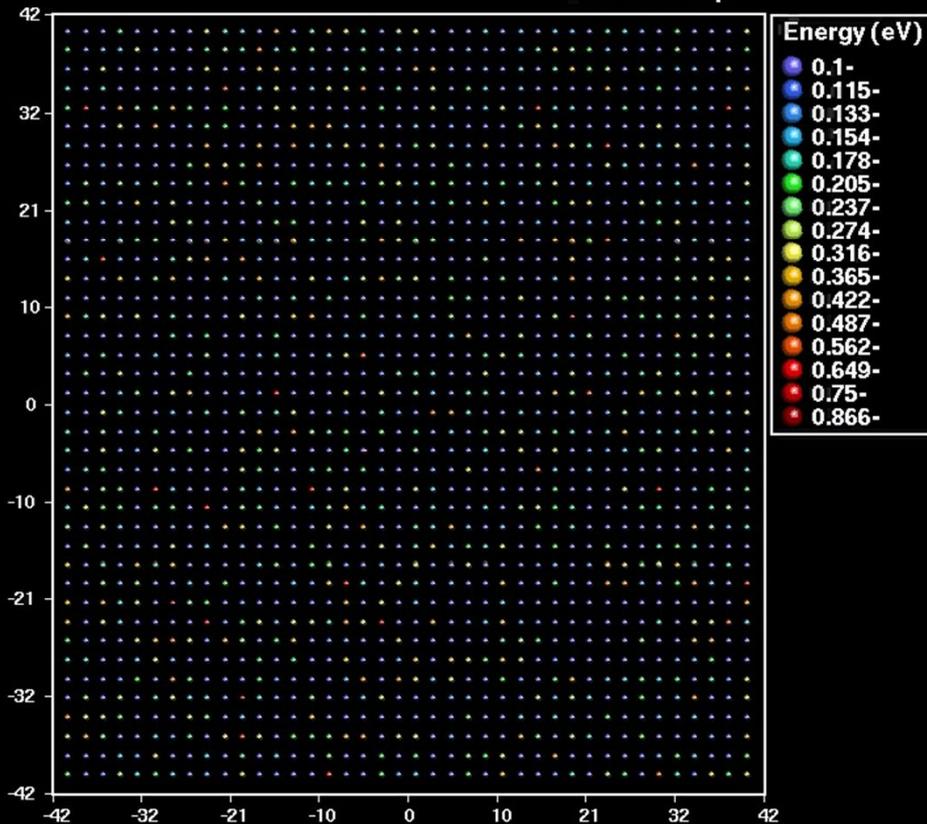


Example: 3 keV cascade in Au

- As an illustrative example, I did an MD simulation of a cascade in Au with *all periodic boundaries* at 600 K
 - => defects cannot escape, perfect recombination likely eventually
- Animation of damage evolution:

3 keV Au recoil in Au @ 600 K, view of all atoms in cubic cell

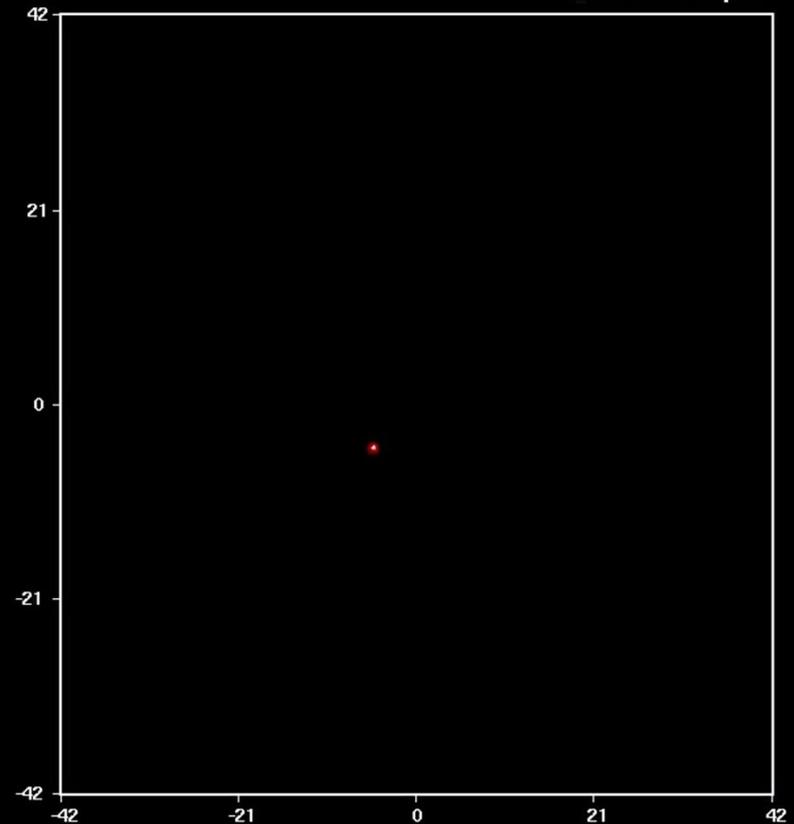
time 0.00018 ps



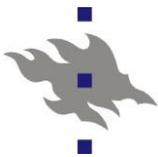
Kai Nordlund (2014)

Same recoil event, only defects plotted

time 0.00018 ps

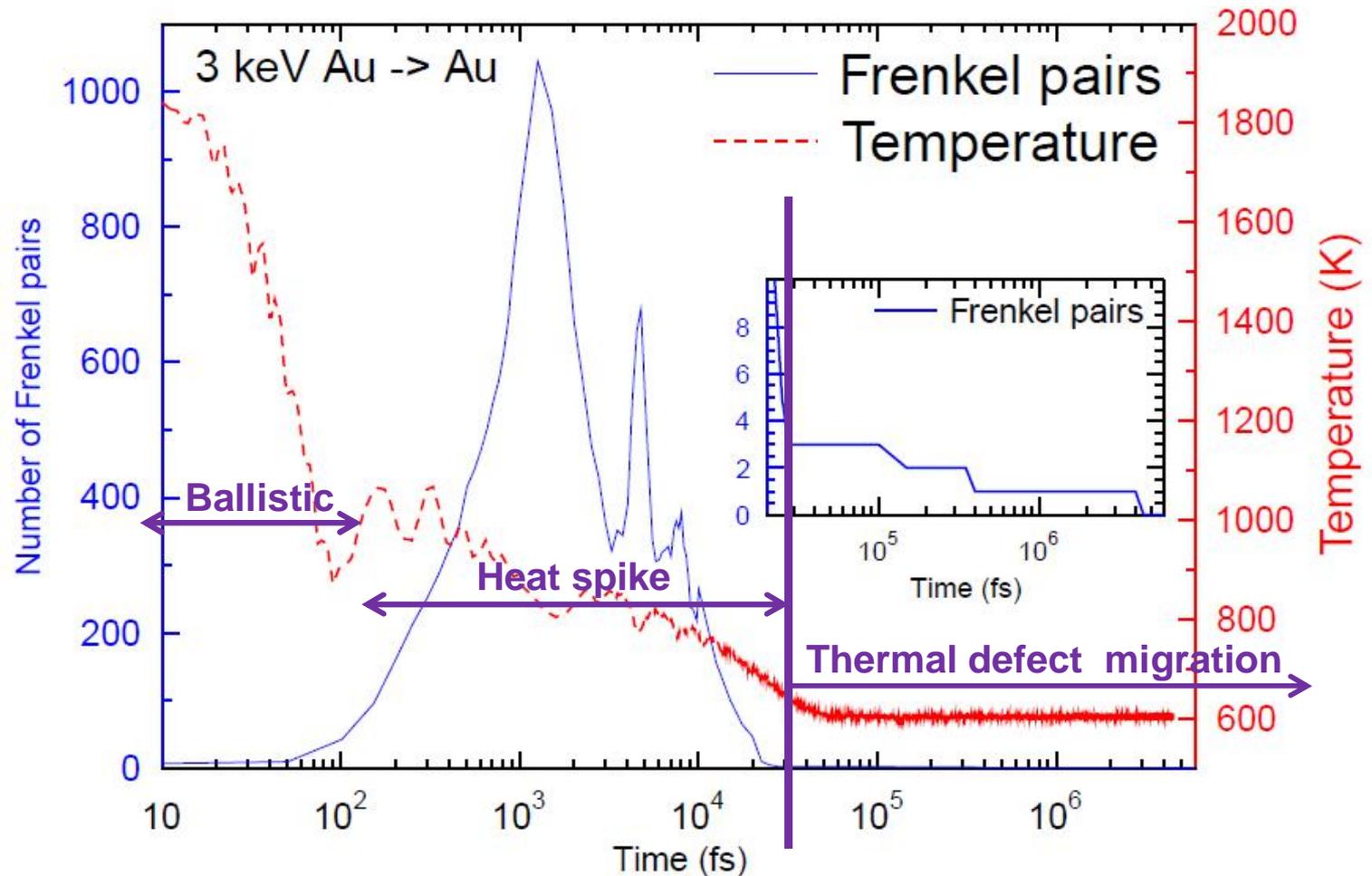


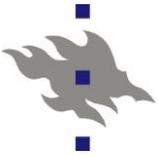
Kai Nordlund (2014)



Example: 3 keV cascade in Au

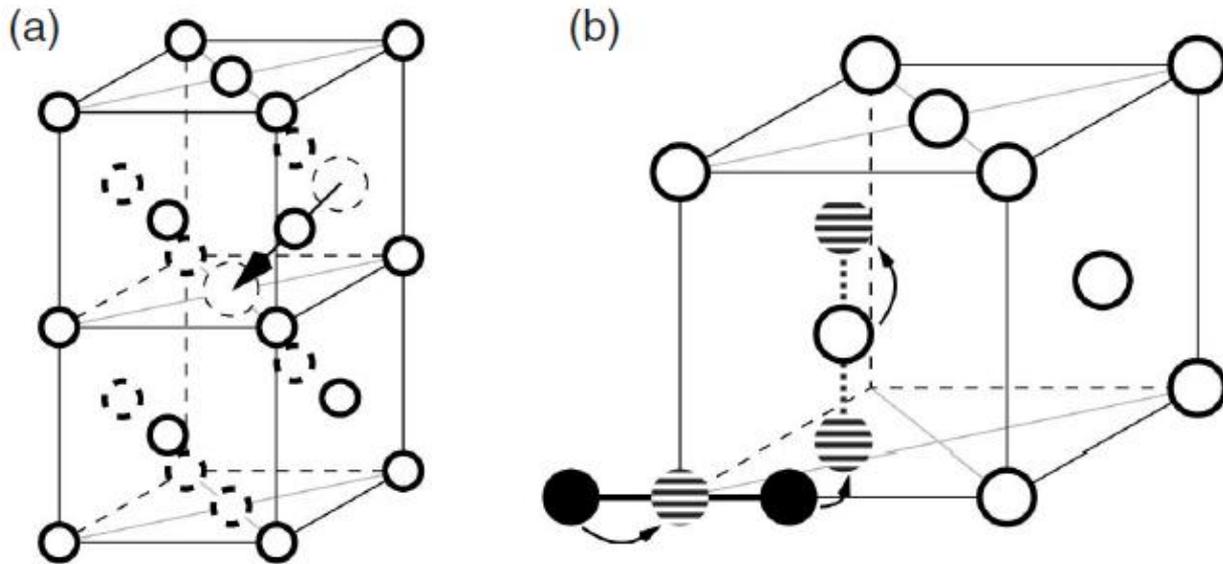
- Number of defects and temperature vs. time in this same event:



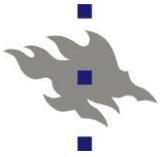


How do the defects move?

- The defect mobility mechanism depends a lot on defect structure
- For vacancies usually a simple atom jump into empty site
- For dumbbell interstitials more complex pathways, e.g:



[K. Nordlund and R. S. Averback, Handbook of Materials Modeling, edited by S. Yip (Kluwer Academic, Dordrecht, The Netherlands, 2005), Vol. 1, Chap. 6.2. Point defects in metals]



When are defects mobile?

- A crucial question for the long-term evolution is hence, when and how fast are defects mobile?
- Simple defect mobility (migration, diffusion) is almost always Arrhenius-like, i.e. follows a Boltzmann-like activation energy function of the type

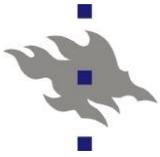
$$\text{Jump rate} = \text{Prefactor} \times e^{-E_m/k_B T}$$

which more commonly is written as

$$f = f_0 e^{-E_m/k_B T}$$

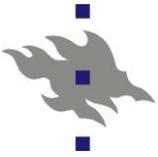
where f is the jump rate (in units of jumps/time), f_0 is the migration prefactor, E_m is the migration activation energy (barrier) and T is the temperature of the environment

- For simple defects, f_0 is close to the lattice vibration rate which can be estimated e.g. from the Debye model
 - In typical hard metals and ceramics, $f_0 \sim 10^{13}$ 1/s (Hz)



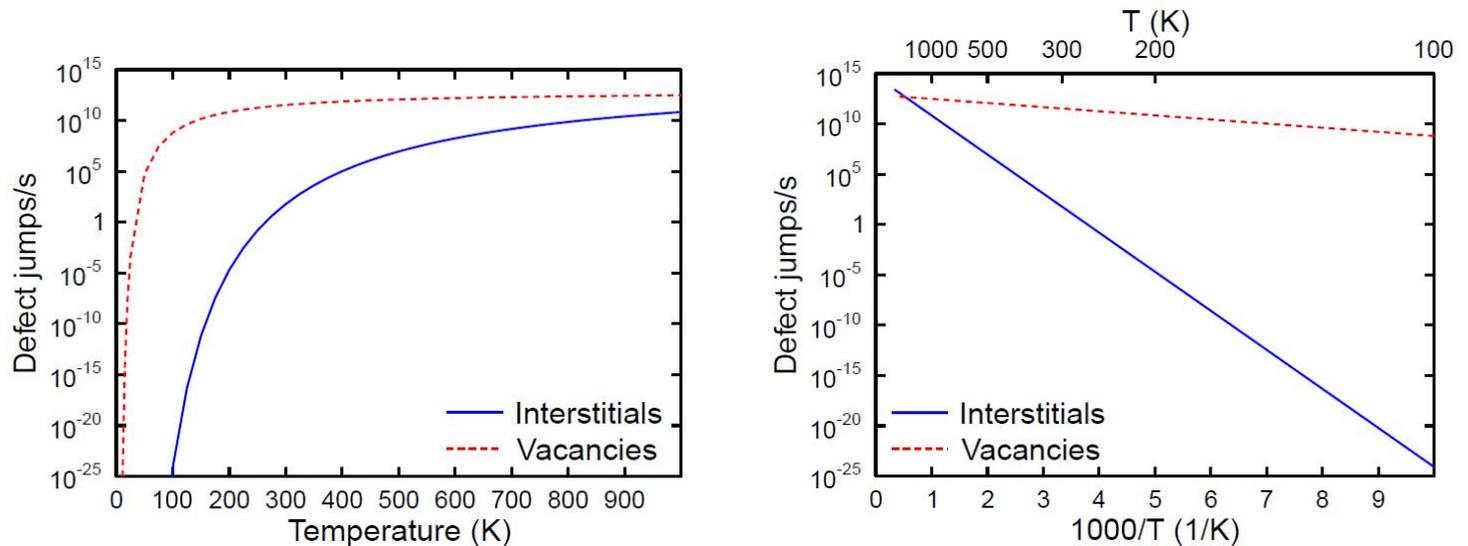
Terminology note

- *Nota bene*: some scientist maintain that the word diffusion should only be used for equilibrium diffusion due to thermally generated defects, and any other kind of atom or defect motion is migration
- However, there is no consensus on this, and many other scientists use the terms mobility, migration and diffusion as if they were identical in meaning
 - In these lecture notes we follow the latter practice, i.e.
mobility = migration = diffusion

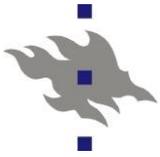


Arrhenius temperature dependence

- This is a very strong temperature dependence!
- Example: migration of vacancies in Cu [factors from Phys. Rev. Lett. **80**, 4201 (1998)], same data plotted on a log-lin and Arrhenius plot:

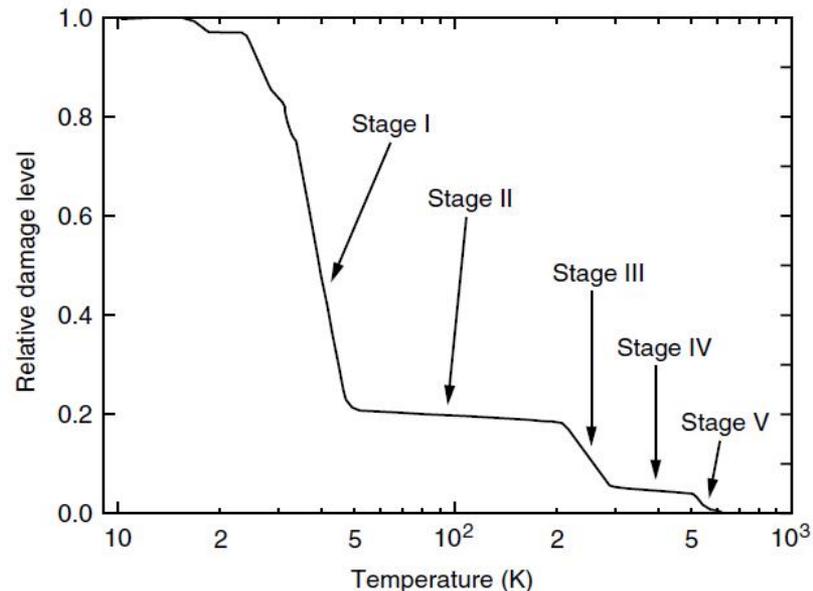


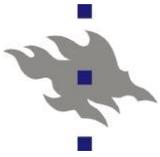
- Note how migration rates change > 10 orders of magnitude in a narrow < 100 K T interval!!
 - Due to this strong temperature dependence, on heating there is a fairly narrow temperature interval when a defect becomes efficiently mobile.



Stages for damage recovery

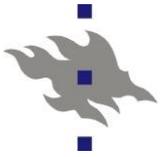
- The damage recovery after irradiation thus often occurs in distinct stages
 - Typical experiment: irradiate sample at very low temperature (e.g. liquid He, 4 K) when there is no migration, then heat it up at a constant rate and measure defect concentrations
- This has led to naming of defect annealing stages: I, II...





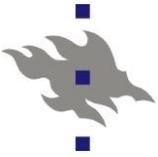
Physical interpretation

- In typical metals:
 - Stage I: interstitial mobility: anneal with vacancies or cluster
 - Stage II: interstitial clusters mobile, some annealing with vacancies, may migrate to surface
 - Stage III: vacancies mobile, anneal with interstitials or cluster
 - Stage IV: vacancy clusters mobile, anneal or cluster to form big vacancy clusters
 - Stage V: Vacancy clusters start to emit free vacancies, which move and anneal with interstitials or at surface => no defects left



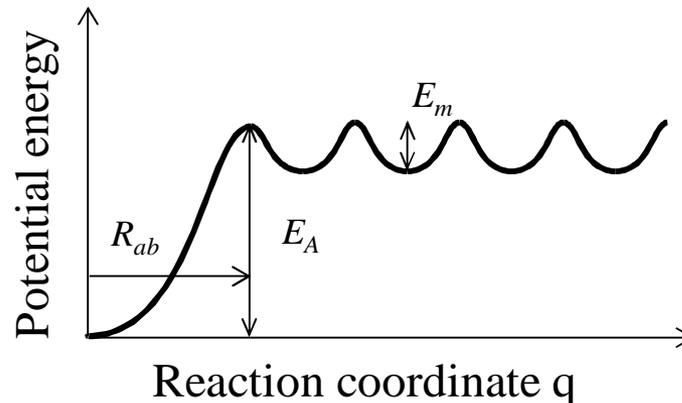
Sinks, trapping etc.

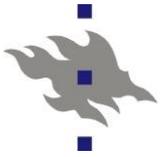
- The mobile defects can interact with each other in a number of ways
- Using Kroger-Vink notation, for self-defects only:
 - Annihilation: $I + V = 0$ (no defect left)
 - But this is not automatic, e.g. in Si possible to have: $I + V = IV$ pair, in graphene: $I + V =$ Stone-Wales defect
 - Cluster formation: $I + I = I_2, I + I_2 = I_3, V_7 + V_4 = V_{11}$ etc....
 - Cluster shrinkage: $I + V_3 = V_2, V_2 + I_7 = I_5$ etc....
 - Defect emission: $V_{25} = V_{24} + V, I_2 = I + I, \text{ etc...}$
- Surfaces and interfaces often act as defect **sinks** (*sänka/nielu*): $I + S = S$
- Defects can be **trapped** (*infångning/loukkuuntuminen*) at impurities, or drag them along: $I + C = IC$ complex



Sink strength, emission activation energy

- The defect reactions are usually treated as instantaneous once the two defect types a and b come within some radius R_{ab} of each other
- The emission of atoms from a defect (**detrapping** (*oinfångning / epäloukkuuntuminen*)), on the other hand, requires that the atom overcomes a barrier, so this process is thermally activated and has a rate of the type $f_0 e^{-E_A/k_B T}$
- The motivation to this difference is the following (quite realistic) idea of the energy landscape:



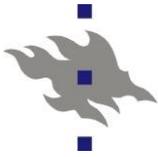


Solution of diffusion equation (rate equations)

- All of this can be described by the solution of the diffusion equation with added term for the irradiation source, trapping and detrapping reactions
- The equation in 1D for a specific defect species a and its interactions with other species b is:

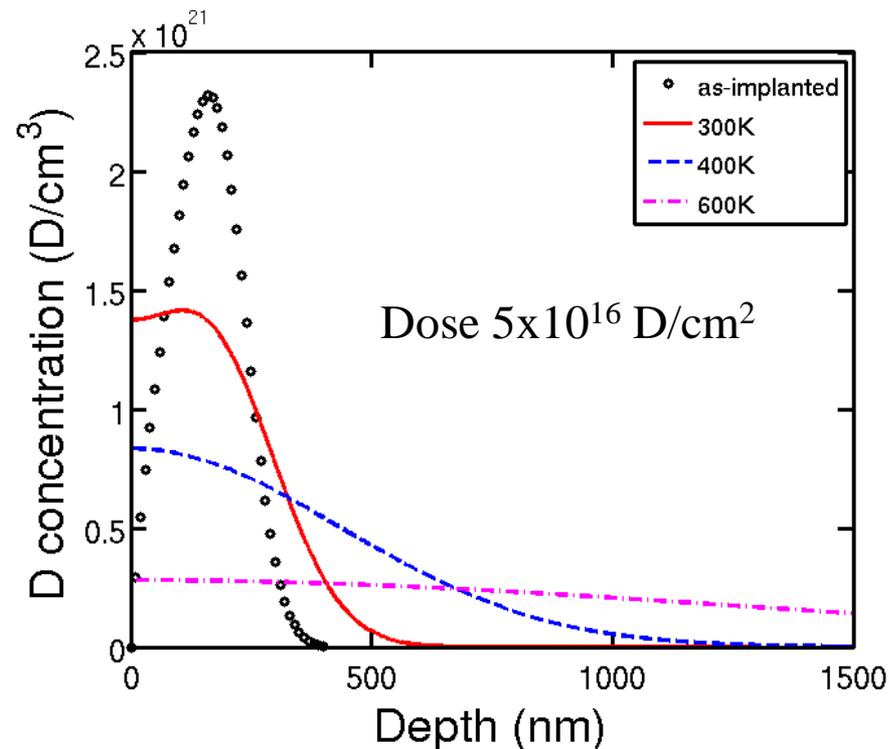
$$\begin{aligned} \frac{\partial C_a}{\partial t} = & D_a \frac{\partial^2 C_a}{\partial x^2} && \text{diffusion} && (\text{free particles } D = D_0 e^{-E_m/kT}) \\ + & S_{a,b} && \text{source term} && (\text{implantation } \rightarrow \text{ ions, defects}) \\ - & 4\pi R_{ab}(D_a + D_b)C_a C_b && \text{trapping} && (R_{ab} \text{ from MD}) \\ + & \nu_{ab} e^{-E_A/kT} C_{ab} && \text{detrapping} && \end{aligned}$$

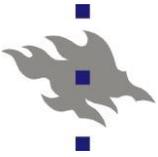
[Equations courtesy of Tommy Ahlgren]



Example of diffusion

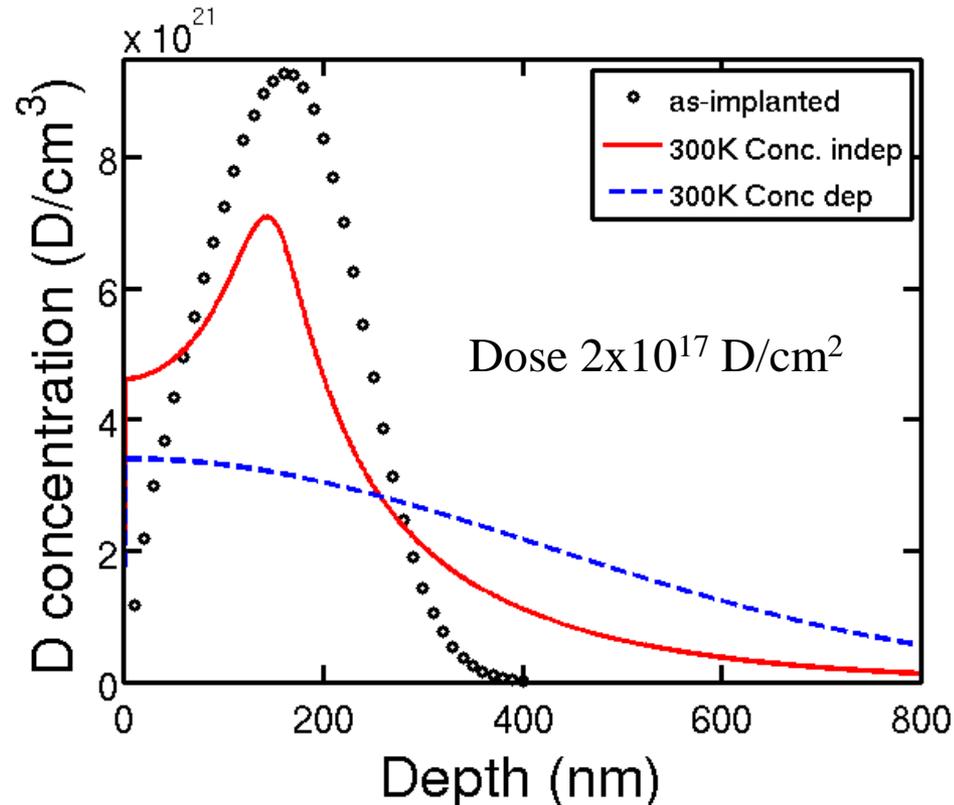
- Example of direct solution of the diffusion equation for deuterium (D) implantation of W
 - Source term which is the initial implantation depth profile, and annealing at different temperatures for 1 ms

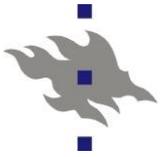




Example of concentration-dependent diffusion

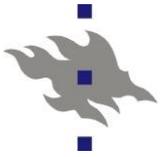
- Similar case but taking into account that at high D concentrations the diffusion depends on concentration – faster at high concentrations



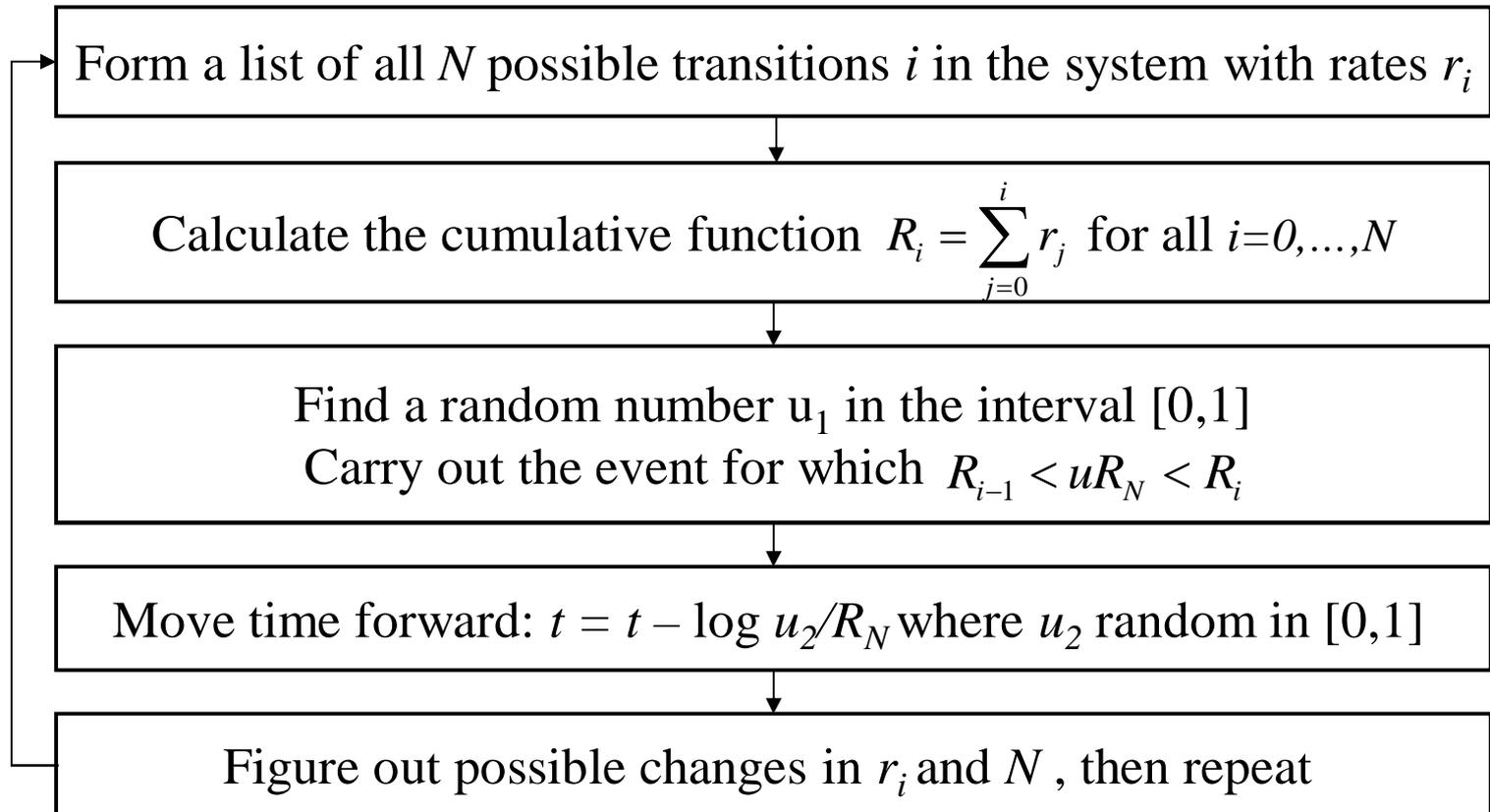


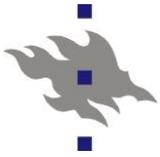
8.2 Kinetic Monte Carlo

- Another, completely independent approach is to simulate the defect migration explicitly with the kinetic Monte Carlo approach
- Like in rate equations, the defect types and their migration and reaction parameters need to be known in advance
- Once they are, the evolution of the system can be simulated as a set of stochastic processes



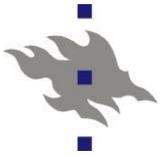
Kinetic Monte Carlo algorithm





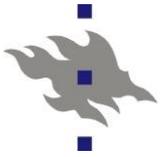
Comments on KMC algorithm

- The KMC algorithm is actually exactly right for so called Poisson processes, i.e. processes occurring independent of each other at constant rates
 - Stochastic but exact
- Typical use: atom diffusion: rates are simply atom jumps
- But the big issue is how to know the input rates r_i ??
 - The algorithm itself can't do anything to predict them
 - I.e. they have to be known in advance somehow
- From experiments, DFT simulations, ...
- Also knowing reactions may be difficult



Comments on KMC algorithm

- Many varieties of KMC exist:
 - object KMC (OKMC): only treat defects, impurities as the objects of the simulation
 - Atomic KMC (AKMC): treat all atoms in system explicitly
 - Reaction KMC (RKMC): speed up OKMC by jumping from one reaction to the next
 - First-passage KMC (FPKMC): well motivated way to speed up KMC
- There are also many varieties of ‘adaptive’ KMC where a barrier-detecting calculation of some sorts is run within the KMC to find the barriers ‘on-the-fly’ without having to pretabulate them

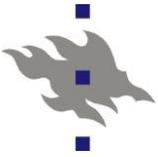


Principles of object KMC for defects

- Basic object is an impurity or intrinsic defect in lattice
- Non-defect lattice atoms are not described at all!
- Basic process is a diffusive jump, occurring at Arrhenius rate

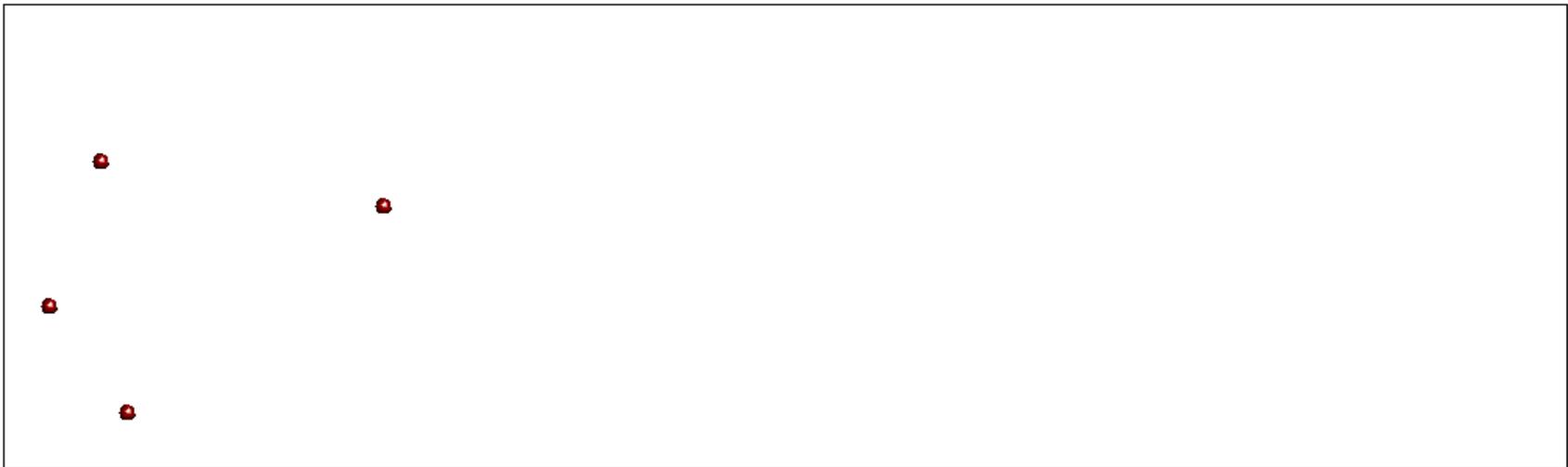
$$r_i = r_0 e^{-E_m / k_B T}$$

- But also reactions are important: for example formation of divacancy from two monovacancies, or a pair of impurities
- Reactions typically dealt with using a simple recombination radius: if species A and B are closer than some recombination radius r_{AB} , they instantly combine to form defect complex



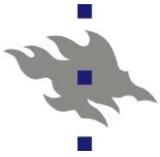
Example animation of KMC

- Simple example: He mobility and bubble formation in W
 - Inputs: experimental He migration rate, experimental flux, recombination radius of 3 Å
 - All clusters assumed immobile



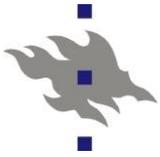
x (0 - 1000) y (-500 - 500) z (-500 - 500)

[K. O. E. Henriksson, **K. Nordlund**, A. Krasheninnikov, and J. Keinonen, Fusion Science & Technology **50**, 43 (2006).]



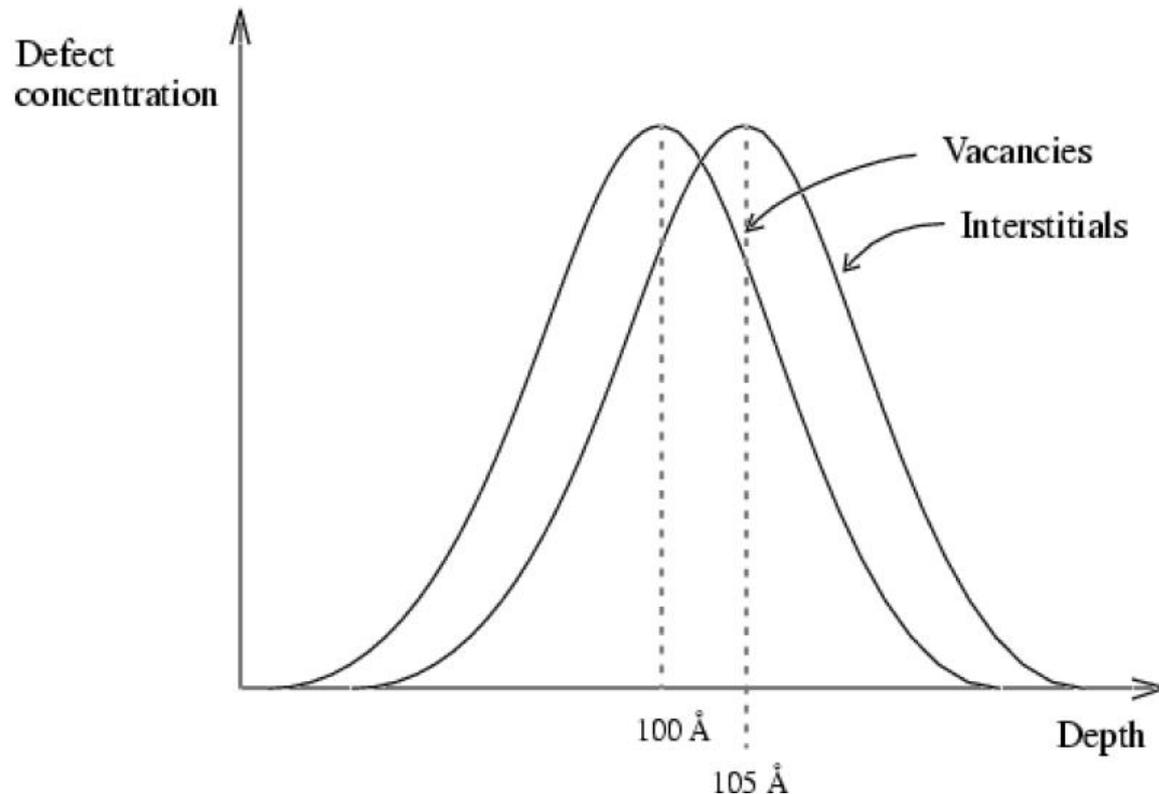
Example 2: i and v migration in Si

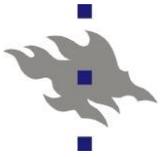
- A more advanced example: defect mobility in Si with recombination and clustering reactions
 - However, no detrapping or cluster mobility
- Parameters for i and v mobility from Tang et al. [Phys. Rev. B. 55 (1997) 14279] as follows:
 - $f_0^i = 1.717 \text{ 1/fs}$
 - $E_m^i = 1.37 \text{ eV}$
 - $f_0^v = 0.001282 \text{ 1/fs}$
 - $E_m^v = 0.1 \text{ eV}$



Initial defect depth profiles

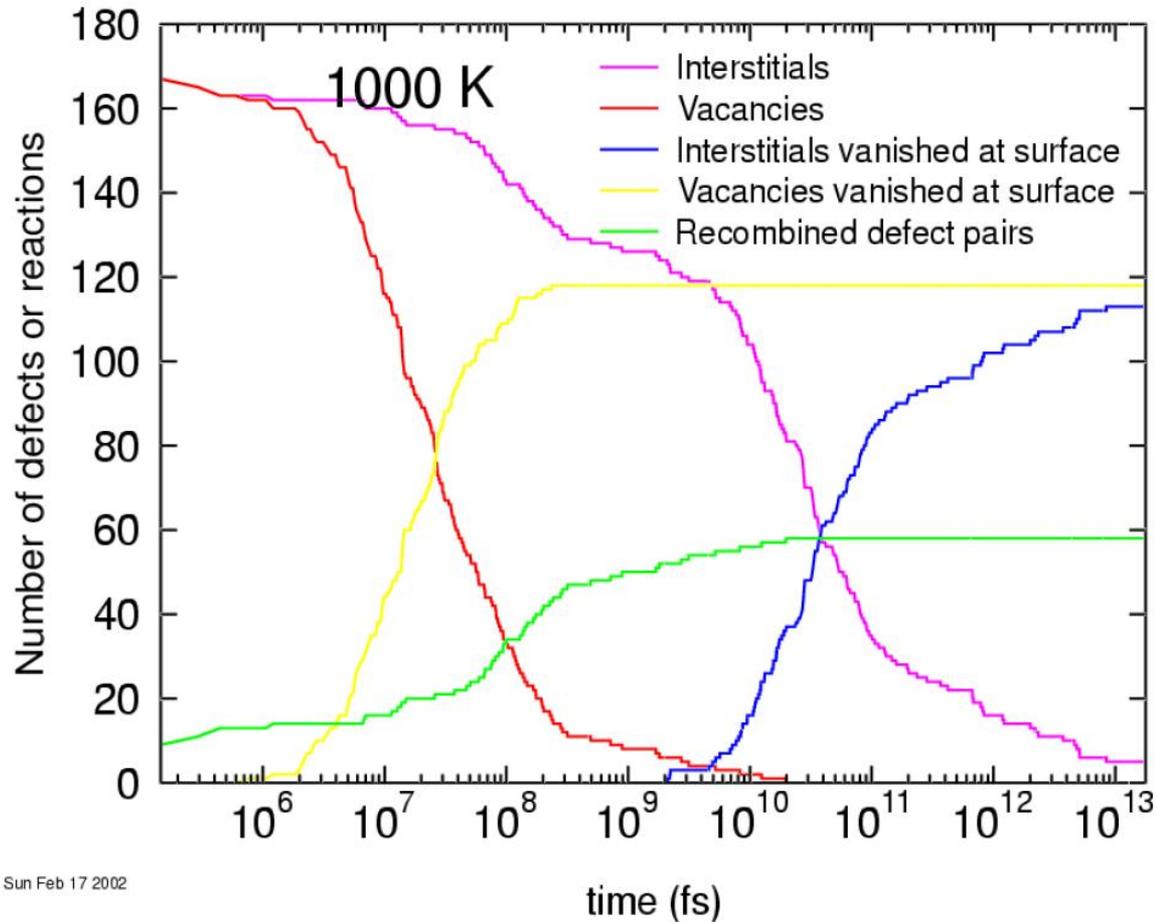
- Initial state: v and i concentration profiles, with interstitials slightly deeper in due to ballistic collisions pushing them frontwards





Results for defect numbers

■ At 1000 K:



Sun Feb 17 2002

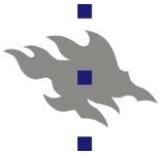
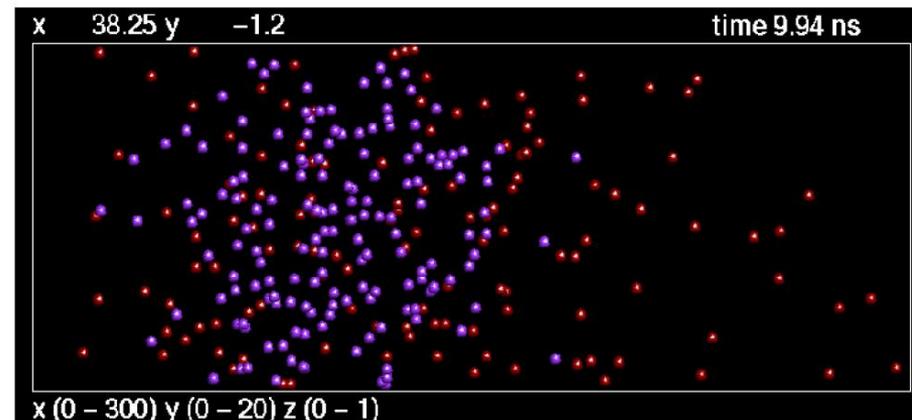
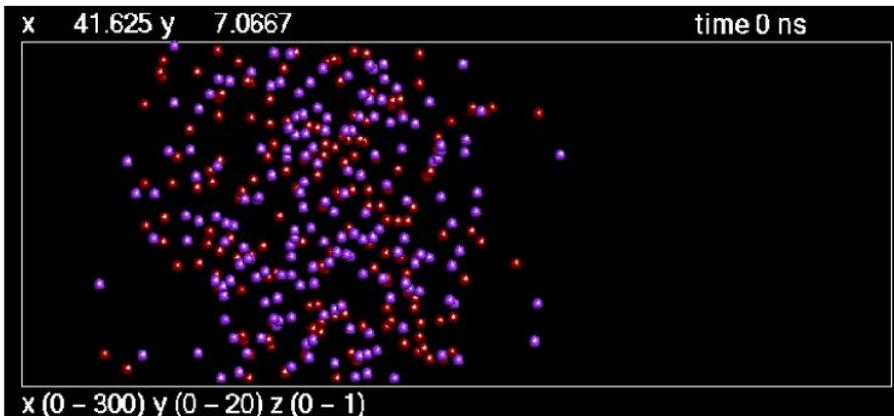


Illustration of evolution at 1000 K

- The red dots are vacancies, the purple ones interstitials. The plotting region is 0-20 Å in the y direction, 0-300 Å in the x (depth) direction. The surface $x = 0$ is to the left.
 - Initially the interstitials do not move essentially at all in this phase, so what happens is just that the vacancies vanish by recombination and at the surface. But a few vacancies go deep into the bulk.
 - But on longer time scales, these vacancies have a chance to come back to the interstitial layer and recombine.



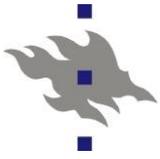
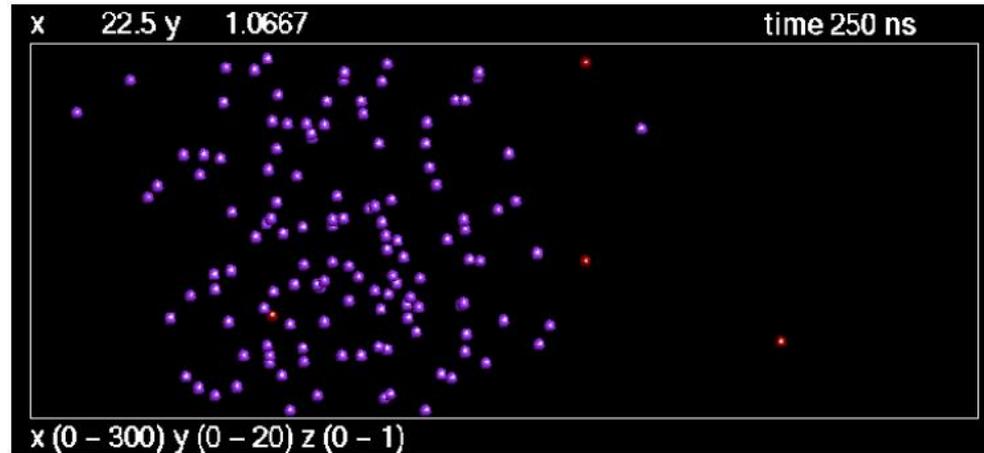
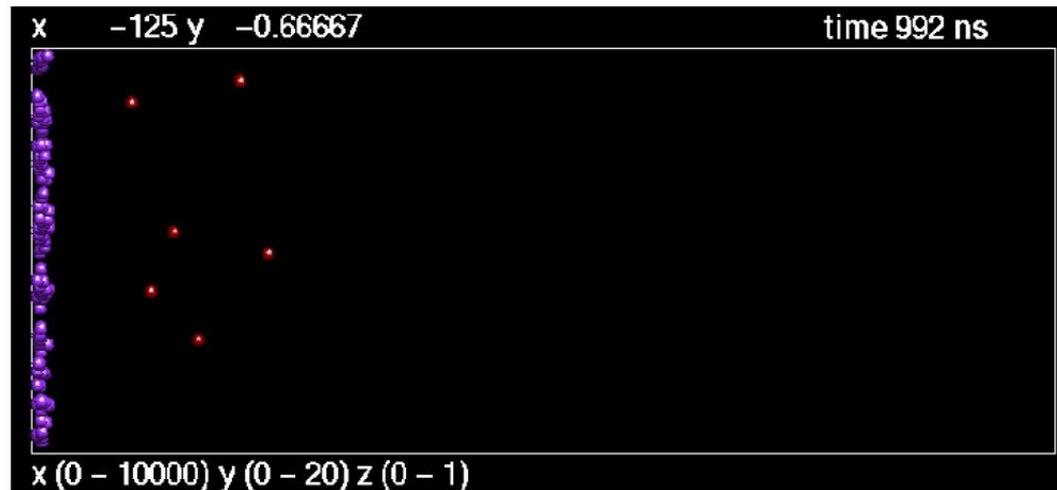


Illustration of evolution at 1000 K

- State when vacancies have almost all vanished in surface or to the bulk:



- Below is a plot of the state at 1 μs (note that the z scale is now extended from 0 to 10000 \AA):



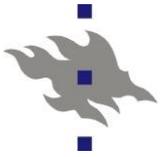
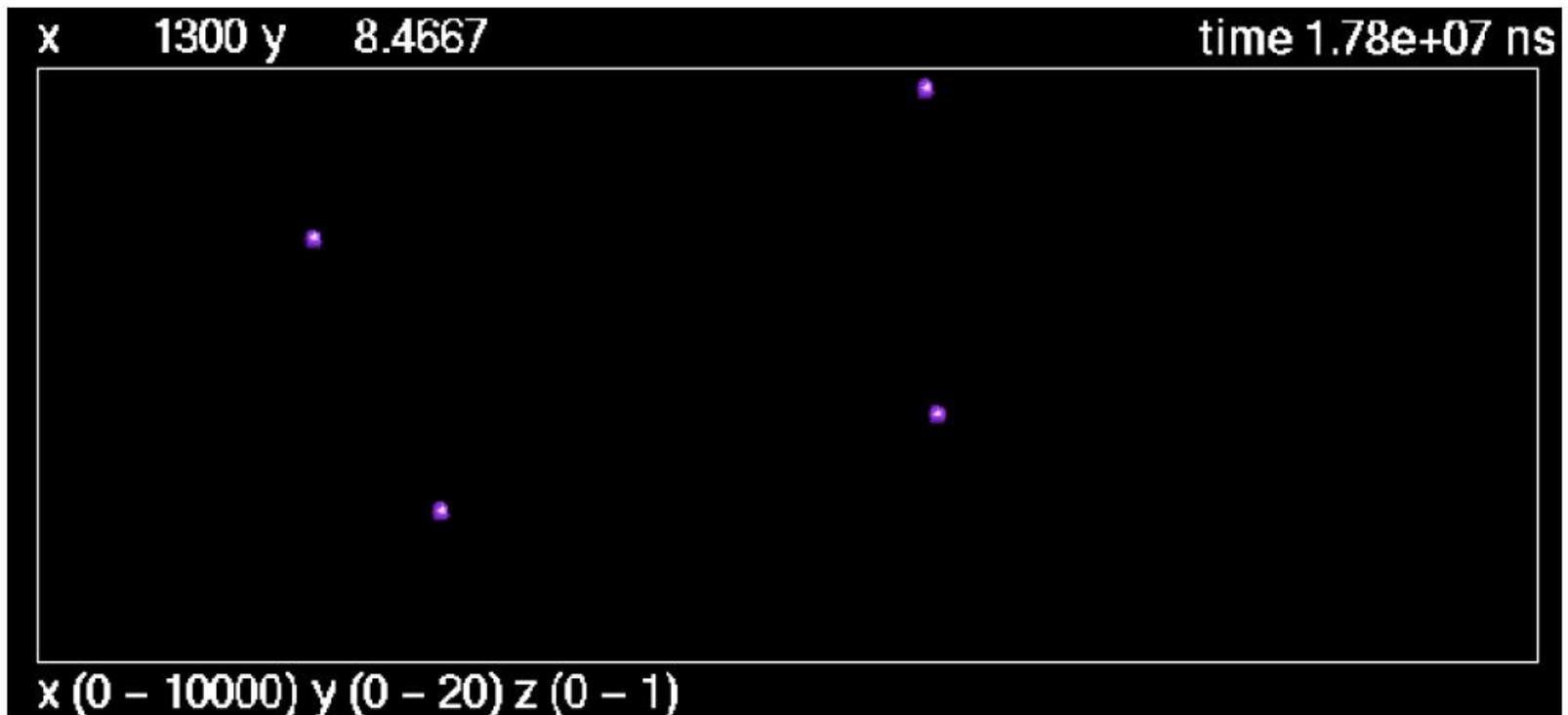
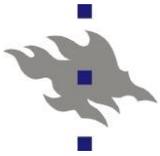


Illustration of evolution

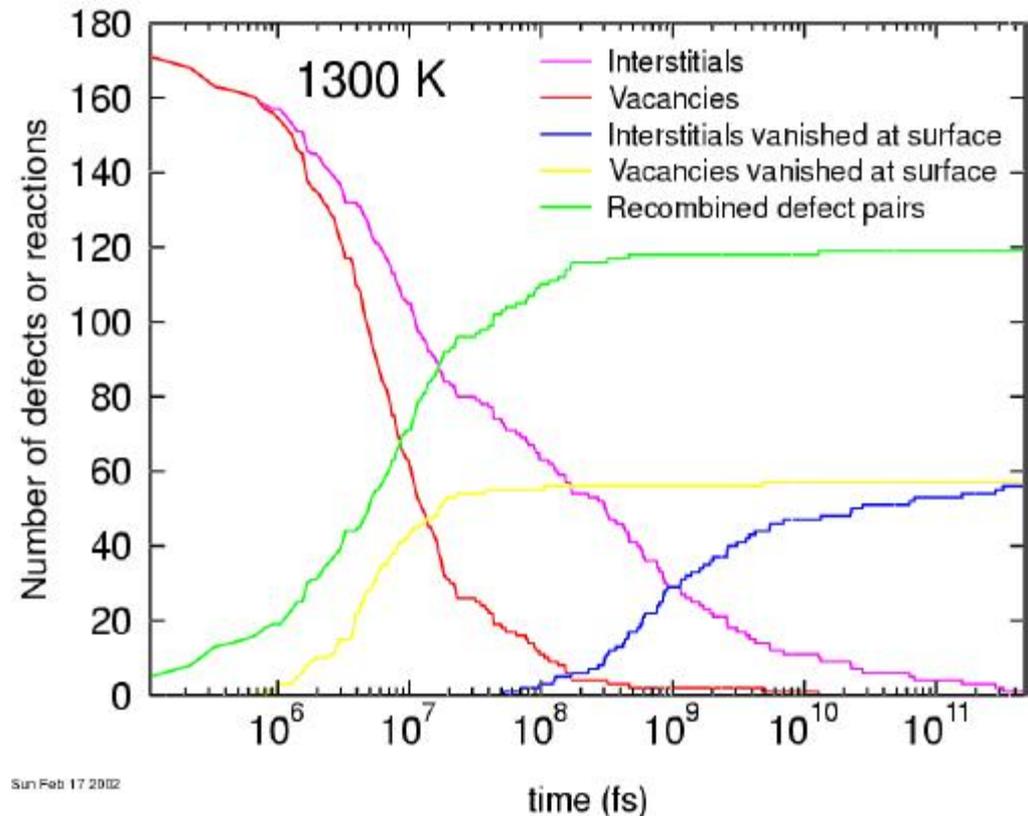
- Finally, given enough time the vacancies find their ways back to the interstitials and recombine with them, so that after a very long time only a few slowly moving interstitials are left:



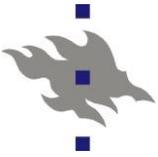


Evolution at 1300 K

- At a higher temperature, the interstitials and vacancies are mobile on comparable time scales and the behaviour changes
- More recombination, less vacancies vanishing at surface

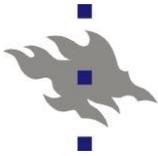


Sun Feb 17 2002



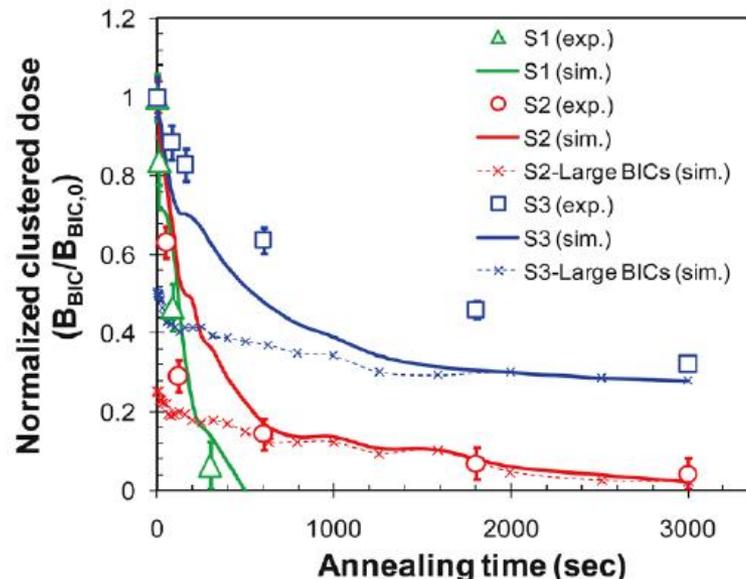
8.3. Radiation enhanced diffusion

- The defects introduced by irradiation can also enhance the mobility of impurities above their normal irradiation values!
- They can form agglomerates, for instance a self-interstitial I may bind with an impurity X to form a mobile mixed defect => radiation enhanced diffusion (RED)

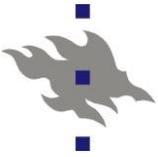


Example of RED KMC: B in Si

- Lourdes Pelaz group have done extensive works on parametrizing the mobility of all significant defects in Si, and also B-containing defects
- B has a major RED-effect due to interaction with interstitials
- Example data (details not important on this course):

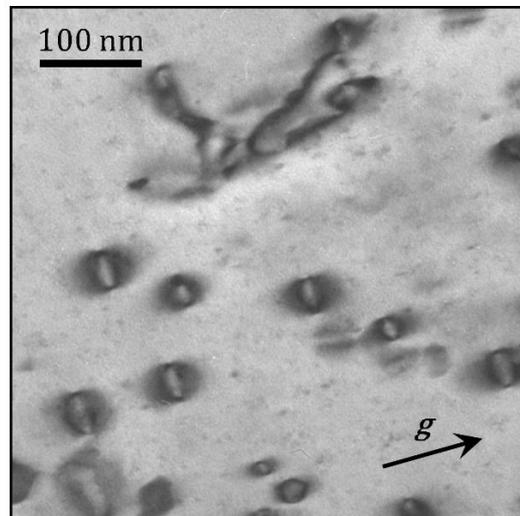


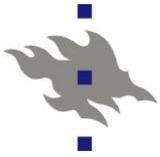
[M. Aboy, L. Pelaz, E. Bruno, S. Mirabella, S. Boninelli, J. Appl. Phys. 110, 073524 (2011)]



8.4. Long-term end results of irradiation

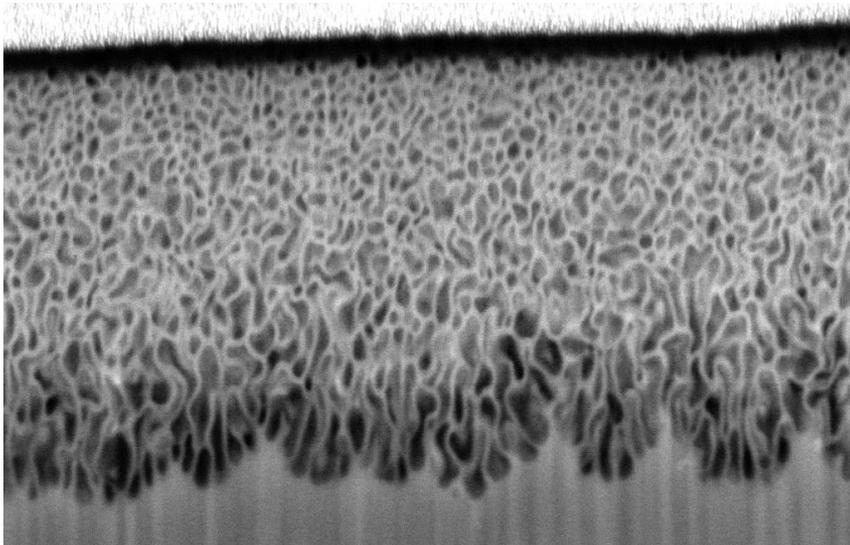
- As we saw in the examples, a clear majority of defects do recombine
- However, some can cluster to form localized dislocation structure, dislocation lines starting and ending on themselves
- These are often roughly circular and hence called **dislocation loops** (*dislokationsslinga / dislokaatiosilmukka*)





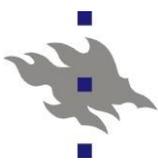
Long-term end results: porosity

- In some cases, vacancies can also agglomerate to form voids in the material
- These can eventually make the material completely porous
- For instance long-term irradiation of Ge by pretty much any kind of ions makes it eventually porous



c-Ge:Ge 1MeV
 $1.5 \times 10^{17} \text{cm}^{-2}$

[Image: Thomas Bierschenk, Australian National University]

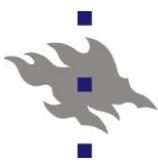


Voids in reactor materials

- In nuclear reactors, one of the worst long-term effects of the neutron irradiation is that some materials start forming voids, which can lead to a macroscopic **swelling** (*svullnad* / *paisuminen*) of the material
 - Up to factor of ~ 3 reported (after decades of irradiation)
- Fortunately, not all metals exhibit swelling
- For instance, so called Ferritic-Martensitic steels do not show almost any swelling, and hence are a material of choice for nuclear reactors

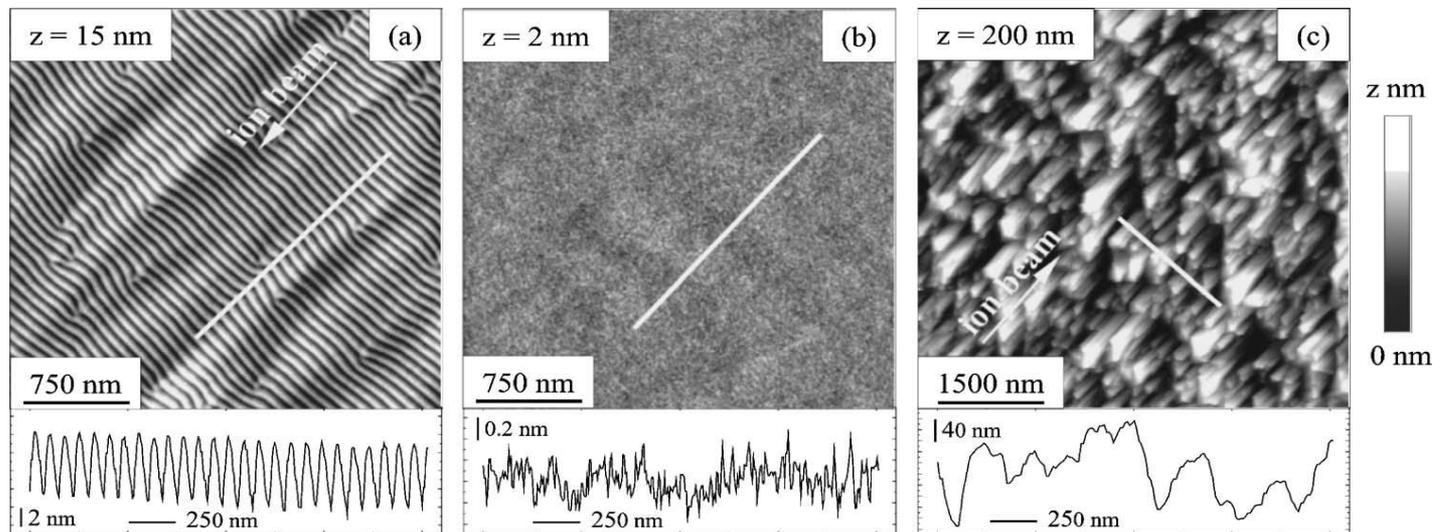


<http://cmcsn.phys.washington.edu/book/export/html/467>

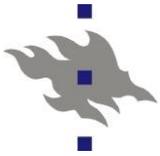


8.5. Surface long-term effects: roughening, ripples

- Surfaces can under long-term irradiation roughen randomly, but also in many cases show a formation of ordered wave-like structures, **ripples** (*rippel?? / väre*)



[Xe bombardment of silicon: Patterns induced by 5, 45, and 75 degree ion beams. Ziberi et al. PRB 72 (2005) 235310]

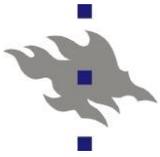


Ripple formation equations

- Formation mechanism either sputtering [Bradley, Harper, J. Vac Sci. 1982] or atom flow leading to an instability in the surface height function [Norris et al, Nature Communications 2 (2011) 276]
- The ripple formation can in both the sputtering and material flow pictures be described by a differential equation in height h with second and fourth derivatives in space
 - Suitable combinations of the prefactors predict formation of ripples

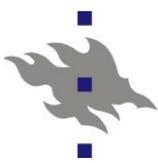
$$\frac{\partial h(x, y, t)}{\partial t} = \left(S_X(\theta) \frac{\partial^2 h}{\partial x^2} + S_Y(\theta) \frac{\partial^2 h}{\partial y^2} \right) - B \nabla^4 h,$$

- (details in equation not important on this course)



8.6. Segregation

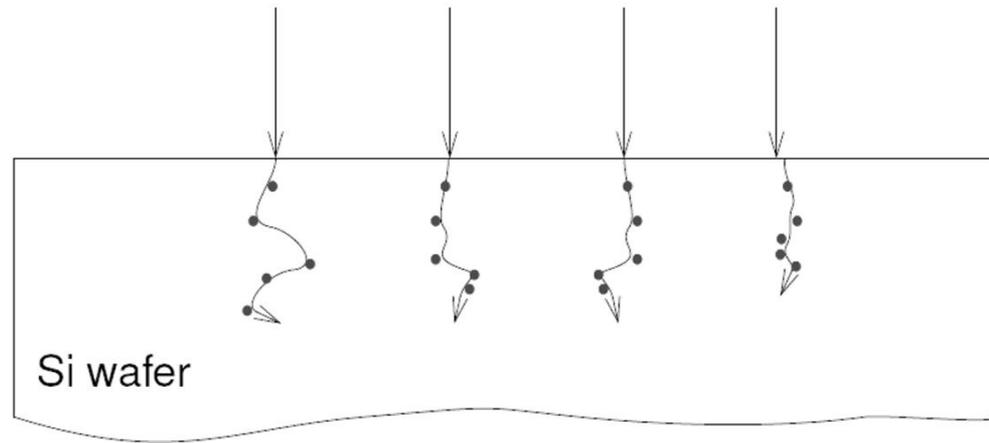
- In case the ion implanted species is not thermodynamically **soluble** (*lösbar / liukeneva*) in the material, it may (if the temperature is high enough for mobility) separate from the material into precipitates
 - This is called (phase) **segregation** (*segregering / segregaatio*)
- In case the material itself is thermodynamically metastable, radiation may drive the material to segregate even at temperatures where it normally would not
- Segregation can be used to make nanocrystals



Example of useful segregation: Embedded nanoclusters by ion implantation

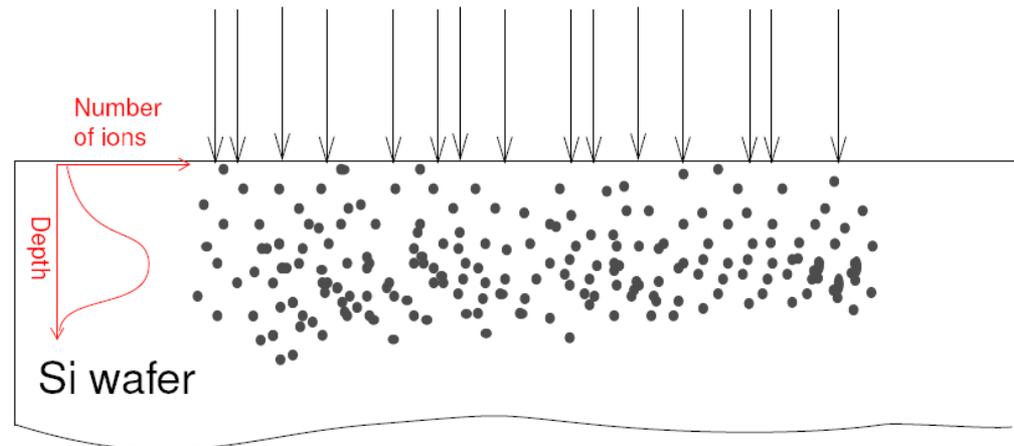
1. Ion implantation

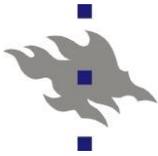
- Ion implantation means using an ion accelerator to shoot ions into a material
- The ions move randomly in the material and then stop somewhere inside the samples
- The process is stochastic



2. Implantation profiles

- After a high dose implantation, a **depth distribution** of implanted ions is formed, with some mean depth \bar{R}
- Typical energies: 0.1 - 1000 keV
- Typical mean depth \bar{R} : 10 nm - 10 μm

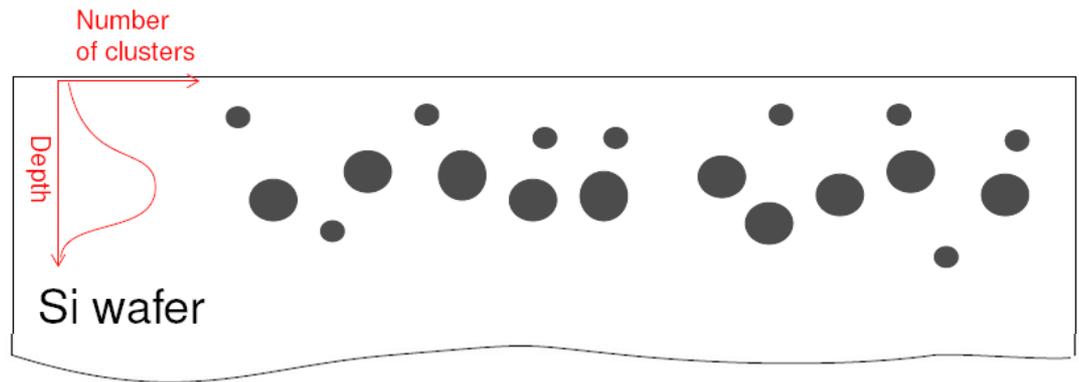




Embedded nanoclusters by ion implantation

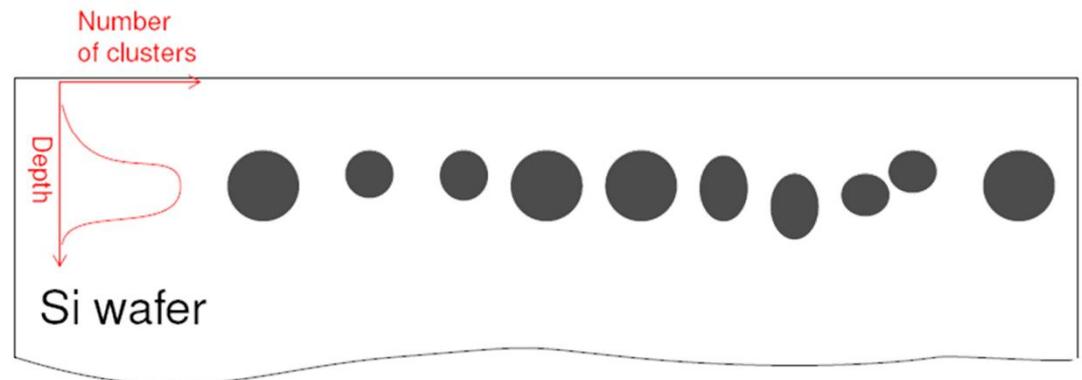
3. Nanocluster formation

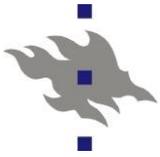
- By heating the sample after (or during) the implantation, one can make the ions mobile in the material. They can then (provided the material choice is suitable) join together to form nanoclusters



4. Ostwald ripening

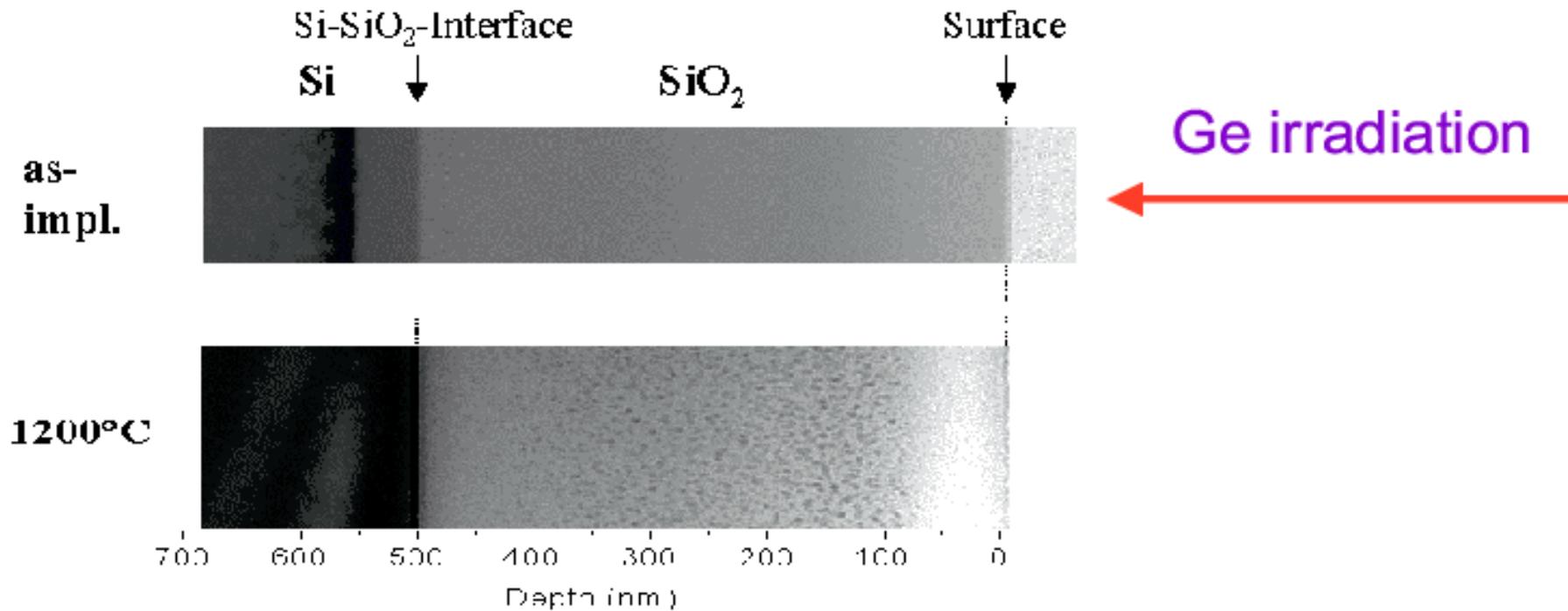
- Moreover, if the heating temperature is high enough, the clusters start to emit atoms with some probability
- Emission is more probable the smaller the cluster is (higher curvature => less surface binding energy)
- This so called **Ostwald ripening** causes the larger clusters to grow at expense of the smaller



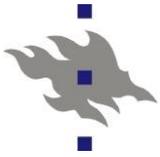


Embedded nanoclusters by ion implantation

- An experimental realization of this looks like follows:

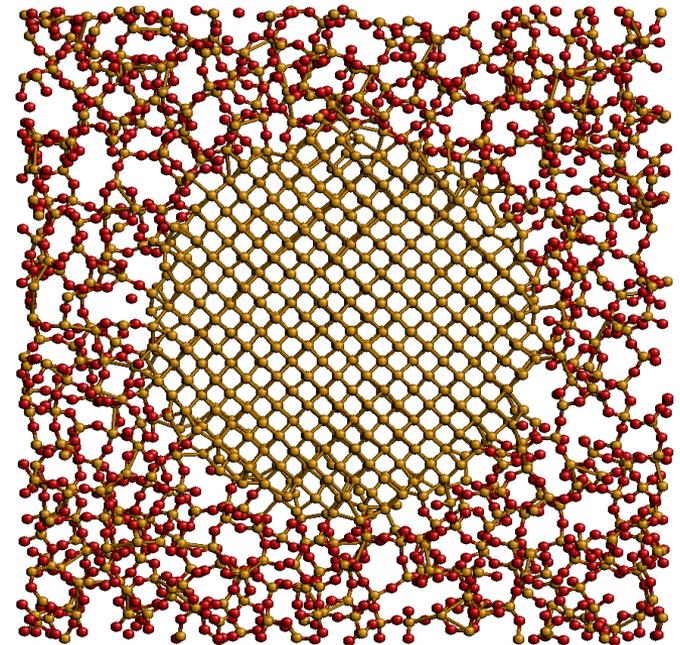
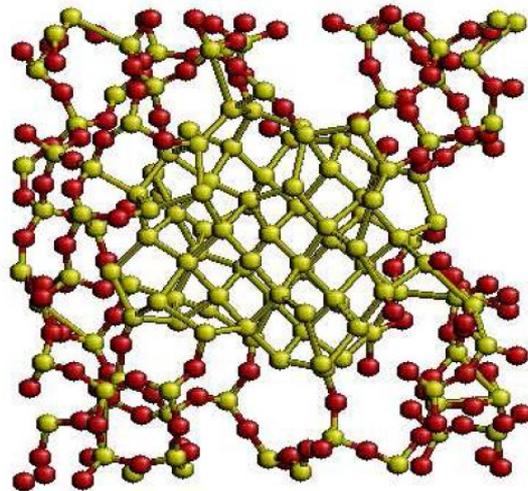


[L. Rebohle et al, FZ Rossendorf]



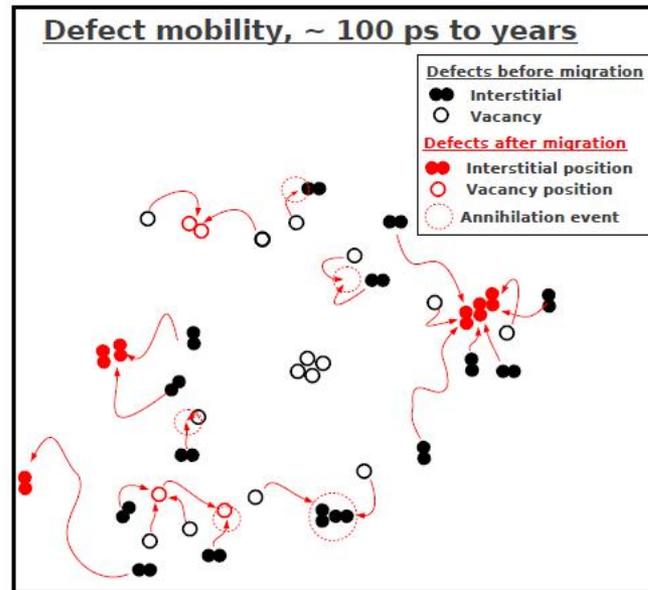
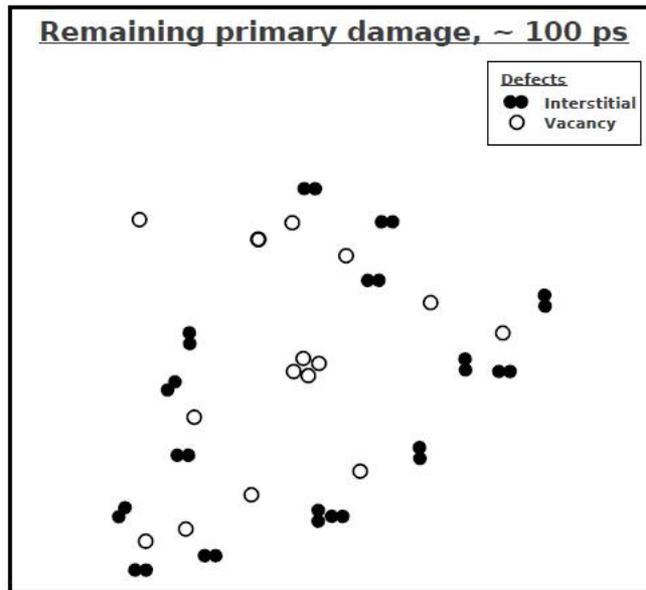
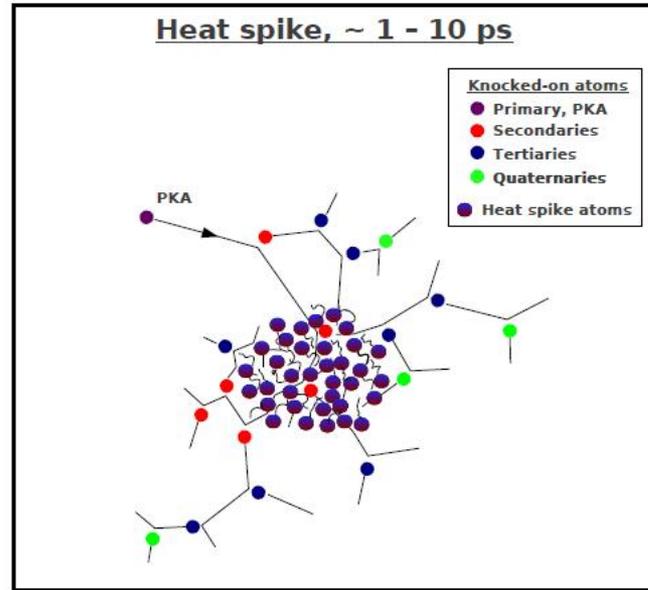
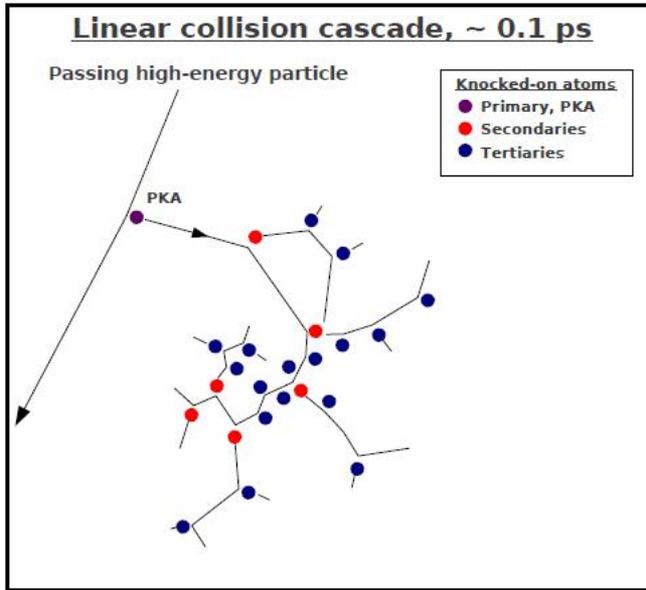
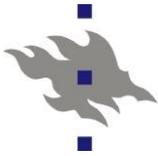
Embedded nanoclusters by ion implantation

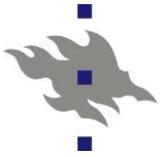
- End result: structure of small and large Si nanocrystal embedded in Si obtained from molecular dynamics simulations



[F. Djurabekova and K. Nordlund, Phys. Rev. B 77, 115325 (2008)]

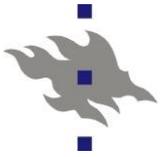
Summary of sections 4, 5 and 8





Further reading

- Good review articles with extensive data sets
- P. Ehrhart, K.H. Robrock, and H.R. Shober, “Basic defects in metals,” In: R.A. Johnson and A.N. Orlov (eds.), *Physics of Radiation Effects in Crystals*, Elsevier, Amsterdam, p. 3, 1986.
- [2] P. Ehrhart, “Properties and interactions of atomic defects in metals and alloys,” In: *Landolt–Börnstein, New Series III*, vol. 25 Springer, Berlin, Chapter 2, p. 88, 1991.



What should you have learned from this section?

- When does the athermal cascade end and the subsequent thermal migration start
- How the defect behaviour is fundamentally different in the two phases
- You know how diffusion can be modelled
- You know that the end result of defect evolution tends to be dislocation loop formation, void formation, trapping or annihilation at surfaces or grain boundaries
- You know what ion-beam induced ripples are
- You know that ion irradiation + diffusion can lead to segregation and that this can be used to make nanocrystals