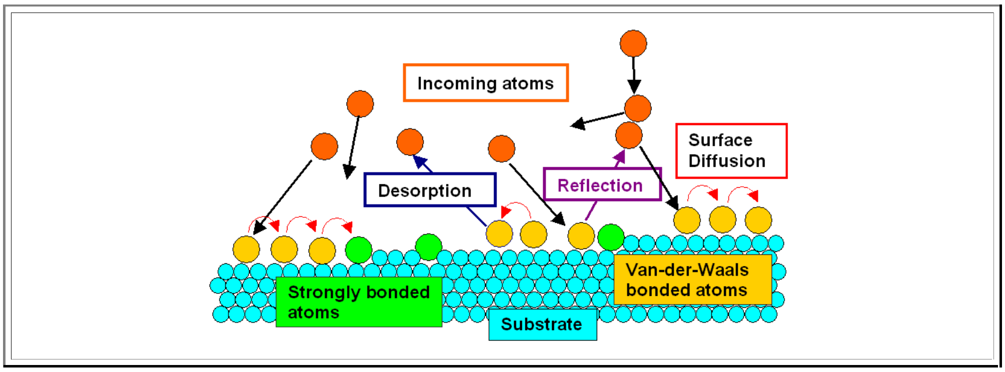
3.3 Nucleation and Growth

3.3.1 In the Beginning

First Condensation

- In the beginning of a thin layer we have a substrate with a "receptive" surface (being pretty clean at the minimum) and a source of atoms or molecules that are supposed to build up on the substrate.
- How do we build up a thin layer? Let's do it in a very simple manner. We put on our good glasses, the ones that allow us to see atoms. (*Hint*: you don't see with your eyes, you actually *see* with your brain. Eyes are just one source of input to the seeing center of the brain). Moreover, we do the most perfect experiment we can imagine, because here we will work with perfect materials in a perfect world - in our minds, where this is easy.
    - So we have a perfect substrate crystal with a perfect surface - no oxide on it, no other dirt, no whatever Also no **surface reconstruction** (if you want to find out what that means - activate this link). But perfect, in the sense of minimum free enthalpy, still entails some vacancies even in thermal equilibrium; being of a gentle disposition we also allow mild deviations from perfection as required by thermal equilibrium and allow a few surface steps and the occasional dislocation.
    - From some unnamed source we produce a constant stream of atoms (or molecules) that are supposed to form our thin film on the substrate. They have some average velocity and move more or less in the direction of the substrate.
- What happens when an incoming atom hits the surface of the substrate? Well, just about anything you care to imagine:
    - The atom may just be reflected like at solid wall and then runs away to infinity.
    - The atom may just be reflected like at solid wall but then hits an incoming atom and is redirected to the substrate.
    - The atom may loosely bond to one or two of the substrate atoms (by one or the other of the **secondary bonding** mechanisms, like "**van der Waals**"), or, to use surface science terminology, it will become **"physisorbed"**.
    - At finite temperatures, it may now jump to equivalent positions in its neighborhood, i.e. it diffuses in a **2-**dimensional random walk manner on the surface.
    - On occasion, while running around at random, it may just get **desorbed** again and flies off into the wide world out there.
    - But then it may also find a cozy place where it can *seriously* bond to more than just one (or two) substrate atoms, it will get **chemisorbed**; i.e. bonded by one of the strong bonding mechanisms.
    - This *chemisorption* will happen with higher probability if our so far loosely bonded or physisorbed atom is seriously cornered by the substrate atoms - at a **step** or a surface vacancy, for example



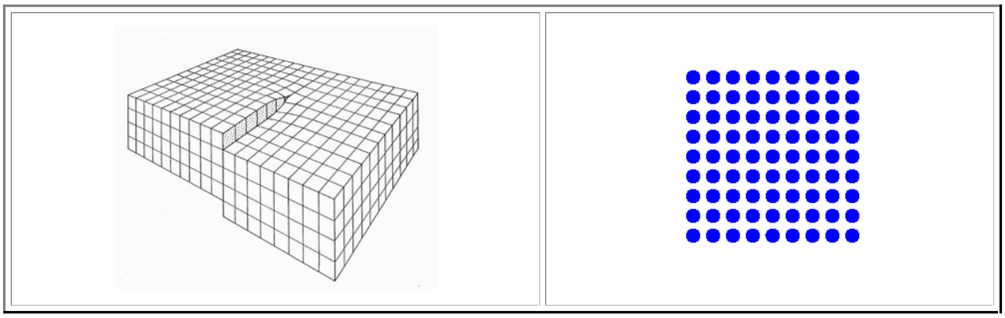
- It's all in the picture, and all of that (and more) is really happening.
    - Atoms, as the saying goes, are only human after all (or was it: humans are only atoms, after all?). They fool around if they can, and only get seriously stuck if they fall into "traps", or to put it more positively, if they find highly attractive situations.
- All in all, we can draw two major conclusions from this simple picture:
    1. Not all atoms reaching the substrate "get stuck". The percentage of "**B**" atoms (or molecules) remaining on the substrate **A** (the **sticking coefficient**") depends on many things, but the probably most important parameter is the binding energy between **A** and **B**.
    2. In the initial phase of layer growth - the **nucleation** phase - first clusters of **B** atoms (or molecules) most likely form at irregularities of the substrate, in particular at (atomic) steps.
- The question coming up now is how many steps (per **cm^2**) we might have on a given substrate and how we can optimize the step density if that is what it takes.

  - This is easy to answer on a first glance. You can even take off your sharp glasses and just imagine a *perfect* **{100}** or **{111}** oriented surface of a **fcc** crystal, for example. There will be no steps. But look at the picture above. Steps in regular intervals are an unavoidable consequence of a substrate simply orientation that is off a bit from - in the picture - precise **{110}**.
  - If d_{111} is the distance between **{111}** lattice planes, and d_{step} is the average distance between steps like in the picture above, the **misorientation** α is simply given by

$$\boxed{\sin\alpha \;=\; \frac{d_{111}}{d_{step}}}$$

  - At this point, we get a first idea why semiconductor companies making **Si** chips order their wafers on occasion with a specification like "**2^{o}** off **{100}**".

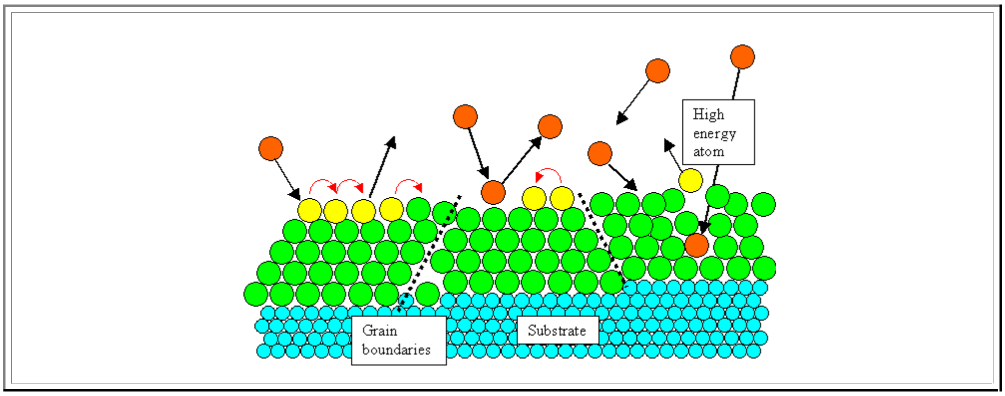
- Not so easy perhaps, on a second glance, is to imagine that even surfaces with *no* misorientation from, for example, **{100}**, might still have a certain density of steps.
  - This step density, to give you a hint, is identical to the density of screw dislocations terminating at that surface. Below is an picture of a screw dislocation ending at a surface; a Burgers circuit running around it shows that the Burgers vector is parallel indeed to the dislocations line direction.



- If you now recall that **edge dislocations** that left the crystal, automatically produced a step in the surface, you finally get the picture:
  - If your substrate contains defects - dislocations, grain boundaries, and so on, you might have steps even for a perfect low index surface orientation.
- What happens in the beginning of a deposition process where some atoms (or molecules) are brought in contact with a substrate surface, thus depends on many parameters. All the processes that take place in parallel, and with some possible interaction, may produce an exceedingly complicated situation. Mind, its complicated - but not difficult.

During Growth

- This module is not really the right place to discuss what happens *during* the growth of a layer, but this topic fits here very nicely with what has been described so far.
- We simply ask ourselves: How does the general situation change after we - somehow - have already produced a thin layer of **B** and, keeping the process running, now just make it thicker?
- The answer is. Not much changes. Look at the picture below:



  - It's pretty much the same as the picture form above, For varieties sake one more process has been added: A relatively energetic **B** atoms hits the **B**-layer so hard that it penetrates into the layer, causing some damage, and kicking one (or more) already physisorped **B**-atom out again.
  - It is also quite clear that you will produce grain boundaries and other defects in the **B**-layer because things - atom size, lattice constants, lattice types - just don't match.

- Of course, *sticking coefficients* and all other numbers you can attach to the atomic processes might be quite different in the "**B** hits **B**" case in comparison to the "**B** hits **A**" case.

How Do We Know

- It's easy (and amazingly cheap) to look at what is going during thin film growth at atomic dimensions with your good glasses, the ones that allow you to see atoms. But how do we *know* that what we "see" is the *truth*?
  - Your choices are limited. If you are convinced that what you "see" is the truth, but you cannot corroborate your finding with independent evidence, you must either found a new religion or become a philosopher.
  - If you prefer to remain a scientist or engineer, you now must find some way to prove in a mathematical sense that what we discussed so far is the truth. Well - Good Luck to you!
- It's generally not so easy to *really* see on an atomic scale, and to make things worse, you want to see a dynamic process, where things change rapidly.
  - This is just not possible with the usual tool, the **High-Resolution Transmission Electron Microscope** (***HRTEM***) - it just can't give "surface dynamics".
  - The big boost to this topic came with the invention of the **Scanning Tunneling Microscope** (***STM***) in **1980** by **Gerd Binnig** and **Heinrich Rohrer** (Nobel prize **1986**) and the whole family of "Needle scrapers" following, in particular the **Atomic Force Microscope** (***AFM***). Before that, one could draw pictures like the ones here easily, but back in the Lab it was guess work.
- We will come back to these instruments, but already now you can appreciate how important the invention and development of these instruments was to the thin film communities (and others).
  - Finally, you may enjoy to look at some spectacular pictures produced by these instruments in the link to the company Omicron. A few selected examples are also found in this (future) advanced module.