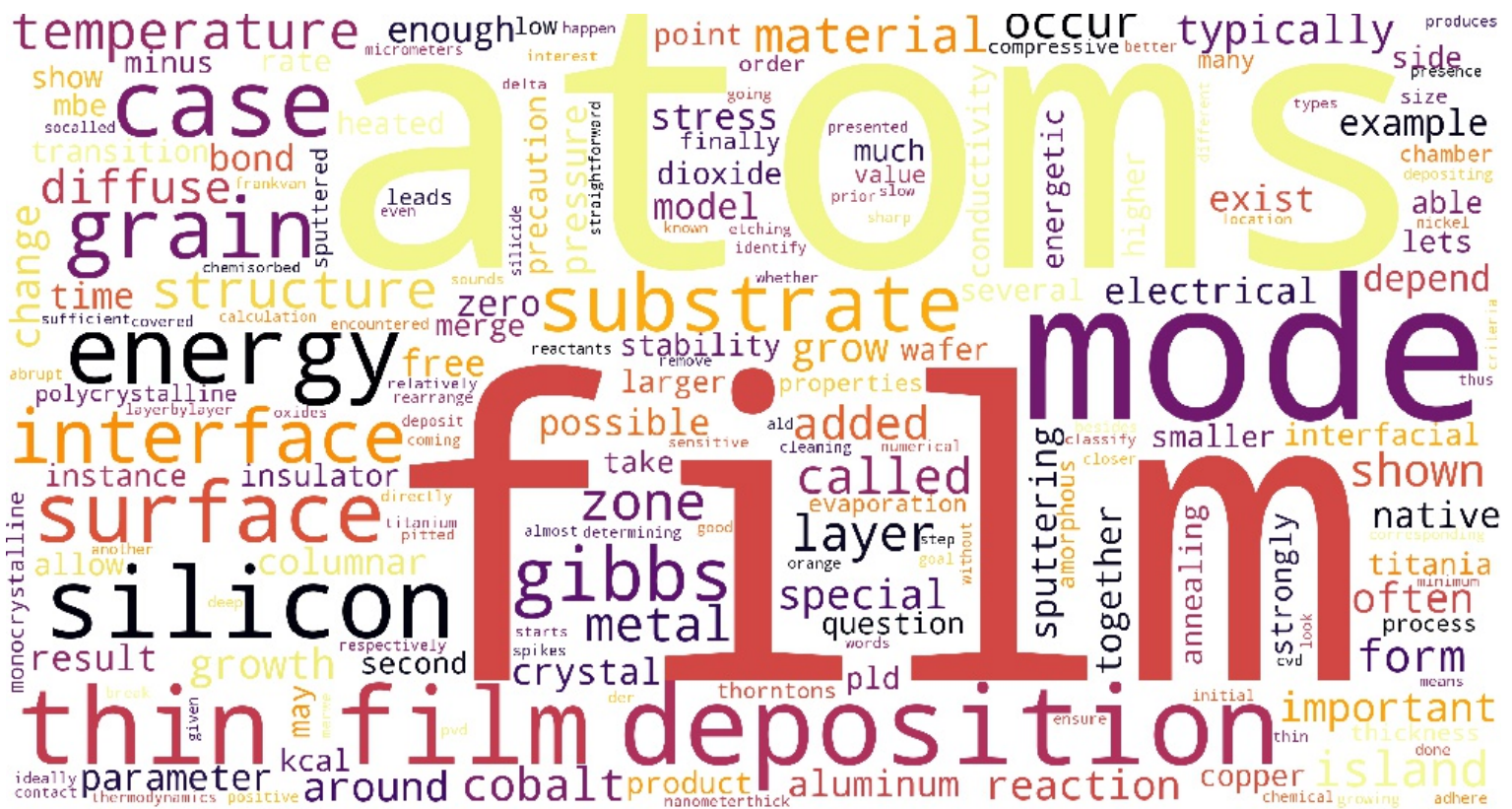


III. Growth modes and crystal structure

PVD 8: Film growth

III. Growth modes and crystal structure

Prof. Jürgen Brugger & Prof. Martin A. M. Gijs



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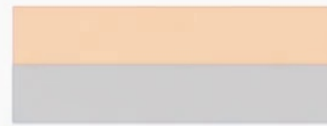
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Film-substrate interface

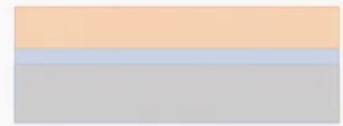
- Interface stability:

- Ti deposition on SiO_2

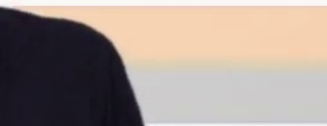
ΔG = Gibbs free energy difference in [kcal]
 G_{products} = products Gibbs free energy in [kcal]
 $G_{\text{reactants}}$ = reactants Gibbs free energy in [kcal]



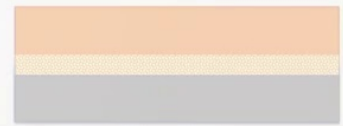
Abrupt



Interfacial layer



Diffused



Reacted



Pitted

Micro and Nanofabrication (MEMS)

Once there are enough atoms on the substrate surface, the film starts growing. A very important parameter here is the interface stability. Or in other words, the question whether the layer will adhere to the substrate or not. Thermodynamics allows determining if the atoms will be chemisorbed on the surface or not.

Film-substrate interface

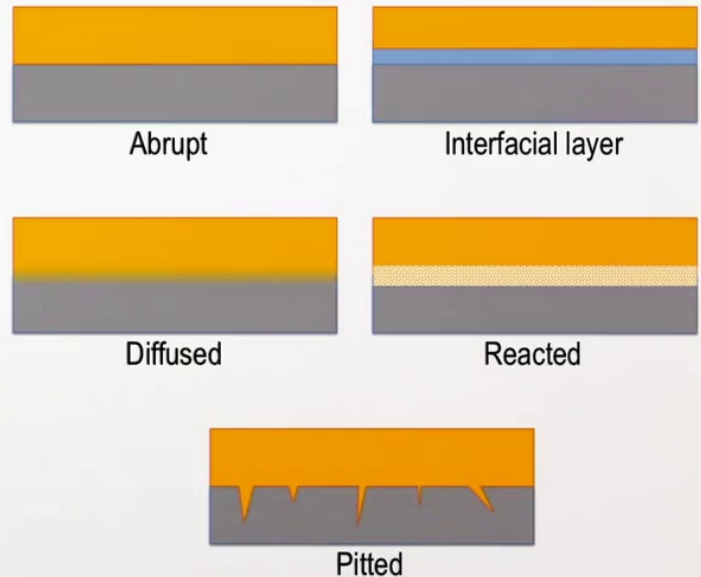
- Interface stability:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} < 0$$

- Ti deposition on SiO_2

$$\begin{aligned} \Delta G &= G_{\text{TiO}_2} - G_{\text{SiO}_2} \\ &= (160 - 165) \text{ kcal} = -5 \text{ kcal} \\ &< 0 \end{aligned}$$

ΔG = Gibbs free energy difference in [kcal]
 G_{products} = products Gibbs free energy in [kcal]
 $G_{\text{reactants}}$ = reactants Gibbs free energy in [kcal]



Micro and Nanofabrication (MEMS)

So if the change in Gibbs energy, which is given by the Gibbs energy of the products minus the Gibbs energy of the reactants, is smaller than zero, then the reaction is possible. Let's take the example of titania on SiO_2 . So the Gibbs free energy is the product Gibbs free energy of TiO_2 minus Gibbs of SiO_2 which is, in numerical values, known to be 160 - 165 Kcal, which is -5 Kcal which is smaller than zero, so this reaction can happen. It means we can deposit titania on SiO_2 .

Film-substrate interface

- Interface stability:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} < 0$$

- Ti deposition on SiO_2

$$\begin{aligned}\Delta G &= G_{\text{TiO}_2} - G_{\text{SiO}_2} \\ &= (160 - 165) \text{ kcal} = -5 \text{ kcal} \\ &< 0\end{aligned}$$

ΔG = Gibbs free energy difference in [kcal]
 G_{products} = products Gibbs free energy in [kcal]
 $G_{\text{reactants}}$ = reactants Gibbs free energy in [kcal]



Another material of interest may be cobalt. Depositing cobalt on silicon is also possible, as a corresponding Gibbs free energy calculation would show. But the deposition of cobalt on SiO_2 is not possible as the ΔG is larger than zero. Thus, the cobalt deposition on silicon is very sensitive to the presence of native oxides.

Film-substrate interface

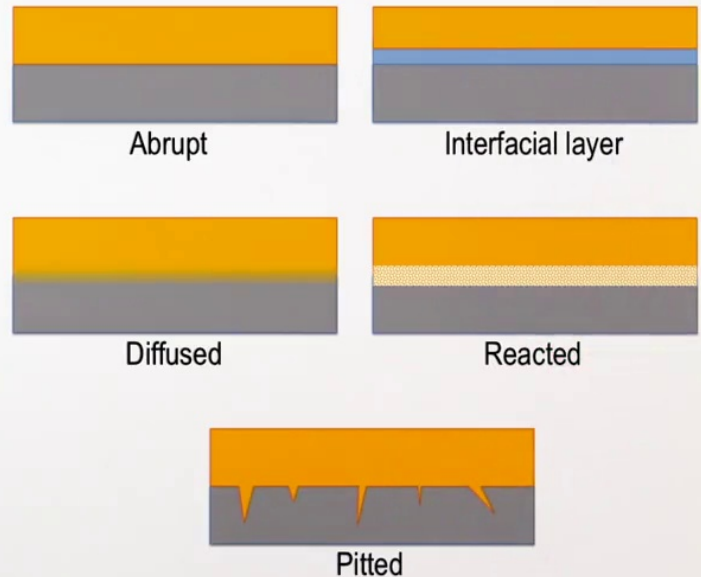
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Micro and Nanofabrication (MEMS)

Besides the initial interface stability criteria, different types of interfaces exist. An abrupt interface, shown here, is encountered in most PVD and CVD depositions and it produces an almost ideally sharp material transition. However, if the goal is to grow a thin film directly on silicon, this is not as straightforward as it sounds, because without special precaution, silicon is often covered by a few nanometer-thick native SiO_2 layer. In this case, an interfacial layer exists between the substrate and the added film. Shown here. To remove the interfacial SiO_2 layer, typically, a special surface etching and cleaning has to be done prior to the deposition. So in some other cases, for instance during the deposition of copper on silicon dioxide, the added copper atoms diffuse into the substrate. Chemical reactions between the thin film and the wafer may also occur. This is the case of nickel, cobalt and titanium deposition on silicon which forms a so-called "silicide" at 400°C , 500°C and 600°C , respectively. There is a reaction going on at the interface. In some cases, an annealing step is sufficient to ensure a good electrical conductivity between the added thin film and the silicon. See the case of the pitted interface, for example. This is the case of silicon in aluminum when heated over 425°C . The spikes of the film into the wafer can be several micrometers deep. On the positive side, they allow for better electrical contact between aluminum and silicon and is even able to break through this thin native silicon dioxide interface that we have presented here before.

Growth modes

- 2D / Layer-by-layer mode (Frank-van der Merwe)

- Strong atom-surface interaction
- E.g. MBE, ALD

- 3D / Island mode (Volmer-Weber)

- Strong atom-atom interaction
- E.g. evaporation on a wetting substrate

- Columnar mode

- Not wetting
- E.g. evaporation on a dry substrate



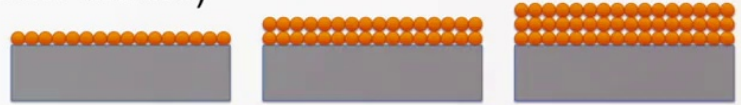
Micro and Nanofabrication (MEMS)

Now let's have a closer look at how the thin films grow classify their modes, and identify the important parameters on which this depends. The 2D, or layer-by-layer mode, also called "Frank-van der Merwe mode",

Growth modes

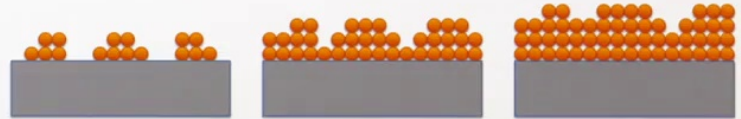
- 2D / Layer-by-layer mode (Frank-van der Merwe)

- Strong atom-surface bonds
- E.g. MBE, ALD, *PLD*



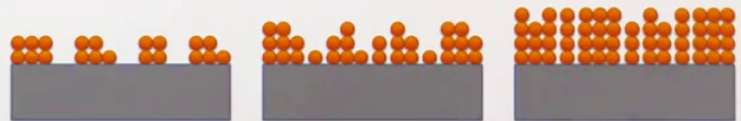
- 3D / Island mode (Vollmer-Weber)

- Strong atom-atom bonds
- E.g. evaporation and sputtering with heated substrate or ionic bombardment



- Columnar mode

- Not enough energy to merge islands together
- E.g. deposition at room temperature

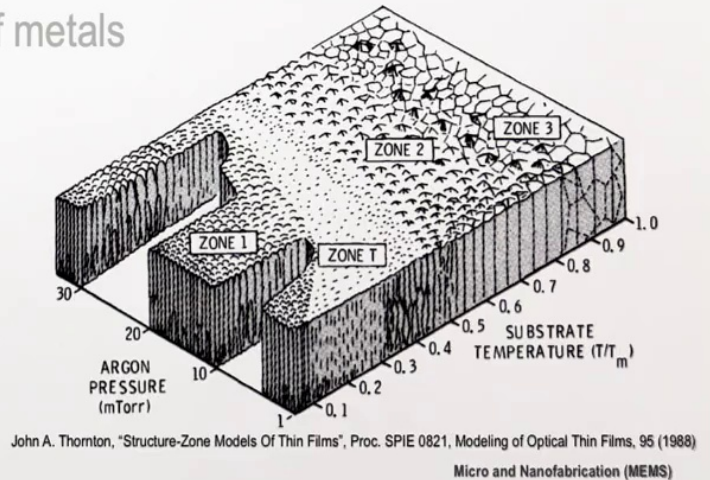


Micro and Nanofabrication (MEMS)

occurs when the added atoms, here in orange, bond more strongly with the substrate than with other atoms and when they have enough energy and time to diffuse around to their energetic minimum location. This is the case in ALD, MBE, and also PLD. Here, we have a relatively slow growth rate, so that the atoms have time to rearrange themselves before the atoms for the second layer are coming. The second growth mode is the 3D, or island mode. Also called "Vollmer-Weber mode". It typically occurs during the deposition of metal atoms onto an insulator, since bonds between metal atoms are stronger than bonds between insulator and metal atoms. In the island mode, surface atoms have enough energy and time to diffuse around but not as much as in the 2D mode, because the growth rate is higher than in the previous case. As a result, a few surface atoms nucleate together and form clusters, or islands. At some point, islands merge together and form a uniform film. For films formed by sputtering and evaporation, a continuous thin film forms at around 10 to 20 nm thickness. Before this threshold value, the film does not yet cover the entire surface. Island mode more typically occurs with sputtering deposition or with evaporation when the substrate is heated. A mixed mode, combining 2D and 3D modes also exists. It is then called the "Stranski-Krastanov mode". Finally, when the surface atoms' energy and mobility is low, atoms stick where they land, and islands are not able to merge together. In this last mode, which is called the "columnar mode", grains grow upwards and voids between the grains can remain. Columnar mode typically takes place when the deposition is performed at room temperature.

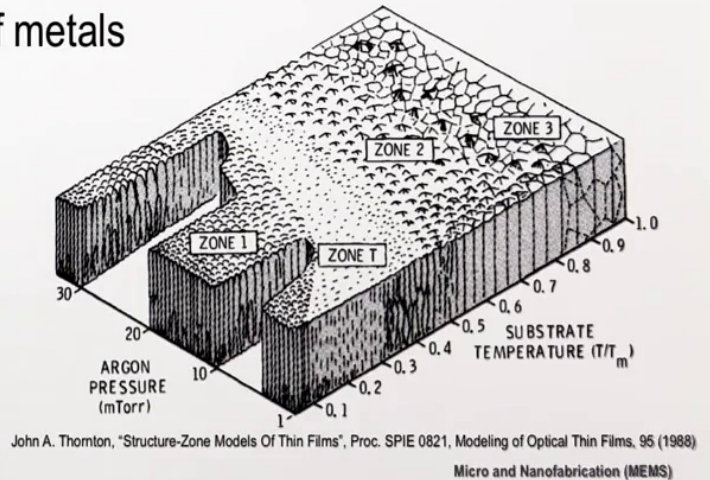
Crystal structure

- Will the film be amorphous, polycrystalline or monocrystalline?
 - Silicon, covalent materials, compounds (TiN, Al_2O_3) and alloys (TiW, SiCr) are often amorphous
 - Metals (Al, Au, Cu, Ag, Pt) are often polycrystalline
- Thornton's zone model for sputtering of metals
 - Zone 1
 - Low
 - Low
 - Zone 2
 - Intermediate
 - Zone 3
 - High
 - Film loses



The growth mode determines the way in which the film forms. For us as users, what is more important is actually the resulting film intrinsic structure. It plays a key role for many physical properties of the thin film, such as electrical band structure, conductivity, hardness, transparency, and piezoelectric properties. The first important question to ask is if the film is amorphous polycrystalline or monocrystalline?

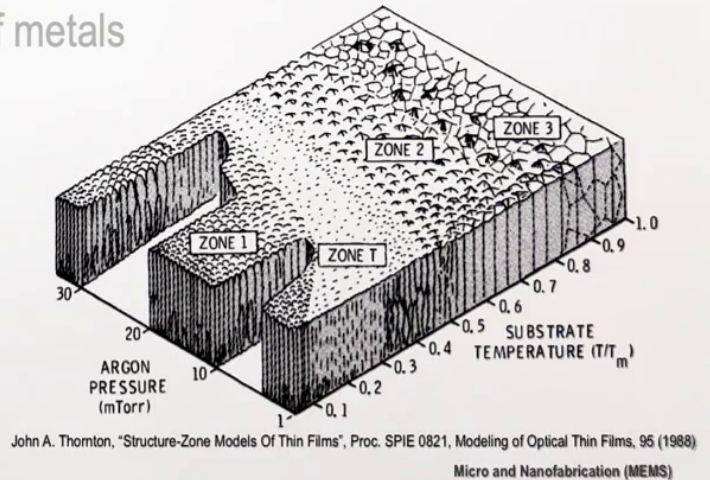
- Will the film be amorphous, polycrystalline or monocrystalline?
 - Silicon, covalently bonding materials, compounds (TiN, Al_2O_3) and alloys (TiW, SiCr) are often amorphous
 - Metals (Al, Au, Cu, W, Ti, Cr, Pt) are often polycrystalline
- Thornton's zone model for sputtering of metals
 - Zone 1
 - Low temperature and/or high pressure
 - Low energetic atoms $\rightarrow$ porous tensile films
 - Zone T and zone 2
 - Increase temperature and/or decrease pressure
 - More energetic atoms $\rightarrow$ denser compressive films
 - Zone 3
 - High temperature $\rightarrow$ annealing
 - Film lose process details memory



As a rule of thumb, thin films made of silicon covalently bonding materials, compounds and alloys are often amorphous if no special precaution is taken during the deposition. Metals, on the other side, are often polycrystalline. In order to grow monocrystalline films very special deposition techniques, such as MBE or PLD, are required. However, it is sometimes difficult to predict the exact structure of the thin film, as it depends on so many several parameters, such as the material itself, the deposition method, and the process. In case of sputtering of metals, for instance, a well-known model, called the "Thornton's zone model", shown here, can be used. It shows in empirical diagrams the morphology of thin films as a function of the chamber pressure, shown here on this axis, and the substrate temperature, normalized by the melting temperature of the thin film (T_m), shown here. Sputtered metal thin films have a poorly crystalline structure. At high pressure, or low temperature, zone one, atoms do not have much energy to diffuse around. Which results in columnar grains. We see them here. Usually, this leads to porous films with tensile stress unless oxygen is present in the chamber, which leads to compressive stress in the film. At lower pressure and higher temperature, impinging atoms are more energetic and can knock out loosely attached atoms and diffuse on the surface. This results in denser films with compressive stress. Simultaneously, the film grain structure moves from zone 1 to the zone T, for transition, and zone 2, where the grains are larger. At some point, if the temperature is further increased the film crystal structure reaches zone 3, where annealing occurs, and the film loses memory of the deposition process, as it is called in technical terms. In the case of sputtered aluminum, typical grain size can go up to $0.5 \mu\text{m}$ and can be in the order of the film thickness. Processes which depend on grain boundaries such as diffusion and electromigration, are strongly affected by the ratio between grain size and the characteristic dimensions of the thin film in the microdevice. For some materials, the film crystal structure does not change continuously as described in the Thornton's zone model. Instead, it changes abruptly due to a phase change occurring at specific temperatures. An example of such a material is tantalum.

Crystal structure

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 - Metals (Al, Au, Cu, Pt) are often polycrystalline
- Thornton's zone model for sputtering of metals
 - Zone 1
 - Low temperature
 - Low pressure
 - Zone 2
 - Intermediate temperature and pressure
 - Zone 3
 - High temperature and pressure



Finally, it is relevant to note that the texture of the added thin film is inherited from the underlying film. Seed layers are therefore often used to obtain a well defined crystal orientation on the subsequent deposition of a thicker film.