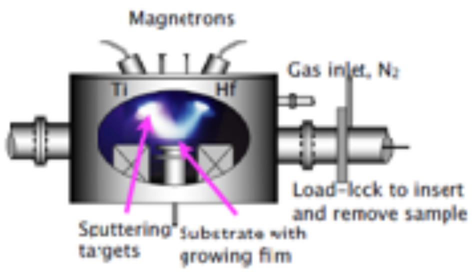
MATERIALVETENSKAP/PHYSICAL METALLURGY TFYA21

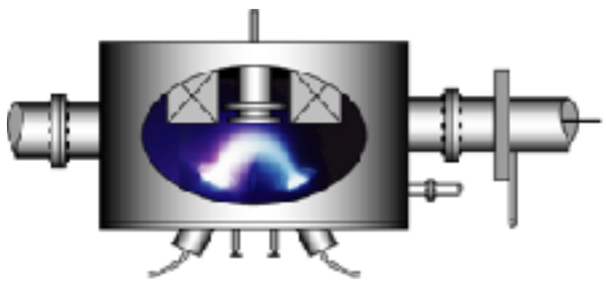
VT:1 2020; Björn Alling

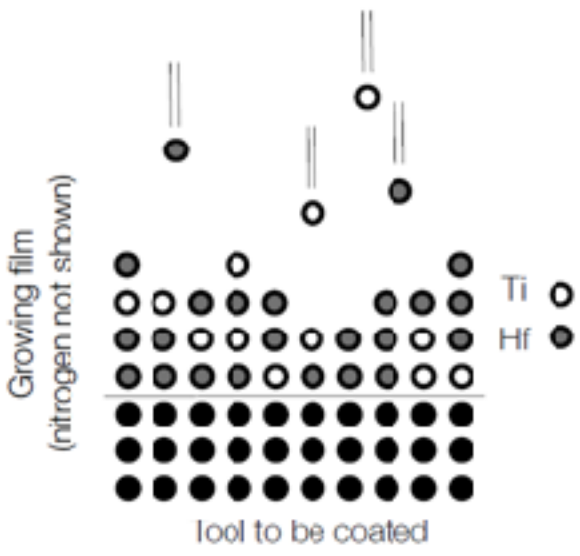
Home assignment 1
Effect of gravity on the synthesis of a thin film of a pseudo-binary alloy

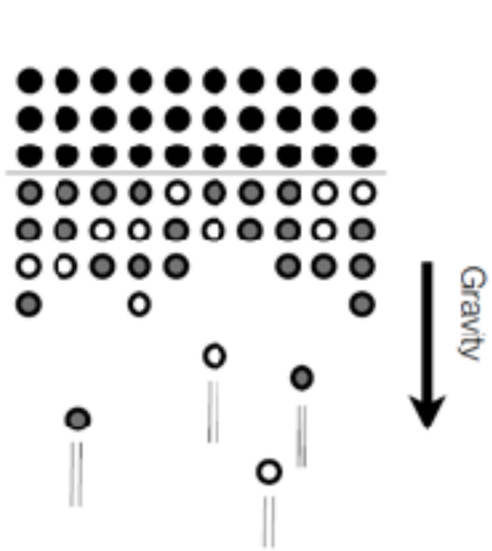
Introduction: this home assignment is about understanding the fundamental thermodynamic concepts of (mixing) enthalpy, (mixing) entropy, (mixing) Gibbs free energy, and chemical potential, and how important they are compared to other forces/energies. Chapter 1 in the textbook contains all necessary thermodynamic background for the course and should be used as reference. Relevant numerical values can be found in databases or in e.g. Physics Handbook.

Background: Thin films of transition metal nitrides, such as titanium nitride, TiN, and hafnium nitride HfN are of practical importance as wear resistant coatings on cutting tools. Both these two materials crystalize in a NaCl type cubic structure. This structure, also designated as B1, can be viewed as a face centered cubic structure of Ti or Hf with interstitial N sitting on a separate fcc sublattice shifted with respect to the metals.









In order to improve the performance of the coatings one might try to alloy TiN and HfN into the so called pseudo-binary $(Ti_{1-x}Hf_x)N$ alloy. One way of synthesizing thin films, a couple of micrometers thick, of this alloy on a tool is with magnetron sputtering inside a vacuum chamber. Two typical designs of such sputtering systems setup are used in laboratories. One is with the sources **above** the substrate, as displayed in Fig. 1 (left). The other is the opposite configuration, with the sources **above** the substrate (Fig1, right).

The Ti and Hf atoms are sputtered out of the metallic targets by ionized argon that is accelerated into the targets by a strong voltage. These Ti and Hf metal atoms travel through the vacuum chamber and impinge on the chamber walls but also on the tool that we want to coat. On this tool an alloy film grows more or less atom by atom as metal atoms siting on the surface react with nitrogen molecules added to the chamber. A heater make sure that the tool and the growing film is kept at a constant temperature of 800 K.

Hafnium nitride is believed to form an almost ideal solid solution with titanium nitride, that is Hf and Ti mix as an ideal binary solid solution on the metal fcc sublattice of $(Ti_{1-x}Hf_x)N$, while N is just a spectator atom in the mixing process. The lattice spacing, the side of the conventional cubic unit cell, is 4.40 Å in the alloy with equal amount of Ti and Hf.

However, the effect of gravity has this far been forgotten and the question is: is it of importance? Hf has a different mass than Ti and the chosen geometry of the thin film growth can induce a difference in the film. In particular, gravity will either pull the atoms towards or away from the tool.

Problem:

Consider a 1 micrometer thick film of $(Ti_{0.5}Hf_{0.5})N$ alloy grown in the setup to the left. Use the concepts of Mixing enthalpy, Mixing Entropy, Mixing Free energy and chemical potentials to discuss how the Ti-Hf concentration gradient will look like due to gravity and the mass differences. Use the information above and numerical data from e.g. Physics Handbook.

Consider only thermodynamic aspects of the film here, not diffusion or kinetics of the metals, Assume that the films can be viewed as if in equilibrium. Assume that no intermixing with the material of the tool will take place.

Can you come up with any other materials science consideration why either the left or right setup should be used in any specific cases, besides any gravity-induced concentration gradient in the film?

Hand in your solution no later than Friday 14 February 23:59.