Exercise 1 Growth of Selenium Nanowires - Experimental Facts

Selenium is a non-metal that is often used in semiconductor devices, in particular in photocells. Selenium crystal habit is an elongated prism, as shown in the sample below:



Figure 1: Selenium crystals, from www.periodictable.ru

Selenium has a low melting point, just above 200°C, and it can be processed using fiber technology, giving the possibility to integrate optoelectronic devices inside an optical fiber. To this aim, in the laboratory of Prof. Fabien Sorin at EPFL, researchers are experimenting on the re-crystallization of the Se core of the fiber (that emerges from the process in an amorphous form) into selenium nanowires. It turns out that, by soaking the tip of the fiber in alcohol (specifically, isopropanol), the material spontaneously forms nanowires, that appear as below under a scanning electron microscope.

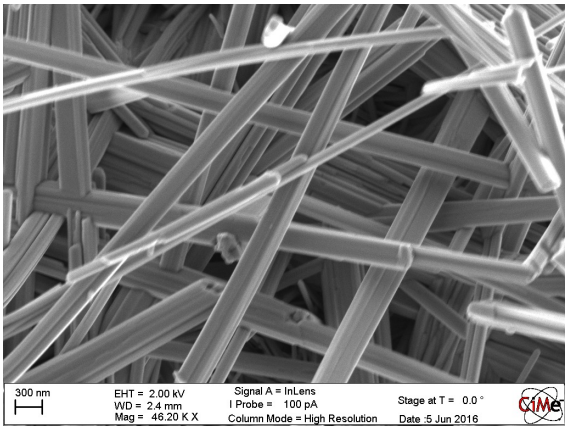


Figure 2: Se nanowires formed by recrystallization of the amorphous selenium fiber in the presence of isopropanol, from W. Yan (FIMAP).

(a) Discuss with your colleagues a few possible explanations for this observation. Which properties of selenium could play a role? How could the presence of isopropanol play a role? Make a hypothesis - in the following exercises we will collect more data that will allow you to verify it, disprove it, or formulate an alternative one.

** Exercise 2 Structure-property relations: crystal habit

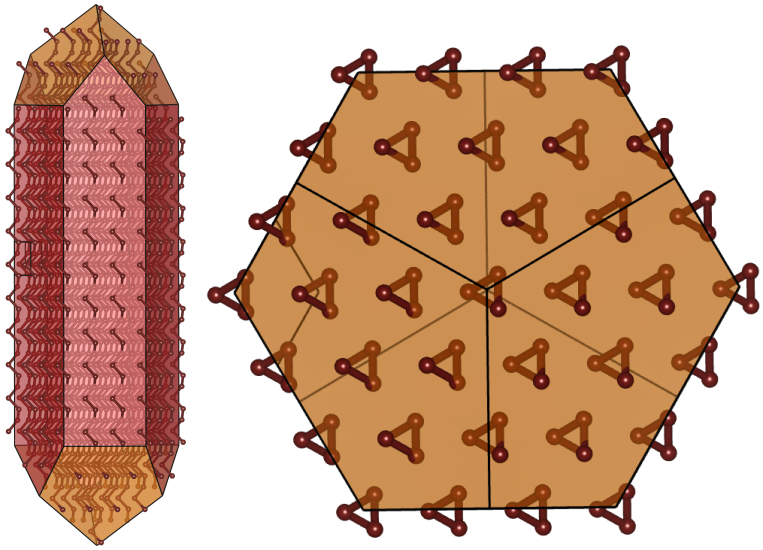


Figure 3: Observed crystal habit of trigonal selenium, together with a representation of its molecular structure.

Selenium crystallizes in a trigonal space group, and is characterized by the presence of polymer-like 1D chains stretching along the [001] direction.

(a) Can you explain qualitatively why Se crystals typically have an elongated crystal shape? *Hint: think about the crystal structure, and the energetic cost of breaking a covalent bond within the polymer chains*

For simplicity, we will assume that the crystal has a prismatic shape, with the side of the hexagon labelled by a and the height of the prism labelled by c. We will work out the relation between the aspect ratio $r = c/a$ and the ratio between the surface energies $\gamma_{001}/\gamma_{010}$.

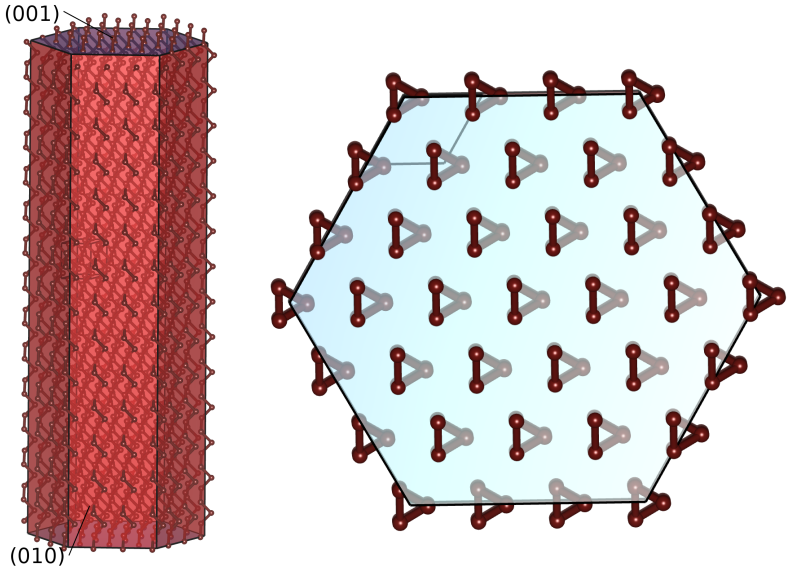


Figure 4: A simplified model of the crystal shape of Se.

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(b) Write the expression of the volume of the prism and of its surface area as a function of c and a.

(c) Write the expression of the total surface energy G_{surf} leaving the energy of the basal and prismatic planes expressed as γ_{001} and γ_{010}, respectively.

(d) The crystal shape is determined by the minimization of G_{surf} at constant volume. To do so, use the relation between volume, a and c to write c as a function of a and V.

(e) Plug this result into G_{surf} to obtain an expression that depends only on a and V. Derive with respect to a to find the value of a that corresponds to the energy minimum at constant V.

(f) Use this expression to write the aspect ratio as a function of $\gamma_{001}/\gamma_{010}$. By means of ab initio calculations, one can compute the values of γ_{001} – which is equal to 39 meV/Å^2 – and that of γ_{010} – which is equal to 9 meV/Å^2.

(g) What is the aspect ratio? Does it compare well with the crystals observed in air? And what about the nanowires? Discute more about your initial hypothesis. Is it verified or falsified by the analysis in this exercise?

** Exercise 3 Effect of the solvent

Now you probably start to see that the habit of the crystals is determined by the surface energies of different facets. Nanowires can be regarded as crystals with a very large aspect ratio, so perhaps the thermodynamic drive towards nanowire growth can be explained by the changes in interface energy when the crystal is immersed in isopropanol. Unfortunately it is hard to grow large crystals of selenium so as to measure the interface energy on different surfaces. Instead, we'll try to see how it can be estimated by simple ab initio calculations.

(a) Write the Dupré equation for the surface energy between selenium and isopropanol. What terms enter it? A quick Google search (and some units conversion!) will tell you that the surface tension of isopropanol is 1.35 meV/Å^2. Which is the missing term?

(b) Consider two materials A and B separated from each other. Write the internal energy between the two materials in terms of pair interactions V_{AA} and V_{BB} between their atoms (not necessarily the first neighbors).

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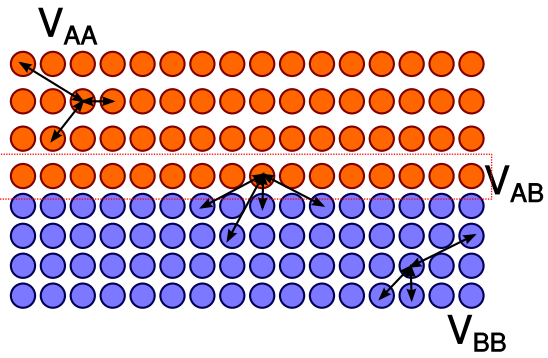


Figure 5: A scheme of the adhesion between the two materials in terms of pair interactions. It is assumed that only the first layer of A interacts with (all) the molecules in B.

(c) Now put into contact the two materials, and write the total energy including also the interactions between the two materials V_{AB}. We will make the approximations that (1) only the first layer of molecules in A interacts with B and (2) that the conformation and interactions between molecules in the two materials don't change upon joining the materials.

(d) Explain how this approximation allows us to estimate the work of adhesion based only on the adsorption energy of a single molecule of isopropanol on a selenium surface.

(e) The adsorption energy of an isopropanol molecule on selenium $\{001\}$ can be computed to be $E_{001} = -0.28$ eV, and on $\{010\}$ $E_{010} = -0.30$ eV. Assume that the area occupied by a molecule at the interface is of the order of 30Å^2. Estimate the interface energies $\gamma_{010,\mathrm{iso}}$ and $\gamma_{001,\mathrm{iso}}$.

(f) What aspect ratio do you predict for a crystal growing in isopropanol? Does this help explain the experimental findings? Did your initial hypothesis match with what you discovered in this exercise?

**** Exercise 4 The real thing

Only after you finish all the other exercises, if you are up for a challenge, you can try to repeat these exercises using the real crystal habit of selenium given in Fig. 3. Nothing changes from the conceptual point of view, and it is mostly a (difficult but fun) exercise in solid geometry. You should know the following additional pieces of information

(a) The pentagonal facets expose $\{01\bar{1}\}$ planes, and have an angle of about 90 degrees at the apex.

(b) The surface energy of $\{01\bar{1}\}$ is $\gamma_{01\bar{1}} = 27$ meV/Å^2.

(c) The adsorption energy of an isopropanol molecule on $\{01\bar{1}\}$ is -57 meV.

The End.