Popular Science Summary

In a rapidly globalizing world, the progress and success in the electronics industry are inextricably linked to the miniaturization of electronics. The smaller the size of an electronic device, the more such devices can be fit into the same area. For example, the current type of transistor, invented in 1947, was 40 micrometers long, while IBM announced in May 2021 a chip with 2 nanometer transistors. The difference in the length scale is 20000 times (the same as the difference between the length of a Pharaoh ant and an African bush elephant). Somewhere in between, humanity made a step into the nanoscale world. The prefix “nano” comes from ancient Greek for “dwarf” and denotes 1/1 000 000 000, or one billionth.

In addition to a higher packing density of the electronic chips, which results in higher performance and lower energy use, the transition to nanoscale enables the materials to exhibit unique properties directly connected to its small size. When the size is small enough, that is on the nanometer scale, quantum mechanical effects start to dominate and one such effect is that the motion of electrons get restricted and this is known as quantum confinement. Considering the size, there are three main types of nanostructures, namely 0-dimensional with quantum confinement in all three spatial directions, 1-dimensional, with quantum confinement in two directions, and 2-dimensional with quantum confinement in one direction. The 0-dimensional nanostructures are known as quantum dots, the 1-dimensional ones as quantum wires or nanowires, and the 2-dimensional ones as quantum wells. Even if nanostructures cannot be seen with the naked eyes, their influence is more and more perceptible: they incorporate into our daily life and change it. For example, a regular customer can buy a high-resolution TV with quantum dots or glossy printing paper with ceramic nanoparticles.

Among the nanostructures of different shapes and dimensions, the nanowires are of particular interest and importance. They are whisker-like crystals with the radius of 10-100 nanometers and the length of a few micrometers. Despite there are no nanowire-based devices in today’s industry, many prototypes have been developed such as solar cells, sensors, transistors, light emitting diodes and silicon nanowire-based batteries announced by Tesla. Such a variety of applications can be explained by the possibility of controlled growth of nanowires, including their morphology (the radius and length), chemical composition (sort and number of atoms which form a nanowire) and crystal structure (the arrangement of the atoms in the crystal). This allows one to tune the optical and electrical properties of nanowires. For example, combining two binary compounds, such as indium arsenide (InAs) and gallium arsenide (GaAs), one may obtain ternary InGaAs nanowires whose properties are a combination of those of the binary compounds (InAs and GaAs). To be more specific, the properties of ternary nanowires are determined by the ratio of the number of the InAs and GaAs units in the solid. In this perspective, an important question arises: how to make a nanowire with a given chemical composition?

To answer this question, we should understand the underlying growth mechanism and know how to control the process using experimental conditions such as temperature and fluxes. The most popular way to fabricate nanowires is by so called vapor-liquid-solid growth. Within this approach, the fluxes of atomic species are directed towards a sample surface containing liquid metal droplets. Then, atoms dissolve into the liquid droplets, and when the concentration of atoms exceeds the solubility limit, it is energetically favourable for crystalline material to form. This formation process takes place at the contact area between the sample surface and the liquid drop. Continuing this process, a nanowire takes form, one atomic layer after another, until the fluxes of atomic species from the vapor are turned off.

Now, when we understand the principle behind nanowire formation, we would like to know how the composition of the liquid drop is related to the composition of the vapor, and how the composition of the solid nanowire is related to the liquid. If we know this, we can predict, on average, which atom, red or white (see Figure 1), will incorporate into the nanowire depending on the conditions.

One of the purposes of this thesis is to find the relationships between these compositions using a variety of models, which are based on different assumptions and limiting steps. Another purpose is to explain the crystal structure of ternary nanowires. The research procedure is the following. When considering nanowire growth, I assume the most critical elementary processes, which I translate into equations. Then I solve these equations and analyse their solutions under the variation of different, experimentally relevant parameters, such as concentrations and nanowire growth temperature.

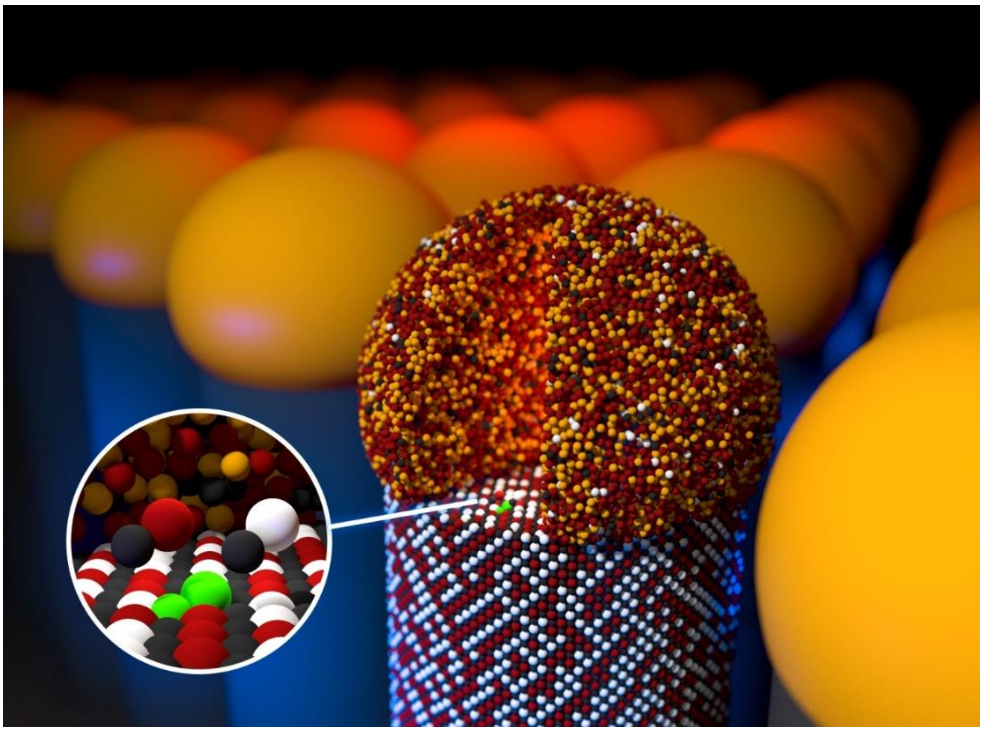

Figure 1. Schematic illustration of a ternary nanowire array. The structure in the "focus" is a nanowire and the droplet situated on the nanowire tip. Both of them are built by a large number of the small spheres, which denote atoms. Their colour corresponds to one of the sorts of atoms. For example, the nanowire is made of three sorts of atoms, namely indium (red spheres), gallium (white spheres) and arsenic (black spheres). As discussed earlier, a ternary nanowire can be considered as a combination of binary compounds, or the atom pairs (InAs and GaAs). The droplet consists of four sorts of atoms. The fourth component (yellow spheres) is gold, which serves as a solvent. The atoms in the crystal are well arranged, while the atoms in the droplet are randomly distributed. A piece of the droplet is cut for illustrative purpose. The main question, shown in the inset, is, 'which pair of atoms (InAs or GaAs) should be instead of the "unknown" green pair'? Reprinted with permission from The Royal Society of Chemistry 2018 (Paper: "Nucleation-limited composition of ternary III-V nanowires forming from quaternary gold based liquid alloys" Egor D. Leshchenko, Masoomeh Ghasemi, Vladimir G. Dubrovskii and Jonas Johansson, CrystEngComm, 2018, 20, 1649 – 1655.)