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Nanowires produced by laser ablation of binary metal alloys in superfluid helium

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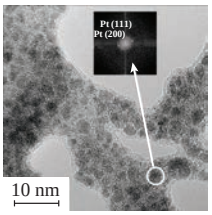
Method based on laser ablation of metals in superfluid helium was applied to prepare thin nanowires from binary alloys. The possibility of production of different types of nanostructures *via* this technique was demonstrated. The thin nanowires with periodic alternation of elemental composition and core–shell nanostructures were obtained for different alloys.



As it was already demonstrated,[1–3] the laser ablation of any metals in superfluid helium resulted in appearance of thin nanowires with a regular shape and of good quality. In this work, on the typical examples, we analyzed the structure of nanowires produced by ablation of binary alloys and estimated the promises of their application in science and technology.

The mechanism of nanowire formation in superfluid helium is briefly as follows. Atoms and small metal clusters, like any other impurities embedded into superfluid helium, tend to get into the core of 1D quantized vortices existing therein.[4–6] Moving inside a vortex strictly towards each other, these particles have much greater probability to collide than in the bulk of liquid, where their motion is chaotic.[7] At low temperatures, any collision leads to coagulation, and the longer the coagulation product becomes, the stronger it attaches to the vortex.[3,8] Eventually, whole coagulation of impurities occurs inside of the vortices and its products are long nanowires. For some reasons, the coagulation process proceeds adiabatically rather than isothermally, despite the fact that superfluid helium has unbeatably high thermal conductivity.[2] Therefore, as it is valid for vacuum, the coagulation product of two small enough cold metallic clusters acquires the heat sufficient for its melting. Naturally, then this product becomes spherical due to surface tension.[2] For each metal, depending on its thermal properties, there is such a critical size of cluster, that larger clusters could not be melted, but simply adhered to each other in the vortex to form a nanowire. Just this size determines the diameter of growing nanowire.[2] Based on the thermodynamic properties of the bulk metal, simple formula is proposed[2] to correctly predict the wire diameter of all nanowires so far obtained in our lab. The structures of nanowires made of various metals are different, *viz.* crystalline, polycrystalline or amorphous, but, due to their formation from molten clusters, their structure is close to dense packing.

In general, the mechanism of nanowire formation in quantized vortices when the target is made of binary alloy, due to the universal nature of processes occurring in superfluid helium should be the same as for pure metals. However, the structure of nanowires thus formed is to be much more diverse, and may be of large interest for science and engineering.

The technique of the nanowires production by laser ablation of metals immersed into superfluid helium was described elsewhere.[†,1–3]

Note that the spherical protoclusters served as the bricks for nanowire growth possess diameters at least higher than 2 nm; so they are large enough for spatial phase separation to occur.[9,10] Only rarely, if the alloy is a solid solution even in nanoclusters, the phase separation does not proceed, the example is alloy of indium and lead of any elemental composition (Figure 1). The nanowires produced from In : Pb [see Figure 1(*c*)] possess a crystalline structure, and even the temperature of its transition to superconducting state smoothly varies between those of individual indium and lead depending on the elemental composition.

The phase separation in nanoclusters with size of a few nanometers occurs even in eutectic alloys.[9,11] This is due to the fact that the phase diagram of a nanocluster correlates rather with surface tension than with free energy.[12] Therefore, the protocluster just before its sticking to nanowire already represents the solidified nanocluster of core–shell structure,[9] where the shell is more fusible

[†] The target represented the strip of corresponding alloy prepared from chemically pure (99.99%) metals. In_{88} : Pb_{12} alloy was prepared by joint heating the pieces of metals *in vacuo* up to temperature (350 °C) exceeding their melting points, subsequent incubation during 2 h and cooling. Ag_{90} : Cu_{10} alloy was obtained *via* slow sintering of metals at 980 °C using borax as a flux.[10] The most difficult problem was to make alloy of platinum and tungsten due to high melting temperature of the latter. Eventually Pt_{50} : W_{50} alloy was produced by zone melting method.

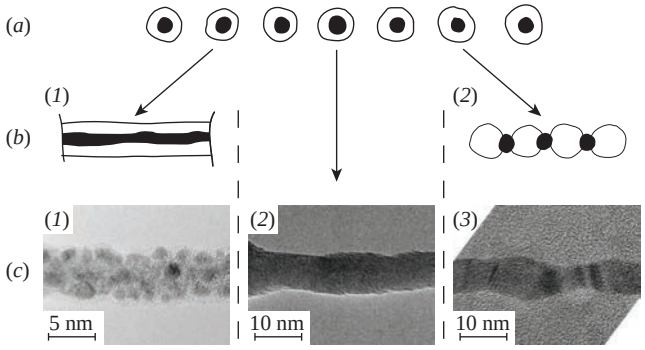


Figure 1 Different structures of nanowires produced from binary metal alloys: (*a*) schematic representation of protoclusters; (*b*) schematic image of nanowires with (*1*) core–shell and (*2*) heterostructures; (*c*) structures of wire made of (*1*) $Pt_{50}:W_{50}$, (*2*) $In_{88}:Pb_{12}$, and (*3*) $Ag_{90}:Cu_{10}$.

phase [see Figure 1(*a*)]. As shown in Figure 1(*b*), there are two extreme types of nanowire structure, namely the core–shell wire (picture *1*) and the periodic heterostructure (picture *2*); the intermediate structures are of course possible.[13,14] Note that for all elemental compositions, even if one of the elements is in excess, the period of the heterostructure should be close to the wire caliber.

A typical example of the wire with core–shell structure is the nanowire obtained by the ablation of platinum–tungsten alloy, with the volume ratio of elements close to 1 : 1. Although being far from a perfect solid solution, the target has the size of grains determined by an optical microscope, which did not exceed a few micrometres, that is sufficient because the laser spot on the target surface has a diameter of 100 μm. According to a transmission electron microscope (TEM) micrograph, the wire originally represents the tungsten core coated by platinum cladding. However, as it is shown in Figure 1(*c*) (picture *1*), the heating up to 300 °C in air atmosphere leads to platinum shell decay into separate nanocrystals with size about 2 nm regularly arranged on the core surface, whole tungsten then was oxidized to WO_3. FFT measurements revealed that the individual clusters possessed *fcc* structure with interplanar distances of 2.0 and 2.3 Å, corresponding to Pt (200) and Pt (111).

Such a structure is of great interest for application in nanocatalysis. Indeed, the platinum nanoweb, which we already used as a catalyst,[15] decays into separate nanoclusters at 300 °C. The composite nanoweb manufactured from binary alloy is stable at least up to 500 °C due to the formation of a core of refractory tungsten oxide. The size of platinum nanocrystals is close to the optimal one for nanocatalysis,[16–18] and their regular arrangement, unattainable by simple deposition of nanoparticles on the substrate, allows us to study the proximity effects, whose importance is noted by several authors.[19,20] Apparently, one should keep in mind that it is possible to change over a wide range the components of alloy, the catalyst precursors, and support to satisfy the optimal conditions for any catalytic reaction.

The example of a different type of nanowire structures, *viz.*, heterostructure, where a fusible phase was gathered between the fragments of refractory phase, was the nanowire produced by ablation of $Ag_{90}:Cu_{10}$ alloy. Despite the fact that in the bulk this composition relates to a solid solution, the corresponding micrograph [Figure 1(*c*), picture *3*] shows that nanowire consists of quasiperiodically alternating crystals of silver and copper. The possible applications of these objects are wide. For example, the nanowires with superconducting and ferromagnetic properties may be manufactured creating a magnetically controlled resistor due to a combination of known negative mutual influence of superconductivity and ferromagnetism with known proximity effect, imposing on the order of nanometer distances neighboring metals. Using binary alloys of metal with the semiconductor, one can also produce a structure serving as logic elements.

In conclusion, the above examples illustrate the variety of quasi-1D heterostructures, which can be obtained by laser ablation of different alloys in superfluid helium. A variety of metals and semiconductors, especially germanium and silicon, may be the components of alloys. The alternation period of the elemental composition in the wire is close to its caliber and amounts to several nanometers. No reagents are used in the synthesis other than the material of alloy and superfluid helium, which in principle contains no contaminants. This is important for the prospects of using the method in microelectronics, where purity is known to play a pivotal role.

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