Nano-Structures & Nano-Objects 16 (2018) 104–109

Contents lists available at ScienceDirect

Nano-Structures & Nano-Objects

journal homepage: www.elsevier.com/locate/nanoso

Disintegration of nanostructured metals with the formation of nanoparticles in electron microscope

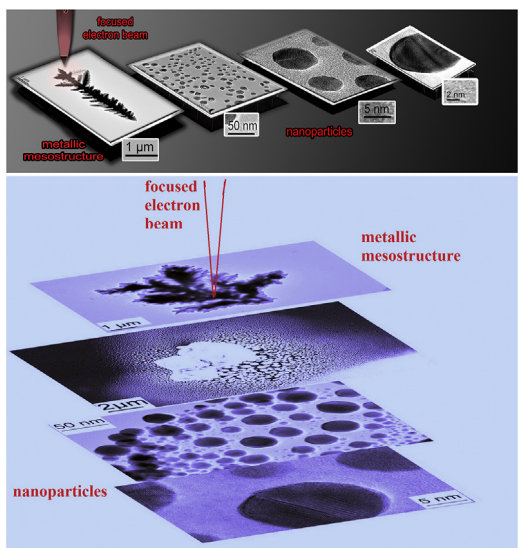
G.K. Strukova [a,*], G.V. Strukov [a], I.I. Khodos [b], S.A. Vitkalov [c]

[a] Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia
[b] Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences, 142432 Chernogolovka, Russia
[c] Physics Department, City College of City University of New York, NY 10031, USA

HIGHLIGHTS

- 3D hierarchical metallic mesostructures disintegrate in transition electron microscope.
- Samples containing $FeNi_3$ nanowires, silver nanowafers or Pb–In nanorods were irradiated.
- Explosive disintegration leads to form of metallic nanoparticles on a holding substrate.
- Direct atomic resolution images exhibit the single crystal structure of nanoparticles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 November 2017
Received in revised form 13 March 2018
Accepted 18 April 2018

Keywords:
Nanostructured mesostructure
Disintegration
Metallic nanoparticles

ABSTRACT

In this paper we report on an explosive disintegration of metallic 3D samples with built-in nanoscaled hierarchical order under electron beam irradiation in a transmission electron microscope. The objects of our investigation are novel 3D mesostructures containing either $FeNi_3$ intermetallic nanowires, or silver wafers of nanoscale thickness, or Pb–In nanorods. These structures were fabricated via a self-organization of metallic nanowires growing on templates during the pulsed electro-deposition process. The disintegration of 3D mesostructures yields an array of 2–50 nm metallic crystalline nanoparticles scattered on a holding substrate in the vicinity of the contact of the electron beam with samples. Direct atomic resolution images made in-situ reveal the monocrystalline structure of the nanoparticles. The observed rapid disintegration of 3D mesostructures in the electron beam is related to the internal energy significantly enhanced in the nanostructured samples. Possible applications of the phenomenon are discussed.

1. Introduction

Recently we have reported on 3D mesostructures obtained by a self-organization of nanowires growing on templates in electrolytes under the action of programmed electric pulses. These

* Corresponding author.
E-mail address: strukgalina@gmail.com (G.K. Strukova).

https://doi.org/10.1016/j.nanoso.2018.04.004
2352-507X/

novel objects, having size of few microns to few hundred microns, demonstrate intriguing structural similarity with biological objects such as plants, fungi, seashells (biomimetics) [1]. SEM and TEM studies of Pd–Ni seashell-shaped samples revealed a hierarchic order of densely packed conical bundles of metallic nanowires. The nanowires themselves consist of 4–15 nm nanocrystals embedded in an amorphous matrix [2]. During the TEM study of branch-shaped metallic mesostructures with nanoscale needles we have observed a rapid disintegration of the samples, which appear locally in the vicinity of the contact with a focused electron beam. The disintegration results in an array of nanoscale metallic particles arises near the contact on a substrate supporting samples. This fascinating behavior of 3D nanostructured metallic samples in an electron microscope, i.e. their disintegration and an appearance of the nanoparticles, to the best of our knowledge, was not described in the literature. This issue has initiated the study presented below. The usefulness of metallic nanoparticles in modern technologies stimulates the development of new methods for their production [3]. Accomplishments in this field have been demonstrated recently [4,5]. An explosion of wires in a liquid media produces nanoparticles of s- and p-type metals [4]. A microwave assisted synthesis of Pt-nanoparticles on graphene oxide facilitates a creation of effective electrodes for dye sensitized solar cells [5]. A wide variety of metal nanoparticles obtained by methods of a chemical reduction of metal ions in solutions as well as microbiological methods have been utilized in a diversity of applications [6]. The current state of art in the nanocrystal synthesis, including metal growth in a non-thermal plasma, as well as examples of applications, using the nanocrystals, are presented in a recent review [7]. The synthesis of powders of metal nanoparticles via action of a powerful focused electron beam on a massive metal target in an industrial scale is described in Ref. [8].

Furthermore during last 15 years a technique of metal deposition by a focused electron beam (FEBID) is developed, that allows to synthesize nanostructures using metallic atoms produced in decomposition processes with gaseous precursors [9,10]. Organometallic compounds (metal carbonyls) used as precursor are thermodynamically unstable under the e-beam irradiation. This property allows to conduct FEBID process in an electron microscope in-situ, since the microscope beam power is sufficient for a rapid decomposition of the precursor. As mentioned above, our nanostructured samples obtained via a pulsed electrodeposition on templates have a complex multiscale architecture with building blocks containing both amorphous and nanocrystalline phases. This leads to an increased internal energy and, as a consequence, may enhance significantly the disintegration of the samples under the electron beam irradiation. Presented below study of the novel 3D nanostructured materials under a relatively weak electron beam irradiation in an electron microscope both sheds a light on the stability of these structures and demonstrates an effective and clean method of the synthesis of crystalline metallic nanoparticles in the electron microscope.

2. Experiment

The fabrication of the studied 3D metallic nanostructured materials is described in detail in [1,2]. The nanostructured metal samples are obtained onto templates by an electroplating from aqueous solutions of metal salts using programmable electric current pulses. In such conditions, the electroplating leads to both the metal deposition and a self-organization of growing nanowires, yielding nanostructured samples with a built in 3D hierarchical order propagating up to several hundred microns. Shapes of the obtained structures are often similar to the shapes of natural objects such as mushrooms, plants, seashells. In the presented work we used three different sets of samples: (1) "shells", obtained as a result of self-organization of nanowires of intermetallic $FeNi_3$, (2) "branches", consisting of silver nano-plates, and (3) "branches" of the Pb–In alloy nanorods. The SEM and TEM studies of the samples were performed using JEM-2100 electron microscope. For these studies the grown samples were rinsed in an ultrasonic bath twice. The first rinse was in acetone. The second was in alcohol to make a suspension of the grown structures. A droplet of the alcohol suspension was then placed on a holding substrate (a carbon-coated copper grid) and after the alcohol evaporation the substrate with the nanostructured samples was placed into the electron microscope column. All experiments were carried in the electron microscope at 200 kV accelerating voltage. An electron beam carrying total electric current (4 pA) was focused on the samples area of 20–50 nm^2. The disintegration of the sample occurs promptly upon a contact of the focused electron beam with the sample. Metal nanoparticles were observed on holding substrate in the vicinity of the contact of the sample with the focused electron beam. High resolution images of individual nanoparticles obtained via the sample disintegration were made in-situ in the same electron microscope.

3. Results

All studied samples have demonstrated the explosive disintegration under irradiation by the focused electron beam. Fig. 1a, b present a hierarchical 3D mesostructure composed of nanowires of magnetic intermetallic compound $FeNi_3$ (permalloy). The sample is shaped as a seashell. The studied sample was a single-phase $FeNi_3$ -intermetallide, that has been confirmed by an analysis of the X-ray diffraction (not shown).

Fig. 1c demonstrates the edge of the sample and the array of nanoparticles disjected onto the substrate during the electron beam irradiation of the sample. The inset to Fig. 1c shows the electron diffraction pattern indicating the crystalline structure of these particles. Fig. 1c, d show that the particles have sizes less than 20 nm. The particle shape is identical to rounded polyhedrons. The nanoparticles form single crystals. This is seen from the direct high resolution images presented in Fig. 1e, f.

A single-crystal $FeNi_3$-flake with a nano-sized thickness was found in a mortar produced by grounding of the permalloy mesostructures (Fig. 2a).

After the explosive disintegration in the focused electron beam, this sample was dispersed into nanoparticles of several nanometers in size shown in Fig. 2b, c.

Fig. 3 presents the image of a hierarchical 3D structure made of silver.

The structure looks as a conifer branch with elements of fractal self-similarity. It is a single crystal as shown in the inset to Fig. 3a presenting the electron diffraction image of the structure. A localization of the focused electron beam on a "branch" of the structure induces the explosive evaporation of the metal producing an array of nanoparticles placed on the substrate near the beam. Fig. 3b shows the substrate with the array of nanoparticles scattered near the contact between the electron beam with the sample. Fig. 3c demonstrates that the scattered particles are shaped as polyhedrons with different linear sizes less than 50 nm. The electron diffraction images of the scattered particles reveal that these particles are nanocrystals. This is presented in the inset to Fig. 3c. Finally, Fig. 3d shows the direct resolution image of a single nanoparticle indicating the ordered arrangement of the atomic planes and confirming the single crystal structure of the nanoparticle.

In a similar experiment, using a mesostructure consisting of gold wafers of nanoscale thickness as a target for a focused electron beam in the microscope, we have obtained gold nanoparticles on a substrate.