Chemical Physics 478 (2016) 2–7

Contents lists available at ScienceDirect

Chemical Physics

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

Nanocluster metal films as thermoelectric material for radioisotope mini battery unit

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ARTICLE INFO

Article history:
Received 15 February 2016
In final form 14 July 2016
Available online 16 July 2016

Keywords:
Thermoelectric conversion
Nanostructured films
Metal nanoclusters
Electronic percolation
Thermopower
Radioisotopes
Nuclear batteries

ABSTRACT

The paper is devoted to studying the thermoelectric and structural properties of films based on metal nanoclusters (Au, Pd, Pt). The experimental results of the study of single nanoclusters' tunneling conductance obtained with scanning tunneling spectroscopy are presented. The obtained data allowed us to evaluate the thermoelectric power of thin film consisting of densely packed individual nanoclusters. It is shown that such thin films can operate as highly efficient thermoelectric materials. A scheme of miniature thermoelectric radioisotope power source based on the thorium-228 isotope is proposed. The efficiency of the radioisotope battery using thermoelectric converters based on nanocluster metal films is shown to reach values up to 1.3%. The estimated characteristics of the device are comparable with the parameters of up-to-date radioisotope batteries based on nickel-63.

1. Introduction

Micro- and nano-electromechanical systems (MEMS and NEMS) bringing together such nanoelectronic and mechanical elements as actuators, pumps and motors are of great interest because they can be used as microscopic physical, biological and chemical sensors [1–3]. One of the main constraints to wide-scale introduction of the devices is the problem of producing miniature power supplies for MEMS and NEMS. Nowadays, the solution to this problem is closely connected with up-to-date miniaturization capabilities of standard lithium-ion batteries, solar cells, fuel cells, and capacitors of various types (see., e.g., [4,5]). Unfortunately, the advances in this area are not concerned with developing effective micro- and nano-sized systems, as minimal allowable lateral dimensions of such power sources are of the order of several millimeters.

An alternative solution to the problem of MEMS and NEMS power supply is the application of radioisotope batteries [6]. The most efficient ones are based on thermoelectric conversion of the energy released during nuclear decay into electric energy [7]. It is one of the shortest energy conversion chains that potentially allows reducing energy losses. The well-known physical and chemical techniques ranging from lithography to local electrochemical deposition [8] can be used to form a radioisotope source of micrometer dimensions. The main difficulty lies in developing a highly efficient thermoelectric material which would act as a converter of thermal energy of nuclear decay into electric energy.

Currently nanostructured materials based on semiconductor elements, e.g. SiGe, Bi_2Te_3 [9,10] are widely used to increase the efficiency of thermoelectric materials. However, it is not possible to apply these materials in radioisotope batteries for MEMS and NEMS for the following reasons. First, an attempt to reduce the size of semiconductor thermoelectric elements to the nanoscale leads to a sharp decrease in their conductivity up to the manifestation of the dielectric properties [9]. Secondly, the characteristic feature of radioisotope batteries is a rather stringent requirement for radiation resistance of the materials used [7].Therefore, for example, the use of germanium, tellurium, and bismuth as structural materials seems to be inappropriate because of their relatively low radiation resistance, especially in thin films. Thus, the thermoelectric material used in radioisotope batteries should have sufficient current conductivity at nanometer size scales, as well as good radiation resistance, i.e. it should be analogous to metal.

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http://dx.doi.org/10.1016/j.chemphys.2016.07.010
0301-0104/

In this paper, we consider the possibility of creating a radioisotope thermoelectric power source based on the thorium-228 isotope with power density of 26 W/g. Thin films up to several microns thick, consisting of metal nanocluster of sizes in the range of 1 to 10 nm are proposed to use as a thermoelectric material for converting the thermal energy of thorium-228 decay. Such structure is estimated to strongly suppress phonon heat transfer (phonons are "locked" inside metal clusters). The surface contact of metal nanoclusters with each other is enough to maintain electronic conductivity similar to metallic one, which is caused by percolation effects [11], but it is not sufficient for propagation of phonons. The change in the electronic properties due to quantum effects in small-sized nanoclusters leads to an increase in the thermoelectric power value. It is shown that the efficiency of the proposed micron sized radioisotope power unit based on the thorium-228 isotope as a heat source, and the thermoelectric transducer based on nanocluster metal film, can reach values up to 1.3%.

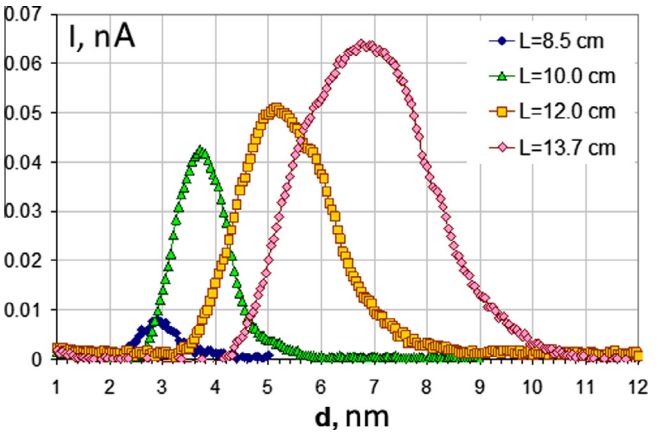

Fig. 1. Typical size distributions of gold nanoclusters in Ar plasma for various aggregation zones: $L = 8.5$ cm, 10.0 cm, 12.0 cm and 13.7 cm at gas flow of 25 sccm, voltage supply of 224 V, and current of 144 mA.

2. Experimental techniques

The experimental research aimed at the development of a prototype of radioisotope battery included both the technique of formation of nanocluster films and the radioisotope source.

2.1. Formation of nanocluster films

Formation of thin film samples composed of metal nanoclusters, on the surface of silicon oxide SiO_2/Si(001) (1 μm), was conducted by cluster deposition in the gas phase using the cluster source Nanogen-50 with the quadrupole mass spectrometer MesoQ (Mantis Deposition Ltd., UK) integrated in the UHV surface analysis system Multiprobe MXPS VT AFM (Omicron NanoTechnology GmbH, Germany). Formation of nanoclusters in the source was a result of magnetron sputtering of a target in an inert gas stream at sufficiently low pressure $p \simeq 1 \times 10^{-3}$ Torr. Cooling of atoms of sputtered target resulted in the formation of the metallic phase nucleation, and subsequent growth of nucleating centers during the passage through the aggregation area. The analysis and size separation of charged clusters were carried out in real time using the quadrupole mass spectrometer MesoQ at the outlet of the aggregation zone. Typical mass spectra of gold nanoclusters are shown in Fig. 1. The figure shows that the size range of formed nanoparticles depends on the length of the aggregation area, and may vary from 1 to 10 nm. If the mass spectrometer is adjusted to the filtering mode, the nanoclusters beam emitted from the source will have a very narrow size distribution with a variance of about 15%.

The chemical composition and electronic structure of nanocluster films deposited on SiO_2/Si(001) surface were controlled *in situ* by X-ray photoelectron spectroscopy (XPS). To this purpose, immediately after the deposition the sample was moved in the chamber of UHV ($p \simeq 1 \times 10^{-10}$ Torr) analyzer Multiprobe MXPS VT AFM by means of the rod. The size and shape of the clusters were measured *ex situ* by analyzing SEM images obtained with the scanning electron microscope JSM 7001F (JEOL, Japan).

Typical SEM images of gold films formed from nanoclusters with size of 10 nm after 10 min of deposition are shown in Fig. 2. The left panel shows that the deposited nanoparticles are rounded and quite tightly packed. The average size of nanoparticles can be estimated at the level of 10 nm, which corresponds to the predetermined value in the mass filter. It should be noted that the cluster size of 10 nm was chosen for visualization, since the maximum resolution used in this work was 2 nm, and it was not possible to obtain a SEM image of good quality for such small particles. The right panel (b) of Fig. 2 shows the image of the cleavage of the same sample obtained by mechanical means. It can be seen that a sufficiently loose film composed of individual clusters is formed. The shape and size of the clusters which are in contact with the substrate do not differ from the shape and size of the cluster lying on the surface. Thus, these images show that the films produced consisted of individual nanoclusters, which are in contact with each other without aggregation.

2.2. Formation of radioisotope source

It is to be recalled that the requirements for sources of radioisotope batteries for MEMS and NEMS are quite specific, namely: high power density (>10 W/g), small size (battery size should not exceed the size of the system), and a long service life (several months to hundreds of years). In our opinion, one of the most promising batteries satisfying these requirements is a radioisotope thermoelectric generator of micron size, currently being developed by our research group. It is obvious that the radioisotope source of this power unit must meet the safety requirements (absence of intense gamma radiation). Therefore, we considered the following candidates for the radioisotope material: Po-210 (α-source; $T_{1/2} = 138$ days; $E = 5.4$ eV; $P = 124.9$ W/g), and Th-228 (α-source; $T_{1/2} = 1.9$ years; $E = 5.5$ eV; $P = 26.0$ W/g) [7]. In this work, the thorium-228 isotope-based generator of the radioisotope source was proposed. This choice was determined by high power density of thorium-228 (26 W/g) and low emission of gamma radiation as thorium-228 decays with creation of alpha particles. If necessary, all the techniques can be transferred to other radioisotope materials.

The formation of the radioisotope source as the thermal element of micron size was conducted on a specially prepared surface of silicon by electrochemical deposition of thorium at room temperature according to the technique described in [12]. Because of the high radiation activity of the thorium-228 isotope, the formation of model thorium batteries was carried out using the salt of stable thorium-232 isotope. This substitution reduced the level of radioactivity of the sample to the level permitted under normal laboratory conditions, and allowed conducting series of experiments to determine the optimum deposition parameters.

The element of novelty in the preparation of SiO_2/Si(001) substrates was in etching of disc-shaped hole with the diameter of 200 μm, and 1 μm deep (the latter dimension is determined by the thickness of the substrate) in the thickness of silicon oxide. During the electrochemical deposition the space between the cathode (silicon substrate with a mask of the oxide film) and the anode