INDIUM ANTIMONIDE NANOWIRE ARRAYS FOR PROMISING THERMOELECTRIC CONVERTERS

G. G Gorokh¹, I. A. Obukhov², A. A. Lozovenko¹
Belarus, Minsk, ¹Belarusian State University of Informatics and Radioelectronics, BSUIR
Russia, Moscow region, ²System Recourses Ltd.
gorokh@bsuir.by, i_obukhov@systemres.ru

The paper presents a theoretical substantiation of the possibility to create promising thermoelectric converters based on quantum wires. The authors have developed and tested technological methods for manufacturing InSb nanowire arrays with a high diameter to length aspect ratio in modified nanoporous anodic alumina matrices. The microstructure and composition of the formed nanostructures were investigated. The authors present the results of electrophysical studies of InSb nanowire arrays in the pores of anodic alumina, and consider the prospects of their practical application in the manufacture of new types of generating and cooling devices.

Keywords: nanowire array, quantum size effects, anodic alumina, indium antimonide, thermoelectric converter

Modern nanotechnologies even now allow creating nanoscale objects with dimensions commensurable with or even smaller than the size quantization length \( L_{dq} \) in such materials [1]. In cases if the lateral dimensions of one-dimensional conductors are less than \( L_{dq} \), their potential reliefs for electrons change, nonequilibrium quantum effects occur at the boundaries between quantum wires with different cross sections, and other quantum effects appear [2]. It was theoretically shown in [3—5] that nonequilibrium phenomena arising at the boundaries of a conducting channel and contacts of a quantum wire (QW) can be used for thermoelectric transformations. With the appropriate choice of the QW design parameters, the flow of current through the device will lead to the cooling of the emitter contact and heating of the collector contact [3]. If many such QWs are present, this effect multiplies many times, which makes it possible to achieve cooling of the emitter junction by tens of degrees. Accordingly, if there is a temperature difference between the contacts of the QW, an electric current appears.

The indium antimonide having a small band gap (0.18 eV) and high electron mobility (7.8 m²/(V∙s)) [6] is the most preferable material for the QW construction [6]. InSb-based devices are able to receive infrared radiation with wavelengths up to \( \lambda \approx 7 \) μm and possess the best frequency properties [7]. Another important feature of the InSb material is that its nanostructures have the maximum value of dimensional quantization of electrons among \( \text{A}^{III}\text{B}^{V} \) semiconductors, which is 58 nm at room temperature. Therefore, a decrease in the linear dimensions of InSb nanostructures below 60—50 nm at a temperature \( T = 300 \) K leads to a change in the nature of the quantum states of electrons and to manifestation of quantum-size effects [8, 9]. Reducing the size of InSb nanostructures to the order of tens and units of
nanometers allows changing the width of their effective band gap from 0.5 to 3.2 eV, which is the widest possible range for semiconductors of this group [10].

Among the physicochemical methods for the production of InSb nanostructures, the most attractive method is the electrochemical deposition on metal bases and films (Au, Ag, Pt, Ni, Cu) into specially prepared "templates", in particular nanoporous films of anodic alumina (AA) [11, 12]. However, the specific structure of the AA does not allow it to be used directly as a template for the electrochemical deposition of InSb. In order to do that, it is necessary to replace the dielectric barrier oxide layer at the pore base with a conductive film. Earlier, we developed methods for the electrochemical deposition of metals (Ni, Cu) and semiconductors (InSb) into modified 0.5—1 μm thick AA matrices on metallized silicon substrates [13, 14]. The development of methods for the controlled formation of indium antimonide nanowires of a given dimension opens prospects for the use of a wide range of quantum phenomena as the basis for the functioning of microelectronic devices, including those that efficiently convert thermal energy to electric energy and vice versa.

The aim of this work was to substantiate the possibility of creating thermoelectric converters based on nonequilibrium effects in quantum wires, to form quantum-wire arrays with a large length to diameter aspect ratio using nanoporous templates of anodic alumina, and to study their structure, composition and electrophysical characteristics in order to then create new types of generating and cooling devices based on such structures.

**Theoretical prerequisites for creating microelectronic devices based on quantum nonequilibrium effects**

In order to explain the nonequilibrium effects in nanowires, let us imagine a quantum wire in the form of a conducting channel — a rectangular parallelepiped with emitter and collector QW contacts at its ends (Fig. 1). The threshold for quantum effects in solids is the dimension quantization of $L_{dq} = \pi \cdot (1.5\hbar\tau_0/m^*)^{1/2}$ (where $\tau_0 = \hbar/kT$ is the time during which the electron gas relaxes to thermodynamic equilibrium [5, 8]; $\hbar$ is the Planck constant); therefore, in cases where the lateral dimensions of the conducting channel are less than $L_{dq}$, when the current flows through the QW, its emitter contact will cool down, and the collector contact will heat up.

![Fig. 1. Schematic representation of a quantum wire](image-url)
The described phenomena are based on the Peltier effect, which is manifested at the boundaries of the emitter and collector channels of the QW contacts. If the lateral dimensions of the QW are sufficiently small, then such QW is a potential barrier for electrons in the direction of charge transfer. As a result of dimensional quantization an energy gap appears \( \Delta = (E_1 - E_F) > 0 \) between the Fermi energy of the electrons in the contacts \( E_F \) and the first allowed level of the energy of these electrons in the conducting channel of the quantum wire \( E_1 \). The value of \( \Delta \) is the lower energy limit, which can be either absorbed or emitted by electrons upon transition from a state with an energy level not higher than the Fermi energy to a state with energy level allowed in the conducting channel.

As it is clearly seen in Fig. 2, the levels are separated by energy gaps exceeding the energy of the thermal fluctuations \( k_B T \) \( (k_B \) is the Boltzmann constant, \( T \) is the temperature) of about 0.026 eV at room temperature. Since the height of the potential barrier created by the electrons conducting channel in the QW is a function of the lateral dimensions of this channel, the electrophysical properties of the wire will depend on these dimensions. In addition, the injection of electrons from the contact into the channel is equivalent, in its physical sense, to the evaporation emission [3, 8].

If the order of the values of \( \Delta \) and \( k_B T \) is the same, then by applying an external voltage to the QW it is possible to cool the emitter contact due to the charge transfer and collector contact cooling. Thus, this effect is caused by the "evaporation" of electrons in a narrow region near the emitter contact and subsequent transfer of the electrons through a conducting channel to another contact [3—5, 15]. Fig. 3 shows the distribution of the ratio \( n/n_{eq} \) along the quantum wire \( (n \) is the electron concentration at a voltage \( V = 0.38 \) V, \( n_{eq} \) is the equilibrium electron concentration that is calculated at \( V = 0 \) V). It is evident from the Figure that in the region of the conducting channel adjacent to the emitter contact, the concentration of electrons "evaporated" from the emitter is several times higher than the equilibrium concentration. At the same time, the depletion of the conducting channel by electrons is observed in the region of the collector contact.

As a result of the injection of electrons from the contact regions in the conducting channel, the energy of thermal fluctuations is absorbed and emitted by the electrons. Upon absorption, the electrons pass from a state with a lower height of the potential barrier to a state with higher energy. Reverse transitions occur in the same way with the emission of thermal energy. If a non-zero offset is applied between the emitter and collector channels, QW has an electric current produced in it. Electrons that absorb thermal energy are carried by this current from the contact with a smaller applied voltage into the conducting channel. Here, electrons cannot radiate heat energy, since this region does not contain states with a lesser energy than the height of the potential barrier. Radiation of thermal energy and a decrease in the energy of electrons occurs only in the region of the opposite contact. It should be noted that the described phenomena can be used to create nanorefrigerators or (which is the same) heat pumps based on quantum wire arrays. Theoretical estimates show that in such devices it is possible to cool objects adjacent to the emitter junctions of quantum wires by tens of degrees [3, 5].
In addition to the evaporation emission in the transition region between the emitter contact and the conducting channel, absorption of infrared range photons is observed, which makes it possible to use QW as a photocell [16]. With the corresponding power of external electromagnetic radiation, one QW can generate approximately 10 nW of electric power. The calculated values of the maximum power being taken from one QW and of the efficiency of such a cell are proportional to the ratio $R_0/R$, where $R_0 = \hbar/e^2 \approx 4.1 \, \text{k} \Omega$; $\hbar$ is the Planck constant; $e$ is the electron charge; $R$ is the resistance of the quantum wire. Thus it is obvious that the lower is the QW resistance, the higher is the conversion efficiency.

The combination of a heat pump and a photocell based on quantum wires makes it possible to build a quantum thermoelectric converter — its probable scheme is shown in Fig. 4, a. It consists of a quantum wire array adjacent to the cooled surface and a similar matrix that converts infrared radiation into electric current. It also includes the accumulating and control
devices. A thin-film functional device schematically depicted in Fig. 4, b can be used as the basic element for a nanorefrigerator, photocell, and quantum thermoelectric converter.

Fig. 4. Schematic representation of a quantum thermoelectric converter (a) and the simplest cooling device based on nanowire arrays (b)

The part of quantum wires in this device is performed by an array of nanowires formed in a porous matrix of anodic alumina with emitter and collector contacts on its opposite sides. The cooling temperature in such a device can be controlled by the applied voltage: the greater the applied voltage and the electron concentration in the emitter contact — the more is the increase in the cooling extent. Calculations show that during the formation of an InSb QW with lateral dimensions of less than 58 nm the emitter contact of the quantum wire can be cooled considerably — by tens of degrees.

**Manufacturing of InSb nanowire arrays in the AA matrix**

Templates for deposition of InSb nanowires were obtained by two-step electrochemical anodizing of aluminum foil (99.99%), which was previously subjected to chemical and mechanical treatment. The sequence of steps required to prepare InSb nanowires in AA matrices is shown in Fig. 5. At the first stage, the prepared polished blanks were anodized to a depth of 5 μm in a 0.5 M aqueous oxalic acid electrolyte at a constant voltage of 35 V (Fig. 5, a). The electrical parameters of the electrochemical process were determined with the help of stabilized power sources and controlled by high-precision voltmeters and registered and monitored using a GPIB controller connected to a personal computer with the HP Vee 6.01 software installed. The formed sacrificial layer of AA was selectively removed (Fig. 5, b) in a solution of a mixture of 20 g/l of CrO₃ and 35 ml/l of H₃PO₄ [17].

Repeated two-sided anodization of the aluminum blanks with the surface structured by oxide cells imprints was carried out for 270 min under the same electrochemical conditions as the first anodizing (Fig. 5, c). During this time, a 35±1 μm thick AA layer was formed. Then the obtained AA samples were treated in a 2 M sulfuric acid solution at a temperature of 50°C for 3—5 min, which resulted in the pores being cleaned and increased in diameter to 35 nm. Then a 2 μm layer of copper was sprayed in vacuum onto one side of the anodized blank with a porous AA layer (Fig. 5, d).
Fig. 5. Sequence of steps for preparing samples with InSb nanowires in AA matrices for measuring the current-voltage characteristics

a) Formation of the sacrificial AA
b) Selective dissolution of AA
c) Double-sided deep anodizing of Al
d) Copper layer coating
e) Masking of copper with a CRV layer, AA selective dissolution
f) Aluminum selective dissolution
g) Photolithography
h) Dissolution of BOL
i) Primary deposition of copper contacts
j) InSb deposition
k) Copper deposition to create a contact pad
l) Photoresist and CRV removal
After that, the copper surface was covered with a layer of chemically resistant varnish (CRV) and dried first in air for 40 min, then in a heat chamber at a temperature of 90°C for 10 min. In the next step, a selective dissolution was performed on the back of the blank: first, a layer of porous AA was dissolved in a solution based on orthophosphoric acid and chromic anhydride (Fig. 5, e), then the aluminum remaining after anodizing was dissolved for 25 min in a solution of 1.25 g/l chloride copper, 1 l of hydrochloric acid, and 158 ml/l of distilled water (Fig. 5, f).

In order to perform electrophysical measurements it was necessary to create regions with nanowires locally deposited in a certain area. Using photolithography, a pattern with 1×1 mm photoresistless windows was formed on the side of the barrier oxide layer (BOL) (Fig. 5, g). In the AA layers remaining free, the BOL was dissolved for 10 min through the photoresist mask in a 5% solution of orthophosphoric acid at 50°C (Fig. 5, h). In the pores of the prepared templates, a thin layer of copper was electrochemically deposited for 4.5 min in a 0.5 M solution of CuSO₄ at a current density of 20 mA/cm² and an electrolyte temperature of 20±2°C at a rate of about 0.3 μm/min. Thus were formed copper contacts of about 1.4 μm in thickness (Fig. 5, i).

Indium antimonide was electrochemically deposited on copper contacts in AA pores in an aqueous solution of 0.1 M SbCl₃, 0.18 M InCl₃, 0.35 M C₆H₈O₇ and 0.17 M K₃C₆H₅O₇, brought to the level of pH = 2.0 with a 20% HCl solution [11]. A three-electrode electrochemical cell with a silver chloride reference electrode was used for electrochemical deposition. A carbon electrode was used as the anode for the deposition. InSb deposition was carried out for 25 min at a constant current of 20 mA/cm² at an electrolyte temperature of 20±2°C and a pH of 2.0. The cathode potential with respect to the reference electrode (Ag/AgCl) was 1.6 V. For the indicated time, InSb completely filled the AA pores. After InSb started to leave the pores, the current density decreased, and when the voltage was reduced to 1.53 V, the process was stopped (Fig. 5, j). Additionally, copper was electrolytically deposited on the InSb surface for 20 min at a current density of 10 mA/cm² in order to ensure good ohmic contact (Fig. 5, k). Finally, the photoresist mask and the CRV layer were removed from the back of the template (Fig. 5, l), and the finished samples were rinsed in distilled water and dried in a thermostat.

Fig. 6 shows electron microscopic images of sections of nanoporous templates from AA membranes with InSb deposited nanowires, as well as of the nanowire array after selective removal of the matrix. As can be seen from the images, nanowires of about 35 nm in diameter were formed along the entire length of each pore, which corresponded to the pore size of the initial AA templates. According to the density of the pores of the AA matrix, under each contact there were about 2.568×108 nanowires connected by a copper sublayer.
Fig. 6. Electron microscopic images of cross-section of AA with InSb nanowires (a) and nanowires after dissolution of AA arrays (b).

Fig. 7 shows the results of an investigation of the composition of InSb nanowires in a porous AA template that were obtained by electron probe X-ray spectral microanalysis using a scanning electron microscope equipped with a special AN 10000 add-on from Princeton Gamma-Tech, Inc. The add-on records the characteristic X-ray radiation from all components that fall under the action of the primary electron beam of the microscope when the beam is decelerated on the surface of the prepared sample, causing the generation of such radiation. The characteristic spot size from the primary beam is $10 \times 10 \mu m$, the penetration depth of the beam is from 0.1 $\mu m$ to several micrometers.

The obtained spectrum contains lines corresponding to the elemental composition of the original matrix: the line with a maximum of 1.62 eV corresponds to aluminum in the structure of the AA membrane; 8.16 eV corresponds to the copper sublayer, on which InSb was deposited; 1.26 eV is oxygen; 1.48 eV corresponds to partially oxidized copper in the pores. The composition of nanowires in the pores of AA is characterized by the presence of several lines in the spectrum corresponding to different forms of indium (2.87, 3.52, 3.72 and 3.9 eV) with a maximum band of 3.22 V, and antimony (3.2 3.82, 4.15, and 4.6 eV) with a maximum band of 3.52 eV. In addition, chlorine (2.6 and 2.87 eV) was found in the sample, which was probably embedded in the structure of the composite from the electrolyte.

The measured data were computer processed, which allowed calculating the following percentage of indium and antimony in the composition of the deposited InSb nanowires: the mass ratio was 36.89% In and 63.11% Sb; the atomic ratio was 38.26% In and 61.74% Sb.
Fig. 7. Results of the electron-probe X-ray spectral microanalysis of InSb nanowires in AA matrices

**Measurements of the I-V characteristic of InSb nanowire arrays**

The current-voltage (I-V) characteristics of InSb nanowire arrays in the AA matrix were investigated by using the Hewlett-Packard 4061 automated system, equipped with a probe device with copper microcontacts, a current and voltage source with a digital interface (GPIB, IEEE 488), and an Agilent 34401A multimeter. The measurement modes and parameters were controlled using a personal computer connected to the devices with the Agilent Technologies USB-GPIB Card controller, which allows recording and processing of readings from recording devices in real time. Lower parts with a continuous copper layer (see Fig. 5, l) of the samples of the investigated matrices were placed on a copper-covered plate. Upper areas of the samples in the form of 1×1 mm windows were attached to a working contact by means of a spring-loaded copper probe. During the measurements, the voltage at the working contact was linearly increased/decreased at a rate of 0.1 V/s, and the reading of the current flowing between the lower and upper contacts was recorded on the monitor and multimeter.

The investigations have shown that the current was increased nonlinearly in the Cu–InSb–Cu system, when first connected, and that there were sharp current steps in the form of oscillations at the voltage of about 1 V (Fig. 8, a, curve 1), while when the voltage was decreased the current linearly dropped to zero (Fig. 8, a, curve 2). After the reversal of polarity at the contacts of the sample, the current behaved in the same way, only in negative ordinates (Fig. 8, a, curves 3, 4). This behavior of the current is probably related to the contact phenomena at the interface of InSb nanowires and Cu contacts. In an anodized matrix with electrochemically deposited nanowires, there is some amount of hydroxides and uncompensated oxygen which can interact with copper contacts [18] resulting in the formation of thin plate corrosion zones.
Cu₂O/Cu and CuO/Cu at the contacts during anodic connection [19]. Anodically formed on Cu thin Cu₂O and CuO layers have a $p$-type conductivity [20], therefore a barrier contact is formed at the boundary of $n$-type nanowires InSb, which are an $n$-type semiconductor and a copper contact coated with a copper acceptor, which begins to break through at a voltage close to 1 V. After repeated inclusions at high voltages, the current oscillations disappeared and the I-V characteristics acquired the form shown in Fig. 8, $b$: the current practically linearly increased and decreased, respectively, with increasing and decreasing voltage at the contacts in the range of ±2 V. At the same time, the current values increased insignificantly.

![Graph a) and b)](image)

Fig. 8. Current-voltage characteristics of InSb nanowires in AA matrices at various measurement stages

A further increase in the voltage led to a near-exponential increase in current, while at $U = 7$ V a sharp current step was observed (Fig. 8, $c$). This must have been caused by the run-in of InSb/Cu contact transitions, since during subsequent switchings the I-V characteristics of the structures were stable and had an exponential character in both direct and reverse switchings (Fig. 8, $d$). At the same time, the characteristic control voltage was significantly reduced, and the current values were time stable and reached 320 mA, which corresponded to a current density of 129.8 A/cm² through the cross sections of all nanowires.
In the course of measurement of current, the infrared temperature meter DT-8380 was used to record the temperature of the upper (collector) contact in the positively switched nanowire array and of the lower (emitter) contact in the negatively switched nanowire array. With a short-term direct switching at a voltage of 3 V, there was a current of about 250 mA, and the collector contact was heated up to 73°C during 150 s. With the reverse switching the temperature of the emitter contact reached 55°C. Presumably, this phenomenon is due to two nonequilibrium effects: the injection of electrons from the emitter contact into the conducting channel and the local chemical disbalance between the phases of the "emitter" and "collector" electrons. Both of the observed effects are a consequence of current flow through regions with a high electron concentration gradient. Sources of nonequilibrium are localized in \( n^+ - n^− \)-junctions between contacts and the nanowire array. The values of this gradient are determined by the concentration of electrons in the contact materials. It should be noted that the temperature effect would be much higher either in case of the greater structural perfection of nanowires, or in case if the contact was made of another material, e.g. gold.

The obtained results prove the possibility of producing InSb nanowire arrays with good electrical characteristics. They confirm the earlier theoretical and experimental conclusions about the strong influence of contact phenomena on these characteristics [1—3, 8]. In order to use nanowire arrays as thermoelectric converters efficiently, it is necessary to fine-tune the technology for stable formation of contacts with maximum tunnel transparency, thereby increasing the current density in nanowires up to \( 10^4—10^5 \) A/cm².

**Conclusion**

The study of the structures with quantum wire arrays with lateral dimensions that are smaller than the size quantization, made of a material with a high concentration and mobility of electrons, has shown that it is possible to significantly (by tens of degrees) cool one of the contacts in such structures at room temperature. The templating method of electrochemical deposition of indium antimonide into nanoporous matrices of anodic alumina that was used in this study has proved to be promising for forming InSb quantum wires with a large diameter to length aspect ratio.

The electron microscope study and the electron probe X-ray spectral microanalysis of the formed low-dimensional systems have shown that whisker nanostructures are formed in each pore on a copper sublayer, their diameters corresponding to the pore sizes, and their length being determined by the duration of deposition. It was established that the InSb binary semiconductor compound is present in the nanostructure in different forms, and the atomic content of indium and antimony is 38.26 and 61.74%, respectively.

The carried out current-voltage studies of the produced structures with 35 nm InSb nanowires in a 35 \( \mu \)m AA matrix have shown that the structures can pass an electric current of up to 129.8 A/cm² at a voltage of 3 V. The collector contact is heated up to 60—70°C. Thus, the experimental results confirm theoretical conclusions about the strong influence of contact phenomena on the electrical characteristics of quantum wire arrays that can be used to create thermoelectric devices. Cooling devices based on such quantum wire systems allow thermal controlling of electrical circuits by the applied voltage and can find wide application in engineering, in particular, in cooling integrated circuits (processors).
REFERENCES