One-dimensional Silicon-Based Crystals For Thermoelectrics

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Abstract – **The review of modern semiconductor thermoelectric materials development and methods of their thermoelectric efficiency enhancement has been conducted. Prospects of practical use of silicon and $Si_{1-x}Ge_x$ solid solutions whiskers and nanowires in thermoelectrics have been estimated.**

Keywords – **thermoelectric figure of merit, $Si_{1-x}Ge_x$ solid solutions, nanowire, whisker, thermal conductivity, Seebeck coefficient.**

I. INTRODUCTION

The performance of thermoelectric material depends on its Seebeck coefficient S, electrical conductivity σ and thermal conductivity κ [1]:

$$ZT = \frac{S^2 \sigma T}{\kappa}, \qquad (1)$$

where Z is thermoelectric figure of merit and T stands for temperature. Today's requirements to thermoelectric materials are their figure of merit to be at least $Z = 0{,}01K^{-1}$ at room temperature, i.e. $ZT = 3$ [1]. However this limit has not been yet achieved for any of the known mass produced semiconductor thermoelectrics. Such a situation demands a comprehensive search of new cheap and highly efficient thermoelectric materials for mass production and monolithic integration with silicon microelectronic technologies.

II. MODERN STATE OF THERMOELECTRIC MATERIALS DEVELOPMENT

The best bulk thermoelectric materials in the temperature range of up to 600K are still considered to be bismuth tellurides [1]. But tellurium is a rare, toxic and very volatile element.

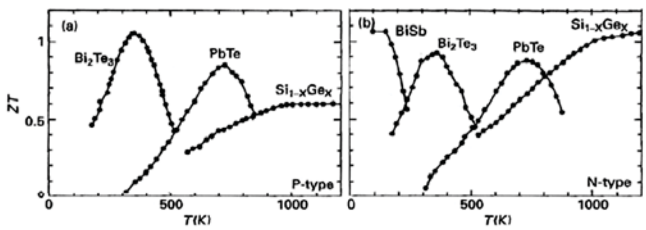

Fig.1. Thermoelectric efficiency of main modern thermoelectric materials [2]

Bulk silicon is known to be not a promising material from the thermoelectrical point of view. Despite the high value of Seebeck coefficient its ZT is not higher than 0,01 [2]. Meanwhile the $Si_{1-x}Ge_x$ solid solutions with prevalent content of silicon are the best candidates for temperatures above 1000°C (Fig. 1). The best known bulk $Si_{1-x}Ge_x$ at these temperaures has ZT = 0,65 for p-type crystals [3] and ZT = 0,93 for n-$Si_{1-x}Ge_x$ [4] and is used in radioisotope thermoelectric generators (RTG) for space missions. Moreover $Si_{1-x}Ge_x$ solid solutions possess a high chemical and thermal stability, besides they are ecologically safe.

Recent investigations of semiconductor nanosized crystals have proven, that thermoelectric efficiency may be even sufficiently higher than ZT = 3. In fact, if to take into account, that the mean free path of phonons, which are the main heat carriers in semiconductors (over 60% of silicon thermal conductivity [5]) is equal to few hundreds nanometers, while for electrons (holes) this value is not higher than 10 nm, in nanoscaled semiconductors the phonon transport is sufficiently suppressed. This means that the crystal thermal conductivity would be much lower while its Seebeck coefficient and electrical conductivity will remain unchanged.

For example, the thermal conductivity of nanostructured bulk n-$Si_{1-x}Ge_x$ is two times lower in comparison with convenient n-$Si_{1-x}Ge_x$ for RTGs, resulting in ZT arise up to 1,3 at 1000°C [4]. In nanostructured p-$Si_{1-x}Ge_x$ thermoelectric efficiency arises to ZT = 0,95 [3]. It has been shown that 50 nm thick silicon nanowires possess a thermoelectric performance 100 times higher than a bulk material [6].

III. OUR RESULTS

We have found that decrease in $Si_{1-x}Ge_x$ whiskers' diameter leads not only to the decrease of their thermal conductivity, but also increases the Seebeck coefficient (Fig. 2). This gives us additional opportunities to enhance the thermoelectric efficiency of $Si_{1-x}Ge_x$ wires and is urgent for thermal sensors applications.

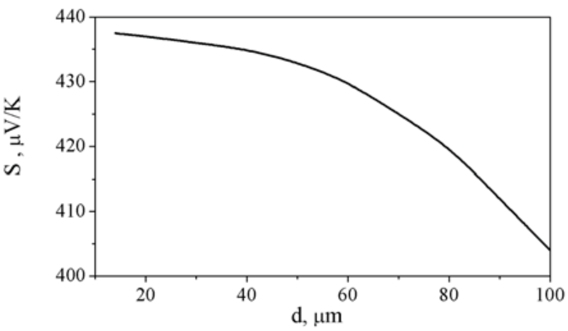

Fig. 2. Size dependence of the Seebeck coefficient of $Si_{1-x}Ge_x$ solid solutions whiskers

As it has been shown earlier, the applying of compressive thermal deformation to $Si_{1-x}Ge_x$ whiskers allows to stabilize the value of Seebeck coefficient in a wide range of cryogenic temperatures (Fig. 3, a) [7]. By optimizing the doping of $Si_{1-x}Ge_x$ whiskers with boron and gold one can achieve a highly stabilized Seebeck coefficient of 750 μV/K in the temperature

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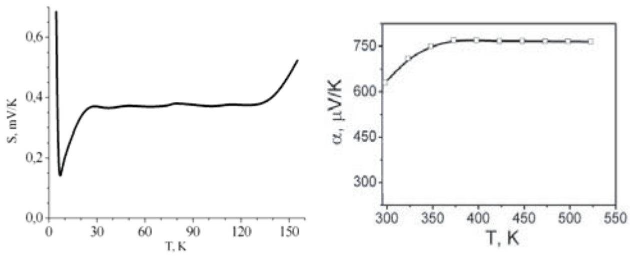
range of 350-525K (Fig. 3, b). These observations have been used for creation of thermal sensors for cryogenic and elevated temperatures with thermoelectric operation principles [7, 8].

We have developed a methodology for Si and $Si_{1-x}Ge_x$ nanowires synthesis using the chemical vapor deposition on a silicon substrate covered with ultrathin gold film. The gold was used as a catalyst for nanowire growth by the VLS-mechanism [9]. The substrate was heated to the "Si-metal" eutectics temperature in order to form the silicon-gold alloy droplets, which were the seeds for silicon wires growth according to the VLS-mechanism. At the next stage formation of Si nanowires starts. After passing the mixture of $SiCl_4$ and H_2 gases above the <100> silicon substrate at the temperature of 600°C the ensemble of Si nanowires 3 to 10 nm thick arises at the substrate (Fig. 4). The grown nanowires have been investigated with an atomic-force microscope.



a) b)

Fig. 3. Temperature dependencies of the Seebeck coefficient for p-$Si_{1-x}Ge_x$ whiskers: (a) at cryogenic temperatures and compressive deformation; (b) at elevated temperatures

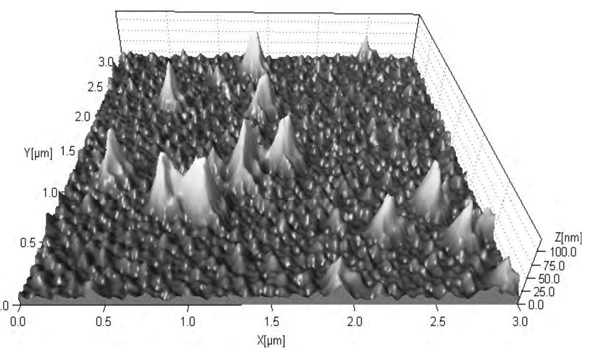


Fig. 4. Formation of Si nanowires on the silicon substrate covered with 9-nm thick gold film at the temperature of 600°C (growth time - 10 min) [9]

The formation of contacts to nanosized semiconductors is the main problem in investigation of thermoelectric properties of Si and $Si_{1-x}Ge_x$ nanowires in a wide range of temperatures, magnetic fields and deformations. Besides, the thermal conductivity measurements are still a very hard task, but are necessary for estimating the thermoelectric efficiency of Si or $Si_{1-x}Ge_x$ whiskers and nanowires for thermoelectric power generators or thermal sensors. We believe that a wide and comprehensive cooperation with scientists and specialists, who work in the field of previously named problems, would be a great step towards the mass manufacturing and integration of nanoscaled thermoelectric devices.

IV. Conclusions

The problem of achieving the Ioffe criteria of ZT = 3 has not been solved yet. That is why the creation of high-perfomance thermoelectric devices for space missions and on-land applications, e.g. waste heat utilization, is sufficiently limited. These circumstances demand the development and investigation of new micro- and nanostructures with suppressed phonon transport, in particular based on the $Si_{1-x}Ge_x$ solid solutions, which has been proven to be a promising thermoelectric material for low and high temperature applications. An urgent task is also to create a highly sensitive thermal radiation sensors with high values of Seebeck coefficient on the basis of $Si_{1-x}Ge_x$ solid solutions whiskers and nanowires.

References

[1] A.A. Yepremyan, V.M. Arutyunyan, A.I. Vaganyan, "Figure of merit of modern semiconductor thermoelectric materials", *International scientific journal «Alternative energetic and ecology »*, №5(25), pp.7-18, 2005 (in Russian).

[2] J. Tervo, A. Manninen, R. Ilola, H. Hänninen, "State-of-the-art of Thermoelectric Materials: Processing, Properties and Applications" in *VTT Working Papers 124*, VTT Technical Research Centre of Finland, Finland: Julkaisija – Utgivare – Publisher, 2009.- 29p.

[3] G. Joshi *et al.*, "Enhanced Thermoelectric Figure-of-Merit in Nanostructured p-type Silicon Germanium Bulk Alloys", *Nano Lett.*, Vol.8, No.12, pp.4670-4674, 2008.

[4] X. W. Wang *et al.*, "Enhanced thermoelectric figure of merit in nanostructured n-type silicon germanium bulk alloy", *Appl. Phys. Let.*, V.93, pp.193121-1–193121-3, 2008.

[5] C.J. Glassbrenner, G.A. Slack, "Thermal conductivity of silicon and germanium from 3°K to melting point", *Phys.Rev.A.*, Vol.134, №4A, pp.A1058–A1069, 1964.

[6] A. Hochbaum *et al.*, "Enhanced Thermoelectric Performance of Rough Silicon Nanowires", *Nature Letters*, Vol. 451, pp. 163–167, 2008.

[7] A. Druzhinin, I. Ostrovskii, Iu. Kogut, "Thermoelectric properties of Si-Ge whiskers", *Materials Science in Semiconductor Processing*, № 9, pp. 853-857, 2006.

[8] A.A. Druzhinin, A.P. Dolgolenko, I.P. Ostrovskii, Yu.M. Khoverko, Iu.R. Kogut, "Thermoelectric sensors based on Si-Ge whiskers", *J.Thermoelectricity*, №4, pp.82-85, 2009.

[9] A.A. Druzhinin, I.P. Ostrovskii, Yu.M. Khoverko, S.I. Nichkalo, "Growth of nanoscaled silicon chrystals by vapor-phase epitaxy", *Visnyk of Lviv National Polytechnic University: "Electronics"*, №646, pp. 11–16, 2009 (in Ukrainian).