Digest Journal of Nanomaterials and Biostructures Vol. 16, No. 3, July - September 2021, p. 907 -913

Influence of environment on thermoelectric properties of n-type silicon-germanium alloy

K. Fatima[a,*], X. Song[b], A. Maryam[a], M. N. Rasheed[c], F. Iqbal[a], E. V. Monakhov[b], M. Asghar[d]
[a]*Institute of Physics, The Islamia University of Bahawalpur, 63100, Pakistan*
[b]*Department of Physics, Centre for Material Science and Nanotechnology, University of Oslo, P. O. Box 1048, Blindern, Oslo N-0316, Norway*
[c]*Department of Physics, University of Education, Lahore, 54770, Pakistan*
[d]*Department of Physics, Khwaja Fareed University of Engineering and Information Technology, Rahim Yar Khan, 64200, Pakistan*

Environmental stability of material properties is an important factor for its utilization for electronic devices. Gases in air such as oxygen can react chemically with material and cause degradation of its properties. This work reports on effect of air on thermoelectric properties of nanostructured n-type silicon-germanium (SiGe) alloy: a well-known high temperature thermoelectric material with superior properties. Phosphorous doped SiGe alloy was synthesized via mechanical alloying followed by hot-press and characterized by powder X-ray diffraction, scanning electron microscopy, and thermoelectric measurements. The average grain size of alloyed powder was in the range 50 - 400 nm. The reduction in grain size caused decrease in thermal conductivity of SiGe alloy (2.044 W/mK at ~ 900K). To study the effect of air on the transport properties of alloy measurements were carried out in presence of air and in inert (argon) atmosphere. Interesting results have been obtained and discussed with the available literature.

(Received May 5, 2021; Accepted July 30, 2021)

Keywords: Silicon-germanium alloys, Thermoelectric properties, Environment, Mechanical alloying, Nanostructures

1. Introduction

Thermoelectrics belong to a class of materials that can convert waste heat into electrical energy by thermoelectric effect. Some novel applications wherein thermoelectric materials can be utilized are space and automotive power generation, bio-thermal batteries, optoelectronic devices and solid-state thermoelectric cooling and refrigeration. They have become focus of revived research because of theoretic predictions [1,2] and experimental confirmations of nanostructured materials with improved thermoelectric properties[3-10].. Both n-type and p-type thermoelectric materials can be obtained with suitable doping. The thermoelectric efficiency of these materials is characterized by dimensionless parameter, figure of merit $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity [11,12] A given material has better thermoelectric performance for higher ZT. Depending upon nature of doping (n-type or p-type), majority of materials have different ZT values for same temperature range[13].

For high conversion efficiency, materials with high electrical conductivity, low thermal conductivity and high Seebeck coefficient are required. Therefore, the suitable materials for thermoelectrics are degenerate semiconductors with 'S' in range 150-250 μV/K[14]. Most of semiconductor materials do not have suitable values of 'σ' and 'S' simultaneously, which makes availability of good thermoelectric material difficult. Modification of band structures and controlling carrier concentration of materials has been useful in improving the electron transport properties. A thermoelectric material works well for a specific temperature range. There are various thermoelectric materials, operating at different temperature ranges, including bismuth

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[*] Corresponding author: fatima_kaneez34@yahoo.com

telluride, lead telluride, SiGe alloys, Te-Ag-Ge-Sb, etc.[13]. Research is also being done on some other classes of materials like skutterdites, chevrel phases, clathrates, semi-Heusler phases, etc. to acquire a nanostructured form[13].

Silicon-germanium (SiGe) alloys are extensively used in transistors[15], solar cells, photo-detectors and have studied for thermoelectric applications[16-19]. Unlike conventional thermo-electric materials (e.g. Bi_2Te_3 or PbTe), they are non-toxic and environment friendly. From application perspective, SiGe alloys exhibit low mismatch in coefficient of thermal expansion, high-temperature stability, high mechanical strength, and scalability with the silicon technology [20-22].

For high-temperature thermoelectric applications different materials have been studied such as rhodium oxides, layered cobalt[23], boron-rich cluster compounds [24-26], SiGe alloys etc. Among these materials, SiGe alloys are prominent and very promising thermoelectric materials. Particularly, $Si_{80}Ge_{20}$ composition owns best thermoelectric properties for power generation [27-29,11,30] . Suitable doping and nanostructuring can further enhance the thermoelectric properties of alloy. Using nano-structuration approach the thermal conductivity of bulk polycrystalline nanomaterial with large number of grain boundaries can be lowered significantly[31]. Besides good thermal and electronic transport properties, stability of these thermoelectric properties in working temperature range is an important key factor to device thermoelectric coolers or generators.

It is widely known that some materials, when exposed to air, can get oxidized or react with its constituents. Consequently, this exposure can cause degradation, and leads to decrease in their transport properties. Therefore, it is important to keep in mind the environmental effect on properties of the material for its use in electronic devices. The purpose of this work is to study the influence of environment on the thermoelectric properties of nano-structured n-type silicon-germanium alloy, prepared by mechanical alloying and hot-press technique. For that purpose measurements were carried out both in air and Inert (Argon) atmosphere. The scheme of the manuscript is: Experimental Details, Results and Discussion and Conclusions.

2. Experimental Details

2.1. Synthesis

The nanopowder of n-type SiGe was prepared by mechanical alloying of Si, Ge and P. Powder mixture of Si (99.99% pure), Ge (99.99% pure,) was taken in stoichiometric ratio 80:20 and red phosphorous lumps (99.999% pure) were taken for doping with 2 at %. The powder mixture is then loaded in tungsten carbide bowl. The bowl was sealed in Ar filled glove bag. Mixture was then milled in planetary ballmill for 2hrs with 5min milling and 3min break at speed of 400 rpm. Milled nanopowder was loaded into graphite die (inner diameter:13.5mm) inside the glove bag and heated with heating rate of 43°C/min up to 875°C under uniaxial pressure of ~ 50MPa. The soak time was 5min.

2.2. Characterization

The structural characterization of milled powder and hotpressed sample was performed by X-ray diffraction (XRD) and by scanning electron microscopy (SEM) /energy dispersive spectroscopy(EDS) using SEM(JEOL JSM-IT300). Electrical resistivity (ρ) and Seebeck coefficient (S) were simultaneously measured using ProboStat setup one pellet under argon atmosphere and second pellet in air. Thermal conductivity (κ) was measured using NETZSCH, LFA 457 MicroFlash setup.

3. Results and Discussion

XRD patterns of ballmilled powder and hotpressed pallet are shown in figure 1. XRD spectrum of as-prepared ballmilled powder of SiGe shows that ballmilling was insufficient for complete alloying because Ge was not completely dissolved in Si array which was accomplished by hot pressing. Average crystallite size D for ballmilled and hotpressed SiGe was calculated using Scherrer`s formula[32,33]:

$$D = 0.9\lambda/\beta\cos\theta$$

where β is full width at half maximum FWHM of diffraction peaks.

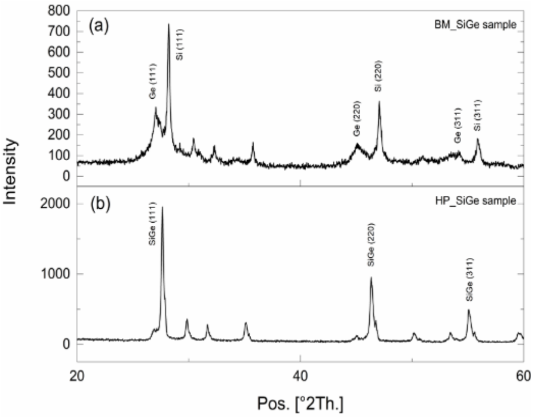

Fig. 1. XRD patterns of (a) ballmilled SiGe powder and (b) hotpressed SiGe pellet.

The average crystallite size for ballmilled powder was ∼16nm. After hotpress average crystallite size increased to ∼ 24 nm which is due to lower micro strain and dislocation density. The stress produced during ballmilling process was relaxed due to hotpress at high temperature, which increased the crystallite size of the SiGe alloy[19].

SEM images of ballmilled SiGe powder and hotpressed pellet are shown in Fig. 2. It can be seen that the grain size of most of the grains of SiGe ballmilled powder is ranging from 50 to 400nm. These grains are in actual agglomerates of several small crystallites. Small grains with different crystallite orientations are thought to be more effective in promoting phonon scattering in nanostructured materials.

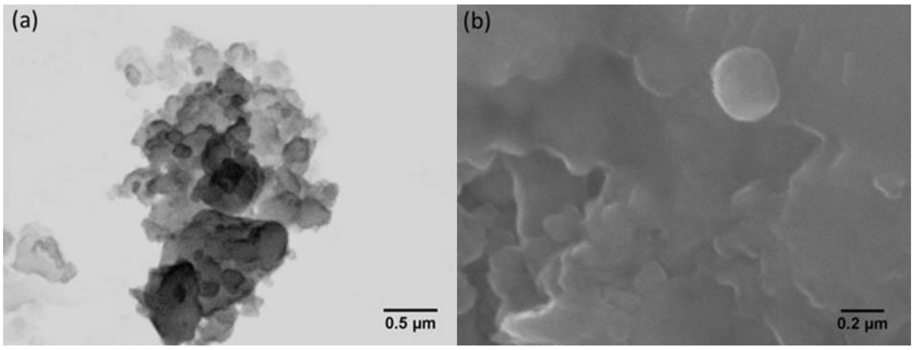

Fig. 2. SEM images of (a) ballmilled SiGe powder (b) hotpressed SiGe pellet.

The increase in phonon scattering due to small grains results in reduced thermal conductivity. The key advantage of using nanostructuring to enhance the thermoelectric performance of SiGe alloy is associated with huge difference in mean free path of phonon (2-300 nm) and electron (about 5 nm) in highly doped SiGe alloy at room temperature[31,19]. Therefore, thermal conductivity can be reduced without significant change in electrical conductivity of nano-SiGe alloy. The SEM image of hotpressed SiGe pellet Fig. 2 (b) shows that but sample is porous and there is no significant increase in grain size due to hot-press.

Temperature dependencies of thermoelectric properties of nanostructured n-type SiGe alloy are shown in Fig.3. The electrical conductivity σ of SiGe sample shows metallic behavior, decreasing σ with increasing temperature, due to high doping concentration. The data of NASA radioisotopic thermoelectric generator RTG sample having typical grain size of 1-10 μm is added as a reference [11]. The electrical conductivity of SiGe sample is lower than that of the reference sample, and changes from 3.96×10^4 S/m to 2.18×10^4 S/m for temperature range 300-900K. The decrease in electrical conductivity is mainly due to increase in density of grain boundaries. Also nano-grained porous material has low electrical conductivity due to increased charge carrier scattering from scattering sites [34].

Fig.3 (b) shows dependency of Seebeck coefficient on temperature. It can be seen that Seebeck coefficient of hotpressed and reference sample shows similar behavior up to ~ 650K and increases with temperature. For temperature range of 650-750K there is slight decrease in Seebeck coefficient from199 μV/K to 180μV/K which and then it increases again up to ~203μV/K at 900K, which is a different behavior from that of a typical n-type SiGe alloy and could be result of unintentional impurity addition from the vial or formation of secondary phase as indicated by extra unidentified peaks in XRD patterns. The negative sign of Seebeck coefficient shows that the conduction is caused by electrons.

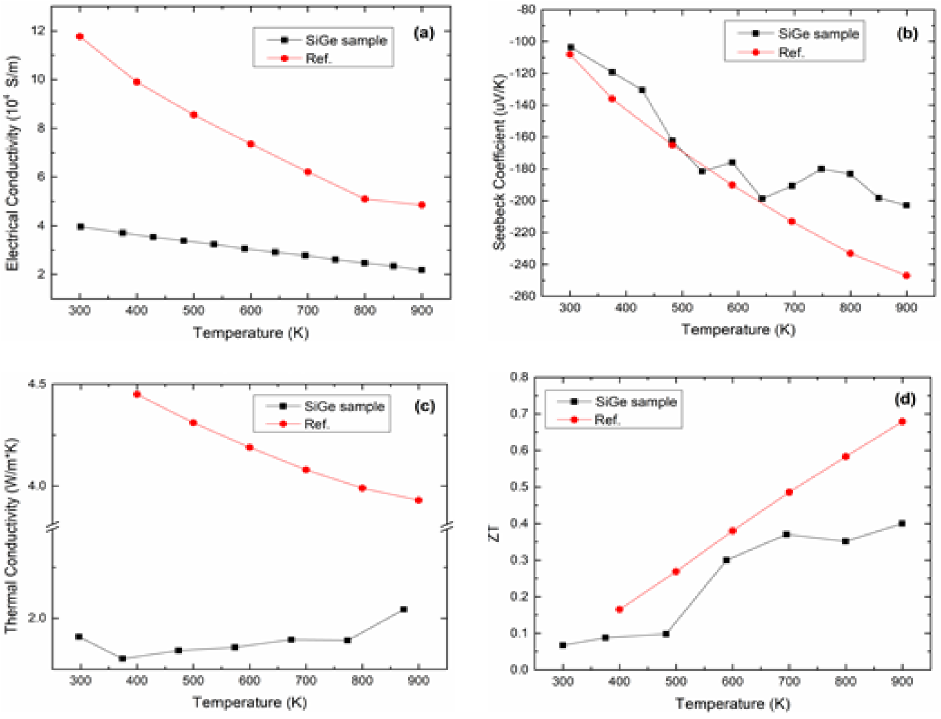

Fig. 3. Thermoelectric properties of n-type SiGe alloy and reference sample: (a) electrical conductivity, (b) Seebeck coefficient, (c) thermal conductivity and (d) Figure of merit ZT.

Variation in thermal conductivity of hotpressed sample with temperature is shown in Fig.3 (c). There is large reduction in thermal conductivity of nanostructured SiGe alloy as compared to reference sample. At room temperature 300K thermal conductivity of hotpressed sample is 1.91 W/mK. Using Wiedemann-Franz law ($k_e = L_o \sigma T$), electronic contribution to thermal conductivity can be estimated, with Lorenz k_e number L_o equal to 2.14×10^{-8} W Ω/K^2(for SiGe system at 300K). For SiGe sample estimated = 0.25 W/mK at room temperature with $\sigma = 3.96 \times 10^4$ S/m, whereas a typical nanostructured SiGe sample has $k_e = 0.55$ W/mK at room temperature for $\sigma = 0.85 \times 10^5$ S/m [11]. The lattice thermal conductivity k_L can be found by subtracting electronic contribution k_e from total thermal conductivity 'κ'. For hot-pressed sample calculated $k_L = 1.66$ W/ mK at 300K, 43% of that for a typical n-type SiGe sample ($k_L \sim 3.8$ W/ mK). The reduction in k_L is attributed to enhanced phonon scattering from grain boundaries.

Dimensionless figure of merit *ZT* as a function of temperature is shown in Fig.3 (d). Despite of large reduction in thermal conductivity there is no enhancement in *ZT* due to low electrical conductivity and Seebeck coefficient. The value of *ZT* at 900K ~ 0.4 which is less than that of reference sample (*ZT* ~ 0.67 at 900K). Due to nano-porosity and low density there is significant drop in electrical conductivity of the sample which causes low figure of merit *ZT*.

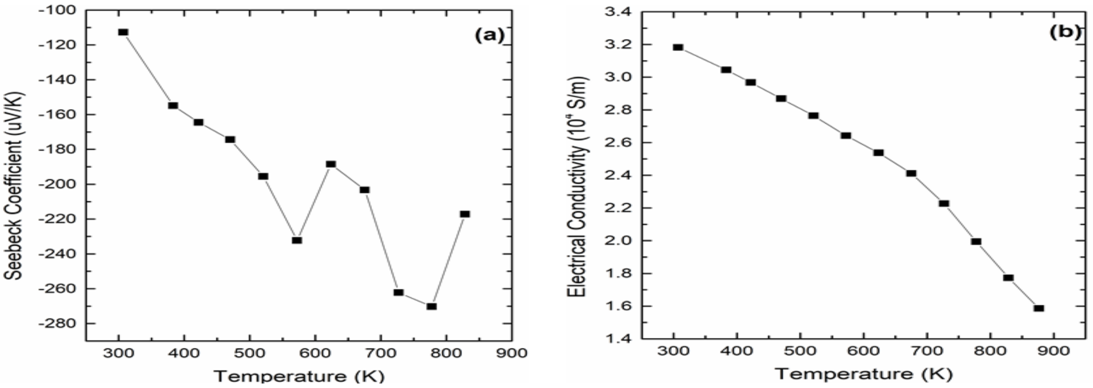

Fig. 4. Transport properties of hot-pressed SiGe alloy in presence of air (a) Seebeck coefficient (b) electrical conductivity.

For environmental stability investigation, transport properties of hotpressed sample were measured in presence of air. Fig. 4 shows temperature dependent Seebeck coefficient and electrical conductivity measured in air. It can be seen that the Seebeck coefficient has almost same trend as for measurements taken in argon environment. Its value is higher in air as compared to that in argon environment and also higher than that of reference sample except for temperature range from 600K to 700K. The increase in value of Seebeck coefficient in air could be result of sublimation of dopant.

Fig. 4(b) shows variation in electrical conductivity of hotpressed SiGe sample in air with respect to temperature. Its value varies from ~ 3.18×10^4 S/m to 1.59×10^4 S/m for temperature range 300K - 875K. In presence of air there is small decrease in value of electrical conductivity caused by dopant sublimation and formation of silicon oxide layer on surface of the sample as indicated by increase in Seebeck coefficient. As there is no significant degradation of transport properties of SiGe alloy in air, the overall thermoelectric performance of SiGe alloy will remain unchanged and it shows that the nano-structured bulk SiGe alloy is stable under air.

4. Conclusions

The effect of environment on thermoelectric properties of nanostructured n-type silicon-germanium alloy synthesized using mechanical alloying and hot-press was studied. The structural characterizations revealed that mechanical alloying reduced the grain size of alloyed SiGe powder in the range 50 - 400nm. The reduction in grain size resulted in significant decrease in thermal conductivity (2.044 W/mK at ~ 900K). The effect of environment on transport properties was studied by carrying out measurement in air and inert (argon) atmosphere. The calculated figure of merit *ZT* was 0.4 at 900K for measurements taken under argon atmosphere. High charge carrier scattering in porous nanograind sample caused low electrical conductivity, which results in low figure of merit. The measurements taken in presence of air showed increase in Seebeck coefficient and small decrease in electrical conductivity possibly caused by dopant sublimation. Overall no significant degradation in properties of SiGe alloy was observed, which indicated that synthesized SiGe alloy was stable in air.

Acknowledgements

The financial support from IRSIP HEC Pakistan for working at University of Oslo, Norway is highly acknowledged.

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