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Review

The Impact of Nanostructured Silicon and Hybrid Materials on the Thermoelectric Performance of Thermoelectric Devices: Review

Rehab Ramadan [1] and Raúl J. Martín-Palma [2,3,*]

1 Department of Physics, Faculty of Science, Minia University, Minia 61519, Egypt; rehabramadan@mu.edu.eg
2 Departamento de Física Aplicada, Universidad Autónoma de Madrid, 28049 Madrid, Spain
3 Instituto de Ciencia de Materiales Nicolás Cabrera, Universidad Autónoma de Madrid, 28049 Madrid, Spain
* Correspondence: rauljose.martin@uam.es

Abstract: Nanostructured materials remarkably improve the overall properties of thermoelectric devices, mainly due to the increase in the surface-to-volume ratio. This behavior is attributed to an increased number of scattered phonons at the interfaces and boundaries of the nanostructures. Among many other materials, nanostructured Si was used to expand the power generation compared to bulk crystalline Si, which leads to a reduction in thermal conductivity. However, the use of nanostructured Si leads to a reduction in the electrical conductivity due to the formation of low dimensional features in the heavily doped Si regions. Accordingly, the fabrication of hybrid nanostructures based on nanostructured Si and other different nanostructured materials constitutes another strategy to combine a reduction in the thermal conductivity while keeping the good electrical conduction properties. This review deals with the properties of Si-based thermoelectric devices modified by different nanostructures and hybrid nanostructured materials.

Keywords: thermoelectric devices; phonon scattering; nanostructured Si; hybrid nanostructures

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Citation: Ramadan, R.; Martín-Palma, R.J. The Impact of Nanostructured Silicon and Hybrid Materials on the Thermoelectric Performance of Thermoelectric Devices: Review. *Energies* **2022**, *15*, 5363. https://doi.org/10.3390/en15155363

Academic Editor: Dmitri A. Bulushev

Received: 23 June 2022
Accepted: 22 July 2022
Published: 24 July 2022

1. Introduction

Thermoelectric devices allow power generation from waste heat. The thermoelectric effect is the direct conversion of a temperature difference to electricity or vice versa [1]. Among many other materials, bismuth telluride alloys are considered the most efficient thermoelectric materials [2]. However, these alloys are costly due to the enormous amount of expensive telluride material the alloys have, in addition to their toxicity. Crystalline Si was used to expand the power generation via the thermoelectric effect. Si is a non-toxic, inexpensive, and earth-abundant material. Various thermoelectric alloys based on Si were designed, including Si-Ge and Mg_2Si alloys [3–6]. Although bulk Si has high electrical conductivity, it has a high thermal conductivity, which yields a low figure of merit (ZT) for thermoelectric devices [7].

Therefore, researchers focused on modifying methods to improve the performance of Si-based thermoelectric devices by reducing their thermal conductivity. The growth of nanostructured Si is one of the sufficient approaches to minimizing the thermal conductivity of bulk Si. Porous silicon (PSi), Si nanoparticles (SiNPs) or Si nanowires (SiNWs) are nanostructured instances suitable for enhancing the Seebeck coefficient of Si-based thermoelectric devices by reducing the thermal conductivity [8–10]. However, texturing the surface of Si wafers leads to a reduction in the electrical conductivity [11,12]. This behavior is attributed to the performance of the texturing in the heavily doped regions of Si substrates.

For that, the combination between two thermoelectric materials or two thermoelectric nanostructures is another way to combine the good electrical conductivity and the low thermal conductivity for the improvement of the Seebeck coefficient. Numerous strategies were developed by researchers based on hybrid materials or hybrid nanostructures. For instance, PEDOT:PSS thin films capped with SiNPs at different concentrations of SiNPs [13], hybrid graphene-mesoporous silicon nanocomposite [14], Phenylacetylene capped with SiNPs [15], TiO_2 nanostructures grown inside the PSi layer [16], atomic layer deposited (ALD) PbTe/PbSe nanolaminate structures deposited inside the PSi layer [17] and silicon-germanium nanocomposite alloys [4,6].

The present review article outlines a comparison between the thermoelectric properties of various reported thermoelectric devices based on Si, porous silicon and hybrid nanostructures of Si and other thermoelectric materials.

2. Characteristic Features of Thermoelectric Devices

The thermoelectric effect takes place when a thermoelectric material is subjected to a temperature difference. Accordingly, electrons in the material start to follow from the hot side to the cold one, creating an electric current. The amount of generated electrical power depends on the transport properties of the carriers in the thermoelectric material. The conversion efficiency of thermal energy to electricity is defined by the figure of merit (*ZT*). The figure of merit is related to the electrical and thermal properties of a material through the following relation [7]:

$$ZT = \frac{S^2}{k}\sigma T \quad (1)$$

$$S = \frac{V}{\Delta T} \quad (2)$$

where S is the seebeck coefficient, which quantifies the amount of voltage (V) generated across a given temperature gradient (ΔT), σ is the electrical conductivity, k is the thermal conductivity and T is the absolute temperature.

3. Si-Based Thermoelectric Materials

Non-toxicity, high industrial compatibility, low price compared with other materials, and the chemical and mechanical stability of silicon make this material a good candidate for thermoelectric applications. In addition, it shows good electrical conductivity which depends on the doping level. However, monocrystalline silicon has a high thermal conductivity of ~150 W m^{-1} K^{-1} at 300 K, which hinders the high conversion efficiency of thermoelectric devices. Thermoelectric properties of silicon were previously reported by researchers. For instance, Bux et al. measured the thermoelectric properties of bulk silicon with a Seebeck coefficient of 0.008 at 300 K [9]. This reduction in the Seebeck coefficient for silicon-based thermoelectric devices is attributed to the increase in the thermal conductivity of silicon [9,18]. Many strategies were developed to improve the thermoelectric properties of silicon material. One way is by texturing or etching the surface of the silicon substrate to increase phonon scattering in the interfaces and on the boundaries of the walls of nanostructured silicon [7,9,18]. Another perspective is by combining silicon nanostructures with another effective thermoelectric material, such as Ge and Mg [3–6,13].

4. Thermoelectric Devices Modified by Nanostructured Silicon

Nanostructured silicon can take many different forms, including porous silicon (PSi), silicon nanoparticles (SiNPs) or silicon nanowires (SiNWs). The morphology of nanostructured Si depends on the fabrication method and the fabrication parameters [19]. The increase in the surface-to-volume ratio of nanostructured Si greatly improves the thermoelectric performance due to an increased number of scattered phonons at the interfaces and boundaries of the nanowires or nanoparticles of Si. The number of surface defects is also increased. Furthermore, the reduction in the dimensions of Si nanostructures leads to increased surface roughness, resulting in a reduction in thermal conductivity. Figure 1 shows the comparison between *ZT* values of heavily doped single crystal Si and nanostructured n-type Si studied by Sabah K. Bux et al. in the form of pellets approximately 12.7 mm in diameter and 15 mm long [9]. An enhancement in *ZT* values by 3.5-fold was achieved due to texturing the Si material. This behavior is attributed to the increase in the density of the interfaces, in addition to increasing boundary defects around the nanostructures, increasing the mean free path for phonon scattering.

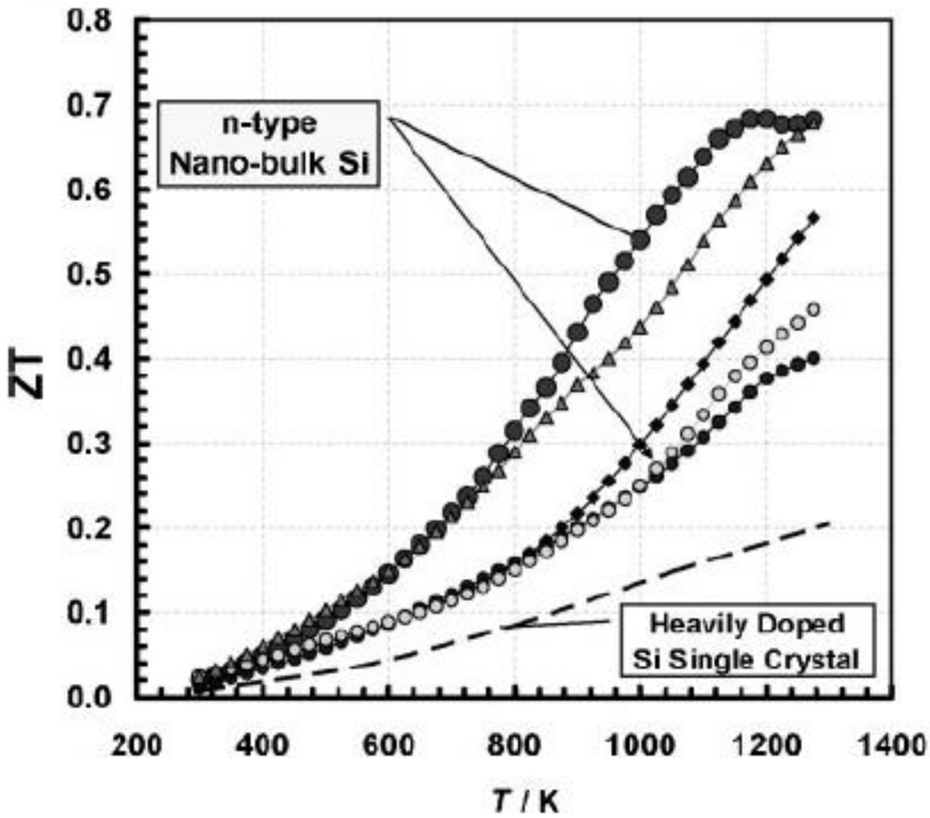
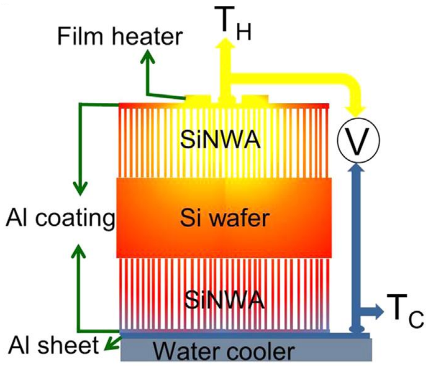
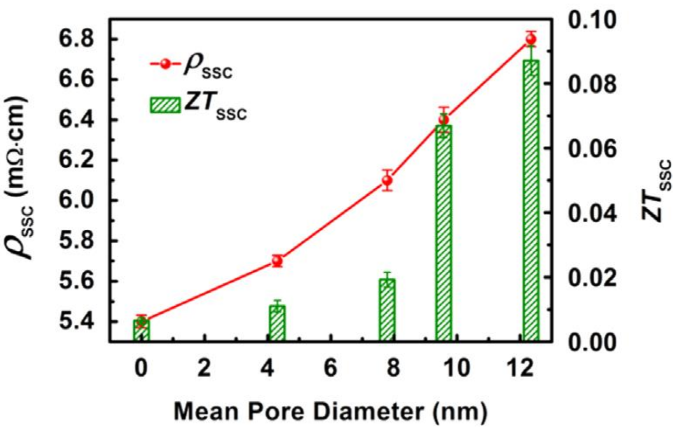


Figure 1. Comparison between *ZT* values for heavily doped single-crystalline Si (dashed lines) and nanostructured n-type silicon (n-type Nano-bulk Si) (Circles) as a function of temperature. Reprint with permission [5318650473494]; Copyright Year 2022, John Wiley and Sons Publisher [9].

From another perspective, nanostructured silicon in different forms has been studied as an effective thermoelectric material by many researchers in a wide range of different porosities [7,10,18]. For instance, Ting Zhang et al. presented a remarkable enhancement in the *ZT* values due to texturing the front and back sides of Si substrate performing Si nanowire arrays (SiNWAs). The structure of the modified device is SiNWAs/Si/SNWAs sandwich structured composites (SSC) [18]. *ZT* values were remarkably increased from 0.006 for bulk Si devices to 0.493 for the modified SSC at room temperature. Figure 2a shows a schematic representation of the fabricated SSC and the measuring unit. Furthermore, Figure 2b shows the effect of mean pore diameter (MPD) on the electrical resistivity (ρssc) and the *ZT* values of the performed SSC thermoelectric devices. The increase in the pore diameter leads to an increase in the electrical resistivity due to performing the nanopores in the heavily doped Si regions. Moreover, the thermoelectric properties were found to improve with increasing the pore diameter due to the increase in the surface-to-volume ratio, which leads to increasing the mean free path for phonon scattering.



(a)



(b)

Figure 2. (**a**). Schematic representation of the modified structure of thermoelectric devices based on SiNWs. (**b**) Chart representing the effect of mean pore diameter on the electrical resistivity and *ZT* values of the fabricated thermoelectric devices. Reprint with permission [5283611435296]; Copyright Year 2022, Elsevier Publisher [18].

5. Thermoelectric Materials Modified by Hybrid Nanocomposites

Nanostructured Si remarkably contributes to reducing the thermal conductivity of thermoelectric devices. However, etching the surface of Si substrate occurs in the heavily doped Si regions. As a result, the electrical conductivity of nanostructured Si remarkably decreases with the increase in porosity; likewise, fast oxidation of the porous silicon layer in ambient air. Accordingly, hybrid silicon nanostructures with another effective thermoelectric material dramatically reduced the thermal conductivity of nanostructured Si and maintained adequate electrical conductivity due to the other thermoelectric material, in addition to preventing nanostructured Si from oxidation due to the growth of the other thermoelectric material into the nanostructured Si layer.

Figure 3 shows a schematic representation of some of the possible hybrid nanostructures suitable for enhancing the thermoelectric properties of thermoelectric devices. Each material has a valuable effect in improving the thermoelectric properties of the implemented thermoelectric devices. For instance, Nitin Saxena et al. reported the combination of the organic PEDOT:PSS material with SiNPs. This combination leads to improving the *ZT* value of the fabricated thermoelectric device from 5.3×10^{-3} without SiNPs to 8.0×10^{-3} at 0.5 wt% SiNPs at 300 K [13]. Furthermore, Gitanjali Kolhatkar et al. observed the stability and reduction in the thermal conductivity due to the combination of graphene and nanostructured mesoporous Si to 13 WmK^{-1} [14]. From another perspective, the Seebeck coefficient of the atomic layer-deposited PbTe/PbSe nanolaminate structures deposited inside PSi templates significantly increased in both vertical and horizontal directions compared with the growth of the same nanolaminate on planar Si (143 μV/K), 370.556 μV/K in horizontal directions and 78,670 μV/K in vertical directions at 300 K [17].

Figure 4 shows the enhancement in the Seebeck coefficient of ALD PbTe/PbSe (10/10 nm) nanolaminates deposited on the PSi substrate with two different porosities compared with the values of the same layer and deposited on the planar Si substrate as a function of temperature [17]. From the recorded data, the Seebeck coefficient of PbTe/PbSe (10/10 nm) nanolaminates deposited on PSi substrate is about four times higher than that of the planar sample. This enhancement is attributed to the presence of the regular arrays of nanopores. These pores lead to the increase in the surface-to-volume ratio for Si and for the grown nanolaminates, which results in a reduction in thermal conductivity. Moreover, the increase in porosity leads to an increase in the number of defects and surface roughness. So, the Seebeck coefficient increases, particularly at low temperatures.

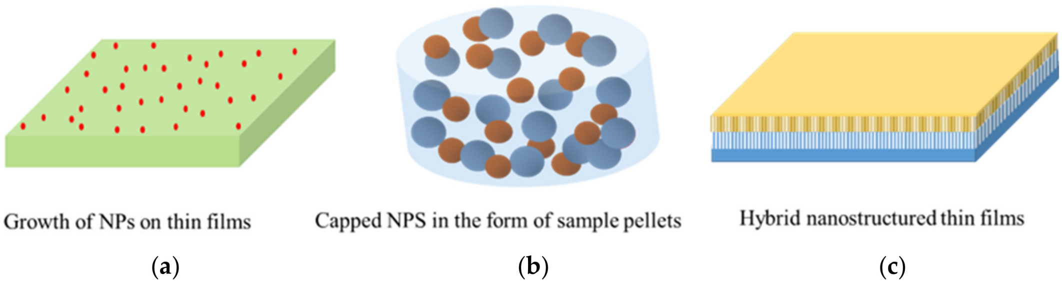


Figure 3. Schematic representation of different hybrid nanostructures. (**a**) Compose of NPs/thin films, (**b**) Hybrid NPs in the form of pellets and (**c**) Hybrid nanostructured thin films for the development of efficient thermoelectric devices.

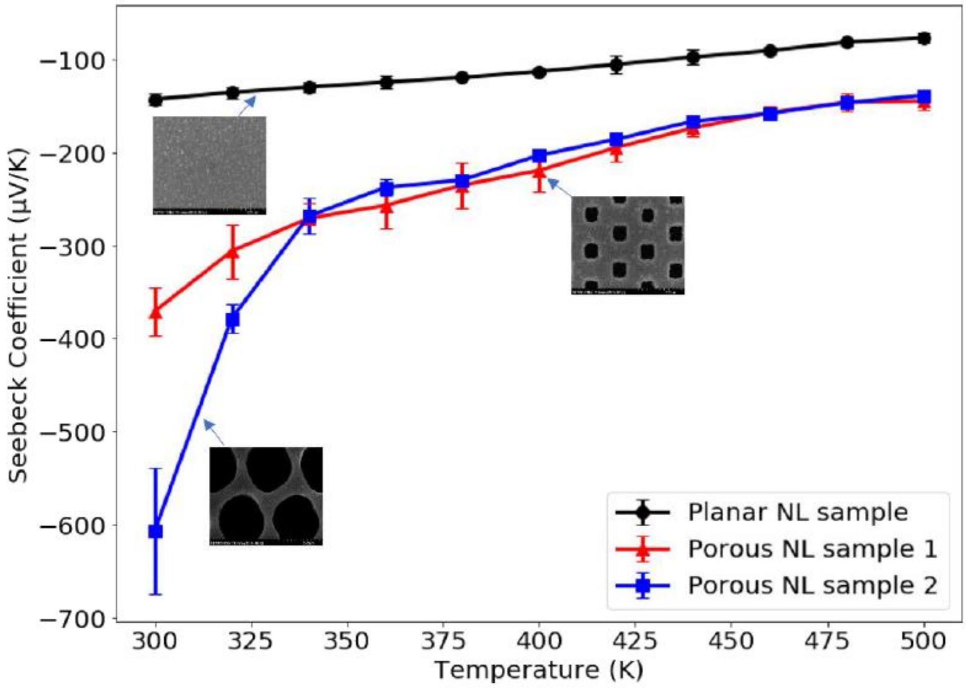
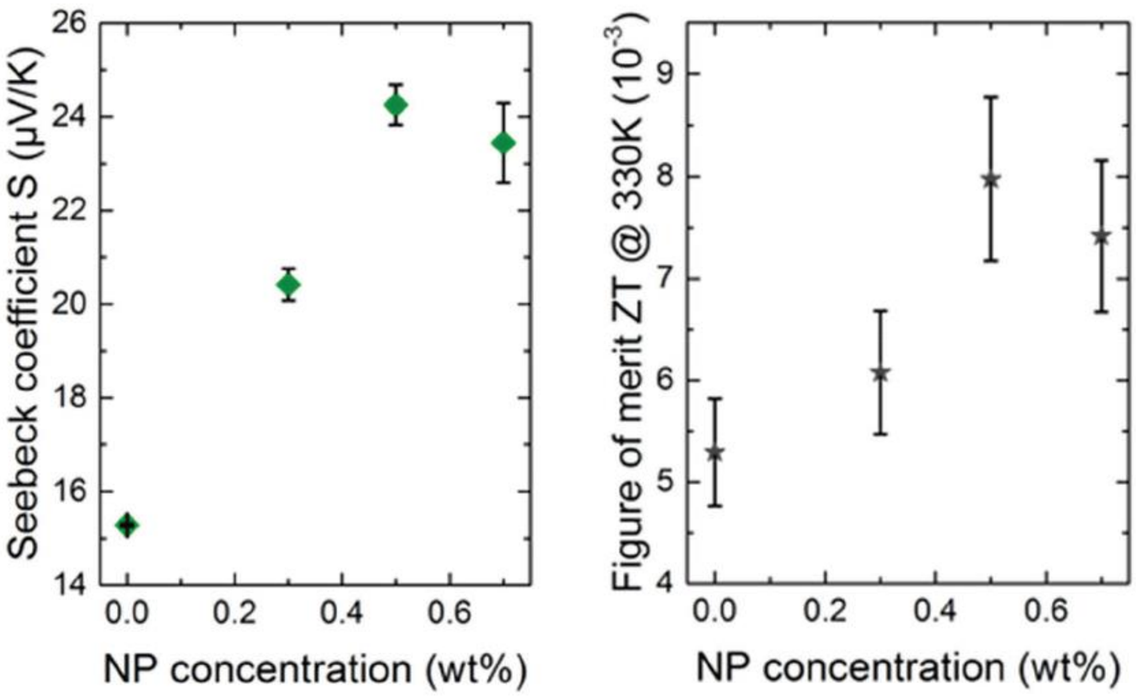


Figure 4. Comparison between the Seebeck coefficient as a function of temperature for ALD PbTe/PbSe layer deposited on planar Si and porous silicon, at two different porosities [17].

Additionally, SiNPs show a remarkable enhancement in the thermoelectric properties compared with the bulk material. This enhancement is attributed to the increase in the number of surface defects, which leads to increasing phonon scattering between the interfaces. However, the increase in the density of SiNPs leads to a reduction in the electrical conductivity due to the formation of an oxide layer on the outer surface. Figure 5a,b present the reported thermoelectric properties of PEDOT:PSS thermoelectric material conjugated with different concentrations of SiNPs. From the reported data, it is clear that the combination with SiNPs leads to a remarkable enhancement in the thermoelectric properties. However, the large density of SiNPs results in a reduction in conversion efficiency due to the reduced electrical conduction [13].



(**a**) (**b**)

Figure 5. Thermoelectric properties as a function of SiNPs concentration grown on PEDOT:PSS thin films. (**a**) Seebeck coefficient for PEDOT:PSS/SiNPs at different concentrations of SiNPs. (**b**) Figure of merit values for PEDOT:PSS/SiNPs thermoelectric samples at different concentrations of SiNPs. Reprint with permission [5324900718582]; Copyright Year 2022, John Wiley and Sons Publisher [13].

Silicon-germanium (SiGe) alloy has been one of the thermoelectric materials most widely used for Radioisotope Thermoelectric Generators (RTGs) at high temperatures since 1976 [20]. The thermoelectric properties of SiGe alloys can be enhanced by nanostructuring the composite. For instance, the *ZT* values of p-type SiGe nanostructured alloy were improved by 50% due to the nanostructuring of the composite [21]. Subsequent work shows the effect of fabrication parameters on the thermoelectric properties of SiGe nanocomposites [22]. The thermal and electrical conduction change is a function of the average crystallite size, porosity, and doping concentration, in addition to the precise control of the milling and sintering conditions. Figure 6a–c show the comparison between the electrical conductivity, Seebeck coefficient and figure-of-merit, respectively, for five different samples at different preparation conditions in comparison with the thermoelectric properties of the RTG sample. The preparation conditions are available in ref. [22]. Figure 6a shows the enhancement in the electrical conduction in a wide range of temperatures for sample 2, which consists of $Si_{80}Ge_{20}$. The increase in the concentration of nanostructured Si to 95% leads to a notable reduction in electrical conductivity (sample 1 $Si_{95}Ge_{5}$) due to a reduction in the electrical conduction of nanostructured Si compared with bulk Si. This behavior is attributed to performing the nanostructures in the heavily doped Si regions. Accordingly, Figure 6c shows the remarkable enhancement in the *ZT* values of sample 2 ($Si_{80}Ge_{20}$) in a wide range of temperatures. This variation in the thermoelectric performance of the reported samples indicates the high sensitivity of the thermoelectric properties to the composition of the nanostructured alloys and the fabrication parameters.

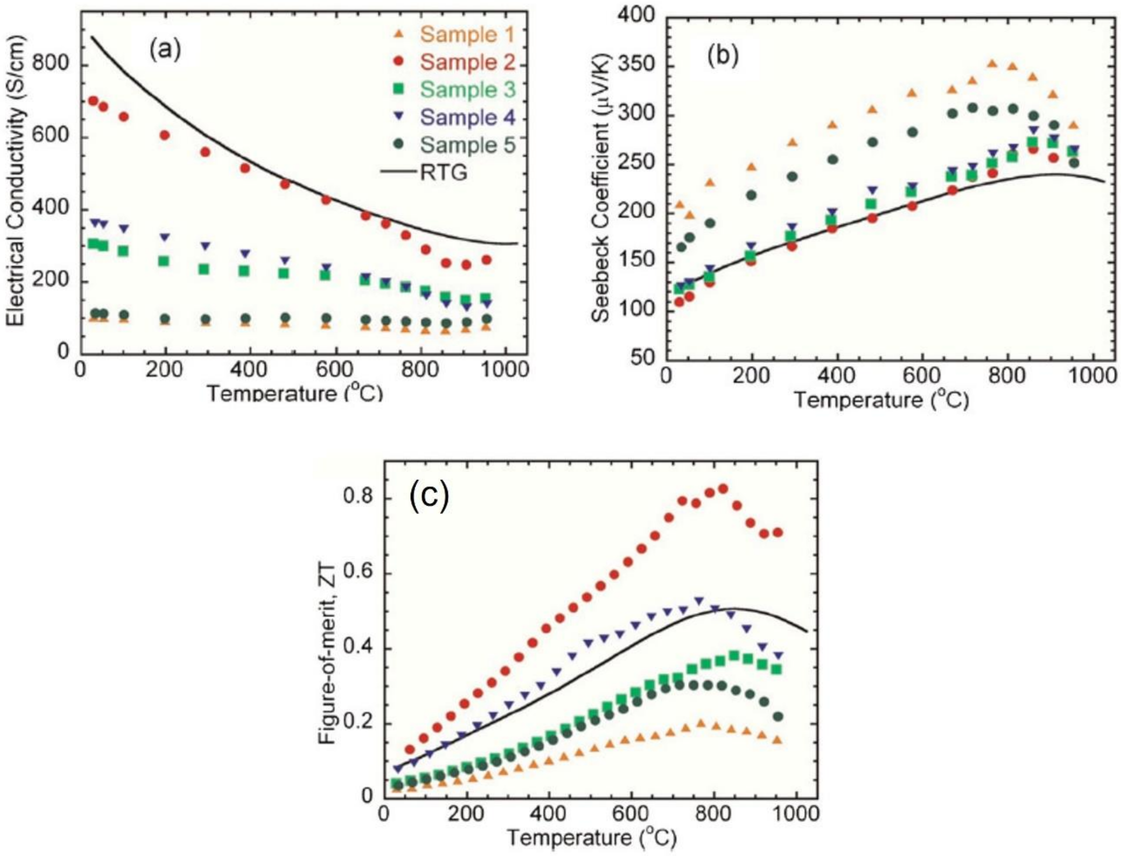


Figure 6. Thermoelectric properties of nanostructured SiGe alloys ate different preparation conditions as a function of temperature. (**a**) The electrical conductivity for 5 samples and RTG sample, (**b**) The seebeck coefficient for the same 5 samples and RTG one, and (**c**) *ZT* values, Reprint with permission [5326930875021]; Copyright Year 2022, John Wiley and Sons Publisher [22].

6. Conclusions

Monocrystalline silicon has high thermal conductivity, which hinders the high conversion efficiency of thermoelectric devices. Many strategies have been developed to improve the thermoelectric properties of silicon materials. One way is by texturing the surface of the silicon substrate to increase phonon scattering at the interfaces. Nanostructured silicon can take many different forms, including porous silicon (PSi), silicon nanoparticles (SiNPs) or silicon nanowires (SiNWs). Nanostructured Si remarkably contributes to reducing the thermal conductivity of thermoelectric devices. However, etching the surface of the Si substrate leads to a reduction in the electrical conductivity of nanostructured Si; likewise, the fast oxidation of the porous silicon layer in ambient air. Accordingly, hybrid silicon nanostructures with another effective thermoelectric material can dramatically reduce the thermal conductivity of nanostructured Si and maintain adequate electrical conductivity due to the other thermoelectric material, in addition to preventing nanostructured Si from oxidation. For instance, PEDOT:PSS combined with SiNPs at a specific concentration, the growth of graphene into nanostructured PSi, atomic layer-deposited PbTe/PbSe nanolaminate structures deposited inside PSi templates and Phenylacetylene capped with SiNPs and alloys of SiGe at suitable percentages are some of the reported hybrid nanostructured materials that have resulting in remarkable improvements in the thermoelectric properties of modified thermoelectric devices.

Author Contributions: R.R. contributed to Investigation, Resources, Validation, Visualization, Writing—original draft and Writing—review and editing and R.J.M.-P. contributed to Conceptualization, Project administration, Supervision, Visualization and Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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