



Thermoelectric performance of silicon with oxide nanoinclusions

D. Coleman, T. Lopez, S. Exarhos, M. Mecklenburg, S. Bux & L. Mangolini

To cite this article: D. Coleman, T. Lopez, S. Exarhos, M. Mecklenburg, S. Bux & L. Mangolini (2018) Thermoelectric performance of silicon with oxide nanoinclusions, Materials Research Letters, 6:8, 419-425, DOI: [10.1080/21663831.2018.1477846](https://doi.org/10.1080/21663831.2018.1477846)

To link to this article: <https://doi.org/10.1080/21663831.2018.1477846>



© 2018 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.



View supplementary material [↗](#)



Published online: 06 Jun 2018.



Submit your article to this journal [↗](#)



Article views: 1496



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 1 View citing articles [↗](#)



ORIGINAL REPORT



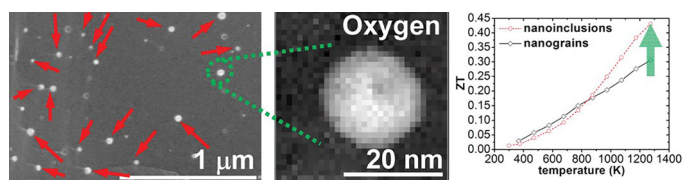
Thermoelectric performance of silicon with oxide nanoinclusions

D. Coleman^{a*}, T. Lopez^{b*}, S. Exarhos^b, M. Mecklenburg^c, S. Bux^d and L. Mangolini^{b a, b}

^aMaterials Science and Engineering Program, University of California Riverside, Riverside, USA; ^bMechanical Engineering Department, University of California Riverside, Riverside, USA; ^cCenter for Electron Microscopy and Microanalysis, University of Southern California, Los Angeles, USA; ^dThermal Energy Conversion Research and Advancement group, Jet Propulsion Laboratory/California Institute of Technology, Pasadena, USA

ABSTRACT

Silicon nanoparticles produced via a plasma-based technique have been sintered into bulk nanostructured samples. These samples have micron-sized crystalline domains and contain well-dispersed oxide nanoinclusions. We have compared the thermoelectric performance of such structure to that of a control sample produced by sintering ball-milled silicon powders. The control sample has lower precipitate density and is composed of nanograins. Despite the stark difference in nanostructure, both samples have comparable thermal conductivity, and the sample with nanoinclusions has higher power factor and ZT. This result confirms that grain size engineering is not the only promising route to achieving improved thermoelectric performance.



IMPACT STATEMENT

By controlling the feedstock powder processing technique, it is possible to obtain well-dispersed nanoinclusions in sintered bulk samples. These are as effective at reducing thermal transport properties as grain boundaries.

ARTICLE HISTORY

Received 6 December 2017

KEYWORDS

Thermal transport;
nanoinclusions; plasma
synthesis

Introduction

The design and realization of materials for efficient thermoelectric energy conversion has attracted the attention of several research groups. From a fundamental point of view, it requires gaining an intimate understanding of the transport of heat and charge carriers in potentially complex materials. Reducing grain size is an effective way to preferentially increase the phonon over the charge carrier scattering rate, thus improving the thermoelectric figure of merit ZT [1,2]. Sintering of fine powders has become a common approach for the realization of bulk materials with nanoscale grains [3–6]. Despite this progress, recent reports have suggested that this tactic has limitations. Grain boundaries have been shown to scatter low frequency phonons less efficiently than high frequency

ones [7], and low frequency phonons can carry a significant amount of heat even at high temperatures [8]. There are also unsolved issues with respect of the processing science of such materials. Bulk nanostructured silicon can be obtained by sintering powders produced using a wide range of techniques, such as ball milling [3,7] and plasma [9–11], and the influence of processing parameters on the transport properties of the resulting bulk samples is far from being fully understood. This contribution focuses on both of these issues. Silicon nanoparticles synthesized using a low temperature plasma-based technique [12,13] have been hot-pressed into bulk silicon samples. The resulting sample has large grains (micron-sized) and ~20 nm well dispersed silicon oxide precipitates. When compared to a control sample with submicron grains,

CONTACT L. Mangolini ✉ lmangolini@engr.ucr.edu Materials Science and Engineering Program, University of California Riverside, Riverside CA 92521, USA; Mechanical Engineering Department, University of California Riverside, Riverside CA 92521, USA

*D. Coleman and T. Lopez equally contributed to this work.

Supplemental data for this article can be accessed here. <https://doi.org/10.1080/21663831.2018.1477846>

© 2018 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

the sample with nanoinclusions has similar thermal conductivity but higher power factor, leading to a markedly higher thermoelectric figure of merit ZT .

Experimental

The nanoparticle synthesis technique utilized here is a scaled-up version of the reactor discussed in other contributions [12–14]. It is composed of a continuous flow non-thermal plasma reactor, tube furnace, and roughing pump, and is capable of producing powder at a rate of the order of grams per hour. The plasma reactor is composed of a 5 cm diameter quartz tube with a 5 cm wide copper electrode wrapped on its outside. The electrode is RF biased at 13.56 MHz. For this study, the plasma power is constant and equal to 160 W. At the gas inlet, 850 sccm of a mixture of 1.37% silane in argon is flown at a pressure of 3.5 torr. After the plasma synthesis step, the particles are crystalline, have a hydrogen terminated surface and are 5–10 nm in size [15]. Any attempt to sinter the as-produced particles into bulk samples has resulted into extremely brittle samples that shatter during handling. We hypothesize that this is due to the hydrogen surface termination of the particles and the consequent hydrogen-induced embrittlement of the sintered sample. For this reason, we have introduced an in-flight annealing step to thermally remove hydrogen from the particle surface. This is achieved by flowing the particles through a tube furnace with a heated length of 20 cm and kept at 1100°C. This in-flight post-processing step allows us to reproducibly sinter the particles into bulk samples with > 99% relative density. Figure S1 in the supplementary material shows TEM micrographs and particle size distribution of the silicon nanoparticles produced with this approach. The average particle size is 50 nm with a standard deviation of 8 nm. They are significantly larger than the 5–10 nm nanoparticles that are typically obtained from non-thermal plasma reactors [12,13,15]. Particle charging, which slows down agglomeration in the plasma reactor [16], is absent once the particles leave the plasma and enter the in-flight annealing step, with the same annealing mechanism enhancing the agglomeration and coalescence kinetics thus leading to rapid growth in size. The particles are collected on a filter downstream of the furnace, sealed in an inert argon atmosphere and transferred to a glove box where they are then mechanically mixed with 2% red phosphorus [17].

We have also sintered silicon powder produced via ball-milling to compare our samples to a more standard structure [3]. Silicon ingot fragments and red phosphorus are sealed in a tungsten carbide vial with 3 tungsten carbide balls of 10 mm diameter in a 50 mL WC vial (Spex industries) and milled in the Spex for 24 h. It is important

to note that the particles produced with our synthesis technique have significantly larger specific surface area than the ones obtained via ball milling: 41.7 m²/gram versus 9 m²/gram respectively.

Both powders are then sintered using the same procedure. They are loaded into a 12.7 mm inner diameter graphite dies with boron nitride dry lubricant, and sintered in a hydraulic hot press at 1160°C and 120 MPa with a linear heating rate of $\sim 20^\circ\text{C}/\text{min}$ and a hold time of 30 min. After sintering, the pressure is released and the system is passively cooled to room temperature over a period of a few hours. The consolidated pucks are then cut and polished for characterization. X-ray Diffraction (XRD) is performed by a PANalytical EMPYREAN diffractometer with a CuK_α source. Transmission Electron Microscopy (TEM) is performed by a Tecnai T12 and Electron Energy Loss Spectroscopy (EELS) is performed on a JEOL JEM-2100F with a Gatan Quantum SE GIF operating with an accelerating voltage of 200 kV. Thermoelectric characterization is performed at the Jet Propulsion Laboratory using both commercial (for thermal diffusivity) and specialized custom equipment (for electrical conductivity, carrier concentration and Seebeck coefficient), as listed below. Thermal conductivity is calculated using the thermal diffusivity measured via Laser Flash Analysis (LFA). A commercial Netzsch LFA 404 is used for the measurement. To obtain the thermal conductivity, we have used the temperature-dependent heat capacity values measured in [18]. We have performed independent differential scanning calorimetry (DSC) measurements to confirm that the heat capacities of our samples are close to the values reported in [18] (see Figure S2 in the supplementary information file). Reports in the literature confirm that nanostructuring does not lead to deviation in the heat capacity compared to that of bulk silicon [19,20]. The density is measured via Archimedes method and corrected for thermal expansion [21]. Electrical conductivity and carrier concentration are measured by high temperature Hall Effect using the 4 point probe Van der Pauw method described in details in [22]. Seebeck coefficient is measured using the system and procedure described in details in [23]. All thermoelectric measurements (thermal diffusivity, electrical conductivity, carrier concentration, Seebeck coefficient) are taken with the same heating rate of 180 K/hr to maintain consistent contributions from carrier concentration effects such as dopant precipitation.

Results and discussion

Figure 1 shows SEM and TEM images for the samples after sintering. Figure 1(a,b) are respectively the cross-section SEM and TEM of the sample obtained by

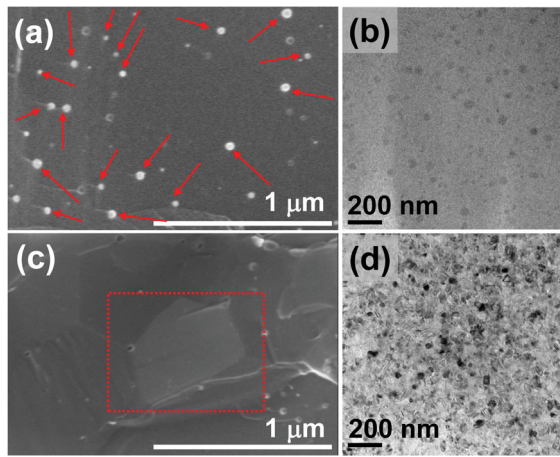


Figure 1. (a) Cross-sectional SEM image for the samples obtained by hot-pressing the plasma-produced particles. (b) TEM of sample obtained using the plasma-produced particles, after FIB-ing. (c) and (d) show the same analysis but for the sample produced by hot-pressing the powder obtained by ball-milling of silicon ingots.

sintering the plasma-produced nanoparticles. The SEM image is acquired from a fracture surface, and the TEM analysis is performed after focused ion beam (FIB) processing. The presence of inclusions, which we highlight with red arrows, is clear in both Figure 1(a,b). Grains are not clearly distinguishable in Figure 1(a). The lack of background contrast in Figure 1(b) suggests that the sample in the field of view is oriented along the same crystallographic direction. Figure 1(c,d) show the same analysis on the sample obtained by sintering the powder produced via ball-milling. The density of inclusions is much lower than in Figure 1(a), and grain boundaries (see red box) are clearly distinguishable. The TEM image in Figure 1(d) shows strong contrast, suggesting that the sample is composed of small domains. The XRD spectra for the two samples, not shown for brevity, are consistent with polycrystalline diamond silicon. Williamson-Hall analysis is performed by fitting the first seven diffraction peaks with a two-peaks pseudo-voigt profile to account for the $\kappa\alpha 1$ and $\kappa\alpha 2$ contributions. The analysis suggests that the sample with nanoinclusions has $\sim 3 \mu\text{m}$ crystal domain sizes, while the sample with nanograins has $\sim 200 \text{ nm}$ crystal domain sizes. This result is consistent with the results in Figure 1. We attribute the large grain size for the sample produced using the plasma-produced nanoparticles to the much larger surface area of this powder. The reduced activation energy for diffusion at the nanoparticle surface has been proposed as the mechanism justifying the enhanced sintering kinetics of small particles [24,25].

We have performed electron energy loss spectroscopy (EELS) spectrum imaging on the sample shown in Figure 1(a,b) to better characterize the nanoinclusions.

From the acquired spectrum images the counts from the oxygen and silicon K-edge were extracted, producing the images shown in Figure 2(a,b). This analysis indicates that the inclusions are oxygen rich. Their composition, small size and spatial uniformity in the silicon matrix are consistent with oxide precipitates. Such structures are actually well known in silicon processing science, with early reports suggesting that oxide contamination can lead to the formation of small inclusions in silicon [26–28]. The presence of oxygen contamination in our sample is likely the result of the high-temperature in-flight treatment, which removes the hydrogen termination from the nanoparticle surface. The resulting ‘bare’ surface is extremely sensitive to oxidation. Although the particles are kept nominally air-free during processing, the presence of even trace amounts of oxidizing species, which is unavoidable even in a glove-box with few ppm levels of oxygen and water, is expected to lead to partial oxidation of the particles surface. In Figure 2(c) we show the histogram of the distances between the oxide nanoinclusions. This was obtained by measuring the nearest neighbor distance between the particles from cross-sectional SEM images such as the one shown in Figure 1(a). Care was taken not to double-count particle pairs. A modified Saltykov algorithm was used to convert the raw distance distribution to the three-dimensional distribution [29]. This procedure assumes that the spatial arrangement is isotropic, which based on our observation is a safe assumption. We find that the average spacing between the particles is $\sim 160 \text{ nm}$. Given a size of 20 nm , this implies a nanoinclusion density and volume fraction of $2 \times 10^{14} \text{ cm}^{-3}$ and 0.1% respectively.

From these measurements, it is clear that different powder preparation techniques lead to very different structures after hot-pressing. We should stress that we produced our best effort at doping the samples with similar amount of phosphorous. The room temperature carrier concentrations as measured via Hall Effect are $4.9 \times 10^{20} \text{ cm}^{-3}$ and $4.5 \times 10^{20} \text{ cm}^{-3}$ for the ‘nanoinclusions’ and the ‘nanograins’ samples respectively. The transport properties are shown in Figure 3.

Despite the clear difference in nanostructure, the two samples have practically identical thermal conductivity (Figure 3(a)), with a minimum value of $\sim 12 \text{ W/m K}$ at 1000 K . The lattice thermal conductivities for the two samples are close (inset of Figure 3(a)), reaching a minimum value of $\sim 9 \text{ W/m K}$ at 1200 K . The electronic contribution was calculated using the Wiedemann-Franz law using a Lorenz factor equal to $2.2 \times 10^{-8} \text{ J}^2 \text{ K}^{-2} \text{ C}^{-2}$ [3]. The room temperature electrical resistivities are $4.25 \mu\Omega \text{ m}$ and $5 \mu\Omega \text{ m}$ for the ‘nanoinclusions’ and the ‘nanograins’ samples respectively, and the room temperature Seebeck coefficients are $60 \mu\text{V/K}$ and $78 \mu\text{V/K}$.

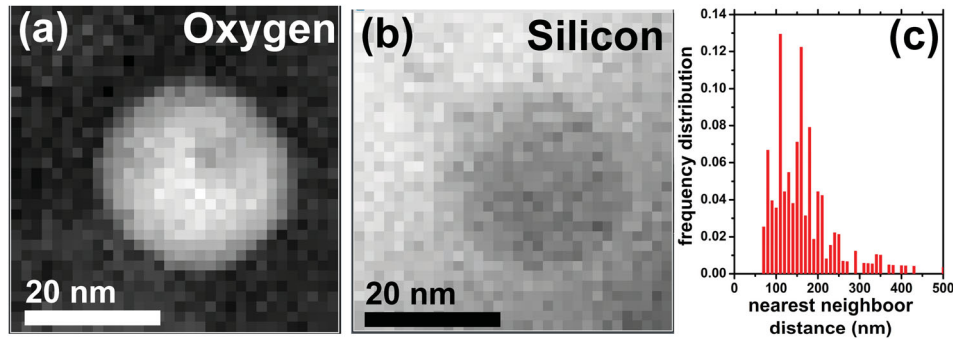


Figure 2. EELS-filtered TEM micrographs of the nanoinclusions. (a) Corresponds to the oxygen signal, while (b) to the silicon signal. (c) Distribution of distances between nearest neighbor inclusions.

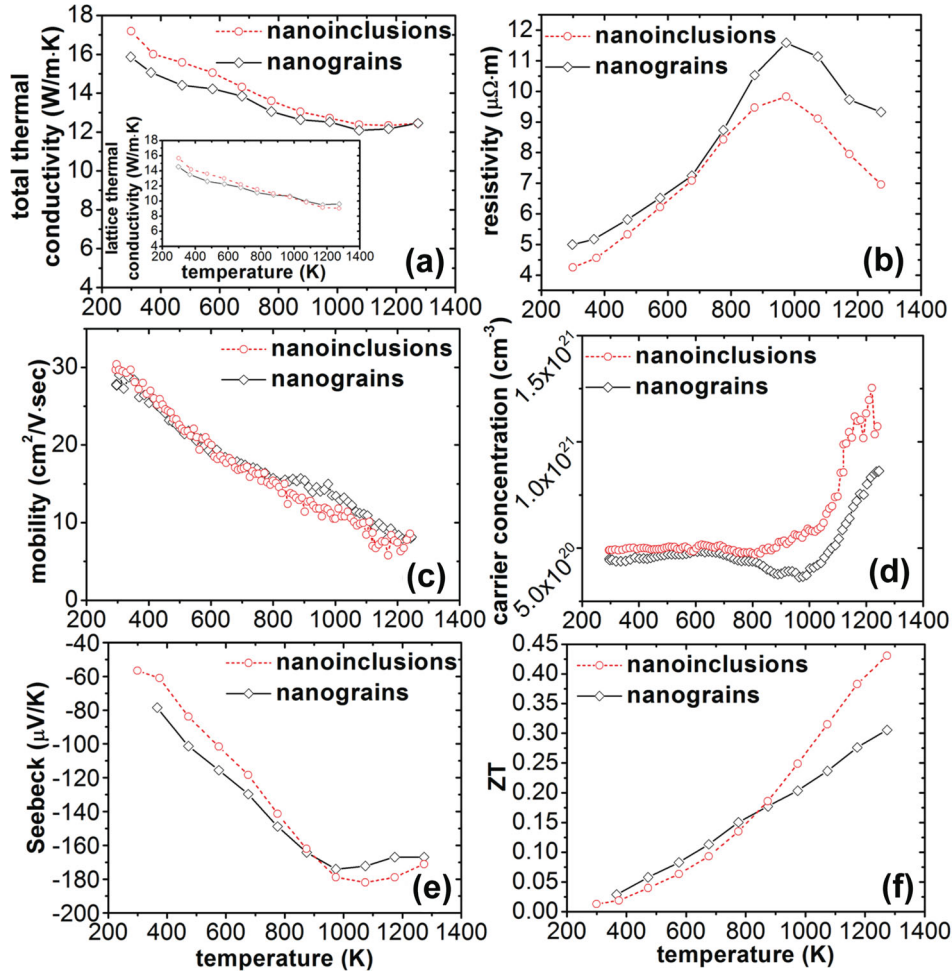


Figure 3. Summary of the transport properties of the samples under investigation. (a) Full and lattice thermal conductivity. (b) Electrical resistivity. (c) Charge carrier mobility. (d) Carrier concentration. (e) Seebeck coefficient. (f) Figure of merit ZT.

respectively. This difference is justified by higher carrier concentration of the ‘nanoinclusions’ sample. The main difference between the two samples is in the temperature dependence of the electrical resistivity. For both samples, it first increases at higher temperature because of increased electron–phonon scattering, and then decreases because of the increased solubility of phosphorous in the lattice [17]. While similar behavior

has been observed in other bulk silicon samples [3,30], the resistivity does not increase with temperature as much for the ‘nanoinclusions’ samples compared to the ‘nanograins’ sample. The difference between the two curves is significant at temperatures higher than 800 K (Figure 3(b)). While the mobilities are practically identical (Figure 3(c)), the carrier concentration dependence (Figure 3(d)) is quite different between the two

samples. For the ‘nanograins’ sample, there is first a decrease in carrier concentration starting at 800 K, which is attributed to dopant precipitation effects in heavily doped silicon [3,31], followed by an increase at 1000 K due to increased solubility of phosphorous in silicon [17]. For the ‘nanoinclusions’ sample, the dopant precipitation effect is practically absent, and the carrier concentration starts increasing at 800 K. Two mechanisms may contribute to this difference in behavior. First, the ‘nanograins’ sample has a much larger density of grain boundaries compared to the ‘nanoinclusions’ sample, and phosphorous is well-known to segregate at boundaries in polycrystalline silicon samples [32,33]. Second, the oxide nanoinclusions may act as a phosphorous reservoir. This is to be expected given the known capability of phosphorous-rich silica to act as a dopant source to silicon [34]. It is also important to notice that despite the larger increase in carrier concentration with temperature for the ‘nanoinclusions’ sample, the Seebeck coefficients remain close for the two samples (Figure 3(e)). This leads to an overall improvement in power factor for the ‘nanoinclusions’ sample. Similar improvements in power factor for samples with inclusions and precipitates have been reported for more complex chemistries. Bulk nanostructured PbSe with CdSe nanoinclusions shows an improved power factor because of the effect of the inclusions on the valence band structure [35,36]. Metallic inclusions in chalcogenides also lead to an improvement in the power factor, this time induced by energy filtering of the charge carriers [37,38]. Similar effects may be at play in our ‘nanoinclusions’ sample. Overall, this results in a thermoelectric figure of merit of 0.45 at 1300 K for the ‘nanoinclusions’ sample, considerably higher than the 0.3 at the same temperature for the ‘nanograins’ sample.

The formation of oxide inclusion in silicon has been observed previously for samples obtained by sintering of nanoparticles with a native oxide layer [30,39]. For these studies, the oxygen content is as high as $\sim 25\%$ by mass, and the grain size is small (~ 100 nm). Therefore both nanoinclusion and grain boundaries contribute to the reduction in thermal conductivity, making it difficult to separate their roles. On the other hand, our samples have been processed by avoiding air exposure as much as possible. The oxygen content is sufficiently low that it is difficult to quantify reliably via SEM-EDS. While determination of the oxygen content is challenging (extensive EELS characterization is prohibitive considering that it requires advanced sample preparation via FIB), the grain size in our samples is large (microns). Grain boundaries are not expected to contribute significantly to the reduction in thermal transport. This study therefore provides a more direct comparison between the role of grain boundaries and nanoinclusions on transport

properties. We should also stress that high ZT values have been measured on multiple samples processed identically to the one discussed earlier in the manuscript, as shown in Figure S3 in the supplementary material.

Conclusions

We have compared the thermal and charge transport properties of two samples with starkly different nanoscale structures: a sample with relatively small crystalline domains and a sample with much larger crystals but with well-dispersed nanoinclusions. Our results suggest that nanoinclusions can be effective at scattering heat carriers (phonons), confirming that improved strategies for the reduction of heat conductivity in bulk materials are within reach, for instance by combining the use of nanograins and nanoinclusions within one sample. Most importantly, the device with nanoinclusions shows a higher power factor. Further improvements in ZT may be attainable by optimizing the doping level for the structure with nanoinclusions.

Acknowledgements

This work was primarily supported by the National Science Foundation via grant number 1351386 (CAREER). Electron microscopy shown in Figure 1 was performed on a Tecnai T12 in the Central Facility for Advanced Microscopy and Microanalysis at UC Riverside. Part of this work was performed at the California Institute of Technology/Jet Propulsion Laboratory under contract with the NASA Science Missions Directorate, under the Radioisotope Power Systems Program’s Thermoelectric Technology Development Project. The EELS data in Figure 2(a,b) was acquired at the Center for Electron Microscopy and Microanalysis, at the University of Southern California.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was primarily supported by the National Science Foundation via [grant number 1351386] (CAREER); Division of Civil, Mechanical and Manufacturing Innovation.

ORCID

L. Mangolini  <http://orcid.org/0000-0002-0057-2450>

References

- [1] Dresselhaus MS, Chen G, Tang MY, et al. New directions for low-dimensional thermoelectric materials. *Adv Mater*. 2007;19(8):1043–1053. doi:10.1002/adma.200600527. PubMed PMID: ISI:000246432800002; English.

- [2] Dresselhaus M, Dresselhaus G, Sun X, et al. Low-dimensional thermoelectric materials. *Phys Solid State*. 1999;41(5):679–682. doi:10.1134/1.1130849.
- [3] Bux SK, Blair RG, Gogna PK, et al. Nanostructured bulk silicon as an effective thermoelectric material. *Adv Funct Mater*. 2009;19(15):2445–2452. doi:10.1002/adfm.200900250. PubMed PMID: ISI:000269021500012; English.
- [4] Zebarjadi M, Joshi G, Zhu GH, et al. Power factor enhancement by modulation doping in bulk nanocomposites. *Nano Lett*. 2011;11(6):2225–2230. doi:10.1021/nl201206d. PubMed PMID: WOS:000291322600006; English.
- [5] Joshi G, Lee H, Lan YC, et al. Enhanced thermoelectric figure-of-merit in nanostructured p-type silicon germanium bulk alloys. *Nano Lett*. 2008;8(12):4670–4674. doi:10.1021/nl8026795. PubMed PMID: ISI:000261630700100; English.
- [6] Poudel B, Hao Q, Ma Y, et al. High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys. *Science*. 2008;320(5876):634–638. doi:10.1126/science.1156446. PubMed PMID: WOS:000255454300037; English.
- [7] Wang Z, Alaniz JE, Jang W, et al. Thermal conductivity of nanocrystalline silicon: importance of grain size and frequency-dependent mean free paths. *Nano Lett*. 2011;11(6):2206–2213. doi:10.1021/nl1045395
- [8] Yang L, Minnich AJ. Thermal transport in nanocrystalline Si and SiGe by ab initio based Monte Carlo simulation. *Sci Rep*. 2017;7:44254. doi:10.1038/srep44254.
- [9] Petermann N, Stein N, Schierning G, et al. Plasma synthesis of nanostructures for improved thermoelectric properties. *J Phys D Appl Phys*. 2011;44(17):174034. doi:10.1088/0022-3727/44/17/174034. PubMed PMID: ISI:000289512700034; English.
- [10] Schwesig D, Schierning G, Theissmann R, et al. From nanoparticles to nanocrystalline bulk: percolation effects in field assisted sintering of silicon nanoparticles. *Nanotechnology*. 2011;22(13):135601. doi:10.1088/0957-4484/22/13/135601. PubMed PMID: ISI:000287578800008; English.
- [11] Miura A, Zhou S, Nozaki T, et al. Crystalline–amorphous silicon nanocomposites with reduced thermal conductivity for bulk thermoelectrics. *ACS Appl Mater Interfaces*. 2015;7(24):13484–13489. doi:10.1021/acsami.5b02537.
- [12] Lopez T, Mangolini L. On the nucleation and crystallization of nanoparticles in continuous-flow nonthermal plasma reactors. *J Vac Sci Technol B*. 2014;32(6):061802. doi:10.1116/1.4899206.
- [13] Mangolini L, Thimsen E, Kortshagen U. High-yield plasma synthesis of luminescent silicon nanocrystals. *Nano Lett*. 2005;5(4):655–659.
- [14] Yasar-Inceoglu O, Mangolini L. Characterization of Si–Ge alloy nanocrystals produced in a non-thermal plasma reactor. *Mater Lett*. 2013;101(0):76–79. doi:10.1016/j.matlet.2013.03.080.
- [15] Yasar-Inceoglu O, Lopez T, Farshihagro E, et al. Silicon nanocrystal production through non-thermal plasma synthesis: a comparative study between silicon tetrachloride and silane precursors. *Nanotechnology*. 2012;23(25):255604.
- [16] Kortshagen U, Bhandarkar U. Modeling of particulate coagulation in low pressure plasmas. *Phys Rev E*. 1999;60(1):887–898.
- [17] Olesinski RW, Kanani N, Abbaschian GJ. The P–Si (Phosphorus-Silicon) system. *Bull Alloy Phase Diagr*. 1985;6(2):130–133. doi:10.1007/bf02869224.
- [18] Shanks HR, Maycock PD, Sidles PH, et al. Thermal conductivity of silicon from 300 to 1400 K. *Phys Rev*. 1963;130(5):1743–1748.
- [19] Claudio T, Schierning G, Theissmann R, et al. Effects of impurities on the lattice dynamics of nanocrystalline silicon for thermoelectric application. *J Mater Sci*. 2013;48(7):2836–2845. doi:10.1007/s10853-012-6827-y.
- [20] Claudio T, Stein N, Stroppa DG, et al. Nanocrystalline silicon: lattice dynamics and enhanced thermoelectric properties. *Phys Chem Chem Phys*. 2014;16(47):25701–25709. doi:10.1039/C3CP53749H.
- [21] Swenson CA. Recommended values for the thermal expansivity of silicon from 0 to 1000 K. *J Phys Chem Ref Data*. 1983;12(2):179–182. doi:10.1063/1.555681.
- [22] Borup KA, Toberer ES, Zoltan LD, et al. Measurement of the electrical resistivity and Hall coefficient at high temperatures. *Rev Sci Instrum*. 2012;83(12):123902. doi:10.1063/1.4770124.
- [23] Wood C, Zoltan D, Stapfer G. Measurement of Seebeck coefficient using a light pulse. *Rev Sci Instrum*. 1985;56(5):719–722. doi:10.1063/1.1138213.
- [24] Möller HJ, Welsch G. Sintering of ultrafine silicon powder. *J Am Ceram Soc*. 1985;68(6):320–325. doi:10.1111/j.1151-2916.1985.tb15233.x.
- [25] Greskovich C, Rosolowski JH. Sintering of covalent solids. *J Am Ceram Soc*. 1976;59(7-8):336–343. doi:10.1111/j.1151-2916.1976.tb10979.x.
- [26] Kaiser W. Electrical and optical properties of heat-treated silicon. *Phys Rev*. 1957;105(6):1751–1756.
- [27] Kissinger G, Kot D, Dabrowski J, et al. Analysis of the nucleation kinetics of oxide precipitates in Czochralski Silicon. *ECS Trans*. 2008;16(6):97–108. doi:10.1149/1.2980296.
- [28] Borghesi A, Pivac B, Sassella A, et al. Oxygen precipitation in silicon. *J Appl Phys*. 1995;77(9):4169–4244. doi:10.1063/1.359479.
- [29] Lewis HD, Walters KL, Allan Johnson K. Particle size distribution by area analysis: modifications and extensions of the Saltykov method. *Metallography*. 1973;6(2):93–101. doi:10.1016/0026-0800(73)90001-3.
- [30] Schierning G, Theissmann R, Stein N, et al. Role of oxygen on microstructure and thermoelectric properties of silicon nanocomposites. *J Appl Phys*. 2011;110(11):113515. doi:10.1063/1.3658021.
- [31] Vining CB. A model for the high-temperature transport properties of heavily doped n-type silicon-germanium alloys. *J Appl Phys*. 1991;69(1):331–341. doi:10.1063/1.347717.
- [32] Rose JH, Gronskey R. Scanning transmission electron microscope microanalytical study of phosphorus segregation at grain boundaries in thin-film silicon. *Appl Phys Lett*. 1982;41(10):993–995. doi:10.1063/1.93368.
- [33] Mandurah MM, Saraswat KC, Helms CR, et al. Dopant segregation in polycrystalline silicon. *J Appl Phys*. 1980;51(11):5755–5763. doi:10.1063/1.327582.

- [34] Hartiti B, Slaoui A, Muller JC, et al. Phosphorus diffusion into silicon from a spin-on source using rapid thermal processing. *J Appl Phys.* **1992**;71(11):5474–5478. doi:10.1063/1.350519.
- [35] Zhao L-D, Hao S, Lo S-H, et al. High thermoelectric performance via hierarchical compositionally alloyed nanostructures. *J Am Chem Soc.* **2013**;135(19):7364–7370. doi:10.1021/ja403134b.
- [36] Tan G, Zhao L-D, Shi F, et al. High thermoelectric performance of p-Type SnTe via a synergistic band engineering and nanostructuring approach. *J Am Chem Soc.* **2014**;136(19):7006–7017. doi:10.1021/ja500860m.
- [37] Martin J, Wang L, Chen L, et al. Enhanced seebeck coefficient through energy-barrier scattering in PbTe nanocomposites. *Phys Rev B.* **2009**;79(11):115311.
- [38] Ko D-K, Kang Y, Murray CB. Enhanced thermopower via carrier energy filtering in solution-processable Pt–Sb₂Te₃ nanocomposites. *Nano Lett.* **2011**;11(7):2841–2844. doi:10.1021/nl2012246.
- [39] Petermann N, Stötzl J, Stein N, et al. Thermoelectrics from silicon nanoparticles: the influence of native oxide. *Eur Phys J B.* **2015**;88(6):163. doi:10.1140/epjb/e2015-50594-7.