possible solutions of this problem is to add dopant after the synthesis (ex situ doping) and to promote its diffusion into the Mg2Si matrix upon consolidation. In some cases, however, this procedure may appear unsuccessful because of thermodynamic stability of foreign intermetallics. This work will demonstrate thermodynamic background of selected Mg-Si-dopant systems to better understand and optimize relevant manufacturing processes.

Keywords: magnesium silicide, thermodynamic stability of Mg-Si-dopant systems

Acknowledgements: The authors wish to acknowledge financial support from the ThermoMag Project, which is co-funded by the European Commission in the 7th Framework Programme (contract NMP4-SL-2011-263207), by the European Space Agency and individual partner organizations and partly from the Ministry of Science and Higher Education in Poland (project 6099/B/T02/2010/38 -18.18.160.910).

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Macro-Micro-Nano Features in Magnesium Silicide/Stannide/Germanide Compounds

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Recent reports of good thermoelectric properties with high thermoelectric figures of merit, (ZT), have added to the interest in $Mg_2(Si,Sn)$ and their doped compounds as promising thermoelectric materials. Nevertheless, the reports dealing with the morphology in-homogeneities of these materials are scarce over the published literature. In the present study, a comparative study is attempted, dealing with the in-homogeneities monitored in the cases of $Mg_2(Si,Sn)$ based ternary compounds as well as the quaternary system based on $Mg_2(Si,Sn,Ge)$. In-homogeneities may occur at different scale lengths; at atomic scale (as dopant and alloying), at nano-scale (as nano-inclusions and nano-crystals), at meso-scale (as grains of different composition) and at macro-scale (as dopant modulated structures and dopant grated materials). Structural in-homogeneities were monitored by using Transmission Electron Microscopy of moderate and high resolution (TEM&HRTEM), Scanning Electron Microscopy (SEM) equipped with EDS analyzer, X-Ray diffraction analysis as well as conventional Fourier transform infrared spectroscopy in the reflectivity mode. X-Ray diffraction indicates that all materials subjected to the present study exhibit two phases, one Sn-rich and another Si-rich. Compositional in-homogeneities extend from nano-scale to macro-scale, as observed with HRTEM (nano-scale), SEM studies and EDS (micro-scale) and IR Reflectivity mappings (macro-scale). The results are discussed in the framework of existing models about the constitution of the alloys for the Sn composition range $0.4 < x < 0.6$. Finally, the implications of these in-homogeneities to the thermoelectric properties of these compounds are also discussed, indicating that both phases are participating in the enhancement of ZT through the lowering of the thermal conductivity.

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Paradoxical Enhancement of the Power Factor in Polycrystalline Silicon Due to the Formation of Nanovoids

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Holey silicon has been considered a viable candidate as a thermoelectric material [1] in view of its low thermal conductivity. However, since voids are efficient scattering centers not just for phonons but also for the charge carriers, achievable power factors (PFs) are normally too low for its most common embodiment, namely porous silicon, to be of practical interest [2]. In this communication we show that the presence of nanopores themselves is not incompatible with thermoelectric efficiency in highly doped silicon. High power factors, up to a huge 22 mW $K^{-2}m^{-1}$ (more than 6 times higher than bulk values), were observed in heavily boron doped nanocrystalline silicon films where nanovoids (NVs) were generated by He^+ ion implantation. Differently than in single-crystalline silicon [3, 4], He^+ implantation followed by annealing at 1000 °C led to the formation of a homogeneous distribution of NVs with final diameters of about 2 nm and densities in the order of 10^{19} cm^{-3}. Its morphology shows silicon nanograins of ≈50 nm in diameter decorated by SiB_x 5-nm precipitates. The details of this remarkable PF enhancement are currently under investigation. We recently reported that PFs up to 15 mW $K^{-2}m^{-1}$ can be achieved in silicon-boron nanocomposites (without the NVs) [5, 6] due to a simultaneous increase of the electrical conductivity and Seebeck coefficient [7,8]. In that case, high Seebeck coefficient was achieved by potential barriers on the grain boundaries, and high

electrical conductivity by extremely high doping values. The additional increase in the PF observed in the case of the new structures with NVs (that also include SiB_x precipitates) might be attributed to several possible reasons, currently under investigation: i) a further increase of the mechanism described above, ii) increase of strain in the grains, iii) increase in active dopant density, iv) change in the electronic and phononic spectrum, v) reduction of carrier energy relaxing mechanisms. Experimental and computational evidence will be put forward to elucidate this paradoxical effect of NVs on silicon PF.

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Reduction of Thermal Conductivity in Compositionally-Graded $Si_{1-x}Ge_x$ Superlattices

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SiGe superlattices (SLs), in which phonon transport is dominated by a high density of interfaces, have been previously reported in an effort to reduce the thermal conductivity below the alloy limit. In this work, we explore the effect of compositionally-modulated Si1-xGex layers, grown in direct and reverse order. Several sets of samples have been prepared by molecular beam epitaxy at 450oC ; one consisting in a (Si1-xGex)/Si superlattice on Si(001) with a continuously increasing Ge content (x from 0 to 0.55 or 0.70) in the growth direction and the others with the compositional gradient in exact reversed order. The SLs consist of 4 periods of 40 nm of graded Si1-xGex alloy separated by 5 nm of Si. The growth starts and ends with Si layers of 60 nm and 5 nm thickness, respectively. We use the 3ù method to obtain ê in the T range 50-400 K. Under a temperature gradient from the top surface, heat will travel across different interfaces and different compositional gradients. We demonstrate this asymmetry has a remarkable effect in the heat flow. The compositionally-graded Si1-xGex SLs also show a significant reduction of phonon transport compared to traditional SLs superlattices or even quantum dot superlattices, with conductivity values below 2.5 W/mK at room temperature. We discuss our results in terms of the asymmetry of the compositional modulation and the thermal boundary resistance and about the possible influence of extended defects. We also use X-ray diffraction tools to map the strain in the superlattice.

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Effect of Pore Sizes on the Reduction in Lattice Thermal Conductivity of Nano to Micro Scale Porous Materials

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We study the effect of thermal phonon scattering on the reduction of lattice thermal conductivity (LTC) in porous semiconducting materials with nonconnected spherical hole pores of varying diameter from nano to micro scale sizes. We use a model based on the Gamma distributions of the nondimemsional pore diameters. The volume fraction (porosity) of each pore group is proportional to the second moment of the distribution. We have calculated effective cross-section area and phonon mean free paths at scattering on randomly distributed pore boundaries and obtained a general relationship for the LTC in porous materials for an arbitrary number of pore groups with various size scales. We have shown that the presence of the pores with all-scale hierarchical disorder leads to a considerable reduction in the LTC and have estimated that in the presence of nano and microscale pores. Particularly, we have shown a possibility for the reduction of the LTC more than in two orders in several specific cases, which can be very useful for a large enhancement in the thermoelectric figure of merit of porous semiconductors.

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Monte Carlo Simulations Of Thermal Conductivity Nanoporous Si Membranes

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Nanoporous membranes made of single-crystalline Si (otherwise referred to as 'holey' Si) are promising candidates for thermoelectric materials as they can provide extremely low thermal conductivities, relatively