# DS 42: Thermoelectric Materials

Time: Thursday 15:00–19:00 Location: CHE 89

DS 42.1 Thu 15:00 CHE 89

**Thermoelectric Property Modification in Hybrid Semiconducting/Metal Superlattices and Local Characterization by SThM** — •Guodong Li[1,2], Daniel Grimm[1,2], and Oliver. G Schmidt[1,2] — [1]Institute for Integrative Nanosciences, IFW Dresden, Germany — [2]Technische Universität Chemnitz, Material Systems for Nanoelectronics, Germany

Nanostructured materials show great promising applications in thermoelectric industry not only owing to their intrinsic quantum confinement effects but also related to the enhanced boundary or interface scattering to phonon transport. The ideal modified thermoelectric structures should have much decreased thermal conductivity while keeping thermal power unaffected or even enhanced. Here, we combine the self-rolling and compressing technique to demonstrate a straight forward route to make hybrid superlattices consisting of a large number of nanomembranes that are mechanically stacked on top of each other. Depending on what kind of material we choose as the interfacial layer, we have successfully fabricated superlattices composed of different kinds of hybrid interfaces. Together with conventional time-domain thermoreflectance (TDTR) method that shows the cross-plane thermal conductivity of as-fabricated superlattice being nearly two orders of magnitude smaller than the thin film, we also characterize the local thermal transport property by using scanning thermal microscopy (SThM) technique. By taking the standard thermal samples as references, we are purposing to develop a quantitative model to characterize the cross-plane thermal transport property of fabricated superlattices.

DS 42.2 Thu 15:15 CHE 89

**Thermoelectric properties of meso-porous thin films from laser-assisted wet-chemically doped group-IV nanoparticles** — •Anton Greppmair[1], Benedikt Stoib[1], Tim Langmann[1], Nils Petermann[2], Hartmut Wiggers[2], Martin Stutzmann[1], and Martin S. Brandt[1] — [1]Walter Schottky Institut, Technische Universität München, Am Coulombwall 4, 85748 Garching — [2]Institut für Verbrennung und Gasdynamik, Universität Duisburg-Essen, Lotharstraße 1, 47048 Duisburg

We present recent studies on the morphology and the thermoelectric properties of thin films of laser-sintered group-IV nanoparticles. The structure size of the meso-porous network can be controlled by the laser fluence used for sintering, doping is achieved by immersing the nanoparticle film in a liquid containing the dopants prior to sintering. Conductivity and thermopower measurements provide insight into the doping efficiency and confirm n- and p-type doping. For the doping with group-V elements we find a threshold concentration, above which the conductivity can be increased by several orders of magnitude using different dopant concentrations in the dopant solution. Adsorption of the dopant atoms to the nanoparticles is the limiting process for the doping efficiency. The doping process was successfully transferred to various SiGe alloy compositions ranging from pure Ge to pure Si. Thermal properties were also investigated by microscopic infrared thermography.

[1] B. Stoib et al., Physica Status Solidi A **210**, 153 (2012)

DS 42.3 Thu 15:30 CHE 89

**Thermoelectric transport in $Sb_2Te_3$ thin films** — •Nicki F. Hinsche[1], Florian Rittweger[2], Tomáš Rauch[1], Jürgen Henk[1], and Ingrid Mertig[1,2] — [1]Martin-Luther-Universität, Institut für Physik, Von-Seckendorff-Platz 1, DE-06120 Halle — [2]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, DE-06120 Halle

Bulk chalcogenides, e.g. $Bi_2Te_3$ and $Sb_2Te_3$, as well as related heterostructures and ternary alloys are well known as efficient thermoelectric materials [1,2]. Today these chalcogenides are known to be strong topological insulators, i.e. their bulk is insulating, while their surface is metallic due to the presence of robust gapless surface states [3]. While the spin structure and the low-temperature electrical transport gained much attention, the physics at room temperature and the thermoelectric transport is still under debate. To contribute on this, we studied the electronic structure of $Sb_2Te_3$ thin films, with 3-36nm thickness, with a fully relativistic screened Korringa-Kohn-Rostoker Green's function method. The thermoelectric transport properties were calculated within the relaxation time approximation of the Boltzmann theory. The influence of thickness, temperature and doping on the thermoelectric transport properties of the surface states were analysed in detail.

[1] T. M. Tritt *et al.*, MRS bulletin **31**, 188 (2006); [2] N. F. Hinsche *et al.*, Phys. Rev. B **86**, 085323 (2012); [3] H. Zhang *et al.*, Nature Phys. **5**, 438 (2009);

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**Reduction of Thermal Conductivity in Si-Isotope-Multilayers** — •Michael Bachmann, Michael Czerner, and Christian Heiliger — I. Physikalisches Institut, Justus Liebig University Giessen, D-35392, Germany

The electronic parameters of Silicon show that Silicon is a promising thermoelectric material. The only drawback of using Silicon as a thermoelectric material is its high lattice thermal conductivity. One idea to reduce the lattice thermal conductivity is the manufacturing of Si-isotope-multilayers. It is expected, that in such structures the phonon-phonon scattering is enhanced due to the mass change at the interfaces between the layers, whereas the electronic transport is unaffected. We present phonon transport calculations based on an atomistic Greens function method [1] for $^{28}Si/^{29}Si$ and $^{28}Si/^{30}Si$ isotope-multilayer. These results show that a periodic arrangement of the layer-system cannot decrease the phonon thermal conductivity substantially, whereas a random arrangement of the layer-system can lead to a strong decrease in the phonon conductivity. We also show that small deviations from the periodic arrangement are enough to end up in the random regime.

[1] W. Fisher, T.Mingo, N.Numerical Heat Transfer, Part B: 2007, 51, 333

DS 42.5 Thu 16:00 CHE 89

**Full ZT and Crystallographic Characterization of Individual Bismuth Telluride Nanowires** — •Danny Kojda[1], Rüdiger Mitdank[1], Anna Mogilatenko[2], William Töllner[3], Zhi Wang[4], Michael Kröner[4], Peter Woias[4], Kornelius Nielsch[3], and Saskia F. Fischer[1] — [1]AG Neue Materialien, Humboldt-Universität zu Berlin, D-10099 Berlin — [2]Ferdinand-Braun-Institut, Leibniz-Institut für Höchstfrequenztechnik, D-12489 Berlin — [3]Institut für Angewandte Physik, Universität Hamburg, D-20355 Hamburg — [4]Laboratory for Design of Microsystems, University of Freiburg - IMTEK, D-79110 Freiburg

Thermoelectrical properties of nanowires (NWs) have been investigated because of their potential in energy conversion. In order to determine the thermoelectric figure of merit $ZT$ of NWs, individual electrochemically grown bismuth telluride ($Bi_2Te_3$) NWs [1] are transferred to a micro device (TNCP)[2] and contacted using electron beam induced deposition (EBID) of platinum. The TNCP design allows a complete thermoelectric characterization and structural and compositional analysis by transmission electron microscopy (TEM) for the same NW. We measured the electrical and thermal conductivity $\lambda$ ($3\omega$-method) as well as the Seebeck coefficient for an individual $Bi_2Te_3$ NW at room temperature. These measurements give $\lambda = 0.8$ W/(mK) and $ZT \approx 0.1$. TEM measurements reveal a textured crystal orientation preserved along the whole NW and a rough surface morphology.

[1] W. Töllner *et al.*, Adv. Func. Mater. **22**, 151 (2012)
[2] Z. Wang *et al.*, IEEE 26th Intern. Conf. on MEMS 2013, pp. 508.

DS 42.6 Thu 16:15 CHE 89

**Full thermoelectric characterization and Lorenz number of individual metallic nanowires** — •Rüdiger Mitdank[1], Danny Kojda[1], Zhi Wang[2], Michael Kröner[2], Peter Woias[2], and Saskia F. Fischer[1] — [1]AG Neue Materialien, Humboldt-Universität zu Berlin, D-12489 Berlin, Newtonstr. 15 — [2]Laboratory for Design of Microsystems, University of Freiburg , IMTEK, D-79110 Freiburg

A full characterization of the thermo electrical properties of nanowires (NWs) needs information about Seebeck coefficient as well as electrical and thermal conductivity. In order to determine the thermoelectric figure of merit of NWs, individual NWs are transferred to a micro machined measurement platform (TNCP) [1] and contacted by electron beam induced deposition (EBID) with platinum. A special issue of such measurements consists in the determination of the thermal conductivity (3-Omega-method). The compliance with boundary conditions and the presence of thermal contact resistances are discussed.

Especially, we present a technique to determine the Lorenz number L from the ratio of two voltages. We observed a Lorenz number L smaller than the Sommerfeld value Ls. This difference increased with decreasing temperature. The deviation of L from Ls is compared with different models.

[1] Z. Wang et al., IEEE 26th Intern. Conf. on MEMS 2013, pp. 508.

DS 42.7 Thu 16:30 CHE 89

**Phonon thermal conductivity in cross-section modulated Si wires: A transition from nano- to microscale regime** — Alexandr I. Cocemasov[1], Denis L. Nika[1], •Vladimir M. Fomin[2], Daniel Grimm[2,3], and Oliver G. Schmidt[2,3] — [1]E. Pokatilov Lab., Dep. Theor. Phys., Moldova State University, Chisinau MD-2009, Rep. of Moldova — [2]Institute for Integrative Nanosciences, IFW-Dresden, D-01069 Dresden, Germany — [3]Material Systems for Nanoelectronics, Chemnitz University of Technology, D-09107 Chemnitz, Germany

Periodically modulated nanowires are perspective for thermoelectric applications due to low values of phonon thermal conductivity [1-2]. At present, modulated profiles can be fabricated at the scale of tens and hundreds nm. We have studied a transition of phonon thermal transport in cross-section modulated Si wires from nano- to microscale regime, considering phonon spectra for modulated nanowires obtained within an atomistic model of lattice dynamics and scattering of bulk Si phonons on external faces of the modulated segments for microstructures. For a Si wire of a square cross-section with side $d$, modulation depth of $d/10$, modulated segment width of $d/4$ and distance between neighboring modulated segments of $3d/4$, the transition from the nano- to microscale transport regime at room temperature occurs at $\sim$ 100 nm. The work was supported by Moldova State Projects 11.817.05.10F and 12.819.05.18F. A.I.C. acknowledges the support by DAAD.
[1] D. L. Nika, A. I. Cocemasov, C. I. Isacova, A. A. Balandin, V. M. Fomin, O. G. Schmidt, PRB 85, 205439 (2012). [2] D. L. Nika, A. I. Cocemasov, D. V. Crismari, A. A. Balandin, APL 102, 213109 (2013).

DS 42.8 Thu 16:45 CHE 89

**Phonon processes in silicon crystalline quantum wires with amorphous surface** — Dmitrii V. Crismari[1], Denis L. Nika[1], •Vladimir M. Fomin[2], Daniel Grimm[2,3], and Oliver G. Schmidt[2,3] — [1]E. Pokatilov Lab., Dep. Theor. Phys., Moldova State University, MD-2009 Chisinau, Republic of Moldova — [2]Institute for Integrative Nanosciences, IFW-Dresden, D-01069 Dresden, Germany — [3]Material Systems for Nanoelectronics, Chemnitz University of Technology, D-09107 Chemnitz, Germany

Advancements in high-tech fabrication have attracted interest to the investigation of amorphous microstructures, e.g., Si-based microtubes and radial superlattices with amorphous silica layers [1]. We study phonons in crystalline Si quantum wires with amorphous surface using the Valence Force Field approach with stochastic parameters of interatomic interactions. The phonon thermal conductivity (PTC) is calculated taking into account the phonon-phonon and phonon-surface scattering. Non-zero-velocity phonons, which penetrate amorphous coating, are strongly scattered there and removed from the heat transport. A considerable suppression of the PTC is revealed for experimentally feasible structures. Even for wide (cross-section sizes of 0.5 to 1 $\mu$m) quantum wires with amorphous surface, the PTC is suppressed by a factor of 1.5 to 2 as compared with fully crystalline ones. The suppression significantly increases in quantum wires of smaller cross-section. The work was supported by Moldova State Project 11.817.05.10F. D.V.C. acknowledges the support by DAAD. [1] R. Songmuang, A. Rastelli, S. Mendach, and O. G. Schmidt, APL 90, 091905 (2007).

**Coffee break (15 min)**

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**Half Heusler compounds as high performance thermoelectric materials** — •J Schmitt[1,2], Z Gibbs[2], J Snyder[2], and C Felser[1,3] — [1]Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg-University, Mainz, Germany — [2]Materials Science, California Institute of Technology, Pasadena, USA — [3]Max Planck Institute for Chemical Physics of Solids, Dresden, Germany

Half Heusler compounds with the general formula $X$NiSn crystalize in a $C1_b$ cubic structure. They are considered to be promising thermoelectric materials because of their low costs and they consist of environmentally friendly elements. Those with 18 valence electrons are expected to be narrow band gap semiconductors. Numerous compounds have been studied focusing on their high thermoelectric properties. The majority of these materials in the class of $X$NiSn-systems are n-type thermoelectrics. In this study we investigated the thermoelectric behavior of the $Zr_{1-x}Sc_x$NiSn (x¡0.15) solid solutions, a p-type counterpart of the high $zT$ n-type ZrNiSn family. Measurements of the carrier concentration, Hall mobility, electrical resistivity, thermal diffusivity and thermopower were measured up to 850K. The substitution of Zirconium by Scandium, which possesses one valence electron less, lead to a domination of holes as charge carriers changing the sign for the Seebeck coefficient and the Hall carrier concentration. From the Hall measurements lower mobilities as expected were observed. This observation can be understood within the model of mixed conduction, leading to a depression of the thermopower or bipolar effects in thermal transport measurements.

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**Simulation Study on Thermoelectric Half Heusler Materials** — •Heiko G. Schoberth, Heike Emmerich, and Thomas Gruhn — Material- und Prozesssimulation, Universität Bayreuth, 95447 Bayreuth, Germany

One major task in the development of new thermoelectric materials is to increase the figure of merit by lowering the thermal lattice conductivity. This can be achieved with nanostructured thermoelectrics, in which the phonons are damped at the cluster interfaces. Of special technological interest of thermoelectric materials are CoSb- or NiSn-based half Heusler compounds, in which a complex domain structure forms by partial demixing of the material during the production process [T. Graf et. al., Scripta Mater. 63, 625 (2010)]. We have studied the miscibility of (Ti,Z)CoSb with Z=Cr,Fe,Mn,V,Sc and (Ti,Zr,Hf)NiSn with the help of ab initio calculations. On the one hand, (Ti,Z)CoSb does not show a miscibility gap in the equilibrium state. Therefore, domain structures found in the experiments must result from the preparation method. On the other hand, demixing is found for (Ti,Zr)NiSn and (Ti,Hf)NiSn, while (Zr,Hf)NiSn mixes. We have used a cluster expansion method which provides pseudo-hamiltonians from the first-principles calculations. They are used to perform Monte Carlo Simulations to analyze statistical properties and the phase diagram of the systems, as well as the structure of the domain boundaries. The results will enter later on into phase field simulation to cover the full range from atomistic to micrometer length scale.

DS 42.11 Thu 17:45 CHE 89

**Long term stability of Half Heusler compounds at high temperatures** — •Julia Krez[1,2], Benjamin Balke[1], and Claudia Felser[1,3] — [1]Johannes Gutenberg University Mainz, Mainz, Germany — [2]Graduate School of Excellence MAINZ, Mainz, Germany — [3]Max Planck Institute for Chemical Physics of Solids, Dresden, Germany

Half-Heusler compounds attracted much attention to be a promising materials for thermoelectric applications in a medium temperature range (470 - 770 K). The recovery of waste heat from e.g. automotive and industrial devices requires not only powerful materials in a particular temperature range but also long term stability regarding to a commercial success. Recent works have shown approaches for an up-scaling of the material synthesis and first constructions for thermoelectric modules with Half-Heusler. This work presents the latest results on a long term stability study of Half-Heusler compounds in a temperature range from room temperature up to 873K. The thermoelectric properties of n- and p-type materials were measured in a cycle test after 50, 100 and 500 cycles.

DS 42.12 Thu 18:00 CHE 89

**Phase separation as the key to thermoelectric highly efficient Heusler compounds** — •Benjamin Balke — Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg - University, Mainz, Germany

The Half-Heusler compounds are one of the most promising candidates among the high-temperature thermoelectric materials being investigated for automotive and industrial waste heat recovery applications. For n- as well as p-type materials ZT values with peak values larger than one have been published recently and first modules have been built. In this talk, we will give an overview about our recent investigations about phase separation in the thermoelectric Heusler compounds. We will present the most recent results on our studies on the phase separations in the quasi-ternary system TiNiSn-ZrNiSn-HfNiSn. Studying

patents and publications the last two years carefully one could read a lot about not-single phase samples inside of the TiNiSn-ZrNiSn-HfNiSn system. Furthermore, we will show how we adapted this knowledge to design a p-type Heusler compound which led to a ZT increase of 50% compared to the best published bulk p-type Heusler compound in the literature. This results strongly underline the importance of phase separations as an important tool in the design of highly thermoelectric efficient materials which fulfill the industrial demands for a thermoelectric converter. In the end, I will briefly discuss the most recent development of thermoelectric modules using Heusler compounds.

DS 42.13 Thu 18:15 CHE 89

**Reduced thermal conductivity in Half-Heusler superlattices** — •Paulina Holuj[1], Tino Jaeger[1], Benjamin Balke[2], Sascha Populoh[3], Anke Weidenkaff[3], Claudia Felser[2], and Gerhard Jakob[1] — [1]Institute of Physics, University of Mainz, Germany — [2]Institute of Inorganic and Analytical Chemistry, University of Mainz, Germany — [3]EMPA, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

Research on thermoelectric materials has strongly increased in recent years due to their high application potential in production of a clean energy from wasted heat. Despite many advantages, their weakness is the limited efficiency, that is related to the dimensionless figure of merit $ZT = \alpha^2\sigma\kappa^{-1}T$. One of the approaches to enhance $ZT$ is the reduction of the thermal conductivity by phonon scattering at the interfaces of a superlattice (SL), keeping electrical parameters ($\alpha^2\sigma$) unchanged.

The ability to produce good quality SLs made out of Half-Heusler compounds is demonstrated by a clearly visible satellite peaks in X-ray diffractograms. Additionally, measured data are in good agreement with simulated patterns. Expected reduction of the thermal conductivity of TiNiSn/$Zr_{0.5}Hf_{0.5}$NiSn SLs has been obtained by the differential $3\omega$ method. High temperature measurements of the Seebeck coefficient show a reversible behavior up to 550 K, revealing the stability of SLs up to this temperature range.

Currently HfNiSn, another member of the family of Half-Heusler materials is under investigation, where the ratio of interface scattering to atomic disorder scattering is enhanced.

DS 42.14 Thu 18:30 CHE 89

**Thermal conductivity of nano-structured thermoelectric materials** — •Chandan Bera[1], Lasse Bjerg[2], Ankita Katre[1], Georg K. H. Madsen[1], and Ralf Drautz[1] — [1]Department of Atomistic Modelling and Simulation, ICAMS, Ruhr-Univesität Bochum, Germany — [2]Center for Materials Crystallography, Department of Chemistry & iNANO, Aarhus University, Denmark

Manipulating the thermal properties of materials by nano-structuring is new successful route to improve the performance of thermoelectric materials. We present a new parameter free model to predict anharmonic scattering in bulk and nanoscale materials. Velocities and anharmonic scattering rates are calculated from the Grüneisen parameter of the full phonon dispersions and used to calculate the lattice thermal conductivity using the phonon Boltzmann transport equation in the relaxation time approximation. We find good agreement with experiments for a range of materials. Furthermore, we show that our model, as opposed to simple models based on only the acoustic bands, finds the correct trend in the thermal conductivity of Mg2Si, Mg2Ge and Mg2Sn. We also examine thermal transport in more complex materials like Type-I Si clathrates and zinc-antimonides. Finally, discuss how nano-structure and disorder effect the thermal conductivity.

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**Phonon drag effect in $FeGa_3$** — Maik Wagner-Reetz[1], •Deepa Kasinathan[1], Walter Schnelle[1], Raul Cardoso-Gil[1], Helge Rosner[1], Peter Gille[2], and Yuri Grin[1] — [1]MPI CPfS, Dresden, Germany — [2]LMU Munich, Germany

The thermoelectric properties of single and polycrystalline $FeGa_3$ are systematically investigated over a wide temperature range. At low temperatures, below 20 K, pronounced peaks in the thermal conductivity ($\approx$800 $W K^{-1} m^{-1}$) with corresponding maxima in the thermopower ($\approx$16000 $\mu$V/K) were found. Such large values have previously not been reported in $FeGa_3$. Measurements along [100] and [001] directions indicate only a slight anisotropy in both the electrical and thermal transport coefficients. From susceptibility and heat capacity measurements, a structural or magnetic phase transition as a possible reason for the low temperature enhancement in thermopower and thermal conductivity can be exculded. After careful considerations, we assign the peaks in the thermopower as a manifestation of the phonon-drag effect. Using density functional theory based calculations, we have revisited the electronic structure of $FeGa_3$ and compared the magnetic (including correlations) and non-magnetic electronic structure. Thermopower at fixed carrier concentrations are calculated using semi-classical Boltzmann transport theory and the calculated results match fairly with our experimental data.

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