Executive Summary:
NanoHiTEC is a concerted effort to develop advanced thermoelectric converters based on thin-film technology. Three aspects of the project are noteworthy: First, a focus on nanostructures of comparatively inexpensive materials as the basis for high performance thermoelectric materials. Second, an account of integration issues at the device level, including the appropriate design of all device-components and materials, as required by their function in a specific fabrication process and device layout. And three, an emphasis on the economic viability of the designs and associated fabrication processes, given the present market for waste-heat energy recovery, including the environmental impact of the devices and recycling. Extensive work was carried out to model thermoelectric nanostructures down to atomistics, in order to identify materials’ design guidelines. These helped refine the goals of the materials development
processes, especially for n-type Si/SiGe multilayers and p-type B4C/B9C multilayers. The fabrication was based on industrially relevant thin film deposition techniques, specifically magnetron sputtering and electrodeposition. Expressly avoided were atomic layer deposition techniques, which, though effective (cf. results from Hi-Z, San Diego, CA, USA), are inherently inadequate for industrial-scale production on account of their exceedingly low deposition rates. Electrodeposition was however found inadequate as well, as a method for fabricating the desired Si/SiGe multilayers, on account of the insufficient film quality, exceedingly low tolerance to chemical impurities at all stages of the process, and insufficient rates. The physical processes during deposition in conventional magnetron sputtering further proved to be incompatible with the fabrication of highly doped, nano-crystalline Si- and Ge-based thermoelectric semiconductors. Nevertheless, a modified magnetron sputtering processes successfully yielded the desired materials.

From a device-level point of view, it was found that significant power output gains could be realized even retaining conventional thermoelectric materials (particularly in automotive applications), provided the heat flow through the device was optimized. That places constraints on the geometry of the thermoelectric materials and requires improving heat exchanger performance. Two different thin-film TEC designs proposed take advantage of these conclusions. A first design uses thin film TEC elements that can be assembled with conventional chip assembly techniques. TECs derived from this design are currently in the final stages of commercial production. A second design exploits the possibilities from a greater use of thin-film techniques. Both the use of thin film forms, with correspondingly reduced need for raw materials, and the fabrication by sputtering, which reduces scrap and simplifies recycling, concurrently address the final objective of NanoHiTEC concerning economic viability and low environmental impact.

Project Context and Objectives:
Thermoelectric converters (TECs) are devices that can exploit a temperature difference to produce electric power, or conversely, utilize a current for heating or cooling. The TEC’s component that converts a temperature difference into an electric potential difference is a pair of n-type and p-type semiconducting materials bridging the hot and cold temperature reservoirs, in essence like a set of daisy-chained thermocouples. Ideal thermoelectric materials will feature a low thermal conductivity, a large electrical conductivity, and a large Seebeck coefficient. State of the art materials for temperature ranges up to about 300 °C are based on BiTe.

To-date thermoelectric converters have been confined to niche applications, such as coolers for comparatively costly electronic components. These TEC devices are largely assembled from macroscopic thermoelectric material pieces, a characteristic that is behind a large assembly cost. Likewise, the large amount of thermoelectric material per device constitutes a large cost. The problem is exacerbated by the fact that due to its better performance, about 80% of the market in thermoelectrics is served by Bi2Te3-based technology, and hence is reliant on Tellurium, the abundance of which is 10-9 g Te/g on the earth’s crust. (For comparison, the abundance of Platinum is 3.7 x 10-8g Pt/g). Furthermore, Te is a toxic material, and disposal and safety measures add to the cost of a TEC device.

Against this backdrop researchers have long searched for alternative thermoelectric materials with the aim of increasing the output per cost, mainly through a performance increase of the thermoelectric material. Nanostructured materials have been predicted theoretically to display a very good performance at low cost. Based on this prediction, it was shown that atomic layer deposition (ALD) of Si-Ge multilayers yields good thermoelectric materials. Unfortunately, the deposition rate in these processes is low, whereby the
effective cost of fabrication becomes prohibitive. Alternative fabrication methods are needed. Driven by the goal of increasing the thermoelectric figure of merit (ZT) of the thermoelectric materials, research placed a smaller emphasis on the design of the TEC device as a whole. Yet that is necessary to optimize the amount of heat flowing through the thermoelectric materials, which is what is ultimately converted to useful power, or conversely, to optimize the cooling/heating effect from a current sent through the device. Consequently, potential performance gains exceeding those attainable by thermoelectric materials’ improvements have not been realized.

NanoHiTEC addresses the above problems. For effectiveness, the emphasis is set on a particular application, even though the solutions developed in this work can be transferred to other applications and thermoelectric materials. We identified automotive energy recuperation as a target application for the thermoelectric devices developed within NanoHiTEC, and a long term goal of the consortium’s industrial partners includes taking this application to market. Also other fields of application were recently identified, that would be well-suited for the TEC devices that are closest to commercialization. In line with this objective, NanoHiTEC worked on developing alternative thermoelectric materials which have a better cost-to-performance ratio.

We have developed analytical modelling tools to describe and explain electrical and heat transport in SiGe-based thermoelectric materials. Our findings reveal that channeling carriers can give rise to a significant increase in ZT values.

We have made progress in developing the most promising types of thermoelectric nanostructured materials, in particular n-type Si/SiGe multilayers and p-type B4C/B9C multilayers. Note that Si/SiGe has been successfully fabricated by ALD by Hi-Z of San Diego, CA, USA, but such a process is not economically viable. We have focused instead on magnetron sputtering and electro-deposition, which could be used in commercial-scale production.

With magnetron sputtering we fabricated Si, Ge, and SiGe films. These films are the basis for the multilayered thermoelectric materials. The dopant levels however remained lower than desired for a high performance thermoelectric material. For example concerning doping with Sb, one problem identified in the course of the work was grain boundary segregation and diffusion of the dopant atoms. Inasmuch as the doping largely determines the electrical conductivity, especially in Si- or Ge-nanostructures, this strongly affects the power factor of the materials, as our theoretical results show.

To circumvent these problems, we investigated the fabrication of these films with very high deposition rates or with very low energies, as a route to producing denser films with higher degree of crystallinity and doping. We designed and fabricated the appropriate changes in the film deposition hardware, which has led to a patent application.

Parallel to this development run efforts to fabricate p-type B4C/B9C films, a possible counterpart to the Si-Ge structures, which ultimately will be n-type doped. We have investigated the reaction mechanism of boron-rich boron-carbides, as well as the reactions leading to the formation of an n-type compound, creating the basis for materials’ optimization. For the preparation of nano-sized boron carbide powders we have developed three synthesis approaches. By variation of corresponding molar ratio of starting materials different boron carbides with average particle size around 100 nm within the homogeneity range could be achieved. Up scaling of obtained powder quantity is now in development. Using Spark-Plasma-Sintering (SPS) technology we have studied the sintering properties of the prepared nano-sized powders, a manufacture process of nanostructured bulk boron carbide with small grain growth is established.

As alternative to sputtering for the preparation of B4C/B9C films, manufacture routes were carried out using conventional mixing of B4C/B9C powders and tape casting technique. Furthermore, dense B4C and
B9C sputter targets with large size were successfully produced. Sintering of boron carbide bulks was successful. The grain size of boron carbide was kept in sub-micron range by using a field assisted sintering technology (FAST). Targets for sputtering of B-C containing thin films are available now and have been delivered to project partners. Thus, NanoHiTEC has provided the basic boron carbide materials technology that could now be utilized in thermoelectric devices.

NanoHiTEC also helped to improve a sputtering process for Bi-Te-based thermoelectric materials. Very favorable material properties with grain sizes in the nanometer scale could be achieved by the collaboration between the sputter tool manufacturer, the sputter tool user and groups with profound analytical know-how. Grain sizes down to 5 nm made by sputtering are a convenient way to manufacture material that fulfils the phonon glass-electron crystal concept. Although this materials’ system was a priori deemed inadequate in the long run on account of cost- and environmental considerations, it allows the fabrication of actual devices. From these we can gain valuable insight into the issues affecting the TEC design, before the other parts of the project are completed. Using passive components designed to accommodate the strains expected from thermal cycling, we are currently at the stage of characterizing the assembled TECs. The commercialization of products based on these prototypes is currently being discussed with potential customers.

This Bi-Te development becomes even more important in light of our recent conclusions from a theoretical analysis of waste heat harvesting at the device level. As we point out, the optimal designs call for thermoelectric materials operating at significantly lower temperatures than originally expected. Only half the available temperature difference between the exhaust gases and the coolant will be sustained over the thermoelectric materials. Furthermore, under the assumption that in automotive TECs the coolant will be water, the thermoelectric material will be closer to the coolant temperatures than the hot exhaust temperatures. This brings it within the temperature window where BiTe-based materials have peak performance. Moreover, we can see that what is limiting performance in this application is not the thermoelectric material but the heat exchangers. There are important consequences to this. First, criteria other than the thermoelectric figure of merit may guide the selection of a thermoelectric materials’ system, in particular cost per volume and environmental impact. Second, the importance of good thermal connections between heat exchangers and thermoelectric materials is raised to a high priority. NanoHiTEC has adapted to this new scenario by increasing the priority assigned to the alternative thermoelectric materials’ development, work which was purposely included in the project to allow rapid response to the present situation. In particular, we are now pushing the development of Cu2-xSe, a thermoelectric material that was unknown at the start of NanoHiTEC. It combines low cost and low toxicity with potentially good thermoelectric performance at temperatures expected to prevail in power-optimal automotive applications. Cu2-xSe films were grown by RF-sputtering Cu in a controlled Se gas atmosphere, and the crystallinity and Seebeck coefficients optimized.

Addressing the importance of thermal connection quality, we have designed a thin-film fabrication process which relies almost entirely on magnetron sputtering. Given the relation between power output and thermal impedance of the heat exchangers, a sizeable performance enhancement is expected. Test devices using Si legs instead of thermoelectric materials have been fabricated and passed preliminary thermal cycling strain tests. Numerical simulations of device designs with this technology indicate a good match between our estimates and expected performance in application.

Perhaps most importantly in view of commercial embodiments of these technologies and insight, the
proposed fabrication method for the devices is expected to allow maintaining per-part costs low, and to simplify recycling of scrap – thereby indirectly also improving the environmental impact of the technology. An important aspect of the project has been to achieve worldwide publicity for our work, such that the results could be adopted by an extensive community of industry and academia. To that end we have disseminated the results internally at company/institute level; we have organized internal workshops/meetings between partners; created links with other European projects in the area of TE. Part of this activity was organized through the dissemination plan that was updated periodically every 6 months. Further, in the course of the project we produced a total of 28 presentations and 12 publications reaching worldwide audiences. Additional publications are being prepared. The work included a best paper award for TU Vienna, presentations at automotive OEM customers and regular attendance to the Nano4TE cluster meetings, as well as ICT and ECT conference (note the plenary talk by H. Rohrmann). Leveraging on the project results the Christian Doppler Laboratory for TE was founded at TU Vienna, and new TE design concepts have been introduced by Partner EMPA and a joined patent application has been prepared among project partners.

Thus NanoHiTEC has successfully addressed all aspects of the proposed work, largely achieving its goals. We also identified the materials characteristics and physical processes that hinder TEC layer fabrication. Then we proposed and explored alternative fabrication processes where cost considerations did not rule out prima facie the commercial exploitation of the techniques. Devices based on sputtered Bi-Te films are now being rolled out commercially. The insight gained from this work has yielded device designs and fabrication processes which are expected to be ideally suited for the automotive market.

Project Results:

4.1.3.1 Modelling work

The ability of a material to convert heat into electricity is measured by the dimensionless figure of merit ZT. Its definition, \( ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_l} \), contains the electrical conductivity \( \sigma \), the Seebeck coefficient \( S \), the lattice thermal conductivity \( \kappa_l \), and the electronic part of the thermal conductivity, \( \kappa_e \).

The numerator in the expression above is referred to as the electronic power factor, \( PF = \sigma S^2 \). It is an electronic property of the material and can be influenced by band structure engineering, location of the Fermi level, and tailoring the carrier scattering mechanisms. The dominant term in the denominator is the thermal conductivity \( \kappa_l \), which needs to be reduced by the introduction efficient scatterers for phonons, i.e. the carriers of heat. The best thermoelectric bulk materials are exhibiting \( ZT \approx 1 \). In the past it has been challenging to increase \( ZT > 1 \) since the parameters controlling \( ZT \) are generally interdependent and optimizing one physical parameter often adversely affects another. Nanotechnology offers an opportunity to mitigate the interdependence of the parameters and thus to increase TE performance.

In this workpackage, we studied the TE properties of ultra-thin layers of Si or Ge. Using an atomistic description of the layers (Fig. 1.1) a simulator was developed to extract the properties of channels in different transport orientations, confinement orientations, and confinement length scales.

Figure 1.1: The atomistic description of the semiconductor thin films

Typical results of electronic structure calculations using the tight-binding model are shown in Fig. 1.1. Figures 1.1c-d show the electronic structure for the (110)/(110) channel of width \( W=15\text{nm} \) and \( W=3\text{nm} \), respectively. The most important observation here is that for this channel the electronic structure changes dramatically in the [110] orientation as the width is reduced.
For the extraction of the electronic transport properties (i.e. mobility and electrical conductivity) of thin films, we couple the sp3d5s* tight-binding model and a linearized Boltzmann transport model. Fermi’s Golden rule is used to extract the momentum relaxation rates. We include scattering due to acoustic phonons (ADP), inelastic optical phonons (ODP), and surface roughness (SRS).

The electronic and thermoelectric properties of semiconductor thin films have been thoroughly investigated. Figure 1.3a shows the electrical conductivity of p-type Si layers as a function of the layer thickness W. Clearly, the (110)/[110] channel is advantageous at all thicknesses compared to the other channels considered. The dependence of the Seebeck coefficient on the layer thickness is shown in Fig. 1.3b. At larger thicknesses, S is very similar for all channels. As the thickness is reduced, S decreases in the (110) layers, slightly decreases in the (112) layers, and increases in the (100) layers. The power factor trend with W is shown in Fig. 1.3c. The (110)/[110] channel outperforms the rest of the channels by more than 2X in the entire range of the examined thicknesses, despite the fact that S decreases for that channel at smaller thicknesses.

Important findings for ultra-thin Si layers from band structure engineering:
(i) Large anisotropy is observed in the thermoelectric properties of Si thin layers. The p-type (110)/[110] channel has the highest power factor, more than 2x higher than the rest of the channels. Moreover, the power factor in this channel increases with downscaling of the width.
(ii) The power factor is more controlled by the electrical conductivity, than by the Seebeck coefficient. Our work demonstrates that to achieve high power factors at the nanoscale, the quantity to be maximized is the electrical conductivity. This may even come at the expense of a small reduction of the Seebeck coefficient. This goes against the current view, which seeks to maximize the power factor by maximizing the Seebeck coefficient.

Including thermal transport: We have implemented the atomistic valence force-field method to calculate the thermal conductivity of the thin layers. As the layer thickness is reduced, the thermal conductivity decreases significantly. The thermal conductivity of a W=10nm thin layer is reduced to ~7 W/mK, a large reduction compared to the bulk value 142 W/mK. As the thickness is reduced even further to W=3nm, the thermal conductivity drops down to 2-3 W/mK, in good agreement with experimental data. Boundary scattering of phonons is the dominant factor for this large reduction.

After calculating the power factor and the thermal conductivity of the thin layers, ZT can be extracted, see Fig. 1.4. The (110)/[110] channel has the highest ZT, peaking at ZT~0.5 at carrier densities of 1019/cm3. The solid lines in Fig. 1.4 indicate results for which we exclude the influence of SRS. The ZT in this case is much lower, indicating that strong boundary scattering is the reason which provides large thermoelectric performance because it strongly degrades the thermal conductivity. Part of the reason why the (110) surface is so advantageous, however, is that boundary scattering does not affect its electrical conductivity significantly.
The thermoelectric properties in the case of n-type low-dimensional channels are summarized in Fig. 1.5. The figure shows ZT versus diameter for n-type nanowires in [100], [110], and [2.3.] orientations. A ZT maximum of ZTmax=1 can be achieved in all channels, with little orientation dependence. In solid lines we include scattering by phonons, SR, and impurities. Electron-phonon interactions and the strength of surface roughness scattering increase at lower diameters, which reduce the ZT. Ionized impurity scattering is the strongest scattering mechanism, and strongly degrades the electrical conductivity.

From these results it is obvious, that direct doping of the channel will cause large degradation in performance, and alternative strategies to achieve high carrier densities should be employed. One such method is gating of the channels (e.g. by modulation doping), in which case the high carrier densities are achieved by the field effect. We compared the performance of gated versus doped p-type nanowires. Our results show that remarkable power factor improvements up to ~5x can be achieved in the gated p-type channels. These improvements will be noticeable only for NWs with diameter below ~40nm.

Thermoelectric SiGe-based thin films
Sputtered SiGe tends to be amorphous, and is usually subject to an annealing step at high temperatures for crystallinity to develop, typically 600°C – 700°C. Furthermore, high dopant levels are needed because the dopant provides the extrinsic charge carriers that dominate electronic conduction in this semiconductor and give rise to an enhanced thermoelectric effect. However, the dopant atoms must be part of the SiGe crystalline lattice, substituting for either Si or Ge (i.e. the dopant must be activated), because only so can its additional carriers participate in the semiconductor’s electronic conduction, and then eventually reside in its quantum well states, where they become useful for thermoelectrics.

This is problematic. Our results show that at the temperatures needed to crystallize SiGe alloys in a thermal treatment, there is a severe dopant loss, mainly enabled by grain boundary diffusion processes. Neither the usual deposition and annealing temperature optimizations, and tuning of other deposition parameters such as pressure rate, etc. could prevent dopant loss. Also unsuccessful were ion implantation techniques and HIPIMS. Potential solutions were found with implementations of off-axis sputtering, and more preferably by using facing target cathodes, the designs of which have led to a patent application for future commercialization by Oerlikon. Finally, we obtained adequate results using sputter deposition for a metal induced crystallization process based on Al metallic interlayers, for which IP protection was similarly sought (US provisional). Figure 2.1. shows the electrical characterization of representative samples.

Figure 2.1.: Comparison of a) electrical resistance and b) Seebeck coefficient for samples of the scaling series (dA/dSiGe=0.1) measured after an annealing at 600 °C for 1 h.
As discussed in previous reports, the semiconductor-like electrical resistance behavior likely stems from grain boundary potentials inhibiting the charge carriers’ transport. Therefore the electrical resistance is the
lacking performance factor. One possible approach for this predicament would be to further increase the layer thicknesses in the multilayer system while keeping \( \frac{dAl}{dSiGe} \approx 0.1 \) to possibly increase the grain size and such decrease the influence of the grain boundaries. It would be important to not increase the grain size too much, so that the effect of phonon scattering at the grain boundaries is kept intact to lower the thermal conductivity. The effect of scaling up the single layer thickness for constant \( \frac{dAl}{dSiGe} \) can be seen in the x-ray diffractograms shown in Fig. 2.2. All peaks except for the indexed SiGe peaks belong to the polycrystalline LTCC substrate. The diffractograms show an increase in crystallinity of the SiGe for increased Al thickness. For sample LTCC_400SiGe_40Al_600QRO (2.3.)-texturized SiGe is detected.

Figure 2.2.: X-ray diffractograms (2.2) of the samples of the scaling series.

These results appear late in the course of NanoHiTEC, and are a testimony to the difficulty of fabricating thin-film alternatives to conventional BiTe thermoelectric materials by industrial processes. They also suggest a competitive advantage and thus an opportunity to further establish the technological leadership displayed by the NanoHiTEC partners.

Electrodeposition of thermoelectric thin films

Bi2Te3 nanowires arrays were produced by electrodeposition onto alumina templates (Figs. 1b) and c)), optimizing the deposition conditions for a desired crystallographic orientation, e.g. [110] direction (Fig. 2.3.a). The SEM image of the cross-section (see fig. 2.3.b) shows nanowires of 40 microns in length and around 200 nm in diameter. They show an electrical conductivity of 1338 S/cm, and a Seebeck coefficient of -50 µV/K, amounting to a power factor of 335 μW/(m K2). These values are comparable to the film’s.

Figure 2.3.: - Example of the Bi2Te3 nanowire array obtained.

Sb2Te3/Bi2Te3 bilayer nanowires have been produced by electrodeposition using commercial nanoporous alumina templates. The technique offers a high degree of control of experimental conditions, does not require high vacuum and woks at room temperature. In particular, clear interfaces were obtained. Multilayers of pure Sb2.10Te2.90 and Bi1.96Te3.04 nanowires arrays can be observed in Figure 2.4.

Figure 2.4. (left) SEM image of a Sb2Te3/Bi2Te3 multilayer of nanowires composed of 4 distinct layers. (right) TEM of the Bi2Te3/Sb2Te3 interface.

Literature reports on the electrodeposition of Si and Ge films (R. Al-Salman et al. Phys. Chem. Chem. Phys. 10, 4650-4657, 2008) could not be reproduced. Instead, SiGe films could be electro-deposited using an ionic liquid from Io-Li-Tec as solvent for the GeCl4 and SiCl4 precursor salts, provided the water and oxygen levels were kept below 0.1 ppm.

Various deposition conditions, film stoichiometry, substrates, and electrodes were assessed to identify the parameters for which good quality films could be grown. However, there are disparities in the basic characteristics of Si-, Ge-, and SixGe1-x-films.

Germanium films presented nanocrystalline character, as evidenced by XRD (Fig. 2.5). The size of the obtained nanocrystals increased with a post-deposition thermal treatment of 30 minutes at 400ºC, as is indicated by the narrowing peaks in Figure 2.5b (the silicon peak corresponds to the substrate).

Figure 2.5. XRD- (left) and Raman spectra (right) of electrodeposited Germanium films.

The electrodeposition of Silicon films resulted in amorphous material, as can be observed in Fig. 2.6. This material did not crystallize after thermal treatments.
The electrodeposition of Si1-xGex thin films has been also thoroughly studied, in particular with various concentrations of GeCl4 and SiCl4 in [PY,4]Tf2N. Figure 2.7 shows a cyclic voltammogram for 0.8M SiCl4 and 0.2M GeCl4 in [PY1,4]Tf2N, 99%, displaying the peaks corresponding to the deposition of Ge and Si. Nevertheless, the obtained films are stable only during some hours inside protective atmosphere, and degrade almost immediately in contact with air. Moreover, these amorphous materials show very high resistivity, well above 106 Ωcm, and they are not useful in their current form for the implementation of a thermoelectric device.

Figure 2.7. Cyclic voltammogram of gold electrode of 0.8M SiCl4 and 0.2M GeCl4 in [P Y1,4]Tf2N, 99%. Scan rate = 0.01 V.s-1 reference electrode Pt wire.

Additional tests were carried out using molten salts, e.g. 1-butylpyridinium chloride (C9H14ClN), which melts at 120°C and allows working at temperatures conducive to avoiding water. However, we only obtained amorphous films, which furthermore oxidized in matter of hours when exposed to air and had resistivity > 106 Ωcm.

Regarding the fabrication of nanowires, the electrodeposition was accomplished using porous alumina templates and commercial polycarbonate templates. No deposit was observed on the alumina templates (insufficient wetting of the template pores). On polycarbonate templates 500 nm Ge nanowires could be observed in 12 h. The deposit likely becomes too resistive for the electrodeposition process to further continue beyond that.

To summarize this part of the work, Si- and Ge-based electrodeposited films and nanowires have insufficient crystallinity, electrical conductance and stability to be applied in thermoelectric devices. High temperature thermoelectric materials

Thermoelectric materials compatible with high temperature applications (T > 600°C) were developed on the basis of boron carbides. First the synthesis process for nano sized boron carbide particles was established, based on the investigation of the reaction mechanism of boron-rich boron carbides from B4C to BxC. The method uses medium temperatures up to 1400 °C to generate boron carbide from boric acid, boron and starch precursor materials. The particle size can be kept below 100 nm. The powders become available in high quality with controlled B:C stoichiometry in adequate amounts. Figure 2.8 shows a schematic of the processes utilized to fabricated the BC parts.

Figure 2.8: Scheme of experimental approach of preparation of B4C-B9C-Composite

These powders are the basis for manufacturing nanostructured B4C and B9C materials, which could potentially increase the thermo-electrical efficiency significantly. Sintering experiments showed that the densification of nanosized powders is associated with grain growth from 100 up to 400 nm. Further experiments showed that the sintering of B4C and B9C composites leads to a homogenization of the material to an average B-C content. Other experimental series investigated the manufacture of layered B4C/B9C composites. Ceramic tapes have been prepared in advance and were combined with each other (Figure 2.9).

Figure 2.9: Depiction of tape casting B4C-B9C-Composite tapes

Examples of the Seebeck coefficient and conductivity can be seen in Figure 2.10

Figure 2.10: (a) Seebeck coefficient and (b) electrical conductivity for BC-based materials.
Finally, sputter targets of B4C and B9C material were produced for further investigation of the fabrication of BCX-based nanostructures by sputtering.

Passive components and packaging

For a rational selection of passive components in the TEC device various substrate materials and the interaction of the substrates with braze materials was investigated.

Concerning the hot-side contacting, particularly alumina, aluminum nitride and silicon nitride ceramics were tested with various brazes as silver and silver-copper based. Materials for metallization were copper, nickel, stainless steel, molybdenum and tungsten. Defect free ceramic-metal compounds are created for most of the combinations. Simulations helped optimize the design of the TEC modules with regard to reliability and efficiency. Test modules build from the considered passive components and using boron carbide thermoelectric materials as test components (Fig. 3.1) were characterized. The test was performed by cycling between 100°C and 600°C on the hot side and constant temperature of about 100°C on the cold side for more than 1000 cycles. The modules showed outstanding performance with only a slight degradation of power output and thermoelectric voltage.

Figure 3.1: (top left) Images of the stages of bonding BC based thermoelectric materials and the hot and cold-side plates. (top right) Detailed section of the high temperature joint. (Bottom left) Close up image of the joint between BC-thermoelectric and heat exchanger plate.

On the cold side the TE-chip and TE-carrier were successfully joined with a soldering process step, as seen in Fig. 3.2. The TE carrier comprises a compliant part which can absorb the mechanical deformations arising from the necessarily inhomogeneous temperatures. However, thermal cycling revealed degradation in the active components. Replacing the hot side heat exchanger serving the TE-chips with individual fins, directly attached to the TE-chip reduced the thermo-mechanical stresses to more convenient levels.

Figure 3.2: Photo of TE-Chips (Bi2Te3) soldered onto carrier

Further alternative designs more thoroughly rely on magnetron sputtering throughout the fabrication process, and were found to be compatible with various materials systems, in particularly also with the current state of the art Bi-Te based thermoelectric materials. These designs exploit the advantages of additive manufacturing, and are currently in the process of securing IP rights.

Overall, it must be recalled that the primary energy source for thermoelectric generators is thermal energy. Therefore the passive materials and joined interfaces must secure the optimum heat flow through the active materials (for a given cost constraint). The design of the device and especially the passive parts must take this into consideration, whereby different applications will lead to different optimal designs. Efficient heat contacts to the thermoelectric material are desirable and conversely also good insulators between hot and cold sources. The mechanical stability, the thermo-mechanical stability must be given, and a simple manufacturing process must be possible. One way to do that is to use inexpensive and simple structures to compensate thermal expansion, which allows direct material joining instead of clamping. NanoHiTEC developed several solutions to this problem. Two of the approaches benefit from the extensive use of thin film deposition for the fabrication, resulting in fabrication processes that are cheaper and more environmentally friendly. Further, we successfully employed standard IMS as cold plate for TEGs, and tested several combinations of metallized ceramics for the use as hot or cold plate, including Al2O3, AlN, and Si3N4. We also tested several conductive pastes optimized for low temperature.
TEC Device Design

We have identified automotive waste energy recovery as an interesting application from the point of view of the available temperature differentials, potential environmental impact, and economic volume. NanoHiTEC designs of thermoelectric converters were primarily aimed at this application. For energy harvesting applications such as this one, it is important to take into consideration the typical temperatures attainable at cold and hot-side heat exchangers, account taken of the available exhaust heat. Thus it can be seen that the typical temperature differential spanned by a TEC operating in this application is given by exhaust gas temperatures of 500°C and cooling fluid temperatures of 100°C. From the point of view of power generation the optimal temperature drop on the thermoelectric elements under these circumstances is 200°C, with the remaining half of the difference occurring on the heat exchangers. For liquid cooling-fluid systems the heat transfer is more efficient, and hence the temperature drop on the thermoelectric device is situated closer to the low temperatures than to the hot ones. The important consequence of this observation is that Bi-Te based thermoelectric materials have a performance peak in the temperature range of interest, contrary to what was initially assessed.

We designed thermoelectric converters based on magnetron sputtering thin-film deposition, wherein the fabrication technique is not specific to any thermoelectric material. In particular, state of the art Bi-Te based materials, but also the Si-, Ge- and SiGe-based advanced materials developed in NanoHiTEC could be used. The detailed shape and of the heat exchangers and the geometry of the thermoelectric elements has been attuned to the materials development work and the optimization of the passive components and structures.

We fabricated devices that specifically account for the mounting in the exhaust line of gasoline vehicles. As devices featuring BiTe-thermoelectrics and based on the same considerations that went into the prototypes are in the initial stages of commercialization through partner O-Flexx, it becomes possible to estimate costs of production. Set at about EUR 2.-/W power output these preliminary values leave room for economies of scale and optimization, primarily because of the greatly reduced volume of thermoelectric material, the comparatively large fraction of recyclable scrap, and the potential for additional automating of fabrication steps.

Characterization

We have measured various new European driving cycles, to get a better understanding of the energy available as heat in the exhaust gases for a standard driving situation. Determining the crystallographic structure and the microstructure of the thermoelectric materials developed within NanoHiTEC (as for instance revealed in Figure 5.1) was instrumental for understanding the detailed effects of the optimization of the thermoelectric materials.

Figure 5.1: TEM images of n-type Bi-Te film samples. (a), (b) and (c): high resolution images showing polycrystalline microstructure, with grain sizes of the order of 20 – 60 nm delineated by yellow contours. (d) Composition mapping by EDX on selected areas of the film show its inhomogeneity. The electrical characterization of samples with slight compositional and heat treatment variations, in particular of BiTe-based alloys, allowed us to obtain phenomenological rules for the material’s design. One example can be seen in Figure 5.2 where the electrical resistivity and Seebeck coefficients are measured. Typical for these materials, the power factor reaches a maximum at around 150°C (slightly below in this case), as in the example of Fig. 5.3.
Figure 5.2: Electrical resistivity and Seebeck coefficient for different BiTe-based n-type thermoelectric materials from O-Flexx.

Figure 5.3: Electrical resistivity, Seebeck coefficient and power factor for a BiTe-based n-type thermoelectric material from O-Flexx.

The thermal conductivity has been determined with a 3ω-method, using a measurement stage designed for that purpose, as for example for Figure 5.4. From these and the above electrical measurements, ZT values have been determined. In this particular case of BiTe-based n-type films, ZT ranges between 0.22 and 0.62.

Figure 5.4: Thermal conductivity of thin film BiTe samples, from 3ω-type measurements.

A key set of measurements concerns the SiGe-based films, which triggered the materials development effort in NanoHiTEC.

For this material Sb atoms are desired dopants, but because Sb atoms are larger than the atoms in the host lattice, once in it they would strain it. This constitutes a thermodynamic driving force for dopant loss, inhibiting incorporation of Sb into the lattice. Rather, we found be extensive TEM and resistivity measurements on samples constructed for that purpose that dopant atoms diffuse to grain boundaries where they cannot contribute to the thermoelectric properties of the ensemble in the desired way. To try to counteract this effect the strategies discussed above were pursued, all the while minding the need to have appropriately sized crystallites, and foregoing methods that clearly cannot be scaled up (e.g. ALD methods).

MIC-based Al-doped SiGe could be shown to have appropriate dopant characteristics, as discussed above. We could measure the thermal conductivity of these systems on different substrates, for example on sapphire in Figure 5.5.

Figure 5.5: Thermal conductivity of substrates and substrates with MIC SiGe films.

The thermoelectric performance and the electric output of different power strips from O-Flexx has also been investigated in detail.

Bismuth Telluride devices with pn-junctions have shown a considerably higher generated voltage compared to devices without pn-junctions. This higher voltage opens the potential of increasing the power output and the efficiency by a factor estimated at two, depending on the internal resistance achieved. Work on optimizing the TEC devices for pn-junction architectures is ongoing.

Work has also been carried out to characterize other thermoelectric materials, in particular BC-based materials up to about 600°C, e.g. sintered B5C/B9C, and CuSe-based materials.

Potential Impact:

O-Flexx Technologies, partner in NanoHiTEC, is a German technology company that specializes in the field of thermoelectric generators. As such, it has pushed the development of thermoelectric converter technology and Bi-Te based thermoelectric thin films in particular, which it produces by magnetron sputtering from partner Oerlikon. As a result of the work from NanoHiTEC, and with the collaboration of other NanoHiTEC partners, patent application no. 10 2014 110 048.4 has been filed on behalf of O-Flexx and NovaPack. O-Flexx is now beginning to roll out the first commercial products (cf. Figure 6.1) which have benefitted from NanoHiTEC (for more information visit http://www.o-flexx.com/) while the product exploiting the patent pending IP is at sampling and pre-production stage within the 2 SMEs, O-Flexx and...
Another thin film based TEC module construction, mostly sampled between EMPA and NovaPack, still is under consideration for future developments.

Last, an IKTS Ceramic materials based construction is under evaluation for possible exploitation.

Figure 6.1: close up view of a commercially available power strip from O-Flexx mounted on corresponding heat exchangers and hot/cold fluid lines.

With the involvement in NanoHiTEC of tier 1 automotive supplier FECT and CRF, it is expected that the insight gained during the project will contribute to the development of exhaust systems with thermoelectric converters. These in turn should contribute to meeting the guidelines for CO2 emissions, as harvesting electrical energy from the exhaust implies that less fuel is burnt to drive the dynamos that power the car electronics. For example, a 250W TEC in a 1.4l engine car (Alfa Romeo) results in around 6,0 g CO2/km emission savings. With the proposed emission limits for the EU for cars, manufacturers are obliged to ensure that their new car fleets do not emit more than an average of 130 grams of CO2 per kilometer (g CO2/km) by 2015 and 95g CO2/km by 2021.

Clearly however, the potential savings are not sufficient for reaching the emission goals. In fact, an estimated bigger reduction potential hinges on reducing the overall vehicle weight. This is a line of work that is currently pursued with intensity by the automotive industry.

At any rate, the wide spread adoption of thermoelectric converters in cars will hinge on cost per performance. From this perspective, a thin-film approach to fabricating the thermoelectric elements presents significant advantages, as we have shown. First, the amount of raw material can be greatly reduced vis-à-vis bulk-element converters. This is particularly relevant for systems relying on rare elements, such as Te. Second, scrap recovery is relatively simple in these cases and expected to further contribute to cost reductions. Third, there is more room for performance enhancement because it is easier to distribute and adapt the converters to the local heat sources, and to ensure a better heat conduction to and from the thermoelectric elements. Lastly, and somewhat independent from the aforementioned arguments, the development of new thin-film thermoelectric materials systems reduces costs associated with hazardous materials.

These are but examples of the potential for thermoelectrics. Apart from automotive applications, others are envisioned e.g. in the area of distributed sensors as well as autarkic heating systems (Duisburg, 22. März 2013). These applications exploit the access to electrical power without externally wiring the device to a remote power source, that is enabled by thermoelectric converters which only need a temperature differential to operate, and are part of the strategy of O-Flexx for market development.

Advantageously, this technology relies on advanced manufacturing with proprietary methods, whereby its commercial exploitation can more readily get under way.

Processes for the industrial deposition of Si-Ge thermoelectric materials, as developed within NanoHiTEC, could be the start of a new generation of thermoelectric devices based on non-toxic, non-scarce materials, and concrete cases are currently under consideration.

List of Websites:
http://www.nanohitec.eu/

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