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ABSTRACT BOOK

ORAL PRESENTATIONS
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Session XIII - Auditorium

MATERIALS & PROCESSING VII

ID: 04971
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Exceptional thermoelectric power factor in hyper-doped nanocrystalline silicon thin films upon dehydrogenation

Dario Narducci[1] , Laura Zulian[1] , Bruno Lorenzi[1] , Federico Giulio[1] , Elia Villa[1]

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Single-crystalline silicon is known to be a poor thermoelectric material due to its high thermal conductivity. This is especially unfortunate, as silicon is a geo-abundant material, differently from tellurium. Most excellent research has focused on ways to decrease silicon thermal conductivity while retaining large power factors (PFs). As an alternate route, one may consider the possibility of promoting silicon efficiency moving from nanocrystalline samples, already showing low thermal conductivity, and attempting to increase their PFs. Among the possible strategies, energy filtering is especially promising. In previous publications we reported how annealing at temperatures > 800 °C of heavily boron-doped nanocrystalline silicon films leads to a concurrent increase of the Seebeck coefficient and the electrical conductivity. We correlated this effect with the precipitation of boron at grain boundaries (GBs). Precipitates set a double potential barrier that filters charge carriers, enabling hot carriers only to diffuse upon application of a thermal gradient. As a result, mobile carriers move as if no GB were present while cold carriers are trapped within grains. Thus, the mobile carrier density decreases, causing an increase of the Seebeck coefficient. At the same time, their mobility increases since mobile carriers overcoming the potential barrier have energies larger (in absolute value) than thermalized holes. PF values of 16.5 mW K^{-2} m^{-1} were achieved. Here we show that the PF may be further increased up to 33 mW K^{-2} m^{-1} at 300 K when hydrogen (embedded in the film during CVD) is removed. Hydrogen binds to boron and to dangling bonds at GBs, impeding precipitates to fully decorate them. Strategies to remove hydrogen, either by optimizing fluid dynamics of the annealing chamber or by aging, are presented. All in all, hydrogen removal amplifies energy filtering, therefore making nanocrystalline silicon a realistic competitor for low-temperature heat harvesting.

ID: 05019
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Thermoelectric properties of CMOS compatible (Si)GeSn/Ge heterostructures for on-chip devices

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Sn-based group-IV alloys have recently attracted a great deal of attention due to their compatibility with existing microelectronics processing and their applications, but have not received much attention as thermoelectric (TE) semiconductors. Alloying Sn with (Si)Ge can be a key breakthrough step toward efficient room temperature TE applications since Sn-based alloys provide low thermal conductivity via alloy disorder and high electrical conductivity.

Here, high-quality epitaxial (Si)GeSn layers deposited by industry-grade Chemical Vapor Deposition (CVD) are investigated regarding their thermoelectric properties by Raman Thermometry. During the measurement, a laser beam is employed for localized heating and the energy of a phonon mode is measured as a function of laser beam power. Calibration is carried out by measuring the phonon mode energy *E* as a function of temperature *T*. It is determined that *E(T)* follows a linear trend and does not vary with Sn content. The thermal conductivity ? is determined by a semi-analytical model specifically developed for simulating the heat transport in epitaxial thin films. With the described methodology, ? is determined for $Ge_{1-x}Sn_x$ layers with x =5 at.% to x=14 at.%. It decreases with increasing Sn content, from 56 W m^{-1} K^{-1} for pure Ge to 4 W m^{-1} K^{-1} at x=14at.% Sn. The ternary alloy SiGeSn was also investigated. $Si_{1-x-y}Ge_ySn_x$ samples with fixed Sn content of x=5% and various Si/Ge ratio 0.05, 0.14 and 0.17 were measured. The addition of the third component to the alloy resulted in a lowering of the thermal conductivity to 2.4 W m^{-1} K^{-1}. The results presented here highlight the potential of epitaxial (Si)GeSn as a thermoelectric material in the temperature range typical for on-chip devices. That could be the first step towards an integration of electronic, photonic, and thermoelectric applications on one chip.

ID: 05055
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Realising enhanced thermoelectric performance in partially substituted higher manganese silicides crystals

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1) Tohoku University

Higher manganese silicide (HMS) based materials are prospective *p*-type thermoelectric materials for mid to high-temperature range power generation applications owing to their remarkable refractory and semiconducting properties. In substitutional alloys, partially compensated co-doping offers a higher degree of freedom for optimizing the electrical transport and enhancing the phonon scattering synergistically. We propose and present the efficacy of compensated co-doping by a combination of Ru, V, and Fe substitution in highly oriented and partially substituted $MnSi_{1.74}$ single crystal synthesized employing the Bridgman method. The synthesized compensated co-doped HMS specimens exhibited a higher power factor and a synergistic reduction in lattice thermal conductivity resulting in an enhanced thermoelectric figure-of-merit (zT)~0.6 at 800K for the specimen directed perpendicular to the *c*-axis. The melt-grown HMS boule on partial substitution was found to be crack-free and exhibited a high mechanical strength, which embarks the remarkable prospects of the compensated co-doping approach and the synthesized HMS single crystals in thermoelectric applications.

ID: 05136
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Thermoelectric performance of nanostructured ?–FeSi2 alloys synthesized by “in situ” SPS

Linda Abbassi[1,2] , David Mesguich[2] , David Berthebaud[3] , Bhuvanesh Srinavasan[3,4] , Sylvain Le Tonquesse[3] , Takao Mori[4] , Geoffroy Chevalier[2] , Claude Estournès[2] , Emmanuel Flahaut[2] , Romain Viennois[1] , Mickaël Beaudhuin[1]

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Iron disilicide ?-$FeSi_2$ can be considered as an outstanding candidate for thermoelectric application as it is composed of abundant, inexpensive and non-toxic chemical elements.

However, its performances are limited mainly by its quietly high thermal conductivity reaches 10.3 W/mK at 440 K. After alloying with Al (n-type) or Co (p-type) its power factor is similar to the best thermoelectric materials in the mid-temperature range. However its thermal conductivity remains high, about 4.3 W/mK [3], and 6.2 W/mK at 425 K respectively.

In this study, the multi-scale approach has been used to obtain a large spectrum of phonons scattered using different length scales, in order to decrease the thermal conductivity. As most of the phonons are scattered below several hundreds of nm, we focused this work on the nanostructuring and point defects. To achieve our goal, we investigated both top-down and bottom-up approaches to obtain nanostructured ?-$FeSi_2$ pellets by spark plasma sintering. Both strategies enabled us to obtain pellets with high relative density (>93%) and to maintain the nanostructuring after the sintering step, with a crystallite size as low as 50 nm. Consequently, a significant reduction of the lattice component of the thermal conductivity has been shown [1,2].

The main advantage of the bottom-up approach is the decrease of the synthesis duration (divided by a factor ~5) to obtain nanostructured ?-$FeSi_2$. We will also present the impact of this multi-scale approach on the thermoelectric performances of ?-$FeSi_2$ alloys with Co.

[1] Abbassi, L. Mesguich, D. Coulomb, L. Chevalier, G. Aries, R. Estournès, C. Flahaut, E. Viennois, R. Beaudhuin, M. Journal of Alloys and compounds, 2022, 902, 163683.

[2] Abbassi, L. Mesguich, D. Berthebaud, D. Le Tonquesse, S. Srinavasan, B. Mori, T. Coulomb, L. Chevalier, R. Estournès, C. Flahaut, E. Viennois, R. Beaudhuin, M. Nanomaterials 2021, 11, 2852.

ID: 05186
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Ultrafast High-temperature Sintering of Mg2Si

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Recently a rapid pressure-less technique has been proposed [1], Ultrafast High-temperature Sintering (UHS), able to produce dense samples of a large set of ceramics, metals and intermetallics within tens of seconds. Among the advantages of this technique, there are the unprecedented versatility and control on the grain growth and the possibility to scale down by orders of magnitude both the time (and energy consumption) for sintering and the experimental setup cost. In this work possibly the first application of this technique to a thermoelectric material, Mg_2Si, is presented.
Despite the relatively low sintering temperature used, full dense samples with good mechanical properties were typically produced with 20 seconds holding time at temperature in the 1050 – 1110 °C range.
The morphology and composition analysis (SEM – EDS), thermal conductivity (Laser Flash Analysis) and electrical properties (conductivity and thermopower) of dense pellets were studied and compared to conventionally (pressure assisted) SPS results.
Perspectives and limits of this new sintering technique for thermoelectric applications are discussed.

[1] A general method to synthesize and sinter bulk ceramics in seconds, C. Wang et al., *Science,* **368**, 521-526 (2020).

ID: 05265
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

SiGe nanowires epitaxially integrated into thermal micro-harvesters

Jose Manuel Sojo-Gordillo[1] , Alex Morata[1] , Carolina Duque Sierra[1] , Gerard Gadea Diez[1,5] , Jaime Segura[2] , Valentina Bonino[2] , Marc Nuñez Eroles[3] , Juan Carlos Gonzalez-Rosillo[3] , Denise Estrada-Wiese[3] , Marc Salleras[3] , Luis Fonseca[3] , Albert Tarancon[1,4]

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Thermoelectric generators are candidates to fulfil the increased necessity of batteryless, delocalized power supply in the booming field of the Internet of Things (IoT). So far, commercial TE devices present a number of weaknesses that have restricted their implementation to niche applications. It is essential to develop materials and processes with an appropriate balance of performance, cost-effectiveness and environmentally friendliness, with integrability underlying as a crucial factor simultaneously impacting these three elements. In this context, silicon-based nanostructures are promising materials for TE harvesting applications since they combine abundancy and non-toxicity with an easy integration in electronic devices, providing an enhancement of thermoelectric performance conferred by nanostructuring.
In this work, a bottom-up Vapour-Liquid-Solid methodology is optimized to integrate in-situ heavily boron-doped SiGe nanowires on thermoelectric generators. The effect of precursors gases is studied to determine the optimal parameters, and these conditions are then used to obtain fully epitaxially integrated nanowires into silicon-made microdevices. Highly accurate elemental maps obtained with nano-X-ray fluorescence and tip-enhanced Raman spectroscopy shed light on the mechanisms hindering electric transport and helps heading appropriate processing conditions. The thermoelectrical properties - i.e. the electrical, thermal conductivity, and Seebeck coefficient - of the fabricated nanowires are fully characterized at temperatures ranging from 300 to 600 K, hence, allowing the complete determination of the Figure-of-merit, zT, with values up to 0.4 at 600 K. Likewise, the power harvesting capability of dense packaged microdevices including the described NWs is evaluated. These devices include several thermoelectric elements connected in different electrical configurations - i.e standalone, series or parallel -. Maximum open circuit voltages 3.6 mV in a series configuration and absolute power outputs of 0.11 µW in a parallel configuration were achieved we operating upon natural thermal gradients generated with hot heat sources at 200 °C. Moreover, voltages as high as 13.8 mV in a series configuration and powers of 1.25 µW in a parallel configuration were obtained under improved heat dissipation conditions with air flows of 1.5 m/s.

ECT'22

Session XIV - Parallel room

ADVANCED CHARACTERIZATION

ID: 05079
Type: Oral Presentation
Topic: Advanced characterization

Development of the thermo-reflectance method for thermal conductivity measurements of thin films & small crystals and elucidating interfacial thermal resistance

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In the thermo-reflectance (TD-TR) method, a transient change in surface temperature of a thin film can be observed and thermal diffusivity in the cross-plane direction of the thin film can be determined by fitting a mathematical model to the transient change. In order to carry out the TD-TR measurement, metallic layer of around 100-nm-thick are typically deposited on the film for absorbing heating laser pulse and for temperature detection for probe laser pulse. It is necessary to evaluate interfacial thermal resistance between metallic thin film and thermoelectric thin film to determine thermal effusivity of the thermoelectric thin film with small uncertainty. However, it has been difficult to distinguish contribution of thermal effusivity and interfacial thermal resistance from the shape of temperature response curve after pulse heating by the measurement and analysis of conventional time domain thermo-reflectance method. Recently the method achieved remarkable developments. Thanks to the rise of electrical delay technique, thermo-reflectance method can observe transient changes of longer period than pulse interval. To make full use of thermo-reflectance signals observed by the electrical delay technique, we improved mathematical models and achieved all-range fitting to the signals by applying Fourier analysis. Importantly, we could also determine interfacial thermal resistance by extending the mathematical model. We have found examples where the thermal conductivity nominally determined by a simple TD-TR method could be seriously underestimated without taking into account this interfacial thermal resistance. We could also measure small crystals by using customized focused thermal analysis system based on thermo-reflectance method. This system enables us to probe small area less than 10 microns square of sample’s surface. We are going to present such recent developments of thermo-reflectance method and some notable results of thermal conductivity measurement with actual samples.

ID: 05158
Type: Oral Presentation
Topic: Advanced characterization

Towards a complete characterization of thermoelectric materials by micro four-point probe (M4PP) technique

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The complete characterization of thermoelectric materials, which is the determination of electrical conductivity, Seebeck coefficient, thermal conductivity, and hence *ZT*, is key to develop thermoelectric devices with higher efficiency. However, it is a time-consuming task that usually requires the use of several instruments and/or complex setups.

Micro four-point probe (M4PP) based metrology has over the past two decades developed into a highly reliable tool for the characterization of electrical conductivity, sheet resistance, electron mobility, carrier density and tunnel magnetoresistance. In the most basic form, an M4PP consists of four electrodes with micrometer scale separation. Two electrodes are used to apply an alternating current and the other two for recording voltage with lock-in technique.

Recently, we have shown the potential of M4PP to determine thermal effects using self-induced Joule heating; in particular, the ratio between the Seebeck coefficient and the thermal conductivity in bulk materials, and the temperature coefficient of resistance of metallic thin films. Here, we present the state-of-the-art of the technique by covering these recent developments, and discussing the challenges and opportunities in the thermoelectric field. This new method could eventually be used to determine all the properties that define *ZT* in a single measurement.

ID: 05170
Type: Oral Presentation
Topic: Advanced characterization

Thermoelectric Characterization of Electrodeposited Materials and its Application in Micro Thermoelectric Devices

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Micro-thermoelectric devices have a high potential for future applications in the biomedical field, powering internet-of-things devices, and thermal management. Successful optimization of the thermoelectric figure of merit, zT, is a key enabler for the introduction of these devices to application. Especially, the TE characterization of films grown by electrochemical deposition, which is a common technique for the fabrication of micro TE devices, remains a great challenge. For such cases, TE materials are deposited onto an electrically conductive seed layer leading to in-plane short-circuit, hindering unambiguous determination of the transport coefficients. Here we present characterization techniques to determine the thermoelectric properties and contact resistance of electrochemical deposition materials, including a platform for the full in-plane zT characterization of electrochemically deposited TE materials.[1] This characterization platform allows the materials zT characterization whilst eliminating the impact of the electrically conducting seed layer as well as the substrate. The in-plane transport characterization could be realized using a suspended TE material within a transport device prepared by a combination of photolithography and etching processes. This full in-plane zT characterization provides an inevitable milestone for a materials optimization under realistic conditions in micro TE devices. Furthermore, a Cox-Strack setup to determine the contact resistance will be presented and the TE characterization of electrochemically deposited materials and its application in micro TE devices will be discussed.[2]

[1] Barati et al., *Advanced Electronic Materials* **6**, 1901288 (2020).

[2] Dutt et al., *Advanced Electronic Materials*, 2101042 (2022).

ID: 05176
Type: Oral Presentation
Topic: Advanced characterization

Novel methods for the thermoelectric characterization of microgenerator-integrable individual nanowires

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Currently employed materials in Thermoelectric Generators (TEGs) such as bismuth telluride or lead telluride are scarce, expensive, toxic, and environmentally harmful. In recent years, the thermoelectrics paradigm has changed mainly due to the introduction of low-dimensional materials able to reduce the thermal conductivity by phonon scattering. Semiconductor nanowires have demonstrated fascinating properties with application in various fields, including energy and information technologies. In particular, increasing attention has been focused on Si and silicon alloy nanowires (NWs) for applications in thermoelectric generation after recent successful implementation in miniaturized devices. Despite this interest, a proper evaluation of such nanostructures' thermoelectrical properties still represents a great challenge, especially when the complete characterization of the device-integrated nanowire is desired.

In this work, we present alternative techniques to measure the thermoelectrical properties of Si and Si alloys epitaxially integrated NWs. In particular, we describe the use of a novel combined Scanning Electron Microscopy and a Scanning Thermal Microscopy analysis to determine the mechanical and thermal properties. Additionally, we also describe the fabrication and testing process of a micro-machined device for the complete evaluation of a single bottom-up integrated NW. This new presented approach allows advanced morphological and structural in-operando characterization (via Transmission Electron Microscopy, X-Ray Fluorescence, X-ray diffraction, or micro-Raman scattering) of the exact same NWs that can be thermoelectrically characterized using conventional electrothermal techniques.

In conclusion, the combination of all this set of techniques – some of them not previously reported in literature – allows us to optimize the properties of the NWs in the same configuration as those used into micro-thermoelectric generators, yielding a direct improvement in the output power of the latter.

ID: 05224
Type: Oral Presentation
Topic: Advanced characterization

Mapping local Seebeck variations in 2D materials devices

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The discovery of 2D materials opened tremendous possibilities for tailored thermoelectric applications. We recently demonstrated[1] that graphene devices exhibit local Seebeck coefficient variations solely arising from the device geometry. This new geometrical thermoelectricity arises from the carrier's mean free path modification. Nearby materials edges change the mean free path and thus affects the local Seebeck coefficient of the material.

To map at the nanoscale thermoelectric effects, we introduced[2] scanning thermal gate microscopy (STGM). This novel method uses a heated scanning probe moving across the sample surface of a device. The electrical potential build-up resulting from the local sample heating can be measured at the edges of the device. This produces thermovoltage maps associated to local Seebeck coefficient variations[2].

Building on our previous experiments, we report here new results of devices based on novel 2D materials and heterostructure. We explored various effects arising selectively from geometry, interfaces and electromagnetic fields. This provides us with better understanding of the fundamental impact of these parameters and opens several new routes for research and industry applications ranging from nanoscale sensors and heat management structures to power sources for wearable electronics.

[1] A. Harzheim, J. Spiece, C. Evangeli, E. McCann, V. Falko, Y. Sheng, J. Warner, A. Briggs, J. Mol, P. Gehring and O. Kolosov, Nano Letters, **18**, 7719 (2018).

[2] A. Harzheim, C. Evangeli, O. Kolosov and P. Gehring, 2D Materials, **7**, 041004 (2020).

ID: 05246
Type: Oral Presentation
Topic: Advanced characterization

Impact of nanostructuring on effective thermal conductivity studied by scanning thermal microscopy

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Minimizing thermal conductivity is required in order to reach high thermoelectric figure of merits. Nanostructuring is a known to be a key way allowing to decrease the mean free path of phonons, but it is not always clear by which amount effective thermal conductivity can be reduced. We report on strategies for confining phonons and determining the reduction factor. We first discuss suspended silicon membranes, ranging from pristine [1] to perforated ones known as thermophononic crystals and paying a particular attention to the design of the shapes of the holes [2]. Effective thermal conductivity can be reduced by a factor 20. We then report on the thermal properties of porous silicon samples, which can be further locally amorphized by irradiation in order to reach a reduction by 100 [3]. Third, we underline that the effect of interface roughness on the overall thermal transport has not been fully exploited yet [4]. Finally, we study the weak thermal contact of a supported Van Der Waals 2D material, MoS_2 [5]. Most reported experimental investigations have been obtained by scanning thermal microscopy, a local thermal characterization technique derived from AFM, while theoretical analyses are based on the Boltzmann transport equation solved by the Discrete Ordinate Method or phonon Monte Carlo ray tracing.

[1] A.M. Massoud et al., APL 111, 063106 (2017). [2] A.M. Massoud et al., APL Materials, in press. [3] A.M. Massoud et al., JAP 128, 175109 (2020). [4] E. Guen et al., APL 119, 161602 (2021). [5] C.M. Frausto Avila et al., submitted.

Contributors : A.M. Massoud, E. Guen, M. Frausto Avila, N.J. Gaur (PhD students), A. Alkurdi (post-docs), P. Klapetek, A. De Luna Bugallo, J.M. Yanez Limon, J.M. Bluet, S. Gomes (colleagues).

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Session XV - Auditorium

MATERIALS & PROCESSING VIII

ID: 05017
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Improved thermoelectric properties in mesograined Fe2VAl

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Upon (self)doping, the Heusler alloy Fe_2VAl displays very large values of power factor: *PF* = 6.8 and 9.0 mW m^{-1} K^{-2} at 300 K in *n*-type $Fe_2V_{1.03}Al_{0.97}$ [1] and $Fe_2V_{0.95}Ta_{0.05}Al_{0.9}Si_{0.1}$ [2] respectively. These values are larger than in Bi_2Te_3 (*PF* = 5 mW m^{-1} K^{-2} at 300K) and this makes consider Fe_2VAl as a potential substitute to Bi_2Te_3. However, its TE performances are hampered by its large thermal conductivity, 29 W m^{-1} K^{-1} in pristine Fe_2VAl at 300 K. Alloying and decreasing the grain size increase the phonon scattering rate by the mass fluctuations and the grain boundaries respectively, and both lead to the decrease of the thermal conductivity required for the improvement of a thermoelectric material.

We thus undertook an investigation of the microstructural and thermoelectric properties of *n*-type Ta-substituted Fe_2VAl, with an average grain size ~ 1 micron obtained by ball-milling and spark plasma sintering. Upon mesostructuration, the lattice thermal conductivity is reduced from 7.1 W m^{-1} K^{-1} to 4.2 W m^{-1} K^{-1} and the power factor reaches *PF* = 7.9 mW m^{-1} K^{-2} at 300 K. This leads to a figure of merit *ZT* = 0.3 at 300 K in meso-$Fe_2V_{0.96}Ta_{0.07}Al_{0.97}$, a value larger than in other Fe_2VAl alloys previously obtained by powder metallurgy [3].

[1] A. Diack-Rasselio et al., submitted

[2] F. Garmroudi et al., Phys. Rev. B **103**, 085202 (2021).

[3] M. Mikami et al., J. Appl. Phys. **111**, 093710 (2012).

ID: 05059
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Optimisation of the thermoelectric properties of Fe2VAl thin films obtained by co-sputtering

Geoffrey Roy[1] , K Muthu Karuppasamy[2] , Vedi Dupont[3] , Jean-François Trelcat[3] , Ankush Kashiwar[1] , Camille van der Rest[1] , Hosni Idrissi[1] , Jean-Pierre Erauw[3] , Philippe Guaino[2] , Pascal J. Jacques[1]

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The Fe_2VAl Heusler compound is attracting increasing interest from the scientific community due to its excellent performance in terms of power factor [1-2] around room temperature, coupled with the high availability and non-toxicity of its constitutive elements. Thermoelectric thin films are of interest from a fundamental point of view, especially owing to the possibilities of nano-structuring, but also from an application point of view where it could facilitate the integration of thermoelectric modules for powering low power electronic devices such as autonomous sensors. Nevertheless, studies on Fe_2VAl thin films are relatively scarce and some recent results still raise some questions [3-4].

In this study, Fe_2VAl thin films were processed by a co-sputtering method allowing to easily control the stoichiometry of the films. After process optimisation, p- and n-type layers have been obtained with power factors of 0.8 and 1.6 10^{-3}W/mK², respectively. In addition, we determined using advanced microstructure analysis that the increase of thermoelectric performances is related to crystal ordering during annealing.

[1] Miyazaki, H. et al. "Thermoelectric properties of Heusler-type off-stoichiometric $Fe_2V_{1+x}Al_{1?x}$ alloys." *Materials Research Express* 1.1 (2013): 015901.

[2] Garmroudi, F., et al. "Boosting the thermoelectric performance of Fe_2VAl? type Heusler compounds by band engineering." *Physical Review B* 103.8 (2021): 085202.

[3] Hinterleitner, B., et al. "Thermoelectric performance of a metastable thin-film Heusler alloy." *Nature* 576.7785 (2019): 85-90.

[4] Alleno, E., et al. "On the structure and electronic properties of $Fe_2V_{0.8}W_{0.2}$ Al thin films." *Physical Chemistry Chemical Physics* 22.39 (2020): 22549-22554.

ID: 05067
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Pseudo 3D-Printed Half-Heuslers

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The go to materials for thermoelectrics are Bi_2Te_3 and PbTe for room temperature and mid-temperature applications respectively. ZT was shown to be ~1 in these materials in the 1950s. Te is, however, a rare element with an Earth abundance similar to Pt (1 µg kg^{-1}). This along with the toxicity of Te, and the high embodied energy of material fabrication are some of the reasons that have prevented the wide scale use of thermoelectrics.

In recent years, other semiconductors have been discovered to have discovered to be high-performing thermoelectric materials, including tin selenide, copper sulfide, and half heulsers. Typical fabrication techniques such as hot pressing and spark plasma sintering, however, still require high pressure, high temperature and lengthy fabrication times. In contrast, printing can be achieved at ambient temperature and pressure and yield fast fabrication times. Printing has primarily focused on the production of films (~300 µm), due to the limitations of printing techniques being studied for thermoelectrics, e.g. screen printing. More recently, 3D printing has been investigated initially for Bi_2Te_3. I have demonstrated a pseudo-3D printing system that has worked for both tin selenide, and copper sulfide.

In this work, we have expanded the pseudo-3D printing system to print Hf free half-Heuslers. Polycrystalline half Heuslers were fabricated by low-cost ball milling of the constituent elements. Thermoelectric elements were printed from a water-based ink using carboxymethyl cellulose as a binder, with the aim of producing a commercially viable thermoelectric device. The effect of variation of stoichiometry on properties (including electrical conductivity, the Seebeck Coefficient and thermal conductivity all up to 1000 K) were studied. We compare thermoelectric performance to other polycrystalline half-Heuslers. A half-Heusler thermoelectric generator consisting of pseudo-3D printed n-type and p-type legs was produced and characterised for the first time.

ID: 05095
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Ultimate phonon scattering of half-Heusler compounds by high pressure sintering

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Thermal management is of vital importance in various modern technologies such as portable electronics, photovoltaics, and thermoelectric devices. Impeding phonon transport remains one of the most challenging tasks for improving the thermoelectric performance of certain materials such as half-Heusler compounds. Herein, a significant reduction of lattice thermal conductivity ($?_L$) is achieved by applying a pressure of ~1 GPa to sinter a broad range of half-Heusler compounds. Contrasting with the common sintering pressure of less than 100 MPa, the gigapascal-level pressure enables densification at a lower temperature, thus greatly modifying the structural characteristics for an intensified phonon scattering. A maximum $?_L$ reduction of ~83% is realized for HfCoSb from 14 W m^{-1} K^{-1} to 2.5 W m^{-1} K^{-1} at 300 K with more than 95% relative density. The realized low $?_L$ originates from a remarkable grain-size refinement to below 100 nm together with the abundant in-grain defects, as determined by microscopy investigations. This work uncovers the phonon transport properties of half-Heusler compounds under unconventional microstructures, thus showing the potential of high-pressure compaction in advancing the performance of thermoelectric materials.

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ID: 05169
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Investigating the relationship between composition, structure and thermoelectric properties of thin-film Fe2VAl Heusler alloys

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Thermoelectric thin films show promising benefits compared to their bulk analogon, reaching from 2D-type conduction and properties [1] to a larger range of possible applications, including flexible thermoelectric generators [2]. On the other hand, they often show a lower performance than the bulk compound, caused by various reasons. A common issue of films made by sputtering is the deviation of the composition from that of the target. While this problem can be circumvented in case of two or three different elements by using multiple single-element targets, different strategies are mandatory for more elements. Here, we present the successful approach of shifting the targets' composition in an iterative step-by-step way to outweigh the target-to-film deviation. This process is elucidated with both Ti-doped and off-stoichiometric full-Heusler Fe_2VAl, whose thermoelectric properties are compared between bulk and thin film. Furthermore, we address how the annealing conditions can be tuned to influence the structure-properties relationship of the film.

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[2] Wang, Yuan, et al. "Flexible thermoelectric materials and generators: challenges and innovations." *Advanced Materials* 31.29 (2019): 1807916.

ID: 05243
Type: Oral Presentation
Topic: Thermoelectric materials and materials processing

Synthesis, Characterization and thermoelectric properties of n-type half Heusler materials via Mechanical Alloying

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Thermoelectric technology has been studied for more than two centuries for energy conversion of waste heat into electricity. The discovery of new compounds and their optimization for maximum figure of merit is significant for the community. The half Heusler compounds have attracted the interest of the community for energy conversion into medium temperature ranges. Due to their mechanical and thermal stability, half Heusler compounds can be used in waste heat recovery applications such as automotive. The major problem in these materials is their high thermal conductivity that fluctuates in the order of 10W/m·K.

Half Heusler compounds are usually synthesized in several ways such as arc melting, induction melting and microwave heating. Additional treatments, including annealing and milling, can contribute significantly to the reduction of the thermal conductivity. The main obstacles of these methods are the material loss due to the evaporation of Sn and Sb as well as the time-consuming annealing process. On the other hand, mechanical alloying is an alternative method to directly fabricate this type of materials avoiding additional steps. The limited processing steps, the possibility of scaling up as well as the formation of nanostructured materials with low lattice thermal conductivity are some advantages of this method. In the few past months, mechanical alloying method was applied in n-type $Zr_{1-x}Ti_xNiSn$ compounds and high figure of merit was reached (ZT~0.7) for the $Ti_{0.4}Zr_{0.6}NiSn_{0.985}Sb_{0.015}$. In this presentation, the synthesis conditions of solid solutions through mechanical alloying compared to the synthesis of arc melting as well as the thermoelectric performance of different compositions are discussed.

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Session XVI - Parallel room

EMERGING TOPICS

ID: 05005
Type: Oral Presentation
Topic: Emerging topics

Exploring new concepts to try to reach Seebeck coefficient values above 1 mV/K in metals

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Metals show very high electrical conductivity, high thermal conductivity and very low Seebeck coefficients. The last two properties make them unsuitable as thermoelectric materials. Although this is typically the case, however, there are alloys with not very high thermal conductivities [e.g. stainless steels with values around 14 W/(Km)], but suitable Seebeck coefficients (above 100 ?V/K) are missing.

Here, we present new concepts under exploration in order to enhance the Seebeck coefficient of metals above 1 mV/K without significantly affecting their electrical conductivity. These concepts consist in the combination of metallic films with redox electrolytes. These redox electrolytes are employed in thermogalvanic cells (thermocells), which exhibit Seebeck coefficient values above 1 mV/K [1]. However, the electrical current flow in these devices is much lower than in solid-state thermoelectrics due to their high electrical resistance. Combining metals with electrolytes in order to fabricate a device with the best of each element (high Seebeck coefficients with high electrical conductivity) is our goal. The progress on this endeavour will be shown, which is part of the UncorrelaTEd EU project [2].

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ID: 05060
Type: Oral Presentation
Topic: Emerging topics

Solid-state/optical alternatives to thermoelectricity for thermal-to-electrical energy conversion

Christophe Lucchesi[1] , Julien Legendre[1] , Dilek Cakiroglu[2] , Jean-Philippe Perez[2] , Thierry Taliercio[2] , Eric Tournié[2] , Rodolphe Vaillon[2] , P-Olivier Chapuis[1]

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Thermoelectricity (TE) is the most advanced technology for solid-state thermal-to-electrical energy conversion, but competing technologies involving optical and radiative channels are currently under development. In this talk we systematically compare the performances of these less-mature technologies with TE.

We report on advances in thermophotovoltaics, which is close to photovoltaics (PV) – the cold side is a pn or pin junction acting as a PV cell - but where the emitter is a hot source as in thermoelectricity. The efficiency is typically higher than that of TE (up to 40% [1]), but the output power density is lower due to the Planck/Bose-Einstein bound of thermal radiation. Recent experimental progresses toward near-field operation, where the hot emitter is brought very close to the cell, allow transferring much more heat than this bound and indicate that the W/cm^2 power density typically reached in TE can be obtained for hot temperatures lower than 1000 K [2].

A technology derived from TPV termed thermophotonics [3], where the emitter is another pn/pin junction acting as a light-emitting diode (LED), is also making progress. The hot source emits above the PV-cell bandgap, in order to convert efficiently, by means of electroluminescence. Theoretical reports indicate that such technology is interesting for heat sources in the range 200-300°C, especially when hot and cold sides are brought in the near-field distance range [4], which is promising as TE and TPV performances are limited in this temperature range.

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ID: 05245
Type: Oral Presentation
Topic: Emerging topics

Thermoelectric coeffient dependency on chemical composition of ionic liquid based ferrofluids

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In recent years, complex fluids are attracting attention as an alternative thermoelectric (TE) material. Unlike in solids, several inter-dependent TE effects take place in such fluids; most notably, the electrochemical (thermogalvanic) reactions of redox salts, the thermodiffusion of charged species and the electronic double-layer formation of ions near the electrodes. They possess Seebeck (or temperature) coefficient values that are generally an order of magnitude larger, and are made of cheap and abundant raw materials compared to the semiconductor counterparts, their TE power-output remains quite low with a limited operational temperature range (e.g., 100 °C). To this end, ionic liquids with high ionic conductivity and boiling points (e.g. > 200 °C) are auspicious candidates to overcome these issues. Additionally, the inclusion of highly charged colloidal nanoparticles has been shown to further enhance the Seebeck coefficient and the power output by proper tailoring [1].
In this work, the thermoelectric properties of ionic liquid (EMI-TFSI) based maghemite ferrofluids (colloidal suspension of magnetic nanoparticles (NP)) with tris(2,2'-bipyridine) $[Co(bpy)_3]^{3+/2+}$ redox couple were studied with varying combinations of NP surface coating molecules and counter-ions. The results shed light on the intricate balance between the NP concentration and the solvation shell of redox salts affecting the fluids' overall TE energy conversion process and performance. A discussion on some key experimental parameters for improving the efficiency of liquid thermoelectrochemical cells will also be given.

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ID: 05250
Type: Oral Presentation
Topic: Emerging topics

Recent Advancements in Complex Fluid Thermoelectric Research

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Thermoelectric effects in liquid electrolytes is receiving increased attention as a potential source of renewable energy in recent years. Indeed, the Seebeck coefficients (or temperature coefficients) of complex fluids are one to two orders of magnitude larger than that of conventional solid-state thermoelectric materials stemming from the thermogalvanic effect, the internal thermoelectric field, the ionic double layer formation at the electrodes, or the combination of these effects (see, for example [1]–[4]. Ionic liquids in particular, present many promising features such as high electrical conductivity, large temperature and electrochemical windows, low vapor pressure and toxicity, and raw material abundance [2] [5] for low-grade waste heat recovery applications. In the case of ionic nanofluids, the thermodiffusion (Soret effect) of charged nanoparticles is also known to produce non-negligible contribution to the fluid’s overall Seebeck coefficient [6], [7].

In this presentation, I will review recent advancements in the complex fluid thermoelectric research and applications. The current theoretical and phenomenological understanding on the compound thermo-electro-chemical processes, as well as future research directions and technological possibilities where thermoelectric complex fluids should become advantageous will also be discussed.

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ID: 05261
Type: Oral Presentation
Topic: Emerging topics

Flexible ?-thermoelectric devices towards emerging technologies on the Era of Internet of Things

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The Energy Harvesting is emerging in the Age of Internet of Things for placing sensor systems, monitoring in many remote places. Thermal systems that can convert heat into electricity are of great importance given the numerous hot spots exposed to heat release.
In order to be of easy adaptation, the flexible systems of thermoelectrics introduce diverse advantages that have an enormous potential that may pass through monitoring systems sensors.
In this scope, in this work we address the various methodologies undertaken within our working group in the field of thermoelectrics, which includes two distinct approaches:
1- **Printable methods** by screen printing or stencil printing, in which we will address the influence of changing parameters such as different polymers involved, types of materials of different stoichiometry or sizes (micro & nanoparticles) or the influence of the fillers.

2- Fabrication of devices by **Physical Vapor Deposition** methods with variation of composition and type of material.

It will be also compared with emerging areas like thermochargable supercapacitors systems.Finally, towards the technological applications it will be mainy focus on the wireless transference of energy.

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