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論　文　要　旨
Thesis Abstract

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主論文題名　（Title）

Growth and Characterization of Thermoelectric Thin Films for Heat Harvesting

内容の要旨　（Abstract）

The increasing worldwide demand for energy and the resultant depletion of fossil fuels have brought new challenges for the scientific community [1]. One of the major issues is to develop high-efficiency devices for capturing energy from abundant natural sources such as solar wind and geothermal energy. Another surplus, but mostly unused, source of energy is waste heat. There are huge waste heat sources in our environments covering a wide range of temperatures (300~1200 K): industrial processes, domestic stoves and radiators, lighting, pipelines, electrical substations, subway networks, automotive exhaust tubes, but also geothermal heat, body heat, and so on: about 66 % of the of annual world energy consumption is lost as waste heat, and the loss corresponds to the stellar amount of $3 \cdot 10^{20}$ J per year, just considering the past 10 years [2,3]. A highly promising method for energy recovery from such heat sources is the utilization of thermoelectric (TE) devices that can convert various types of waste heat flows into electricity.

The TE performance of a material is expressed by means of the concept of figure of merit, Z, defined by E. Altenkirch at the beginning of the XX century [4], a relation expressed by means of the electrical conductivity σ, Seebeck coefficient S and thermal conductivity κ. Seeing that Z differs with absolute temperature T, an advantageous way to display the efficiency is the non-dimensional figure-of-merit ZT. Commonly, ZT values of both the *n*-type and *p*-type TE materials contribute to the definition of the efficiency of a thermoelectric device. State-of-the-art TE materials for heat conversion can operate at T = 300 ~ 1200 K, with ZT = 0.1 ~ 2.6, corresponding to an efficiency in the range of 1 ~ 20%. Therefore, after two centuries, TE devices are seldom utilized in daily life. TE modules have obtained brilliant success, though in niche applications (powering space probe Cassini [5]) while high-conversion modules to harvest waste heat of car engines remained at the state of prototypes [6].

[1] S. Chu, A. Majumdar, "Opportunities and challenges for a sustainable energy future", *Nature* **2012**, *488*, 294–303.
[2] BP statistical review of world energy **2021**, https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html
[3] Annual energy flow charts by Lawrence Livermore Nat. Lab.　https://flowcharts.llnl.gov/commodities/energy
[4] CRC *Handbook of Thermoelectrics* (ed. D.M. Rowe), CRC Press Inc. **1995**.
[5] V. Mireles J. W. Stultz, "Radioisotope Thermoelectric Generator Waste Heat System for the Cassini Propulsion Module", *Journal of Aerospace* **1994**, SAE Transactions, *103*(1), 548-556.
[6] D. Crane, J. LaGrandeur, V. Jovovic, M. Ranalli, M. Adldinger, E. Poliquin, J. Dean, D. Kossakovski, B. Mazar, C. Maranville, "TEG On-Vehicle Performance and Model Validation and What It Means for Further TEG Development", *Journal of Elec. Materi*. **2013**, *42*, 1582–1591.

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The efficiency of TE must be strongly improved to make them competitive with the common thermodynamic cycles based on fossil fuel burning, solar conversion and nuclear power plants. The improvement of ZT can be obtained by enhancing σ and/or S, or the product σS^2 which is called power factor, and/or by decreasing the total thermal conductivity.

In the past decade, due to their amazing advantages, such as lightweight, flexibility and small sizes, thin films emerged in the thermoelectric research field. They can be considered competitive in meeting the requirements for micro-machines and small-scale accessories, such as micro-coolers, micro-power generators, micro-sensors [7]. Flexible thin films have the potential to be useful for wearable devices, while transparent thin films, like ZnO, can be employed on external glass walls or electronic screens for heat harvesting purposes. Regarding efficiency, thin films are interesting for TE applications because their structure opens various paths to enhance thermoelectric properties. It is common knowledge that the interface between the film and the substrate, or the ones between multilayers, have a significant effect on the grain growth, which tunability can be used to control TE performances.

This thesis is articulated into seven chapters. In Chapters 1, 2 and 3 a general introduction about thermoelectricity is followed by some experimental details of interest regarding the research conducted during the doctoral program. Thermoelectric thin films of various materials were prepared and characterized with various techniques. In Chapter 4, two complementary works regarding novel Fe,Ni-based filled skutterudites thin films deposited via Pulsed Laser Deposition (PLD) are reported. Substrate temperature and consecutive annealing were optimized in order to tune the thermoelectric properties of the material. Moreover, a preliminary study of the performances of a thin film module composed of only Fe,Ni-based filled skutterudite's legs was carried out as well. Chapter 5 is dedicated to aluminium-doped zinc oxide (AZO) and the study is aiming to investigate the effect of SnO_2 doping on thermoelectric properties of PLD AZO thin films. A preliminary study regarding Co-doped copper aluminium oxide is the main topic of Chapter 6. Best conditions to deposit the desired phase by PLD were explored, including annealing processes. Chapter 7 is dedicated to a general summary of conclusions and perspective of all the previous themes part of this doctoral thesis.

[7] X. Chen, Z. Zhou, Y.H. Lin, C. Nan, "Thermoelectric thin films: Promising strategies and related mechanism on boosting energy conversion performance", *Journal of Materiomics* **2020**, *6*(3), 494-512.

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