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(54) Title: METHOD OF MANUFACTURING THERMOELECTRIC MODULE

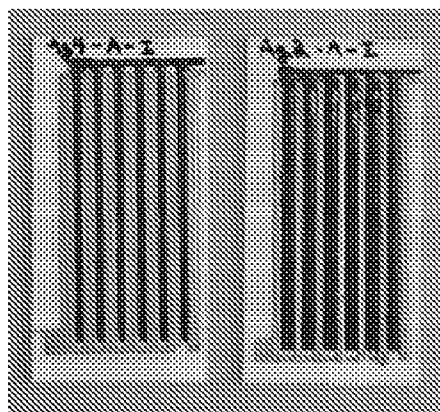


Fig. 3

(57) Abstract: Method of manufacturing transversal thermoelectric modules comprising tilted lines of N-type and P-type semiconducting materials on a substrate. The method comprises applying on the substrate a plurality of inclined layers of anisotropic materials by a printing technique. The produced thin and readily processible thermoelectric modules have interesting properties and can be used for energy harvesting and in electric heating and cooling applications.



Method of manufacturing thermoelectric module**Background of Invention****5 Field of Invention**

The present invention relates to thermoelectric modules. In particular, the present invention concerns methods of manufacturing thermoelectric modules with a dispensing method, such as a paste dispensing or inkjet dispensing method or combinations thereof.

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Description of Related Art

Thermoelectrics can be utilized for energy harvesting as well as for cooling or even heating. There are needs for technical solutions which allow for generation of electricity from waste heat in efficient manner. High power density for such an energy harvester is frequently sought. In addition, the cost of electricity should be low – this concerns in particular consumer appliances, electronics. It is frequently stated that the cost of energy harvester (e.g. thermoelectric module) should be < 1USD/W. The aim of developing new manufacturing techniques is to lower the cost of thermoelectric modules, as well as to utilize them in wider variety of substrates and shapes.

20

Concept of transversal thermoelectric modules for cooling has been described by several authors (cf. Goldsmid, 2010, and Kyarad and Lengfellner, 2006).

25 Different methods for manufacturing has been suggested, including thin film deposition utilizing masking and mask shifting (Figure 2). Panasonic has introduced a transversal thermoelectric tube. It is suggested here, in connection with the present invention, that such a structure can be manufactured also in a manner not stated in original patents (cf. WO10058553 A1, WO12014366 A1, WO12066788 A2, WO12137446 A1, US2012263207 A1 and US2012266930 A1), i.e. by utilizing paste dispensing .

30

In known technology, materials have been attached to each other by sintering after which the piece of material thus obtained has been cut to the desired orientation. The known methods are tedious and expensive.

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Summary of Invention

It is an aim of the present invention to provide an alternative and simple method for thermoelectric module manufacturing by utilizing above mentioned methods.

10

In particular, the present invention is based on the concept of providing a method of manufacturing structures of the above kind without masking by utilizing semiconducting material dispensing, printing or spraying by an application method. In spraying methods masking may be utilized.

15

Invention describes a method that makes low cost manufacturing of transverse TE-modules on 2-dimensional or 3-dimensional substrates possible. There are no similar methods being applied.

20

More specifically, the present method is characterized by what is stated in the characterizing part of claim 1.

Advantages of the Invention

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The present technology provides a simple and efficient solution for production of thermoelectric modules. More particularly, the present technology provides a rapid and scalable production method of the present kind for producing thermoelectric modules at low temperatures.

30

It can be estimated that thermoelectric technology of the present kind will be cost efficient because the cost of produced energy drops below the indicated limit. Utilizing transversal technology the thickness of the modules and thus energy density can be considerably

improved.

A particular value-adding feature resides in the protection against atmospheric degradation which stands for increased service life. The present technology also gives the possibility to
5 utilize inexpensive substrates (e.g. polymer films, in particular films of thermoplastic materials).

The produced thin and readily processible thermoelectric modules have good properties and can be used for energy harvesting and in electric heating and cooling applications.

10

Next embodiments are examined with the aid of the attached drawings.

Brief Description of the Drawings

15 Figure 1 is a schematic drawing of a synthetic transverse thermoelement as presented in literature (Goldsmid 2010);

Figure 2 is a schematic representation of a synthetic anisotropic thermoelement, produced by thinfilm technology. The mask is shifted in regular steps as each half-layer is deposited (Goldsmid, 2010);

20 Figure 3 shows a photograph of first layers of silver and Bi_2Te_3 lines;

Figure 4 shows a tilted structure after dispensing several shifted layers;

Figure 5 is a depiction of a demonstrator with wires;

Figure 6 is a depiction of a demonstrator with wires;

Figure 7 shows in a perspective view a zigzag- or labyrinth-structure, as depicted in
25 Goldsmid, 2010. Each line consists of tilted layers of N- and P-type materials; and

Figure 8 shows a transversal thermoelectric module on a 3-dimensional pipe structure. Such a structure can be manufactured also by utilising spraying, paste dispensing and inkjet method as described here.

30

Description of Embodiments

As discussed above, the present technology provides for dispensing or spraying of materials on substrates. Thus, dispensing or application of paste (e.g. n-scrpt) by a printing method,
5 e.g. a method similar to inkjet technology, makes it possible to produce transversal thermoelectric modules.

Examples of suitable substrates include thermoset and, in particular, thermoplastic films, such as polyester, polyamide or polyimide films, examples being poly(ethylene terephthalate, PET)
10 and polyimide (e.g. of the poly-oxydiphenylene-pyromellitimide type, Kapton). Also semiconductor and ceramic substrate surfaces are possible.

The substrate can be configured as an adhesive surface, a sheet or plate or any planar surface or a 3D surface.

15 A particularly interesting printing method is the roll-to-roll technology which can be used for polymer films and other films and sheet-like or planar materials.

A method of the instant kind can be carried out using various application techniques, such as
20 printing, ink or paste spraying, thermal spraying and dispensing. During manufacturing (especially when spraying) different masking operations may or may not be used.

In the present context, the term “printing” is intended to cover all methods utilized in technology called “printed electronics”, i.e. sheet-based and roll-to-roll-based methods. Sheet-
25 based methods include inkjet, paste dispensing and screen printing. Roll-to-roll-based methods include gravure, offset and flexographic printing. All these methods can be applied for manufacturing transversal modules on 2D-substrates, whereas paste dispensing, inkjets and spraying can be applied on 3D-substrates as well. Thermal spraying methods include so called Direct Write Thermal Spray – a technology developed and marketed by Mesoscribe Inc. If
30 utilizing inks and pastes the method may require sintering depending on materials.

Generally, in the present technology, on a substrate anisotropic materials are printed to form inclined surfaces. The material to be applied is in the form of a paste (pasty material having a high consistency, typically having a consistency of more than 10 % by weight, preferably 20 % or more, in particular 30 % or more, the percentage being calculated from the total weight of the solid material and the liquid phase) . Optionally masking can be utilized. It is also possible to print parallel wires into a second matrix material or to utilize nanothreads or nanotubes.

In modules produced by the present technology the temperature difference (heat flux) will give rise to an electric flux due to the Seebeck effect. This is caused by the interfaces of the anisotropic material. Alternatively an electric current will give rise to a temperature difference on the surfaces of the module (by the Peltier effect).

As indicated above, the application can be carried out by, for example, dispensing, spraying or printing. Specific examples include screen printing, inkjet, offset, rotogravure, flexography and spraying (including thermal spraying) and combinations thereof.

Various embodiments are possible:

The thermoelectric modules can comprise thermoelectric modules on 2D surfaces. It is also possible to provide thermoelectric modules on 3D- or conformal surfaces. Thus, a preferred embodiment comprises utilizing spraying, inkjets or dispensers module for manufacturing on 3D- or conformal surfaces.

The layers are printed in steps on a substrate to produce tilted lines of N-type and P-type semiconducting materials.

Other one of the materials can also be metallic.

The substrate material can be any, but should not be electrically conductive.

After printing the layers are cured or sintered.

Examples include:

- 5 Dispensing a comb-shaped structure using a commercial silver conductive paste on a ceramic substrate (Al_2O_3)

Dispensing a reversed comb-shaped structure using a polyacrylate based Bi_2Te_3 paste on the substrate so that lines are in contact to each other (Figure 3)

10

Generally, drying is carried out in an oven at increased temperature, preferably at about 50 °C, in particular at 100 °C or more, for example about 120 °C, for a time period of 1 to 120 min, for example about 10 min.

- 15 Figure 4 shows an embodiment similar to that above, wherein dispensing and drying the next layers has been carried out in the same way but shifting the starting point in regular steps so that in the cross section of the structure lines are in a 45° angle.

Trimming the line heads can be performed by cutting, for example by cutting with a scalpel.

- 20 Sintering is carried out at a temperature higher than used for drying, for example sintering can be carried out in a vacuum oven, at a temperature of 250 to 600 °C, for example at 350 °C, for 1 min to 24 h, for example about 4 h.

Finally, conductor wires can be attached for example using electrically conducting adhesives

- 25 (cf. Figure 5 and Figure 6)

Various embodiments are possible. Thus, for example, drying and porosity issues during sintering due to evaporation of binder can be dealt with by controlling conditions.

- 30 By utilizing a relatively "thick" paste (i.e. a paste having high consistency), drying after each layer may be omitted.

Manufacturing can be made faster if optical curing (UV) is used during printing (optically curing binder).

- 5 Sintering after printing can be avoided if laser sintering is applied during printing (or if conductive polymer is used as a binder, or if the printed mixture is readily conductive enough).

- 10 By making a zigzag- or labyrinth-structure after printing the power density of the structure can be enhanced considerably (Figure 7). Laser cutting may be utilized in this task. On the other hand the structure can be made such by utilizing printing several consequent layers on top of each other.

- 15 Utilizing two (or more) nozzles (two materials) simultaneously printing speed can be further enhanced.

Manufacturing is also possible on 3-dimensional substrates as depicted in Figure 8 (by other means).

- 20 It is also possible to carry out the dispensing or application by using other methods, including printing methods selected from the group of offset, gravure, and flexo techniques and combinations thereof.

References**Patent Literature**

- 5 US 2010326487A
 WO12014366
 WO10058553 A1
 WO12014366 A1
 WO12066788 A2
10 WO12137446 A1
 US2012263207 A1
 US2012266930 A1

Non-patent Literature

- 15 Goldsmid, H.J., Introduction to Thermoelectricity. Springer Series in Materials Science,
 Springer-Verlag, 2010, 242 p.
 Kyarad and Lengfellner, *Appl.Phys.Lett.* 89 (2006), p. 192103.

Claims:

1. Method of manufacturing transversal thermoelectric modules comprising tilted lines of N-type and P-type semiconducting materials on a substrate, comprising applying on the substrate a plurality of inclined layers of anisotropic materials by a printing technique.
2. The method according to claim 1, wherein the layers are printed in steps.
3. The method according to claim 1 or 2, wherein at least one inclined layer of a metallic material is printed.
4. The method according to any of the preceding claims, wherein the anisotropic material is printed using a paste, in particular a semiconducting paste.
5. The method according to any of the preceding claims, wherein the anisotropic materials are printed from a suitable, in particular semiconducting, paste by dispensing, spraying or printing, for example using a technique selected from screen printing, inkjet, offset, rotogravure, flexography, spraying and combinations thereof.
6. The method according to any of the preceding claims, comprising manufacturing thermoelectric modules on 3D- or conformal surfaces, for example by spraying, inkjet or dispensing.
7. The method according to any of the preceding claims, comprising the steps of dispensing a comb-shaped structure using a silver conductive paste on a substrate (Al_2O_3), or dispensing a comb-shaped structure using a polyacrylate based Bi_2Te_3 paste on a substrate.
8. The method according to claim 7, comprising dispensing a reversed comb-shaped structure wherein the lines are in contact to each other.

9. The method according to any of the preceding claims, wherein, after printing, the layers are cured or sintered.

10. The method according to any of the preceding claims, comprising producing
5 thermoelectric modules in which the inclination of the lines is about 10 to 80°, in particular about 25 to 75°, for example about 30 to 60°, with respect to the direction of a temperature gradient or current flux applied to the modules.

11. The method according to any of the preceding claims, wherein the lines are printed such
10 that they form a zigzag- or labyrinth-structure or pattern.

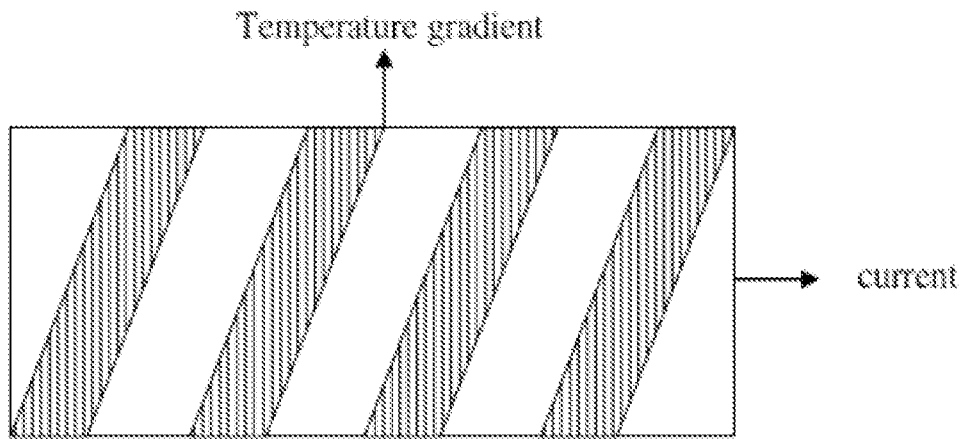


Figure 1 Schematic drawing of a synthetic transverse thermoelement.

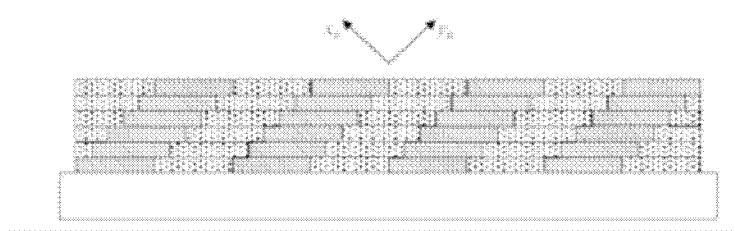


Fig. 2

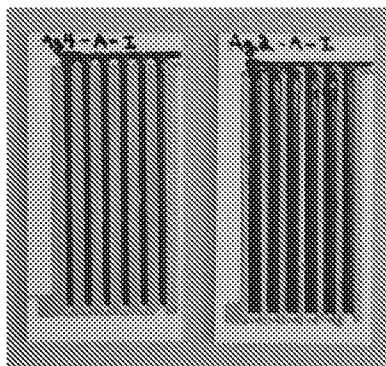


Fig. 3

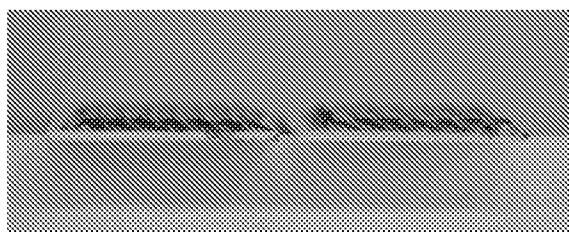


Fig. 4

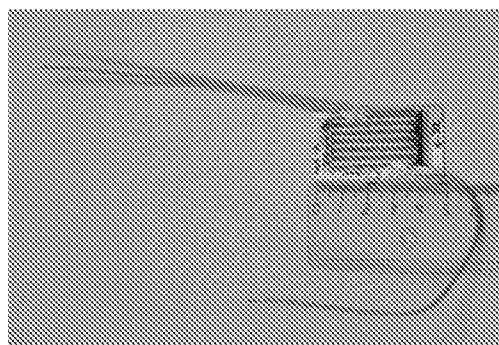


Fig. 5



Fig. 6

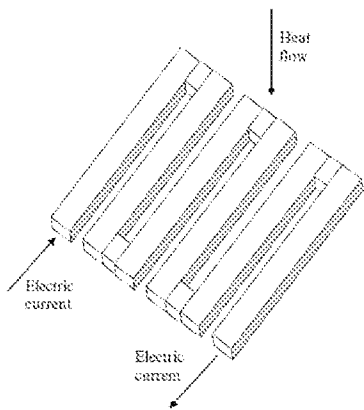


Fig. 7

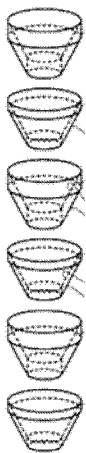


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2013/051125

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, , WPI, INSPEC, XPAIP, XPESP, XPESP2, XPI3E, XPIEE, XPIOP, Google scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Goldsmid, H. Julian. Introduction to Thermoelectricity, Chapter 11 Transverse Devices. Springer Series in Materials Science, Volume 121, Springer-Verlag Berlin Heidelberg, 2010 ISBN 978-3-642-00715-6 DOI: 10.1007/978-3-642-00716-3 cited in the application abstract, sections 11.3 "Materials for Transverse Thermoelements" and 11.4 "Alternative Configurations"; Table 11.1; Figures 11.1, 11-5, and 11.6	1-6, 9-11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier application or patent but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2013/051125

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Navone, C. et al. "Development of (Bi,Sb) ₂ (Te,Se) ₃ -Based Thermoelectric Modules by a Screen-Printing Process" Journal of Electronic Materials, Volume 39, number 9, 1 september 2010, pages 1755-1759 Print ISSN 0361-5235 DOI: 10.1007/s11664-010-1187-3 abstract, sections "INTRODUCTION" and "Thick-Film Thermoelectric Module Manufacturing"	1-5, 10, 11
Y	Chen, A et al. "Dispenser-printed planar thick-film thermoelectric energy generators" Journal of Micromechanics and Microengineering, Volume 21, Number 10, article id. 104006, October 2011, pp. 104006-104013 ISSN 0960-1317 DOI: 10.1088/0960-1317/21/10/104006 sections 1. "Introduction", 2.2. "Material synthesis" and 5. "Conclusion"	1-3, 6, 9-11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2013/051125

CLASSIFICATION OF SUBJECT MATTER

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