(19) Octrooicentrum Nederland

(11) 2020545

(12) B1 OCTROOI

(21) Aanvraagnummer: **2020545**

(22) Aanvraag ingediend: **7 maart 2018**

(51) Int. Cl.:
H01L 35/04 (2018.01) **H01L 35/22** (2018.01)

(41) Aanvraag ingeschreven:
13 september 2019

(43) Aanvraag gepubliceerd:
-

(47) Octrooi verleend:
13 september 2019

(45) Octrooischrift uitgegeven:
16 september 2019

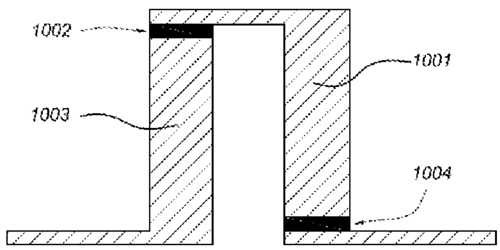
(73) Octrooihouder(s):
RGS Development B.V. te Broek op Langedijk.

(72) Uitvinder(s):
Axel Georg Schönecker te Alkmaar.
Pierre-Yves Pichon te Alkmaar.
Wilhelmus Gerardus Adrianus van Schaik te Maastricht.

(74) Gemachtigde:
ir. M.F.J.M. Ketelaars c.s. te Den Haag.

(54) Thermoelectric conversion device

(57) A thermoelectric device includes active elements containing thermoelectric materials of silicon, an alloy of silicon, a metal-silicide or silicon composite and an interconnection zone consisting of a metal interconnect and a re-crystallized phase consisisting of material from the active thermoelectric elements. The metal interconnect is from a metal that does not form metal silicides in a solid state, has a certain solubility for components of the thermoelectric elements in the liquid phase and a low solubility of these components in the solid phase. The active thermoelectric elements are shaped with a first and a second contact interface. The interconnection between the different thermoelectric elements consists of at least two phases of material, one of which is mainly the metallic interconnection material, the other is formed by the re-crystallized components of the thermoelectric materials.



Dit octrooi is verleend ongeacht het bijgevoegde resultaat van het onderzoek naar de stand van de techniek en schriftelijke opinie. Het octrooischrift komt overeen met de oorspronkelijk ingediende stukken.

NL B1 2020545

Thermoelectric conversion device

Field of the invention

The present invention relates to a thermoelectric conversion device made from a silicon containing material. Additionally, the invention relates to a method for manufacturing such a thermoelectric conversion device.

Background

Thermoelectric elements based upon bismuth telluride containing materials are well known and largely applied in different applications. However due to the material properties of bismuth telluride materials, such devices are typically limited to a maximum operating temperature of 250°C. In the so called high-temperature range with hot side device operating temperatures of more than 500°C, these materials are no longer useful.

On the other side, silicon, silicon composites, silicon alloys and metal-silicide based thermoelectric conversion devices offer the promise to become low cost, environmentally benign thermoelectric devices that are very well suited for high temperature operation with device hot side temperatures above 500°C. Consequently, such devices are ideal candidates for applications in e.g. the process industry where large amounts of waste heat are generated at very high temperature levels (often between 800°C and 1200°C) or in co-generation situation where heat and electricity are produced by combustion of gas or biomass. A promising material class for such high temperature thermoelectric devices is the group of silicon, silicon composites, silicon alloys or metal-silicides, denoted here as silicon containing materials, especially silicon with enclosed nano-structures, silicon germanium alloys (SiGe), higher manganese silicides (HMS), iron silicide ($FeSi_2$) and magnesium silicide (Mg_2Si) (silicides). These silicides are normally tuned to desired properties such as Seebeck voltage, electrical resistivity and thermal conductivity by addition of small traces of dopant materials. A well known example is boron doped SiGe in combination with phosphorous doped SiGe which allows the manufacturing of a p-type conductive material (boron doped SiGe) and a n-type conductive material (phosphorous doped SiGe). Other examples are aluminum doped higher manganese silicide as p-type conductive material or iron doped manganese silicide as n-type material.

As the voltage generated by the Seebeck effect over one thermoelectric element in such a thermoelectric conversion device is typically in the order of 100 mV, a thermoelectric conversion device consists typically of a plurality of thermoelectric elements connected electrically in series by an electrically conductive interconnection. Most preferably such a thermoelectric conversion device consists of two types of thermoelectric elements with a so called p-type conductive element and a n-type conductive element. Alternating these thermoelectric elements in a electrical series interconnection is a preferred method to manufacture a thermoelectric conversion device. However, as is known to the skilled in the art, parallel interconnections and devices consisting of only one type of thermoelectric elements (i.e., p-type or n-type) are possible. In many practical cases such an electrically conductive interconnection makes use of high temperature resistant metals such as nickel or copper. Under oxygen free environments also molybdenum and tungsten are useful elements for electrical interconnection. However due to the high operating temperatures and the long intended operational lifetime of a thermoelectric generator the technical requirements for these electrically conductive interconnections are extremely demanding.

In the process of making thermoelectric conversion devices, thermoelectric elements of at least one but preferably two silicon containing materials comprising silicon, silicon composites, silicon alloys or metal-silicide based materials (one n-type one p-type material) are connected in series using an electrical interconnection with low electrical resistance. These interconnections must fulfill a number of requirements such as:

- low electrical resistivity
- preferably none, or at least acceptably small, performance degradation under high temperature operation
- sufficient mechanical stability to allow the continuous operation of the thermoelectric module both under cyclic temperature operation as also under long time constant high temperature operation.

The accepted state-of-the-art is that a direct silicon containing material – metal interconnection cannot meet the technical requirements above. The reasons for that are that metals from the metal interconnection layer will diffuse into the thermoelectric (silicide) material and degrade the electrical properties while silicon from the thermoelectric material will react with the metal interconnection forming often very brittle metal silicides at the interface. As these diffusion processes will continue during device operation, such an interconnection is not stable under operation. Additionally silicon, silicon composites, silicon alloys or metal-silicide based material – metal interconnects often show differences in thermal expansion coefficient that lead to thermal stress in the interconnection and to crack formation or breakage of the interconnection.

Consequently, layered interface structures are used to overcome the stability issue and to produce the required properties.

WO2013145843 discloses a thermoelectric conversion module comprising manganese silicide as active material in contact with a Ni, Mo or W electrode using a Cr-Cu alloy stress relief layer in combination with a Ni diffusion barrier layer to prevent the solid-state diffusion of Cr or Cu into the manganese silicide. However, in our test results the proposed structure including a manganese silicide – Ni interface was not stable under long term operation in a high temperature environment. Such a system is expected to have a limited lifetime under high temperature operation.

Publication TW201234688 discloses a low resistivity electrical contact on e.g. magnesium silicide where the electrode material itself is a transition metal silicide or a mixture of transition metal silicide (e.g. nickel silicide, chromium silicide, cobalt silicide, titanium silicide) and possibly a metal. Such a structure provides low electrical resistance contacts to the thermoelectric material itself, however it is not useful for thermoelectric module manufacturing, as transition metal silicides are mechanically not sufficiently stable and in combination with a metal such e.g. Ni will not prevent silicon diffusion into the metal and finally conversion of the metal layer into metal silicide.

Publication JP2005317834 discloses a thermoelectric transformation module that comprises a thermoelectric transformation element of p-type iron silicide ($FeSi_2$); a thermoelectric transformation element of n-type iron silicide ($FeSi_2$); and an electrode member whose surface layer at least is of copper, molybdenum, cobalt, or tungsten. At least, the high temperature side of the thermoelectric transformation element is connected with the electrode member via an interposed layer of silver by a brazing filler metal member. The melting point of the brazing filler metal member is 600-820°C. In this publication a method is described where Ag particles are sintered in the above temperature range. Such a method will not produce a stable silver metal interconnection and is subject to further sintering of the Ag particles during thermoelectric operations and thus very likely unstable.

In general the prior art disclosures to produce low resistivity electrical contacts to silicides lack long term stability due to the diffusion of either metal components of the contacts into the thermoelectric silicide material or silicon from the thermoelectric material into the metallization layer where undesired or detrimental silicides are formed that often form a mechanically brittle material. In addition differences in thermal expansion coefficient lead to high thermal stress in the interconnection and can result in crack forming and finally breakage of the contacts.

An alternative approach to connect different materials based on silicon, silicon composites, silicon alloys or metal-silicides is the direct connection of the two thermoelectric elements without an interconnection metal by a so called p-n junction. This can be achieved by laser welding of the semiconductor metals, or by crystallizing a connected p-n type leg from a melt, or by diffusion of dopants from the surface of the material at high temperature. An example of such a device is described in WO0184641 (A1). Due to the omittance of a metal interconnection contact at the hot side of the elements, such technology overcomes the technical problems around the interconnection between a silicon or metal silicide material with a metallic interconnection. However, p-n junctions are less conductive compared to a metal contact and the conductivity is strongly temperature dependent, changing its rectifying p-n junction behavior to a more ohmic behavior when sufficiently thermally generated charger carrier concentrations are reached. At lower temperatures such a p-n junction is not sufficiently conductive, therefore p-n junction based thermoelectric devices are limited in performance at low and medium temperatures (depending upon the bandgap of the materials, ohmic conduction of a p-n junction might require temperatures of at least 500°C or above).

In summary, the state of the art in thermoelectric devices based upon silicon containing materials such as silicon, silicon composites, silicon alloys or metal-silicides based materials is that high conductivity Schottky type contacts between the semiconductor and an interconnection metal are not sufficiently stable due to metal silicide formation at the interface and metal interdiffusion into the semiconductor materials. The direct interconnection between two silicon, silicon composites, silicon alloys or metals silicides thermoelectric elements in the form of a p-n junction can result in a stable interconnection, however at a reduced device performance due to the higher resistivity of a p-n junction.

Summary of the invention

It is an object of the present invention to provide a thermoelectric conversion device based on silicon, silicon composites, silicon alloys or metal-silicide based materials and a method for manufacturing a thermoelectric conversion device that overcomes or mitigates the above detrimental effects.

The above object is achieved by a thermoelectric conversion device comprising a first and a second active element containing silicon, silicon composites, silicon alloys or metal-silicides. In dependence of the desired conduction type such first and second active element can be doped with different dopants to allow for a combination of a n-type conductive and a p-type conductivity. The elements are interconnected by an interconnection layer that consists of a combination of an interconnection metal and a recrystallized material phase consisting of constituents of the silicon, silicon composites, silicon alloys and metal-silicide based elements. The interconnection metal has the following properties:

- The interconnection metal does not react with silicon in the form of an interconnection metal-silicide phase in the solid phase.
- The interconnection metal will melt at a temperature below the melting point of any of the first or second thermoelectric elements.
- In the molten state the interconnection metal will dissolve at least one of the components of the thermoelectric elements, preferably the silicon element, or all components of the thermoelectric elements in the composition as exists in the elements. The solubility of components of the thermoelectric elements in the molten interconnection metal will be limited to a certain value, but will increase if the temperature of the liquid interconnection metal is increased.
- In the solid state the interconnection metal has a low solubility for any of the components of the thermoelectric elements.

As is described below in the examples, such metals that do not form an interconnection metal-silicide do exist in the case of silicon, silicon composites, silicon alloys and metal-silicide based thermoelectric materials. Examples are tin, zinc, aluminum, silver, germanium.

Such thermoelectric elements in combination with the interconnection metal will allow for an interconnection process where an assembly of two thermoelectric elements with the interconnection metal between them is heated to a temperature above the melting point of the interconnection metal. In contrast to the interconnection processes as outlined in the patents above, the interconnection metal is completely melted and liquid in this process. During the heating up of the liquid interconnection metal, a certain amount of at least one component but preferably all components of the thermoelectric elements are dissolved in the melt. After some time in the interconnection process the assembly will be cooled down, causing the dissolved components of the thermoelectric materials to crystallize from the liquid interconnection metal melt due to the reduced solubility. At the solidification point of the interconnection metal melt, the remaining components of the thermoelectric elements in the liquid interconnection melt also have to crystallize due to the low solubility of the elements in the solidified interconnection metal.

As a result of this process an electrical and mechanical interconnection between at least two thermoelectric elements is produced that consists of at least two different phases, a recrystallized phase of components from the thermoelectric elements and a solidified interconnection metal phase.

The advantages of such a process compared to the state of the art are that due to the properties of the selected interconnection metals the assembly becomes chemically inert in the solid state. In the areas where the interconnection metal connects the two thermoelectric materials a low electrical resistance interconnect is realized due to the Schottky contact behavior at the metal – thermoelectric element interface. The connected recrystallized thermoelectric material forms a less electrically conductive p-n junction that provides a high mechanical stability to the interconnection system.

The ratio between recrystallized thermoelectric elements and interconnection metal can be adjusted by process parameters such as the maximum temperature during the interconnection metal melting process. The form of the recrystallized thermoelectric elements phase can be adjusted by the resolidification temperature traject. Doing so the recrystallized phase can be controlled to form a homogeneous layer on the thermoelectric elements with a solidified metal layer in between. Such conditions would result in high electrical conductivity with reduced mechanical strength of the interconnection. If the recrystallization process is done at a different cooling rate, the recrystallization front is destabilised resulting in recrystallized interconnections between the thermoelectric elements. Such a system has an advantage with respect to mechanical stability at the expense of a slightly lower electrical conductivity. As a consequence such process yields the necessary process adjustments to allow the manufacturing of a thermoelectric generator according to its functional requirements.

Another advantage of this system is that the amount of metal in the metal interconnection is typically low with a preferred interconnection metal layer thicknesses between 5 μm and 500 μm.

Brief description of drawings

The invention will be explained in more detail below with reference to drawings in which illustrative embodiments thereof are shown. They are intended exclusively for illustrative purposes and not to restrict the inventive concept, which is defined by the appended claims.

Figure 1 shows a cross-sectional view of a thermoelectric conversion device according to an embodiment of the present invention;

Figure 2 shows a cross-sectional view of another thermoelectric conversion device according to an embodiment of the present invention;

Figure 3 shows a cross-sectional view of the interconnection scheme of a thermoelectric conversion device according to an embodiment of the present invention before the manufacturing process;

Figure 4 shows a cross-sectional view of the interconnection scheme of a thermoelectric conversion device according to an embodiment of the present invention after the manufacturing process;

Figure 5 shows a cross-sectional view of the interconnection scheme of a thermoelectric device according to another embodiment of the present invention after the manufacturing process;

Figure 6 shows a cross-sectional view of the interconnection scheme of a thermoelectric device according to another embodiment of the present invention after the manufacturing process;

Figure 7 shows a photograph of a cross-sectional microscopic view of an actual interconnection of a thermoelectric conversion device according to an embodiment of the present invention after the manufacturing process;

Figure 8 shows the phase diagram of the silver-silicon system, and

Figure 9 shows diagramatically a perspective view of a thermoelectric device build according to an embodiment of the present invention.

Detailed description of embodiments

Figure 1 shows a cross-sectional view of a thermoelectric conversion device according to an embodiment of the present invention.

According to an embodiment, a thermoelectric conversion device comprises a plurality of thermoelectric elements 1001 and 1003, also denoted as “active elements”, from a silicon, silicon composites, silicon alloys or metal-silicide based material. Such thermoelectric elements may have a shape of a bar.

Each thermoelectric element 1001; 1003 comprises a contact interface to an interconnection zone 1002 and a second interconnection zone 1004; For example, these contact and counter interfaces are formed at the respective ends of the bar shape. During use of the thermoelectric element one contact interface (e.g., the first contact interface) is kept at a relatively high temperature, i.e., a hot side positioned in a zone with relatively high temperature and the other, first counter interface as cold side is kept at relatively low temperature, positioned in a zone with, in comparison to the zone with high temperature, a relatively low temperature.

The thermoelectric elements 1001; 1003 are connected in series by providing a metal interconnect zone 1002. According to the invention, the interconnection zone 1002 which may be a strip-like element, consists of a volume of interconnection metal and a volume of re-crystallized components of the thermoelectric elements.

The second interconnection zone 1004 may preferably be made of the same components as the first interconnection zone 1004. However due to the difference in operation temperature other interconnection metals may be applied.

In an embodiment, the thermoelectric elements 1001; 1003 are “L”-shaped and made of one piece. Alternatively, the thermoelectric elements 1001; 1003 may each consist of two legs of the same material that are jointed by heat treatment to form the L-shape.

Figure 2 shows a cross-sectional view of a thermoelectric conversion device according to an embodiment of the present invention.

According to an embodiment, a thermoelectric conversion device comprises a plurality of thermoelectric elements 2001 and 2003, also denoted as “active elements”, from a silicon, silicon composites, silicon alloys or metal-silicide based material. Such thermoelectric elements may have a shape of a bar.

Each thermoelectric element 2001; 2003 comprises a contact interface to an interconnection zone 2002 on the hot side and the cold side; According to the invention, the interconnection zone 2002 which may be a strip-like element, consists of a volume of interconnection metal and a volume of re-crystallized components of the thermoelectric elements.

Figure 3 shows a cross section scheme of the interconnection prior to the manufacturing process. The thermoelectric elements 3001; 3003 are positioned with a metal interconnection layer 3002 in between the respective contact interfaces.

Figure 4 shows a cross section of the interconnection after the manufacturing process. The thermoelectric elements 4001; 4003 were partially dissolved in the liquid interconnection metal and re-crystallized during the cooling process. Such re-crystallization can be in form of pillars 4004 connecting the thermoelectric elements 4001; 4003. In between the pillars the solidified interconnection metal 4002 forms the conductive contact.

Figure 5 shows a cross section of the interconnection after the manufacturing process. One of the two thermoelectric elements 5001, is connected via a recrystallized elements - interconnection metal layer 5005 to a connecting element 5003 of the same material. The connecting element 5003 is than connected to the second thermoelectric element via the recrystallized elements – interconnection metal layer 5004.

Figure 6 shows a cross section of another thermoelectric device after the manufacturing process. The thermoelectric elements 6001 and 6002 are connected together via the recrystallized thermoelectric elements – metal interconnection layer 6003. On the thermoelectric element 6001 a third silicon, silicon composites, silicon alloys or metal-silicide based component 6004 is conductively connected using the same interconnection process 6005. Such structures are useful as heat exchangers in cases where the heat flux over the thermoelectric system is transferred from a liquid or gaseous material.

Figure 7 shows a microscopic picture of an actual cross section of two thermoelectric elements 7001; 7003 connected in accordance with an embodiment of this invention. In the re-crystallized interconnection zone, the interconnection metal 7002 is visible as light areas. In between the interconnection metal 7002 the thermoelectric material is re-crystallized 7004.

Figure 8 shows the phase diagram of the silver-silicon system according to R.W. Olesinski and G.J. Abbaschian (Binary Alloy Phase Diagrams, American Society for Metals, 1986). The dashed line 8004 indicates a processing temperature at 1000°C. In a typical embodiment of the invention, there would be a large amount of silicon in the thermoelectric elements and a limited amount of liquid silver. Therefore the system would be at the thermodynamic steady state point 8001. During cooling down, the system would develop along the solid Si-liquid Ag line towards the eutectic point 8002. During this cooling down period, the grey area 8003 indicates the amount of silicon that has to solidify under steady state conditions. It might be clear that this binary system is a simplification of a real system and only serves to illustrate the principle.

Figure 9 shows shows schematically a cross section of an actual thermoelectric conversion device manufactured according to an embodiment of the present invention.

As an example: phosphorous doped SiGe alloy can be used to manufacture a first type of n-type conductive thermoelectric elements 9001; boron doped SiGe can be used as a second type of p-type conductive thermoelectric elements 9002; these first and second elements 9001; 9002 can be interconnected using a connecting element 9003 and a silver interconnection metal between the first element 9001 and the connecting element 9003 and between the second element 9002 and the connecting element 9003, similar as shown in Figure 5.

All components are mounted in a positioning tool with a layer of the Ag interconnection metal in between the contacting surfaces. During a furnace process, where the Ag interconnection metal layer is melted, the interface is manufactured in accordance with the invention. The furnace process could have a top temperature above the melting point of Ag at 962°C such as 1000°C. After holding the top temperature for a certain amount of time to allow the dissolution of material from components of the thermoelectric elements in the interconnection metal melt, the recrystallization process is started by cooling down. Depending upon the change in solidification temperature due to the dissolved components of the thermoelectric elements, the solidification temperature will vary from the melting temperature of Ag.

For manufacturing purposes, the Ag interconnection metal layer in this example may be applied in form of a Ag foil that is positioned in between the thermoelectric elements; other application methods are evaporation of Ag on the surfaces, plating of a Ag layer or screen printing an Ag particle containing paste. However many other manufacturing processes such as chemical or physical vapor deposition, plasma deposition or sputtering are well known in industry and can be applied in accordance with this invention.

It is also possible to use other metals or metal alloys that have the characteristics that such an interconnection metal:

- does not react with silicon in the form of an interconnection metal-silicide phase in the solid phase;
- will melt at a temperature below the melting point of any of the first or second thermoelectric element;
- that in the molten state will dissolve at least one of the components of the thermoelectric elements, preferably the silicon element, most preferably all components of the thermoelectric elements in the composition as exists in the elements, with a solubility of components of the thermoelectric elements in the molten interconnection metal that is limited to a certain value, but will increase if the temperature of the liquid interconnection metal is increased;
- that in the solid state has a low solubility for any of the components of the thermoelectric elements.

Commercially available examples of such interconnection metal alloys are e.g., AgAl, or AgGe. Other metals that show the desired characteristics are e.g. Zn, Sn, Al, Ge. Obviously, alloys or mixtures of metals from these families can also be applied.

It is also possible to use mixtures or alloys of such interconnection metals with components of the thermoelectric elements. Such compositions can be useful to control melting and solidification temperature and the amount of dissolved components of the thermoelectric elements.

Additionally, it should be mentioned that it can be advantageous to apply different interconnection metals for e.g. the hot side of the thermoelectric generator and the cold side of the thermoelectric generator as the operating temperature within the thermoelectric device of the interfaces will typically be different. Such a thermoelectric device could use a Ag interconnection metal to establish the interconnection of elements of the thermoelectric device in the areas operating under high temperatures in combination with the lower melting temperature Zn to establish the interconnection of parts of the thermoelectric device in the colder areas. It is now obvious that by using this invention for the high temperature interconnection, thermoelectric devices that combine this invention with other well known interconnection processes in colder parts are possible.

The interconnection method of this invention also allows the mechanical, thermal and electrical interconnection of thermoelectric elements of the same type or other structural components as part of a thermoelectric generator. Therefore this method can be used to attach structural components such as highly thermally conductive fins of a heat exchanger to the thermoelectric elements. Another possibility is to produce more complex geometrical shapes of the same type of thermoelectric element by connecting them together with the interconnection process of this invention. This enables the design of thermoelectric generators in a very efficient and flexible way as is obvious to the skilled in the art.

Another example uses higher manganese silicide material with e.g. vanadium, chromium or aluminum dopant as p-type thermoelectric element in combination with higher manganese silicide with iron or ruthenium dopant as n-type thermoelectric element.

It is also possible to combine silicides from different families in a manufacturing process as described in this invention under the condition that the silicide materials are sufficiently matched in thermal expansion coefficient. Such material combination are typically found when the thermoelectric or structural materials differ only in minor components such as addition of dopants or small percentages of an alloying component.

In an embodiment, the method of this invention uses a single high temperature process that allows to manufacture thermoelectric devices in a controlled way. The process itself can be described as mechanically stacking the thermoelectric silicon alloy in contact with the interconnection metal material. This mechanical stack is heated in a gas atmosphere that substantially prevents the formation of surface oxides, in a furnace, where the mechanical stack is heated to a temperature where only the interconnection metal as the lowest melting temperature component becomes liquid. As soon as the interconnection metal is liquid, components from the thermoelectric materials will be dissolved up to the solubility limit in the interconnection metal. The amount of dissolved components of the thermoelectric elements can be controlled by the amount of liquid interconnection metal and the overheating of the melt in dependence of the solubility. After a certain holding time the furnace temperature will be reduced to allow solidification of the dissolved components of the thermoelectric elements from the interconnection metal melt. At the solidification temperature of the mixture of molten interconnection metal and dissolved components of the thermoelectric elements, the system will solidify.

It will be obvious to the skilled in the art, that this process can be easily varied by changing process environments (vacuum, protective gas, reducing atmosphere), process times and process temperatures. It might be useful to foresee a time interval with a holding temperature during heating up to allow surface contaminations such as water to leave the surface of the components in the furnace. Also, surface oxides of the silver or metal components can be removed in a suitable heating up cycle. It is also possible and advantageous to lower the melting temperature of the interconnection metal by adding alloying materials. There are many other mixtures or alloying compositions possible for an interconnection metal, as long as the interconnection metal components do not form a silicide phase. Such non-silicide forming materials are e.g. Ag, Al, Ge, Sn, Zn.

With this process the desired layered structure is formed in a single process step however two step processes using different interconnection metals at different furnace temperatures will now be obvious.

In the foregoing description of the figures, the invention has been described with reference to specific embodiments thereof. It will, however, be evident that various modifications and changes may be made thereto without departing from the scope of the invention as summarized in the attached claims.

In addition, modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiments disclosed, but that the invention includes all embodiments falling within the scope of the appended claims.

In particular, combinations of specific features of various aspects of the invention may be made. An aspect of the invention may be further advantageously enhanced by adding a feature that was described in relation to another aspect of the invention.

It is to be understood that the invention is limited by the annexed claims and its technical equivalents only. In this document and in its claims, the verb "to comprise" and its conjugations are used in their non-limiting sense to mean that items following the word are included, without excluding items not specifically mentioned. In addition, reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element is present, unless the context clearly requires that there be one and only one of the elements. The indefinite article "a" or "an" thus usually means "at least one".

Conclusies

1. Thermoelektrische omzettingsinrichting omvattend ten minste een eerste en een tweede actief thermoelektrisch element, waarbij elk van de eerste en tweede actieve thermoelektrisch elementen is gebaseerd op een silicium bevattend materiaal, en een verbindingszone welke een verbindend metaalfasemateriaal en een gerekristalliseerd thermoelektrisch element componentfasemateriaal bevat tussen het eerste en het tweede actieve thermoelektrisch element, met het kenmerk, dat het verbindend metaalfasemateriaal:
   - niet reageert met silicium om een metaal-silicidefase in de vaste stof te vormen;
   - bij een temperatuur smelt onder het smeltpunt van welke dan ook van de materialen van de eerste of tweede thermoelektrisch elementen;
   - in de gesmolten toestand ten minste één van de samenstellende chemische elementen van de thermoelektrisch elementen oplost, bij voorkeur silicium, meer bij voorkeur alle samenstellende chemische elementen van de thermoelektrisch elementen, terwijl een oplosbaarheid van de een of meer samenstellende chemische elementen van de thermoelektrisch elementen in de smelt beperkt is, maar toenemend met hogere temperatuur, en
   - een lage oplosbaarheid bezit voor willekeurig welke van de samenstellende chemische elementen van de thermoelektrisch elementen in de vaste stof, lager dan de oplosbaarheid daarvan in de gesmolten toestand.

2. Thermoelektrische omzettingsinrichting volgens conclusie 1, waarbij het silicium bevattend materiaal er één omvat die geselecteerd is uit een groep omvattend silicium, silicium composiet, silicium legering of metaal-silicide.

3. Thermoelektrische omzettingsinrichting volgens conclusie 1 of 2, waarbij het verbindend metaalfasemateriaal een contact vormt tussen twee delen van het eerste of tweede actieve thermoelektrisch element.

4. Thermoelektrische omzettingsinrichting volgens willekeurig welke van de voorgaande conclusies 1 – 3, waarbij het verbindend metaalfasemateriaal contact maakt aan één of meer andere functionele componenten van de thermoelektrische

omzettingsinrichting die thermische of elektrische geleiding in de inrichting verschaffen; waarbij de andere functionele componenten elk zijn gebaseerd op het silicium bevattend materiaal.

5. Thermoelektrische omzettingsinrichting volgens willekeurig welke van de voorgaande conclusies 1-4, waarbij het verbindend metaalfasemateriaal is gebaseerd op ten minste een element uit een groep van Ag, Al, Ge, Sn, Zn, of mengsels of legeringen van ten minste twee elementen uit de groep.

6. Thermoelektrische omzettingsinrichting volgens willekeurig welke van de voorgaande conclusies 1-5, waarbij het verbindend metaal is gebaseerd op ten minste één element uit een groep van Ag, Al, Ge, Sn, Zn, of mengsels of legeringen van ten minste twee elementen uit de groep met toevoeging van één of meer van de samenstellende chemische elementen van de thermoelektrische materialen.

7. Thermoelektrische omzettingsinrichting volgens willekeurig welke van de voorgaande conclusies 1-6, waarbij het verbindend metaalfasemateriaal een dikte heeft tussen 5 µm en 500 µm bij aanvang van het verbindingsproces.

8. Thermoelektrische omzettingsinrichting volgens willekeurig welke van de voorgaande conclusies 1-7, omvattend een eerste verbindende metaalfase en een gerekristalliseerd thermoelektrisch element componentfase om componenten van de thermoelektrische inrichting te verbinden in het gebied van een contact aan de hoge temperatuurkant en een tweede verbindende metaalfase en een tweede gerekristalliseerd thermoelektrisch element componentfase om componenten van de thermoelektrische inrichting te verbinden in het gebied van een contact aan de lage temperatuurkant.

9. Werkwijze voor het vervaardigen van en thermoelektrische inrichting volgens willekeurig welke van de voorgaande conclusies 1-8,
omvattend:
plaatsen van ten minste een eerste actief thermoelektrisch element en een tweede

actief thermoelektrisch element in een samenstel met een gewenste geometrie van de te vormen thermoelektrische inrichting, met een eerste verbindend metaal aangebracht tussen eerste oppervlakken waar de eerste en tweede actieve thermoelektrische elementen dienen te worden verbonden;

verhitten van het samenstel van de eerste en tweede actieve thermoelektrische elementen op een eerste temperatuur boven een stollingspunt van het eerste verbindend metaal om een eerste vloeibaar verbindend metaal te vormen terwijl samenstellende chemische elementen van de eerste en tweede thermoelektrisch elementen wordt toegestaan om op te lossen in het eerste vloeibare verbindend metaal;

afkoelen van het samenstel op een bestuurde wijze voor het vormen van een eerste verbindingszone die bestaat uit een eerste verbindend metaalfasemateriaal en een eerste gerekristalliseerd thermoelektrisch element componentfasemateriaal tussen de eerste oppervlakken van het eerste actieve thermoelektrische element en het tweede actieve thermoelektrische element.

10. Werkwijze voor het vervaardigen volgens conclusie 9, voorts omvattend dat gedurende het verhitten van het samenstel op een grensvlak tussen het verbindend metaal en één of meer functionele componenten van de thermoelektrische omzettingsinrichting, samenstellende chemische elementen of het silicium bevattend materiaal oplossen in het vloeibaar verbindend metaal, en

dat gedurende het afkoelen bij het grensvlak een verbindingszone die bestaat uit een gerekristalliseerde metaalfase en een gerekristalliseerd silicium bevattend materiaal, wordt gevormd.

11. Werkwijze voor het vervaardigen volgens conclusie 9 of 10,

voorts omvattend:

gedurende het plaatsen van ten minste het eerste actieve thermoelektrisch element en het tweede actieve thermoelektrisch element in het samenstel met de gewenste geometrie van de te vormen thermoelektrisch inrichting:

het aanbrengen van een tweede verbindend metaal tussen tweede oppervlakken waar de eerste en tweede actieve thermoelektrische elementen dienen te worden verbonden;

waarbij het verhitten van het samenstel van de eerste en tweede actieve thermoelektrisch elementen op de eerste temperatuur boven een stollingspunt van het tweede verbindend metaal omvat: het vormen van een tweede vloeibaar verbindend metaal terwijl samenstellende chemische elementen van de eerste en tweede actieve thermoelektrisch elementen wordt toegestaan om op te lossen in het tweede vloeibaar verbindend metaal;

en

waarbij het afkoelen van het samenstel op bestuurde wijze omvat: het vormen van een tweede verbindingszone die bestaat uit een tweede gerekristalliseerd metaalfasemateriaal en een tweede gerekristalliseerd thermoelektrisch element componentfasemateriaal tussen de tweede oppervlakken van het eerste en het tweede actieve thermoelektrisch element,

waarbij het tweede verbindend metaalfasemateriaal verschilt van het eerste verbindend metaalfasemateriaal.

12. Werkwijze voor het vervaardigen volgens conclusie 9 of 10,

voorts omvattend na het vormen van de eerste verbindingszone die bestaat uit het eerste gerekristalliseerd metaalfasemateriaal en het eerste gerekristalliseerd thermoelektrisch element componentfasemateriaal tussen de eerste oppervlakken van het eerste actieve thermoelektrisch element en het tweede actieve thermoelektrisch element:

aanbrengen van een tweede verbindend metaal tussen de tweede oppervlakken waar de eerste en tweede actieve thermoelektrisch elementen dienen te worden verbonden;

verhitten van het samenstel van de eerste en tweede actieve thermoelektrische elementen op een tweede temperatuur boven een stollingspunt van het tweede verbindend metaal om een tweede vloeibaar verbindend metaal te vormen terwijl samenstellende chemische elementen van de eerste en tweede actieve thermoelektrische elementen wordt toegestaan om op te lossen in het tweede vloeibaar verbindend metaal;

afkoelen van het samenstel op bestuurde wijze voor het vormen van een tweede verbindingszone die bestaat uit een tweede gerekristalliseerd metaalfasemateriaal en een tweede gerekristalliseerd thermoelektrisch element component-

fasemateriaal tussen de tweede oppervlakken van het eerste en het tweede actieve thermoelektrisch element,
waarbij het tweede verbindend metaal verschilt van het eerste verbindend metaal en de tweede temperatuur lager is dan de eerste temperatuur.

13. Werkwijze voor het vervaardigen volgens willekeurig welke van de voorgaande conclusies 9 - 12, waarbij het verbindend metaalfasemateriaal hoofdzakelijk is gebaseerd op ten minste één element uit een groep van Ag, Al, Ge, Sn, Zn, of mengsels of legeringen van ten minste twee elementen uit de groep.

14. Werkwijze voor het vervaardigen volgens willekeurig welke van de voorgaande conclusies 9 - 12, waarbij het verbindend metaal is gebaseerd op ten minste één element uit een groep van Ag, Al, Ge, Sn, Zn, of mengsels of legeringen van ten minste twee elementen uit de groep met toevoeging van één of meer van de samenstellende chemische elementen van de thermoelektrische materialen.

15. Werkwijze voor het vervaardigen volgens willekeurig welke van de voorgaande conclusies 9 - 14, waarbij het verbindend metaal een aanvankelijke dikte heeft tussen 5µm en 500µm wanneer het is aangebracht tussen oppervlakken waar de eerste en tweede thermoelektrisch elementen dienen te worden verbonden, vóór het verhitten van het samenstel.

Fig. 1

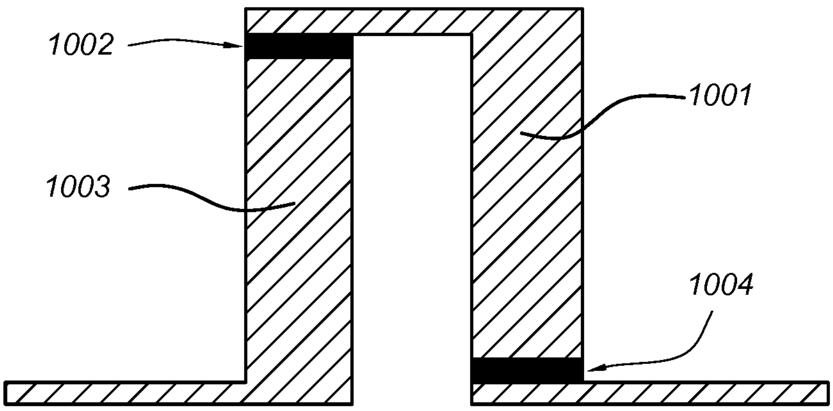


Fig. 2

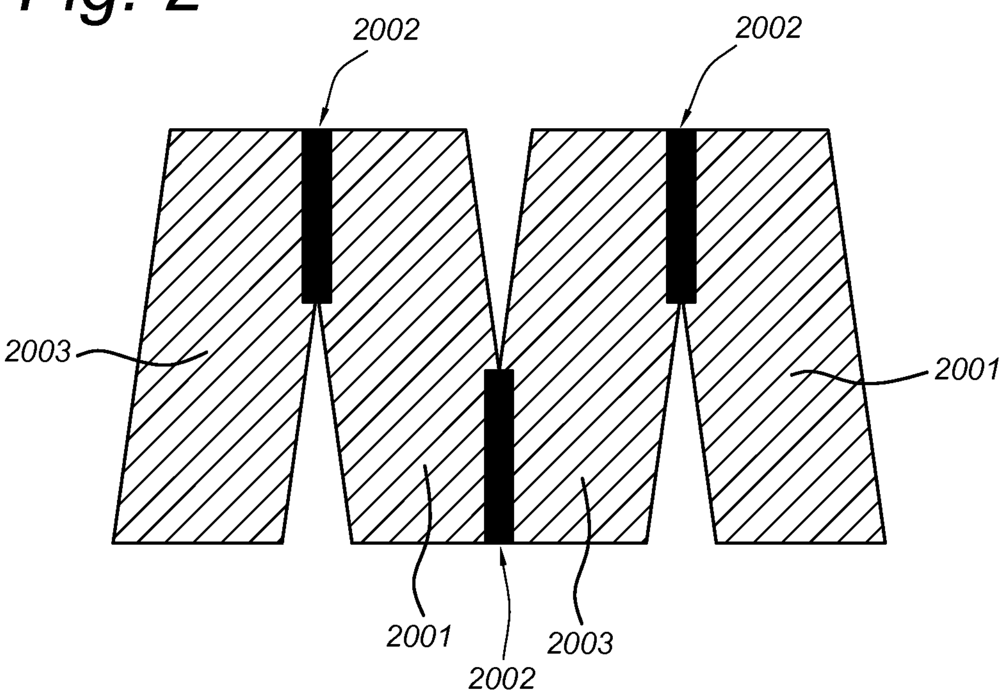


Fig. 3

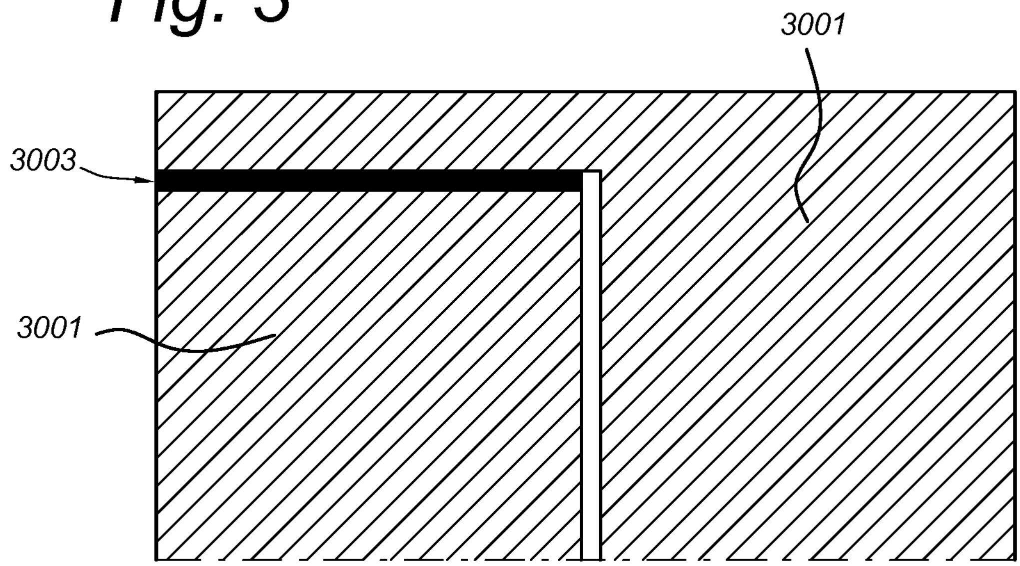


Fig. 4

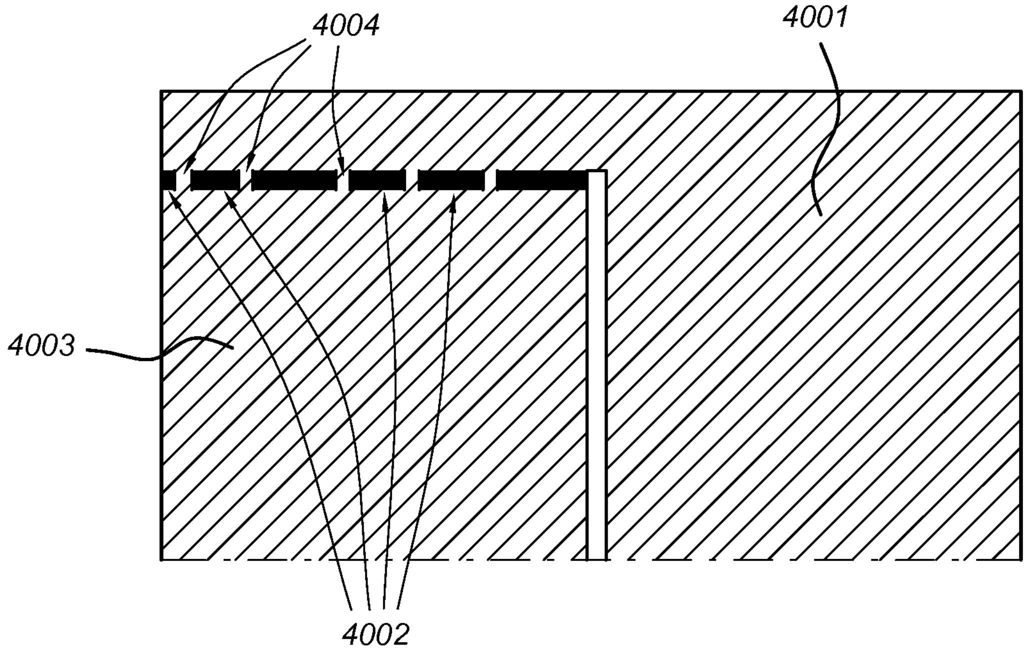


Fig. 5

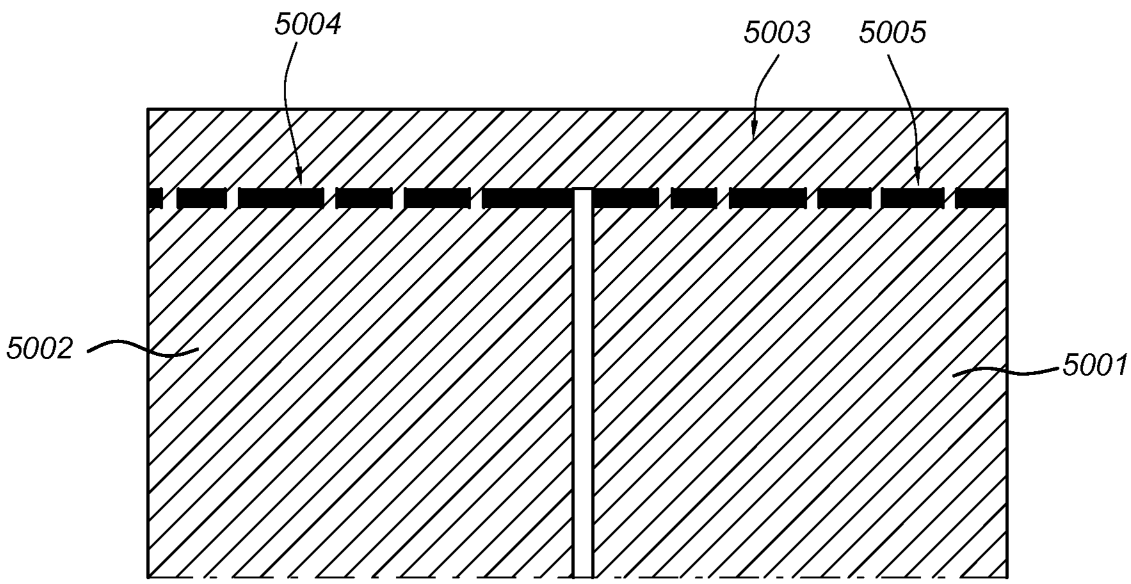


Fig. 6

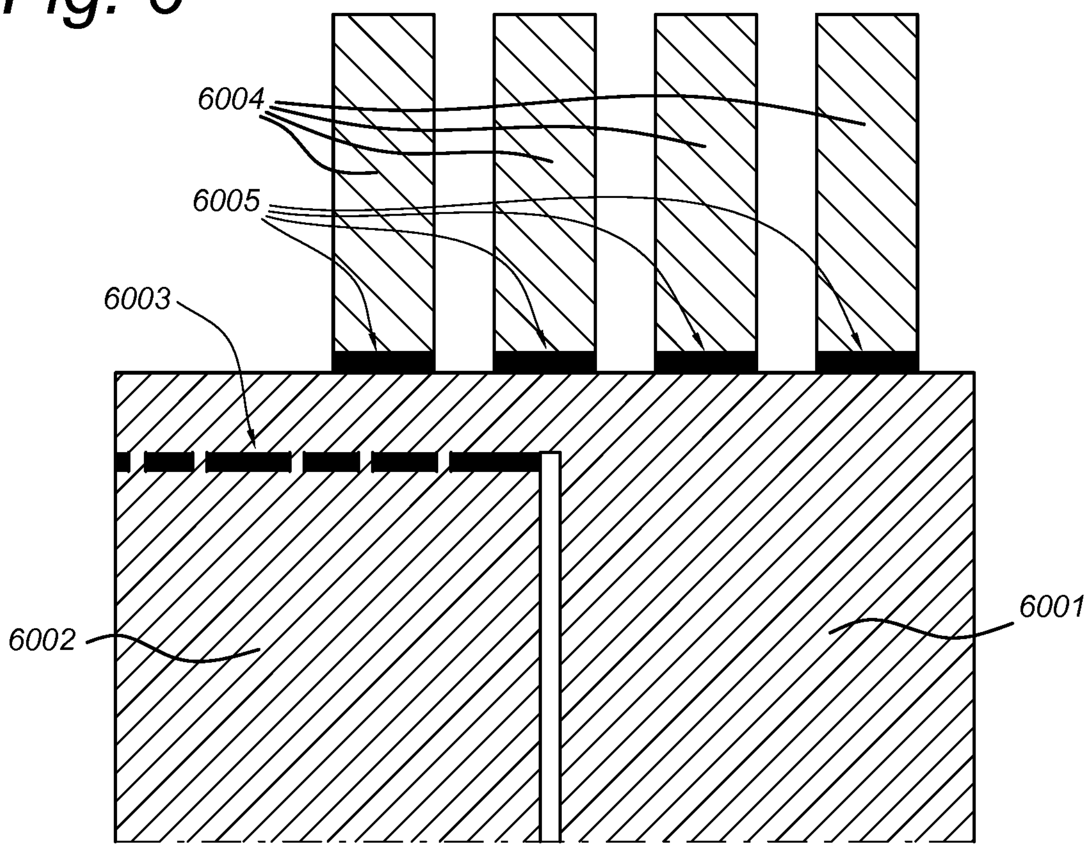


Fig. 7

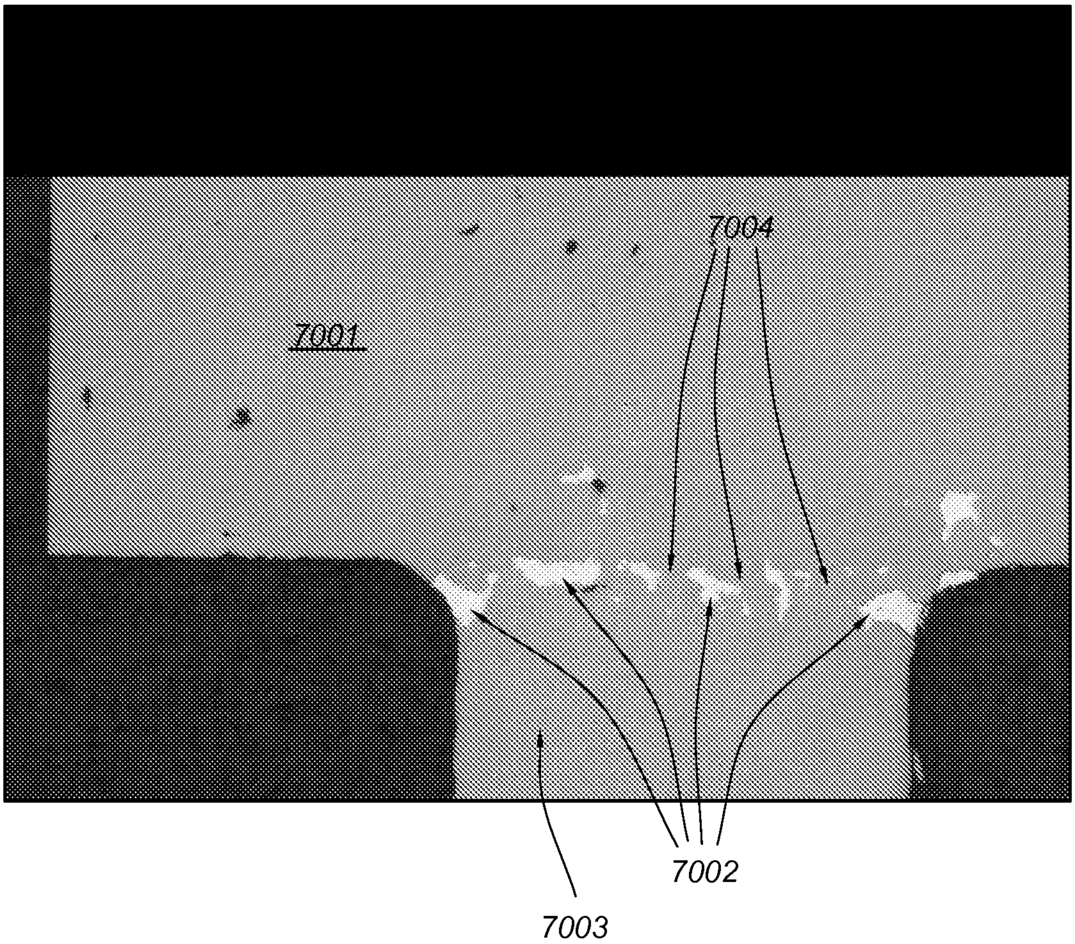
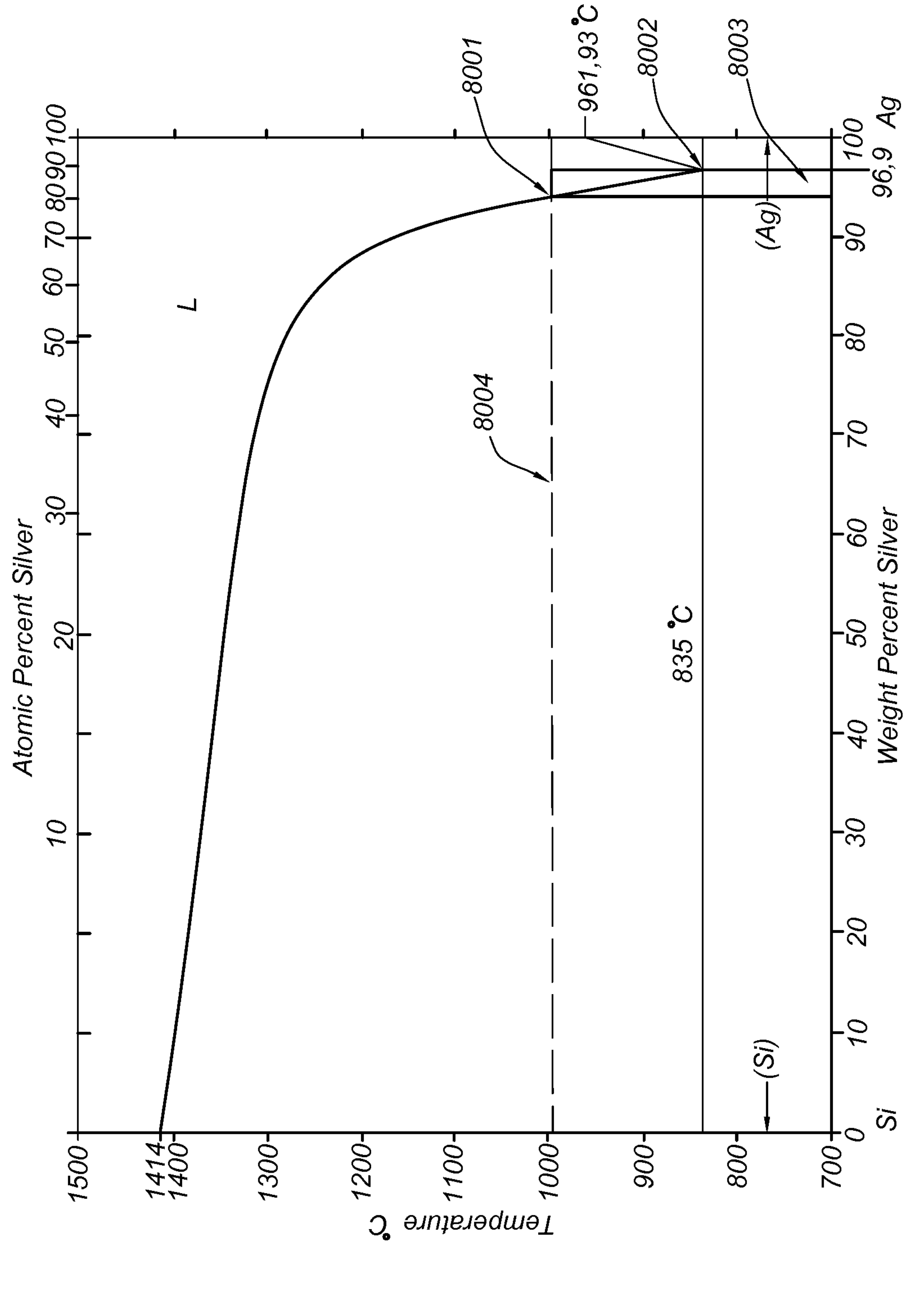
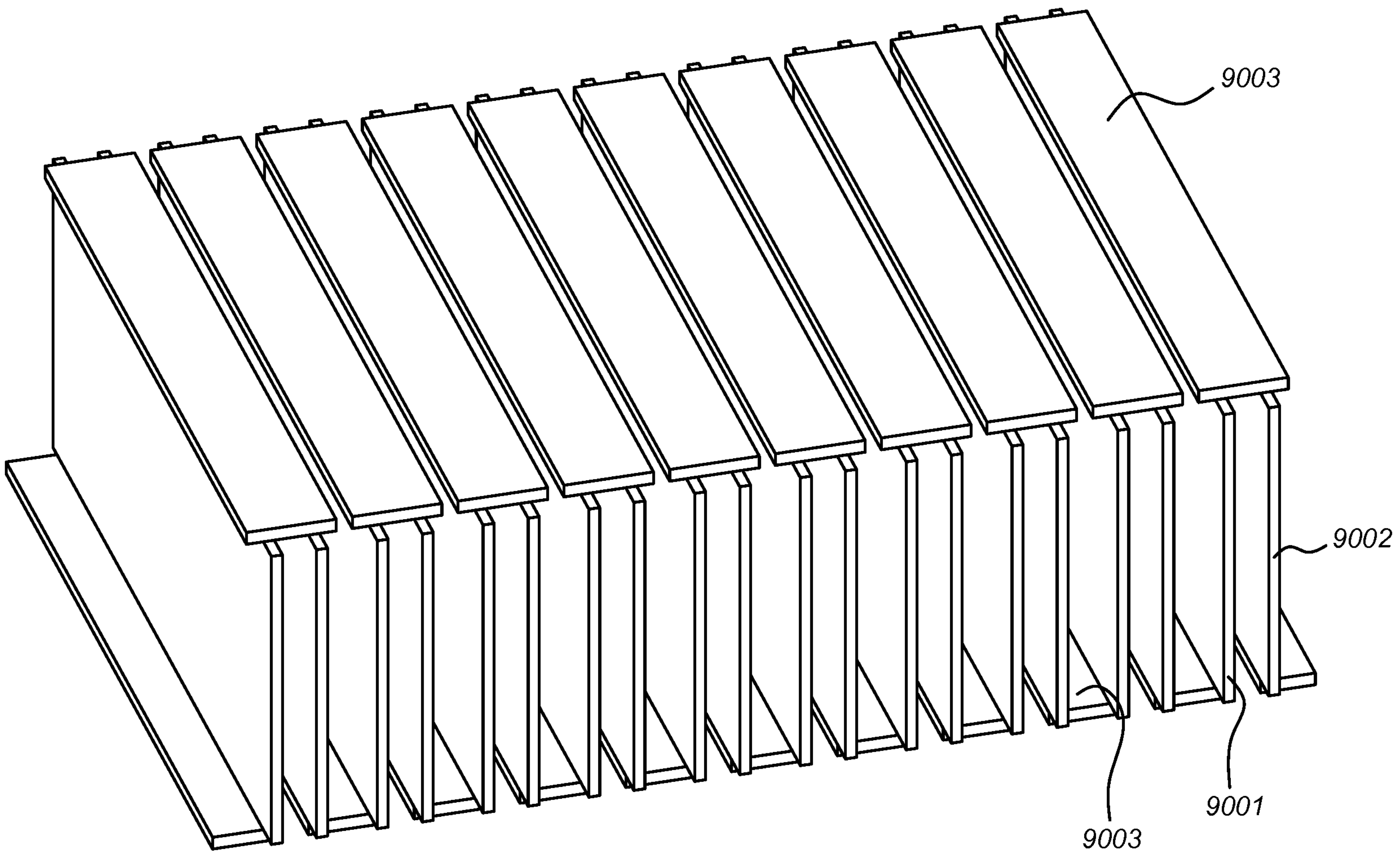


Fig. 8



Atomic Percent Silver
10
20
30
40
50
60
70
80
90
100
L
8001
961,93 °C
8002
8003
8004
835 °C
(Ag)
(Si)
96,9
Ag
Si
Weight Percent Silver
0
10
20
30
40
50
60
70
80
90
100
Temperature °C
1500
1414
1400
1300
1200
1100
1000
900
800
700

Fig. 9



Abstract

A thermoelectric device includes active elements containing thermoelectric materials of silicon, an alloy of silicon, a metal-silicide or silicon composite and an interconnection zone consisting of a metal interconnect and a re-crystallized phase consisisting of material from the active thermoelectric elements. The metal interconnect is from a metal that does not form metal silicides in a solid state, has a certain solubility for components of the thermoelectric elements in the liquid phase and a low solubility of these components in the solid phase. The active thermoelectric elements are shaped with a first and a second contact interface. The interconnection between the different thermoelectric elements consists of at least two phases of material, one of which is mainly the metallic interconnection material, the other is formed by the re-crystallized components of the thermoelectric materials.

[fig.1]

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE **P6073049NL**
Nederlands aanvraag nr. **2020545**	Indieningsdatum **07-03-2018**
	Ingeroepen voorrangsdatum
Aanvrager (Naam) **RGS Development B.V.**	
Datum van het verzoek voor een onderzoek van internationaal type **12-05-2018**	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. **SN71220**

I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)

Volgens de internationale classificatie (IPC)

H01L35/22;H01L35/04

II. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimumdocumentatie	
Classificatiesysteem	Classificatiesymbolen
IPC	**H01L**

Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

III.	☐	**GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES**	(opmerkingen op aanvullingsblad)
IV.	☐	**GEBREK AAN EENHEID VAN UITVINDING**	(opmerkingen op aanvullingsblad)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2020545

A. CLASSIFICATIE VAN HET ONDERWERP
INV. H01L35/22 H01L35/04
ADD.

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte mimimum documentatie (classificatie gevolgd door classificatiesymbolen)
H01L

Onderzochte andere documentatie dan de mimimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)

EPO-Internal, WPI Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
A	JP H10 22530 A (SUMITOMO SPEC METALS) 23 januari 1998 (1998-01-23) * alineas [0011] - [0013] * * tabel 1 * * figuren 1,2 * -----	1-15
A	EP 0 969 526 A1 (SUMITOMO SPEC METALS [JP]) 5 januari 2000 (2000-01-05) * alineas [0019] - [0021] * * conclusie 1 * * alineas [0041] - [0045] * * alinea [0085] * * figuur 2 * -----	1-15
A	JP H08 148726 A (NGK SPARK PLUG CO) 7 juni 1996 (1996-06-07) * het gehele document * ----- -/--	1-15

[X] Verdere documenten worden vermeld in het vervolg van vak C.

[X] Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

° Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"D" in de octrooiaanvrage vermeld

"E" eerdere octrooi(aanvrage), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermelde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"&" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid

28 november 2018

Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type

Naam en adres van de instantie

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

De bevoegde ambtenaar

Deconinck, Eric

1

Formulier PCT/ISA/201 (tweede blad) (Januari 2004)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2020545

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN

Categorie *	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
A	US 2003/091092 A1 (ENGEL CHRISTINE [DE] ET AL) 15 mei 2003 (2003-05-15) * samenvatting * * alineas [0018] - [0024] * * conclusie 5 * -----	1-15
A	JP H09 100166 A (TOKUYAMA CORP) 15 april 1997 (1997-04-15) * samenvatting * * figuur 1 * -----	1-15

1

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2020545

In het rapport genoemd octrooigeschrift		Datum van publicatie	Overeenkomend(e) geschrift(en)		Datum van publicatie
JP H1022530	A	23-01-1998	GEEN		
EP 0969526	A1	05-01-2000	AU 743474	B2	24-01-2002
			CA 2282547	A1	08-07-1999
			CN 1251689	A	26-04-2000
			EP 0969526	A1	05-01-2000
			JP 4285665	B2	24-06-2009
			KR 20000075805	A	26-12-2000
			US 6271460	B1	07-08-2001
			WO 9934450	A1	08-07-1999
JP H08148726	A	07-06-1996	GEEN		
US 2003091092	A1	15-05-2003	DE 10030354	A1	10-01-2002
			EP 1297580	A1	02-04-2003
			JP 4314028	B2	12-08-2009
			JP 2003536277	A	02-12-2003
			US 2003091092	A1	15-05-2003
			WO 0199204	A1	27-12-2001
JP H09100166	A	15-04-1997	GEEN		

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
SN71220	07.03.2018		NL2020545

International Patent Classification (IPC)
INV. H01L35/22 H01L35/04

Applicant
RGS Development B.V.

This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the application
- ☒ Box No. VIII Certain observations on the application

Examiner
Deconinck, Eric

WRITTEN OPINION

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	1-15
	No:	Claims	
Inventive step	Yes:	Claims	1-15
	No:	Claims	
Industrial applicability	Yes:	Claims	1-15
	No:	Claims	

2. Citations and explanations

   see separate sheet

WRITTEN OPINION

Box No. VIII Certain observations on the application

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following documents:

D1 JP H10 22530 A (SUMITOMO SPEC METALS) 23 januari 1998 (1998-01-23)

D2 EP 0 969 526 A1 (SUMITOMO SPEC METALS [JP]) 5 januari 2000 (2000-01-05)

D3 JP H08 148726 A (NGK SPARK PLUG CO) 7 juni 1996 (1996-06-07)

2 **D1** (see [0011] - [0013]; table 1; fig 1,2) which is considered to represent the most relevant state of the art with respect to independent claim 1 and discloses

Thermoelektrische omzettingsinrichting omvattend ten minste een eerste (1) en een tweede (3) actief thermoelektrisch element, waarbij elk van de eerste en tweede actieve thermoelektrisch elementen is gebaseerd op een silicium bevattend materiaal ([0011]), en een verbindingszone welke een verbindend metaal (5) bevat tussen het eerste en het tweede actieve thermoelektrisch element,

from which the subject-matter of claim 1 differs in that

de verbindingszone een verbindend metaalfasemateriaal en een gerekristalliseerd thermoelektrisch element componentfasemateriaal bevat; en dat

dat het verbindend metaalfasemateriaal:

- niet reageert met silicium om een metaal-silicidefase in de vaste stof te vormen;

- bij een temperatuur smelt onder het smeltpunt van welke dan ook van de materialen van de eerste of tweede thermoelektrisch elementen;

- in de gesmolten toestand ten minste één van de samenstellende chemische elementen van de thermoelektrisch elementen oplost, bij voorkeur silicium, meer bij voorkeur alle samenstellende chemische elementen van de thermoelektrisch elementen, terwijl een oplosbaarheid van de een of meer samenstellende chemische elementen van de thermoelektrisch elementen in de smelt beperkt is, maar toenemend met hogere temperatuur, en

- een lage oplosbaarheid bezit voor willekeurig welke van de samenstellende chemische elementen van de thermoelektrisch elementen in de vaste stof, lager dan de oplosbaarheid daarvan in de gesmolten toestand.

The subject-matter of claim 1 is therefore new.

3 **D1** is also considered to represent the most relevant state of the art with respect to independent claim 9 and discloses

Werkwijze voor het vervaardigen van en thermoelektrische inrichting omvattend (see [0012],[0013]):

plaatsen van ten minste een eerste actief thermoelektrisch element (1) en een tweede actief thermoelektrisch element (3) in een samenstel met een gewenste geometrie ([0013]: sandwiched in a jig using a clamp) van de te vormen thermoelektrische inrichting, met een eerste verbindend metaal (5, [0013]: Ag metal film) aangebracht tussen eerste oppervlakken (2,4) waar de eerste en tweede actieve thermoelektrische elementen (1,3) dienen te worden verbonden;

verhitten van het samenstel ([0012] van de eerste en tweede actieve thermoelektrische elementen op een eerste temperatuur boven een stollingspunt ([0012]: 900-150°C) van het eerste verbindend metaal om een eerste vloeibaar verbindend metaal te vormen terwijl samenstellende chemische elementen van de eerste en tweede thermoelektrisch elementen wordt toegestaan om op te lossen in het eerste vloeibare verbindend metaal (holding for 5-20 minutes the thermoelectric elements and metal film at a temperature of 1050°C it is understood that Si from the thermoelectric material will dissolve in the molten Ag metal film; see also Ag-Si phase diagram).

from which the subject-matter of claim 1 differs in that

afkoelen van het samenstel op een bestuurde wijze voor het vormen van een eerste verbindingszone die bestaat uit een eerste verbindend metaalfasemateriaal en een eerste gerekristalliseerd thermoelektrisch element componentfasemateriaal tussen de eerste oppervlakken van het eerste actieve thermoelektrische element en het tweede actieve thermoelektrische element.

The subject-matter of claim 9 is therefore new.

4 The differences of claim 1 and claim 9 with respect to the closest prior art have the technical effect that a more stable interconnection and a p-n junction with a lower resistivity can be obtained. The problem to be solved by the present invention may be regarded as to improve reliability and performance of a thermoelectric conversion device as such.

5 The subject-matter of independent claims 1 and 9 is considered involving an inventive step for the following reasons:

5.1 According to the process of claim 9 a controlled cooling provides an electrical and mechanical interconnection between at least two thermoelectric elements is produced that consists of at least two different phases, a recrystallized phase of components from the thermoelectric elements and a solidified interconnection metal phase. The advantages of such a process compared to the state of the art are that due to the properties of the selected interconnection metals the assembly becomes chemically inert in the solid state. In the areas where the interconnection metal connects the two thermoelectric materials a low electrical resistance interconnect is realized due to the Schottky contact behavior at the metal - thermoelectric element interface. The connected recrystallized thermoelectric material forms a less electrically conductive p-n junction that provides a high mechanical stability to the interconnection system.

5.2 **D1** is silent about a controlled cooling and the therewith related how the microstructure at the interface will look like and if a recrystallized phase of components from the thermoelectric elements and a solidified interconnection metal phase are formed.

5.3 **D2** relates to a similar configuration of silicon containing thermoelectric elements forming a p-n junction bonded by an Al or Ag metal layer (see [0085]). Also **D2** is silent about the cooling down process and the resulting difference in microstructure at the p-n junction.

5.4 **D3** discloses iron silicide thermoelectric elements and bonding them by use of a Ag-Cu-Ti brazing material (see Table 1) discloses brazing temperature of 1060°C so Ag will be liquid and be able to form a intermetallic compound with the thermoelectric material. **D3** is silent about the cooling down process and the resulting difference in microstructure at the p-n junction.

5.5 Further **D1**, **D2** nor **D3** give a hint or indication to a possible alteration of the mechanical and electrical properties at the junction. One could suggest that to some extent at cooling down different phases are formed but it would not lead the skilled person to a process according to claim 9 and also not to a thermoelectric device according claim 1 with the specific characteristics of the interconnection metal phase as defined. The combination of the features of independent claims 1 and 9 is is not rendered obvious by, the available prior art and therefore involves an inventive step

5.6 Claims 2-8 and 10-15 are dependent on claim 1 and 9 respectively and as such also meet the requirements of novelty and inventive step.

Re Item VIII

Certain observations on the application

6 Claims 1-15 are not clear.

6.1 The description and examples do not support all possible combinations of metals / metal compositions used for the interconnection metal and forming the interconnection metal phase at the p-n junction. The description on page 6, lines 1-2 and page 11, lines 24-30 only supports the use of Ag, Al, Sn, Zn, Ge or alloys thereof.

6.2 The same applies for the possible silicon containing thermoelectric materials. It considers such a wide range of possible materials containing silicon, i.e. with a silicon content ranging from from 99,99% up to 0,01% whereas the description and the way of carrying out the invention seems to not support such a broad definition, especially when considering the formation of an interconnection metal phase.

6.3 The applicant has the opportunity to demonstrate in a convincing manner that the description is enabling on the entire scope of the claims, while also considering the problem to be solved. Should that not be possible, the applicant is required to limit the scope of the claims to the extent of the description and the specific compositions mentioned there.

* * *