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(54) Title: MULTILAYER THIN FILM AND THE PREPARATION THEREOF

(57) Abstract: The present invention relates to a multilayer thermoelectric structure, the method of preparation thereof, and the use thereof. The multilayer thermoelectric structure of the present invention can be used, for example, as a heat recovery system in a Thermoelectric Generator (TEG) which converts heat energy to electric energy, or as a Peltier cooling/heating module which can be used in seat heater, humidity controller, or compact refrigerator. The present invention relates to a multilayer thermoelectric structure comprising a plurality of alternated layers of: (A) : crystalline thermoelectric material; and (B) : a material of separation which is a material different from (A); wherein at least one of the two end layers is a layer of (B); and wherein the crystalline thermoelectric material (A) is selected from the group consisting of: Bi₂Te₃, GaTe, Bi₂S₃, Bi₂Se₃, MoS₂, TiS₃, TiSe₃, TiTe₃, MnPS₃, CdPS₃, CdPS₃, NiPS₃, ZnPS₃, Mn_{0.5}Fe_{0.5}PS₃, GaS, GaSe, InS, InSe, InTe, TiS₂, MnS, MnTe, ZnS, ZnSe, GaSb, GeSb, GeTe, CdS, CdSe, CdTe, In₂S₃, In₂Se₃, InSb, Sb₂Te₃, and Ge₂Sb₂Te₅. The present invention also relates to a use of the multilayer thermoelectric structure, in a thermoelectric module, superconducting cable, secondary battery or nonlinear optical device.

Multilayer thin film and the preparation thereof

Field of Invention

The present invention relates to a multilayer thermoelectric structure, the
5 method of preparation thereof, and the use thereof. The multilayer thermoelectric structure of the present invention, which may also be referred to herein as a "multilayer thin film", can be used, for example, as a heat recovery system in a Thermoelectric Generator (TEG) which converts heat energy to electric energy, or as a Peltier cooling/heating module which can be used in
10 seat heater, humidity controller, or compact refrigerator.

Background Art

Over the past decade, there has been heightened interest in the field of thermoelectrics, driven by the need for more efficient materials for power
15 generation. A thermoelectric system is an environment-friendly energy conversion technology with the advantages of small size, high stability, no pollutants and feasibility over a wide temperature range. The demand for alternative energy technologies to reduce our dependency on fossil fuels has led to important programs of research in several technical fields.

20 For example, in the automotive industry, power-generation applications are currently investigated, for example, as a means to develop electrical power from waste engine heat from the radiator and exhaust system for use in next-generation vehicles. In addition, thermoelectric refrigeration applications include seat coolers for comfort and electronic component cooling.

25 Among different thermoelectric materials, alloys based on the Bi_2Te_3 system $[(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-x}\text{Se}_x)_3]$ and the $\text{Si}_{1-y}\text{Ge}_y$ system have been extensively studied and optimized for their use as thermoelectric materials to perform in a variety of solid-state thermoelectric refrigeration and power-generation applications over the past 30 years.

Bi₂Te₃ in the crystallized state has a layer structure (Figure 1) with rhombohedral-hexagonal symmetry, wherein the layers are stacked along the c-axis (...Te₁-Bi-Te₂-Bi-Te₁...), and wherein the Bi and Te layers are held together by strong covalent bonds, whereas the bonding between adjacent Te layers is of the van der Waals type.

A key goal for thermoelectric research is increasing the material figure-of-merit ZT, which is directly related to the efficiency of the thermal/electrical energy conversion.

$$ZT = \frac{S^2 GT}{(K_e + K_l)} \quad (1)$$

where S is the Seebeck coefficient, G is the electrical conductance, T is the temperature and K_{e/l} is the electronic/lattice thermal conductance.

J. Maassen and M. Lundstorm disclose, in the non-patent literature [1], that in a computer-simulated Bi₂Te₃ system, a 1 quintuple layer-thickness (i.e. Te₁-Bi-Te₂-Bi-Te₁) is a superior thermoelectric compared to bulk Bi₂Te₃.

However, when a thermoelectric material is used for example in a thermoelectric module, superconducting cable, secondary battery or nonlinear optical device, it is desirable that the thickness of the thermoelectric layer is more than 100 μm, in order to obtain low electric resistance in the case of thermoelectric module.

It is possible to obtain a desired crystalline orientation and thickness by using a single crystal as substrate, as disclosed in non-patent literature [2], wherein the substrate can be for example, a single crystal of Si, quartz, ZnO, KCl, BaF₂, MgO.

However, such a method is not appropriate for industrial scale production.

Venkatasubramanian et al. disclose, in a non-patent literature [2], a single crystal substrate, which gives a good TE performance, but which is not appropriate for mass production on an industrial scale.

A "2D nano-sheet" is a multilayered structure consisting of several unit layers, said unit layers are separated from one another by Van der Waals gaps and wherein the thickness is less than 1 μm . In case of using a 2D nano-sheet, it would be necessary to stack several 2D nano-sheets to achieve the desirable thickness of more than 100 μm , even though a 2D nano-sheet generally has a good thermoelectric property. However, simple stacking of the 2D material creates bonding interaction between adjacent layers, since it is difficult to keep crystalline orientation, resulting in the stacked 2D nano-sheet becoming a usual bulk material, and not a 2D nano-sheet, thus losing the thermoelectric properties of a 2D nano-sheet.

Non-Patent Literature References

[1] J. Maassen and M. Lundstorm: Appl. Phys. Lett., Vol. 102, 093103 (2013).

[2] E. Venkatasubramanian, E. Siivola, T. Colpitts and B. O'Quinn: Nature 413, 597-602 (2001).

Therefore, there is a continuous need for a thermoelectric material/structure with high energy conversion efficiency, having a sufficient thickness, and which can be produced on an industrial scale.

Summary of the Invention

The present invention relates to a multilayer thermoelectric structure comprising a plurality of alternated layers of:

(A): crystalline thermoelectric material; and

(B): a material of separation which is a material different from (A);

wherein at least one of the two end layers is a layer of (B); and

wherein the crystalline thermoelectric material (A) is selected from the group consisting of: Bi_2Te_3 , GaTe , Bi_2S_3 , Bi_2Se_3 , MoS_2 , TiS_3 , TiSe_3 , TiTe_3 , MnPS_3 , CdPS_3 , NiPS_3 , ZnPS_3 , $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$, GaS , GaSe , InS , InSe , InTe , TiS_2 ,

MnS, MnTe, ZnS, ZnSe, GaSb, GeSb, GeTe, CdS, CdSe, CdTe, In₂S₃, In₂Se₃, InSb, Sb₂Te₃, and Ge₂Sb₂Te₅.

The present invention also relates to a use of the multilayer thermoelectric structure, in a thermoelectric module, superconducting cable,
5 secondary battery or nonlinear optical device.

Brief Description of the Figures

Figure 1 is a schematic representation of the crystalline structure of Bi₂Te₃.

10 Figures 2 and 3 (a)-(c) are schematic representations of a non-limiting illustrative multilayer thermoelectric structure of the present invention.

Figures 4 to 9 are X-ray diffraction patterns of the multilayer thermoelectric materials of Examples, Reference Example and Comparative Examples.

15 Figure 10 (a) is a Transmission Electron Microscopy (TEM) image of the multilayer thermoelectric material of Example 1.

Figure 10 (b) is an enlarged view of the Bi₂Te₃ layer of Figure 9 (a).

Figure 11 presents an example of a thermoelectric device in which a multilayer thermoelectric structure of the present invention is used.

20

Detailed Description of the Invention

<Definition>

The term "thermoelectric material", as used herein, refers to a
25 semiconductor which can convert heat to electricity and electricity to heat, this definition comprising not only well-known inorganic materials such as Bi₂Te₃, but also polymer materials.

The term "amorphous", as used herein, refers to having no real or apparent crystalline form.

The term "unit layer" as used herein, refers to a composite layer consisting of several atomic layers, separated from adjacent unit layers on both sides respectively by a Van der Waals gap.

C-planes are represented with (00l), which is perpendicular to c-axis
5 [001] of the crystal, i.e. (00l) planes are stacking in parallel to the stacking direction of the multilayer thermoelectric structure, and in other words, (00l) planes are in parallel to the separating layer. They can be detected by diffraction technique, such as XRD or Electron Diffraction with TEM. With XRD, a c-plane growth can be identified from (00l) reflections e.g. (006). Those
10 crystals which are not c-plane oriented, give other reflections, e.g. (015). Preferred c-plane growth can be defined with the following condition: the peak intensity ratio of (006)/(015) is greater than 1, when the diffraction plane is perpendicular to the stacking direction of the multilayer thermoelectric structure.

The stacking direction, as used herein, corresponds to the direction
15 perpendicular to the plane of a multilayer thermoelectric structure.

In the case of the crystalline layers of advantageous embodiment of the present invention, c-planes are parallel to the unit layer, divided by Van der Waals gaps. The electron or holes can be transported much faster in the c-
20 plane than across the c-planes.

<Multilayer thermoelectric structure>

The present invention relates to a multilayer thermoelectric structure comprising a plurality of alternated layers of:

25 (A): crystalline thermoelectric material; and

(B): a material of separation which is a material different from (A);

wherein at least one of the two end layers is a layer of (B); and

wherein the crystalline thermoelectric material (B) is selected from the group consisting of: Bi_2Te_3 , GaTe, Bi_2S_3 , Bi_2Se_3 , MoS_2 , TiS_3 , TiSe_3 , TiTe_3 , MnPS_3 , CdPS_3 ,

CdPS₃, NiPS₃, ZnPS₃, Mn_{0.5}Fe_{0.5}PS₃, GaS, GaSe, InS, InSe, InTe, TiS₂, MnS, MnTe, ZnS, ZnSe, GaSb, GeSb, GeTe, CdS, CdSe, CdTe, In₂S₃, In₂Se₃, InSb, Sb₂Te₃, and Ge₂Sb₂Te₅.

5 **(A) Thermoelectric material**

The thermoelectric material used herein can be a thermoelectric material, chosen among Bi₂Te₃, Bi₂S₃, Bi₂Se₃, transition metal dichalcogenides such as MoS₂, transition metal trichalcogenides such as TiS₃, TiSe₃, TiTe₃, Metal phosphorus trichalcogenides such as MnPS₃, CdPS₃, NiPS₃, ZnPS₃,
10 Mn_{0.5}Fe_{0.5}PS₃, III-VI layered semiconductor such as GaS, GaSe, GaTe, InS, InSe, and InTe. Alternatively, it is possible to use TiS₂, MnS, MnTe, ZnSe, GaSb, GeSb, GeTe, CdS, CdSe, CdTe, In₂S₃, In₂Se₃, InSb, and Sb₂Te₃, Ge₂Sb₂Te₅ as the thermoelectric material in the present invention. The thermoelectric material used herein is not particularly limited, but preferably is selected taking into
15 consideration the reactivity with the layer of separation.

Preferably, the thermoelectric material used in the present invention is Bi₂Te₃ or GeTe. Most preferably, the thermoelectric material used in the present invention is Bi₂Te₃.

Possible precursors used for depositing by ALD (atomic layer deposition)
20 a layer of thermoelectric material can be, for example, BiCl₃ and (Et₃Si)₂Te or (Me₃Si)₂Te for Bi₂Te₃.

Possible precursors for depositing other thermoelectric materials are listed in Table 1.

25 Table 1: Examples of possible precursors for depositing thermoelectric material

Thermoelectric material	Reactant A	Reactant B
TiS ₂	TiCl ₄	H ₂ S
MnS	MnCl ₂	H ₂ S
MnTe	Mn	Te
ZnS	Zn	S

	ZnCl ₂	H ₂ S
	ZnEt ₂	
	ZnMe ₂	
ZnSe	Zn	Se
		H ₂ Se
	ZnCl ₂	H ₂ Se
	ZnEt ₂	Et ₂ Se
GaSb	GaCl ₃	(Et ₃ Si) ₃ Sb
GeSb	GeCl ₂ (C ₄ H ₈ O ₂)	(Et ₃ Si) ₃ Sb
GeTe	GeCl ₂ (C ₄ H ₈ O ₂)	(Et ₃ Si) ₂ Te
CdS	Cd	S
	CdCl ₂	H ₂ S
CdSe	Cd	Se
	CdMe ₂	H ₂ Se
CdTe	Cd	Te
	CdMe ₂	Et ₂ Te
In ₂ S ₃	InCl ₃	H ₂ S
In ₂ Se ₃	InCl ₃	(Et ₃ Si) ₂ Se
InSb	In	Sb
Sb ₂ Te ₃	SbCl ₃	(Et ₃ Si) ₂ Te
Ge ₂ Sb ₂ Te ₅	GeCl ₂	SbCl ₃ (R ₃ Si) ₂ Te

The thickness of one layer is advantageously be chosen from the performance point of view.

The minimum thickness of thermoelectric material layer is preferably half the thickness of one unit layer, and preferably the thickness of one unit layer.

The maximum thickness of thermoelectric material layer is preferably 20 times of the thickness of a unit layer, and preferably 3 times the thickness of one unit layer.

Preferably, the thickness of thermoelectric material is half the thickness of one unit layer or more, and 20 times of the thickness of a unit layer or less.

Still more preferably, the thickness of the thermoelectric material is the thickness of one unit layer or more, and 3 times the thickness of a unit layer or less.

When the thickness is in the above-mentioned ranges, higher carrier mobility and low lattice thermal conductivity can be obtained, resulting in a higher ZT value.

Preferably, for layers of thermoelectric material in the invention, and for example, in the case of Bi_2Te_3 , the thickness of thermoelectric material layer is at least 0.5 nm and at most 50 nm, preferably of at least 0.5 nm and at most 30 nm, more preferably at least 0.5 nm and at most 20 nm, and most preferably, at least 1 nm and at most 10 nm, in order to have a higher ZT value.

10 **(B) Material of separation**

The layer of separation used herein can be of any material different from the thermoelectric material used for (A). An appropriate material can be, for example, a solid organic material, a solid polymer and an amorphous inorganic material.

15 The said solid organic material can be, for example, pentacene.

The said solid polymer can be, for example, polyimide, poly(p-phenylene terephthalamide), polyimide-amide and PET.

The said amorphous inorganic material can be, for example, MgO , Al_2O_3 , SiO_2 , CaF_2 , TiO_2 , Y_2O_3 , ZrO_2 , and Sb_2O_5 .

20 Preferably, the layer of separation is made of a solid organic material, a solid polymer and an amorphous inorganic material, since these materials reduce more effectively the interaction between thermoelectric material layers, thus enhancing thermoelectric performance.

Still more preferably, the layer of separation is made of Al_2O_3 or polyimide.

Possible precursors used for depositing a layer of Al_2O_3 can be, for example, Me_3Al and H_2O , or O_2 or O_3 .

Possible precursors used for depositing a layer of polyimide can be, for example, DAH(diaminohexane) and PMDA (pyromellitic dianhydride).

Possible examples of precursors for other materials of separation are indicated in Table 2.

Table 2: Examples of possible precursors for depositing a layer of separation

5

	Reactant A	Reactant B
MgO	MgCp ₂ (bis(cyclopentadienyl)magnesium)	H ₂ O
	Mg(CpEt) ₂ (bis(ethylcyclopentadienyl)magnesium)	
	Mg(thd) ₂ (bis(tetramethylheptanedione)magnesium)	H ₂ O ₂
Al ₂ O ₃	AlCl ₃	O ₃
		H ₂ O
		O ₂
		ROH
SiO ₂	SiCl ₄	Al(OEt) ₃ (triethoxyaluminium)
		H ₂ O
	Si(OMe) ₄ (tetramethoxy silane)	H ₂ O
CaF ₂	Ca(thd) ₂ (bis(tetramethylheptanedione)calcium)	HF
		TiF ₄
TiO ₂	TiF ₄	H ₂ O
	TiCl ₄	H ₂ O ₂
	Ti(OMe) ₄ (tetramethoxy titanium)	
	Ti(CpMe ₅)(OMe) ₃ (pentamethylcyclopentadienyl)trimethoxytitanium)	O ₃
	Ti(OMe) ₄	H ₂ O
	Ti(OEt) ₄ (tetraethoxy titanium)	H ₂ O
	Ti(OPr) ₄ (tetraisopropoxy titanium)	H ₂ O ₂
		H ₂ O
		O ₃
Y ₂ O ₃	YCp ₃ (bis(cyclopentadienyl)yttrium)	H ₂ O
	Y(CpMe) ₃ (tri(cyclopentadienylmethyl)yttrium)	H ₂ O
		O ₃

	Y(thd) ₃ (tris(tetramethylheptanedione)yttrium)	O ₃
ZrO ₂	ZrCl ₄	H ₂ O
	ZrCp ₂ Me ₂ (bis(cyclopentadienyl)dimethyl zirconium)	H ₂ O ₂
		O ₃
	ZrCp ₂ Cl ₂ (bis(cyclopentadienyl)dichloro zirconium)	O ₃
	ZrCp ₂ Me(OMe)	
	ZrCp(NMe ₂) ₃ (tris(dimethylamino)cyclopentadienyl zirconium)	
	Zr(CpMe) ₂ Me ₂ (cyclopentylmethyl)dimethylzirconium	
	Zr(CpMe)(NMe ₂) ₃ (cyclopentylmethyl)tri(dimethylamino) zirconium)	
	Zr(CpEt)(NMe ₂) ₃ (cyclopentylethyl)tri(dimethylamino) zirconium)	
Sb ₂ O ₅	SbCl ₅	H ₂ O
pentacene	pentacene	
Polyimide	PMDA (pyromellitic dianhydride: (1,2,4,5-benzenetetracarboxylic anhydride)	DAH (diaminoheptane)
		EDA (ethylenediamine)
		ODA (oxydiamine)
		PDA (1,4-phenylenediamine)
poly(p-phenylene terephthalamide)	terephthaloyl chloride	p-phenylenediamine
polyimide–amide	PMDA	terephthaloyl dichloride

The thickness of the layer of separation is at least 1 nm and at most 100 nm, preferably at least 2 nm and at most 50 nm, more preferably at least 4 nm and at most 20 nm, and most preferably at least 4 nm and at most 10 nm.

When the thickness of a layer of separation is in the above-mentioned range, the layer of separation keeps each 2D nano sheet isolated, resulting in a high ZT value.

5 **(C) Substrate**

The multilayer thermoelectric structure of the present invention optionally comprises a substrate.

The substrate is not particularly limited and can be made of any material suitable for depositing thermoelectric material. An appropriate substrate can be,
10 for example, single crystal Si, quartz, natural oxidized Si, a single crystal of Si, soda lime glass, SiO₂/Si, ZnO, KCl, BaF₂, MgO, polyethyleneterephthalate (PET) or a mask for photo lithography.

Preferably, the substrate is SiO₂/Si substrate.

15 **Structure**

The multilayer thermoelectric structure of the present invention comprises a plurality of alternated layers of (A) and (B), wherein at least one of the two end layers is a layer of (B).

Here, the term "alternated" means that none of two adjacent layers are
20 of the same type, i.e. two layers of (A) or two layers of (B) are never adjacent in the multilayer structure of the present invention.

Here, the term "end layers" means the uppermost and the lowermost layers of the multilayer structure in the direction of stacking, which have one of its surfaces not in contact with a surface of its adjacent layer. The end layers
25 are indicated by arrows in Figures 2.

In the present invention, any one of the above-mentioned thermoelectric materials (A) can be combined with any one of the above-mentioned materials of separation (B), and the preferred thickness ranges indicated above for thermoelectric materials (A) are applicable to any one of the above-mentioned

thermoelectric materials, and the preferred thickness ranges indicated above for materials of separation (A) are applicable to any one of the above-mentioned material of separation: any one of the above-mentioned thermoelectric materials (A) having a length falling within any one of the above-mentioned preferred thickness ranges for thermoelectric material (A) can be used in combination with any of the above-mentioned materials of separation (B) having a length falling within any of the above-mentioned preferred thickness ranges for materials of separation (B).

Figures 3 (a)-(c) are schematic presentations of some examples of multilayer thermoelectric structures of the present invention.

In Figure 3 (a), a undercoat layer consisting of an amorphous separating material (2') is deposited on a substrate (1), and 2 sets of layers consisting of a layer of separation made of the same amorphous material (2) and a layer of thermoelectric material (3) are deposited on the undercoat layer (2').

In Figure 3 (b), 2 sets of layers consisting of an amorphous layer of separation (2) and a layer of thermoelectric material (3) are deposited directly on the substrate (1).

In Figure 3 (c), a undercoat layer consisting of an amorphous material (2') is deposited on a substrate (1), and 5 sets of layers consisting of a layer of separation made of the same amorphous material (2) and a layer of thermoelectric material (3) are deposited on the undercoat layer (2').

As long as the c-plane growth can be maintained, the thickness of the layer of separation is preferably thinner, i.e. the thickness ratio of a thermoelectric layer to a layer of separation (i.e. the thickness of a layer of thermoelectric material: thickness of a layer of separation) is preferably 70% : 30% or more, more preferably 80% : 20% or more, and most preferably 90% : 10% or more.

With the multilayer structure of the present invention, it is possible to achieve a thickness of more than 100 μm desired for industrial applications for

example in a thermoelectric module, superconducting cable, secondary battery or nonlinear optical device, without losing the thermoelectricity of the 2D nano-sheet.

5 Here, the stacking of alternated layers may be achieved by a depositing process as explained below, such that two adjacent layers are bonded, and not simply placed on top of one another without any interaction between them.

When the multilayer thermoelectric structure of the present invention is used, it is preferably the layer of separation that is exposed to the outside.

The optional substrate layer can be removed before use.

10

Number of layers

The number of layers is not particularly limited. The thickness of one layer of separation and of thermoelectric material may appropriately be chosen from the performance point of view.

15

<Method for preparing the thermoelectric material>

The present invention also relates to a method for preparing the thermoelectric material, comprising the steps of:

- 1) providing a substrate;
 - 20 2) depositing a layer of thermoelectric material on a substrate; and
 - 3) depositing a layer of separation on the thermoelectric layer deposited in step 2);
- wherein steps 2) and 3) are carried out at least once, and
- 4) optionally removing the substrate.

25

1) Preparing a substrate

The first step of the method for preparing the multilayer thermoelectric material consists in preparing a substrate. The substrate is not particularly limited, and for example, single crystal Si, quartz, natural oxidized Si, a single

crystal of Si, soda lime glass, SiO_2/Si , ZnO, KCl, BaF_2 , MgO, polyethyleneterephthalate (PET) or a mask for photo lithography can be used.

When a substrate having a very flat substrate is used, a layer of thermoelectric material obtained may have a smoother surface, and higher mobility.

2) Depositing a layer of thermoelectric material on the substrate

The second step of the method consists in depositing a thermoelectric layer. Any method can be used for depositing a first thermoelectric layer, for example, atomic layer deposition (ALD), Metalorganic Chemical Vapour Deposition (MOCVD) or sputtering.

The thickness of the layer can be controlled, in the first place, by adjusting the number of deposition cycles, in the case of ALD. The thickness can also be controlled, for example by, adjusting the feeding time of the precursors, the purge times and the substrate temperature, in the case of ALD.

Possible precursors used for depositing a layer of Bi_2Te_3 can be, for example, BiCl_3 and $(\text{Et}_3\text{Si})_2\text{Te}$ or $(\text{Me}_3\text{Si})_2\text{Te}$.

Possible precursors for depositing other thermoelectric materials are listed in Table 1 above.

3) Depositing a layer of separation on the thermoelectric layer deposited in step 2)

The third step of the method consists in depositing a layer of separation. Any method can be used for depositing a thermoelectric layer, for example, atomic layer deposition, MOCVD or sputtering.

The thickness of the layer can be controlled, in the first place, by adjusting the number of deposition cycles, in the case of ALD. The thickness can also be controlled, for example by, adjusting the feeding time of the precursors, the purge times and the substrate temperature, in the case of ALD.

Possible precursor used for depositing a layer of Al_2O_3 can be, for example, Me_3Al and H_2O , or O_2 or O_3 .

Possible precursor used for depositing a layer of polyimide can be, for example, DAH(diaminohexane) and PMDA (pyromellitic dianhydride).

5 Possible precursors for depositing other thermoelectric materials are listed in Table 2 above.

Steps 2) and 3) are repeated several times for obtaining a thicker multilayer structure. Preferably, steps 2) and 3) are repeated 3 times or more,
10 and more preferably 5 times or more.

Here, the number of cycles corresponds to the number of repeating units of layers.

4) Removing the substrate

15 Optionally, the substrate is removed before use.

<Use of the thermoelectric material>

The multilayer thermoelectric structure of the present invention can be used, for example, in a thermoelectric module, superconducting cable,
20 secondary battery and nonlinear optical device. The multilayer thermoelectric structure of the present invention can also be used, for example, as a heat recovery system in a Thermoelectric Generator (TEG) which converts heat energy to electric energy, or as a Peltier cooling/heating module which can be used in a seat heater, humidity controller, or compact refrigerator.

25 Figure 11 presents an example of a thermoelectric device in which the multilayer thermoelectric structure of the present invention is used.

When the multilayer thermoelectric structure of the present invention is used for example in a thermoelectric module, superconducting cable, secondary battery or nonlinear optical device, it is possible to achieve a thermoelectric

layer thickness of more than 100 μm , without losing the thermoelectric property of a 2D nano-sheet.

The semiconductor substance may appropriately be included more than 50 vol% in the material which is used in the thermoelectric module. In the case of automobile application, the working temperature is limited only between -40 $^{\circ}\text{C}$ and 1000 $^{\circ}\text{C}$.

Examples

In the following Examples, the thin films were deposited in a flow type ALD reactor, using nitrogen as the carrier and purge gas with the operating pressure below 10mbar. 5 x 5 cm^2 , and native SiO_2/Si or soda-lime glass were used as substrates.

<Deposition condition>

The following deposition condition was used:

Polyamide amorphous layer

A polyamide amorphous layer was deposited under the deposition condition of 2/3/2.5/3s for DAH/purge/PMDA/purge with 35 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$ of evaporation temperature of DAH (1,6-diaminohexane) and PMDA (1,2,3,5-benzenetetracarboxylic anhydride), respectively.

Bi_2Te_3 layer

A Bi_2Te_3 layer was deposited by evaporating the precursors, i.e. BiCl_3 and $(\text{Et}_3\text{Si})_2\text{Te}$, from open glass vessels inside the reactor at 140 $^{\circ}\text{C}$ and 43 $^{\circ}\text{C}$, respectively, and by pulsing with inert gas valving. The pulse duration was 0.5/2/2/2s for BiCl_3 /purge/ $(\text{Et}_3\text{Si})_2\text{Te}$ /purge. The substrate temperature was 165 $^{\circ}\text{C}$.

Al₂O₃ amorphous layer

For Al₂O₃, 0.5/1/1/2s of Me₃Al/purge/H₂O/purge. The precursors were evaporated at room temperature.

5 **Example 1**

A multilayer structure comprising a polyimide undercoat layer and five Bi₂Te₃ layers each separated by an amorphous polyimide layer deposited on a native SiO₂/Si substrate was prepared in the following manner.

10 The native SiO₂/Si is a single crystal Si, wherein the the surface is naturally oxidized to SiO₂.

- 1) An amorphous polyimide undercoat layer of 6 nm was deposited on a native SiO₂/Si substrate.
- 2) A Bi₂Te₃ layer of 14 nm was deposited on the amorphous polyimide undercoat layer deposited in step 1).
- 15 3) An amorphous polyimide layer of 6 nm was deposited on the Bi₂Te₃ layer deposited in step 2).
- 4) Steps 2) and 3) were repeated five times to form a multilayer structure.

20 **Reference Example 1**

A multilayer structure comprising a Bi₂Te₃ layer and an amorphous polyimide layer deposited on a native SiO₂/Si substrate was prepared in the following manner.

- 25 1) A Bi₂Te₃ layer of 6.5 nm was deposited on a native SiO₂/Si substrate.
- 2) An amorphous polyimide layer of 100 nm was deposited on the Bi₂Te₃ layer deposited in step 1).

Comparative Example 1

A multilayer structure comprising a polyamide undercoat layer and a Bi_2Te_3 deposited on a native SiO_2/Si substrate was prepared in the following manner.

5

- 1) An amorphous polyimide undercoat layer of 6 nm was deposited on a native SiO_2/Si substrate.
- 2) A Bi_2Te_3 layer of 65 nm was deposited on the amorphous polyimide undercoat deposited in step 1).

10

Example 2

A multilayer structure comprising a polyamide undercoat layer and two Bi_2Te_3 layers each separated by an amorphous Al_2O_3 layer deposited on a native SiO_2/Si substrate was prepared in the following manner.

15

- 1) An amorphous Al_2O_3 undercoat layer of 6 nm was deposited on a native SiO_2/Si substrate.
- 2) A Bi_2Te_3 layer of 14 nm was deposited on the amorphous Al_2O_3 undercoat layer deposited in step 1).
- 20 3) An amorphous Al_2O_3 layer of 6 nm was deposited on the Bi_2Te_3 layer deposited in step 2).
- 4) Steps 2) and 3) were repeated two times to form a multilayer structure.

Example 3

25

A multilayer structure comprising a Bi_2Te_3 layer and an amorphous Al_2O_3 layer deposited on a native SiO_2/Si substrate was prepared in the following manner.

- 1) A Bi_2Te_3 layer of 14 nm was deposited on a native SiO_2/Si substrate.

- 2) An amorphous Al_2O_3 layer of 6 nm was deposited on the Bi_2Te_3 layer deposited in step 1).
- 3) Steps 2) and 3) were repeated two times to form a multilayer structure.

5 **Comparative Example 2**

A multilayer structure comprising an Al_2O_3 undercoat layer and a Bi_2Te_3 layer deposited on a native SiO_2/Si substrate was prepared in the following manner.

- 10 1) An amorphous Al_2O_3 undercoat layer of 6 nm was deposited on a native SiO_2/Si substrate.
- 3) A Bi_2Te_3 layer of 130 nm was deposited on the amorphous polyamide undercoat deposited in step 1).
- 15 The structure of Examples 1 to 4 and Comparative Examples 1 and 2 are summarized in Table 3.

	substrate	undercoat (nm)		PI/AO (nm)	BT (nm)	cycle	configuration (nm)	c-plane
Example 1	SiO ₂ /Si	PI	6	PI	6	14	{5x(6/14)}6/SiO ₂ /Si	Yes
Reference Example 1	SiO ₂ /Si	-	-	PI	100	6.5	(100/6.5)/SiO ₂ /Si	Yes
Comparative Example 1	SiO ₂ /Si	PI	6	-	-	65	(65)6/SiO ₂ /Si	No
Example 2	SiO ₂ /Si	AO	6	AO	6	14	{2x(6/14)}6/SiO ₂ /Si	Yes
Example 3	SiO ₂ /Si	-	-	AO	6	14	{2x(6/14)}6/SiO ₂ /Si	Yes
Comparative Example 2	SiO ₂ /Si	AO	6	-	-	130	(130)6/SiO ₂ /Si	No

PI: polyimide, AO: Al₂O₃, BT: Bi₂Te₃

Table 3: multilayer thermoelectric structures of Examples

<Identification of c-plane growth>

Preferred c-plane orientation of the Samples prepared according to Examples 1 to 3, Reference Example 1 and to Comparative Examples 1 and 2 was identified by using X-ray diffraction (XRD) wherein the diffraction plane is perpendicular to the stacking direction of the multilayer thermoelectric structure, i.e. (00l) planes are stacking in perpendicular to the stacking direction of the multilayer thermoelectric structure, and in other words, (00l) planes are in parallel to the separating layer. Preferred c-plane orientation is observed from the intensities of (00l)-peaks [(003), (006), (0015) and (0018)] relative to e.g. (015)-peak: the higher the ratio of (00l) to (015), the stronger the c-plane orientation.

A c-plane growth can be identified by using XRD when the following condition is satisfied: the peak intensity ratio of (006)/(015) is greater than 1, when the diffraction plane is perpendicular to the stacking direction of the multilayer thermoelectric structure.

In cases where it is difficult to apply XRD for the sample due e.g. to small sample size, Electron Diffraction is also applicable.

<Application>

Figure 11 presents an example of a thermoelectric device in which the multilayer thermoelectric structure of the present invention is used.

Claims

1. A multilayer thermoelectric structure comprising a plurality of alternated layers of:
 - 5 (A): crystalline thermoelectric material; and
 - (B): a material of separation which is a material different from (A);wherein at least one of the two end layers is a layer of (B); and
wherein the crystalline thermoelectric material (A) is selected from the group consisting of: Bi₂Te₃, GaTe, Bi₂S₃, Bi₂Se₃, MoS₂, TiS₃, TiSe₃, TiTe₃, MnPS₃,
10 CdPS₃, CdPS₃, NiPS₃, ZnPS₃, Mn_{0.5}Fe_{0.5}PS₃, GaS, GaSe, InS, InSe, InTe, TiS₂,
MnS, MnTe, ZnS, ZnSe, GaSb, GeSb, GeTe, CdS, CdSe, CdTe, In₂S₃, In₂Se₃,
InSb, Sb₂Te₃, and Ge₂Sb₂Te₅.
2. The multilayer thermoelectric structure according to claim 1,
15 wherein the same crystalline thermoelectric material (A) is used for all the layers of (A); and
wherein the same material of separation (B) is used for all the layers of (B).
- 20 3. The multilayer thermoelectric structure according to claim 1 or 2, wherein the crystalline thermoelectric material (A) is one whose (00l) planes are parallel to the separating layer (B).
4. The multilayer thermoelectric structure according to claim 3, wherein the
25 following condition is satisfied in an X-ray diffraction pattern: the peak intensity ratio of (006)/(015) is greater than 1, when the diffraction plane is preferentially perpendicular to the stacking direction of the multilayer thermoelectric structure.

5. The multilayer thermoelectric structure according to any one of claims 1 to 4, wherein the crystalline thermoelectric material (A) is Bi_2Te_3 or GeTe .

6. The multilayer thermoelectric structure according to any one of claims 1 to 5, wherein the layer(s) of (B) is(are) selected from the group consisting of: solid organic material, solid polymer and amorphous inorganic material.

7. The multilayer thermoelectric structure according to any one of claims 1 to 6, wherein the layer(s) of (B) is(are) pentacene.

10

8. The multilayer thermoelectric structure according to any one of claims 1 to 6, wherein the layer(s) of (B) is(are) selected from the group consisting of polyimide, poly(p-phenylene terephthalamide), polyimide-amide and PET.

9. The multilayer thermoelectric structure according to any one of claims 1 to 6, wherein the layer(s) of (B) is(are) selected from the group consisting of MgO , Al_2O_3 , SiO_2 , CaF_2 , TiO_2 , Y_2O_3 , ZrO_2 , and Sb_2O_5 .

10. The multilayer thermoelectric structure according to any one of claims 1 to 9, wherein the layer(s) of (B) is(are) selected from the group consisting of: polyimide or Al_2O_3 .

11. The multilayer thermoelectric structure according to any one of claims 1 to 10, wherein the layer(s) of (B) has(have) a thickness of half the thickness of one unit layer or more, and 20 times of the thickness of a unit layer or less.

12. The multilayer thermoelectric structure according to any one of claims 1 to 11, wherein the layer(s) of crystalline thermoelectric material (A) has(have) a thickness of at least 0.5 nm and at most 50 nm, preferably of at least 0.5 nm

and at most 30 nm, more preferably at least 0.5 nm and at most 20 nm, and most preferably, at least 1 nm and at most 10 nm.

13. The multilayer thermoelectric structure according to any one of claims 1 to 12, wherein the layer(s) of (B) has(have) a thickness of at least 1 nm and at most 100 nm, preferably at least 2 nm and at most 50 nm, more preferably at least 4 nm and at most 20 nm, and most preferably at least 4 nm and at most 10 nm.
14. The multilayer thermoelectric structure according to any one of claims 1 to 13, further comprising a substrate, wherein the at least one composite layer is deposited on the substrate (C) in such a way that a layer of (B) is exposed to the outside, and that if there are two or more composite layers, they are on the same side of the substrate.
15. The multilayer thermoelectric structure according to any one of claims 1 to 14, wherein the substrate (C) is selected from single crystal Si, quartz, natural oxidized Si, a single crystal of Si, soda lime glass, SiO_2/Si , ZnO, KCl, BaF_2 , MgO, polyethyleneterephthalate (PET) or a mask for photo lithography.
16. The multilayer thermoelectric structure according to any one of claims 1 to 15, wherein the material further comprises an undercoat between the substrate (A) and the composite layer (B).
17. A method for preparing the multilayer thermoelectric material according to any one of claims 1 to 16, comprising the steps of:
- 1) providing a substrate;
 - 2) depositing a first layer of thermoelectric material on a substrate; and

3) depositing a second layer of separation on the thermoelectric layer deposited in step 2);

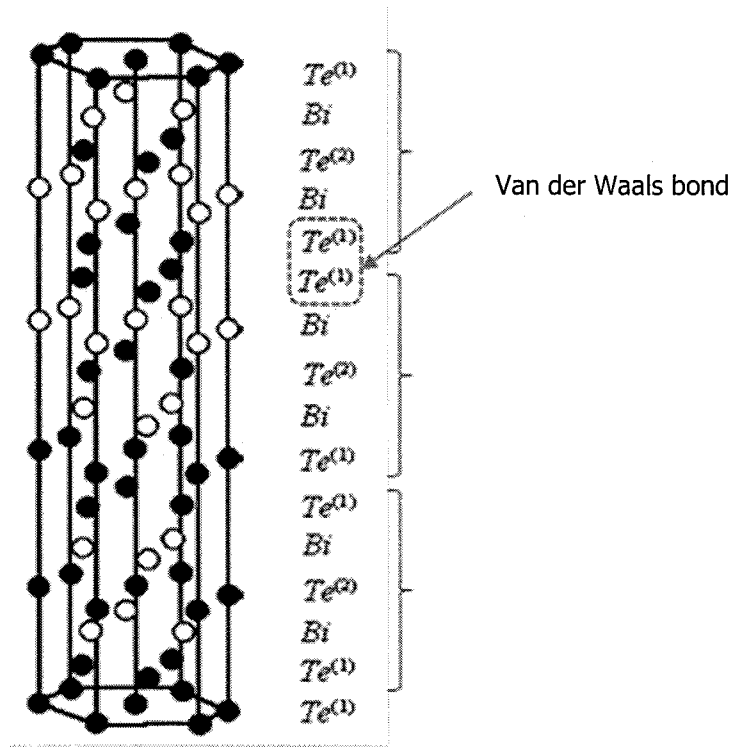
wherein steps 2) and 3) are carried out at least once.

- 5 18. The method according to claim 17, wherein the steps 2) and 3) are repeated 3 times or more.

19. The method according to claim 17 or 18, further comprising a step of depositing an undercoat between the step 1) and step 2).

10

20. A use of the thermoelectric structure according to any one of claims 1 to 16 in a thermoelectric module, superconducting cable, secondary battery or nonlinear optical device.



R-3m, $a=0.439\text{nm}$, $c=3.05\text{nm}$

Figure 1

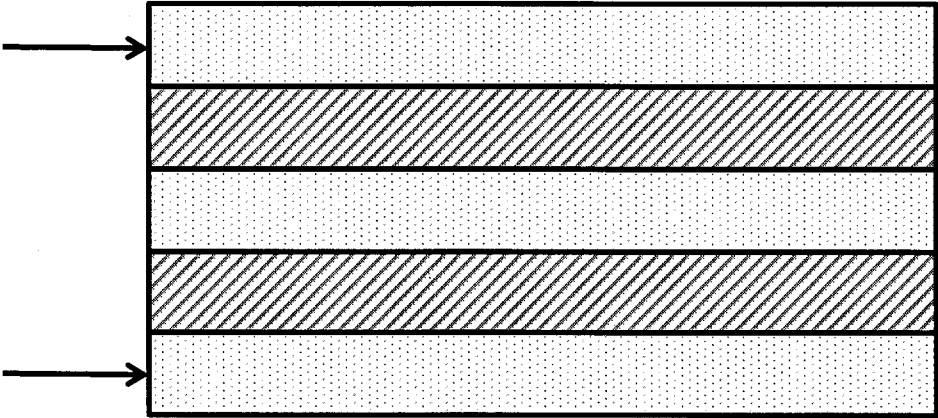


Figure 2

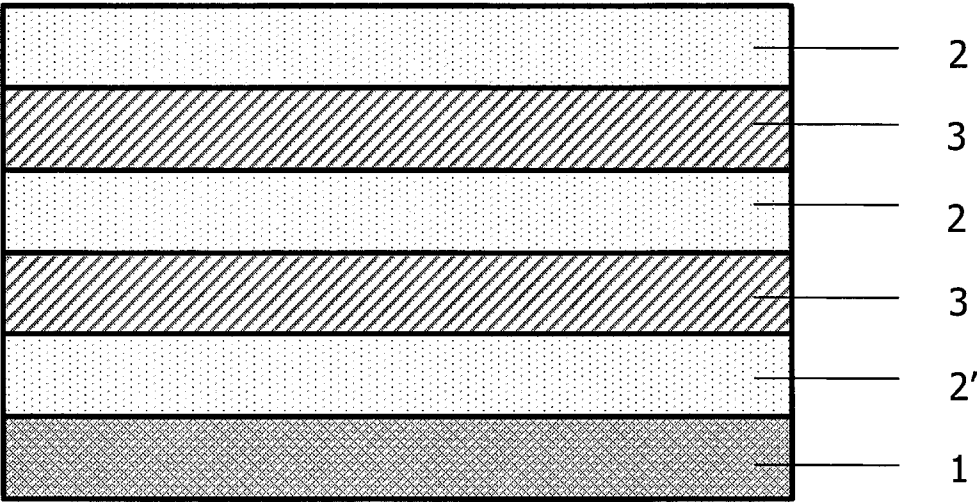


Figure 3 (a)

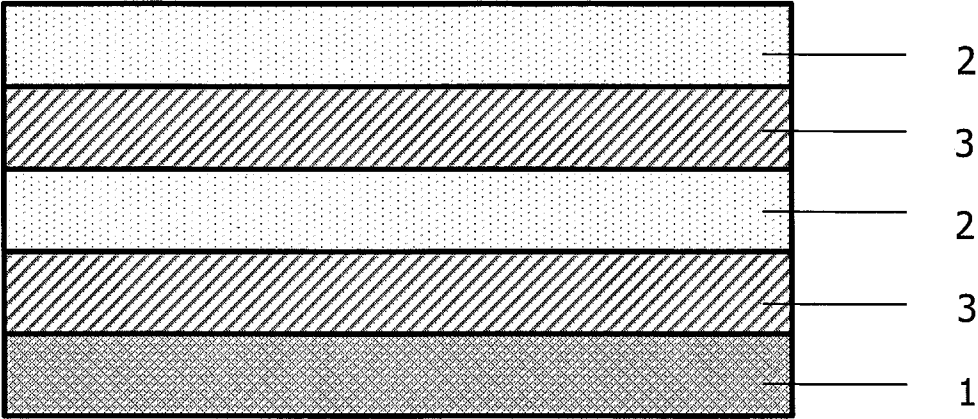


Figure. 3 (b)

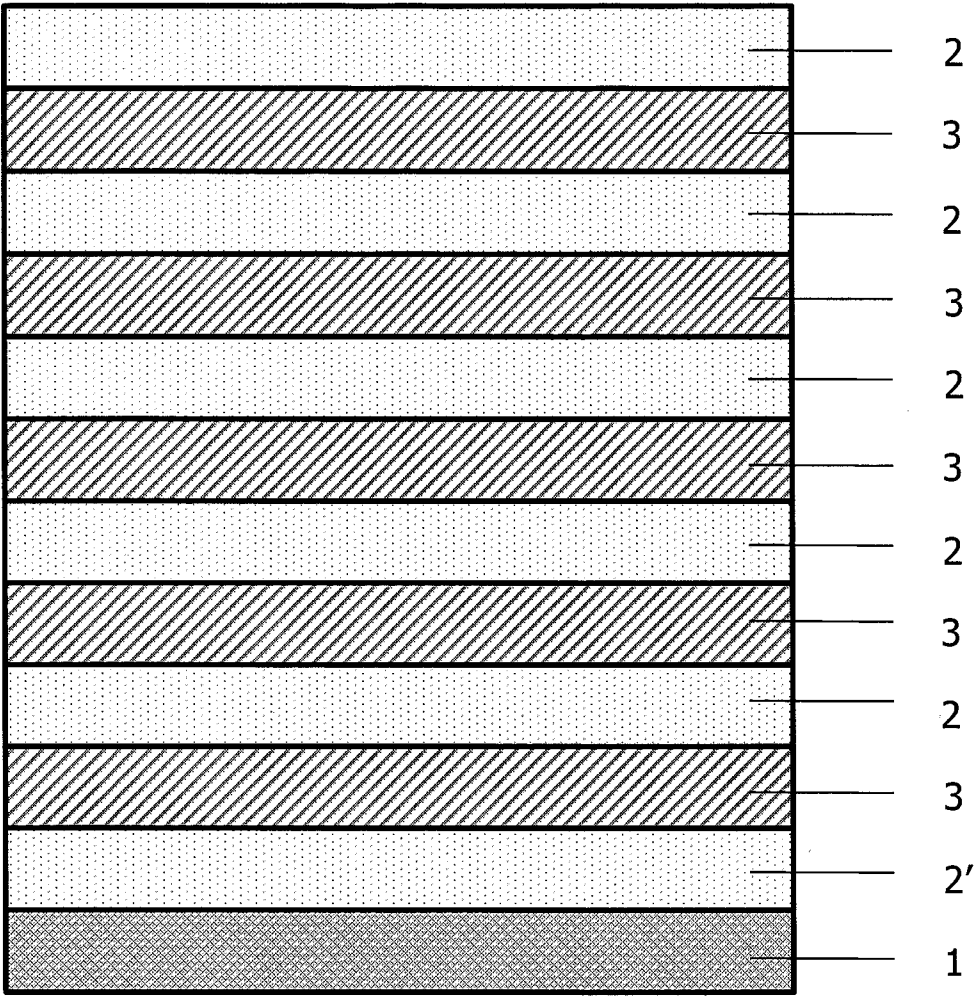
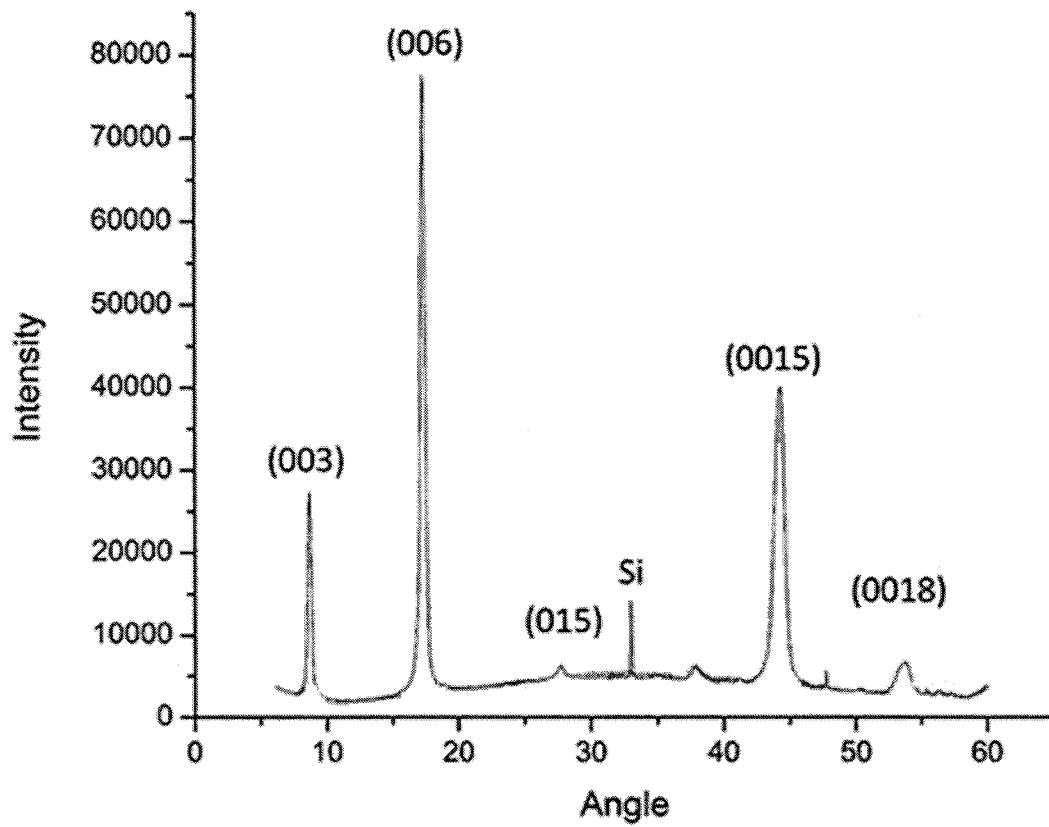
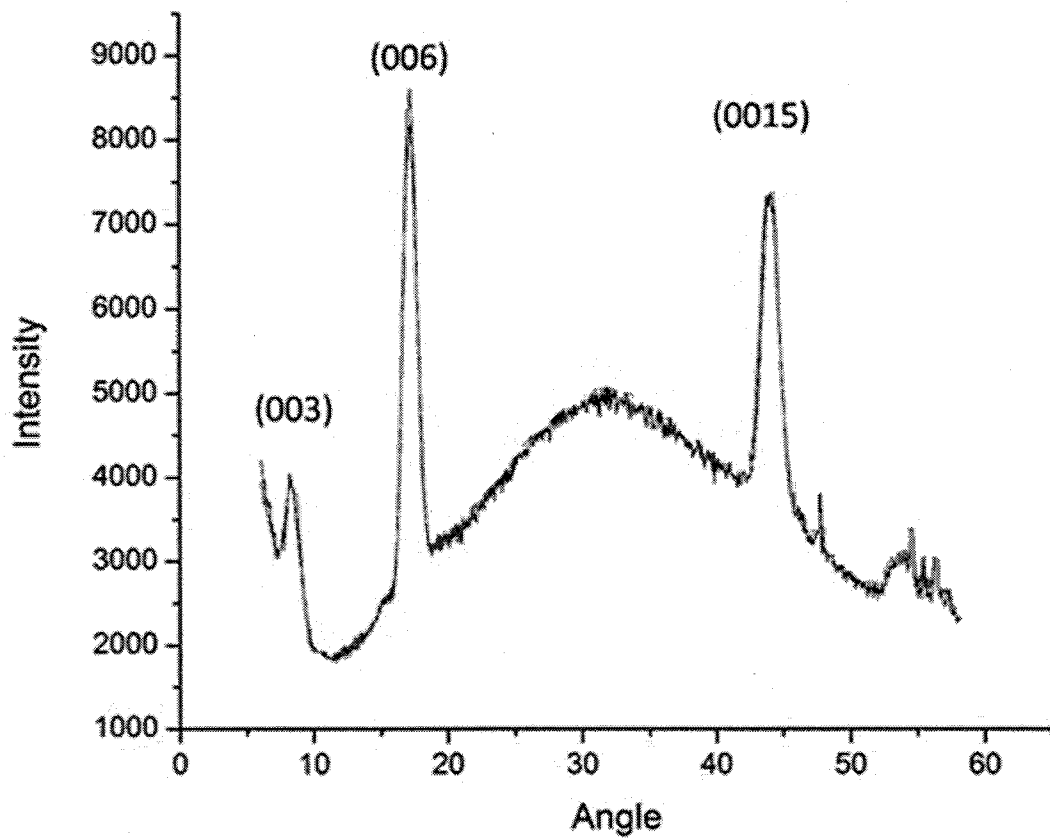
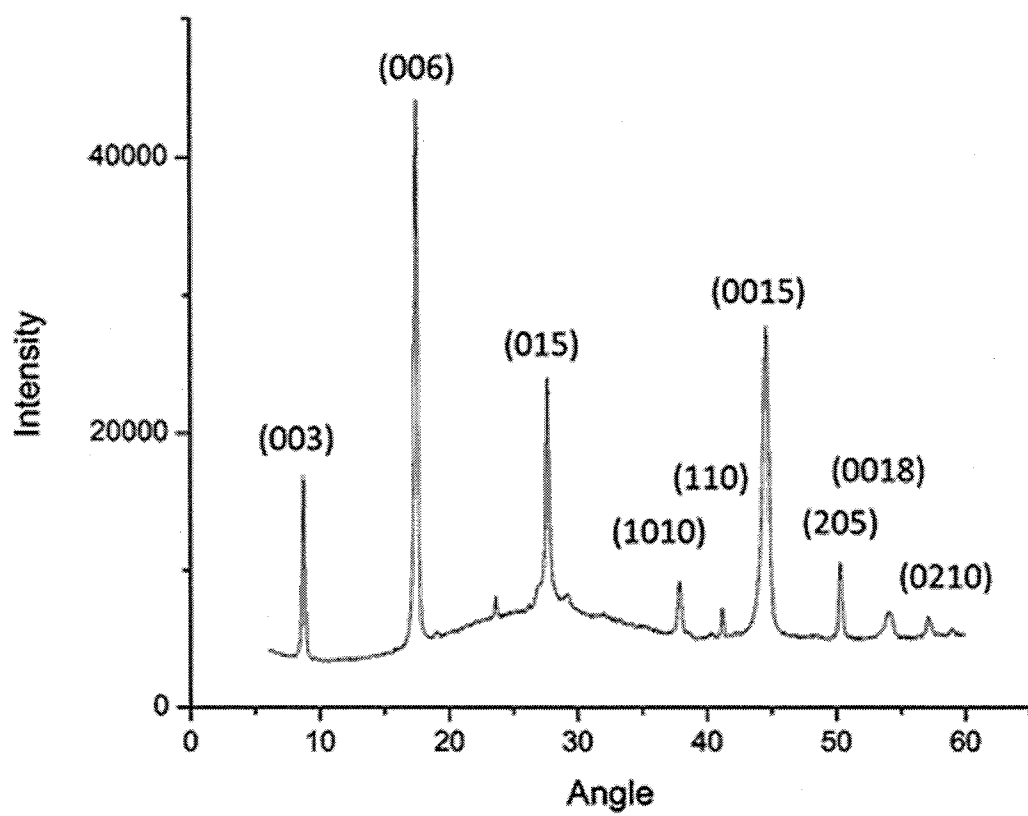
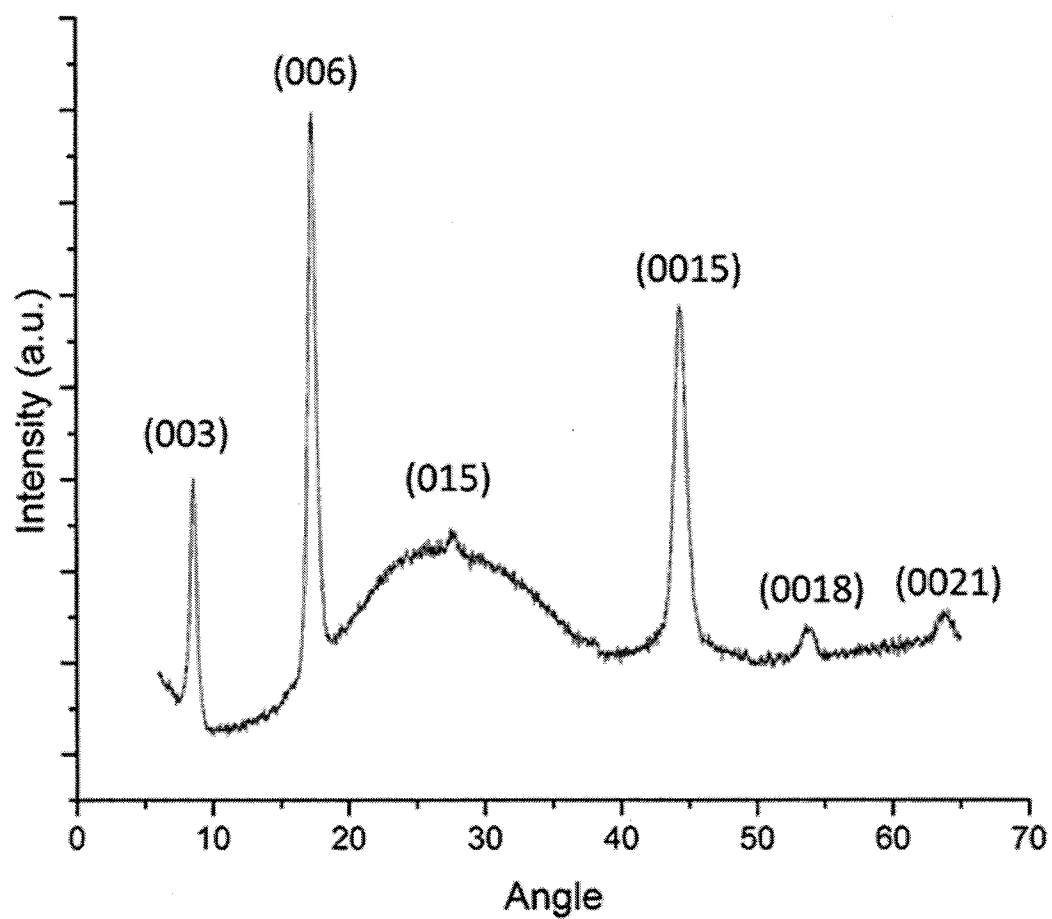


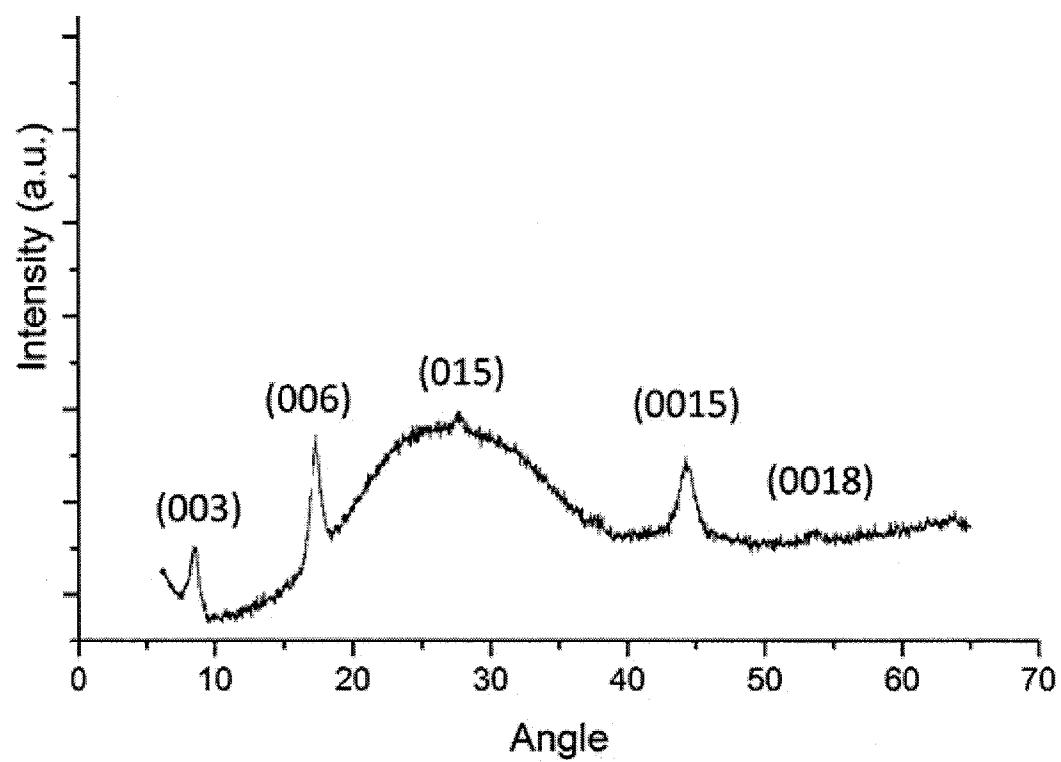
Figure 3 (c)

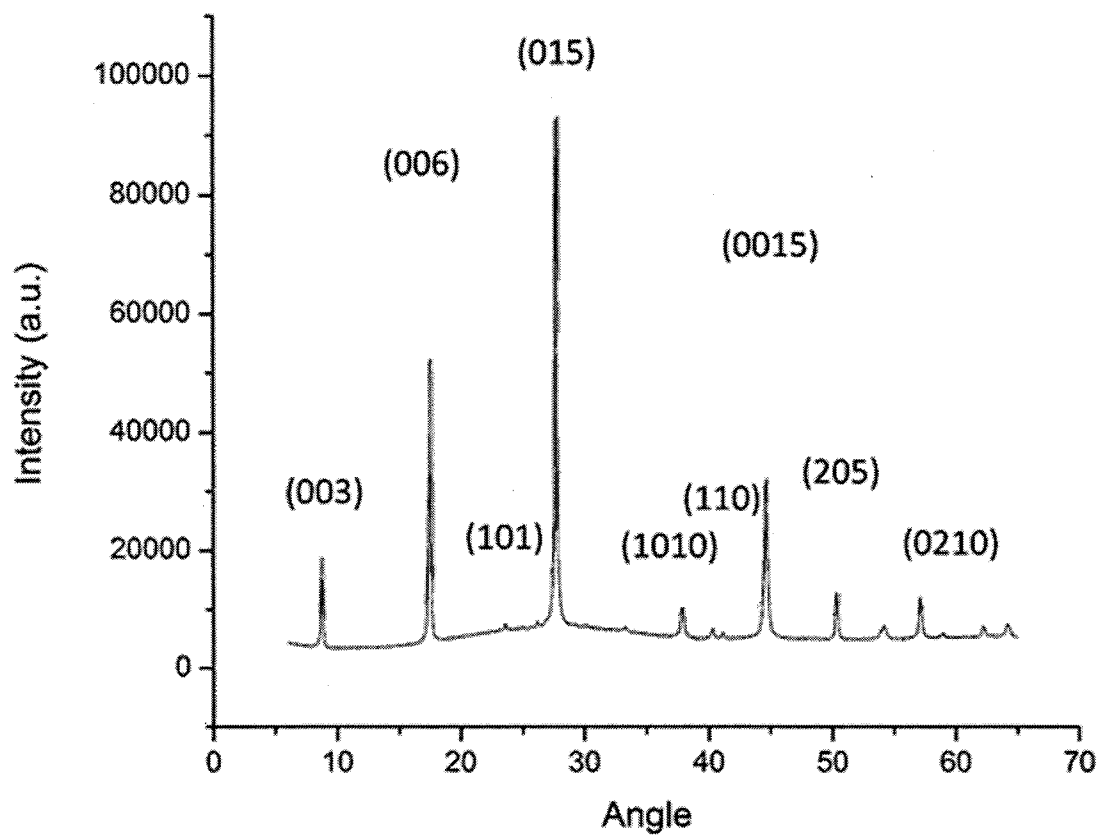
**Figure 4**

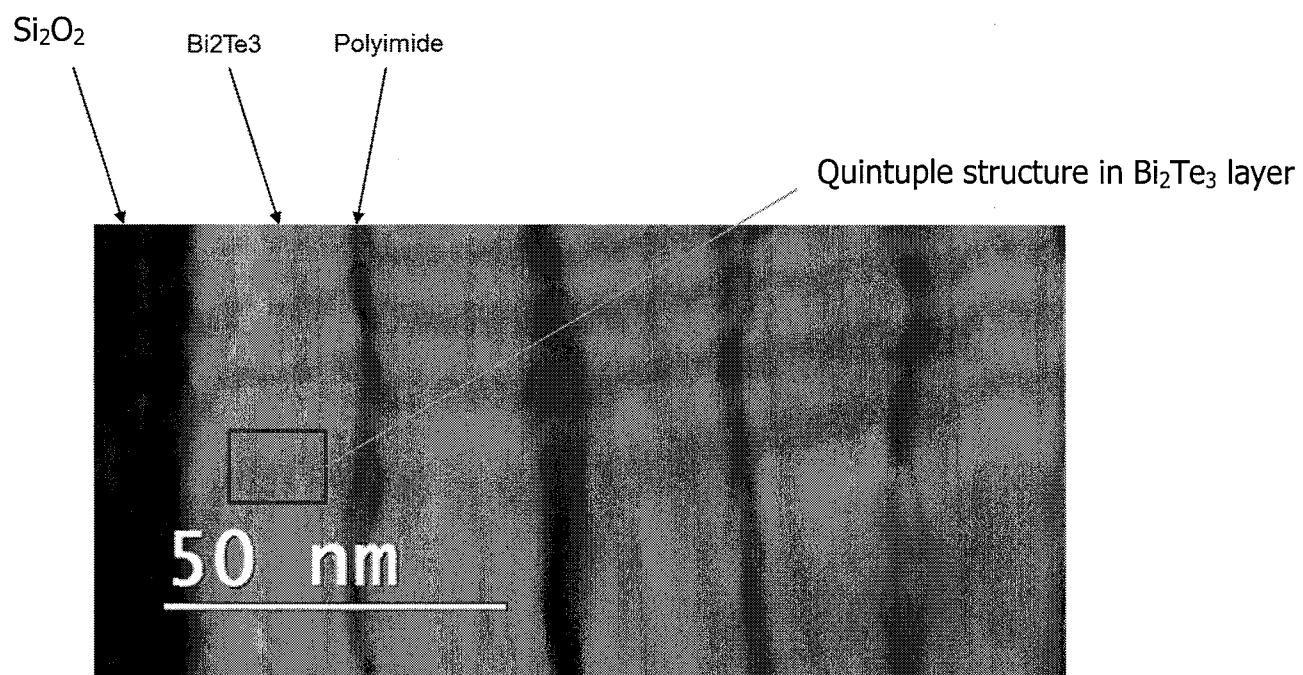
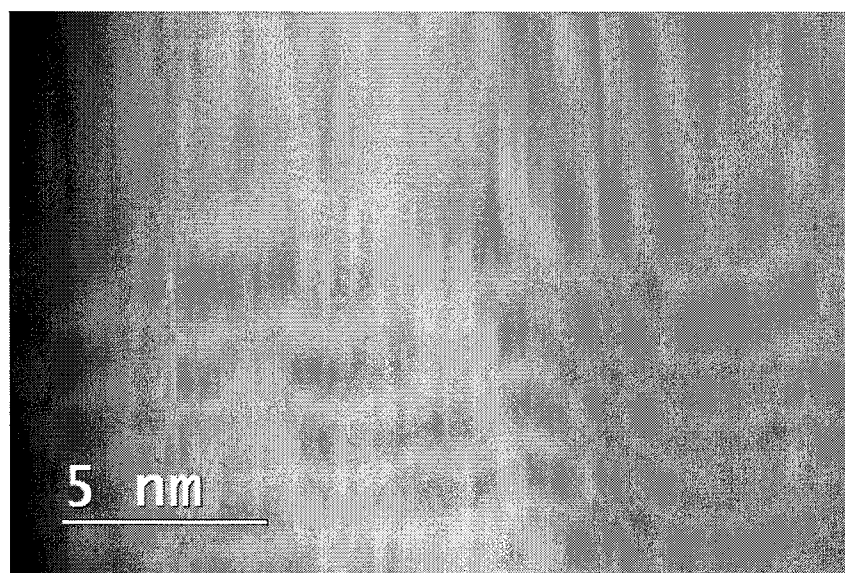
**Figure 5**

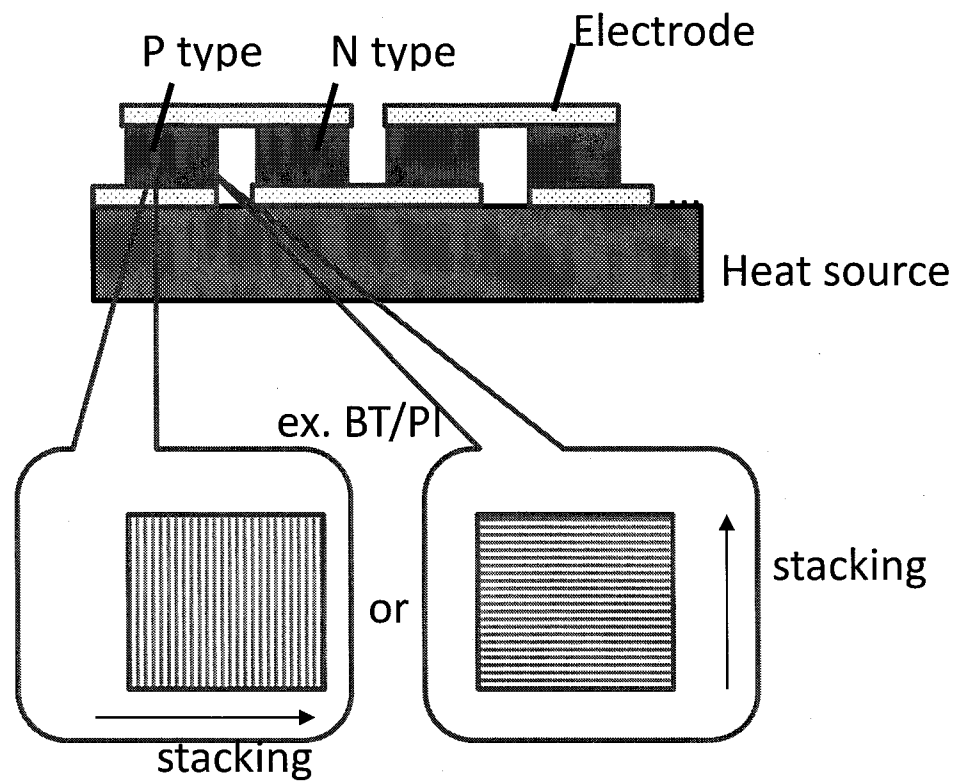
**Figure 6**

**Figure 7**

**Figure 8**

**Figure 9**

**Figure 10 (a)****Figure 10 (b)**

**Figure 11**

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/072469

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B19/00 H01L35/26
ADD.

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)

C01B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/027938 A1 (STOICA VLADIMIR A [US] ET AL) 28 January 2016 (2016-01-28) claims 1-44 paragraphs [0058], [0059] figures 1-4 -----	1-20
X A	US 9 353 445 B2 (PETKIE RONALD R [US]) 31 May 2016 (2016-05-31) claims 1-3,10-19,27-29 figures 1-5 -----	1-5,11, 14-18,20 6-10,12, 13,19
X A	US 6 096 964 A (GHAMATY SAEID [US] ET AL) 1 August 2000 (2000-08-01) claims 1-24, column 3, line 53 - column 4, line 33 column 7, lines 36-42 ----- -/-	1-6, 11-20 7-10



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

30 March 2017

Date of mailing of the international search report

13/04/2017

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/072469

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 104 979 463 A (IND TECH RES INST) 14 October 2015 (2015-10-14) machine translation of CN104979463 (whole document) -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

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