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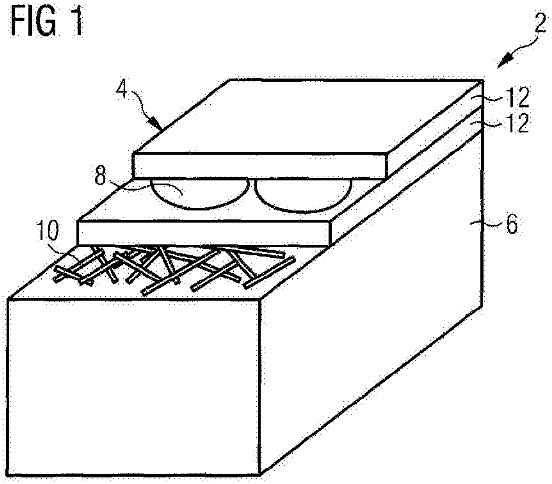
(54) **INFRARED REFLECTIVE AND ELECTRICAL CONDUCTIVE COMPOSITE FILM AND MANUFACTURING METHOD THEREOF.**

(57) The invention is directed to an infrared reflective and electrically conductive composite film (4) to coat on a substrate (6), said composite film (4) comprising at least one infrared reflective layer (8). The composite film further comprises at least one metal layer (10) of connected metal nanowires, each of said at least one infrared reflective layer (8) and at least one metal layer (10) being conformably covered by an optically transparent conductive layer (12).

FIG 1



Description

INFRARED REFLECTIVE AND ELECTRICAL CONDUCTIVE COMPOSITE FILM AND MANUFACTURING METHOD THEREOF

Technical field

[0001] The invention is directed to an optically transparent composite film combining heat reflective properties and electrical conductivity to coat on a substrate, preferably on an optically transparent substrate.

Background art

[0002] Infrared reflective and electrically conductive coatings on glass substrate are used to reduce heat transfer through the substrate and provide resistive heating for defogging and/or defrosting. Said coatings are used in particular in the building and automotive glazing domains.

[0003] Current requirements for infrared reflective and conductive coatings for glazing, in particular in the automotive industry, are very strict, combining low heat transmission given by a high infrared reflection, high optical transmission, low electrical resistance, given by the sheet resistance of the coating, and good visual aspect which is defined by the reflected colour.

[0004] Current technologies are however reaching their physical limits and are not able to meet new requirements in terms of better energy management and/or delivering higher heating power with moderate applied voltage.

[0005] Prior art patent document published US 2011/0268941 A1 discloses a process for manufacturing a glazing unit with 3 or 4 functional layers made of silver that can act on solar radiation and/or infrared radiation, as well as resistive heater. One objective is to provide a multilayer that has a low surface resistivity, a high light transmission and a relatively neutral colour, and that can undergo a heat treatment above 600°C without significant change of the properties. The glazing unit comprises a laminated structure. The glazing unit comprises a transparent glass substrate coated with a composite film comprising an alteration of one functional layer based on silver or metal alloy containing silver and positioned between two antireflection coatings. The coatings are deposited on the substrate by the vacuum technique. The composite film can be used to form heated glazing unit. The limitation of the structure is the absence of versatility on the visual aspect, particularly on the reflected colour. Moreover, the requirement to be able to undergo a heat treatment above 600°C makes the structure complex and difficult to modify as a function of new requirements from the customer.

[0006] Prior art patent document published US 2015/0185382 A1 discloses a transparent infrared reflective and low emissivity composite film. The composite film is configured to be coated on a transparent substrate and comprises at least one silver based layer which provides infrared reflective (IRR) properties, at least one metal based layer and at least one metal oxide based layers and an atomic layer deposited (ALD) metal oxide layer on the top of the composite film. The composite film does not provide any electrical conductivity to said composite and does not reach good optical properties.

[0007] Prior art patent document published US 2015/0183301 A1 discloses an optically transparent and infrared reflecting (IRR) composite film. The composite film is configured to be coated on a glass substrate. The film comprises at least one metal based layer, at least one silver based layer used to reflect infrared radiation and at least one metal oxide based layer. The composite film does not provide any electrical conductivity to said composite and does not reach good optical properties.

[0008] The cited prior art disclosed composite films that show a limited figure of merit in terms of low heat transmission, high optical transmission, low electrical resistance and well defined colour.

[0009] The cited prior art discloses composite films that are deposited by vacuum technology, mainly sputtering, on flat substrates prior to high temperature treatment. The disclosed composite films are complex and contain a lot of layers in order to be able to stand additional processing steps, including high temperature heating and in order to reach good infrared reflective and optical properties and/or electrical conductive properties. Moreover, the process described in this prior art allows only very low versatility for changing the visual parameters of the resulting films.

Summary of invention

Technical Problem

[0010] The invention has for technical problem to provide a solution which overcomes at least one drawback of the cited prior art. More particularly, the invention has for technical problem to provide an optically transparent composite film, to coat on a substrate, comprising a simple structure and which reaches improved optical transmission, infrared reflection and electrical conductive properties, while allowing larger flexibility in terms of visual aspect, in particular reflected colour.

[0011] The invention has also for technical problem to provide a method for the realization of a product coated with a composite film combining heat reflective, electrical conductivity and good optical properties.

Technical solution

[0012] The invention is directed to an infrared reflective and electrically conductive composite film to coat or to be applied or to deposit on a substrate, said composite film comprising at least one infrared reflective layer; remarkable in that said composite film further comprises at least one metal layer of connected metal nanowires, each of said at least one infrared reflective layer and at least one metal layer being conformably covered by an optically transparent conductive layer.

[0013] According to a preferred embodiment, the at least one infrared reflective layer has a surface coverage rate of at least 30%.

[0014] According to a preferred embodiment, the at least one infrared reflective layer is a layer of silver nanostructured particles with irregular shape or disk shape and/or the metal nanowires are silver nanowires.

[0015] According to a preferred embodiment, the nanostructured particles of the at least one infrared reflective layer are separated from each other with a gap inferior to 1 µm, preferably inferior to 100 nm.

[0016] According to a preferred embodiment, the nanostructured particles of the at least one infrared reflective layer have different aspect ratio.

[0017] According to a preferred embodiment, the nanostructured particles of the at least one infrared reflective layer have an average diameter comprised between 1 nm and 10 µm, preferably between 10 nm and 1 µm.

[0018] According to a preferred embodiment, the at least one infrared reflective layer has a thickness comprised between 1 nm and 30 nm.

[0019] According to a preferred embodiment, the connected metal nanowires of the metal layer or each of the metal layer have a surface coverage rate inferior to 20%, preferably inferior to 10%.

[0020] According to a preferred embodiment, the connected metal nanowires have a length superior to 100 nm, preferably superior to 10 µm, a width inferior to 10 µm, preferably inferior to 100 nm and/or a thickness inferior to 300 nm, preferably inferior to 100 nm

[0021] According to a preferred embodiment, each transparent conductive layer is an optically transparent conductive metal oxide.

[0022] According to a preferred embodiment, each transparent conductive layer has a thickness comprised between 10 and 1000 nm.

[0023] According to a preferred embodiment, the composite film further comprises at least one wetting layer, said wetting layer or each wetting layer being coated by an infrared reflective layer or by a metal layer.

[0024] According to a preferred embodiment, the wetting layer or each wetting layer has a thickness inferior to 10 nm.

[0025] According to a preferred embodiment, the composite film comprised between 1 and 5 infrared reflective layers and between 1 and 3 metal layers.

[0026] The invention is also directed to a method for producing a product comprising the steps of providing a substrate, depositing a composite film on said substrate, remarkable in that the composite film of step of depositing a composite film comprises at least one infrared reflective layer and at least one metal layer of connected metal nanowires, each of said at least one infrared reflective layer and at least one metal layer being conformably covered by an optically transparent conductive layer, said composite film being in accordance with the invention.

[0027] According to a preferred embodiment, the method further comprises a step of depositing electrical contacts on said substrate.

[0028] According to a preferred embodiment, in step of depositing electrical contacts on said substrate, said electrical contacts are deposited on the substrate before the composite film or before at least one infrared reflective layer or at least one metal layer.

[0029] According to a preferred embodiment, the step of depositing the composite film is performed by atomic layer deposition and spray deposition.

Advantages of the invention

[0030] The invention is particularly interesting in that the composite film comprises at least one infrared reflective layer preferably of nanostructures particles and at least one metal layer, each of said layers being conformably covered by a transparent conducting layer. The configuration of the composite film according to the invention provides good infrared reflection and electrical conductive properties to said composite film while keeping a good optical transparency of the composite film and thus the optical transparency of the substrate.

[0031] Moreover, the invention provides a higher flexibility of the resulting visual aspect, as compared to the prior art, due to the partial decoupling of the infrared reflective layers and the electrical conductive layers, while keeping a high level of performances due to the synergistical electrical conduction provided by the transparent conductive layers.

[0032] Due to the method described in the invention for providing the afore-mentioned layers with a high degree of accuracy of the thickness on bended substrates, the number of layers can be reduced compared to composite film of the prior art with the same level of performances.

Brief description of the drawings

[0033] Figure 1 illustrates a product comprising a composite film according to the present invention.

[0034] Figure 2 is a cross section of the product represented *on Figure* 1, according to a first embodiment.

[0035] Figure 3 is a cross section of the product represented on Figure 1, according to a second embodiment.

[0036] Figure 4 is a cross section of the product represented on Figure 1, according to a third embodiment.

[0037] Figure 5 illustrates a cross section of an example of a full optically transparent product comprising the composite film and optional layers, in accordance with the invention.

[0038] Figure 6 illustrates a cross section of the product of figure 1 comprising electrical contacts.

Description of an embodiment

[0039] In the following description, the term "optically transparent" is used to mean that a material or a device transmits at least 40%, preferably at least 70%, more preferably at least 90%, of the incident visible light.

[0040] Figure 1 illustrates a product 2 comprising a composite film 4. Figure 2, figure 3 and figure 4 respectively represent a cross section of the product 2 of figure 1 according to different embodiments. The products of figures 2, 3 and 4 are respectively numbered 2.1, 2.2 and 2.3. The product 2 is preferably optically transparent and comprises a substrate 6 and the composite film 4 coated on said substrate. Advantageously, the substrate 6 is optically transparent and is made of glass, PET or any optically transparent material. The substrate 6 can be for example a windshield or a window. The composite film 4 is coated on one face of the substrate but can be coated on more faces of said substrate.

[0041] The composite film 4 comprises at least one infrared reflective layer 8 and at least one metal layer 10 of connected metal nanowires. Each of the at least one infrared reflective layer 8 and the at least one metal layer 10 is conformably coated by an optically transparent conductive layer 12. The term "conformably" is used to mean that the transparent conductive layers cover/fit closely to the at least one infrared reflective layer and the at least one metal layer by adapting to the shape of said at least one infrared reflective layer and said at least one metal layer.

[0042] Figure 1 only shows one infrared reflective layer 8 and one metal layer 10. Preferably, the composite film 4 comprises between 1 and 5 infrared reflective layers 8 and between 1 and 3 metal layers 10.

[0043] The at least one infrared reflective layer 8 has a surface coverage rate of at least 30%. The at least one infrared reflective layer 8 is advantageously a layer of nanostructured particles, as represented in figures 1, 2 and 3. The nanostructured particles are advantageously flat silver nanoparticles with an irregular shape or with a disk shape. Preferentially, the nanoparticles are nanodisks. The term “nanodisk” is well-known by a skilled-man. The term “irregular” is used to describe nanoparticles whose contour does not form a perfect circle or disk. The nanostructured particles have an average diameter comprised between 1 nm and 10 µm, preferably between 10 nm and 1 µm. The nanostructured particles of the at least one infrared reflective layer 8 are separated from each other with a gap inferior to 10 µm, preferably inferior to 100 nm.

[0044] The nanostructured particles of the at least one infrared reflective layer 8 have different aspect ratio and different surface coverage. In each of the at least one infrared reflective layer 8, the nanostructured particles cover different regions of said layer for larger reflection spectrum. The nanostructured particles are advantageously atomic layer deposited nanostructured particles, but not limited to it.

[0045] The connected metal nanowires of the at least one metal layer 10 have a surface coverage rate inferior to 20%, preferably inferior to 10%.

[0046] The connected metal nanowires of the at least one metal layer 10 are preferably connected silver nanowires. The connected nanowires can form a disordered network of nanowires as represented in figure 1 or can be in the form of a metal nanogrid (not represented). The connected metal nanowires have a width inferior to 10 µm, preferably inferior to 100 nm and a thickness inferior to 300 nm, preferably inferior to 100 nm. The width and the thickness of the nanowires are respectively related to a plane parallel to an average plane of the substrate and to a plane transversal to an average plane of the substrate. The connected metal nanowires have a length superior to 100 nm, preferably superior to 10 µm. In case of a nanogrid, the connected metal nanowires form a network with a length between connexions superior to 100 nm, preferably superior to 1 µm. In case of a disordered network of nanowires, the length between the connexions is inferior to the length of the nanowires. The connected nanowires can be deposited by spray-deposition. The metal grid can be a mesh realised by lithography or by dewetting of a metal layer. The use of connected metal nanowires allows to provide an electrical conductive layer in the composite film 4 while keeping a good optical transparency of said layer.

[0047] Each transparent conductive layer 12 conformably covers the nanostructured particles of the at least one infrared reflective layer 8 and the connected metal nanowires of the at least one metal layer 10, in order to form a flattened surface. In order to reach the conformably covering of said layers 8 and 10, the transparent conductive layers 12 are advantageously deposited by Atomic Layer Deposition (ALD) but not limited to it. Each transparent conductive layer 12 is a layer of an optically transparent conductive material, preferentially transparent conductive metal oxide such as but not limited to Al-doped ZnO layer or tin oxide.

[0048] Each transparent conductive layer 12 has a thickness comprised between 10 and 1 µm. Each transparent conductive layer 12 have different thickness, or have the same thickness.

[0049] The combination of at least one infrared layer and at least one metal layer of connected metal nanowires, with conformal transparent conductive layers provides a solution to obtain optimum infrared reflective and electrical resistance properties of the composite film 4, while keeping good optical properties of the composite film in terms of optical transmission and visual aspect.

[0050] The presence of several infrared reflective layers 8 with nanostructured particles of different aspect ratios allows to improve the surface coverage of the nanostructured particles in the composite film, thus improving the infrared reflective properties of the composite film, while maintaining a good optical transparency of said composite film.

[0051] As represented in figures 1 and 2, the infrared reflective layer 8 is under the metal layer 10, said configuration does not limit the invention. Indeed, the metal layer 10 can also be above the infrared reflective layer 8, as represented in figure 3. The terms “above” and “under” are related to the substrate. In case of more than one metal layer 10 and more than one infrared reflective layer 8, many configurations of the composite film 4 are possible. One or several infrared reflective layers 8 can be made of disconnected nanoparticles as represented in figures 1, 2 and 3, or of a continuous metal film corresponding to a surface coverage of 100%, as represented in figure 4.

[0052] The composite film 4 can also comprise at least one wetting layer (not represented). The wetting layer or each wetting layer is coated by an infrared reflective layer 8 or a metal layer 10. The at least one wetting layer promotes deposition of an infrared reflective layer 8 and/or of a metal layer 10. The wetting layer can be made of metal or oxide or nitride or sulfide layer or a combination. Preferably, the at least one wetting layer is made of silver. The at least one wetting layer has a thickness inferior to 10 nm. The composite film 4 can also comprise supplementary layers such as supplementary transparent conductive layers 12, protective insulating layers, anti-reflecting layers or index matching layers, gas barrier layers and/or haze reducing layers (not represented).

[0053] Figure 5 illustrates an example of a product coated with the composite film according to the invention comprising optional additional layers. This example does not restrict any other configuration. The product 102 is a full optically transparent product. The product 102 comprised a substrate 106 which is coated with a composite film 104. The composite film 104 comprises two infrared reflective layers 108 and one metal layer 110, each of said layers 108 and 110 being conformably coated with a transparent conductive layer 112. The composite film 4 can also comprise others transparent conductive layers 112. More particularly, a transparent conductive layer 112 can be coated on the substrate 106 before deposition of the at least one infrared reflective layers 108 or the at least one metal layer 110. The composite film 104 can also comprise optical or barrier layers 114 and a protection layer 116 on the top of the composite film 104, at the opposite side of the substrate 106.

[0054] Generally, the product 2 coated with a composite film 4 according to the invention, can also comprise electric contacts 18, as illustrated in Figure 6. The electrical contacts 18 are deposited on the substrate 6 before the deposition of the composite film 4 on the substrate, or at least before one of the infrared reflective layer or one metal layer. In case of a bended substrate, as a car windshield, the composite film or at least part of the composite film is deposited after the bending of the substrate. The composite film, being mostly deposited by atomic layer deposition, allows to have a direct electrical connection between the electrical contacts and said composite film. The combination of electrical contacts with the composite film provide defogging and defrosting properties to the product.

[0055] The manufacturing described here does not preclude post thermal treatment at a moderate temperature below 300°C.

[0056] In another embodiment of the invention (not represented), the product comprising a glass substrate coated with the composite film according to the invention can also comprise a polymer film such as a polyvinyl butyral film and a counter substrate glass, in order to form a laminated glass.

[0057] The composite film according to the invention can be used to produce low-emissivity windows, glazing in vehicle such as cars, planes or trains, glass for displays and/or transparent polymer substrate (e.g. helmet's eyeshade), all of them can be flat or bended.

Revendications LU100018

1. Film composite (4) réfléchissant l'infrarouge et électriquement conducteur, pour le revêtement d'un substrat (6), ledit film composite (4) comprenant au moins une couche (8) réfléchissant l'infrarouge ;
caractérisé en ce que ledit film composite comprend en outre au moins une couche métallique (10) de nanofils métalliques connectés, chacune desdites au moins une couche réfléchissant l'infrarouge (8) et au moins une couche métallique (10) étant recouverte de manière conforme par une couche conductrice optiquement transparente (12).
2. Film composite (4) selon la revendication 1, caractérisé en ce que la au moins une couche réfléchissant l'infrarouge (8) a un taux de couverture de surface d'au moins 30%.
3. Film composite (4) selon l'une quelconque des revendications 1 et 2, caractérisé en ce que la au moins une couche réfléchissant l'infrarouge (8) est une couche de particules nanostructurées d'argent avec une forme irrégulière ou une forme de disques et/ou les nanofils métalliques sont des nanofils d'argent.
4. Film composite (4) selon la revendication 3, caractérisé en ce que les particules nanostructurées de la au moins une couche réfléchissant l'infrarouge (8) sont séparées l'une de l'autre avec un espace inférieur à 1 µm, de préférence inférieur à 100 nm.
5. Film composite (4) selon l'une quelconque des revendications 3 et 4, caractérisé en ce que les particules nanostructurées de la au moins une couche réfléchissant l'infrarouge (8) ont un rapport d'aspect différent.
6. Film composite (4) selon l'une quelconque des revendications 3 à 5, caractérisé en ce que les particules nanostructurées de la au moins une couche réfléchissant l'infrarouge (8) ont un diamètre moyen compris entre 1 nm et 10 µm, de préférence entre 10 nm et 1 µm.
7. Film composite (4) selon l'une quelconque des revendications 1 à 6, caractérisé en ce que la au moins une couche réfléchissant l'infrarouge (8) a une épaisseur comprise entre 1 nm et 30 nm.
8. Film composite (4) selon l'une quelconque des revendications 1 à 7, caractérisé en ce que les nanofils métalliques connectés de la couche métallique (10) ou de

chacune des couches métalliques (10) ont un taux de couverture de surface inférieure à 20%, de préférence inférieur à 10%. LU100018

9. Film composite (4) selon l'une quelconque des revendications 1 à 8, caractérisé en ce que les nanofils métalliques connectés ont une longueur supérieure à 100 nm, de préférence supérieure à 10 µm, une largeur inférieure à 10 µm, de préférence inférieure à 100 nm et/ou une épaisseur inférieure à 300 nm, de préférence inférieure à 100 nm.
10. Film composite (4) selon l'une quelconque des revendications 1 à 9, caractérisé en ce que chaque couche conductrice transparente (12) est un oxyde métallique conducteur optiquement transparent.
11. Film composite (4) selon l'une quelconque des revendications 1 à 10, caractérisé en ce que chaque couche conductrice transparente (12) a une épaisseur comprise entre 10 et 1000 nm.
12. Film composite (4) selon l'une quelconque des revendications 1 à 11, caractérisé en ce que ledit film composite (4) comprend en outre au moins une couche de mouillage, ladite couche de mouillage ou chaque couche de mouillage étant revêtue par une couche réfléchissant l'infrarouge (8) ou par une couche métallique (10).
13. Film composite (4) selon la revendication 12, caractérisé en ce que la couche de mouillage ou chaque couche de mouillage a une épaisseur inférieure à 10 nm.
14. Film composite (4) selon l'une quelconque des revendications 1 à 13, caractérisé en ce que ledit film composite (4) comprend entre 1 et 5 couches réfléchissant l'infrarouge (8) et entre 1 et 3 couches métalliques (10).
15. Procédé de fabrication d'un produit (2) comprenant les étapes de :

    - fourniture d'un substrat (6)
    - dépôt d'un film composite (4) sur ledit substrat (6)

    caractérisé en ce que le film composite de l'étape de dépôt d'un film composite (4) comprend au moins une couche réfléchissant l'infrarouge (8) et au moins une couche métallique (10) de nanofils métalliques connectés, chacune desdites au moins une couche réfléchissant l'infrarouge et au moins une couche métallique étant recouverte de manière conforme par une couche conductrice optiquement *transparente*, ledit film composite (4) étant conforme à l'une quelconque des revendications 1 à 14.

16. Procédé selon la revendication 15, caractérisé en ce que ledit procédé comprend en outre une étape de dépôt de contacts électriques (18) sur ledit substrat (6).
17. Procédé selon la revendication 16, caractérisé en ce que, lors de l'étape de dépôt de contacts électriques sur ledit substrat, lesdits contacts électriques sont déposés sur le substrat (6) avant le film composite (4) ou avant au moins une couche réfléchissant l'infrarouge (8) ou au moins une couche métallique (10).
18. Procédé selon l'une quelconque des revendications 15 à 17, caractérisé en ce que l'étape de dépôt du film composite est réalisée par dépôt de couche atomique et dépôt par pulvérisation.

FIG 1

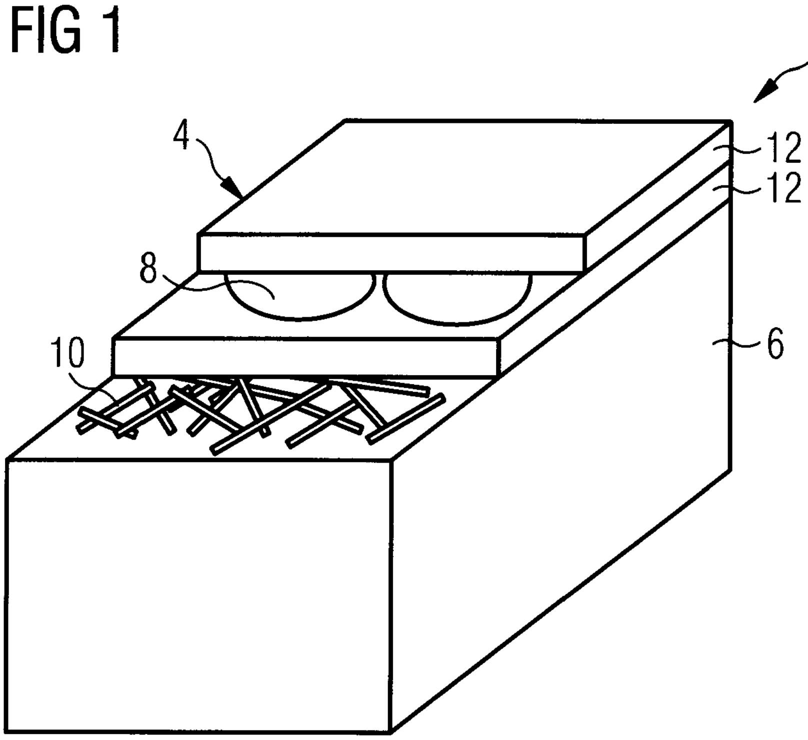


FIG 2

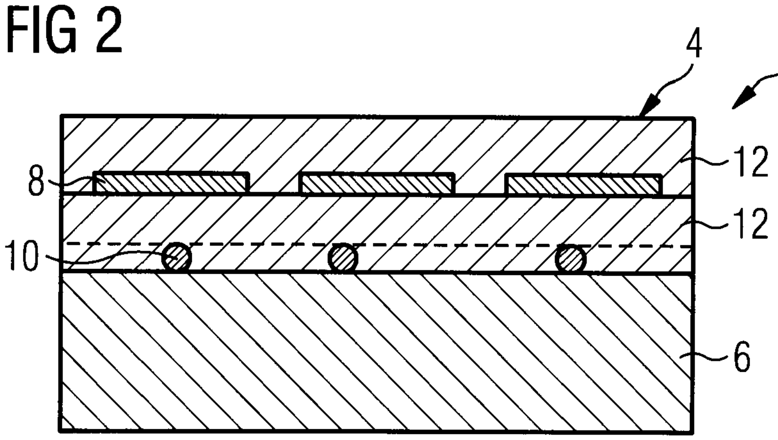


FIG 3

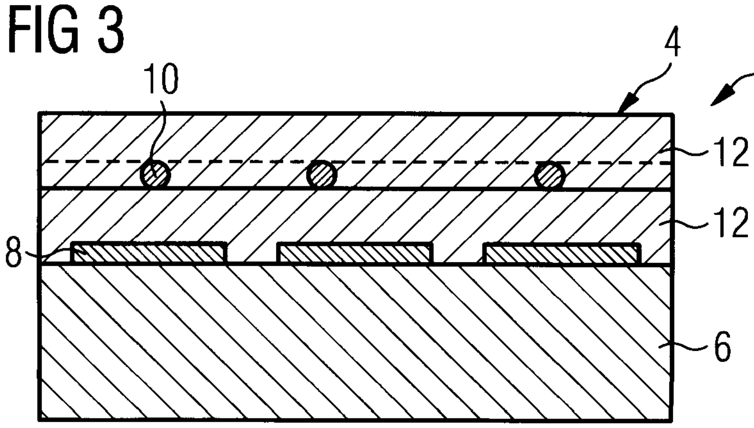


FIG 4

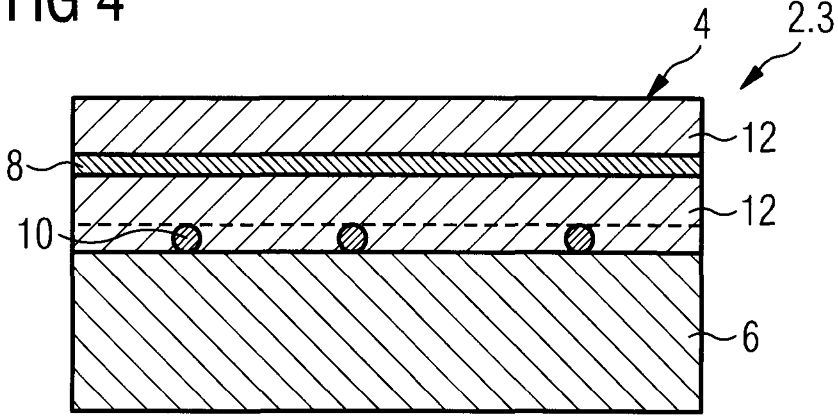

4
2.3
12
8
12
10
6

FIG 5

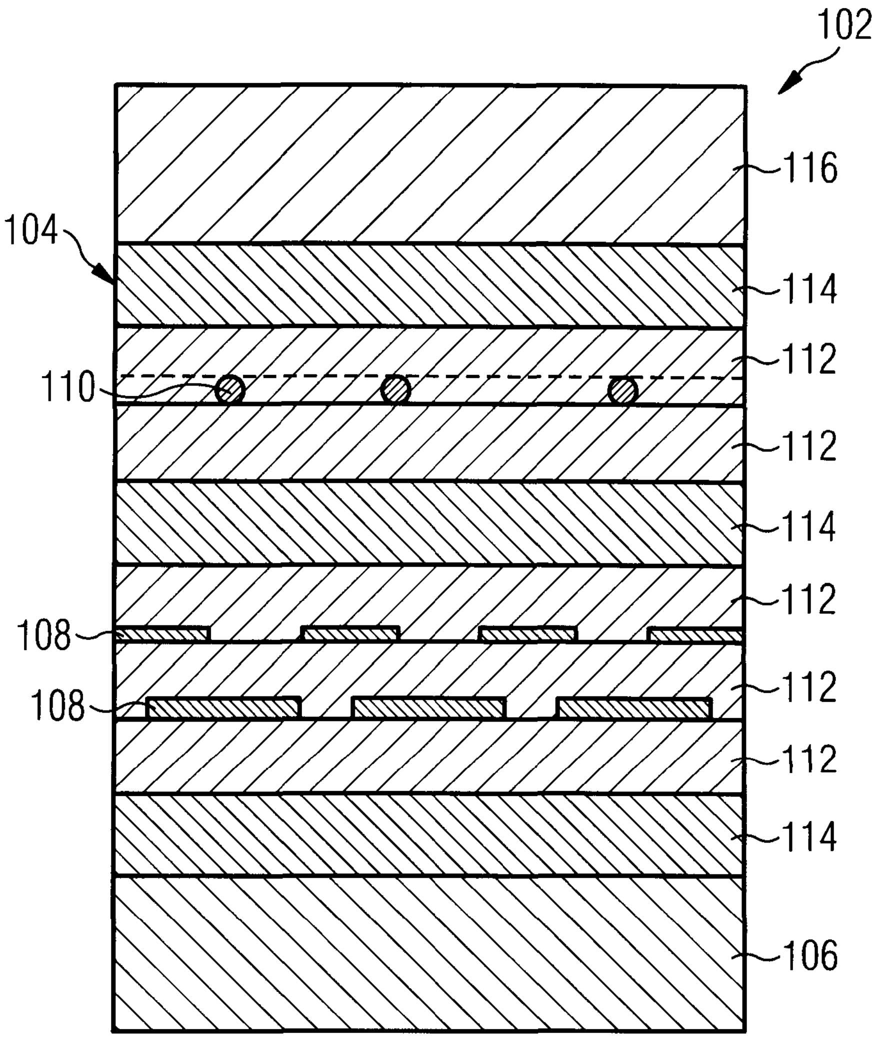

102
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FIG 6

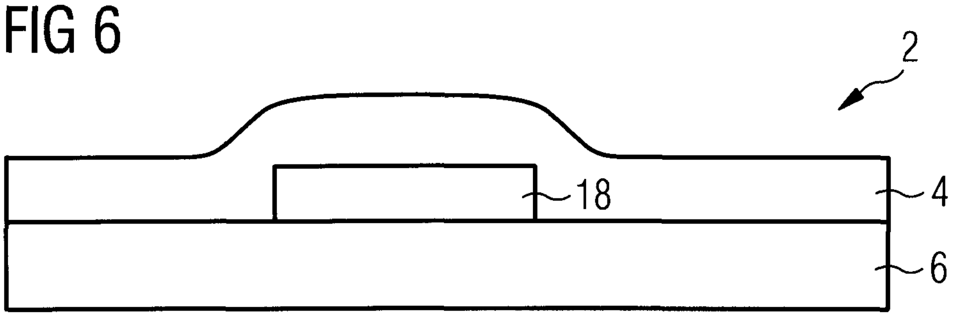

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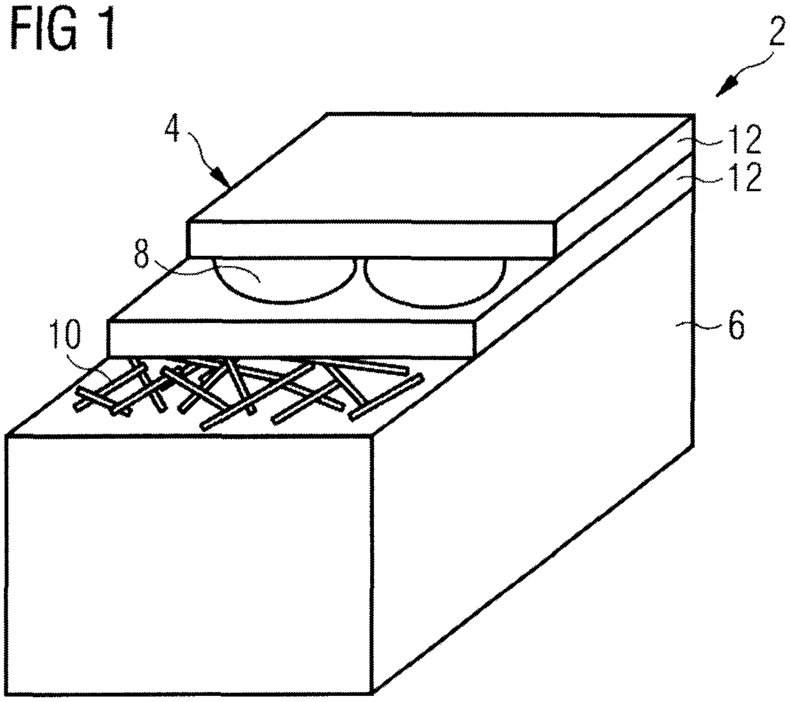
FIG 1



Abstract

INFRARED REFLECTIVE AND ELECTRICAL CONDUCTIVE COMPOSITE FILM AND MANUFACTURING METHOD THEREOF

The invention is directed to an infrared reflective and electrically conductive composite film (4) to coat on a substrate (6), said composite film (4) comprising at least one infrared reflective layer (8). The composite film further comprises at least one metal layer (10) of connected metal nanowires, each of said at least one infrared reflective layer (8) and at least one metal layer (10) being conformably covered by an optically transparent conductive layer (12).

(Figure 1).

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

National Application Number

SEARCH REPORT

in accordance with Article 35.1 a)
of the Luxembourg law on patents
dated 20 July 1992

LO 1559
LU 100018

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	WO 2016/031489 A1 (FUJIFILM CORP [JP]) 3 March 2016 (2016-03-03) * the whole document * *	1-18	INV. G02B5/08 G02B5/28 G02B5/20
E	-& US 2017/145737 A1 (HASEGAWA KAZUHIRO [JP]) 25 May 2017 (2017-05-25) * abstract * * * paragraphs [0077] - [0085], [0089] - [0092], [0147], [0180] - [0196], [0201] - [0261] * * figures 1-3 * -----	1-18	
Y	EP 2 374 559 A2 (FUJIFILM CORP [JP]) 12 October 2011 (2011-10-12) * abstract * * * paragraphs [0009] - [0013], [0039] - [0044], [0091] - [0096] * * figures 1,2 * -----	1-18	
A	WO 2013/056242 A1 (UNIV CALIFORNIA [US]) 18 April 2013 (2013-04-18) * abstract * * * paragraphs [0003] - [0008], [0016] - [0030], [0034] * * figures 1-5 * * claims 29,35 * -----	1-18	TECHNICAL FIELDS SEARCHED (IPC): G02B
A	US 2015/305166 A1 (FRIED ANDREW T [US] ET AL) 22 October 2015 (2015-10-22) * abstract * * ----- -/--	1-18	

The present search report has been drawn up for all claims

	Date of completion of the search	Examiner
	26 September 2017	Moroz, Alexander

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CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C58)

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	TANJA SCHILLING ET AL: "Percolation in suspensions of hard nanoparticles: From spheres to needles", EUROPHYSICS LETTERS: A LETTERS JOURNAL EXPLORING THE FRONTIERS OF PHYSICS, vol. 111, no. 5, 1 September 2015 (2015-09-01), page 56004, XP055409926, FR ISSN: 0295-5075, DOI: 10.1209/0295-5075/111/56004 * abstract * * * tables 1,2 * * figure 3 * -----	1-18	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

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	Date of completion of the search	Examiner
	26 September 2017	Moroz, Alexander

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C38)

ANNEX TO THE SEARCH REPORT ON LUXEMBOURG PATENT APPLICATION NO.

LO 1559
LU 100018

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-09-2017

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016031489 A1	03-03-2016	CN 106575004 A	19-04-2017
		JP WO2016031489 A1	15-06-2017
		US 2017145737 A1	25-05-2017
		WO 2016031489 A1	03-03-2016
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		JP WO2016031489 A1	15-06-2017
		US 2017145737 A1	25-05-2017
		WO 2016031489 A1	03-03-2016
EP 2374559 A2	12-10-2011	CN 102219388 A	19-10-2011
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		JP 2015501534 A	15-01-2015
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		US 2015305166 A1	22-10-2015
		WO 2015164024 A1	29-10-2015

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
LO1559	11.01.2017		LU100018

International Patent Classification (IPC)
INV. G02B5/08 G02B5/28 G02B5/20

Applicant
Luxembourg Institute of Science and Technology (LIST)

This report 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
Moroz, Alexander

Application No.
LU100018

WRITTEN OPINION

Box No. I Basis of the 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.

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 and industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	1-18
	No:	Claims	
Inventive step	Yes:	Claims	
	No:	Claims	1-18
Industrial applicability	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations

   see separate sheet

WRITTEN OPINION

Box No. VII Certain defects in the application

The following defects in the form or contents of the application have been noted:

see separate sheet

Box No. VIII Certain observations on the application

see separate sheet

Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure:

D1: WO 2016/031489 A1 (for the applicant's convenience, passages from a family member US 2017/145737 A1 written in English were quoted)

D2: EP 2 374 559 A2

D3: WO 2013/056242 A1

D4: US 2015/305166 A1

D5: XP055409926 (TANJA SCHILLING ET AL: "Percolation in suspensions of hard nanoparticles: From spheres to needles", EUROPHYSICS LETTERS, vol. 111, no. 5, 1 September 2015 (2015-09-01), page 56004,FRISSN: 0295-5075, DOI: 10.1209/0295-5075/111/56004)

Item V

1 **Inventive step**

The subject-matter of claims **1-18** lacks an inventive step.

1.1 (Regarding independent claim **1**): Document **D1** (abstract; paragraphs [0077] - [0085], [0089] - [0092], [0147], [0180] - [0196], [0201] - [0261]; figures 1-3) discloses (the references in parentheses applying to this document; emphasis added; not applicable alternatives or features strike out)

Infrared reflective and electrically conductive composite film to coat on a **substrate** ([0062]: "*As shown in FIG. 1, it is preferable that the heat insulating film 103 of the invention includes a pressure sensitive adhesive layer 51 on a surface of the support 10 on the window (**glass 61** in FIG. 3) side and it is preferable that the glass 61 and the pressure sensitive adhesive layer 51 are bonded to each other.*"),

said composite film comprising ~~at least one infrared reflective layer (8);~~

~~said composite film further comprises~~ at least one metal layer of connected **metal nanowires** - cf. **D1** (paragraph [0080]): "*In order to easily form more transparent fibrous conductive particles-containing layer, fibrous conductive* *particles having an average short axis length of 1 nm to 150 nm are preferable, for example, as the fibrous conductive particles such as **metal nanowires**.*" Metal nanowires are regarded to be connected because their **aspect ratio is at least 10** - cf. **D1** (paragraph [0180]): "*From a viewpoint of the effect, a content of the fibrous conductive particles such as metal nanowires (preferably, metal nanowires having **an aspect ratio equal to or greater than 10**)*, which in combination with their volume fraction of at least 50% - cf. **D1** (paragraph [0084]): "... *a content of fibrous conductive particles such as metal nanowires ... is preferably equal to or greater than **50%** by mass*) implies that they are above a percolation threshold - cf. **D5** (abstract; tables 1,2; figure 3);

~~each of~~ said ~~at least one infrared reflective layer (8) and~~ at least one metal layer being conformably covered by an **optically transparent conductive layer** - cf. **D1** (paragraph [0147]): "*In the heat insulating film of the invention, it is preferable that the main component of the binder of the fibrous conductive particles-containing layer is a **conductive polymer**. The conductive polymer also effectively shields infrared light and exhibits heat insulating properties.*"

1.1.1 **Difference**: The subject-matter of claim **1** differs from the disclosure of the most relevant state of the art **D1** in that it comprises "*an additional infrared reflective layer*".

In this regard **D1** appears to combine the at least one metal layer of connected metal nanowires and the infrared reflective layer in a **single layer**. See:

- **D1** (paragraph [0180]): "*The fibrous conductive particles-containing layer may include other conductive materials, for example, conductive particles*"

- **D1** (paragraph [0182]): "... "*For example, in a case where the fibrous conductive particles are silver nanowires and the conductive particles are silver particles*" (cf. claim 3 of the application)

1.1.2 Since the closest prior art provides all the technical effects of the invention, the **objective problem to be solved** by the present invention may therefore be regarded as to provide an "*alternative infrared reflective and electrically conductive composite film to coat on a substrate*".

1.1.3 The skilled person would is well aware of the option of having an "*additional infrared reflective layer*". See in this regard **D2** (abstract; paragraphs [0009] - [0013], [0039] - [0044], [0091] - [0096]; figures 1,2), which anticipates all the features of the *infrared reflective layer* of claim **1**.

The *alternative* of having an infrared reflective layer as a **separate** layer to the metal layer (10) of connected metal nanowires in an infrared reflective and electrically conductive composite film, each of said at least one infrared reflective layer and at least one metal layer being conformably covered by an optically transparent conductive layer is regarded to be a constructional detail which comes within the scope of customary practice followed by persons skilled in the art, especially as the achieved advantages can be readily contemplated in advance.

1.2 (Regarding independent claim **15**): The same applies, *mutatis mutandis*, to the independent method claim **15**.

1.3 (Regarding claims **9,11**): Furthermore, **D1** discloses the features introduced by the subject-matter of dependent claims **9,11**.

- **c9**: the connected metal nanowires have a length superior to 100 nm, preferably **superior to 10 µm**, a width inferior to 10 µm, preferably **inferior to 100 nm** and/or a thickness inferior to 300 nm, preferably **inferior to 100 nm** - cf. **D1** (paragraph [0082]): "*The average long axis length of the fibrous conductive particles such as metal nanowires is preferably **5 µm to 50 µm**, in order to easily reflect far infrared rays at a wavelength of 5 to 50 µm, more preferably 10 µm to 40 µm, and even more preferably 15 µm to 40 µm*";

D1 (paragraph [0081]): "*From easiness of handling at the time of the manufacturing, an average short axis length (average diameter) of the fibrous conductive particles such as metal nanowires is preferably **equal to or***

***smaller than 100 nm**, more preferably equal to or smaller than 60 nm, and even more preferably equal to or smaller than 50 nm, and the average short axis length thereof is particularly equal to or smaller than 25 nm*";

- **c11**: transparent conductive layer (12) has a thickness comprised between **10** and **1000 nm** - cf. **D1** (paragraph [0185]): "*An average film thickness of the fibrous conductive particles-containing layer is normally selected from a range of **0.005 µm** to **2 µm**.*"

1.4 (Regarding dependent claims **2-8,10,12-14,16-18**): Given the closest prior art **D1** taken in combination with **D2**, the additional features introduced by dependent claims **2-8,10,12-14,16-18** are regarded minor constructional details and merely some of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill. There appears to be no surprising or synergetic effect resulting from the implementation of any of these additional features.

2 Item VII

The application contravenes the following rules: (identification of relevant prior art **D1,D2,D3,D4**) and two-part form does not properly reflects the cited prior art.

3 Item VIII

3.1 (Regarding claim **2**): A surface coverage rate of what? The feature of: "*the at least one infrared reflective layer (8) has a <u>surface coverage rate</u> of at least 30%*" is **unclear** because the infrared reflective layer has not been defined yet as e.g. "*a layer of silver nanostructured particles with irregular shape or disk shape*" - cf. claim **3**.

The above objection can be overcome by redrafting claim **1** so that it defines "*the at least one infrared reflective layer (8) of <u>silver</u> nanostructured particles with irregular shape or disk shape*".

3.2 (Regarding claims **6,7**): How can "*the at least one infrared reflective layer (8) have a **thickness** comprised between 1 nm and **30 nm***" if "*the nanostructured particles of the at least one infrared reflective layer (8) have an average diameter comprised between 1 nm and **10 µm**, preferably between 10 nm and **1 µm***"?

3.3 (Regarding claim **9**): The technical meaning of metal nanowires which have length shorter than their width and/or thickness is **unclear** - cf. "*the connected metal nanowires have a **length superior to 100 nm**, ..., a **width inferior to 10 µm**, ... and/or a **thickness inferior to 300 nm**, preferably inferior to 100 nm*".

3.3.1 What is a geometrical meaning of a **width** and a **thickness** of a metal nanowire? How one can differentiate between the two?