

PROCESS FOR MANUFACTURING A TWO-DIMENSIONAL FILM OF HEXAGONAL CRYSTALLINE STRUCTURE

5 **FIELD OF THE INVENTION**

The present invention concerns the growth of a two-dimensional film of a material of group IV of the periodic table of elements having a hexagonal crystal structure, in particular graphene, as well as a structure comprising such a film.

10 **STATE OF THE ART**

Graphene films are of growing interest in various technologies, especially electronics, optoelectronics, energy, sensors, biotechnology, composite materials. A graphene film consists of carbon atoms arranged in the form of a two-dimensional hexagonal crystal structure. Among the particularly interesting properties of graphene are
15 the mobility of charge carriers, thermal conductivity in the film plane, optical transparency, good mechanical properties such as high cohesion or tensile strength, flexibility, and biocompatibility.

Processes already exist for growing a graphene film, in the form of a monoatomic layer, or a few atomic layers, on a support substrate.

20 A first technique uses a metal foil, particularly copper or nickel, as a support substrate, and uses a chemical vapor deposition (CVD) process to grow a graphene layer on said support substrate. Optionally, the graphene film thus formed can then be transferred to another support.

A first disadvantage of this technique is that the coefficients of thermal expansion
25 (CTEs) of graphene and the copper or nickel support substrate are very different.

However, since the growth of the graphene film is carried out at high temperature (typically in the range of 1000 to 1100°C), this difference in coefficient of thermal expansion generates high stresses in the graphene film when it returns to room temperature.

30 Since the graphene film consists of no more than a few atomic layers, these stresses cause deformation and damage to the graphene during cooling. These effects may be exacerbated in later process steps of the graphene film.

A second disadvantage of the above technique is that, in order to perfectly and reproducibly control the number of deposited graphene atomic layers (in particular by
35 avoiding the formation of areas where an additional layer begins to form), it must be possible to guarantee that the only source of carbon atoms comes from the deposition atmosphere and not from the growth substrate itself.

However, metal foils tend to absorb carbon atoms that are also deliberately strongly present in the deposition atmosphere and to release them unintentionally during growth or cooling. In the case of copper, this absorption is considered to be localized, mainly through grain boundaries and other defects in the copper foils, which are polycrystalline. In the case of nickel, it is considered that it tends to temporarily absorb carbon to its full thickness, or at least over several micrometers from the surface exposed to the carbon atmosphere. However, the limit solubility of carbon in nickel decreases with temperature, leading to a release of carbon during cooling following the growth of the graphene film.

Finally, to precisely and reproducibly control graphene growth, it is not sufficient for the copper foil to be well textured and/or oriented (for example by presenting only oriented grains (111), because the arrangement of the different grains (like a mosaic) can significantly influence the properties of the graphene film.

A second technique therefore aims to replace the above-mentioned metal foil with a composite substrate consisting of a copper layer deposited on a silicon or sapphire substrate [Miller 2012] [Miller 2013] [Ismach 2010] [Rahimi 2014] [Tao 2012].

However, even when the deposition of the copper layer is optimized to promote orientation (111) along the normal axis to the substrate, said layer remains textured (polycrystalline) with the presence of orientation variants in the plane (twins). Similarly, annealing a layer of copper at high temperature (around 950°C) makes it possible to grow some grains, but their size remains well below a millimeter.

The graphene films deposited on these composite substrates are of comparable quality to those obtained on copper foils.

To overcome the disadvantages of the polycrystallinity of copper, tests were carried out by depositing graphene on small single-crystal copper crystals, naturally free of grain boundaries [Gao 2010].

However, this third technique does not solve the problem of the difference in coefficient of thermal expansion. In addition, the use of copper single crystals, which are very expensive and too small, does not lend itself to industrial application. Finally, this technique does not solve the problem of volume absorption by nickel.

The document US 8,501,531 proposes to avoid deposition of graphene by CVD and describes a process in which a metal layer with a determined carbon concentration is deposited on a substrate, which then undergoes heat treatment comprising a heating step to diffuse carbon inside the metal layer and then a step of sufficiently rapid cooling to migrate carbon out of the metal layer and organize itself as graphene on the surface of said metal layer. However, this technique has certain disadvantages. First, it should be noted that the graphene formation temperature is poorly defined. Indeed, this technique requires exposing the structure to high temperatures in order to incorporate carbon into the metal layer, and graphene is formed during cooling due to over-saturation of carbon.

Wrinkles in the graphene film are therefore generally observed. In addition, the metal layer obtained by deposition is polycrystalline. The roughness of the deposited films is generally high, and may be higher than 10 or so nanometers. Thickness control for deposited films is therefore tricky for small thicknesses, i.e. less than 10 nm.

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DISCLOSURE OF THE INVENTION

One aim of the invention is to overcome the above-mentioned disadvantages and to design a process for manufacturing a two-dimensional film of a group-IV material having a hexagonal crystal structure, in particular graphene, which makes it possible to precisely control the growth of one or more atomic layers and which provides a better quality film than the films currently available.

To that end, the invention proposes a process for manufacturing a two-dimensional film of a group-IV material having a hexagonal crystal structure, said process comprising:

- the formation of a growth substrate, comprising the transfer of a single-crystal metal film adapted for growth of said two-dimensional film on a support substrate, and
- the epitaxial growth of the two-dimensional film on the metal film of said substrate.

Advantageously, the metal film comprises at least one of the following metals: nickel, copper, platinum, cobalt, chromium, iron, zinc, aluminum, iridium, ruthenium, silver.

Preferably, the metal film has a thickness of 1 μm or less, preferably 0.1 μm or less.

The support substrate can be a quartz, graphite, silicon, sapphire, ceramic, nitride, carbide, alumina or metal substrate.

According to one embodiment of the invention, the support substrate has, with respect to the material of the two-dimensional film, a smaller difference in coefficient of thermal expansion than between the metal film and said two-dimensional film.

According to one embodiment of the invention, the transfer of the metal film comprises:

- the provision of a single-crystal metal donor substrate,
- the assembly of the donor substrate and the support substrate,
- the thinning of the donor substrate so as to transfer the metal film to the support substrate.

Said single-crystal metal donor substrate is advantageously obtained by pulling an ingot.

According to one embodiment, the process further comprises a step of formation of an embrittlement zone in the donor substrate, so as to delimit the single-crystal metal film to be transferred, and the thinning of the donor substrate comprises a detachment of the donor substrate along the embrittlement zone.

According to one embodiment, the embrittlement zone is formed by implantation of atomic species in the donor substrate.

According to one embodiment, the assembly of the donor substrate and the support substrate is carried out by bonding.

Alternatively, the assembly of the donor substrate and the support substrate is carried out by deposition of the support substrate on the donor substrate.

5 In a particular embodiment, the single-crystal metal film is in the form of a plurality of blocks, each transferred to the support substrate.

Each block advantageously has the same surface area as the donor substrate, said surface area being less than the surface area of the support substrate.

10 According to one embodiment, the growth substrate comprises a removable interface.

Said interface can be configured to be disassembled by laser lift-off, chemical etching, or mechanical loading.

In addition, the process may comprise, after the growth of the two-dimensional film, a step of separation of said two-dimensional film from the growth substrate.

15 According to one embodiment, said separation may comprise a delamination of the interface between the single-crystal metal film and the support substrate.

Alternatively, said separation may comprise an implantation of atomic species in the support substrate so as to form an embrittlement zone, and then detachment of the growth substrate along said embrittlement zone.

20 In a particular embodiment, the process comprises, after said separation, the transfer of a new single-crystal metal film onto the support substrate so as to form a new growth substrate, and then the growth of a new two-dimensional film of a group-IV material having a hexagonal crystal structure on said new growth substrate.

25 According to another embodiment, said separation comprises a delamination of the interface between the two-dimensional film and the single-crystal metal film of the growth substrate.

In a particular embodiment, the process comprises, after said separation, the reuse of the growth substrate to grow a new two-dimensional film of a group-IV material having a hexagonal crystal structure on said substrate.

30 Optionally, the process may comprise, after the growth of the two-dimensional film, an etching of the metal film so as to transfer the two-dimensional film to the support substrate.

According to an advantageous embodiment of the invention, the two-dimensional film is a graphene film.

35 Another object of the invention concerns a structure obtained by the process just described. Said structure comprises successively a support substrate, a single-crystal metal film and a two-dimensional film of a group-IV material having a hexagonal crystal structure on the metal film.

According to one embodiment, the metal film is in the form of a plurality of blocks distributed over the surface of the support substrate.

Advantageously, said two-dimensional film consists of one or more monoatomic layers.

5 According to one embodiment, the two-dimensional film is a graphene film.

DESCRIPTION OF THE FIGURES

Other features and advantages of the invention will be better understood when reading the detailed description that follows, with reference to the attached drawings on
10 which:

- Figure 1 illustrates a substrate for the growth of a graphene film according to one embodiment of the invention;
- Figure 2 illustrates a substrate for the growth of a graphene film according to a variant of the invention;
- 15 - Figures 3A to 3B illustrate the main features of a process for manufacturing the substrate of Figure 1 according to one embodiment of the invention;
- Figures 4A to 4B illustrate the main steps of a process for manufacturing the substrate of Figure 2 according to one embodiment of the invention;
- Figures 5A to 5B illustrate the main steps of a process for manufacturing the
20 substrate of Figure 2 according to a variant embodiment of the invention;
- Figure 6 illustrates a structure comprising a graphene film formed by epitaxial growth on the substrate of Figure 1;
- Figure 7 illustrates a structure comprising a graphene film on a growth substrate comprising a removable interface;
- 25 - Figure 8 illustrates a structure in which the metal film of the growth substrate has been etched after the growth of the graphene film.

To make the figures easier to read, the different layers are not necessarily represented to scale.

30 DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

For reasons of brevity, the following description refers to the growth of a graphene film, but the invention also applies to the other group IV-elements of the periodic table of elements that form a two-dimensional film of hexagonal crystal structure, namely silicon (the film material being referred to as “silicene”), germanium (the film material being
35 referred to as “germanene”) and tin (the film material being referred to as “stanene”).

Figure 1 illustrates a substrate 100 for the growth of a graphene film according to one embodiment of the invention.

Said substrate comprises a single-crystal metal film 1 adapted for the growth of graphene, on a support substrate 2.

Said substrate is obtained by transfer of the metal film onto the support substrate from a donor substrate. This transfer can be carried out by the Smart Cut™ process as described below, but other transfer processes involving an assembly of the donor substrate on the support substrate and then a thinning of the donor substrate until the desired thickness of the metal film is obtained can be implemented.

The metal film 1 comprises at least one of the following metals: nickel, copper, platinum, cobalt, chromium, iron, zinc, aluminum, iridium, ruthenium, silver. Optionally, the film may consist of an alloy of said metals, or an alloy comprising at least one of said metals and at least one other metal.

The thickness of the single-crystal film is advantageously 1 μm or less, preferably 0.1 μm or less.

This thickness is typically at least 10 times lower than the thickness of the metal foils used conventionally for graphene growth. Thus, the absorption effect of the atoms mentioned above is considerably reduced, especially in the case of nickel, where the absorption phenomenon occurs throughout the thickness of the film.

However, such a thickness is sufficient to fulfil the main function of the metal film, which is to form a seed layer for graphene growth. Indeed, the single-crystal character of the metal film allows the formation of a graphene film with an excellent crystal quality.

Finally, due to its thinness, the metal film has little influence on the thermal expansion of the substrate during the growth of the graphene film, said thermal expansion being essentially due to the thermal expansion of the support substrate.

The main function of the support substrate 2 is to mechanically support the metal film during the growth of the graphene film.

The material of the support substrate 2 must therefore withstand the conditions (especially temperature and chemical environment) of graphene film growth, which may vary depending on the deposition technique chosen. Thus, chemical vapor deposition (CVD) is implemented at a higher temperature than molecular beam epitaxy (MBE).

According to an advantageous but not imperative embodiment, the material of the support substrate 2 is chosen to have, with respect to graphene, a smaller difference in coefficient of thermal expansion than between the metal film and graphene. Preferably, the difference in coefficient of thermal expansion between graphene and the material of the support substrate is minimized, it being recalled, however, that the difference in coefficient of thermal expansion between graphene and the material of the support substrate is all the more acceptable when the graphene growth temperature is low.

The support substrate 2 is advantageously single-crystal because this configuration is more favorable for the polishing of the surface of said substrate before the transfer of

the metal film (when this transfer involves bonding), but this property is not imperative. As indicated below, the support substrate can optionally be formed by deposition.

Advantageously, the preferred materials for the support substrate are in particular quartz, graphite, silicon, sapphire, ceramics, nitrides, carbides, alumina, and metals.

5 Optionally, the support substrate may have, at the interface with the metal film, an encapsulation layer (not shown) to promote adhesion between the metal film and the support substrate, and/or to form a diffusion barrier to prevent pollution of the graphene by elements of the support substrate. Conversely, the material of the support substrate may have in certain cases signs of decomposition or deterioration when exposed directly to the growth atmosphere of the graphene film, or when exposed to the assembly conditions of the metal film. A diffusion barrier also makes it possible in this case to remove or limit these effects. Said encapsulation layer can for example be made of one of the following materials among oxides, nitrides, carbides.

15 After obtaining the graphene film, it can be detached from the substrate used for its growth.

It should be noted that the metal film is not necessarily continuous on the surface of the support substrate. On the contrary, the metal film 1 can be formed by a set of single-crystal metal blocks 10 distributed over the surface of the support substrate 2, said blocks 10 which may be contiguous or distant from each other, as shown in Figure 2. As will be seen below, these blocks allow the use of small metal single crystals in relation to the size of the support substrate. Size, as used here, means the surface area of the surfaces in contact with the blocks and the support substrate. The blocks are advantageously rectangular, but this shape is not limiting. By way of another example, these blocks can also be in the form of strips, discs, hexagons, etc. The skilled person is able to determine the shape of the blocks and their distribution on the surface of the support substrate depending on the geometry of the donor substrates at her disposal and the surface area of the graphene film to be formed.

Examples of growth substrate according to the embodiments of the invention

Example no. 1

30 In this example, the single-crystal metal film 1 is copper and the support substrate 2 is a silicon substrate successively coated with a 0.4- μm SiO_2 film and a 0.1- μm copper film to provide direct Cu/Cu metal bonding between the support substrate 2 and the metal film 1.

Example no. 2

35 In this example, the single-crystal metal film 1 is nickel and the support substrate 2 is a molybdenum substrate, each coated with a 0.2- μm copper film to provide direct Cu/Cu metal bonding between the support substrate 2 and the metal film 1.

Example no. 3

In this example, the single-crystal metal film 1 is nickel and the support substrate 2 is a polycrystalline AlN ceramic coated successively with a 0.3- μm Si_3N_4 film and a 0.5- μm SiO_2 film.

5 Example no. 4

In this example, the single-crystal metal film 1 is copper and the support substrate 2 is sapphire coated with a 0.3- μm SiO_2 film.

Example no. 5

10 In this example, the single-crystal metal film 1 is copper and the support substrate 2 is a 20- μm thick polycrystalline copper film assembled by direct Cu/Cu metal bonding on a donor substrate after formation of an embrittlement zone by implantation therein.

Example no. 5

15 In this example, the single-crystal metal film 1 is copper and the support substrate 2 is a nickel film deposited by electrodeposition to a thickness of 15 μm directly on a donor substrate after formation of an embrittlement zone by implantation therein.

Example no. 6

In this example, the single-crystal metal film 1 is copper and the support substrate 2 is a nickel-copper alloy film deposited by electrodeposition to a thickness of 15 μm directly on a donor substrate after formation of an embrittlement zone by implantation therein.

20 Example no. 7

In this example, the single-crystal metal film 1 is a nickel-copper alloy and the support substrate 2 is a nickel film deposited by electrodeposition to a thickness of 15 μm directly on a donor substrate after formation of an embrittlement zone by implantation therein.

25 Example no. 8

In this example, the single-crystal metal film 1 is in the form of a plurality of single-crystal nickel blocks 10 positioned contiguously on a planar support and the support substrate 2 is a nickel film deposited directly on a side embrittled by hydrogen implantation of the plurality of blocks, the deposition of said nickel film being carried out by
30 electrodeposition to a thickness of 10 μm .

A process for manufacturing a substrate as shown in Figure 1, according to one embodiment of the invention, will now be described.

With reference to Figure 3A, a donor substrate 11 made of a metal single crystal is provided.

35 An embrittlement zone 12 is formed in the donor substrate by implantation of atomic species (schematized by the arrows), said embrittlement zone delimiting, on the surface of the donor substrate 11, the single-crystal metal film to be transferred to the support substrate. Said atomic species may include hydrogen in particular. Helium is another

species of particular interest from this point of view, either as a replacement for hydrogen or in combination with hydrogen.

With reference to Figure 3B, the donor substrate 11 is assembled on a support substrate 2, the metal film to be transferred being at the bonding interface.

5 According to one embodiment, this assembly is achieved by bonding the substrates 2 and 11.

According to another embodiment, this assembly is achieved by deposition of the support substrate 2 on the donor substrate 11, by any appropriate deposition technique depending on the nature of the support substrate.

10 Next, the donor substrate is detached along the embrittlement zone 12, said detachment which may be initiated for example by mechanical, chemical, and/or thermal stress. This detachment results in the transfer of the single-crystal metal film 1 to the support substrate 2. The structure shown in Figure 1 is thus obtained.

15 Optionally, a finishing treatment is carried out on the surface of the single-crystal metal film to make it suitable for subsequent deposition of the graphene film. This may be, for example, a polishing, annealing and/or etching operation.

Naturally, the skilled person is able to define the procedure according to the material of the donor substrate and the thickness of the film to be transferred.

This metal film transfer process comprises variants.

20 A first variant concerns the assembly of the donor substrate and the support substrate. Thus, instead of an assembly by bonding the donor substrate to the support substrate, the assembly may consist of deposition of the support substrate on the donor substrate, with the film to be transferred being on the side of the donor substrate on which the deposition is performed. Optionally, a diffusion barrier layer is formed between the
25 donor substrate and the support substrate to prevent the diffusion of unwanted species from the support substrate to the graphene layer during its growth.

A second variant — optionally combinable with the first — concerns the method for thinning the donor substrate to transfer the metal film to the support substrate. Thus, instead of thinning by detaching the donor substrate along the embrittlement zone, it is
30 possible to remove material (in particular by etching or mechanical removal such as grinding or polishing) from the donor substrate by its side opposite the interface with the support substrate, until the desired thickness is obtained for the metal film to be transferred.

A process for manufacturing a substrate as shown in Figure 2 will now be described.

35 According to one embodiment, the blocks are assembled successively and then collectively transferred to the support substrate. To that end, a donor substrate 11 made of a metal single crystal is provided, the surface area of which is smaller than that of the support substrate 2 intended to receive it.

As already explained in reference to Figure 3A, an embrittlement zone 12 is formed in the donor substrate 11.

With reference to Figure 4A, a first donor substrate 11 is then bonded to the support substrate 2.

5 With reference to Figure 4B, a second donor substrate 11 is bonded to the support substrate 2, and this assembly operation is continued until all the donor substrates necessary to obtain all the blocks on the support substrate 2 are bonded.

Next, all the donor substrates 11 are detached along the respective embrittlement zone 12 to transfer all the single-crystal metal blocks 10 to the support substrate 2.

10 The procedure described above for the transfer of a continuous metal film onto the support substrate is applicable, with possible adaptations within the competence of the skilled person, to the transfer of one or more metal blocks onto the support substrate.

According to one variant (not shown) of this process, after the bonding of a first donor substrate to the support substrate, said donor substrate is detached along the
15 embrittlement zone to transfer a first single-crystal metal block to the support substrate, and this sequence is repeated with a subsequent donor substrate until all the blocks 10 are transferred to the support substrate 2.

The donor substrate may optionally be the same as the one from which the block 10 was collected, and thus be used several times to transfer a block to the same support
20 substrate 2.

Alternatively, the donor substrate may be different from the one from which the block 10 was collected. At the end of the transfer operation of all the metal blocks 10, all the donor substrates 11 can be reused to carry out a new cycle. Recycling operations may be desirable or necessary. For example, a polishing operation will make it possible to start
25 from an adequate surface roughness to a good quality assembly.

In addition, although the new donor substrate 11 is shown at a distance from the already transferred block 10, it could be positioned adjacent to the already transferred block 10.

Thus, a plurality of blocks 10 are successively transferred to the support substrate 2,
30 allowing the structure illustrated in Figure 2 to be obtained.

According to another embodiment, the blocks 10 are assembled and transferred collectively onto the support substrate 2.

To that end, as shown in Figure 5A, a plurality of donor substrates 11 are assembled on an intermediate substrate 13, said intermediate substrate essentially serving as a
35 mechanical support or handling tool for the donor substrates 11. The donor substrates 11 are represented at a distance from each other, but they could also be juxtaposed in a joint manner.

An embrittlement zone 12 is formed in each donor substrate, before or after their assembly on the intermediate substrate 13, so as to delimit a block 10 to transfer the support substrate.

5 With reference to Figure 5B, the intermediate substrate 13 carrying the donor substrates 11 is bonded to the support substrate 2, the free surface of the donor substrates 11 being at the bonding interface.

Next, all the donor substrates 11 are detached along their respective embrittlement zone 12, so as to transfer all the blocks 10 to the support substrate 2. The structure shown in Figure 2 is then obtained.

10 Preferably, the detachment step is performed collectively for all the donor substrates.

According to a variant, the detachment step can be performed successively for each donor substrate.

15 Optionally, the intermediate substrate 13 carrying the remaining donor substrates can be recycled for a new collective transfer of blocks. To that end, the free surface of the donor substrates is treated to remove defects related to detachment, a new embrittlement zone is formed in all the donor substrates, and the intermediate substrate carrying the embrittled donor substrates is bonded to a new support substrate.

20 Advantageously, the preparation of the blocks is organized upstream of the growth substrate manufacturing process. To that end, for example, metal ingots are assembled together before being collectively cut to form donor substrates, then collectively implanted before being assembled to the support substrate.

The growth substrate having a continuous or discontinuous (blocks) single-crystal metal film is then used for the growth of a graphene film.

25 Any technique known for growing graphene can be used.

By way of non-limiting example, mention may be made of chemical vapor deposition (CVD) and molecular beam epitaxy (MBE). The parameters of these processes allowing the growth of a graphene layer are known or determinable by the skilled person and, therefore, will not be described in detail in the present text.

30 Figure 6 shows a graphene 3 film formed on a growth substrate 100.

The graphene film is advantageously composed of one or more monoatomic layers of graphene, said layers which may be complete (i.e. continuous over the entire surface of the metal film) or not.

35 Depending on the applications targeted by the graphene film and the quality required for said film, it may be of interest to form a single atomic layer of graphene, or a stack of two or more monoatomic layers of graphene, making sure that each monoatomic layer is complete and avoiding initiating the formation of a new (incomplete) layer on a complete monoatomic layer.

This quality control of the graphene film is made possible not only by the parameters of the graphene deposition process but also by the excellent crystal quality and/or the thinness of the metal film that serves as the seed for graphene growth.

Indeed, on the one hand, the precise control of the number of monoatomic layers
5 formed is based on the fact that the carbon atoms constituting the graphene layer come only from the deposition atmosphere and not from the growth substrate itself.

Thus, in the case of copper, the single-crystal film used in the invention is of better quality than the copper foils used in the prior art, which are polycrystalline. To the extent that the presence of grain boundaries or other crystal defects is minimized in the copper
10 film according to the invention, the absorption sites of carbon atoms are thus minimized.

In the case of nickel, the superior quality of the single-crystal film used in the invention has the same advantage as in the case of copper, to which is added a minimum volume for the absorption of carbon atoms, due to the considerably reduced thickness of the single-crystal film compared with the foils usually used.

Consequently, since the absorption of carbon atoms into the single-crystal metal film
15 is minimized, the release of such atoms during the growth of the graphene film or subsequent cooling thereof is avoided or at least considerably reduced.

On the other hand, in the case where the support substrate 2 is chosen to have a small difference in coefficient of thermal expansion with respect to the graphene film (the
20 single-crystal metal film being thin enough to have a negligible influence), the mechanical stresses applied to the graphene film during its cooling are minimized. This prevents or reduces relaxation or damage to the graphene film. This also contributes to a better quality of the graphene film.

Finally, in contrast to composite substrates of the prior art in which a polycrystalline
25 copper film is deposited on a support substrate, the fact that the metal film of the invention is single-crystal allows the orientation (for example 111) of the graphene film to be controlled over the entire surface of the metal film.

After the graphene film has formed, it can be separated from the growth substrate in order to be optionally transferred to another support.

30 This separation can be carried out in different ways.

According to one embodiment, the growth substrate comprises a removable interface, i.e. an interface at which the application of a stress (or a treatment) allows a detachment of two parts of the substrate. The term interface is used here in the broad sense, in particular in that it may contain one or more layers of non-zero thickness.

35 In this respect, any known separation technique in the field of microelectronics may be used, the skilled person being able to select the appropriate materials according to the chosen technique.

Possible techniques include (optionally in combination):

- application of mechanical stress,
- chemical attack,
- decomposition,
- fusion,
- 5 - laser lift-off.

Said removable interface can be located between the single-crystal metal film and the support substrate or located inside the support substrate.

Figure 7 thus illustrates an embodiment in which the removable interface I is located within the support substrate 2.

10 For example, said interface I may consist of a bonding interface, a region of a material adapted to confine a mechanical fracture, such as a porous layer (for example silicon), a layer allowing selective etching against another, an embrittlement zone formed by implantation in the support substrate, etc.

Alternatively, the separation of the graphene film from the growth substrate can be
15 based on any known disassembly technique in the graphene domain.

According to one embodiment, the disassembly of the graphene film comprises a delamination of the interface between the metal film and the support substrate, then optionally chemical etching of the metal film. In this case, the support substrate can be reused for the transfer of a new metal film, in order to form a new substrate for graphene
20 growth.

According to another embodiment, the disassembly of the graphene film comprises a delamination of the interface between the graphene film and the metal film. Such a delamination technique is described in [Wang 2011], in the case of a growth substrate consisting of a copper foil. After such delamination, the growth substrate can be reused
25 for the growth of a new graphene film.

It is also possible to transfer the graphene film directly to the support substrate by etching the single-crystal metal film located between the graphene film and the support substrate. The structure shown in Figure 8 is thus obtained. Such a process is described in particular in [Levendorf 2009], in the case where the growth substrate comprises a
30 copper film formed by evaporation on a silicon substrate coated with a thermal oxide.

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CLAIMS

1. Process for manufacturing a two-dimensional film (3) of a group-IV material having a hexagonal crystal structure, comprising:
 - 5 - forming a growth substrate (100), comprising the transfer of a single-crystal metal film (1) adapted for growth of said two-dimensional film on a support substrate (2), and
 - epitaxially growing the two-dimensional film (3) on the metal film of said substrate (100).
- 10 2. Process according to claim 1, wherein the metal film (1) comprises at least one of the following metals: nickel, copper, platinum, cobalt, chromium, iron, zinc, aluminum, iridium, ruthenium, silver.
- 15 3. Process according to claim 1 or claim 2, wherein the metal film (1) has a thickness of 1 μm or less, preferably 0.1 μm or less.
4. Process according to one of claims 1 to 3, wherein the support substrate (2) is a quartz, graphite, silicon, sapphire, ceramic, nitride, carbide, alumina or metal substrate.
- 20 5. Process according to one of claims 1 to 4, wherein the support substrate (2) has, with respect to the material of the two-dimensional film, a smaller difference in coefficient of thermal expansion than between the metal film and said two-dimensional film.
- 25 6. Process according to one of claims 1 to 5, wherein the transfer of the metal film (1) comprises:
 - providing a single-crystal metal donor substrate (11),
 - assembling the donor substrate (11) and the support substrate (2),
 - thinning the donor substrate (11) so as to transfer the metal film to the support
 - 30 substrate (2).
7. Process according to claim 6, wherein the single-crystal metal donor substrate (11) is obtained by pulling an ingot.
- 35 8. Process according to claim 6 or claim 7, further comprising a step of forming a embrittlement zone (12) in the donor substrate (11), so as to delimit the single-crystal metal film (1, 10) to be transferred, and wherein thinning the donor substrate comprises detaching the donor substrate (11) along the embrittlement zone (12).

9. Process according to claim 8, wherein the embrittlement zone (12) is formed by implantation of atomic species in the donor substrate.

5 10. Process according to one of claims 6 to 9, wherein the assembly of the donor substrate (11) and the support substrate (2) is carried out by bonding.

10 11. Process according to one of claims 6 to 9, wherein assembling the donor substrate (11) and the support substrate (2) is carried out by deposition of the support substrate (2) on the donor substrate (11).

15 12. Process according to one of claims 1 to 11, wherein the single-crystal metal film (1) is in the form of a plurality of blocks (10) each transferred to the support substrate (2).

13. Process according to claim 12 in combination with claim 10, wherein each block (10) has the same surface area as the donor substrate (11), said surface area being smaller than the surface area of the support substrate (2).

20 14. Process according to one of claims 1 to 13, wherein the growth substrate (100) comprises a removable interface.

25 15. Process according to claim 14, wherein said interface (I) is configured to be disassembled by laser lift-off.

16. Process according to claim 14, wherein said interface (I) is configured to be disassembled by chemical etching.

30 17. Process according to claim 14, wherein said interface (I) is configured to be disassembled by mechanical loading.

35 18. Process according to one of claims 1 to 17, comprising, after the growth of the two-dimensional film (3), a step of separation of said two-dimensional film (3) from the growth substrate (100).

19. Process according to claim 18, wherein said separation comprises a delamination of the interface between the single-crystal metal film (1) and the support substrate (2).

20. Process according to claim 18, wherein said separation comprises an implantation of atomic species in the support substrate (2) so as to form an embrittlement zone, and then the detachment of the growth substrate along said embrittlement zone.

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21. Process according to one of claims 18 to 20, comprising, after said separation, the transfer of a new single-crystal metal film (1) to the support substrate (2) so as to form a new growth substrate (100), then the growth of a new two-dimensional film (3) of a group-IV material having a hexagonal crystal structure on said new growth substrate (100).

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22. Process according to claim 18, wherein said separation comprises a delamination of the interface between the two-dimensional film (3) and the single-crystal metal film (1) of the growth substrate.

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23. Process according to claim 22, comprising, after said separation, the reuse of the growth substrate (100) to grow a new two-dimensional film of a group-IV material having a hexagonal crystal structure on said substrate.

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24. Process according to claim 23, further comprising, after the growth of the two-dimensional film, an etching of the metal film (1) so as to transfer the two-dimensional film to the support substrate.

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25. Process according to one of claims 1 to 24, wherein the two-dimensional film (3) is a graphene film.

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26. Structure comprising successively a support substrate (2), a single-crystal metal film (1) and a two-dimensional film (3) of a group-IV material having a hexagonal crystal structure on the metal film (1).

27. Structure according to claim 26, wherein the metal film (1) is in the form of a plurality of blocks (10) distributed over the surface of the support substrate (2).

28. Structure according to claim 26 or claim 27, wherein the two-dimensional film (3) consists of one or more monoatomic layers.

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29. Structure according to one of claims 26 to 28, wherein the two-dimensional film (3) is a graphene film.