Using the seed (and possible mask) layers as the scaffold for graphene transfer has another important merit. The layers can be deposited directly after the CVD growth of graphene, and therefore protect the clean graphene surface from further processing that involves the deposition of polymer-based materials such as e-beam resists for graphene transfer. The direct deposition of polymer-based materials on CVD grown graphene always leaves carbon residues on the surface, which results in carbon contamination during NW growth, degrading the doping control and optical properties of NWs as well as contaminating the growth system. It could also affect the NW growth itself.

So the deposition of seed (and possible mask) layers before depositing polymer-based materials makes it possible to have the graphene surface carbon-contamination free. It can also be beneficial to incorporate the polymer-based material into the hole patterning process. It can be e-beam resist (or nano-imprinting resist) if the hole patterning would be done by e-beam lithography (nano-imprinting). Any carbon residues on the seed or mask layers can be thoroughly cleaned by oxygen plasma treatment and wet chemical etching, which would easily destroy the bare graphene without seed or mask layers.

Summary of Invention

Thus, viewed from one aspect the invention provides a composition of matter comprising:

a graphitic substrate optionally carried on a support;

a seed layer having a thickness of no more than 50 nm deposited directly on top of said substrate, opposite any support; and

an oxide or nitride masking layer directly on top of said seed layer wherein the masking layer is different from the seed layer;

wherein a plurality of holes are present through said seed layer and through said masking layer to said graphitic substrate; and wherein

a plurality of nanowires or nanopyramids are grown from said substrate in said holes, said nanowires or nanopyramids comprising at least one semiconducting group III-V compound.

There is also disclosed a composition of matter comprising:

a graphitic substrate optionally carried on a support;

an oxidised or nitridized seed layer having a thickness of no more than 50 nm present directly on top of said substrate, opposite any support; optionally

an oxide or nitride masking layer directly on top of said oxidised or nitridized seed layer;

wherein a plurality of holes are present through said seed layer and through said masking layer, if present, to said graphitic substrate; and wherein

a plurality of nanowires or nanopyramids are grown from said substrate in said holes, said nanowires or nanopyramids comprising at least one semiconducting group III-V compound.

Viewed from another aspect the invention provides a process comprising:

(I) providing a graphitic substrate on a support and depositing thereon a seed layer formed from a single metallic element and having a thickness of no more than 50 nm;

(II) oxidising or nitridizing said seed layer to form a oxidised or nitridized seed layer; optionally

(III) depositing a masking layer on said oxidised or nitridized seed layer, e.g. an oxide or nitride masking layer;

(IV) optionally transferring the graphitic substrate to a different support;

(V) introducing a plurality holes in said oxidised or nitridized seed layer and said masking layer, if present, said holes penetrating to said substrate;

(VI) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metal organic vapour phase epitaxy.

Viewed from another aspect the invention provides a process comprising:

(I) providing a graphitic substrate on a support and depositing thereon a seed layer formed from a single metallic element and having a thickness of no more than 50 nm;

(II) depositing on said seed layer an oxide or nitride masking layer;

(III) introducing a plurality holes in said seed layer and said masking layer said holes penetrating to said substrate;

(IV) optionally transferring the graphitic substrate to a different support;

(V) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

Embodiments of the invention provide a product obtained by a process as hereinbefore defined.

Optionally, the surface of the graphitic substrate can be chemically/ physically modified in the said plurality of holes to enhance the epitaxial growth of nanowires or nanopyramids.

Embodiments of the invention provide a device, such as an electronic device, comprising a composition as hereinbefore defined, e.g. a solar cell, light emitting device or photodetector.

In another aspect, the innovation provides a process comprising: providing a graphitic substrate composed of CVD grown single or multi-layer graphene on a metal catalyst layer, such as Pt, and depositing thereon a seed layer formed from a single metallic element and having a thickness of no more than 50 nm; oxidising or nitridizing said seed layer to form an oxidised or nitridized seed layer; optionally depositing a masking layer on said oxidised or nitridized seed layer; depositing a polymer layer on said masking layer (if present) or said oxidised or nitridized seed layer, said polymer layer being capable of acting as a scaffold for the transfer of said graphitic substrate to another support; transferring the graphitic substrate from said metal catalyst layer to a support; optionally removing the polymer layer, and optionally depositing a further oxide or nitride masking layer on top of the upper layer present; introducing a plurality holes through all layers present penetrating to said substrate; growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

In another aspect, the innovation provides a process comprising: providing a graphitic substrate composed of CVD grown single or multi-layer graphene on a metal catalyst layer, such as Pt, and depositing thereon a seed layer formed from a single metallic element and having a thickness of no more than 50 nm; depositing a masking layer on said seed layer; depositing a polymer layer on said masking layer said polymer layer being capable of acting as a scaffold for the transfer of said

graphitic substrate to another support; transferring the graphitic substrate from said metal catalyst layer to a support; optionally removing the polymer layer, and optionally depositing a further oxide or nitride masking layer on top of the upper layer present; introducing a plurality holes through all layers present penetrating to said substrate; growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

In another aspect, the invention provides a process comprising: (I) providing a graphitic substrate on a support and depositing thereon using thermal or e-beam evaporation a semiconducting or insulating seed layer having a thickness of no more than 50 nm; (II) depositing on said seed layer an oxide or nitride masking layer; (III) introducing a plurality of holes in said seed layer and said masking layer said holes penetrating to said substrate; (IV) optionally transferring the graphitic substrate to a different support; (V) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

In another aspect, the invention provides a process comprising: (I) providing a graphitic substrate composed of CVD grown single or multi-layer graphene on a metal catalyst layer, such as Pt, and depositing thereon using thermal or e-beam evaporation a semiconducting or insulating seed layer having a thickness of no more than 50 nm; (II) depositing on said seed layer an oxide or nitride masking layer; (III) depositing a polymer layer on said masking layer said polymer layer being capable of acting as a scaffold for the transfer of said graphitic substrate to another support; (IV) transferring the graphitic substrate from said metal catalyst layer to a support; (V) optionally removing the polymer layer, and optionally depositing a further oxide or nitride masking layer on top of the upper layer present; (VI) introducing a plurality holes through all layers present penetrating to said substrate; (VII) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

Definitions

By a group III-V compound semiconductor is meant one comprising at least one element from group III and at least one element from group V. There may be more than one element present from each group, e.g. InGaAs, AlGaN (i.e. a ternary compound), AlInGaN (i.e. a quaternary compound) and so on. The term semiconducting nanowire or nanopyramid is meant nanowire or nanopyramid made of semiconducting materials from group III-V elements.

The term nanowire is used herein to describe a solid, wirelike structure of nanometer dimensions. Nanowires preferably have an even diameter throughout the majority of the nanowire, e.g. at least 75% of its length. The term nanowire is intended to cover the use of nanorods, nanopillars, nanocolumns or nanowhiskers some of which may have tapered end structures. The nanowires can be said to be in essentially in one-dimensional form with nanometer dimensions in their width or diameter and their length typically in the range of a few 100 nm to a few μm. Ideally the nanowire diameter is not greater than 500 nm. Ideally the nanowire diameter is between 50 and 500 nm, however, the diameter can exceed few micrometers (called microwires).

Ideally, the diameter at the base of the nanowire and at the top of the nanowire should remain about the same (e.g. within 20% of each other).

Claims

1. A composition of matter comprising:

a graphitic substrate optionally carried on a support;

a seed layer having a thickness of no more than 50 nm deposited directly on top of said substrate, opposite any support; and

an oxide or nitride masking layer directly on top of said seed layer wherein the masking layer is different from the seed layer;

wherein a plurality of holes are present through said seed layer and through said masking layer to said graphitic substrate; and wherein

a plurality of nanowires or nanopyramids are grown from said substrate in said holes, said nanowires or nanopyramids comprising at least one semiconducting group III-V compound.

2. A composition as claimed in any preceding claim in which said seed layer is a metallic layer or a layer of oxidised or nitridized metal.

3. A composition as claimed in any preceding claim in which said substrate is graphene.

4. A composition as claimed in any preceding claim in which said nanowires or nanopyramids grow epitaxially from the substrate.

5. A composition as claimed in any preceding claim in which said substrate is up to 20 nm in thickness.

6. A composition as claimed in any preceding claim in which said seed layer is a metal layer from the first (3d) transition series (Sc-Zn), B, Al, Si, Ge, Sb, Ta, W, or Nb, or an oxidised layer thereof.

7. A composition as claimed in any preceding claim in which said masking layer comprises a metal oxide or metal nitride.

8. A composition as claimed in any preceding claim in which said masking layer comprises Al_2O_3, TiO_2, SiO_2, AlN, BN or Si_3N_4.

9. A composition as claimed in any preceding claim in which support comprises a semiconductor substrate, transparent glass, AlN or silicon carbide.

10. A composition as claimed in any preceding claim in which support comprises a semiconductor substrate comprising crystalline Si or GaAs with a crystal orientation of [111], [110], or [100] perpendicular to the surface with or without oxide or nitride layer such as SiO_2, Si_3N_4 on top; or a transparent glass of fused silica or fused alumina.

11. A composition as claimed in any preceding claim in which said nanowires or nanopyramids are doped.

12. A composition as claimed in any preceding claim in which said nanowires or nanopyramids are core-shell nanowires or nanopyramids or radially heterostructured nanowires or nanopyramids.

13. A composition as claimed in any preceding claim in which said nanowires or nanopyramids are axially heterostructured nanowires or nanopyramids.

14. A composition as claimed in any preceding claim wherein a graphitic top contact layer is present on top of said nanowires or nanopyramids.

15. A composition as claimed in any preceding claim wherein said masking layer comprises at least two different layers, e.g. an oxide layer and a nitride layer.

16. A process comprising:

(I) providing a graphitic substrate on a support and depositing thereon a seed layer formed from a single metallic element and having a thickness of no more than 50 nm;

(II) oxidising or nitridizing said seed layer to form an oxidised or nitridized seed layer; optionally

(III) depositing a masking layer on said oxidised or nitridized seed layer;

(IV) optionally transferring the graphitic substrate to a different support;

(V) introducing a plurality of holes in said oxidised or nitridized seed layer and said masking layer, if present, said holes penetrating to said substrate;

(VI) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via molecular beam epitaxy or metalorganic vapour phase epitaxy.

17. A process comprising:

(I) providing a graphitic substrate on a support and depositing thereon a seed layer formed from a single metallic element and having a thickness of no more than 50 nm;

(II) depositing on said seed layer an oxide or nitride masking layer;

(III) introducing a plurality of holes in said seed layer and said masking layer said holes penetrating to said substrate;

(IV) optionally transferring the graphitic substrate to a different support;

(V) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

18. A process comprising:

(I) providing a graphitic substrate on a support and depositing thereon using thermal or e-beam evaporation a semiconducting or insulating seed layer having a thickness of no more than 50 nm;

(II) depositing on said seed layer an oxide or nitride masking layer;

(III) introducing a plurality of holes in said seed layer and said masking layer said holes penetrating to said substrate;

(IV) optionally transferring the graphitic substrate to a different support;

(V) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

19. A process comprising:

(I) providing a graphitic substrate composed of CVD grown single or multi-layer graphene on a metal catalyst layer, such as Pt, and depositing thereon a seed layer formed from a single metallic element and having a thickness of no more than 50 nm;

(II) oxidising or nitridizing said seed layer to form an oxidised or nitridized seed layer; optionally

(III) depositing a masking layer on said oxidised or nitridized seed layer;

(IV) depositing a polymer layer on said masking layer (if present) or said oxidised or nitridized seed layer, said polymer layer being capable of acting as a scaffold for the transfer of said graphitic substrate to another support;

(V) transferring the graphitic substrate from said metal catalyst layer to a support;

(VI) optionally removing the polymer layer, and optionally depositing a further oxide or nitride masking layer on top of the upper layer present;

(VII) introducing a plurality holes through all layers present penetrating to said substrate;

(VIII) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

20. A process comprising:

(I) providing a graphitic substrate composed of CVD grown single or multi-layer graphene on a metal catalyst layer, such as Pt, and depositing thereon a seed layer formed from a single metallic element and having a thickness of no more than 50 nm;

(II) depositing a masking layer on said seed layer;

(III) depositing a polymer layer on said masking layer said polymer layer being capable of acting as a scaffold for the transfer of said graphitic substrate to another support;

(IV) transferring the graphitic substrate from said metal catalyst layer to a support;

(V) optionally removing the polymer layer, and optionally depositing a further oxide or nitride masking layer on top of the upper layer present;

(VI) introducing a plurality holes through all layers present penetrating to said substrate;

(VII) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

21. A process comprising:

(I) providing a graphitic substrate composed of CVD grown single or multi-layer graphene on a metal catalyst layer, such as Pt, and depositing thereon

using thermal or e-beam evaporation a semiconducting or insulating seed layer having a thickness of no more than 50 nm;

(II) depositing on said seed layer an oxide or nitride masking layer;

(III) depositing a polymer layer on said masking layer said polymer layer being capable of acting as a scaffold for the transfer of said graphitic substrate to another support;

(IV) transferring the graphitic substrate from said metal catalyst layer to a support;

(V) optionally removing the polymer layer, and optionally depositing a further oxide or nitride masking layer on top of the upper layer present;

(VI) introducing a plurality holes through all layers present penetrating to said substrate;

(VII) growing a plurality of semiconducting group III-V nanowires or nanopyramids in the holes, preferably via a molecular beam epitaxy or metalorganic vapour phase epitaxy.

22. A process as claimed in claim 19 or 20 in which said graphene transfer is effected by an electrochemical delamination method employing an aqueous electrolyte comprising an acid, hydroxide, carbonate, or chloride solution.

23. A process as claimed in claim 16 to 22 in which said nanowires or nanopyramids are grown in the presence or absence of a catalyst.

24. A product obtained by a process as hereinbefore defined.

25. A device, such as an electronic device, comprising a composition as claimed in claims 1 to 15, e.g. a solar cell or LED.

26. A composition as claimed in claim 1 to 15 wherein the surface of the graphitic substrate is chemically/ physically modified in the said plurality of holes to enhance the epitaxial growth of nanowires or nanopyramids.