Catalyst deposition for the preparation of carbon nanotubes

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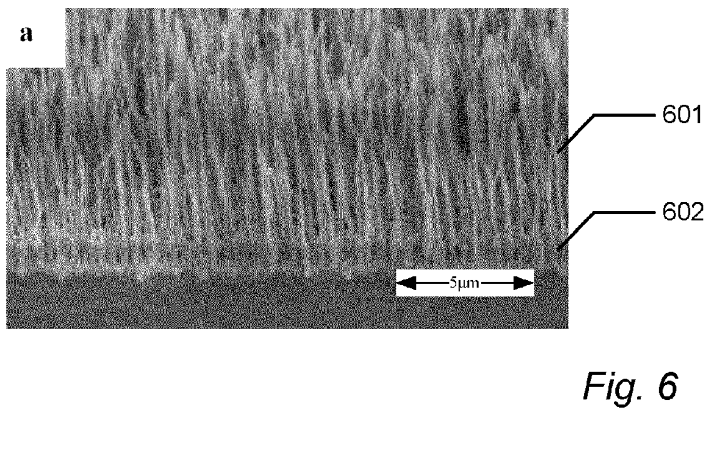

Fig. 6

(57) **Abstract**: Disclosed is a method of depositing islands of catalyst with a predetermined density, wherein in said method comprises the steps of: obtaining a diffusion barrier covered nano patterned surface comprising a plurality of plateaus, having a density of plateaus dependent on the predetermined density of islands of catalyst; depositing catalyst on said diffusion barrier covered nano patterned surface; and heating the diffusion barrier covered nano patterned surface after catalyst has been deposited, to anneal the catalyst, whereby islands of catalyst is formed. Wherein said diffusion barrier covered nano patterned surface is configured to ensure that no more than a single island of catalyst is formed on each plateau, so that a sub sequent growth of carbon nanotubes from the deposited islands result in that no more than a single carbon nanotube is grown from each plateau.

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CATALYST DEPOSITION FOR THE PREPARATION OF CARBON NANOTUBES

Field

The present invention relates to a method for nano-scale deposition of catalyst and to devices for use as templates for nano-scale deposition of catalysts. Additionally, the present invention relates to methods of growing carbon nanotubes.

Background

For a plurality of applications precise nano-scale deposition of catalyst material is of great importance. Examples of such applications are for the creation of various optical devices and/or as a starting point for various chemical processes e.g. growth of carbon nanotubes (CNT).

Carbon nanotubes due to their unique physicochemical properties are a subject of extensive studies in many application fields including electronics, electrochemistry, or biotechnology, to mention the few. For nanotube devices to reach their industrial maturity, economical and high in yield fabrication methods must be accessible. Plasma enhanced chemical vapour deposition (PECVD) is the state of the art approach for growth of sparse CNT forests [Meyyappan, M., *A review of plasma enhanced chemical vapour deposition of carbon nanotubes.* Journal of Physics D-Applied Physics, 2009. 42(21).]. Metal catalysts (nickel, iron, or other) are used in the process, where each single particle nucleates one nanotube, and defines its diameter and structure. Therefore, the catalyst pattern defines distribution of carbon nanotubes in the forest [Meyyappan, M., *A review of plasma enhanced chemical vapour deposition of carbon nanotubes.* Journal of Physics D-Applied Physics, 2009. 42(21).]. Several approaches of patterning the catalyst are available, offering different level of control and feature size. The simplest involves annealing of a thin (few to tens of nm) film of the catalyst, where islands of catalyst agglomerates into nanoparticles with a random non-uniform distribution of droplet size [Meyyappan, M., *A review of plasma enhanced chemical vapour deposition of carbon nanotubes.* Journal of Physics D-Applied Physics, 2009. 42(21).]. However, for certain applications, it may be desirable to have islands of catalyst with a more uniform size and possibly also a more uniform distribution.Thicker films require patterning as surface tension prevents them from breaking up into the particles.

An example of such an application is the growth of carbon nanotubes from the catalysts islands, using the chemical vapour deposition method. For growth of carbon nanotubes, the diameter and the height of the resulting carbon nanotubes are dependent on the size of the catalyst islands. When a surface comprising islands with highly un-uniform sizes is used as a starting point, the resulting forest of carbon nanotubes becomes correspondingly non-uniform.

Photolithography is a well established patterning method for achieving a more uniformly deposition of catalyst material, but unfortunately, it is limited to submicron resolutions. E-beam writing offers ultimate resolution, however, it is too expensive and very time consuming for mass production since each island of catalyst material needs to printed individually.

Alternatively shadow masking has been used for catalyst patterning [Wei, H., et al., *Patterned forest-assembly of singlewall carbon nanotubes on gold using a non-thiol functionalization technique.* Journal of Materials Chemistry, 2007. 17(43): p. 4577-4585.]; yet it suffers proximity errors. Self assembly also offers a good alternative and can provide nanometric patterning [Lee, S.H., et al., *Tailored Assembly of Carbon Nanotubes and Graphene.* Advanced Functional Materials, 2011. 21(8): p. 1338-1354.], but do not allow mesoscale (in the range from 100 to 1000nm) feature sizes. Finally, solid spherical nanoparticles of catalyst metals are commercially available with narrow distribution of the diameters and could be dispersed from a volatile solution; however that approach offers poor control on the particle distribution.

"Photonic Crystals Based on Periodic Arrays of Aligned Carbon Nanotubes, K. Kempa et. al., NANO LETTERS 2003 Vol. 3, No. 1 13-18" discuss a method of depositing Ni dots using a nanosphere based method. However, the use of nanospheres may increase the cost of the method, and further limit the possible distributions of Ni dots to the available sizes of nanospheres.

Thus it remains a problem to provide a flexible, simple and cost effective method for depositing catalyst material.

Summary

According to a first aspect, the invention relates to a method of depositing islands of catalyst with a predetermined density. The method may comprise the step of

obtaining a diffusion barrier covered nano patterned surface comprising a plurality of plateaus, wherein the density of plateaus may be dependent on the predetermined density of islands of catalyst. The density of plateaus may be between 1 and 1000 plateau(s) pr square micrometer. The method may further comprise the step of

depositing catalyst on said diffusion barrier covered nano patterned surface; and

heating the diffusion barrier covered nano patterned surface after catalyst has been deposited, to anneal the catalyst, whereby islands of catalyst is formed.

The diffusion barrier covered nano patterned surface may thus be configured to ensure that no more than a single island of catalyst is formed on each plateau. Hereby a sub sequent growth of carbon nanotubes from the deposited islands may result in that no more than a single carbon nanotube is grown from each plateau.

Consequently, by using a diffusion barrier covered nano patterned surface as a template for depositing catalyst a simple and flexible method of depositing islands of catalyst is provided. This provides a concept for a maskless method of growing vertically aligned carbon nanotube forests with controllable density and diameter distribution of the individual nanotubes.

An island of catalyst may be a connected amount of catalyst material. The catalyst islands may have any shape e.g. round, triangular or rectangular. In some embodiments the catalyst islands is approximately round. The catalyst islands may have a widest width between 10 nm to 1000 nm. The catalyst material may be any material suitable for use as a catalyst. In some embodiments the catalyst material is a metal catalyst material e.g. Nickel (Ni), iron (Fe) or copper (Cu). In some embodiments the catalyst material is a catalyst material suitable for use for subsequent growth of carbon nanotubes. The diffusion barrier may be made of any material suitable for preventing the catalyst from substantially diffusing into the nano patterned surface. The diffusion barrier may be made of a metal material e.g. Titanium Tungsten or titanium nitride (TiN). Titanium tungsten used as the diffusion barrier may be advantageous due to its electric conductivity and chemical stability. This may render the method to be a promising solution for CNT device fabrication, including electrochemical sensors, Raman resonators, or field emission guns. The diffusion barrier may form an outer layer covering the nano patterned surface. The diffusion barrier layer may have an approximately equal thickness, and may have a uniform thickness across the nano patterned surface. The nano patterned surface may be made of a any material suitable to form the base material for e.g. the carbon nantotubes, such as a polymer material, a semi conductor material, such as a group IV material, such as a silicon material, such as a germanium material, etc, such as a group III-V material, such as a gallium arsenide, a silicon dioxide, a glass, etc. The nano patterned surface may comprise a plurality of features having a scale below a micrometer e.g. the height and/or width of the features may be below a micrometer. Each plateau may comprise a plateau surface that may be planar or convex. The plateau surface may face substantially away from the nano patterned surface. A plateau may be elevated compared to at least a part of the nano patterned surface immediately surrounding the plateau. The catalyst may be deposited using a method securing an even distribution of catalyst material over the diffusion barrier covered nano patterned surface. The catalyst may be deposited by using any thin film deposition method, e.g. e-beam deposition, thermal evaporation, sputtering, etc. The step of obtaining a diffusion barrier covered nano patterned surface comprising a plurality of plateaus, having a density of plateaus dependent on the predetermined density of islands, may comprise obtaining a diffusion barrier covered nano patterned surface comprising a plurality of plateaus, having a density of plateaus substantially equal to the predetermined density of islands of catalyst.

The diffusion barrier covered nano patterned surface may be configured to ensure that a single island of catalyst is formed on each plateau by having the plateaus formed on nano scale features having a shape preventing catalyst material from diffusing/travelling from one plateau to another.

The diffusion barrier covered nano patterned surface may be heated to a temperature within the range of 300 degrees to 1000 degrees, for a period of time within the range of 10 seconds to 5000 seconds.

The density of catalyst islands on a surface, e.g. the diffusion barrier covered nano patterned surface, is defined as the average number of catalyst island pr surface area. Correspondingly, the density of plateaus is defined as the average number of plateaus per surface area. In both cases, surface area is defined as the surface area of a 2 dimensional reference plane positioned so that the average distance between the plateaus / islands and the reference plane is minimized.

In some embodiments, the density of plateaus is between 10 and 1000 plateaus pr square micrometer.

By having a density of plateaus within the above specified range, it may be ensured that a single island of catalyst is formed on each plateau, and further that the number of islands not formed on plateaus is low relative to the total number of islands of catalyst. If the density is higher than the above specified range, the chance that catalyst material diffuse from one plateau to the neighbouring plateau is increased. This may result in that the size of the catalyst islands becomes less uniform. If the density is lower than the above specified range, the number of islands not formed on plateaus may increase. This may again result in that the size of the catalyst islands becomes less uniform. The density of plateaus may be measured by using manual or automatic counting methods based on images obtain using electron microscopy.

In some embodiments, the method further comprises depositing islands of catalyst having a predetermined average size, wherein the step of obtaining a diffusion barrier covered nano patterned surface comprises: obtaining a diffusion barrier covered nano patterned surface having plateaus with an average size dependent on the predetermined average size of the catalyst islands.

Consequently, a surface having a predetermined density of catalyst islands and a predetermined average size of the catalyst islands may be formed. By obtaining a diffusion barrier covered nano patterned surface having large plateaus large islands of catalyst material may be created and correspondingly by obtaining a diffusion barrier covered nano patterned surface having small plateaus small islands of catalyst material may be created. An iterative approach may be used to find the necessary average size of plateaus resulting in a predetermined size of catalyst islands.

In some embodiments, the average width of the plateaus is between 10 nanometre and 500 nanometre.

In some embodiments, the average width of the plateaus is between 100 nanometre and 500 nanometre.

In some embodiments, the diffusion barrier covered nano patterned surface comprises gaps between adjacent plateaus.

By having a surface comprising gaps between the plateaus, an efficient solution of preventing catalyst material to travel / diffuse from one plateau to another is provided.

In some embodiments, the average depth of the gaps is between 5 nanometre and 5000 nanometre.

In some embodiments, the average depth of the gaps is between 100 nanometre and 1000 nanometre.

Having gaps with an average depth within the above specified range may secure that the diffusion barrier covered nano patterned surface is especially effective at ensuring that a single island of catalyst is formed on each plateau. Deeper gaps may make the diffusion barrier covered nano patterned surface more difficult to manufacture, and more shallow gaps may increase the chance that catalyst material travels / diffuse from one plateau to the next. In some embodiments, the average width of the gaps is between 1 nanometre and 1000 nanometre.

In some embodiments, the average width of the gaps is between 100 nanometre and 500 nanometre.

It is possible to control the nanograss properties with reactive ion etching (RIE) processing parameters and obtain nearest neighbour distance between the protrusions in the range of between 1 nm and 1000 nm, such as between 150 nm to 700 nm.

The widest width of the plateaus, the depth of the gaps, and the size of the gaps may be measured using electron microscopy images.

In some embodiments, the step of obtaining a diffusion barrier covered nano patterned surface comprises:

- obtaining a nano patterned surface; and
- covering said nano patterned surface with a diffusion barrier.

The nano patterned surface may be covered with a diffusion barrier by thin film deposition methods, e.g. PVD or CVD evaporation, sputtering, electroplating, etc.

In some embodiments, the step of obtaining a nano patterned surface comprises: obtaining a nano patterned surface, comprising a plurality of protrusions protruding from a surface, having a density of protrusions dependent on the predetermined density of catalyst islands, wherein a plateau is formed at the top of each protrusion after the nano patterned surface has been covered with said diffusion barrier.

The protrusions may be randomly distributed over the surface. The nano patterned surface may be created by using a reactive ion etch process anisotropic wet etching, laser or microwave irradiation, shadow masking or lithography (UV, e-beam).

In some embodiments, the density of protrusions is between 1 and 1000 protrusions pr square micrometer, such as between 10 and 700, such as between 50 and 500, such as below 1000, such as below 700 protrusion pr square micrometer.

In some embodiments, the density of protrusions is between 10 and 1000 protrusions pr square micrometer.

The density of protrusions is defined as the average number of protrusions pr surface area, where surface area is defined as the surface area of a 2 dimensional reference plane positioned so that the average distance between the top of the protrusions and the reference plane is minimized.

In some embodiments, the average height of the protrusions is between 5 nanometre and 5000 nanometre.

In some embodiments, the average height of the protrusions is between 100 nanometre and 1000 nanometre.

In some embodiments, the average thickness of the diffusion barrier is between 0.1 nanometre and 1000 nanometre.

In some embodiments, the average thickness of the diffusion barrier is between 1 nanometre and 500 nanometre, such as below 500 nm.

By having a diffusion barrier with an average thickness within the range specified above, effective plateaus are created where islands of catalysts may be formed.

In some embodiments, the ratio between the average thickness of the diffusion barrier and the average distance between protrusions is between 0.25 and 0.5.

Where the ration is defined as the average thickness of the diffusion barrier divided with the average distance between protrusions both measured in nanometres.

If the ratio is below the above specified interval a large number of catalyst islands may be formed between plateaus, and if the ratio is above the specified interval catalyst material may propagate between adjacent plateaus.

In some embodiments, a value V specifying the relationship between the average thickness of the diffusion barrier and the density of protrusions is between 0.25 and 0.5, where V is defined as

$$V = \left(\sqrt{D}\right) \cdot T$$

where D is defined as the density of protrusions pr square micrometer, and T is defined as the average thickness of the diffusion barrier.

If the ratio is below the above specified interval, a large number of catalyst islands may be formed between plateaus, and if the ratio is above the specified interval catalyst material may propagate between adjacent plateaus.

In some embodiments, a catalyst layer is deposited on the diffusion barrier covered nano patterned surface having an average thickness between 1 nanometre and 20 nanometre.

In some embodiments, the step of obtaining a nano patterned surface comprises:

- obtaining a silicon surface; and
- processing said silicon surface with a reactive ion etching process, thereby creating silicon nano grass comprising a plurality of protrusions;

wherein the process parameters of the reactive ion etching process is chosen to create a density of protrusions dependent on the predetermined density of catalyst islands.

According to a second aspect, the invention relates to a method of growing carbon nanotubes, comprising the steps of:

- depositing islands of catalyst with a predetermined density using a method as described in previous sections; and
- growing carbon nanotubes using the chemical vapour deposition method from the deposited islands of catalyst.

Consequently, a flexible and simple method of growing carbon nanotubes is provided. The method allows maskless definition of carbon nanotube forests with control of their density, nanotube diameter and height.
According to a third aspect, the invention relates to a product obtainable by a method as described previously.

In some embodiments, the product is directly obtained by a method as described above.

According to a fourth aspect, the invention relates to a device for use as a template for growing carbon nanotubes, wherein said device comprises a diffusion barrier covered nano patterned surface comprising a plurality of plateaus; wherein said diffusion barrier covered nano patterned surface is configured to ensure, after deposition and annealing of a catalyst, that no more than a single island of catalyst is formed on each plateau, so that a sub sequent growth of carbon nanotubes from the deposited islands result in growth of no more than a single carbon nanotube from each plateau.

In some embodiments, the device further comprises a catalyst deposited on said diffusion barrier covered nano patterned surface.

In some embodiments, the density of plateaus is between 1 and 1000 plateau(s) pr square micrometer.

In some embodiments, the density of plateaus is between 10 and 1000 plateau(s) pr square micrometer.

The density of plateaus is defined as the average number of plateaus per surface area, where surface area is defined as the surface area of a 2 dimensional reference plane positioned so that the average distance between the plateaus and the reference plane is minimized.

In some embodiments, the average width of the plateaus is between 10 nanometres and 500 nanometres.

In some embodiments, the average width of the plateaus is between 100 nanometres and 500 nanometres.

In some embodiments, the diffusion barrier covered nano patterned surface comprises gaps between adjacent plateaus.

In some embodiments, the average depth of the gaps is between 5 nanometres and 5000 nanometres.

In some embodiments, the average depth of the gaps is between 100 nanometres and 1000 nanometres.

In some embodiments, the average width of the gaps is between 100 nanometres and 500 nanometres.

In some embodiments, the average width of the gaps is between 1 nanometre and 1000 nanometres.

In some embodiments, the diffusion barrier covered nano patterned surface comprises:

- a nano patterned surface; and
- a diffusion barrier, covering said nano patterned surface.

In some embodiments, the nano patterned surface comprises a plurality of protrusions, and wherein a plateau is formed, at the top of the protrusions, by the diffusion barrier.

In some embodiments, the nano patterned surface is obtainable by a reactive ion etching process.

In some embodiments, the nano patterned surface comprises silicon nano grass.

In some embodiments, the density of protrusions is between1 and 1000 protrusions pr square micrometer.

In some embodiments, the density of protrusions is between10 and 1000 protrusions pr square micrometer.

The density of protrusions is defined as the average number of protrusions pr surface area, where surface area is defined as the surface area of a 2 dimensional reference plane positioned so that the average distance between the top of the protrusions and the reference plane is minimized.

In some embodiments, the average height of the protrusions is between 5 nanometres and 5000 nanometres.

In some embodiments, the average height of the protrusions is between 100 nanometres and 1000 nanometres.

In some embodiments, the average thickness of the diffusion barrier is between 1 nanometre and 1000 nanometres.

In some embodiments, the average thickness of the diffusion barrier is between 1 nanometre and 500 nanometres.

In some embodiments, the ratio between the average thickness of the diffusion barrier and the average distance between protrusions is between 0.25 and 0.5.

Where the ratio is defined as the average thickness of the diffusion barrier divided with the average distance between protrusions both measured in nanometres.

If the ratio is below the above specified interval a large number of catalyst islands may be formed between plateaus, and if the ratio is above the specified interval catalyst material may propagate between adjacent plateaus.

In some embodiments, a value V specifying the relationship between the average thickness of the diffusion barrier and the density of protrusions is between 0.25 and 0.5, where V is defined as

$$V = \left(\sqrt{D}\right) \cdot T$$

where D is defined as the density of protrusions pr square micrometer, and T is defined as the average thickness of the diffusion barrier.

If the ratio is below the above specified interval a large number of catalyst islands may be formed between plateaus, and if the ratio is above the specified interval catalyst material may propagate between adjacent plateaus.

In some embodiments, the device further comprises a catalyst layer deposited on the diffusion barrier covered nano patterned surface having an average thickness between 1 nanometre and 20 nanometre.

In some embodiments, the device further comprises islands of catalyst, wherein a single island of catalyst is positioned on top of each plateaus.

According to a fourth aspect the invention relates to a carbon nanotube device comprising a device as describe previously, wherein a carbon nanotube is positioned on top of each plateau.

According to a fifth aspect the invention relates to use of a device as described above as a template for depositing catalyst material.

The different aspects of the present invention can be implemented in different ways including the methods for depositing islands of catalyst, and to device for use as a template for depositing catalyst described above and in the following, each yielding one or more of the benefits and advantages described in connection with at least one of the aspects described above, and each having one or more preferred embodiments corresponding to the preferred embodiments described in connection with at least one of the aspects described above and/or disclosed in the dependant claims. Furthermore, it will be appreciated that embodiments described in connection with one of the aspects described herein may equally be applied to the other aspects.

Brief description of the drawings

The above and/or additional objects, features and advantages of the present invention, will be further elucidated by the following illustrative and non-limiting detailed description of embodiments of the present invention, with reference to the appended drawings, wherein:

Fig. 1a-b show a diffusion barrier covered nano patterned surface according to an embodiment of the present invention.
Fig. 2 illustrates the principle of a diffusion barrier.
Fig. 3a-d show different type of diffusion barrier covered nano patterned surfaces according to some embodiments of the present invention.
Fig. 4a-d show a method of depositing catalyst and further growing carbon nanotubes according to an embodiment of the present invention.
Fig. 5a shows an electron microscope image of a nano patterned surface according to an embodiment of the present invention.
Fig. 5b shows an electron microscope image of a diffusion barrier covered nano patterned surface according to an embodiment of the present invention.
Fig. 6a-b show electron microscope images of a carbon nano tube device according to an embodiment of the present invention.

Fig. 7a shows an electron microscope image of a plurality of carbon nano tubes grown from a template for growing carbon nano tubes according to an embodiment of the present invention.

Fig. 7b shows an electron microscope image of a plurality of carbon nano tubes grown without the use of a template according to the invention.

Figure 8 shows SEM top views of the investigated nanograss samples.

Figure 9 shows radial uniformity of two silicon nanograss recipes.

Figure 10 shows nanograss NND control with RIE chamber pressure and processing time.

Figure 11 shows SEM images of the fabricated CNT samples.

Figure 12 shows diameter distributions of the CNT forests.

Detailed description

In the following description, reference is made to the accompanying figures, which show by way of illustration how the invention may be practiced.

Fig. 1a-b show a schematic drawing of a diffusion barrier covered nano patterned surface according to an embodiment of the present invention. Fig. 1a shows a top view of the diffusion barrier covered nano patterned surface, and Fig 1b shows a cross-section of the diffusion barrier covered nano patterned surface taken along the stippled line 106. The diffusion barrier covered nano patterned surface comprises a plurality of plateaus 102. The plateaus 102 are in this embodiment positioned at the top of the protrusions. In this embodiment gaps are present between adjacent plateaus 102. The diffusion barrier covered nano patterned surface is configured to ensure that no more than a single island of catalyst material is formed on each plateau 102, after catalyst material has been deposited and annealed. This may be achieved by having plateaus with a desired shape, size and/or distribution. The diffusion barrier covered nano patterned surface comprises a nano patterned surface 101 and a diffusion barrier 104. The nano pattern of the nano patterned surface 101 is created by a plurality of protrusions 103. The protrusions 103 are in this embodiment positioned in a non-regular fashion e.g. not in a regular grid. However, in other embodiments the nano patterned surface may comprise protrusions positioned in a regular grid.

The density of plateaus 102 is defined as the number of plateaus pr surface area, where surface area is defined as the surface area of a reference plane 105, positioned so that the average distance between the plateaus 102 and the reference plane is minimized e.g. the density is defined as the number of plateaus on/above/below the reference plane 105 divided with the 2 dimensional surface area of the reference plane 105. The surface area of the reference plane 105 may correspond to the surface area of the nano patterned surface before it has been nano patterned e.g. the surface area of the silicon surface before it is patterned using the reactive ion etch process.

Correspondingly, the density of protrusions 103 is defined as the number of protrusions 103 pr surface area, where surface area is defined as the surface area of a reference plane 107, positioned so that the average distance between the protrusions 103 and the reference plane 107 is minimized e.g. the density is defined as the number of protrusions on/above/below the reference plane 107 divided with the 2 dimensional surface area of the reference plane 107. The surface area of the reference plane 107 may correspond to the surface area of the nano patterned surface before it has been nano patterned e.g. the surface area of the silicon surface before it is patterned using the reactive ion etch process.

Fig. 2 illustrates the principle of a diffusion barrier. Shown is a nano patterned surface 201 covered with a diffusion barrier 202. The diffusion barrier 202 prevents a substrate 203, e.g. a catalyst, from vertically diffusing into the underlying surface 201.

Fig. 3a-d shows cross-sections of different type of diffusion barrier covered nano patterned surfaces according to some embodiments of the present invention.

Fig. 3a shows a diffusion barrier covered nano patterned surface, where the nano pattern of the nano patterned surface is created by a plurality of pyramid shaped or conical shaped protrusions 302.

Fig. 3b shows a diffusion barrier covered nano patterned surface, where the nano pattern of the nano patterned surface is created by a plurality of box shaped protrusions 303.

Fig. 3c shows a diffusion barrier covered nano patterned surface, where the nano pattern of the nano patterned surface is created by a plurality of needle shaped or conical shaped protrusions.

Fig. 3d shows a diffusion barrier covered nano patterned surface, where the nano pattern of the nano patterned surface is created by a plurality of hemispherical protrusions 302.

Figs.4a-d illustrate schematically a method of depositing catalyst and further growing carbon nanotubes according to an embodiments of the present invention. Fig. 4a shows a cross-section of a nano patterned surface 401 comprising a plurality of protrusions 402. The protrusions have a height 403 and a distance between them of 404. Fig. 4b shows the nano patterned surface after being covered with a diffusion barrier 405. The diffusion barrier 405 may be applied using the principles described above. The diffusion barrier 405 may have a substantially uniform thickness over the nano patterned surface 401. The diffusion barrier 405 creates a plurality of plateaus 409 positioned above the plurality of protrusions 402.

Fig 4c shows the diffusion barrier covered nano patterned surface after a catalyst 406 has been deposited. The catalyst 406 may be deposited using the techniques described above. The catalyst 406 may be distributed in small droplets over the diffusion barrier 405.

Fig 4d shows the diffusion barrier covered nano patterned surface after the catalyst has been annealed by heating the diffusion barrier covered nano patterned surface. The catalyst material has aggregated into islands of catalyst material 407 having a high uniformity in size, where no more than on island is formed on each plateau. This may be ensured by having plateaus with a desired height, shape, size, and/or distribution.

Fig 4e shows the diffusion barrier covered nano patterned surface after growth of carbon nanotubes 410. The carbon nanotubes 410 may be grown using the plasma enhanced vapour deposition method see “A review of plasma enhanced vapour deposition of carbon nanotubes, Meyyappan, M., Journal of Physics D-Applied Physics, 2009.42(21)”. Using the plasma enhanced vapour deposition method, a single carbon nano tube is grown from each island of catalyst material. As the diameter and height of the resulting carbon nanotubes are dependent on the size of the catalyst islands, a forest of carbon nanotubes with a high uniformity can be grown.

A nano patterned surface may be created using the reactive ion etching (RIE) process. By selecting appropriate parameters different nano patterns may be created e.g. a plurality of protrusions may be formed having a desired density of protrusions pr square micro meter. This may be used to deposit islands of catalyst with a predetermined desired density e.g. as plateaus may be formed on top of the protrusions after deposition of a diffusion barrier.

The RIE process in a commercial ASE (Advanced Silicon Etcher) system may be controlled by the following parameters: etch gas flows, etch time, platen power, coil power, chamber pressure and wafer chuck temperature. To etch silicon a mixture of sulfur hexafluoride (SF6) and oxygen (O2) may be used.

Height of the structures may be controlled by the processing time; the higher the processing time, the higher obtained structures. However, the structure (protrusions) may keep constant aspect ratio (ratio between height and width), so with higher processing time, the structures may become wider, and more sparsely distributed. Thus, the density of the nanograss may be inversely proportional to the processing time. Processing time may be varied in a range from single seconds to half an hour.

To compensate the influence of processing time on the density, the chamber pressure may be changed. The chamber pressure may also influence the density, which may be inversely proportional to the pressure. The pressure may be changed from 1 to 100 mTorr.

It is important to note, that all the process parameters may be cross-coupled. That is, a change of one parameters may change all the features of the nanograss. If only one feature needs to be controlled (i.e. density), all the parameters may need to be tuned accordingly. The chamber pressure may be used to control the density of protrusions. See also “Towards easily reproducible nano-structured SERS substrates, Sensors, 2009 IEEE, On pages: 1763 – 1767”.

Fig. 5a shows an electron microscope image of a nano patterned surface according to an embodiment of the present invention. The nano patterned surface comprises a plurality of protrusions 501. In this embodiment the nano patterned surface is Silicon nanograss. The silicon nanograss was fabricated at a 4” low-doped silicon wafer, using RIE processing in an Advanced Silicon Etching (ASE) system. The following process parameters for RIE were used:

SF6 = 99sccm, O2 = 90sccm, time = 4 minutes, platen power = 16 W, coil power = 2800 W, chamber pressure = 38 mTorr, temperature = -10C.

Fig. 5b shows an electron microscope image of the nano patterned surface shown in Fig. 5a after a diffusion barrier has been applied according to an embodiment of the present invention. The diffusion barrier forms a plurality of slightly convex plateaus 502 on top of the protrusions. The nanograss was coated in a Wordentec system with 150nm of titanium tungsten diffusion barrier, and 8nm of nickel catalyst by magnetron sputtering, and e-beam evaporation, respectively.

Fig. 6a-b show electron microscope images of a carbon nano tube device, according to an embodiment of the present invention. The carbon nano tubes have been grown using the plasma enhanced chemical vapour deposition method. The diffusion barrier covered nano patterned surface shown in 5b has been used a template for depositing catalyst material. The catalyst material has been deposited and subsequently annealed whereby no more than a single island of catalyst material is formed on the plateaus. Carbon nanotubes were grown in Aixtron’s 6” Black Magic system, using PECVD recipe. The sample was annealed at 600C for 60s in pure ammonia (160sccm), and processed at 750C for 15min, with ammonia (160sccm) and acetylene (40sccm).

Fig. 7a shows an electron microscope image of a plurality of carbon nano tubes 701 702 grown from a template for growing carbon nano tubes according to an embodiment of the present invention.

Fig. 7b shows an electron microscope image of a plurality of carbon nano tubes 703 704 grown without the use of a template according to the invention.

It can be seen by comparing the two images that a higher uniformity in distribution, height and diameter may be achieved by using a template for growing carbon nano tubes and/or a method according to the present invention.

In the following the novel cost-effective maskless fabrication method of growing vertically aligned CNT forests on silicon nanograss with controllable density and diameter distribution meeting the needs of well controlled CNT distribution will be explained in more details with details of experimental data. It relies on use of a topographical confinement of the metal catalyst on a nanostructured diffusion barrier. The topographical confinement is created from a silicon black, also known as ‘nanograss’ (Figure 5a), onto which the diffusion barrier is conformally coated with titanium tungsten (Figure 5b). Titanium tungsten used as the diffusion barrier is advantageous due to its electric conductivity and chemical stability. This renders the method to be a promising solution for CNT device fabrication, including electrochemical sensors, Raman resonators, or field emission guns. The density, aspect ratio and height of the nanograss are controlled solely with the parameters of the reactive ion etching (RIE) of the plane silicon wafer [Jansen, H., et al., *The black silicon method – a universal method for determining the parameter setting of fluorine-based reactive ion etcher in deep silicon trench etching with profile control.* Journal of Micromechanics and Microengineering, 1995. 5(2): p. 115-120.]. With a suitable combination of TiW coating and nanograss topography, very limited space is left between the coated nanograss protrusions. The catalyst is deposited with e-beam evaporation and as the deposition is highly directional, it resides mostly on the nanograss hemispherical caps and ideally does not reach the gaps between the protrusions in sufficient amounts to form catalytic particles. Annealing causes the catalyst residing on the peaks to agglomerate into single droplets. As the droplets are isolated from each other their size distribution fits within a narrow range defined by the average amount of the catalyst deposited on each nanograss peak. This leads to creation of a uniform forest of CNTs with one nanotube growing from one nanograss protrusion (Figure 6a). Therefore, the density of the forest is defined by the density of the nanograss, CNT diameter is controlled by the average catalyst thickness and the CNT length by PECVD processing time. This paper presents a proof of concept for that technology, with fabrication details and uniformity analysis.

Silicon nanograss

The RIE method offers maskless fabrication of black silicon nanograss. The masking effect is obtained with the native silicon oxide residing on the wafers and the etched protrusion profiles and densities are controlled with a balance between chemical and physical etching processes present within the RIE. This offers a rich variety of morphologies, densities, aspect ratios and heights [Jansen, H., et al., *The black silicon method – a universal method for determining the parameter setting of fluorine-based reactive ion etcher in deep silicon trench etching with profile control.* Journal of Micromechanics and Microengineering, 1995. 5(2): p. 115-120.]. To control the catalyst distribution well the nanograss protrusions shall be straight or slightly undercut pillars, so the gaps that remain after the diffusion barrier coating are of a minimal size. The aspect ratio of the protrusions shall not be too high, as the coated protrusions are supposed to mechanically support the nanotubes. The density of the protrusions per surface area should be batch repeatable and uniform across the wafers. Finally, the protrusions shall not cluster but be distributed uniformly. Otherwise, large gaps between the protrusions would allow the catalyst to collect and form nanoparticles of uncontrollable sizing.

A recipe known from previous studies [Schmidt, M.S., J. Hübner, and A. Boisen, *Large area fabrication of leaning silicon nanopillars for surface enhanced Raman spectroscopy.* Advanced Materials, In press.] produces protrusions with the above mentioned morphology (RIE_1) and was chosen as a starting point. Three additional recipes were investigated (RIE_2, RIE_3, RIE_4) to evaluate how well the protrusion density can be controlled, the clustering avoided and the morphology preserved. Two 4" wafers were fabricated with each recipe to evaluate wafer-to-wafer repeatability. Chamber pressure and processing time were varied and the other plasma processing parameters were kept constant: SF6 = 30 sccm, O2 = 27 sccm, coil power = 0W, platen power P = 120 W, chuck temperature T = -10ºC (Table 1).

Recipe	Processing time [min]	Chamber pressure [mTorr]	TiW coating [nm]	Nickel deposition [nm]
RIE_1a	4	40	250	8
RIE_1b	4	40	250	10
RIE_2	16	48	-	-
RIE_3	3	20	-	-
RIE_4	3	38	-	-
Control_a	-	-	250	8
Control_b	-	-	250	10

Table 1 Nanograss fabrication recipes. Each recipe was used at Advanced Silicon Etcher (ASE) machine to fabricate two wafers. The other parameters were: SF6 = 30 sccm, O2 = 27 sccm, coil power = 0W, platen power P = 120 W, chuck temperature T = -10ºC.

In Figure 8, SEM top views of the investigated nanograss samples are shown: a) RIE1, b) RIE2, c) RIE3, and d) RIE4. The images were taken in the centers of the wafers. The scale bar is 1 μm and applies to all four structures. Figure 9 shows radial uniformity of two silicon nanograss recipes (RIE_3 and RIE_4). Mean nearest neighbor distance was measured with Delaunay triangulation algorithm.

After fabrication, scanning electron micrographs (SEM) of each nanograss wafer were obtained (Figure 8) at radial distances from the wafers' center: 0, 10, 20, 30, 40 and 50 mm. Images were processed with ImageJ software in order to retrieve the statistical information on peak density and nearest neighbour distance (NND). The images were subjected to Gaussian filter (2 pix), and binary threshold was applied. The threshold value was set for each image manually preserving the least bright peaks. Particles were counted with the particle analysis standard ImageJ function, and the mean and variance of the distances between nearest neighbors (NND) were measured with a Delaunay-Voronoi triangulation algorithm plug-in [Schindelin, J. and L. Paul Chew, *http://fiji.sc/wiki/index.php/Delaunay_Voronoi.*].

On the investigated 4" wafers the morphology of the nanograss is preserved within a radius of 30 mm. Beyond that central region the protrusions are collapsed or undeveloped. This is a common feature of RIE fabricated nanograss: as the edge effects disturb plasma distribution over the wafer, the nanograss exhibits proper morphology over a limited, central area of the wafer [Schmidt, M.S., J. Hübner, and A. Boisen, *Large area fabrication of leaning silicon nanopillars for surface enhanced Raman spectroscopy.* Advanced Materials, In press.]. The mean NND between the protrusions tends to increase slightly outwards the center of the wafer (Figure 9). Wafer-to-wafer mean NND repeatability is within 10%. On the measured wafers and allows control of the distance between 150 and 700 nm for all investigated recipes (Figure 10).

Carbon nanotubes

After the plasma processing each wafer was sputtercoated with TiW, and e-beam evaporated with Ni (Table 1). The wafers were subsequently processed with PECVD in an Aixtron BlackMagic system with ammonia used as a reducing agent and acetylene. The processing recipe was: chamber pressure set to 6 mbar, NH3 soak (250 sccm) for 60 s at room temperature, temperature ramp to 625 ºC, wait for 10 s, DC plasma (800 W), C2H2 feed at 50 sccm, wait for 30 s, temperature ramp to 750 ºC and process for 15 min.

Control samples with a flat TiW surfaces were cofabricated. Images of the CNT forests on samples RIE_1a, RIE_1b and their corresponding control samples were taken with SEM (Figure 11) and analyzed with ImageJ software. Figure 11 shows the SEM images of the fabricated CNT samples.: a) flat control sample with 8 nm of catalyst (Control_a), b) flat control sample with 10 nm of the catalyst (Control_b), c) silicon nanograss coated with 8 nm of catalyst (RIE_1), d) silicon nanograss coated with 10 nm of catalyst (RIE_1b). Scale bar: 2 μm for all images. The diameters and the CNT number density were measured manually. Histograms were used to evaluate the diameter distributions (Figure 12).

A visual inspection as well as histograms indicates a significant difference in CNT formation between the two flat control samples (Figure 11a and Figure 11c). The CNT forest on the sample Control_a with 8 nm of the catalyst is relatively uniform, while the forest grown on sample Control_b from 10 nm of catalyst exhibits high non-uniformities with several CNTs of high diameter present.

Investigation of the CNTs grown on nanograss shows a considerable improvement of the diameter distributions for both RIE_1a and RIE_1b samples, correlated with the fact that most of the nanotubes grow from single nanograss protrusions (Figure 11). While it is unavoidable that part of the CNTs grows from inbetween the nanograss protrusions, or that the catalyst merges on two or more neighboring protrusion peaks forming one CNT, the histograms show considerable narrowing of the diameter distributions at the both samples (Figure 11c). The mean diameter for samples RIE_1a and RIE_1b are 53 and 88 nm respectively. It indicates the expected dependence of the CNT diameters on the catalyst amount; more investigation is needed however in order to quantify this effect.

The narrow end of the histograms can be attributed to CNTs growing from in-between the CNTs, while the thick diameter CNTs seem to be growing from merged protrusion tops (Figure 6a) (growth of the CNTs from large gaps caused by clustering should not be considered, as the nanograss recipe RIE_1 exhibits negligible clustering). Both histograms are fairly symmetrical and that indicates lack of dominance of either of the effects. The diameter distribution is narrower for the sample covered with less catalyst (RIE_1a). This can be explained with lower probability of peak-to-peak particle merging, as well as lower amount deposited into the narrow gaps between the protrusions, and thus lower probability of CNT growth.

It is possible to control the nanograss properties with RIE processing parameters and obtain nearest neighbor distance between the protrusions in the range of 150 to 700 nm. The growth is wafer-to-wafer repeatable and yields ca. 40% of each wafer surface. Growth of the carbon nanotubes on the nanograss highly improves their diameter distribution and NND, and the mean diameter is controllable with the amount of deposited catalyst.

Although some embodiments have been described and shown in detail, the invention is not restricted to them, but may also be embodied in other ways within the scope of the subject matter defined in the following claims. In particular, it is to be understood that other embodiments may be utilised and structural and functional modifications may be made without departing from the scope of the present invention.

In device claims enumerating several means, several of these means can be embodied by one and the same item of hardware. The mere fact that certain measures are recited in mutually different dependent claims or described in different embodiments does not indicate that a combination of these measures cannot be used to advantage.

It should be emphasized that the term "comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

Claims:

1. A method of depositing islands of catalyst with a predetermined density, wherein in said method comprises the steps of:

- obtaining a diffusion barrier covered nano patterned surface comprising a plurality of plateaus, having a density of plateaus dependent on the predetermined density of islands of catalyst, wherein the density of plateaus is between 1 and 1000 plateau(s) pr square micrometer;
- depositing catalyst on said diffusion barrier covered nano patterned surface; and
- heating the diffusion barrier covered nano patterned surface after catalyst has been deposited, to anneal the catalyst, whereby islands of catalyst is formed;

wherein said diffusion barrier covered nano patterned surface is configured to ensure that no more than a single island of catalyst is formed on each plateau, so that a sub sequent growth of carbon nanotubes from the deposited islands result in that a single carbon nanotube is grown from each plateau.

2. A method according to any of claim 1 , wherein the average width of the plateaus is between 10 nanometre and 500 nanometre.

3. A method according to any of claims 1 or 2, wherein the diffusion barrier covered nano patterned surface comprises gaps between adjacent plateaus

4. A method according to claim 3, wherein the average depth of the gaps is between 5 nanometre and 5000 nanometre.

5. A method according to any of claims 1 to 4, wherein the step of obtaining a diffusion barrier covered nano patterned surface comprises:

- obtaining a nano patterned surface; and
- covering said nano patterned surface with a diffusion barrier.

6. A method according to claim 5, wherein the step of obtaining a nano patterned surface comprises: obtaining a nano patterned surface, comprising a plurality of protrusions protruding from a surface, having a density of protrusions dependent on the predetermined density of catalyst islands, wherein a plateau is formed at the top of each protrusion after the nano patterned surface has been covered with said diffusion barrier.

7. A method according to any of claims 5 or 6, wherein a value V specifying the relationship between the average thickness of the diffusion barrier and the density of protrusions is between 0.25 and 0.5, where V is defined as

$$V = \left(\sqrt{D}\right) \cdot T$$

where D is defined as the density of protrusions pr square micrometer, and T is defined as the average thickness of the diffusion barrier.

8. A method according to any of claims 5 to 7, wherein the step of obtaining a nano patterned surface comprises:

- obtaining a silicon surface; and
- processing said silicon surface with a reactive ion etching process, thereby creating silicon nano grass comprising a plurality of protrusions;

wherein the process parameters of the reactive ion etching process is chosen to create a density of protrusions dependent on the predetermined density of catalyst islands.

9. A method of growing carbon nanotubes, comprising the steps of:

- depositing islands of catalyst with a predetermined density using a method according to any of claims 1 to 8; and
- growing carbon nanotubes using the chemical vapour deposition method from the deposited islands of catalyst.

10. A product obtainable by a method according to any of claims 1 to 9.

11. A device for use at a template for growing carbon nanotubes, wherein said device comprises a diffusion barrier covered nano patterned surface comprising a plurality of plateaus; wherein said diffusion barrier covered nano patterned surface is configured to ensure, after deposition and annealing of a catalyst, that no more than a single island of catalyst is formed on each plateau, so that a sub sequent growth of carbon nanotubes from the deposited islands result in growth of no more than a single carbon nanotube from each plateau.

12. A device according to claim 11, wherein the diffusion barrier covered nano patterned surface comprises:

- a nano patterned surface; and
- a diffusion barrier, covering said nano patterned surface.

13. A device according to claim 12, the nano patterned surface comprises a plurality of protrusions, and wherein a plateau is formed, at the top of the protrusions, by the diffusion barrier.

14. A device according to claim 13, wherein a value V specifying the relationship between the average thickness of the diffusion barrier and the density of protrusions is between 0.25 and 0.5, where V is defined as

$$V = \left(\sqrt{D}\right) \cdot T$$

where D is defined as the density of protrusions pr square micrometer, and T is defined as the average thickness of the diffusion barrier.

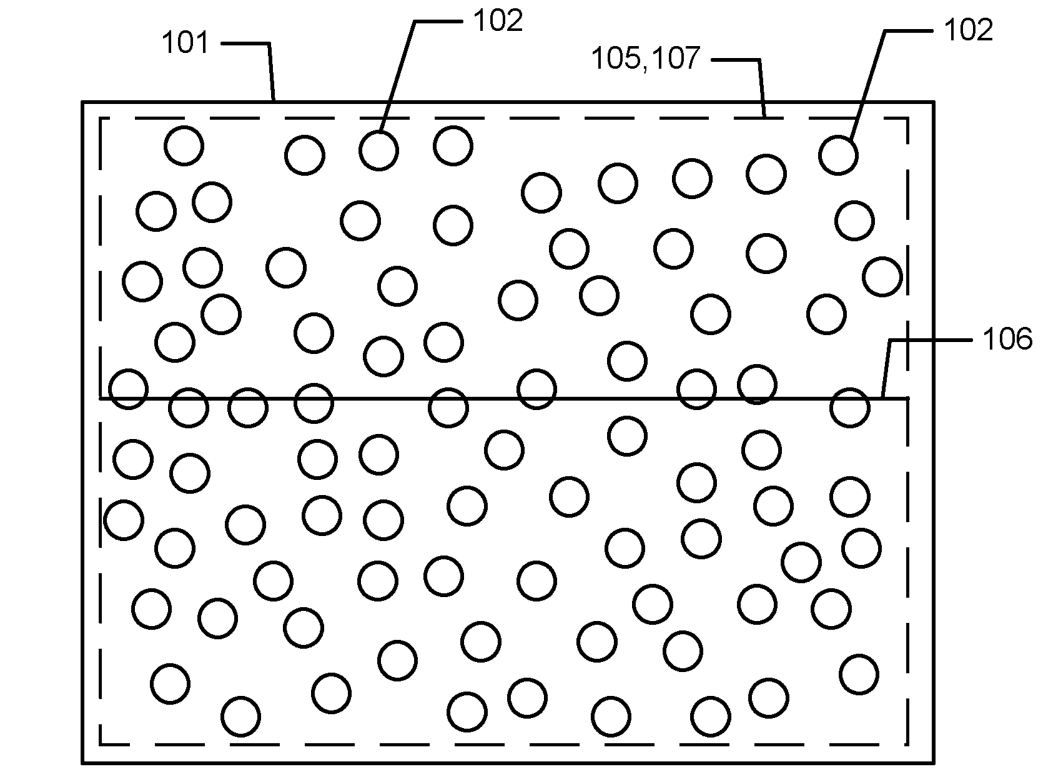

Fig. 1a

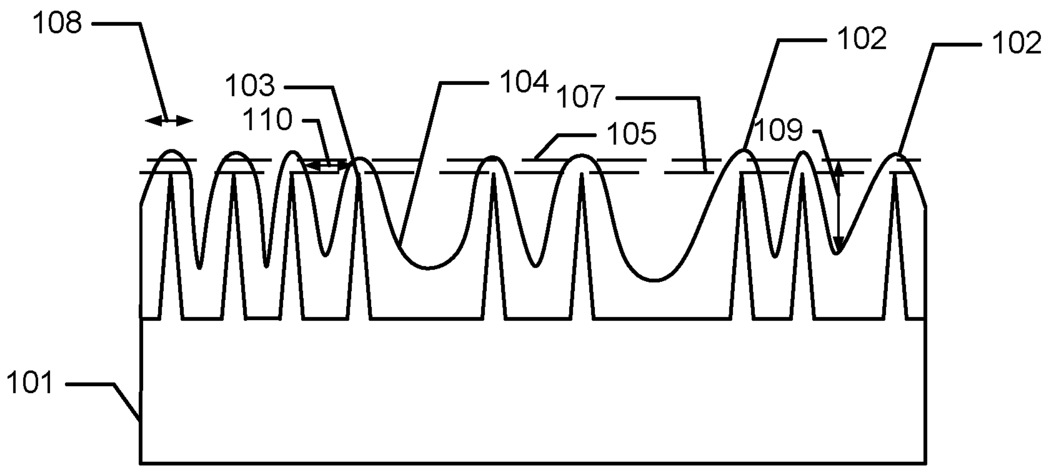

Fig. 1b

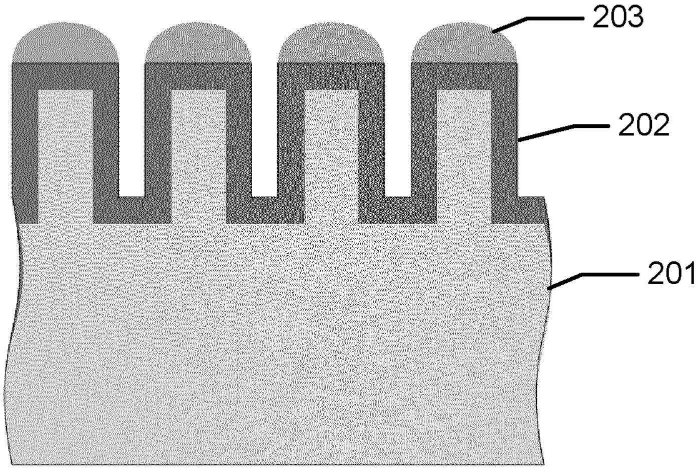

Fig. 2

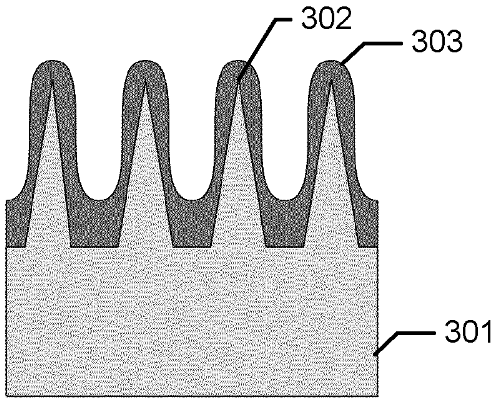

Fig. 3a

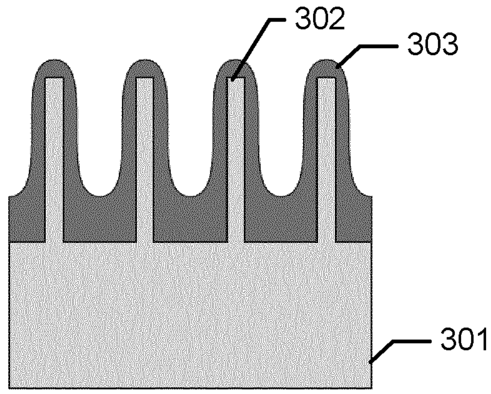

Fig. 3b

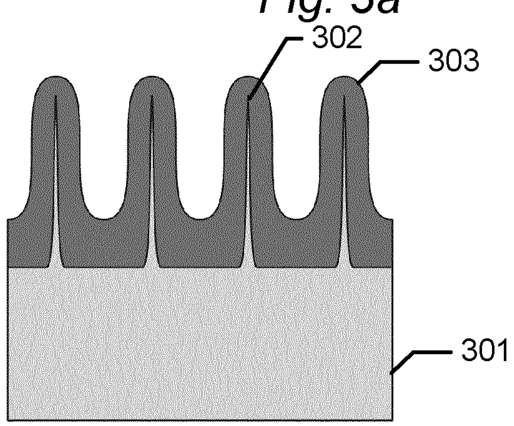

Fig. 3c

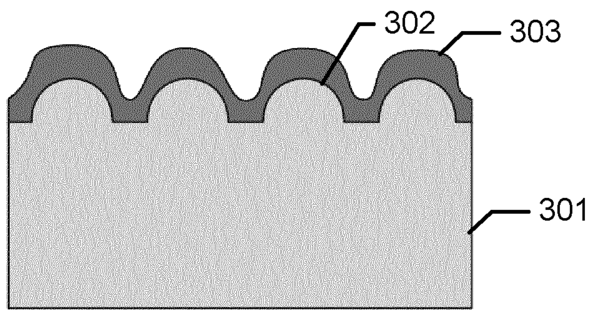

Fig. 3d

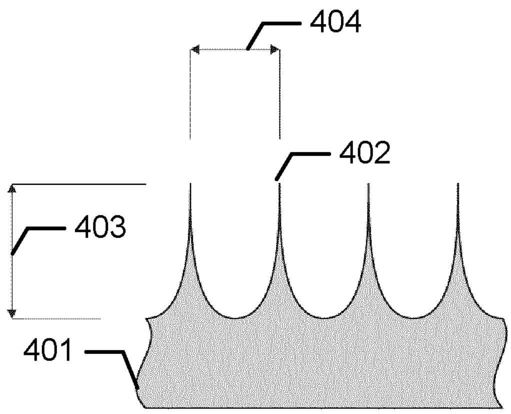

Fig. 4a

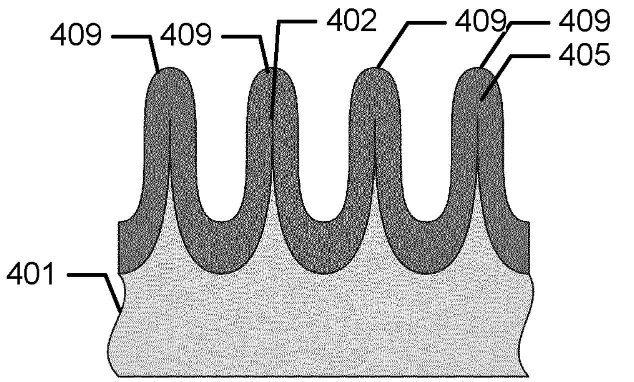

Fig. 4b

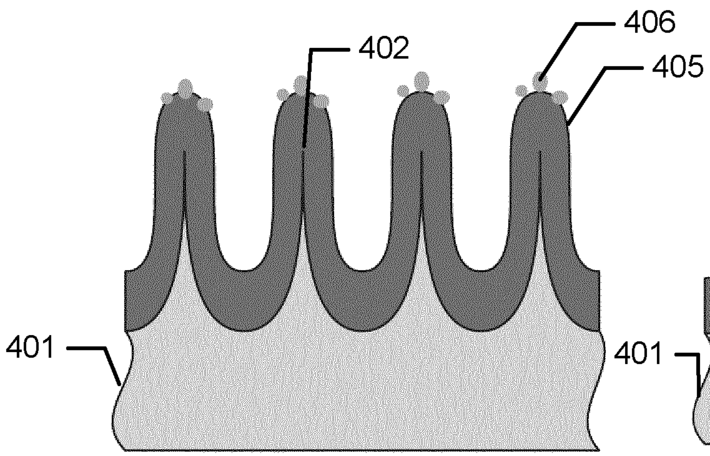

Fig. 4c

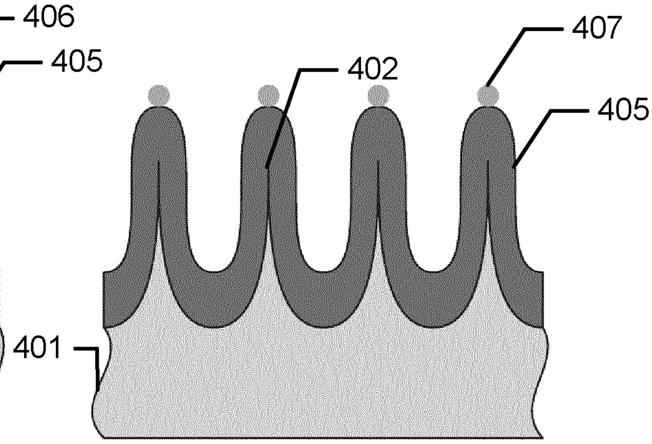

Fig. 4d

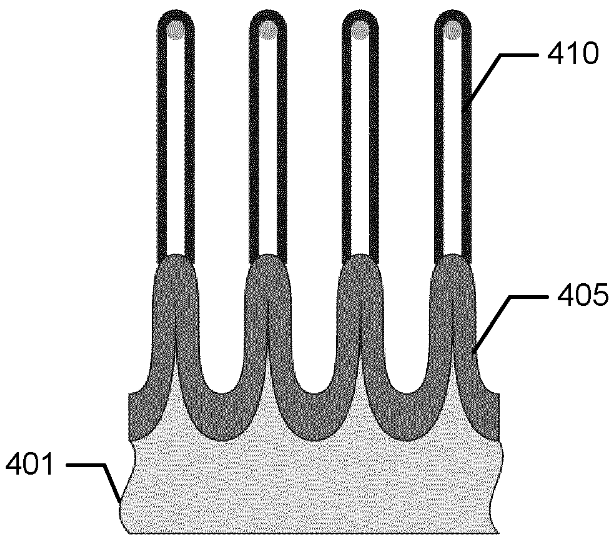

Fig. 4e

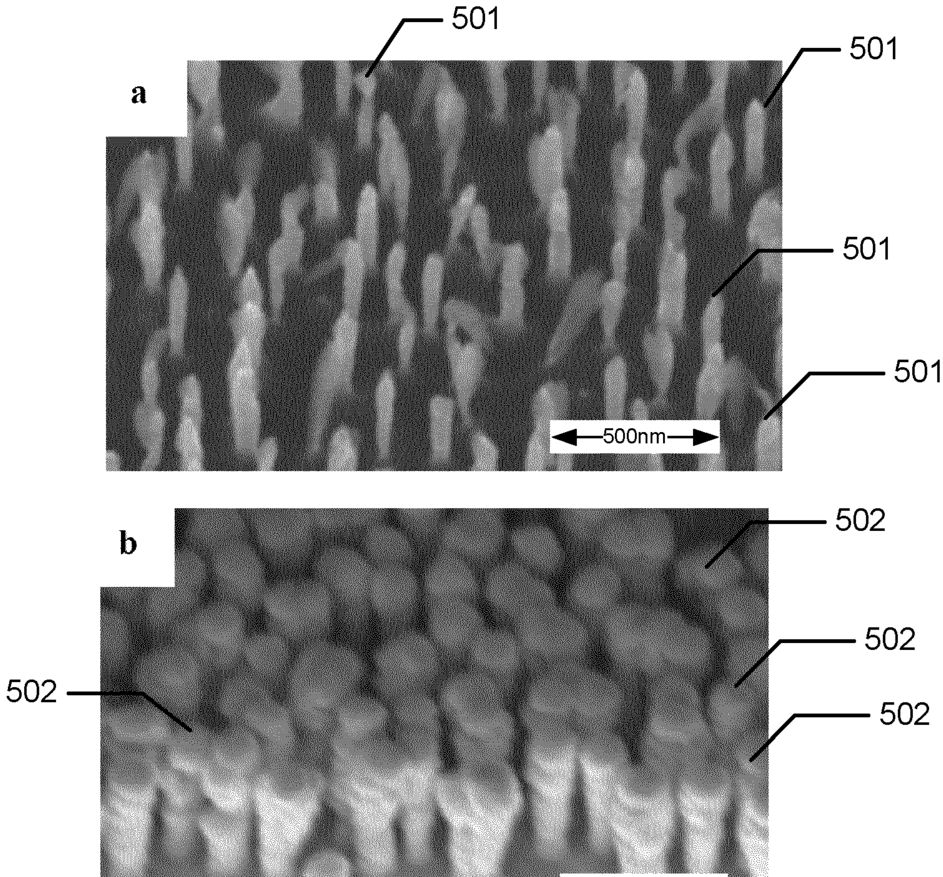
a
501
501
501
501
500nm
b
502
502
502
502
500nm

Fig. 5

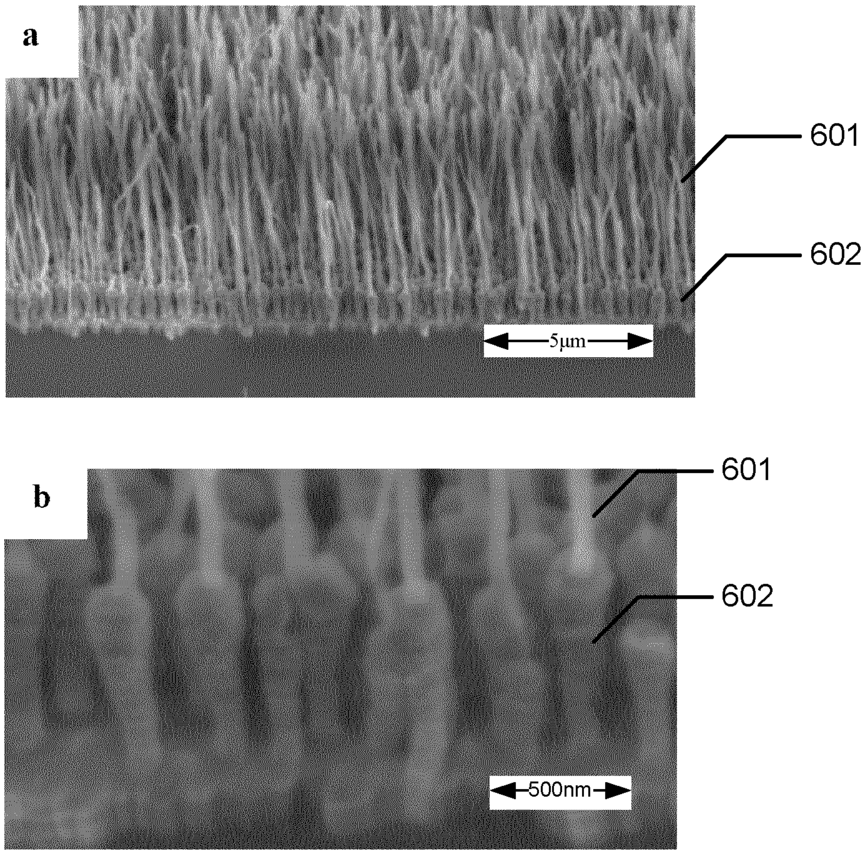
a
601
602
5μm
b
601
602
500nm

Fig. 6

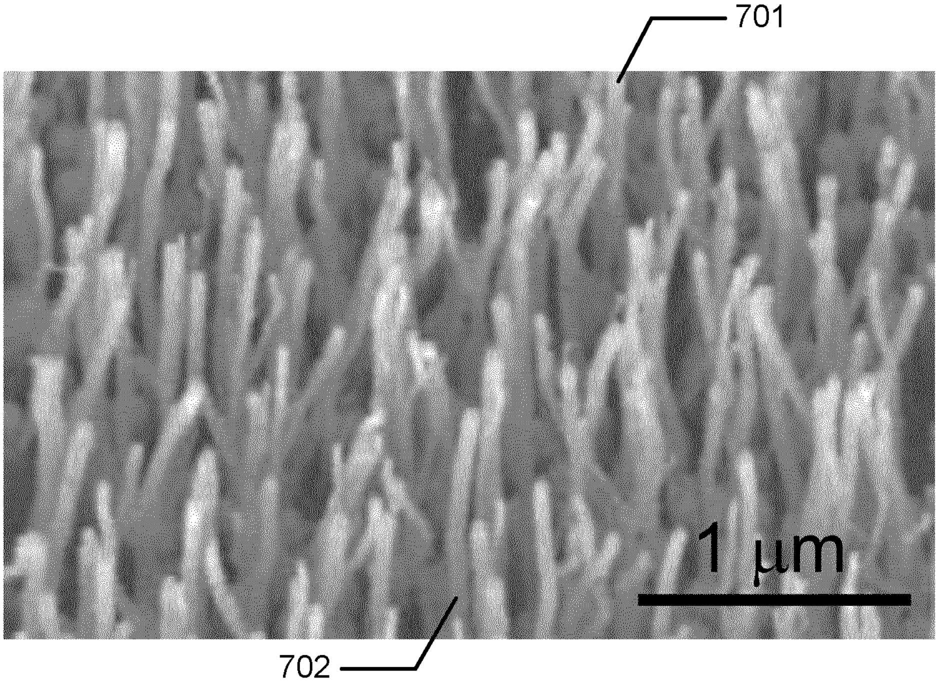

Fig. 7a

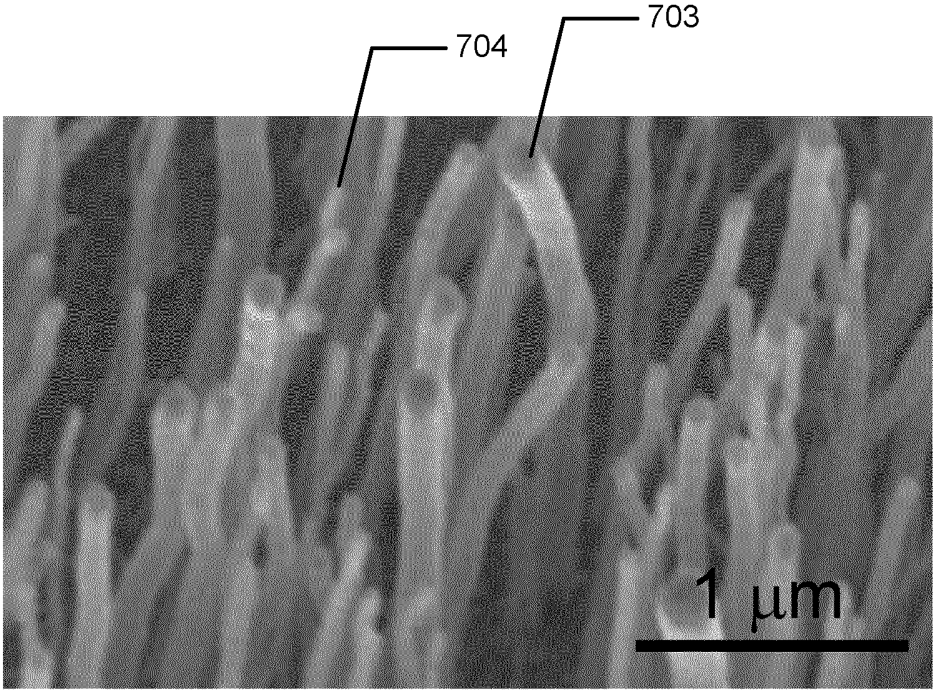

Fig. 7b

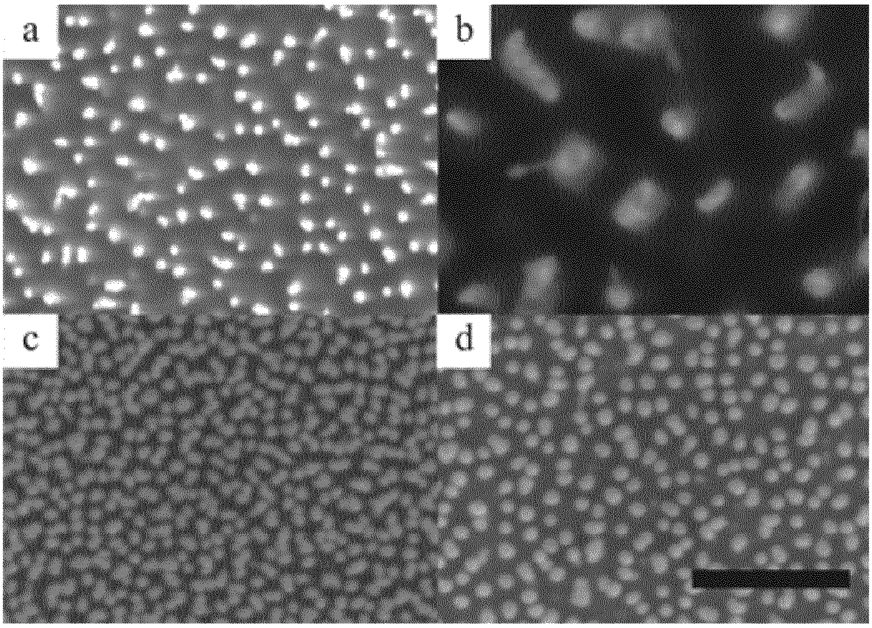
a
b
c
d

Fig. 8

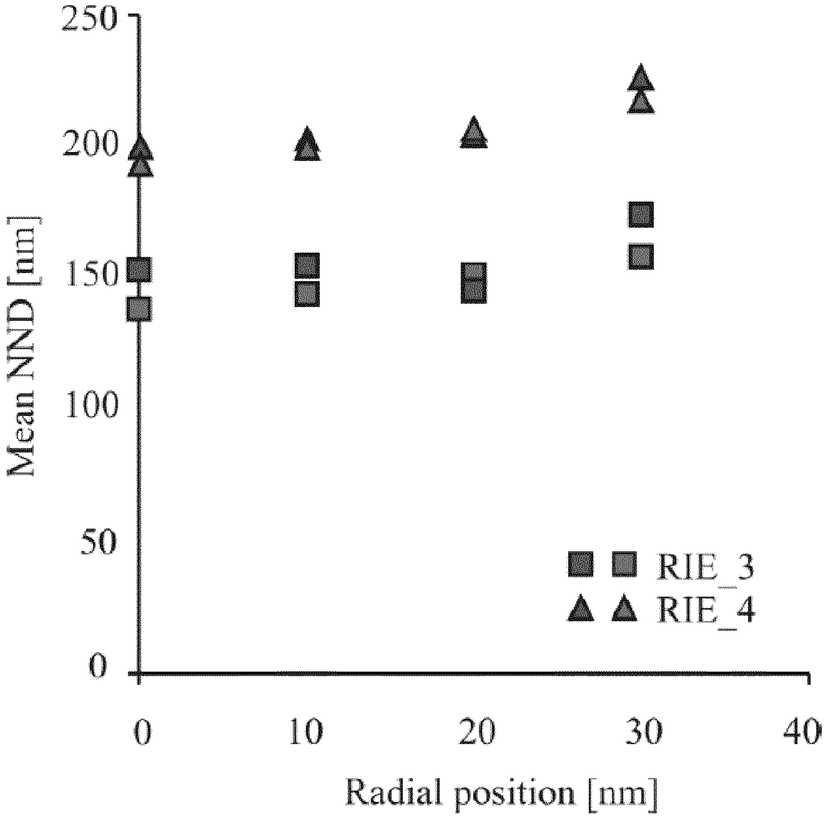
250
200
150
100
50
0
Mean NND [nm]
RIE_3
RIE_4
0
10
20
30
40
Radial position [nm]

Fig. 9

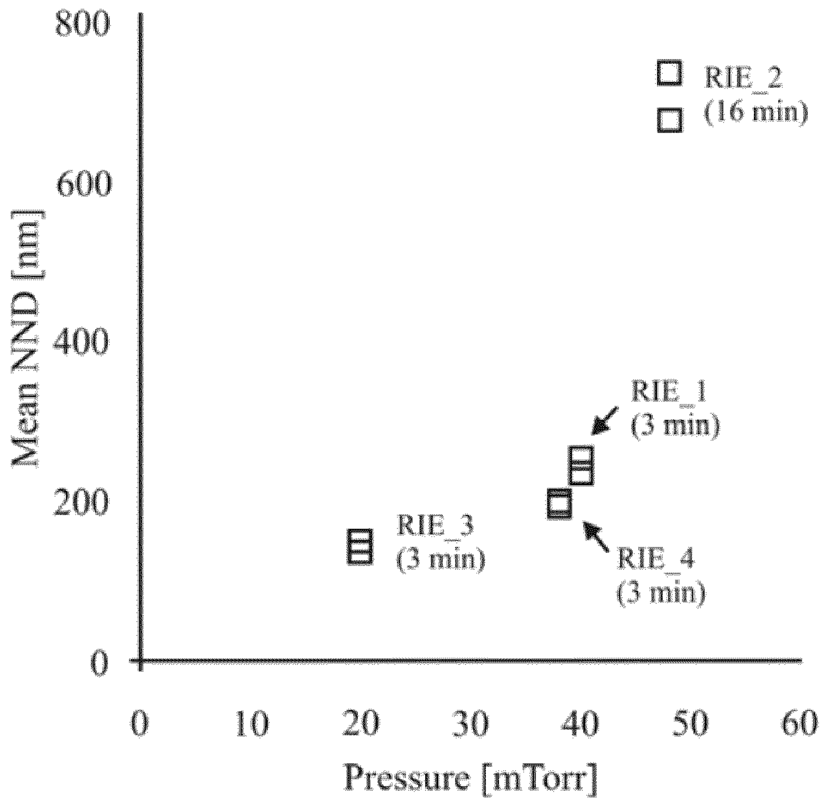
800
600
400
200
0
Mean NND [nm]
RIE_2
(16 min)
RIE_1
(3 min)
RIE_3
(3 min)
RIE_4
(3 min)
0
10
20
30
40
50
60
Pressure [mTorr]

Fig. 10

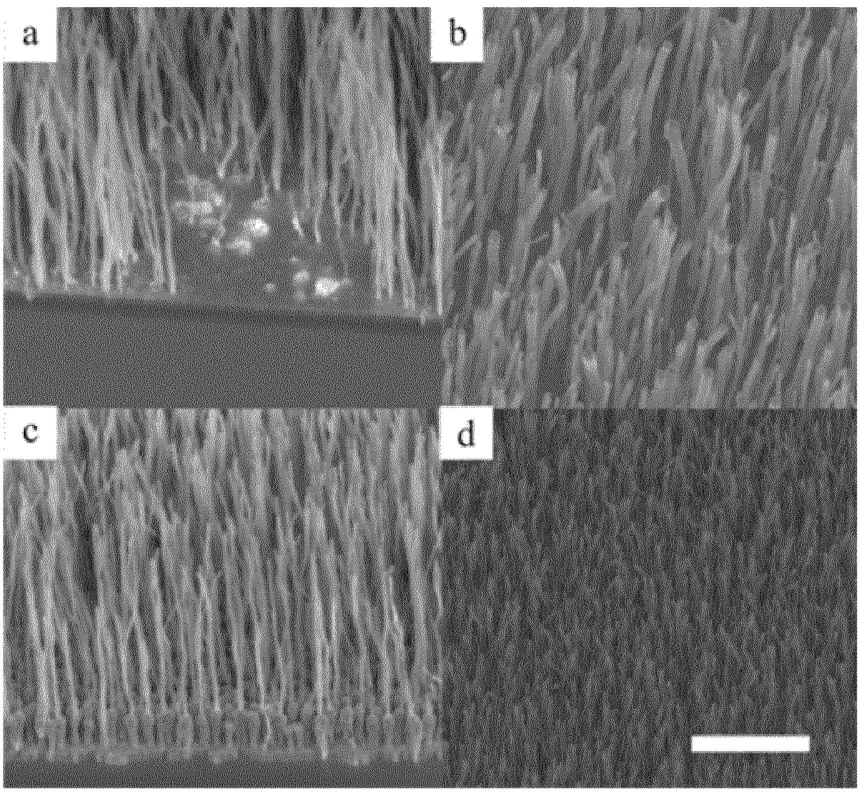
a
b
c
d

Fig. 11

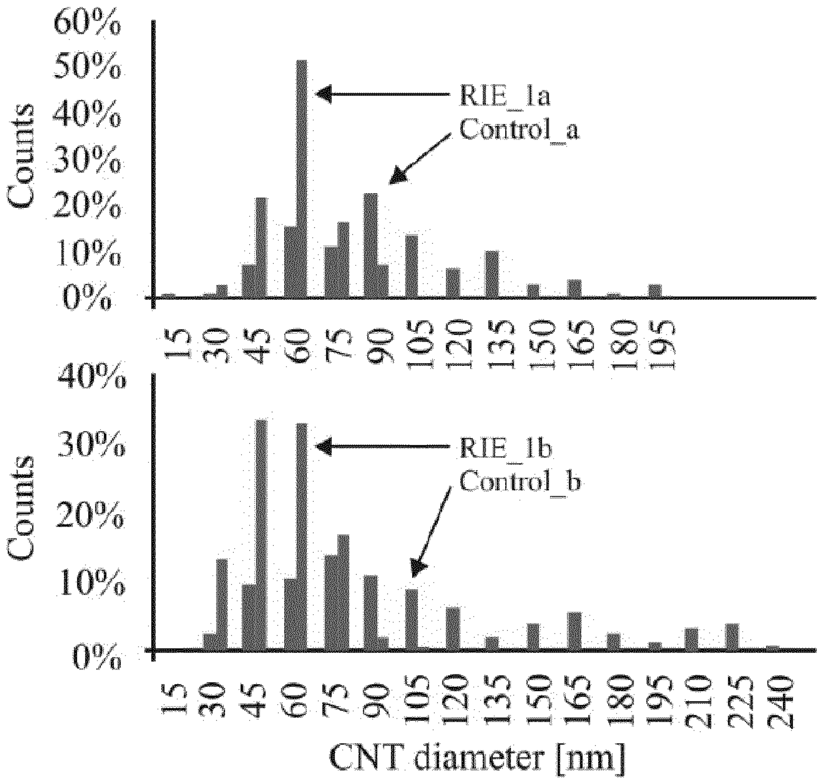
60%
50%
40%
30%
20%
10%
0%
Counts
RIE_1a
Control_a
15
30
45
60
75
90
105
120
135
150
165
180
195
40%
30%
20%
10%
0%
Counts
RIE_1b
Control_b
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
CNT diameter [nm]

Fig. 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068086

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B31/02 B01J37/02 B01J37/34 C23C14/02 C23C14/04
C23C16/02 C23C16/04

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01B B01J C23C

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

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

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHING-HSIANG TSAI ET AL: "Selective carbon nanotSelective carbon nanotube growth on silicon tips with the soft electrostatic force bonding and catalyst transfer concepts", NANOTECHNOLOGY, IOP, BRISTOL, GB, vol. 16, no. 5, 1 May 2005 (2005-05-01), pages S296-S299, XP020091055, ISSN: 0957-4484, DOI: 10.1088/0957-4484/16/5/030 the whole document -----	1-14
A	FR 2 886 284 A1 (COMMISSARIAT ENERGIE ATOMIQUE [FR]) 1 December 2006 (2006-12-01) page 15, line 1 - page 24, line 11; figure 7 -----	1-14
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 November 2012	23/11/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Marucci, Alessandra

1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068086

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/245209 A1 (JUNG HEE TAE [KR] ET AL) 9 December 2004 (2004-12-09) claims; figure 2 -----	1-14

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/068086

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2886284 A1	01-12-2006	EP 1885648 A2	13-02-2008
		EP 1885649 A2	13-02-2008
		FR 2886284 A1	01-12-2006
		JP 2008543008 A	27-11-2008
		JP 2008546146 A	18-12-2008
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