

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 July 2010 (08.07.2010)

(10) International Publication Number
WO 2010/076191 A1

(51) International Patent Classification:
H01L 29/16 (2006.01) *H01L 29/06* (2006.01)
H01L 29/161 (2006.01)

[US/US]; IBM Corporation, M/D 14-242, 1101 Kitchawan Road, Route 134, Yorktown Heights, New York 10598 (US).

(21) International Application Number:
PCT/EP2009/067173

(74) Agent: **WILLIAMS, Julian, David**; IBM United Kingdom Limited, Intellectual Property Law, Hursley Park, Winchester Hampshire SO21 2JN (GB).

(22) International Filing Date:
15 December 2009 (15.12.2009)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/344,696 29 December 2008 (29.12.2008) US

(71) Applicant (for all designated States except US): **INTERNATIONAL BUSINESS MACHINES CORPORATION** [US/US]; New Orchard Road, Armonk, New York 10504 (US).

(71) Applicant (for MG only): **IBM UNITED KINGDOM LIMITED** [GB/GB]; P.O. Box 41, North Harbour, Portsmouth Hampshire PO6 3AU (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ANDERSON, Brent, Alan** [US/US]; IBM Corporation, M/D 972C, 1000 River Street, Essex Junction, Vermont 05452-4299 (US). **BRYANT, Andres** [US/US]; IBM Corporation, M/D 972F, 1000 River Street, Essex Junction, Vermont 05452-4299 (US). **NOWAK, Edward** [US/US]; IBM Corporation, M/D 972F, 1000 River Street, Essex Junction, Vermont 05452-4299 (US). **SLEIGHT, Jeffrey**

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: METHODS OF FABRICATING NANOSTRUCTURES

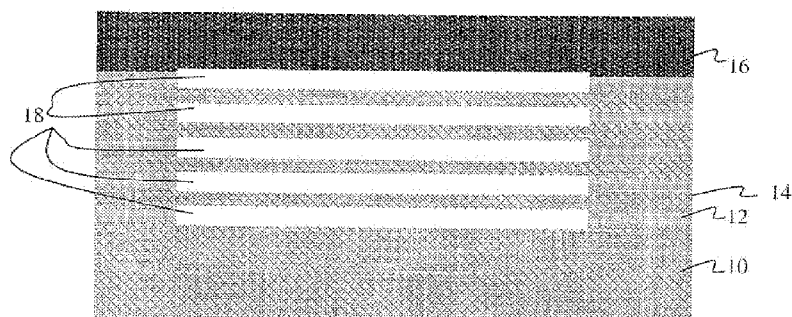


FIG. 4

(57) Abstract: A method is shown for fabricating nanostructures, and more particularly, to methods of fabricating silicon nanowires. The method of manufacturing a nanowire includes forming a sandwich structure of SiX material and material Si over a substrate and etching the sandwich structure to expose sidewalls of the Si material and the SiX material. The method further includes etching the SiX material to expose portions of the Si material and etching the exposed portions of the Si material. The method also includes breaking away the Si material to form silicon nanowires.



WO 2010/076191 A1

METHODS OF FABRICATING NANOSTRUCTURES

FIELD OF THE INVENTION

The invention relates to the fabrication of nanostructures, and more particularly, to methods of fabricating silicon nanowires.

BACKGROUND OF THE INVENTION

Nanotechnology has become a very important tool in the scaling of devices and more particularly in integrated circuit manufacturing techniques. For example, nanowires are now being used to form transistors in integrated circuits, which may be used for various devices such as, for example, LCD panels. Currently, though, nanowires are fabricated using a "top-down" technique. That is, nanowires are fabricated in a vertical orientation. However, this traditional methodology cannot achieve the precision required for certain electronics.

For example, in the top down methodology, a silicon nanowire is formed by etching from a top, downwards into a silicon material. This forms a tightly clustered plurality of vertically oriented nanowires, i.e., perpendicular with respect to the planar surface of the silicon material. However, in this orientation it is very difficult to change the characteristics of the nanowires prior to breaking them from the silicon material. Specifically, as the nanowires are densely packed (e.g., tightly clustered) and formed in a vertical orientation, it is difficult to gain access to them in order to make any modifications such as, for example, change their shapes or provide a silicide implant.

Accordingly, there exists a need in the art to overcome the deficiencies and limitations described hereinabove.

BRIEF SUMMARY OF THE INVENTION

In a first aspect of the invention, a method of manufacturing a nanowire comprises forming a sandwich structure of SiX material and material Si over a substrate and etching the sandwich

structure to expose sidewalls of the Si material and the SiX material. The method further comprises etching the SiX material to expose portions of the Si material and etching the exposed portions of the Si material. The method also comprises breaking away the Si material to form silicon nanowires.

In another aspect of the invention, a method of forming a plurality of nanowires in a horizontal plane comprises growing alternate layers of Si material and SiGe material over a substrate and capping an uppermost layer of the SiGe material with a capping layer. A trench is formed to the substrate by etching through the alternate layers of Si material and SiGe material and the capping layer to expose sidewalls of the alternate layers of the Si material and the SiGe material. The SiGe is selectively etched away to expose planar surfaces of the Si material. The Si material is thinned to form a pattern by etching the planar surfaces the Si material. The Si material is broken away from non-etched portions of the SiGe material to form silicon nanowires.

In another aspect of the invention, a method of forming nanowires, comprises: providing alternate epitaxial SiGe layers and Si layers on a substrate, where a selectively of the SiGe layers to the Si layers is about 100:1; depositing a nitride cap on an uppermost SiGe layer; forming a trench to the substrate by etching an opening in the SiGe layers, the Si layer and the nitride cap to expose sidewalls of the SiGe layers and the Si layers; etching the SiGe layers to expose surfaces of the Si layers; etching the exposed surfaces of the Si layers in order to narrow the Si layers; and breaking away the Si layers attached to any remaining SiGe material at ends thereof.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

The present invention is described in the detailed description which follows, in reference to the noted plurality of drawings by way of non-limiting examples of exemplary embodiments of the present invention.

FIGS. 1-5 show structures and respective processing steps in accordance with aspects of the invention;

FIG. 6 shows alternative processing steps in accordance with aspects of the invention; and

FIGS. 7A-7D show nanowires of various complex shapes formed in accordance with aspects of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to the fabrication of nanostructures, and more particularly, to methods of fabricating silicon nanowires. In embodiments, the method of fabricating the silicon nanowires includes etching several layers of silicon and intervening material (e.g., SiX) to simultaneously manufacture a plurality of silicon nanowires in a horizontal plane. Compared to the fabrication of nanowires in a vertical plane, the method of the present invention provides the flexibility to manufacture complex shapes and make other modifications to the nanowires at a lower cost. Accordingly, in implementation, the invention provides a low cost, flexible method of manufacturing silicon nanowires of different complex shapes and/or with other types of modifications.

FIG. 1 shows a beginning structure and respective processing steps in accordance with aspects of the invention. More specifically, FIG. 1 shows a base substrate (wafer) 10 made from, for example, silicon or other known materials such as, for example, SOI. An epitaxial SiX layer 12 and Si layer 14 are alternately grown on the substrate 10 in a conventionally known manner. This alternate growth forms a sandwich structure of SiX (hereinafter referred to as SiGe) and Si.

X is an impurity such as, for example, Ge. As such, in embodiments, the SiX layers 12 are preferably SiGe. Although only five layers of SiGe and four layers of Si are shown, it is contemplated that more or less than these layers can be provided by the present invention. For example, in one illustrative, non-limiting example, 1- 25 layers each of SiGe and Si are contemplated by the present invention.

In embodiments, the SiGe layers can range in thickness from about 2 nm to about 500 nm, depending on the particular application of the invention. Similarly, the Si layers 14 can range

in thickness from about 2 nm to about 500 nm or more, with no practical limit to the length of the Si layer 14. Additionally, the selectivity of SiGe to Si is about 100:1. This selectivity ensures that subsequent etching processes of the SiGe will not attack the Si to such an extent as to completely etch away or destroy the Si layers, which form the nanowires of the present invention.

A nitride cap 16 is deposited on the final SiGe layer 12. The nitride cap 16 protects the underlying Si layers 12 during vertical etching processes. For example, in this role, the nitride cap 16 will protect an uppermost SiGe layer thereby ensuring that the uppermost SiGe layer will not be etched away during a vertical etching process. This, in turn, protects the underlying Si layers 14, e.g., a vertical etching process will not attack the Si layers. In optional embodiments, the nitride cap 16 can act as a template for the different shapes of nanowires formed from the Si layers 14.

FIGS. 2 and 3 show an intermediate structure and respective processing steps in accordance with aspects of the invention. FIG. 3 is a top view of FIG. 2. More specifically, referring to FIGS. 2 and 3, the structure of FIG. 1 is subject to an etching process which forms vertical trenches 18 through the nitride cap 16 and underlying epitaxial SiGe layers 12 and Si layers 14. The etching stops at the substrate 10. This etching step exposes the sidewalls of the SiGe layers 12 and Si layers 14, which are subject to subsequent etching steps that are used to form the Si nanowires. The trenches 18 can be of any desired shape.

More specifically, using conventional lithography and reactive ion etching processes, a resist (not shown) is deposited over the structure of FIG. 1. Using a light source, for example, openings are formed in the resist (which correspond to the shape of the opening 18 shown in FIG. 3). A reactive ion etching, preferably a dry etching process, attacks the nitride cap 16 and underlying epitaxial SiGe layers 12 and Si layers 14 to form the trenches 18. In embodiments and although more expensive than wet etching techniques, a dry etch can be used in order to provide finer features such as, for example, deep vertical sidewalls.

FIG. 4 shows another intermediate structure and respective processing steps in accordance with aspects of the invention. In FIG. 4, the structure is subject to an etching process to

narrow or reduce the size of the Si layers 14. More specifically, as the sidewalls of the SiGe layers 12 are exposed, a selective etching process to the SiGe layers 12 is performed to attack the SiGe layers 12. This selective etching process will strip or etch away the SiGe layers 12 between (e.g., above and below) the Si layers 14, in order to form free floating portions of the Si layers 14. The etching will also expose planar surfaces of the Si layers 14. The selective etching process can be, for example, an isotropic wet etching process.

A subsequent etching process is performed to thin and/or shape the Si layers 14. More specifically a wet etching process is performed to etch away the planar surfaces, e.g., exposed portions, of each of the Si layers 14. Continuing with this etching process, the Si layers 14 will begin to narrow. In embodiments, the Si layers 14 can have an aspect ratio of width to thickness of about 10:1 to 100:1, for example. Also, there is no practical limit to the length of the Si layers 14, which will form the silicon nanowires. Also, the Si layers 14 can be etched to practically any desired shape by forming a certain resist shape, e.g., forming openings in the resist (using conventional lithography processes) of certain sizes and shapes, prior to the subsequent etching process. The Si layers, as should be understood by those of skill in the art, will form the silicon nanowires of the present invention.

In embodiments, it is also possible to control the crystal orientation of the nanowires by aligning the wires with the X Y ($\langle 100, 110 \rangle$) orientation of the underlying substrate 10. For example, prior to etching, the structure is rotated relative to the mask image to a certain desired orientation. As the structure is now rotated, the etching process can form a wire pattern in a desired orientation with respect to the underlying substrate 10. In this way, the pattern can be aligned with the crystal orientation $\langle 100, 110 \rangle$ of the substrate 10.

FIG. 5 shows another intermediate structure and respective processing steps in accordance with aspects of the invention. In FIG. 5, the nanowires 14a are detached from the structure of FIG. 4 using conventional etching processes. For example, ends 14a₁ of the nanowires 14a are broken off from the remaining structure of FIG. 4 using conventional masking and etching processes. Illustratively, a mask can be placed over the Si layers 14 at a certain distance from the end of the structure of FIG. 5, e.g., near an edge of the SiGe. Thereafter, the structure is subject to an etching process to break away the nanowires 14a. This results in

a plurality of nanowires 14a of uniform length and size. Those of skill in the art should understand that the original number of Si layers 14 will dictate the number of nanowires 14a. Also, the length of the nanowires 14a can be tailored to any length, depending on the placement of the mask.

FIG. 6 shows alternative processing steps in accordance with aspects of the invention. In further embodiments, prior (or after) to the etching process of FIG. 4, for example, the Si layers 14 can be subject to a silicidation or oxidation process. For example, a dielectric material can be placed over the structure of FIG. 4 to protect certain areas. A resist used for the etching process is stripped to expose certain areas of the nanowires 14a. A metal is then deposited and reacted on the exposed areas. Any unreacted metal is then removed resulting in selective silicided areas. The dielectric can then be removed using conventional stripping processes.

FIGS. 7A-7D show nanowires of various complex shapes formed in accordance with aspects of the invention. The nanowires of FIGS. 7A-7D are illustrative of the many different complex shapes of nanowires that can be formed using the methods of the present invention. For example, FIG. 7A shows a triangular shape, whereas, FIGS. 7B and 7C show a bone shape with a narrow central portion and two thicker end portions. FIG. 7C also shows a thicker portion of the nanowire formed with a salicide. FIG. 7D shows a "T" shaped structure with a narrow portion and a thicker end portion. These shapes can be formed easily, as the nanowires are formed in a horizontal plane.

The methods as described above is used in the fabrication of integrated circuit chips. The resulting integrated circuit chips can be distributed by the fabricator in raw wafer form (that is, as a single wafer that has multiple unpackaged chips), as a bare die, or in a packaged form. In the latter case the chip is mounted in a single chip package (such as a plastic carrier, with leads that are affixed to a motherboard or other higher level carrier) or in a multichip package (such as a ceramic carrier that has either or both surface interconnections or buried interconnections). In any case the chip is then integrated with other chips, discrete circuit elements, and/or other signal processing devices as part of either (a) an intermediate

product, such as a motherboard, or (b) an end product. The end product can be any product that includes integrated circuit chips.

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

The corresponding structures, materials, acts, and equivalents of all means or step plus function elements, if any, in the claims below are intended to include any structure, material, or act for performing the function in combination with other claimed elements as specifically claimed. The description of the present invention has been presented for purposes of illustration and description, but is not intended to be exhaustive or limited to the invention in the form disclosed. Many modifications and variations will be apparent to those of ordinary skill in the art without departing from the scope and spirit of the invention. The embodiments were chosen and described in order to best explain the principles of the invention and the practical application, and to enable others of ordinary skill in the art to understand the invention for various embodiments with various modifications as are suited to the particular use contemplated.

CLAIMS

1. A method of manufacturing a nanowire, comprising:
 - (a) forming a sandwich structure of SiX material and material Si over a substrate;
 - (b) etching the sandwich structure to expose sidewalls of the Si material and the SiX material;
 - (c) etching the SiX material to expose portions of the Si material;
 - (d) etching the exposed portions of the Si material; and
 - (e) breaking away the Si material to form silicon nanowires.
2. The method of claim 1, wherein X is an impurity.
3. The method of claim 2, wherein the impurity is Ge.
4. The method of claim 1, wherein the etching of the exposed portions of the Si material is an isotropic etching process.
5. The method of claim 1, wherein the sandwich structure comprises the Si material between the SiX material with at least 1 to 25 layers of the Si material.
6. The method of claim 1, further comprising depositing a capping layer on an uppermost layer of the SiX material prior to step (b).
7. The method of claim 6, wherein the capping is a deposition of nitride.
8. The method of claim 1, wherein a selectivity of the SiX material to the Si material is about 100:1.
9. The method of claim 1, wherein the etching the exposed portions of the Si material comprises depositing a resist layer, forming openings in the resist layer to a desired shape and etching the Si material through the openings to form a predetermined shape of the nanowires.

10. The method of claim 1, further comprising controlling a crystal orientation of the nanowires by rotating the sandwich structure relative to mask alignment prior to the etching of the sandwich structure, the SiX material and the exposed portions of the Si material.
11. The method of claim 1, further comprising saliciding the nanowires.
12. The method of claim 1 wherein step (b) includes forming a trench to the substrate by etching through the alternate layers of Si material and SiGe material and the capping layer to expose sidewalls of the alternate layers of the Si material and the SiGe material; and wherein the following step is performed between steps (d) and (e):
thinning the Si material by etching away the surfaces of the Si material to form a pattern.
13. The method of claim 1, further comprising saliciding the Si material prior to the step (e) of breaking away.

1/4

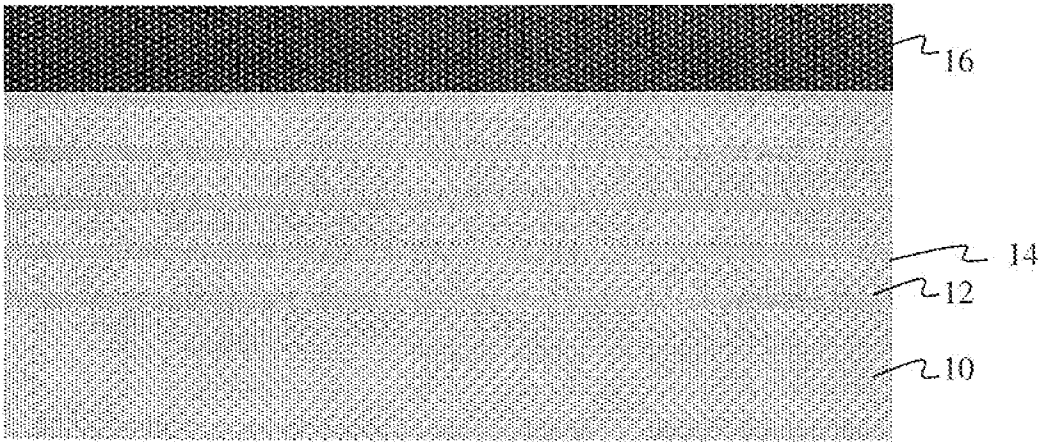


FIG. 1

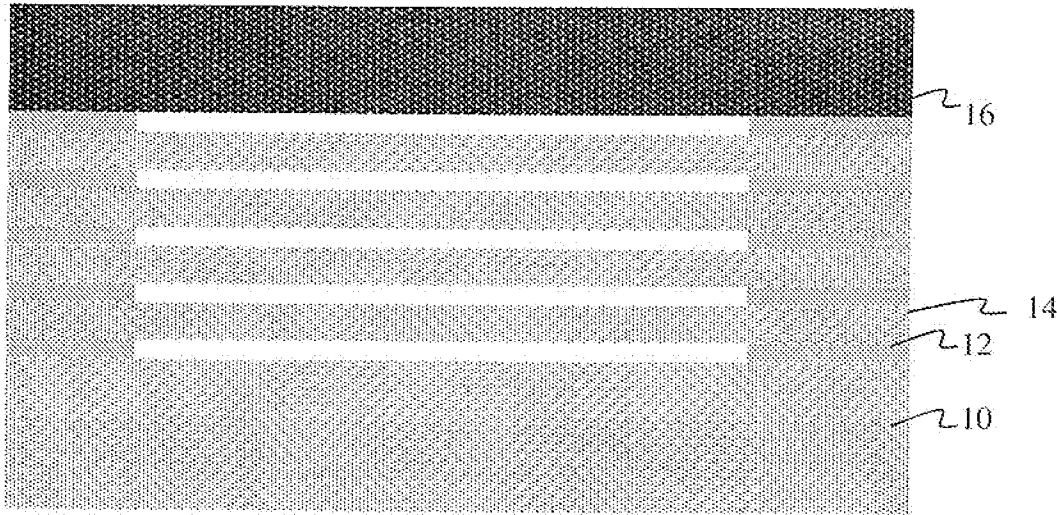


FIG. 2

2/4

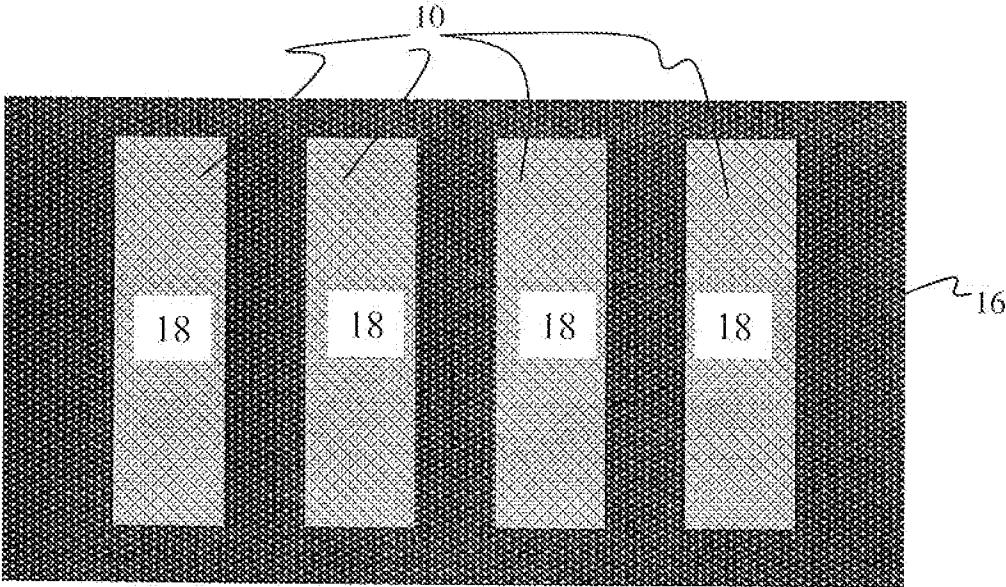


FIG.3

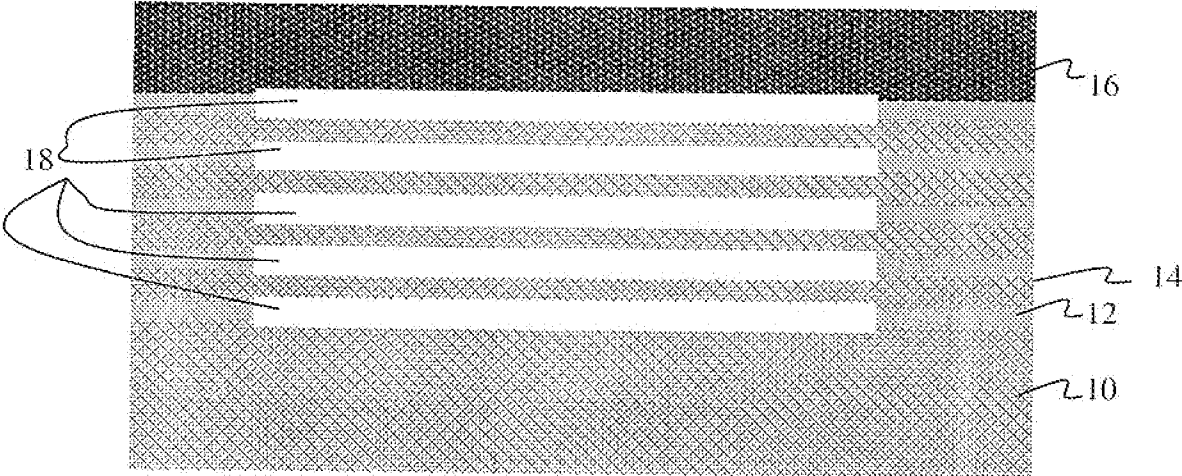


FIG.4

3/4

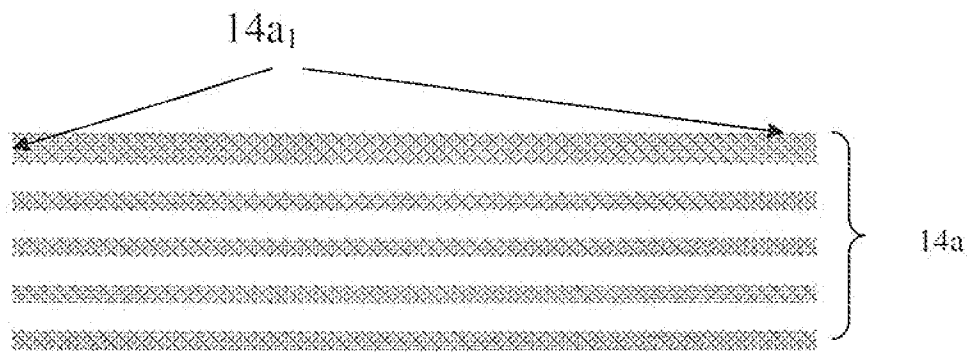


FIG.5

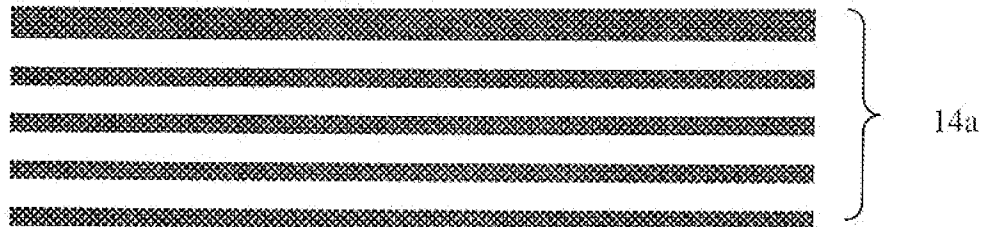
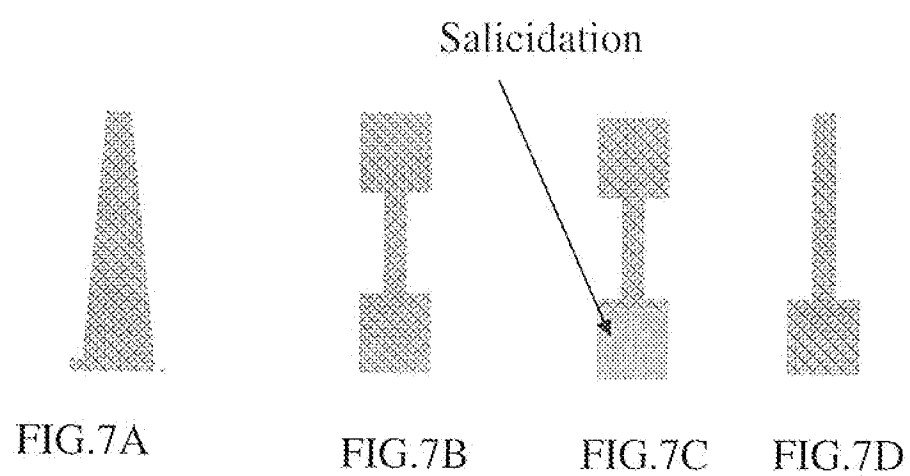


FIG.6

4/4



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/067173

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L29/16 H01L29/161 H01L29/06

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)

H01L

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

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

EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LIU J L ET AL: "STUDY ON THERMAL OXIDATION OF SI NANOWIRES" 1 January 1998 (1998-01-01), PHYSICA STATUS SOLIDI (A). APPLIED RESEARCH, BERLIN, DE, PAGE(S) 441 - 446 , XP009018541 ISSN: 0031-8965 page 442 - page 443 -----	1-13
X	MONFRAY S ET AL: "Applications of SiGe Material for CMOS and Related Processing" BIPOLAR/BICMOS CIRCUITS AND TECHNOLOGY MEETING, 2006, IEEE, PISCATAWAY, NJ, USA, 1 October 2006 (2006-10-01), pages 1-7, XP031047252 ISBN: 978-1-4244-0458-2 page 4 - page 5 -----	1-13



Further documents are listed in the continuation of Box C.



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 document 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

1 March 2010

Date of mailing of the international search report

08/03/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Baillet, Bernard