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[Continued on next page]

(54) Title: A METHOD OF PRODUCING NANOWIRES OF TWO DIFFERENT MATERIALS

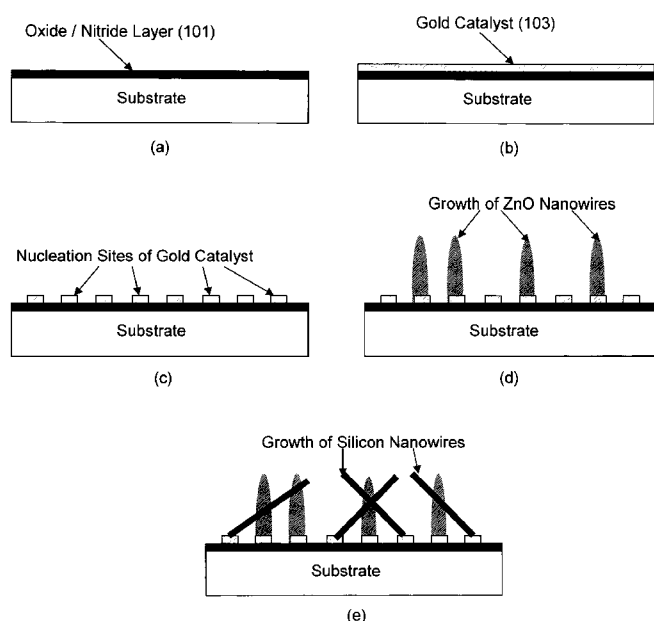


Figure 2.

(57) Abstract: A method of producing vertical nanowires using single catalyst material is provided, the method includes the steps of depositing an insulating oxide or nitride layer (101) on a substrate surface, depositing a gold catalyst layer (103) on top of the insulating oxide or nitride layer (101), annealing the substrate with the gold catalyst layer at temperature above 350°C, such that nanoparticles are formed of a diameter in the range of 1 to 100 nm, growing zinc oxide nanowires from the exposed gold catalyst nanoparticles by chemical vapour deposition (CVD) with diethylzinc as a precursor, and growing silicon nanowires from the remaining gold catalyst nanoparticles with silicon as precursor, such that vertical type zinc oxide nanowires are produced and laterally connected by silicon nanowires wherein the insulating oxide or nitride layer (101) is not required when the substrate is an insulative material.



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A METHOD OF PRODUCING NANOWIRES OF TWO DIFFERENT MATERIALS

FIELD OF INVENTION

- 5 The present invention relates to a method of producing vertical nanowires using single catalyst material.

BACKGROUND OF INVENTION

- 10 There have been significant development efforts by researchers in the area of nanotube and nanowire growth or synthesis for potential applications in the area of electronics, photonics and sensors. These include research in the type of metal catalyst used for growth, wherein the growth techniques and dimensions of the nanotubes and nanowires by controlling the growth temperature, gas ratios, pressure and plasma. Most of these works concentrate on
- 15 the growth of single type nanotube or nanowire in a working area. In the work of sensor technology, if a combination of at least 2 types of nanotube and nanowire selective to the same ions can be grown in the same area, it increases the overall selectivity of the sensing element. In sensor applications in particular, ZnO nanowires are used as sensing elements are typically left exposed to enable detection, of ions. As these nanowires can be of vertical
- 20 type, to connect them to enable electrical measurements and at the same time leaving them exposed for sensing is a challenge.

- US 7608905 describes multiple sets of independently addressable interdigitated nanowires. However, both nanowires are of a vertical type and cannot be used as a gas sensor as all
- 25 the nanowires are enclosed and not contactable with the environment.

US 7344961 describes a method for producing nanowires that includes providing a thin film of a catalyst material with varying thickness on a substrate, heating the substrate and thin

film, such that the thin film disassociates at the relatively thinner regions and vapor depositing a semiconductor onto the substrate to produce nanowires. However, only one type of nanowire is grown in the working area and it does not cover electrical contacts to the nanowires. Therefore the method is not ready for full device application as it will not be able to sense the environment.

Hence this limits the sensors to only lateral type ZnO nanowires where they normally forms bundles which can results in variations between different sensors.

SUMMARY OF INVENTION

Accordingly, there is provided a method of producing vertical nanowires, characterized in that, the method uses single catalyst material, the method includes the steps of depositing
5 an insulating oxide or nitride layer on a substrate surface, depositing a gold catalyst layer on top of the insulating oxide or nitride layer, annealing the substrate with gold catalyst at temperature above 350°C, such that nanoparticles are of diameter in range of 1 to 100 nm, growing zinc oxide nanowires from exposed gold catalyst by chemical vapour deposition (CVD) with diethylzinc as a precursor and growing silicon nanowires from remaining gold
10 catalyst nanoparticles with silicon as precursor, such that vertical type zinc oxide nanowires are produced and laterally connected by silicon nanowires wherein the insulating oxide or nitride layer is not required when the substrate (105) is insulative material.

The present invention consists of several novel features and a combination of parts
15 hereinafter fully described and illustrated in the accompanying description and drawings, it being understood that various changes in the details may be made without departing from the scope of the invention or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be fully understood from the detailed description given herein below and the accompanying drawings which are given by way of illustration only, and thus
5 are not limitative of the present invention, wherein:

Figure 1 shows a cross sectional view of ZnO nanowires grown first before the silicon nanowire contacts in the present embodiment of the invention;

Figure 2 shows a flowchart of cross sectional views showing a method of producing vertical nanowires using single catalyst material in the present embodiment of the invention;

10 Figure 3 shows a top view of vertically grown ZnO nanowires by chemical vapour deposition method with gold catalyst in the preferred embodiment of the invention; and

Figure 4 shows a top view of silicon nanowires that have been grown utilizing the remaining un-used gold catalyst in the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention relates to a method of producing vertical nanowires using single catalyst material. Hereinafter, this specification will describe the present invention according to the preferred embodiment of the present invention. However, it is to be understood that limiting the description to the preferred embodiment of the invention is merely to facilitate discussion of the present invention and it is envisioned that those skilled in the art may devise various modifications and equivalents without departing from the scope of the appended claims.

The following detailed description of the preferred embodiment will now be described in accordance with the attached drawings, either individually or in combination.

Figure 2 illustrates a method of producing vertical nanowires using single catalyst material. The method includes the steps of depositing an insulating oxide or nitride layer (101) on a substrate (105) surface, depositing a gold catalyst layer (103) on top of the insulating oxide or nitride layer (101), annealing the substrate (105) with gold catalyst at temperature above 350°C, such that nanoparticles are of diameter in range of 1 to 100 nm, growing zinc oxide nanowires from exposed gold catalyst by chemical vapour deposition (CVD) with diethylzinc as a precursor and growing silicon nanowires (107) from remaining gold catalyst nanoparticles with silicon as precursor, such that vertical type zinc oxide (ZnO) nanowires (109) are produced and laterally connected by silicon nanowires (107) wherein the insulating oxide or nitride layer (101) is not required when the substrate (105) is insulative material.

25

The gold catalyst was nucleated at temperature of above 350°C to form catalyst nanoparticles prior to the nanowire growth. In this method, not all the gold (Au) catalyst

particles take part in the initial ZnO nanowire growth by chemical vapour deposition (CVD) method. Remaining catalyst materials were then subjected to silicon nanowire growth also by CVD. During the initial ZnO nanowire growth process, not all the gold catalyst is consumed as there is a competing nature of the catalyst with the gas precursor where some catalysts are more reactive thus enabling the nucleation of nanowires much better as compared to the catalyst in its surroundings. Hence, this allows only a single catalyst to be used for growing the two types of nanowires.

Growth sequence is important where the ZnO nanowires (109) are grown first before the silicon nanowire contacts to prevent the silicon nanowires (107) which form a mesh from inhibiting the vertical growth of the ZnO nanowires (109) as seen in Figure 1. For sensor applications, the ZnO nanowires (109) will be used as the sensing elements while the connecting silicon nanowires (107) will measure the change in electrical conductivity during the sensor operation.

The silicon nanowires (107) are doped with n-type or p-type dopant materials to improve electrical conductivity. Detailed process flow is described in the following sections and illustrated in Figure 2. The first step involves depositing an insulating layer onto the substrate (105) surface (Figure 2a). The insulating layer is of silicon dioxide or silicon nitride deposited by physical or chemical vapour deposition (PVD or CVD) or silicon dioxide grown by thermal oxidation method. The oxide/nitride layer acts to isolate the nanotubes and nanowires from the conducting substrate (105), e.g. silicon. The second step involves depositing gold (Au) metal catalyst material on top of the insulating surface (Figure 2b). The catalyst is deposited by physical deposition or sputtering. Thickness of the deposited Au catalyst is typically less than 30nm.

The third step involves annealing the substrate (105) at temperatures 350 to 700°C to allow nucleation of the material across the substrate (105) (Figure 2c). The nucleated catalyst

particles are of diameters in range between 1 to 100nm. The fourth step involves growing of vertical ZnO nanowires (109) from the exposed gold metal catalyst nanoparticles (Figure 2d). These nanowires are grown by chemical vapour deposition method with diethylzinc ($(C_2H_5)_2Zn$) as the growth precursor. The fifth step involves growing of silicon nanowires (107) from the remaining gold catalyst nanoparticles (Figure 2e). Similar to ZnO nanowires (109), the silicon nanowires (107) are also grown by chemical vapour deposition method with silane (SiH_4) as the growth precursor.

The vertically grown ZnO nanowires (109) by chemical vapour deposition method with gold catalyst are as shown in Figure 3. In Figure 4, silicon nanowires (107) has been grown utilizing the remaining un-used gold catalyst.

The invention uses silicon nanowires (107) to connect the vertical ZnO nanowires (109) to measure a change in electrical conductivity and in the meantime leaving the ZnO nanowires (109) exposed which is required for sensor applications. In order to grow ZnO nanowires (109), gold (Au) is typically used as the metal catalyst and to grow silicon nanowires (107), a choice of either aluminium (Al), copper (Cu) or gold (Au) thin films can be used as the catalyst material. However, gold is the common metal catalyst material that can be used to grow both ZnO and silicon nanowires (107). The gold catalyst was nucleated at temperature of above 350 °C to form catalyst nanoparticles prior to the nanowire growth, unlike those of the prior art. Therefore, the invention is an improvement over the prior art where there are two types of nanowires are connected where the silicon nanowires (107) connects the vertical ZnO nanowires (109). The invention also does not require a thin film material for contacts, as the silicon nanowires (107) are the contact to the ZnO nanowire (109) and ready to be integrated for sensor applications. The invention also only requires one catalyst type to grow two nanowire types.

This invention is adapted for producing vertical ZnO nanowires (109). The disclosed invention is suitable, but not restricted to, for use in sensor applications.

CLAIMS

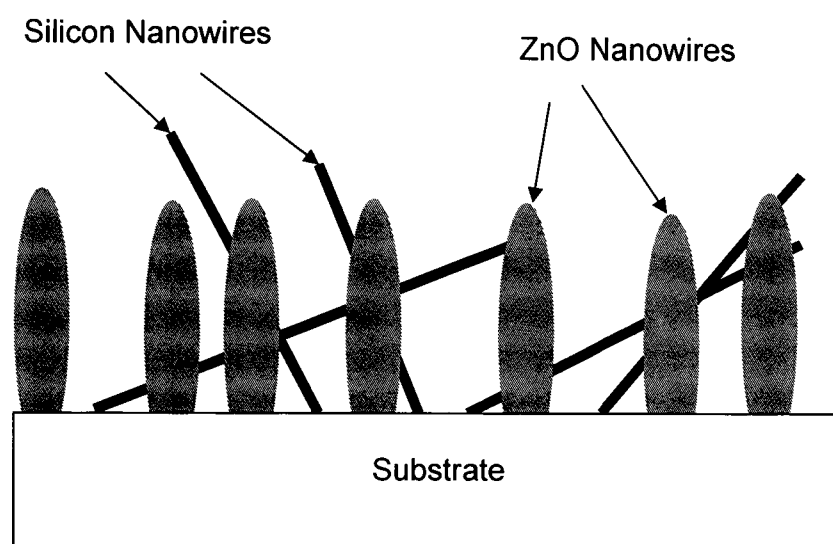
1. A method of producing vertical nanowires, characterized in that, the method uses single catalyst material, the method includes the steps of:

- 5 i. depositing an insulating oxide or nitride layer (101) on a substrate (105) surface;
- ii. depositing a gold catalyst layer (103) on top of the insulating oxide or nitride layer (101);
- iii. annealing the substrate (105) with gold catalyst at temperature above 350°C,
10 such that nanoparticles are of diameter in range of 1 to 100 nm;
- iv. growing zinc oxide nanowires from exposed gold catalyst by chemical vapour deposition (CVD) with diethylzinc as a precursor; and
- v. growing silicon nanowires (107) from remaining gold catalyst nanoparticles with silicon as precursor,
- 15 such that vertical type zinc oxide nanowires are produced and laterally connected by silicon nanowires (107),
- wherein the insulating oxide or nitride layer (101) is not required when the substrate (105) is insulative material.

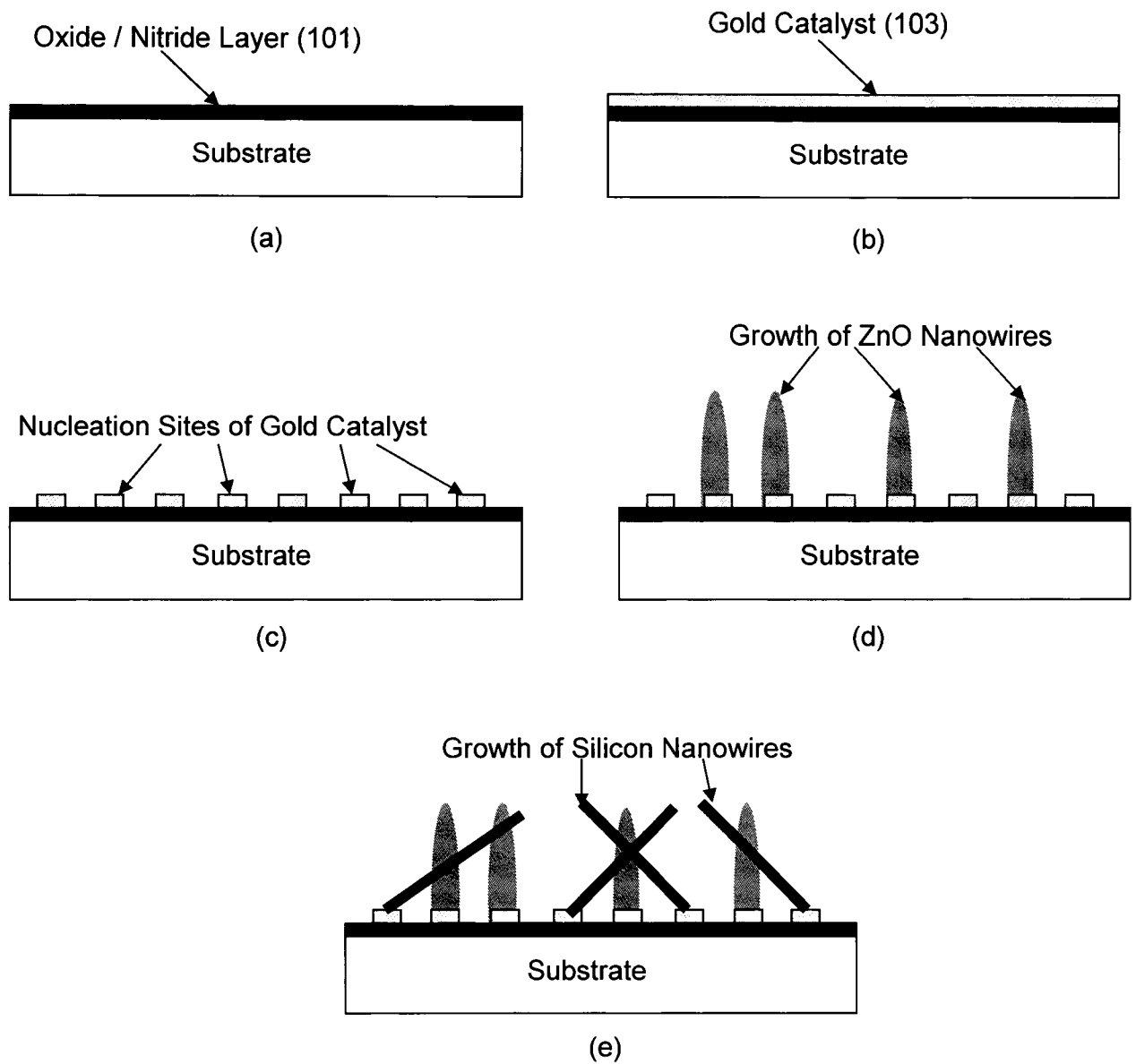
20 2. The method as claimed in claim 1, wherein the deposition of insulating oxide or nitride layer (101) is done by physical vapour deposition (PVD), chemical vapour deposition (CVD) or thermal oxidation method.

3. The method as claimed in claim 1, wherein the deposition of gold catalyst layer (103) by
25 evaporation or sputtering methods.

4. The method as claimed in claim 1, wherein the silicon nanowires (107) are doped with n type or p type materials.

**Figure 1.**

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**Figure 2.**

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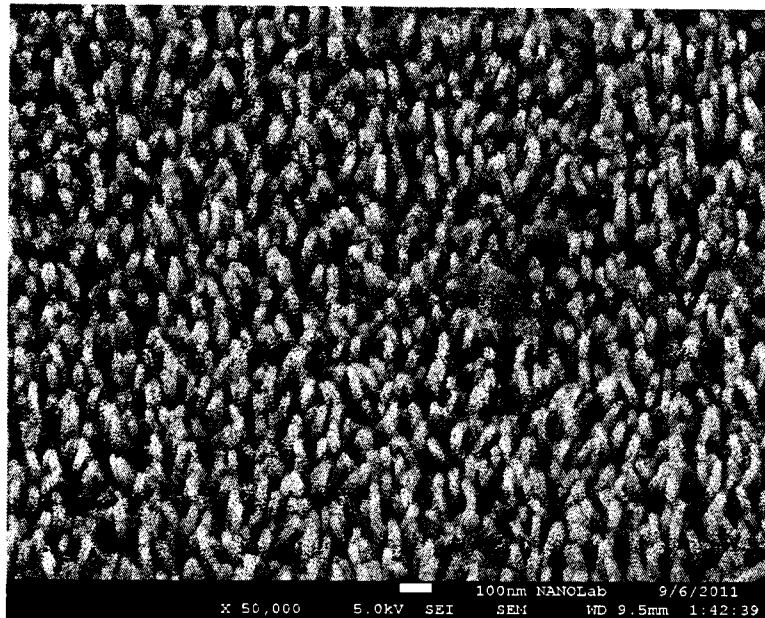


Figure 3.

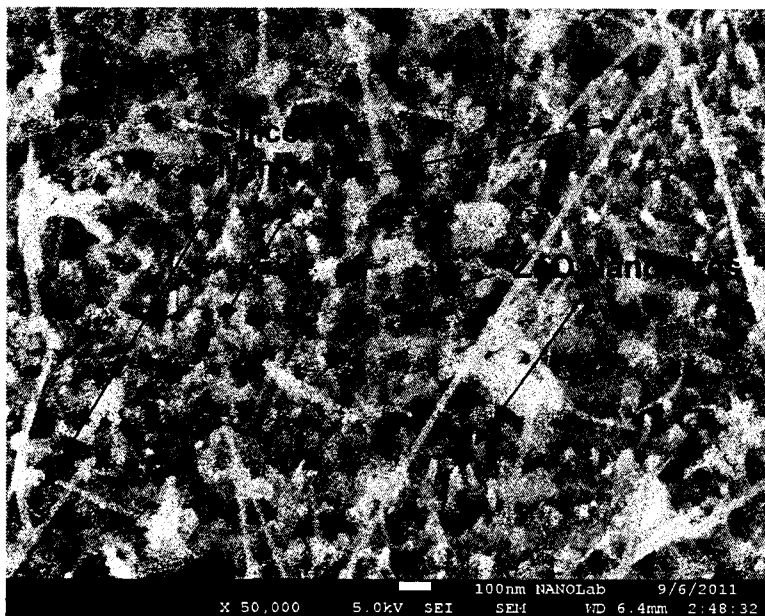


Figure 4.

INTERNATIONAL SEARCH REPORT

International application No
PCT/MY2013/000227

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L21/36 H01L21/20 H01L21/02
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)
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 practicable, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/070924 A1 (MIMOS BERHAD [MY]; SHENG DANIEL BIEN CHIA [MY]; SHIH TEH AUN [MY]) 31 May 2012 (2012-05-31) page 3, line 23 - page 4, line 13; claims 1-5; figures -----	1-4
A	US 2012/070964 A1 (PERRAUD SIMON [FR] ET AL) 22 March 2012 (2012-03-22) paragraphs [0051] - [0061]; figure 2; example 1 -----	1-4
A	US 2011/136288 A1 (DUANE PETER [US] ET AL) 9 June 2011 (2011-06-09) paragraphs [0152], [0169] - [0175] -----	1-4
A	US 2008/283821 A1 (PARK SUNG-SOO [KR] ET AL) 20 November 2008 (2008-11-20) paragraph [0031]; claim 4 -----	1-4

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Further documents are listed in the continuation of Box C.

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See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/MY2013/000227

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