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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 November 2006 (02.11.2006)

PCT

(10) International Publication Number
WO 2006/114781 A2

(51) International Patent Classification:
C23C 18/12 (2006.01)

(21) International Application Number: PCT/IE2006/000041

(22) International Filing Date: 26 April 2006 (26.04.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2005/0254 26 April 2005 (26.04.2005) IE

(71) Applicant *(for all designated States except US)*: **UNIVERSITY COLLEGE CORK - NATIONAL UNIVERSITY OF IRELAND, CORK** [IE/IE]; College Road, Cork (IE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **CREAN, Gabriel, M.** [IE/IE]; The Hawthorns, French Furze, Carrigaline, County Cork (IE). **REDMOND, Gareth** [IE/IE]; 17 Annmount, Friar's Walk, Cork (IE).

(74) Agents: O'BRIEN, John, A. et al.; c/o John A. O'Brien & Associates, Third Floor, Duncairn House, 14 Carysfort Avenue, Blackrock, County Dublin (IE).

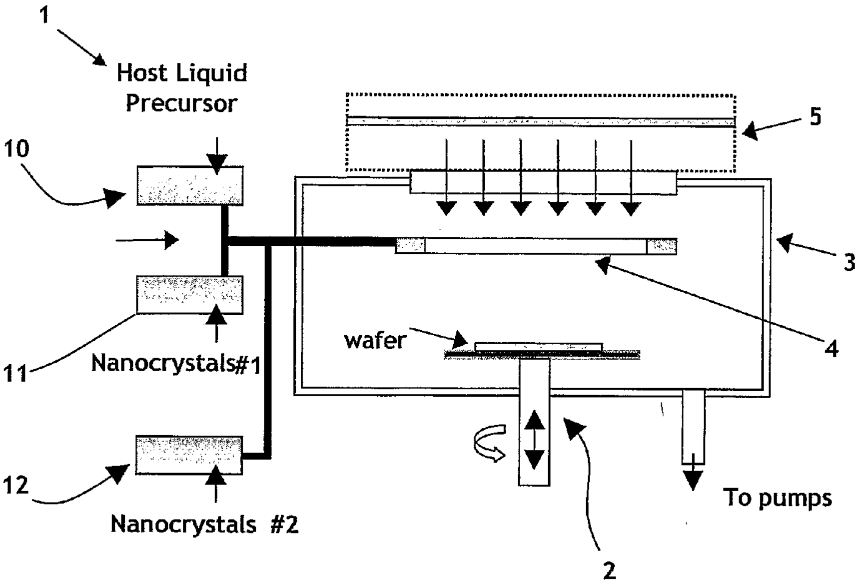
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC,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

(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, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DEPOSITION OF MATERIALS



(57) Abstract: A liquid injection system (10) receives a flow of host material in liquid precursor form and forms the liquid flow into a spray, which is delivered by a head (4) in a chamber (3). Nano-particle carrier liquid injector systems (11, 12) receive flows of nano-particles dispersed in liquid carriers, and form the liquid into a spray which is also delivered over the substrate wafer by the spray head (4). The sprayed material forms a deposit on the substrate in the chamber. A UV source (5) is operated so that the deposited material forms a layer on the substrate. The layer comprises nano-particles embedded in the host material.

WO 2006/114781 A2

"Deposition of materials"

Introduction

The invention relates to deposition of a composite coating or layer on a substrate, the coating having particles embedded in a host material.

It is known to form an oxide layer on silicon in a process involving application of high temperatures, in excess of 800°C.

The invention is directed towards providing for more versatility in composition of coatings which are applied. Another object is to achieve this versatility with low-temperature processing and/or where the composite coating is to include nano-particles.

Statements of Invention

According to the invention, there is provided a method of forming a composite layer on a substrate, the layer comprising a host material in which nano-particles of a different material are embedded, the method comprising the steps of:

> providing the host material in a liquid precursor form,
>
> dispersing the nano-particles in a carrier liquid,
>
> forming the liquids into a spray and directing the spray so that it forms a deposit on the substrate, with relative proportions of the liquids contributing to the spray according to a control scheme to achieve a desired layer composition, and
>
> treating the deposit so that it forms the layer.

In one embodiment, the nano-particles are chemically synthesised to provide the desired nano-particle size and composition in the layer.

In one embodiment, the nano-particles are dispersed in the carrier liquid with a density chosen according to the desired density of nano-particles embedded in the layer.

In one embodiment, the control scheme times inclusion of the liquids to achieve a stratum of nano-particles in the layer.

In one embodiment, the substrate is heated to a temperature of less than 500°C.

In one embodiment, the substrate is a silicon wafer.

In one embodiment, the deposit is treated by irradiation with UV radiation.

In one embodiment, the radiation is generated by an excimer lamp.

In one embodiment, the liquids are formed into a spray by an injection system and the spray is delivered to a spray head.

In another embodiment, there are at least two different nano-particle materials, and the relative proportions are chosen to achieve a desired relative concentration of nano-particles in the layer.

In one embodiment, the host material is in a carrier liquid.

In one embodiment, the host material comprises titanium isopropoxide solution.

In one embodiment, the host material carrier liquid comprises hexane.

In one embodiment, the nano-particle carrier liquid comprises hexane.

In another aspect, the invention provides an apparatus for forming a composite layer on a substrate, the layer comprising a host material in which nano-particles of a different material are embedded, the apparatus comprising:

means for supporting the substrate;

means for receiving the host material in a liquid precursor form,

means for receiving a carrier liquid with the nano-particles dispersed in the carrier liquid,

spray means for forming the liquids into a spray and directing the spray so that it forms a deposit on the substrate, with relative proportions of the liquids contributing to the spray according to a control scheme to achieve a desired layer composition,

a controller for implementing said control scheme; and

means for treating the deposit so that it forms the layer.

In one embodiment, the substrate support comprises a rotating stage.

In one embodiment, the spray means comprises a plurality of injector systems, at least one per liquid.

In one embodiment, the treatment means comprises an irradiation means.

In one embodiment, the irradiation means comprises a UV source.

Detailed Description of the Invention

The invention will be more clearly understood from the following description of some embodiments thereof, given by way of example only with reference to the accompanying drawings in which:-

Fig. 1 is a schematic representation of a process of the invention;

Figs 2 to 6 are diagrams illustrating process steps; and

Figs. 7(a) and 7(b) are 10X bright-field and epifluorescence micrographs respectively (with 200ms integration) of portions of layers formed according to the invention.

Referring to Fig. 1 an apparatus 1 for co-deposition of materials to form a coating on a substrate is shown. The apparatus 1 comprises a rotating stage 2 in a processing chamber 3 at sub-atmospheric pressure. The apparatus 1 also comprises a spray head 4 having an aperture for passage of UV light from a UV source 5 to a wafer on the stage 2.

The apparatus 1 also comprises a liquid injection system 10 for receiving a flow of host material in liquid precursor form. The system 10 forms the liquid flow into a spray, which is delivered by the head 4 in the chamber 3.

The apparatus 1 also comprises nanocrystal injector systems 11 and 12. These receive a flow of nano-particles dispersed in a liquid carrier, and form the liquid into a spray which is also is delivered over the wafer by the spray head 4.

In this specification, the terms “nano-crystal” and “nano-particle” are interchangeable, and mean particles in the nano-particle size range.

Instead of being dispersed in a carrier liquid, the nano-particles may be solubilised as a colloidal sol. This may be achieved by a charged surface coating or by steric hindrance.

The method of manufacture includes the steps of maintaining the substrate at an appropriate temperature. This is preferably below 500°C.

The sprayed material forms a deposit on the substrate in the chamber. The UV source 5 is operated so that the deposited material forms a layer on the substrate. The layer comprises nano-particles embedded in the host material.

An advantage of the invention is that the nano-particles may be chemically synthesised to have the precise chemical and physical properties desired. Also, the nano-particles are dispersed in the carrier liquid with a density chosen according to the desired density of nano-particles in the host material of the layer. As this is done "offline" in a highly controlled process there is very precise control over the nano-particle properties and their density. This is an advantageous departure from the prior art, in which the nano-particles are formed "inline" during the deposition process, such as in CVD processes.

Another advantage is that the pattern of the nano-particles in the host material may be easily and precisely controlled. This is achieved by simply controlling the flows of the host and nano-particle/carrier streams. In one embodiment, the flows are pulsed with inter-leaving according to the desired patterns. There may, for example, be zero flow of the nano-particle stream for a period so that when it is started and subsequently stopped it forms a discrete stratum within the host material.

Instead of use of UV irradiation, the deposited materials may be thermally decomposed at the heated substrate surface in order to form the layer.

Also, there may be removal of stabilising moieties previously attached at the nano-particle surfaces, e.g. alkyl thiol molecules, by UV exposure to facilitate incorporation of the nano-particles in the host matrix.

Fig. 2.shows a substrate 20 onto which a layer 21 is formed. The layer 21 comprises a host matrix 22 with embedded nano-particles 23.

Referring to Fig. 3, the apparatus 1 may be used in a method of co-depositing a host matrix and nano-particles to form a stratum in a layer on a substrate, whereby the host material liquid precursor is introduced to form a host matrix 30 on a silicon substrate 20, and a nano-particle/carrier stream is pulsed for a defined period during the host matrix deposition resulting in the formation of a defined stratum 31 of nano-particles. Subsequent deposition of host material completes a layer 40 having a buried stratum 31 of nano-particles.

Referring to Fig. 4, the apparatus 1 may alternatively be used to perform a method of co-depositing a host matrix and nano-particles to form a compositionally graded layer 50 on a substrate 20. The second nano-particle injection system 12 is operated in a controlled fashion during the host matrix formation to allow a graded concentration of nano-particles 51 within the host matrix as shown in Fig. 4.

Referring to Fig. 5, another method forms a sequentially varying multilayer structure 60 on a substrate 20 with parallel injection of the host liquid and a nano-particle/carrier liquid, but with sequential steps of the different nano-particle injections by the systems 11 and 12. This results in the formation of a multilayer, multifunctional thin film structure 60 on the substrate as shown in Fig. 5.

Referring to Fig. 6, the apparatus 1 may be used in a method of forming a host layer 80 embedded with a plurality of different species of nano-particles 81 and 82 on a substrate. There is parallel injection of the host matrix and a plurality of different nano-particle carrier liquids. This results in the formation of randomly distributed nano-particles of different properties within a host matrix 83.

It is possible to continuously carry out any sequence of process deposition steps to deposit a multilevel, multifunctional structure.

The host material liquid and the nano-particle carrier liquid or liquids may be pre-mixed and injected together for complete dispersion of the nano-particles in the host material in the layer.

The low temperature environment of this process is very well suited to deposition of nano-sized metallic and semiconductor nanocrystals since size effects such as suppression of melting point are well known. Low temperature deposition ensures that the risks of nano-crystal melting or phase change during deposition are minimised.

In an example, a 1:1 ratio of 0.1M titanium isopropoxide solution in hexane and a 2.5 mg/ml CdTe(ZnS) nanocrystal suspension (also in hexane) were mixed together. The resulting mixture was agitated in an ultrasonic bath to ensure homogeneity. A titania film incorporating CdTe(ZnS) nano-particles with thickness = 15nm was then prepared by injection of 300 droplets of this host matrix precursor and nanocrystal mixture into the reaction chamber from a single sample bottle via a single liquid delivery line. The evaporation temperature was fixed at 200°C and the substrate temperature was maintained at 365°C. 15 sccm of N_2O were also used as a reactant gas to avoid carbon incorporation into the film, as a result of hexane cracking. Images of nano-crystals incorporated in the titania host matrix prepared in this way are shown in Figs. 7(a) and (b).

The following summarises some features and advantages of the invention:

Co-depositing a host matrix and nano-particles in a single step process to form a functional layer on a substrate from multiple or single sources.

Co-depositing a host matrix and nano-particles to form a stratum in a layer on a substrate

Co-depositing a host matrix and nano-particles to form a compositionally graded layer on a substrate

Forming a sequentially varying multilayer structure on a substrate

Forming a host layer embedded with a plurality of different nano-particles on a substrate

Forming a range of layer morphologies depending on the concentration of nano-particles injected, ranging from isolated islands through to discontinuous and ultimately continuous films.

It will be appreciated that removal of stabilising moieties facilitated by UV exposure during deposition has several beneficial consequences, including:

a. Reduction of adventitious contaminants e.g. carbon

b. At high concentration deposition, exposure of the reactive (not fully coordinated) surface atoms of the nano-crystals facilitates nano-crystal fusion and formation of coherent films such as. Au.

c. For silicon nano-crystals exposure of the reactive surface atoms in this way may also facilitate wetting of the nanocrystals by simultaneously forming a SiO2 host matrix and passivation of the nanocrystal surface states by covalent bonding to this SiO2 host.

d. Furthermore, hydrogen or another suitable agent may be incorporated into the reaction mixture during host Si NC deposition and incorporated into the SiO2 matrix in order to enhance the passivation of the surface and interface states between the Si NC and oxide host.

The invention is not limited to the embodiments described but may be varied in construction and detail.

Claims

1. A method of forming a composite layer on a substrate, the layer comprising a host material in which nano-particles of a different material are embedded, the method comprising the steps of:

   providing the host material in a liquid precursor form,

   dispersing the nano-particles in a carrier liquid,

   forming the liquids into a spray and directing the spray so that it forms a deposit on the substrate, with relative proportions of the liquids contributing to the spray according to a control scheme to achieve a desired layer composition, and

   treating the deposit so that it forms the layer.

2. A method as claimed in claim 1, wherein the nano-particles are chemically synthesised to provide the desired nano-particle size and composition in the layer.

3. A method as claimed in claims 1 or 2, wherein the nano-particles are dispersed in the carrier liquid with a density chosen according to the desired density of nano-particles embedded in the layer.

4. A method as claimed in any preceding claim, wherein the control scheme times inclusion of the liquids to achieve a stratum of nano-particles in the layer.

5. A method as claimed in any preceding claim, wherein the substrate is heated to a temperature of less than 500°C.

6. A method as claimed in any preceding claim, wherein the substrate is a silicon wafer.

7. A method as claimed in any preceding claim, wherein the deposit is treated by irradiation with UV radiation.

8. A method as claimed in claims 6 or 7, wherein the radiation is generated by an excimer lamp.

9. A method as claimed in any preceding claim, wherein the liquids are formed into a spray by an injection system and the spray is delivered to a spray head.

10. A method as claimed in any preceding claim, wherein there are at least two different nano-particle materials, and the relative proportions are chosen to achieve a desired relative concentration of nano-particles in the layer.

11. A method as claimed in any preceding claim, wherein the host material is in a carrier liquid.

12. A method as claimed in claim 11, wherein the host material comprises titanium isopropoxide solution.

13. A method as claimed in claims 11 or 12, wherein the host material carrier liquid comprises hexane.

14. A method as claimed in any preceding claim, wherein the nano-particle carrier liquid comprises hexane.

15. An apparatus for forming a composite layer on a substrate, the layer comprising a host material in which nano-particles of a different material are embedded, the apparatus comprising:

means for supporting the substrate;

means for receiving the host material in a liquid precursor form,

means for receiving a carrier liquid with the nano-particles dispersed in the carrier liquid,

spray means for forming the liquids into a spray and directing the spray so that it forms a deposit on the substrate, with relative proportions of the liquids contributing to the spray according to a control scheme to achieve a desired layer composition,

a controller for implementing said control scheme; and

means for treating the deposit so that it forms the layer.

16. An apparatus as claimed in claim 15, wherein the substrate support comprises a rotating stage.

17. An apparatus as claimed in claim 16, wherein the spray means comprises a plurality of injector systems, at least one per liquid.

18. An apparatus as claimed in any of claims 15 to 17, wherein the treatment means comprises an irradiation means.

19. An apparatus as claimed in claim 18, wherein the irradiation means comprises a UV source.

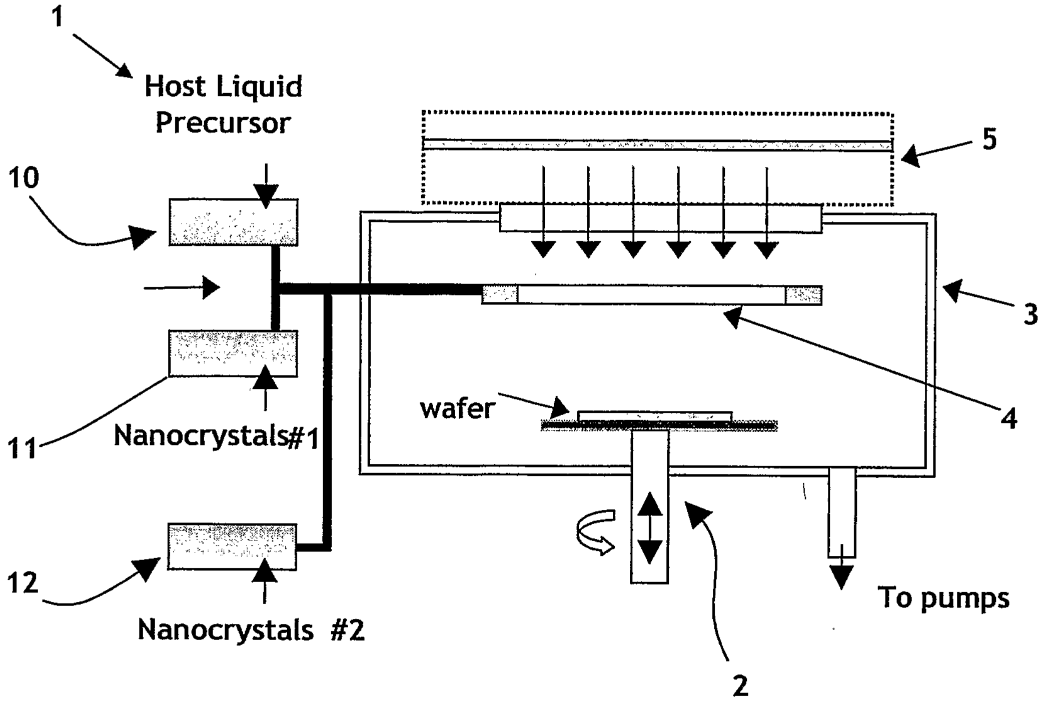

1
Host Liquid Precursor
10
11
Nanocrystals#1
12
Nanocrystals #2
5
3
4
wafer
2
To pumps

Fig. 1

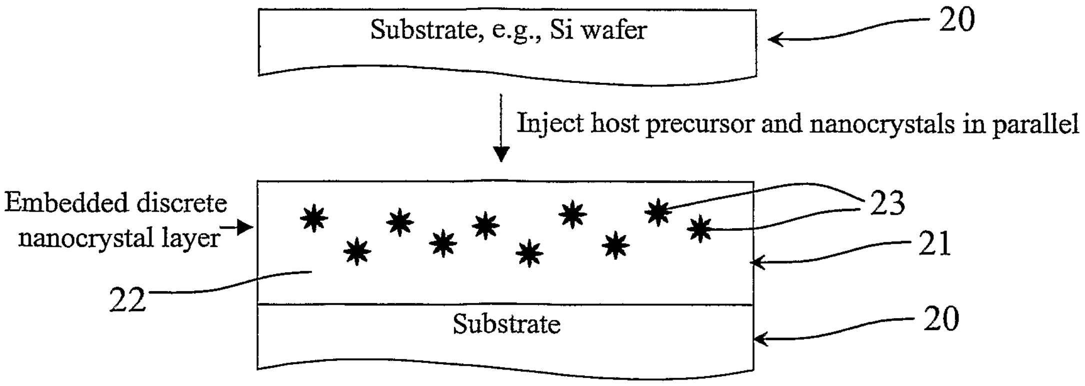

Substrate, e.g., Si wafer
20
Inject host precursor and nanocrystals in parallel
Embedded discrete nanocrystal layer
23
21
22
Substrate
20

Fig. 2

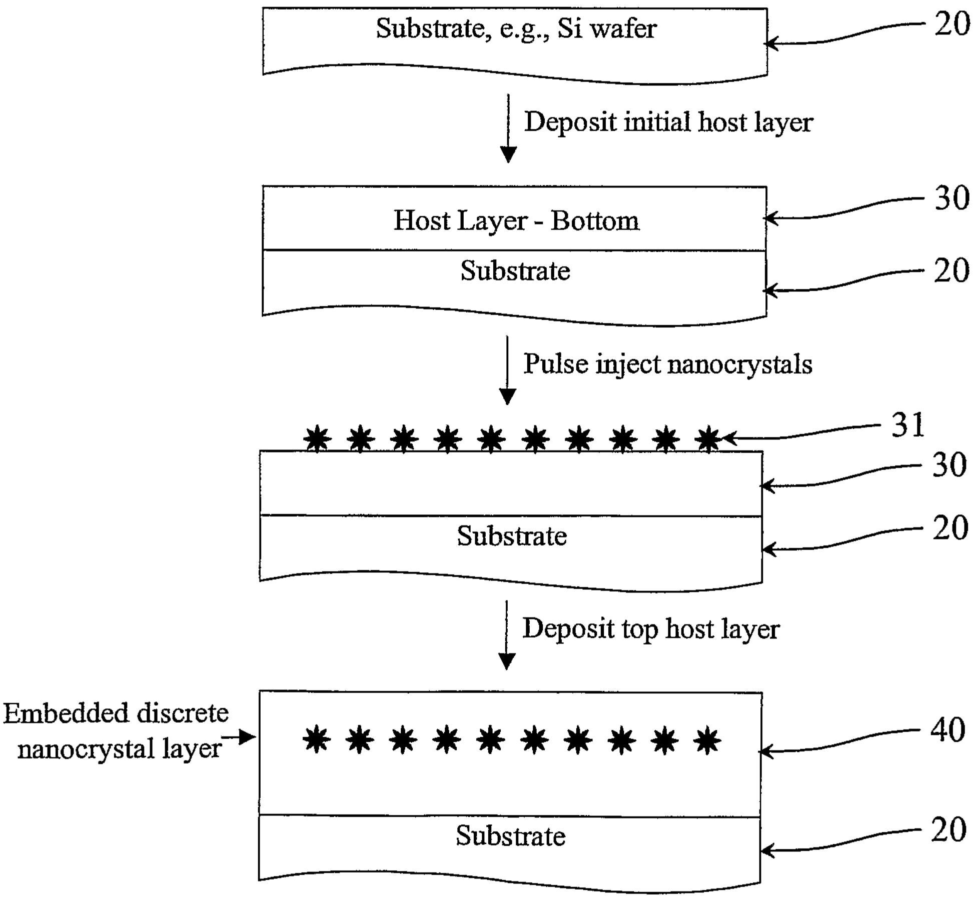

Substrate, e.g., Si wafer
20
Deposit initial host layer
Host Layer - Bottom
30
Substrate
20
Pulse inject nanocrystals
31
30
Substrate
20
Deposit top host layer
Embedded discrete nanocrystal layer
40
Substrate
20

Fig. 3

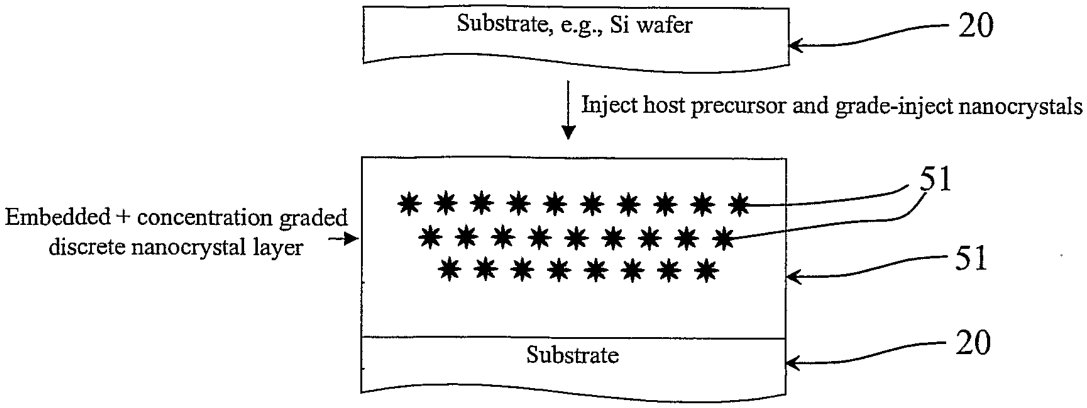

Substrate, e.g., Si wafer
20
Inject host precursor and grade-inject nanocrystals
Embedded + concentration graded discrete nanocrystal layer
51
51
Substrate
20

Fig. 4

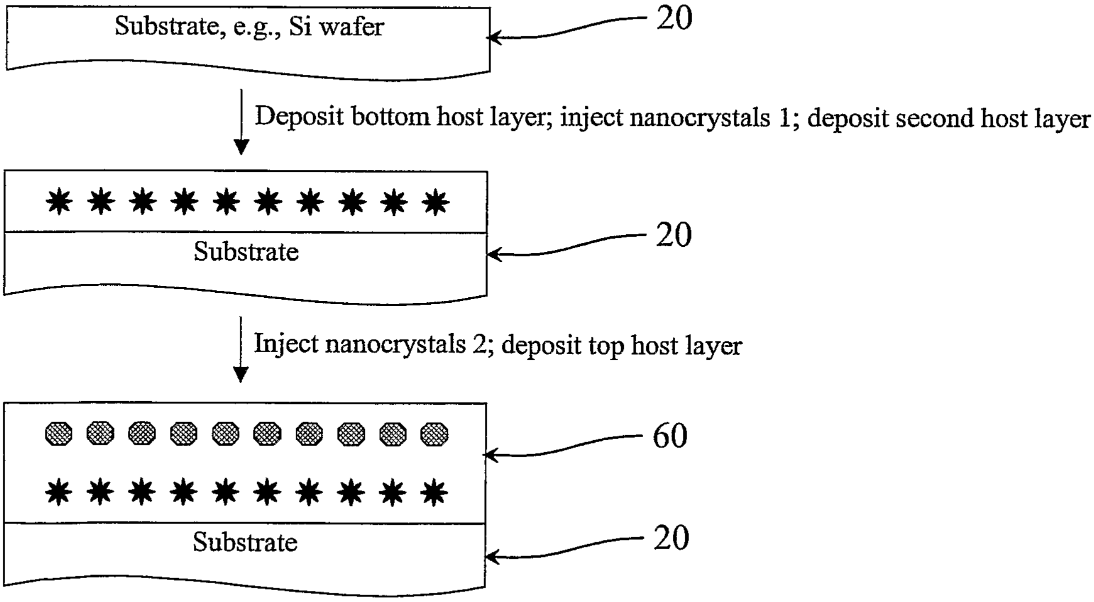

Substrate, e.g., Si wafer
20
Deposit bottom host layer; inject nanocrystals 1; deposit second host layer
Substrate
20
Inject nanocrystals 2; deposit top host layer
60
Substrate
20

Fig. 5

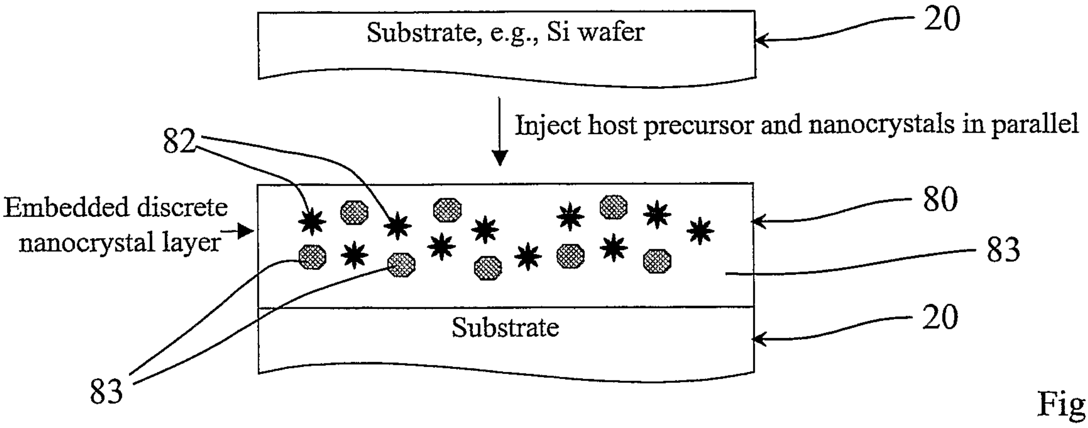


Fig. 6

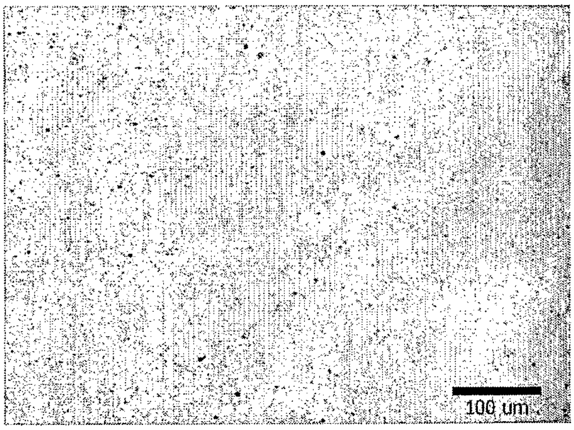


Fig. 7(a)

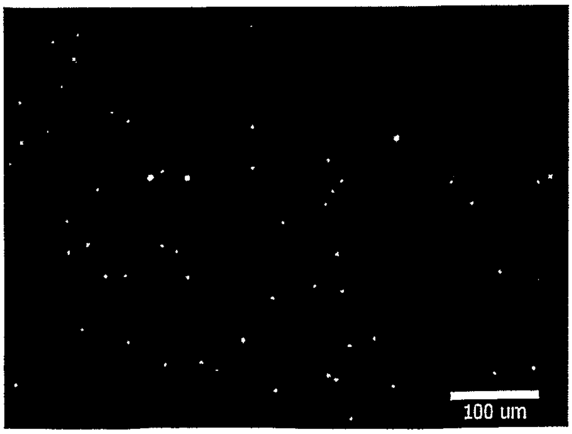


Fig. 7(b)