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[Continued on next page]

(54) Title: METHOD FOR FABRICATING HIGH ASPECT RATIO GRATINGS FOR PHASE CONTRAST IMAGING

(57) Abstract: A method with several options to manufacture high aspect ratio structures is proposed. The method is based on fabrication of high aspect ratio recess structure in silicon by dry or chemical etching and then filling the high aspect ratio recess with metal by using electroplating, atomic layer deposition, wafer bonding, metal casting or combination of these techniques. The gratings can be used for x-ray or neutron imaging, as well as for space applications.

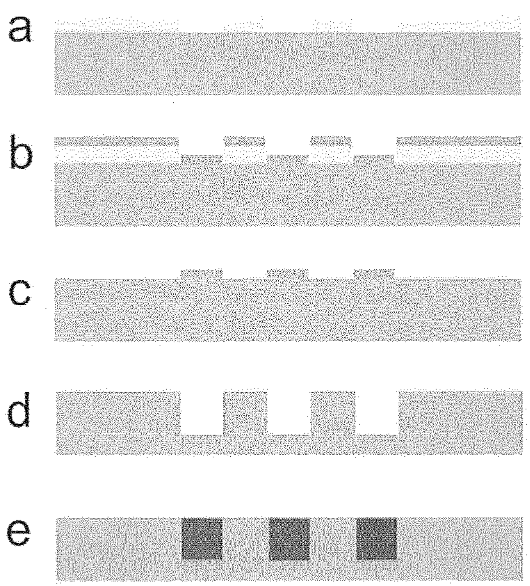

Figure 1

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Method for fabricating high aspect ratio gratings for phase contrast imaging

The present invention relates to several methods for fabricating high aspect ratio gratings for phase contrast imaging.

Interferometric X-ray and neutron phase contrast imaging is based on diffraction gratings. The essential part of the interferometer consists of two (or three) gratings: the source grating G0, eventually used to generate small local coherent spots of the source; the phase grating G1, which generates a Talbot carpet by shifting the phase of illuminating radiation, and the analyzer grating G2 which is used to analyze the Talbot carpet, conventionally using a phase stepping mode. The periods of the gratings depend on the geometry of the whole set-up. If, e.g. the set-up should fit into a standard full body computer tomograph the overall set-up (X-ray source to detector) is in the range of 1 m only. This allows for a period in the micrometer range of 2 μm for the analyzer grating G2.

Gratings' quality and the height of the analyzer grating strongly affect the quality and the contrast of the generated images, while the period depends on the geometry of the whole set-up. There is the need to fabricate gratings with 1) very high aspect ratio (>10, structural width in the micron range); 2) large area (mammography, e.g., asks for a field of view > 20cm x 20cm) and 3) good uniformity (no distortions and change in the period over the full grating area).

Moreover, the fabrication of the analyzer grating G2 is the most challenging part, as the grating period is the μm range, and large areas have to be patterned with good uniformity. The required thickness of the gold absorbing structures must be sufficient to (ideally) fully attenuate the radiation, to provide high fringe visibility and therefore best image contrast.

One of the approaches to realize such gratings is based on forming a high aspect ratio recess structure in polymer on conductive substrate and filling it with metal by electroplating. The drawback of the method is a weak mechanical stability of high aspect ratio polymer structure, which tends to collapse during the wet resist processing.

Another approach is to replace the polymer with a monocrystalline Silicon, which has a much better mechanical properties. It is essential that the filling starts only at the bottom of the grooves to ensure a complete, uniform filling. This would require a sophisticated technique to deposit a first metal seed on the bottom of the grooves, which efficiency is strongly limited to low aspect ratio grooves.

Another approach – Metal-assisted chemical etching (MACE) is an electroless chemical etching technique. MACE is reported as a simple and low-cost method used to fabricate Si nanowires, nanoporous silicon, and nanostructures. The metal catalyst layer stays at the bottom of the formed profile and can be used as a seeding layer for electroplating.

It was proposed recently to use low resistivity wafers and do seedless electroplating directly on a surface of silicon. In order to avoid electroplating on sidewalls and at the top of the structure the wafer is coated by dielectric layer before forming the recess structure in silicon. Then, after forming the recess it is additionally coated by a polymer or a silicon oxide layer. Finally, the coating is opened at the bottom of recess which allows start plating directly at the bottom of the recess, while keeping top and sidewall surfaces isolated.

It was also demonstrated that a high aspect ratio silicon structure can be filled by dipping it into liquid Bismuth. Papers demonstrate that high aspect ratio recess can be filled by Atomic layer Deposition technique and used for x-ray applications.

It is the objective of the present invention to provide method for the fabrication of high aspect ratio gratings for phase contrast imaging.

According to the present invention, several alternative approaches for manufacturing of gratings for x-ray and neutron imaging are suggested based on formation of high aspect ratio recess structures in silicon and filling them with metal:

- A process to form high aspect ratio silicon structure with pitches in micrometer range by Metal Assisted Chemical Etching. The method uses thermal annealing of the gold catalyst, which allows formation of continuous gold mesh structured films, which enables production of structures with large features and deep vertical structures.
- A process which utilizes oxidation and shadow evaporation of high etching resistance material over the high aspect ratio recess in low resistivity silicon, etching the oxide layer at the bottom of the recess structure and electroplating. The process enables relaxed tolerances for the process step parameters and a realization of small pitch sizes and high aspect ratios.
- A process of thermal casting of metal into high aspect ratio recess structure for x-ray applications and neutron applications. The present approach enables a use of materials with better absorbing properties for x-ray and neutrons and utilize less demanding structures with lower aspect ratios.
- A process, which utilizes a combination of deposition metallic and dielectric layers by Atomic Layer Deposition to form electroplating seeding layer in the high aspect ratio recess structure, etching the dielectric layer at the bottom of the recess structure and electroplating. This method allows excluding issues with potentially insufficient conductivity, surface oxidation and uniformity compared to a case of seedless electroplating.

- A process, which utilizes bonded silicon wafers with metal in between the "device" and carrier wafers, forming a high aspect ratio recess structure in the device layer and electroplating. This method allows excluding issues with the oxidation and uniformity compared to a case of seedless electroplating on one hand and a necessity of electrical isolation of the sidewalls in a case of metalized recess structure on the other hand.
- An application of the Phaeble technology (Eulitha, http://www.eulitha.com/technology/phabletm/), as a cost effective method to pattern gratings for x-ray and neutron phase contrast imaging applications on a large scale.

a) Metal Assisted Chemical Etching of microstructures

A method to produce x-ray optical elements with fine feature sizes is reported in literature. However, the method uses thick film catalyst and is limited to small lateral features and limited depth and a small area of the structures. Fabrication of deep recesses with micron scaled features is shown to be difficult either due to the movement of the metal catalyst, excess of porosity due to unbalanced charge carriers and edge bending of the catalyst pattern in case of thicker film catalyst.

Here, it is suggested to form an interconnected metal structure of the catalyst by thermal annealing treatment of the lifted-off layer and to use a solution which does not allow forming silicon structures through the holes in the interconnected metal catalyst. The present method does not need any balancing structures and can be applied to a whole wafer size. Etching of 4" scale wafers was demonstrated, but it can be upscaled to any wafer size providing metal patterning and the etching batch of required size available. Figure 1 show schematic drawing of the process of the Metal Assisted Chemical Etching:

a. Pattern on the substrate;
b. Metal catalyst film deposition;

c. Lift-off and thermal annealing;
d. Metal Assisted Chemical Etching;
e. Electroplating.

Figure 2 demonstrates the effect of the proposed process on quality of the fabricated structures. In top row a surface of the fresh evaporated gold film (left) and a thermally annealed gold film (right) and in the bottom row corresponding structures etched into silicon are shown. A strong out-of-vertical etching is visible (FIG.2, left bottom) in the grating realized without the formation of the metal interconnected structure (step c) of the present invention, the undercut is a consequence of the metal catalyst movement during the etching process. The metal catalyst movement was solved by introducing the formation of the metal interconnected structure (step c in Figure 1) by thermal annealing. For example, metal de-wetting during thermal annealing occurs if a thin film of Au is deposited on Oxygen-terminated Silicon surface. Metal de-wetting (FIG.2, top right) produces an interconnected metal structure that mechanically strengths the metal catalyst avoiding deformation during the MACE process.

b) Seedless electroplating method

In the art, a method is reported to create high aspect ratio recess structures using an oxide or Polymer mask on top of the structures, oxidation, etching of the oxide at the bottom of the recess and electroplating. The key condition in all of these methods is to have an extra dielectric layer on top of the recess structures before the oxidation step. This allows opening the oxide at the bottom without losing the whole dielectric layer on top. However, when decreasing the pitch of the grating and increasing the aspect ratio, the etching ratio in the bottom of recess decreases drastically. Here, a solution is suggested which eliminates the necessity of using oxide on top of the silicon and which can be applied for gratings with high aspect ratio independently on the pitch.

Figure 3 shows a schematic drawing of high aspect ratio formation using a standard lithographic technique. The sample consists of a wafer, an intermediate layer, serving as an etching mask and a resist and undergoes the following steps:

a. Patterning of the photoresist;
b. Pattern transfer into hard mask;
c. Etching of high aspect ratio recess structure;
d. Removal of the mask.

Patterning of photoresist can be done by means of photolithography, interferometric lithography, Talbot displacement lithography or electron beam lithography or other methods allowing to realize the features of required size on a required area. After the exposure and development of the resist the pattern can be transferred to underlying hard mask by chemical etching or by dry etching. The use of an intermediate hard mask allows increasing the selectivity between the substrate material and a mask material in the following step. This material can be either metallic or dielectric. The etching of high aspect ratio recess structure can be realized by several options – anisotropic etching in potassium hydroxide solution or deep reactive ion etching by Bosch process or cryogenic etching. Finally, the mask material is removed. The described process is used as a standard routine to prepare a high aspect ratio recess structure and uses it as a template to be filled with highly absorbing material. In this section it is suggested to do it the way shown in Figure 4:

a. Fabrication of a high aspect ratio recess structure;
b. Isolation of top and sidewall of the recess;
c. Deposition of hard mask by shadow deposition;
d. Removal of the oxidation layer at the bottom of high aspect ratio recess mask with optional removal of the mask on top of the recess.
e. Electroplating.

Step “b” can be performed by thermal oxidation, wet oxidation, atomic layer deposition (ALD) or plasma enhanced chemical vapor deposition (PECVD). In case the substrate material is silicon and the method is thermal or wet oxidation the insulation material is silicon oxide, while in case of ALD or PECVD the insulation material can be chosen from a variety of dielectrics (e.g. aluminum oxide, silicon nitride, silicon oxide or others). After the step “b” an etching mask with high etching resistance is deposited on top of the grating by shadow deposition. The etching mask can be metal, such as Chromium or a dielectric, such as sapphire. In shadow evaporation the evaporated material is approaching the surface of the sample at an angle and is deposited to the top and partly to the sidewalls of the high aspect ratio recess structure. Those angles should be chosen in such a way that the material is not deposited at the bottom of the high aspect ratio recess structure. Depending on the etching selectivity, the required thickness of this layer can be 10-100 times lower than required thickness of the oxide layer in the art. This makes our invention distinct from the above prior art and enables fabrication of higher aspect ratio structures and smaller lateral dimensions.

Alternatively, depending on experimental conditions, the isolation layer deposited in step “b” can readily be deposited in such a way that the thickness of the layer on top of the recess structure is much higher than at the bottom. This, for instance, is given by default in case of deposition by PECVD. In this case, the step “c” can be skipped.

Alternatively, step “b” can include thermal oxidation and deposition of extra insulation layer by PECVD. This would provide a formation of thicker layer on top of the high aspect ratio structure and could also allow skipping the step “c”.

c) Fabrication of gratings utilizing Atomic Layer Deposition and electroplating

Another approach suggested is based on atomic layer deposition (ALD) of a seed layer. This method is known to provide very conformal coating of high aspect ratio structures with metals and dielectrics. Complete or partial conformal filling of the very high aspect ratio recesses by ALD can be achieved by this method. Here, several approaches are suggested to utilize ALD for fabrication of gratings for x-ray and neutron imaging applications. Up to a recent time, the ALD was considered to be slow and expensive process, which is only suitable for deposition of layers in tens or few hundreds of nanometers range. However, a complete filling of micron wide high aspect ratio structures is a costly and time-consuming process. It is suggested to use the ALD for a deposition of a conductive seed layer and filling the high aspect ratio recess structure by electroplating. The process includes deposition of conductive and dielectric layers over the high aspect ratio recess structure and removing the dielectric layer from the bottom of recess structures. By doing that the electroplating can be realized only at the bottom of the recess structure, while keeping other surfaces protected by dielectric. The process steps are shown in Figure 5:

a. Fabrication of a high aspect ratio recess structure;
b. Deposition of metal and dielectric layers by ALD;
c. Shadow deposition of a hard mask on top of the high aspect ratio recess structure;
d. Removal of the dielectric layer at the bottom of high aspect ratio recess structure.
e. Electroplating.

Alternatively, shadow deposition in step “c” can be replaced by PECVD coating of insulating layer. As mentioned above the PECVD layer will mostly deposit on top of the recess structure and will allow performing step “d” without losing the insulating layer on top of the high aspect ratio recess structure. An advantage of this approach compared to seedless electroplating shown above is that the plating seeding layer in this case is a metal, which has much higher conductivity and makes formation of the starting layer during the electroplating much easier.

d) Metal casting

The high aspect ratio structure produced in silicon can be filled by metal casting. Casting of liquid Bismuth into silicon mold has been demonstrated. However, the low absorption of Bismuth requires structures with extreme aspect ratios, which limits their application in realistic systems. Ideally, the material should have high absorption of x-rays, yet maintain good wetting properties. The most common x-ray absorbing materials for hard x-rays reported in literature are Ta, W, Ir, Pt, Au and Bi. Among them, gold is perhaps the most frequently used due to the fact that it can be efficiently deposited by electroplating. While only Bi and Au have melting temperatures below the melting point of silicon. Gold is much more efficient in absorption of x-rays, compared to Bismuth. For example, one needs 30 micron of Gold against 50 microns of Bismuth to have the same absorption level at 30 keV x-ray energy. The melting point of Bismuth is only 271°C, while melting point of Gold is 1064°C. The use of high temperature, as required to melt gold has a risk of diffusion of one material into another or even forming an eutectic alloy. However, a need of higher thickness of metal in case of Bismuth introduces complications both for the fabrication and practical use of such gratings. Here, it is suggested to use an eutectic Au80Sn20 alloy instead of pure Au, which has a melting temperature of only 280°C and absorbing properties even better than that of pure gold. The Au80Sn20 alloy is commonly used in microelectronic industry and has very good wetting properties, especially, on gold surfaces. The soldering is usually done in ambient environment (Nitrogen environment with 5% Hydrogen content), which improves the flow of the solder along the surfaces.

In case of neutron radiation the only suitable metal which substantially absorbs neutrons is Gadolinium. The melting point of Gd (1312°C) is below the melting temperature of

Silicon (1414°C). However, as in case of gold some alloys with lower melting temperature could also be used.

Metal or metal layer or alloy foil can be applied on high aspect ratio recess structure (for example, made of Silicon) and melted in vacuum with, optionally, applying additional pressure. This can be easily controlled in a standard wafer bonding machine. Once melted the liquid metal is filled into silicon recess structure. Several options exist to realize this process (see Figure 6):

- Figure 6 left: Metal casting into pure silicon recess structures, consisting of following steps:
  a. Fabrication of a high aspect ratio recess structure;
  b. Deposition of casting material layer or a foil;
  c. Casting at elevated temperature and, optionally, pressure;
  d. Removal of the excess material.

- Figure 6 center: Melting of metal coating deposited onto sidewalls of the recess structure:
  a. Fabrication of a high aspect ratio recess structure;
  b. Deposition of casting material layer (for example, by electroplating);
  c. Casting at elevated temperature and, optionally, pressure;
  d. Removal of the excess material.

- Figure 6 rights: Metal casting into silicon recess structures coated with a thin layer of material with favorable wetting properties:
  a. Fabrication of a high aspect ratio recess structure;
  b. Coating the recess structure with a layer having good wetting properties;
  c. Deposition of casting material layer or a foil;
  d. Casting at elevated temperature and, optionally, pressure;
  e. Removal of the excess material.

e) Bonded wafers technique

Plating in high aspect ratio recess structure suggests having an electroplating seeding layer at the bottom of the recess. This can be realized by the method suggested here. Two metalized Silicon wafers is used and Metal-Metal bonding is employed to realize sandwiched Silicon-Metal-Silicon wafer as shown in Figure 7 and perform the following process steps:

- The bonded wafer, consisting a carrier wafer, metal layer and device layer of targeted thickness;
- Etching of high aspect ratio recess structure through the device layer;
- Electroplating (The metal between the wafer serves as an etching stop layer and as a seeding layer for the electroplating step);
- Removal of the carrier wafer (optional).

The metal between the wafers can be, for example gold or copper. If the metal is copper, the device layer can be separated from the carrier wafer by wet etching of copper sacrificial layer in nitric acid. If the support layer is transparent (i.e., glass, quartz or sapphire) it allows to inspect the progress of etching of the sacrificial layer.

Alternatively to metal, an additional polymer sacrificial layer can be used between the wafers, which allows chemical or thermal removal of the carrier wafer. The advantage of the removal of the device wafer is, on one hand – an increased x-ray transmission required for low energy applications through a thinner wafer and, on the other hand – an improve of the elasticity of the grating due to thinner substrate required for setups with divergent beams, which requires corresponding bending of the gratings.

f) Fabrication of bended gratings

The visibility of the phase contrast imaging depends on the absorbing power of the absorption gratings G0 and G2. The higher is the energy, the thicker (taller) grating lines are required to achieve a necessary opacity of the lines in the x-ray beam. However, if the x-ray beam is divergent, which is a case in many x-ray tube based source, there is certain limitation for the aspect ratio of the gratings which can be practically used in planar geometry. One of the solutions to address this problem is to bent the grating in such a way that the high aspect ratio lines follow the beam direction. However, during the bending of the high aspect ratio structures filled with metal, a line distortion would appear due to the fact that the bending assumes lateral stretching of the surface. This lateral stretching may cause random irregular separation of the metal inside the high aspect ratio recess structure. In order to avoid this effect we suggest to perform metal filling into the recess structure by electroplating, casting ALD or any other method when the substrate with the high aspect ratio recess is bent. The bending curvature should be designed according to the setup geometry to be used. By doing so, the high aspect ratio recess structures will be filled with metal without distortions, the line directions will correspond to the divergence of the beam and the substrate will keep the bending curvature by itself.

g) Patterning of gratings for x-ray and neutron imaging

The prior art does not say how the small pitch gratings for x-ray or neutron applications can be patterned cost efficiently on a large scale. Standard photolithography can potentially be used down to a pitch size of ~1 micrometer. However, in practice, severe uniformity problems appear when processing pitches of few microns are processed on thin wafers with thickness below 500 micrometers. Here it is suggested to use displacement Talbot lithography to produce gratings for x-ray and neutron applications with a pitch of few microns and below. The advantage of the method compared to a standard photolithography is that it is contactless. This makes it insensitive to imperfections (bow/wrap) or to the presence of particles on wafers and is particularly suitable for processing thin substrates. Features of these dimensions can be also realized by laser holographic exposures. However, the accuracy for the pitch is limited to setting of the angle between the beams, while in case of displacement Talbot lithography the pitch is given by the mask.

Patent Claims

1. A method for fabricating high aspect ratio gratings, comprising:

- providing a substrate and a patterned metal catalyst film disposed on said substrate;
- forming an interconnected structure within the patterned metal catalyst film by heating the substrate at temperature between 100°C and the melting temperature of the substrate;
- etching the substrate by an etchant solution containing a fluoride etchant and an oxidizing agent, thereby controlling the metal catalyst movement during metal assisted chemical etching of high aspect ratio structures.

2. The method according to claim 1, wherein said heating comprises using a process selected from the group consisting of thermal annealing, laser annealing, rapid thermal annealing, furnace, flash annealing, electron beam irradiation, ion beam irradiation, exposure to plasma.

3. The method according to claim 1 or 2, wherein the said metal is selected from the group of gold, silver, platinum and tungsten, wherein the said substrate comprises a material selected from the group consisting of silicon, GaAs, InP, GaP, GaN, and III-V semiconductors and any compounds or alloys of these materials.

4. A method for fabricating high aspect ratio gratings, comprising:

a) providing a high aspect ratio recess structure;
b) generating an electrical insulation on the high aspect ratio recess structure by thermal oxidation, plasma enhanced oxidation, coating a dielectric layer by PECVD or ALD dielectric layer or any combination of these techniques;

c) depositing by shadow deposition of material with high etching resistance on top of the electrical insulation and, partly, on sidewalls of high aspect ratio recess structure;
d) etching the insulation layer at the bottom of the recess structure through a high etching resistance mask; and
e) seedless electroplating into the high aspect ratio recess structure.

5. A method of claim 4, wherein the electroplated metal is selected from a group of gold, nickel, copper, wherein the said substrate comprises of a material selected from the group consisting of silicon, GaAs, InP, GaP, GaN, and III-V semiconductors and any compounds or alloys of these materials.

6. A method for fabricating high aspect ratio gratings, comprising the step of:
a) forming a high aspect ratio recess structure by deep reactive ion etching, anisotropic wet-etching, metal assisted chemical etching or photo-assisted chemical etching;
b) coating the recess structure by a conductive layer by atomic layer deposition;
c) coating the recess structure by an insulating layer by atomic layer deposition or PECVD;
d) shadow deposition of material with high etching resistance on top and, partly, on sidewalls of high aspect ratio recess structure by thermal evaporation or PECVD;
e) etching the insulation layer at the bottom of the recess structure through a high etching resistance mask;
f) filling the high aspect ratio recess structure by electroplating.

7. The method of claim 6, wherein the electroplated metal is selected from a group of gold, nickel, copper, wherein the said substrate comprises of a material selected from the group consisting of silicon, GaAs, InP, GaP, GaN, and III-V semiconductors and any compounds or alloys of these materials.

8. The method of claim 6 or 7, wherein the conductive layer is selected from a group of Ir, Pd, Pt, Ru, W wherein the insulating layer is selected from a group of SiO_2, Al_2O_3, TiO_2, CaO, CuO, Er_2O_3, Ga_2O_3, HfO_2, La_2O_3, MgO, Nb_2O_5, Sc_2O_3, Ta_2O_5, V_XO_Y, Y_2O_3, Yb_2O_3, ZnO, ZrO_2.

9. A method for fabricating high aspect ratio gratings, comprising:
a) forming a high aspect ratio recess structure by deep reactive ion etching, anisotropic wet-etching, metal assisted chemical etching or photo-assisted chemical etching; and
b) casting of metal into recess structure.

10. The method of claim 9, wherein the electroplated metal is selected from a group of gold, nickel, copper, wherein the said substrate comprises of a material selected from the group consisting of Si, GaAs, InP, GaP, GaN, and III-V semiconductors and any compounds or alloys of these materials.

11. The method of claim 9 or 10, wherein the casting material is selected from a group consisting of Au, Sn, $Au_{20}Sn_{80}$, Au-Sn alloy, Au-Si alloy.

12. A method for fabricating high aspect ratio gratings, comprising:
a) forming a high aspect ratio recess structure by deep reactive ion etching, anisotropic wet-etching, metal assisted chemical etching or photo-assisted chemical etching;
b) pre-filling the recess structure by electroplating;
c) melting the electroplated metal into the high aspect ratio recess structure to prevent voids in electroplated layer.

13. The method of claim 12, wherein the electroplated metal is gold or copper, wherein the said substrate comprises of a material selected from the group consisting of silicon, GaAs, InP, GaP, GaN, III-V semiconductors and any compounds or alloys of these materials.

14. A method for fabricating high aspect ratio gratings, comprising:
a) forming high aspect ratio recess structure by deep reactive ion etching, anisotropic wet-etching, metal assisted chemical etching or photo-assisted chemical etching;
b) pre-coating of the recess structure by a material with good wetting characteristic;
c) casting of metal with low melting temperature into the high aspect ratio recess structure.

15. The method of claim 14, wherein the said substrate comprises of a material selected from the group consisting of Si, GaAs, InP, GaP, GaN, and III-V semiconductors or any compounds or alloys of these materials, wherein the electroplated metal is gold wherein the casting material selected from the group consisting of Au, Sn, $Au_{20}Sn_{80}$, Au-Sn alloy, Au-Si alloy.

16. A method for fabricating high aspect ratio gratings, comprising:
a) providing a bonded wafer comprising a carrier wafer, a metal layer and a device wafer;
b) forming a high aspect ratio recess structure in the device layer by deep reactive ion etching, anisotropic wet-etching, metal assisted chemical etching or photo-assisted chemical etching;
c) electroplating into high aspect ratio recess structure.

17. The method of claim 16, wherein carrier and device wafer consist of silicon, GaAs, InP, GaP, GaN, and III-V semiconductors or any compounds or alloys of these materials, wherein the metal layer is selected from a group consisting of Cu, Cr, Au, Ni, Al or combination of these materials.

18. The method of claim 16 or 17, wherein the support wafer is removed by chemical etching of the metal layer between the wafers.

19. A method for fabricating high aspect ratio gratings; comprising:
a) providing a bonded wafer comprising a carrier wafer, a sacrificial layer, a metal layer and device wafer;
b) forming a high aspect ratio recess structure in the device layer by deep reactive ion etching, anisotropic wet-etching, metal assisted chemical etching or photo-assisted chemical etching;electroplating into high aspect ratio recess structure; and
c) removal of the carrier wafer through the chemical dissolving or thermal treatment of the sacrificial layer.

20. A method to fabricate the absorbing grating on bended substrates; comprising the following steps:
a) forming a high aspect ratio recess structure;
b) bending the substrate to an angle corresponding to divergence of the beam and geometry of a setup to be used;
c) filling the high aspect ratio recess structure with metal.

21. A method to produce gratings for x-ray or neutron phase contrast imaging, whereas the patterning of the gratings is performed using displacement Talbot lithography.

22. A method to produce gratings for x-ray imaging, where the high aspect ratio recess structure is filled by atomic layer deposited metal from a group of Ir, Pd, Pt, Ru, W.

23. A method to produce gratings for neutron imaging, where the high aspect ratio recess structure is filled by atomic layer deposited gadolinium, gadolinium oxide or other gadolinium containing compound material.

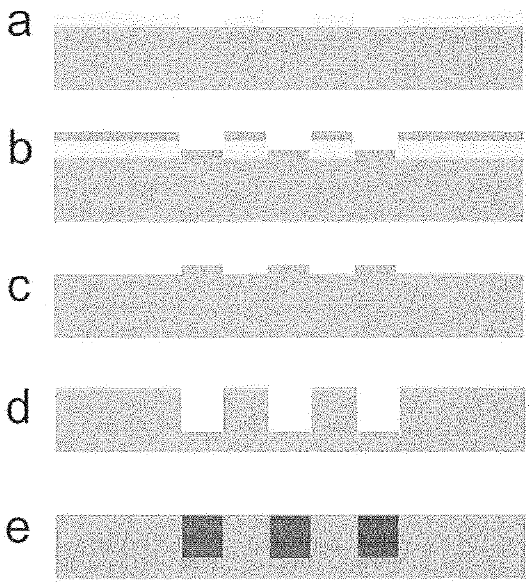

Figure 1

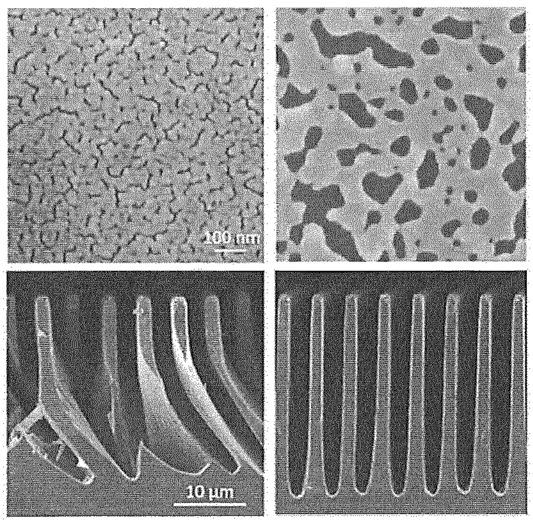

Figure 2

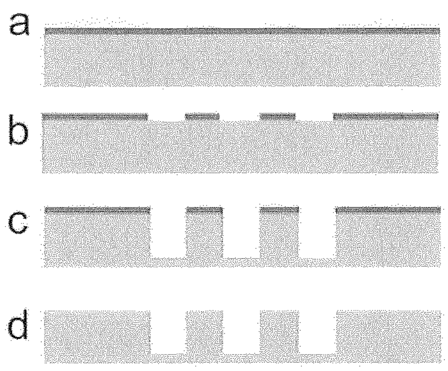

Figure 3

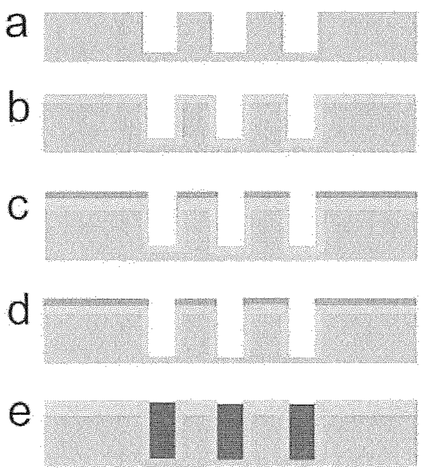

Figure 4

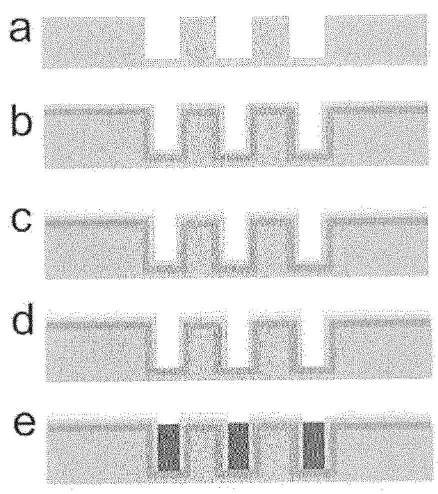

Figure 5

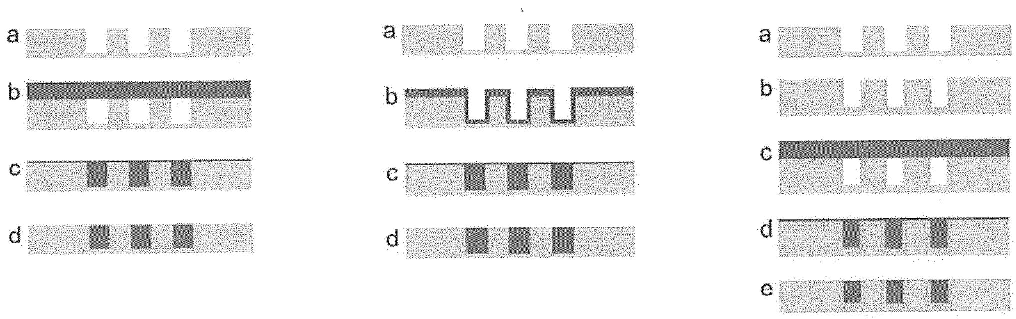

Figure 6

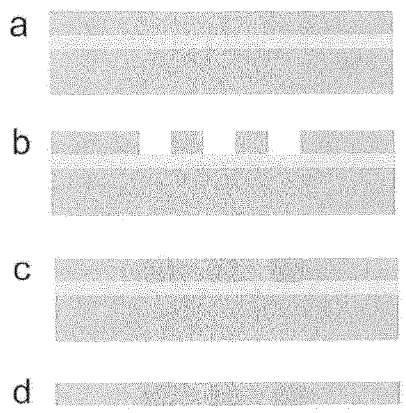

Figure 7

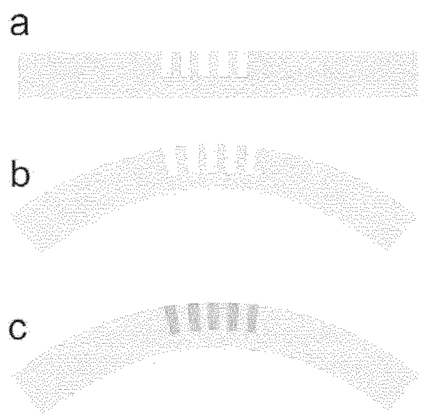

Figure 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/068658

A. CLASSIFICATION OF SUBJECT MATTER
INV. G02B5/18 B82Y10/00 B82Y40/00
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)
G02B B82Y

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHIEH CHANG ET AL: "Ultra-high aspect ratio high-resolution nanofabrication for hard X-ray diffractive optics", NATURE COMMUNICATIONS, vol. 5, 27 June 2014 (2014-06-27), XP055306490, DOI: 10.1038/ncomms5243 abstract figures 1,3 page 4, left-hand column page 5, left-hand column, paragraph 2 -----	1-3

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[X] 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 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
5 October 2016	07/12/2016

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	von Hentig, Roger

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MATT DEJARLD ET AL: "Formation of High Aspect Ratio GaAs Nanostructures with Metal-Assisted Chemical Etching", NANO LETTERS, vol. 11, no. 12, 14 December 2011 (2011-12-14), pages 5259-5263, XP055306544, US ISSN: 1530-6984, DOI: 10.1021/nl202708d abstract page 5259, left-hand column - page 5260, left-hand column, paragraph 2 figure 2 -----	1-3
X	XIULING LI: "Metal assisted chemical etching for high aspect ratio nanostructures: A review of characteristics and applications in photovoltaics", CURRENT OPINION IN SOLID STATE AND MATERIALS SCIENCE, vol. 16, no. 2, 1 April 2012 (2012-04-01), pages 71-81, XP055306568, GB ISSN: 1359-0286, DOI: 10.1016/j.cossms.2011.11.002 abstract page 1, right-hand column - page 2, right-hand column, paragraph 2 -----	1-3
X	LIYI LI ET AL: "Uniform Vertical Trench Etching on Silicon with High Aspect Ratio by Metal-Assisted Chemical Etching Using Nanoporous Catalysts", ACS APPLIED MATERIALS AND INTERFACES, vol. 6, no. 1, 8 January 2014 (2014-01-08), pages 575-584, XP055306611, US ISSN: 1944-8244, DOI: 10.1021/am4046519 page 575, left-hand column - page 580, left-hand column -----	1-3

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Dong Wang ET AL: "Ordered arrays of nanoporous silicon nanopillars and silicon nanopillars with nanoporous shells", Nanoscale Research Letters, 1 December 2013 (2013-12-01), pages 1-9, XP055307298, New York DOI: 10.1186/1556-276X-8-42 Retrieved from the Internet: URL:http://rd.springer.com/content/pdf/10.1186/1556-276X-8-42.pdf [retrieved on 2016-10-04] abstract page 2 figure 1 -----	1-3

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2016/068658

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-3

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-3

refer to a method for fabricating high aspect ratio gratings by providing a substrate and a patterned metal catalyst film disposed on said substrate, forming an interconnected structure within the patterned metal catalyst film by heating the substrate at temperature between 100°C and the melting temperature of the substrate and etching the substrate by an etchant solution containing a fluoride etchant and an oxidizing agent,

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2. claims: 4, 5

refer to a method for fabricating high aspect ratio gratings, by providing a high aspect ratio recess structure, generating an electrical insulation on the high aspect ratio recess structure by thermal oxidation, plasma enhanced oxidation, coating a dielectric layer by PECVD or ALD dielectric layer or any combination of these techniques and depositing by shadow deposition of material with high etching resistance on top of the electrical insulation and, partly, on sidewalls of high aspect ratio recess structure and further etching the insulation layer at the bottom of the recess structure through a high etching resistance mask and seedless electroplating into the high aspect ratio recess structure.

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3. claims: 6-15

refer to a method for fabricating high aspect ratio gratings, by forming a high aspect ratio recess structure by deep reactive ion etching, anisotropic wet-etching, metal assisted chemical etching or photo-assisted chemical etching.

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4. claims: 16-19

refer to a method for fabricating high aspect ratio gratings by providing a bonded wafer comprising a carrier wafer.

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5. claim: 20

refers to a method to fabricate an absorbing grating on bended substrates by bending the substrate to an angle corresponding to divergence of the beam and geometry and filling the high aspect ratio recess structure with metal.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

6. claim: 21

refers to a method to produce gratings for x-ray or neutron phase contrast imaging, whereas the patterning of the gratings is performed using displacement Talbot lithography.

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7. claim: 22

refers to a method to produce gratings for x-ray imaging, where the high aspect ratio recess structure is filled by atomic layer deposited metal from a group of Ir, Pd, Pt, Ru, W.

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8. claim: 23

refers to a method to produce gratings for neutron imaging, where the high aspect ratio recess structure is filled by atomic layer deposited gadolinium, gadolinium oxide or other gadolinium containing compound material.
