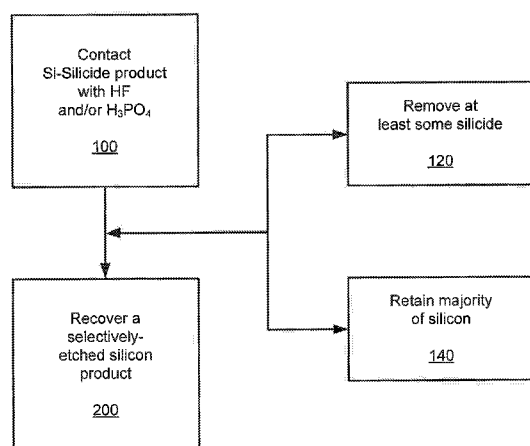




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[Continued on next page]

(54) **Title:** METHODS OF REMOVING SILICIDES FROM SILICON COMPOSITIONS, AND PRODUCTS MADE BY SUCH METHODS



(57) **Abstract:** New methods for selectively etching silicon-silicide materials, and products made therefrom are disclosed. A method may include contacting surfaces of a silicon-silicide product with a fluid (e.g., hydrofluoric acid (HF), phosphoric acid (H₃PO₄) and mixtures thereof). Concomitant to the contacting step, at least some of the silicides may be removed from the silicon-silicide product via the fluid, wherein the average amount of silicides removed during the removing step is a silicide removal rate (MSix-RR). Also concomitant to the contacting step (b), a majority of the silicon of the silicon-silicide product may be retained, wherein the average rate of silicon removal during the retaining step is a silicon removal rate (Si-RR). The ratio of the silicide removal rate to the silicon removal rate may be at least 5.0 (MSix-RR / Si-RR ≥ 5.0).

FIG. 1



TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG). **Published:**

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METHODS OF REMOVING SILICIDES FROM SILICON COMPOSITIONS, AND PRODUCTS MADE BY SUCH METHODS

BACKGROUND

[001] Silicon (Si) eutectic alloys can be fabricated by melting and casting processes (see, e.g., WO 2011/022058). Such silicon eutectic alloys of WO2011/022058 may realize improved fracture toughness.

SUMMARY OF THE DISCLOSURE

[002] Broadly, the present patent application relates to methods of removing one or more silicides from a silicon-silicide product, while retaining a majority of the silicon of the silicon-silicide product. Referring now to FIG. 1, the methods may involve contacting (100) surfaces of a silicon-silicide product with a fluid, the fluid generally being an acid selected from the group consisting of hydrofluoric acid (HF), phosphoric acid (H₃PO₄), and mixtures thereof. The silicon-silicide product may include a first phase comprising silicon and a second phase comprising at least one silicide. During the contacting, the fluid may contact both (A) at least some of the first phase comprising the silicon and (B) at least some of the second phase comprising the at least one silicide. Concomitant to the contacting step, at least some of the silicides may be removed (120) from the silicon-silicide product via the fluid. The average amount of silicides removed during the removing step is referred to herein as the "silicide removal rate" or "MSi_x-RR". Also concomitant to the contacting step, a majority of the silicon of the silicon-silicide product may be retained (140), i.e., a relatively small amount of silicon (or no silicon) is removed. The average rate of silicon removal is referred to herein as the "silicon removal rate" or "Si-RR". Thus, the fluid may "selectively etch" the silicides of the silicon-silicide product, thereby enabling recovery (200) of a selectively-etched silicon product. In one embodiment, the selective etch achieves a ratio of silicide removal rate to silicon removal rate of at least 5.0 (i.e., "MSi_x-RR" divided by "Si-RR" is ≥ 5.0), i.e., the rate at which silicides are removed from the silicon-silicide product is at least 5 times faster than the rate at which silicon is removed from the silicon-silicide product ("the selective etch ratio").

[003] The silicon-silicide product may be any product having both silicon and at least one silicide ("silicide(s)"). The silicide(s) may be proximal to, or adjacent to (in contact with), the silicon. Some examples of silicon-silicide products that might be useful to selectively etch are described in further detail below.

[004] The silicon of the silicon-silicide product may be monocrystalline silicon, polycrystalline silicon, amorphous silicon, and combinations thereof. In one embodiment, the silicon-silicide product comprises monocrystalline silicon. In another embodiment, the silicon-silicide product comprises polycrystalline silicon. In yet another embodiment, the silicon-silicide product comprises both monocrystalline and polycrystalline silicon. In another embodiment, the silicon of the silicon-silicide product consists essentially of monocrystalline silicon. In yet another embodiment, the silicon of the silicon-silicide product consists essentially of polycrystalline silicon.

[005] The silicide(s) of the silicon-silicide product may be any silicide(s) susceptible of removal by HF, H_3PO_4 and combinations thereof. In one embodiment, the silicide(s) comprise a disilicide. In another embodiment, the silicide(s) comprise a monosilicide. In yet another embodiment, the silicide(s) comprise both some monosilicide and some disilicide. Higher order silicides may also potentially be removed. As used herein, "silicide" means a compound comprising at least one metal bonded to silicon.

[006] As noted above, the silicide(s) of the silicon-silicide product may be removed via the fluid comprising HF, H_3PO_4 , and combinations thereof. In one embodiment, the fluid is a liquid. In another embodiment, the fluid is a gas. In another embodiment, the fluid comprises both a liquid and a gas.

[007] In one approach, the fluid is a liquid consisting essentially of HF in water. In this regard, the liquid may have an HF concentration of from 0.5 wt. % to 48 wt. %. In one embodiment, the liquid may have an HF concentration of from 1 wt. % to 30 wt. %. In another embodiment, the liquid may have an HF concentration of from 1 wt. % to 25 wt. %. In yet another embodiment, the liquid may have an HF concentration of from 1 wt. % to 20 wt. %. High concentrations of HF may achieve high etch rates, but may be aggressive and harder to control. Lower concentrations of HF may be more controllable, but may achieve low etch rates. HF in gaseous forms may also / alternatively be used, such as anhydrous HF.

[008] In another approach, the fluid is a liquid consisting essentially of H_3PO_4 in water. In one embodiment, the liquid may have an H_3PO_4 concentration of at least 25 wt. %. In another embodiment, the liquid may have an H_3PO_4 concentration of at least 50 wt. %. In yet another embodiment, the liquid may have an H_3PO_4 concentration of at least 85 wt. %.

[009] The silicon-silicide product is contacted by the fluid to remove at least some of the silicide(s) of the silicon-silicide product. The contacting step may be achieved via any suitable apparatus and methodology, including spraying, immersion, and sonication, among

others. Notably, the contacting step may occur in the absence of an applied electrical current (i.e., is not an electrochemical etch).

[0010] As disclosed above, during the contacting step (100) at least some of the silicide(s) are removed from the silicon-silicide product while at least a majority of the silicon is retained. In one approach, at least 0.5 wt. % of the silicide(s) are removed. Correspondingly, in this approach, less than 0.1 wt. % of the silicon is removed due to the selective etch ratio being at least 5.0 (i.e., " $\text{MSi}_x\text{-RR}$ " divided by " Si-RR " is ≥ 5.0). In one embodiment, at least 1 wt. % of silicide(s) are removed. In another embodiment, at least 5 wt. % of silicide(s) are removed. In yet another embodiment, at least 10 wt. % of silicide(s) are removed. In another embodiment, at least 15 wt. % of silicide(s) are removed. In yet another embodiment, at least 25 wt. % of silicide(s) are removed. In another embodiment, at least 50 wt. % of silicide(s) are removed. In yet another embodiment, at least 75 wt. % of silicide(s) are removed. In another embodiment, at least 90 wt. % of silicide(s) are removed. In yet another embodiment, at least 95 wt. % of silicide(s) are removed. In another embodiment, at least 99 wt. % of silicide(s) are removed. In yet another embodiment, essentially all of the silicide(s) are removed.

[0011] As disclosed above, the selective etch ratio is at least 5.0 (i.e., " $\text{MSi}_x\text{-RR}$ " divided by " Si-RR " is ≥ 5.0). In one embodiment, the selective etch ratio is at least 10. In another embodiment, the selective etch ratio is at least 50. In yet another embodiment, the selective etch ratio is at least 100. In another embodiment, the selective etch ratio is at least 500. In yet another embodiment, the selective etch ratio is at least 1000. In another embodiment, the selective etch ratio is at least 5000. In yet another embodiment, the selective etch ratio is at least 10000. For purposes of determining the selective etch ratio, when no detectable level of silicon is removed due to the contacting step, " Si-RR " is 0.47 angstroms per minute, as per Hu, S. W., Kerr, D. W. "Observation of etching of n-type silicon in aqueous HF solutions", *J. Electrochem Soc.*, 14 (1967), 414.

[0012] As disclosed above, the disclosed methods may be useful in removing at least some silicide(s) of a silicon-silicide product. The silicon-silicide product may be any silicon product having silicide(s) therein, such as silicon-eutectic alloys, semiconductor devices, and microelectro-mechanical systems, to name a few.

[0013] In one embodiment, the silicon-silicide product is a silicon eutectic alloy. As used herein, a "silicon-eutectic alloy" is a material predominately composed of silicon (at least 50.1 at. % Si) and having an aggregation of a first phase comprising one of (A) eutectic

silicon and (B) eutectic silicide(s), and a second phase dispersed within the first phase. The second phase may comprise, for example, a silicide(s) phase or solid solution (which phases may be in stable, metastable, or unstable phase). A silicon-eutectic alloy does not have to be "perfectly eutectic", i.e., a silicon-eutectic alloy does not need to have a composition that is located perfectly on the eutectic point of its corresponding phase diagram. For example, a Si-CrSi₂ eutectic alloy has one eutectic point at about 24 wt. % Cr and 76 wt. % Si. However, compositions outside of this point may produce acceptable silicon-eutectic alloys having a defined aggregation of a first phase and a second phase dispersed within the first phase. Third or more distinct phases may also be present. Some methods for producing silicon eutectic alloy products are disclosed in, for instance, WO2011/022058 to Schuh et al. and U.S. Patent No. 4,724,233 to Ditchek et al, each of which is incorporated herein by reference in its entirety.

[0014] In one embodiment, the first phase of the aggregation is an elemental silicon phase, i.e., the first phase comprises silicon in the form of crystalline silicon and/or amorphous silicon. In another embodiment, the first phase includes silicon and one or more metallic element(s) M in silicide form. In one embodiment, one of the first and second phases of the aggregation comprises one or more colonies of aligned high aspect ratio structures (e.g., 2:1, or larger). In one embodiment, a silicon eutectic alloy body is symmetric about a longitudinal axis, and one of the first and second phases of the eutectic aggregation comprises high aspect ratio structures oriented along a radial direction with respect to the longitudinal axis.

[0015] The solid phases that form upon cooling through a eutectic temperature at a eutectic composition may define a eutectic aggregation having a morphology that depends on the solidification process. For instance, the silicide portion of the silicon eutectic alloy may be in the form of lamella, rods, globes (globular), acicular (needle-like), disks, flakes, dendrites, interpenetrated / percolated, Chinese script and combinations thereof. The phases may be regular (normal) or irregular (anomalous). Examples of normal: regular spacing (e.g., regular lamella spacing, regular rod spacing). Examples of anomalous: no apparent orientation relationship between the silicon and the silicide in the silicon-silicide material (e.g., irregular spacing, broken lamella, fibrous silicides, interconnected-percolated silicides, Chinese script silicides). The form of the silicide(s) may be controlled by, for example, the type of metal(s) used in the silicon-eutectic alloy, and solidification conditions, and/or

eutectic phase growth rates, to name a few. Some non-limiting examples of materials having a partially-etched silicide eutectic phases are illustrated in FIG. 10a-10d.

[0016] In one embodiment, a second phase (silicide phase) may comprise discrete eutectic structures, whereas a matrix phase, or first phase, (silicon) may be substantially continuous. For example, the eutectic aggregation may include a reinforcement (second) phase of rod-like, plate-like (lamella), acicular and/or globular structures, or others of the above-noted silicide phases, dispersed in a substantially continuous matrix phase. Such eutectic structures may be referred to as “reinforcement phase structures.”

[0017] The reinforcement phase structures in the eutectic aggregation may further be referred to as high aspect ratio structures when at least one dimension (e.g., length) exceeds another dimension (e.g., width, thickness, diameter) by a factor of 2 or more. Aspect ratios of reinforcement phase structures may be determined by, for instance, optical or electron microscopy using standard measurement and image analysis software. If useful, the solidification process may be controlled to form and align high aspect ratio structures in the matrix phase. For example, when the eutectic alloy is produced by a directional solidification process, it is possible to align a plurality of the high aspect ratio structures along the direction of solidification.

[0018] The eutectic alloys described herein may be composed entirely or in part of the eutectic aggregation of silicon-containing and silicide(s). Depending on the concentration ratio of the silicon and the metallic element(s) M, at least about 70 vol.%, or at least about 80 vol.%, or at least about 90 vol.% of the eutectic alloy may comprise the eutectic aggregation. In one embodiment, a eutectic alloy body may include at least about 50.1 at. % Si. In another embodiment, the alloy may include at least about 60 at.% Si. In yet another embodiment, the alloy may include at least about 70 at.% Si. In another embodiment, the alloy may include at least about 80 at.% Si. In yet another embodiment, the alloy may include at least about 90 at.% Si.

[0019] The metal (M) of the silicide(s) may be any metal that can form a silicide and that can be selectively etched by the fluid. Examples of some metals that may be used include Li, Na, K, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ba, La, Hf, Ta, Re, Os, Ir, W, Pt, Bi, U, rare earth elements, and mixtures thereof. In one embodiment, the metal comprises chromium. In one embodiment, the metal is titanium. In one embodiment, the metal is cobalt. In one embodiment, the metal is vanadium. In one embodiment, the metal comprises at least one of Cr, Ti, Co, V, & combinations thereof.

[0020] Referring now to FIG. 2, one embodiment of a method for producing selectively-etched silicon-silicide products having preselected characteristics is shown. In the illustrated embodiment, the method includes preselecting one or more silicon-silicide characteristics (70), producing the silicon-silicide product, wherein the silicon-silicide product realizes the one or more preselected silicon-silicide product characteristics (72), and then completing (74) the contacting (100), removing (not shown), and retaining (not shown) steps. Thus, selectively-etched silicon products having preselected characteristics may be recovered (200).

[0021] In one approach, a preselected silicon-silicide characteristic is a pre-etch silicon characteristic. In one embodiment, a pre-etch silicon characteristic comprises one of a silicon type and a silicon grain size (if any). In one embodiment, the preselected silicon type is one of monocrystalline and polycrystalline silicon. In one embodiment, the preselected silicon type is polycrystalline silicon. In these embodiments, a preselected silicon characteristic may include a preselected silicon grain size. By using preselected silicon grain sizes, tailored or preselected porosities and/or surface areas may be achieved in a final selectively-etched product (e.g., by etching or partially etching oxides at the grain boundaries).

[0022] In one approach, a preselected silicon-silicide characteristic is a preselected pre-etch silicide characteristic. In one embodiment, a preselected silicide characteristic may be a pre-etch silicide dimension characteristic and/or a pre-etch silicide type characteristic.

[0023] In one embodiment, a preselected pre-etch silicide characteristic is a pre-etch silicide dimension characteristic. The preselected pre-etch silicide dimension characteristic may be, for instance, one or more of a preselected silicide volume, silicide spacing, silicide characteristic length, and silicide aspect ratio. A preselected silicide volume may be achieved by selection of appropriate metal(s) of the silicide(s). A preselected silicide spacing and/or silicide characteristic length and/or silicide aspect ratio may be achieved by controlling the silicon eutectic alloy manufacturing process. Examples of silicide characteristic lengths and silicide aspect ratios are illustrated in FIGS. 9a-9f.

[0024] As used herein, "silicide volume" refers to the volume of silicides in a silicon-silicide product. For silicon eutectic alloys, the silicide volume may be from, for example, 0.5 to 57 vol. % (prior to the contacting step). After the contacting step, the silicide volume will be less than the initial silicide volume due to the removal of at least some silicide(s).

[0025] As used herein, "silicide spacing" refers to the average characteristic spacing of the silicides of a eutectic silicon-silicide product. Silicide spacing may be from, for example, 0.1 to 50 microns in a silicon eutectic alloy body. Silicide spacing may be controlled by

controlling the cooling rate during the silicon eutectic alloy production process. A higher cooling / solidification rate, in general, results in smaller (closer) silicide spacing and/or smaller silicide grain sizes.

[0026] In one embodiment, a preselected silicide characteristic is a silicide type characteristic. The predetermined silicide type characteristic may be, for instance, a predetermined type and/or amount of monosilicides, a predetermined type and/or amount of disilicides, and combinations thereof.

[0027] Table 1 below, illustrates examples of correlations between produced silicon-silicide products, preselected silicon-silicide characteristics, and properties that may be achieved in a final selectively-etched silicon product due to such preselected silicon-silicide characteristics. One or more of these preselected silicon-silicide characteristics may be selected, and in any combination to achieve a final selectively-etched silicon product having preselected characteristics.

Table 1

Silicon-silicide product	Preselected silicon-silicide characteristic	Correlation to final selectively-etched product
Silicon grain size (for p-Si)	Silicon pre-etch characteristic	Porosity / surface area
Silicide volume fraction (e.g., from 0.5 to 57 vol. % of the silicon-silicide product)	Silicide pre-etch dimension characteristic	Density of pores in the final selectively-etched product
Silicide spacing (e.g., from 0.1 to 50 micrometers)	Silicide pre-etch dimension characteristic	Density of pores in the final selectively-etched product
Silicide characteristic length or aspect ratio (e.g., for silicide rods, the diameter could be from 0.1 to 15 micrometers)	Silicide pre-etch dimension characteristic	Size of the pores in the final selectively-etched product
Silicide type (e.g., type and/or amount monosilicides, disilicides)	Silicide type characteristic	Reactivity, electrical, magnetic and other properties of the final selectively-etched product

[0028] Referring now to FIG. 3, another embodiment of a method for producing selectively-etched silicon products having preselected characteristics is shown. In the illustrated embodiment, the method includes selecting one or more selectively-etched product characteristics (80), and then completing (84) the contacting (100), removing (not shown), and retaining (not shown) steps. Thus, selectively-etched silicon products having preselected characteristics may be recovered (200).

[0029] In one approach, a preselected selectively-etched characteristic is a post-etch silicide characteristic. In one embodiment, the post-etch silicide characteristic is a silicide presence characteristic. The silicide presence characteristic relates to the quantity (or absence) of silicide(s) in the final selectively-etched product. For example, the silicide presence characteristic may be a preselected amount of silicide(s) (volume or weight) in the final selectively-etched product. In one embodiment, the preselected silicide presence characteristic is a "full etch" where substantially all of the silicides are removed from the silicon-silicide product, thereby achieving a substantially silicide-free silicon product (e.g., the silicon product is free of silicides except for trace silicides remaining on silicide etchable surfaces and/or silicides that are not reachable by the etching fluid). In another embodiment, at least some silicides are selected to remain in the selectively-etched product, and from a "light etch" where a relatively small amount of silicides are removed, to a "heavy etch" where a relatively larger amount of silicides (but not all silicides) are removed. Accordingly, the contacting step (100) may be conducted to achieve the preselected silicide presence characteristic (e.g., by controlling duration, concentration and/or temperature parameters of the contacting step, among others).

[0030] In one embodiment, the silicide characteristic may be a post-etch silicide dimension characteristic, such as any of the silicide dimension characteristics described above (e.g., silicide spacing, silicide characteristic length, and silicide aspect ratio). Such characteristics may be related to the pre-etch silicide dimension characteristics

[0031] In another approach, the preselected selectively-etched characteristic is a post-etch silicon characteristic, such as a silicon porosity characteristic and/or a silicon surface area characteristic. In one embodiment, the post-etch silicon characteristic is a silicon porosity characteristic. In one embodiment, the silicon porosity characteristic is one of pore volume and pore size. Such characteristics may be related to the pre-etch silicon characteristics

[0032] Table 2 below, illustrates examples of correlations between selectively-etched silicon products, preselected selectively-etched product characteristics, and example

properties of a final selectively-etched silicon product. One or more of these preselected silicon-silicide characteristics may be selected, and in any combination.

Table 2

Selectively-etched silicon product	Preselected selectively-etched product characteristic	Illustrative Example
Remaining silicide amount	Silicide presence characteristic	• No silicides remain • Predetermined amount of silicides remain
Silicide spacing (e.g., from 0.1 to 50 micrometers)	Silicide dimension characteristic	A silicide spacing useful in an silicon-silicide electronic product
Silicide characteristic length or aspect ratio (e.g., for silicide rods, the diameter could be from 0.1 to 15 micrometers)	Silicide dimension characteristic	A silicide length / aspect ratio useful in an silicon-silicide electronic product
Product porosity	Silicon porosity characteristic	A porosity or pore volume useful in a catalyst, adsorbent or absorbent
Product surface area	Silicon surface area characteristic	A surface area useful in a catalyst, adsorbent or absorbent

[0033] Referring now to FIG. 4, another embodiment of a method for producing selectively-etched silicon-silicide products having preselected characteristics is shown. In the illustrated embodiment, the method combines the methods of FIGS. 2 and 3, and includes selecting one or more silicon-silicide characteristic(s) (70), producing the silicon-silicide product, wherein the silicon-silicide product realizes the one or more preselected silicon-silicide product characteristic(s) (72), selecting one or more selectively-etched product characteristic(s) (80), and then completing (90) the contacting (100), removing (not shown), retaining (not shown) steps. Thus, selectively-etched silicon products having preselected characteristic(s) may be recovered (200). Any of the above described preselected silicon-

silicide characteristics and selectively-etched product characteristics may be selected, and in any useful combination.

[0034] As described above, partially-etched or fully-etched products may be produced. For example, and with reference now to FIGS. 5a-5b, a partially-etched product (1) may include a first phase (10) comprising silicon and a plurality of blind pores (20) dispersed within the first phase (10). The plurality of blind pores (20) include a proximal open end (22) located at a surface of the product (1). The plurality of blind pores (20) also comprise a terminal closed end (24) located within the first phase (10). The product (1) also includes a second phase (30) dispersed within the first phase (10), the second phase (30) including at least one silicide. The second phase includes ends (32) adjacent the terminal closed ends (24) of the plurality of blind pores (20).

[0035] "Blind pores" has the meaning provided for in *Recommendations for the Characterization of Porous Solids* by Rouquerol et al., IUPAC Physical Chemistry Division, Commission on Colloid and Surface Chemistry, Subcommittee on Characterization of Porous Solids, *Pure and Appl. Chem.*, Vol. 66, No. 8, 1739-1758 (© 1994 IUPAC). A blind pore may be, for example, in the form of a channel or disk, and may be tortuous or non-tortuous within the first phase. A blind pore may be interconnected with one or more other blind pores, or may not interconnect with any other blind pores. A channel may have a high length-to-cross-sectional-area ratio. A disk is similar to a channel, but has a lower length-to-cross-sectional-area ratio.

[0036] In another embodiment, masking (or other suitable methods / apparatus) may be used during the contacting step to produce tailored partially-etched products. For instance, and with reference now to FIG. 6a, a mask (40) may be used to cover at least a portion of at least one exposed silicide (30a) during a contacting step (100). The mask (40) may be inert and/or impermeable to the etching fluid, such as a mask made of silicon (for HF and/or H₃PO₄ type fluids) and phosphosilicate glass (PSG) and SiO₂ (for H₃PO₄ type fluids), for instance. Other portions of the product (1a) may have silicides (30b) that remain available for contacting with the etching fluid. Thus, upon conclusion of the contacting step, and now referring to FIG. 6b, a product (1b) may have silicides located (30a') at a first surface (11) of the product (1b), while pores (22') may be located at a second surface (12) due to the silicides being partially etched (30b'), or fully etched (30b'') due to the contacting step (100). Thus, tailored porous, silicon-silicide products may be prepared.

[0037] In yet another embodiment, a product may be a fully-etched product (not illustrated), where essentially all of the silicide(s) are removed. Such fully-etched products may have tailored porosity and surface area, such as when, for example, tailored silicon eutectic alloy products are fully etched. Thus, in one embodiment, a product includes a first phase comprising eutectic silicon and a plurality of pores dispersed within and at least partially surrounded by the first phase, wherein the pores are in the shape of one or more eutectic silicide phases, such as any of the silicide eutectic shapes described above, and combinations thereof. The pores are in the shape of the eutectic silicide phase because the eutectic silicide has been removed due to the contacting step. In one embodiment, at least some of the plurality of pores are in the shape of a eutectic rod phase. In one embodiment, at least some of the plurality of pores are in the shape of a eutectic lamella phase. In one embodiment, at least some of the plurality of pores are in the shape of a eutectic globular phase. In one embodiment, at least some of the plurality of pores are in the shape of a eutectic acicular phase. In one embodiment, at least some of the plurality of pores are in the shape of a eutectic flake phase. In one embodiment, at least some of the plurality of pores are in the shape of a eutectic sphere phase. In one embodiment, at least some of the plurality of pores are in the shape of a eutectic disk phase. In one embodiment, at least some of the plurality of pores are in the shape of a eutectic dendrite phase. In one embodiment, at least some of the plurality of pores are in the shape of Chinese script. In one embodiment, at least some of the plurality of pores are in the shape of interpenetrated/percolated pores.

[0038] The partially-etched or fully-etched products may be useful, for instance, in semiconductor applications, such as in non-planar devices, such as a diode and high voltage switches. For instance, the contacting step could remove the etch stop of silicide but not the silicon. Other applications include field emitters and anodes of freestanding / porous silicon. Metal contacts may be used relative to the selectively-etched products, such as one metal phase on one side and another metal phase on another side (e.g., at least partially filling pores created due to the selective etch.)

[0039] In one aspect, and referring now to FIG. 11a, a method may include depositing (300) a substance (e.g., a third phase) into at least a portion of at least one pore of the selectively-etched product, thereby at least partially covering a surface of the at least one pore of the silicon-silicide product with the substance. In one embodiment, the substance covers at least a portion of a terminal end of the at least one pore. In one embodiment, the substance covers at least a portion of the sidewalls of the at least one pore. In one embodiment, the

substance partially covers outer surfaces of the silicon-silicide product. In one embodiment, the substance covers at least a majority of a terminal end of the at least one pore and at least 25% of the surface of the sidewalls of the at least one pore. In one embodiment, the substance covers at least a majority of a terminal end of the at least one pore and at least 50% of the surface of the sidewalls of the at least one pore. In one embodiment, the substance covers at least a majority of a terminal end of the at least one pore and at least 75% of the surface of the sidewalls of the at least one pore. In one embodiment, the substance covers at least a majority of a terminal end of the at least one pore and at least 95% of the surface of the sidewalls of the at least one pore. In one embodiment, the substance substantially covers the entire surface of the at least one pore (i.e., covers the entire surface of the terminal end and the sidewalls of the at least one pore).

[0040] In one approach, the depositing step (300) comprising forming (310) a film. For instance, and with reference now to FIGS. 11a and 12a, due to the contacting (100), recovering (200) and depositing (300) steps, a functionalized, selectively-etched product (1a) may be produced. As described above, the product (1a) may include a first phase (10) comprising silicon, and a second phase (30). The second phase (30) is dispersed within the first phase (10), and the second phase (30) includes at least one silicide. At least one pore (20a) is dispersed within the first phase (10). The at least one pore (20a) may comprise a terminal closed end located within the first phase (10), the terminal closed end being defined by an end (32) of the second phase (30). Due to the depositing step (300), the product (1a) further includes a film (50) that at least partially covers a surface of the at least one pore (20a).

[0041] For instance, the film (50) may comprise a first portion (50a) located at partially on the end (32) of the second phase (30), which end (32) defines the terminal lower end of the pore (20a). The film 50 may comprise a second portion (50b) located at least partially on an inner sidewall of the first phase (10), which inner sidewall defines sides/sidewalls of the pore (20a). Thus, a functionalized, selectively-etched product (1a) may be produced, which functionalization can be tailored based on the composition of the film (50) and/or the type of silicide of the second phase (30).

[0042] In the illustrated embodiment of FIG. 12a, the film (50) substantially coats all surfaces of the at least one pore (20a). In the illustrated embodiment of FIG. 12a, the film (50) also includes a third portion (50c) located on outer surfaces of the product (1a). However, the film (50) may only include the first portion (50a) and/or the second portion

(50b). Furthermore, the first portion (50a) may coat the entire end (32) or may only coat a portion of the end (32). The second portion (50b) may coat the entire inner sidewall or may only coat a portion of the inner sidewall.

[0043] The depositing step (300) may be completed one or more times to provide multiple film layers. For instance, and with reference now to FIG. 12b, a product (1b) may include a first film (50) and a second film (52) at least partially located on the first film. The first film (50) may comprise a first substance and the second film (52) may comprise a second substance. The first substance may be the same as or different than the second substance. In one embodiment, the first substance is a different material than the second substance. Any number of film layers can be used / deposited, and which films may be deposited onto one another and/or onto surface(s) of the first phase (10) and/or the second phase (30) of the product (1b).

[0044] Referring now to FIGS. 11a and 12c, in another approach, the depositing step (300) comprising forming (320) a mass within at least one pore of the selectively-etched product, thereby at least partially covering a surface of the at least one pore of the silicon-silicide product with the substance. As shown in FIG. 12c, the product (1c) may include a first phase (10) comprising silicon, and a second phase (30). The second phase (30) is dispersed within the first phase (10), and the second phase (30) includes at least one silicide. At least one pore (20a) is dispersed within the first phase (10). The at least one pore (20a) may comprise a terminal closed end located within the first phase (10), the terminal closed end being defined by an end (32) of a second phase (30). Due to the depositing step (300), the product (1c) further includes a mass (60) that at least partially covers a surface of the at least one pore (20a). The mass (60) may be in the form of a plug. For instance, and as illustrated, the mass (60) may cover the end (32) of the second phase (30). The mass (60) may also partially cover inner sidewalls of the first phase (10). In one embodiment, the mass (60) occupies at least 10% of the pore volume of the at least one pore (20a). In another embodiment, the mass (60) occupies at least 25% of the pore volume of the at least one pore (20a). In yet another embodiment, the mass (60) occupies at least 50% of the pore volume of the at least one pore (20a). In another embodiment, the mass (60) occupies at least 75% of the pore volume of the at least one pore (20a). In yet another embodiment, the mass (60) occupies at least 95% of the pore volume of the at least one pore (20a). In another embodiment, the mass (60) occupies substantially the entire pore volume, occupying 99% or more of the pore volume of the at least one pore (20a).

[0045] The depositing step (300) may be completed one or more times to provide multiple mass layers. For instance, and with reference now to FIG. 12d, a product (1d) may include a multi-layer mass, which multi-layer mass includes a first mass (60) and a second mass (62) at least partially located on the first mass (60). The first mass (60) may comprise a first substance and the second mass (62) may comprise a second substance. The first substance may be the same as or different than the second substance. In one embodiment, the first substance is a different material than the second substance. Any number of mass layers can be used / deposited, and which mass layers may be deposited onto one another and/or surface of the first phase (10) and/or the second phase (30) of the product (1d).

[0046] In another approach (not illustrated), a deposit comprises both a film and a mass. In one embodiment, the film is deposited first, the mass is deposited second, and the mass is at least partially located on the film. In another embodiment, the mass is deposited first, the film is deposited second, and the film is at least partially located on the mass.

[0047] In another approach (not illustrated), a substance is deposited on at least a portion of an outer surface of the product, but the substance is not deposited into any pores. In this regard, masking and the like may be used to mask the pores during the depositing step.

[0048] In another approach (not illustrated), a first substance may be deposited into a first pore of the product, and a second substance may be deposited into a second pore of the product. The first pore may be free of the second substance. Likewise, the second pore may be free of the first substance. In this regard, masking and the like may be used to mask appropriate ones of the pores during the various depositing steps.

[0049] Referring now to FIG. 11b, the depositing step (300) may comprise incorporating (350) a precursor into at least a portion of the at least one pore, and converting (360) the precursor into the substance. During the incorporating step (350), the precursor may be a fluid (351), such as a gas (352) and/or a liquid (353), or the precursor may be a solid (354). The converting step (360) generally converts the precursor into a solid (362). Thus, the substance is usually of a solid form.

[0050] In one embodiment, the depositing step (300) comprises one or more of chemical vapor deposition (CVD), chemical vapor infiltration, spaying, immersion, sputtering, electrochemical deposition, electroless deposition, melt infiltration, spin coating, and evaporation, among others. When used, the CVD process may be one or more of atmospheric pressure CVD (APCVD), low-pressure CVD (LPCVD), ultrahigh vacuum CVD (UHVCVD), aerosol assisted CVD (AACVD), direct liquid injection CVD, microwave

plasma-assisted CVD (MPCVD), plasma-enhanced CVD (PECVD), remote plasma-enhanced CVD (RPECVD), atomic-layer CVD (ALCVD), combustion CVD (CCVD), hot-wire CVD (HWCVD) or hot filament CVD (HFCVD), hybrid physical-chemical vapor deposition (HPCVD), metalorganic chemical vapor deposition (MOCVD), rapid thermal CVD, vapor-phase epitaxy (VPE) and photo-initiated CVD (PICVD).

[0051] The substance may be any material useful in at least one pore of the selectively-etched product. In one embodiment, the substance is electrically conductive. For instance, the substance may include metal(s) (e.g., Al, Cu, Ag, Au, W and combinations thereof), conductive metal oxide(s) (e.g. InO), conductive nitride(s) (e.g., tungsten nitride, titanium nitride), conductive silicide(s) (e.g., titanium disilicide, titanium silicide, tantalum disilicide) and which silicide is different than the silicide that was removed via the etching step, conductive polymer(s) (e.g., polyacetylene, polythiophene), graphite, and combinations thereof.

[0052] In another embodiment, the substance is a dielectric (i.e., an insulator). For instance, the substance may include ceramic(s) (e.g., insulative oxide(s) (e.g., alumina, silica), titanate(s), apatite(s), carbide(s), boride(s), nitride(s) (e.g., silicon nitride), and combinations thereof), polymer(s) (e.g., PTFE, PET), carbon-based material(s) (e.g., diamond / diamond-like carbon, organics), and combinations thereof.

[0053] In another embodiment, the substance is semiconductive. For instance, the substance may include silicon, germanium, phosphide(s), semiconductive silicide(s) (e.g., chromium disilicide, iron disilicide, ruthenium silicide and combinations thereof) and which silicide is different than the silicide that was removed via the etching step, silicon carbide, and combinations thereof.

[0054] Other properties may be tailored. For example, the material may have magnetic, optical, and/or structural (e.g., scratch resistance) properties. Further, multiple different materials can be used as the substance. For instance, any combination of the electrical conductors, dielectrics, and semiconductors described above may be used.

[0055] In another approach (not illustrated), the silicon-silicide product comprises a fully-etched product, where essentially all of the silicide(s) are removed, after which the depositing step (300) is completed. Such products may include a first phase comprising eutectic silicon and a plurality of pores dispersed within and at least partially surrounded by the first phase, wherein the pores are in the shape of one or more eutectic silicide phases, such as any of the silicide eutectic shapes described above, and combinations thereof. Due to the depositing

step, at least some of the pores may be at least partially filled with the deposited substance, which substance may be any of the substances described above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0056] FIG. 1 is a flow chart illustrating one embodiment of a method for producing selectively-etched silicon-silicide products.

[0057] FIG. 2 is a flow chart illustrating another embodiment of a method for producing selectively-etched silicon-silicide products.

[0058] FIG. 3 is a flow chart illustrating another embodiment of a method for producing selectively-etched silicon-silicide products.

[0059] FIG. 4 is a flow chart illustrating another embodiment of a method for producing selectively-etched silicon-silicide products.

[0060] FIG. 5a is a perspective, schematic view of one embodiment of a partially-etched product.

[0061] FIG. 5b is a cross-sectional, schematic view of the product of FIG. 5a.

[0062] FIG. 6a is a cross-sectional, schematic view of a masked silicon-silicide product prior to etching.

[0063] FIG. 6b is a cross-sectional schematic view of the silicon-silicide product of FIG. 6a after etching.

[0064] FIGS. 7a through 7d illustrate SEM images of a Si-CrSi₂ eutectic alloy composite before etching (FIGS. 7a-b) and after etching (FIGS. 7c-d) from Example 3.

[0065] FIGS. 8a through 8b are SEM cross-sectional views of a partially etched Si-CrSi₂ eutectic alloy composite from Example 3.

[0066] FIGS. 9a-9f illustrate various examples of silicide characteristic lengths and silicide aspect ratios.

[0067] FIGS. 10a-10d illustrate various example materials having a partially-etched silicide eutectic phase.

[0068] FIG. 11a is a flow chart illustrating one embodiment of a method for producing selectively-etched silicon-silicide products having a substance deposited in at least one pore.

[0069] FIG. 11b is a flow chart illustrating a related embodiment of a method for producing selectively-etched silicon-silicide products having a substance deposited in at least one pore.

[0070] FIG. 12a is a schematic, close-up, cut-away view of a pore of a silicon-silicide product incorporating a deposit in the form of a film.

[0071] FIG. 12b is a schematic, close-up, cut-away view of a pore of a silicon-silicide product incorporating a deposit in the form of a multi-layer film.

[0072] FIG. 12c is a schematic, close-up, cut-away view of a pore of a silicon-silicide product incorporating a deposit in the form of a mass.

[0073] FIG. 12d is a schematic, close-up, cut-away view of a pore of a silicon-silicide product incorporating a deposit in the form of a multi-layer mass.

[0074] FIGS. 13a-13b are SEMs showing a top view (surface view) and a cross-section view, respectively, of an etched material having pores coated with a film of carbon.

[0075] FIGS. 14a-14c are SEMs showing a top view (surface view), a cross-section view, and a top view at a lower resolution, respectively, of an etched material having pores filled with SiC.

DETAILED DESCRIPTION

Example 1 - Separate immersion of CrSi and polysilicon in dilute HF

[0076] Chromium disilicide (CrSi_2) samples were prepared by arc-melting 4.7 g chromium flakes, 99.999 % and 5.0 g polycrystalline silicon (polySi) chunks, 99.999 % in vacuum. An X-ray diffraction pattern of the ground powder confirmed the presence of CrSi_2 phase. The CrSi_2 samples were then immersed in a dilute (about 10 % (v/v)) HF solution for about 24 hours at ambient temperature (about 24°C). The dilute HF solution was produced by mixing about 47-51 % wt. HF with de-ionized water. The solution was free of any oxidizing agents. The samples and HF solution were contained in a Teflon beaker. After the 24 hour period, the clear solution had turned to a deep green solution, and with all the CrSi_2 completely dissolved.

[0077] A polycrystalline silicon bar was prepared and cut into pieces. The silicon bar was then submerged in a dilute (10 % (v/v)) HF solution for about 24 hours at ambient temperature (about 24 °C). After the 24 hour period, the product was then rinsed in deionized water and methanol and then conventionally dried. The dilute HF solution appears to have no material effect on polycrystalline silicon. No visible etching was observed via an SEM analysis. Also, no weight loss was observed (within statistical error). The weight of the sample prior to immersion was about 1.9052 grams and the weight of the sample after immersion and appropriate drying was about 1.9048 g. This result is consistent with an etch

rate of 0.47 angstroms per minute, which has been reported in literature. See, Hu, S. W., Kerr, D. W. Observation of etching of n-type silicon in aqueous HF solutions, *J. Electrochem Soc.*, 14 (1967), 414.

Example 2 - Arc melting of CrSi and Si to form Si-CrSi₂ eutectic alloy composite with subsequent immersion in dilute HF

[0078] A Si-CrSi₂ eutectic alloy composite was prepared by arc melting CrSi₂ and polysilicon raw materials, and in a manner similar to that of Example 1. The amount of CrSi₂ and Si were selected so as to form a eutectic composition upon cooling. After melting and cooling, the Si-Cr eutectic alloy product had a first eutectic phase comprised of polysilicon (Si) and a second eutectic phase comprised of CrSi₂. The second eutectic phase was in the form of rods having an average rod diameter of about 1.0 micrometer, an average inter-rod spacing of about 1.5 micrometers, and occupying about 32 vol. % of the binary Si-Cr eutectic alloy product. From this product, several test coupons were obtained. The coupons size was 20 mm in diameter x 1 mm thickness.

[0079] Next, the coupons were immersed in a (about 10 % (v/v)) HF solution for about 24 hours at ambient temperature (about 24°C). The test coupons were then rinsed in deionized water and methanol and then conventionally dried. The coupons were examined, and the complete selective removal of CrSi₂ was verified by SEM, Energy Dispersive Spectroscopy (EDS). Conversely, none of the silicon appeared to have been removed.

Example 3 - Selective partial etch (removal) of silicides in a directionally solidified binary Si-Cr eutectic alloy product

[0080] A binary Si-Cr eutectic alloy product was made by directional solidification in the form of Czochralski-growth processing. After casting, the Si-Cr eutectic alloy product had a first eutectic phase comprised of polysilicon (Si) and a second eutectic phase comprised of CrSi₂. The second eutectic phase was in the form of rods having an average rod diameter of about 2.0 micrometers, an average inter-rod spacing of about 4.0 microns, and occupying about 32 vol. % of the binary Si-Cr eutectic alloy product. From this product, several test coupons were obtained. The coupons size was 20 mm in diameter x 4 mm thickness.

[0081] Next, the test coupons were immersed in an aqueous solution having about 10 vol. % HF at ambient temperature. The test coupons were immersed for about 24 hours. The test coupons were then rinsed in deionized water and methanol and then conventionally dried.

[0082] The test coupons were then subjected to SEM, Energy Dispersive Spectroscopy (EDS) and XRD testing. FIGS. 7a - 7d show the surface and cross-sectional SEM micrographs of Si-CrSi₂ composites before and after the immersion step resulting in a porous eutectic silicon product with a selective amount of silicide removed, as shown in FIGS. 8a - 8b. This is confirmed by XRD analysis. The calculated average etch rate of the second phase comprising CrSi₂ was about 20 micrometers per hour (um/h). Conversely, the first eutectic phase comprised of polysilicon (Si) remained intact, showing no visible signs of silicon removal. These results are consistent with the results shown in Example 1, above.

Example 4 - Selective full etch (removal) of silicides in directionally solidified, binary Si-Cr eutectic alloy products

[0083] A binary Si-Cr eutectic alloy product was made similar to Example 2. After casting, the Si-Cr eutectic alloy product had a first eutectic phase comprised of silicon (Si) and a second eutectic phase comprised of CrSi₂. From this product, several test coupons were obtained. The coupons size was 20 mm in diameter x 0.6 mm thickness.

[0084] Next, the test coupons were immersed in an aqueous solution having about 10 vol. % HF at ambient temperature. The test coupons were immersed for about 24 hours. The test coupons were then rinsed in deionized water and methanol and then conventionally dried. All measurable CrSi₂ was removed as verified by SEM, Energy Dispersive Spectroscopy (EDS) and XRD, (no detectable CrSi₂ was shown), i.e., essentially pure macroporous polysilicon (p-Si) was obtained. The final product weighed about 44% less than its original starting weight.

Example 5 - Selective etching of rotary cast binary Si-Cr eutectic alloy products

[0085] A binary Si-Cr eutectic alloy product was made using rotational casting. After casting, the Si-Cr eutectic alloy product had a first eutectic phase comprised of polysilicon (Si) and a second eutectic phase comprised of CrSi₂. The second eutectic phase was in the form of rods having an average rod diameter of about 10 micrometers, an average inter-rod spacing of about 20 micrometers, and occupying about 32 vol. % of the binary Si-Cr eutectic alloy product. From this product, several test coupons were obtained. The coupons size was 18 mm x 13 mm x 4 mm.

[0086] Next, the test coupons were immersed in an aqueous solution having about 10 vol. % HF at ambient temperature. The test coupons were immersed for about 24 hours. The test coupons were then rinsed in deionized water and methanol and then conventionally dried. All measurable CrSi₂ was removed as verified by SEM, Energy Dispersive Spectroscopy

(EDS) and XRD, (no detectable CrSi_2 was shown), i.e., essentially pure macroporous polysilicon (p-Si) was obtained.

Example 6 - Selective etching of vacuum cast binary Si-Co eutectic alloy products

[0087] A binary Si-Co (cobalt) eutectic alloy product was vacuum cast. After casting, the Si-Co eutectic alloy product had a first eutectic phase comprised of polysilicon (Si) and a second eutectic phase comprised of CoSi_2 . The second eutectic phase was in the form of irregular lamella and interpenetrated-percolated structures. From this product, several test coupons were obtained. The coupons size was 20 mm x 12 mm x 4 mm.

[0088] Next, the test coupons were immersed in an aqueous solution having about 10 vol. % HF at ambient temperature. The test coupons were immersed for about 24 hours. The test coupons were then rinsed in deionized water and methanol and then conventionally dried. All measurable CoSi_2 was removed as verified by SEM, Energy Dispersive Spectroscopy (EDS) and XRD, (no detectable CoSi_2 was shown), i.e., essentially pure macroporous polysilicon (p-Si) was obtained. The calculated average etch rate of the second phase comprising CoSi_2 was about 4 micrometers per hour (um/h).

Example 7 - Selective etching of vacuum cast binary Si-Ti eutectic alloy products

[0089] A binary Si-Ti (titanium) eutectic alloy product was vacuum cast. After casting, the Si-Ti eutectic alloy product had a first eutectic phase comprised of polysilicon (Si) and a second eutectic phase comprised of TiSi_2 . The second eutectic phase was in the form of a mixture of rods and lamella. From this product, several test coupons were obtained. The coupons size was 23 mm x 4 mm x 3 mm.

[0090] Next, the test coupons were immersed in an aqueous solution having about 10 vol. % HF at ambient temperature. The test coupons were immersed for about 24 hours. The test coupons were then rinsed in deionized water and methanol and then conventionally dried. Partial removal of TiSi_2 was verified by SEM, Energy Dispersive Spectroscopy (EDS). The calculated average etch rate of the second phase comprising TiSi_2 was about 7 micrometers per hour (um/h).

Example 8 - Etching with phosphoric acid

[0091] *Etching of chromium disilicide (CrSi_2)*

[0092] A binary Si-Cr (chromium) eutectic alloy was vacuum cast and had a similar microstructure to the alloys of Example 4. From these products, several test coupons were obtained. The coupons sizes were 23mm x 4mm x 3mm.

[0093] Next, the test Si-CrSi₂ coupons were immersed in a boiling 85 wt. % phosphoric acid solution and a boiling 10 wt. % phosphoric acid solution. The boiling 85 wt. % phosphoric acid solution etched most of the CrSi₂, and showed some oxidation of silicon. The corresponding etch selectivity of CrSi₂ to Si was about 5:1. The boiling 10 wt. % phosphoric acid solution did not etch CrSi₂.

[0094] *Etching of cobalt disilicide*

[0095] A binary Si-Co (cobalt) eutectic alloy was vacuum cast and had a similar microstructure to the alloys of Example 5. From these products, several test coupons were obtained. The coupons sizes were 20 mm x 12 mm x 4 mm. The Si-CoSi₂ coupons were immersed in a boiling 85 wt. % phosphoric acid solution. In this instance, the Si phase etched faster than the CoSi₂ phase. Furthermore, oxidation of both Si and CoSi₂ phases was observed (i.e., boiling 85 wt. % phosphoric acid was found not to be selective to CoSi₂ in a Si-CoSi₂ eutectic system).

[0096] *Etching of titanium disilicide (CrSi₂)*

[0097] A binary Si-Ti (titanium) eutectic alloy was vacuum cast and had a similar microstructure to the alloys of Example 7. From these products, several test coupons were obtained. The coupons sizes were 22mm x 4mm x 3mm.

[0098] Next, the test Si-TiSi₂ coupons were immersed in a boiling 85 wt. % phosphoric acid solution. The boiling 85 wt. % phosphoric acid solution etched most of the TiSi₂ with minor silicon oxidation. The etch rate of the TiSi₂ was about 10 angstroms per second (about 600 angstroms per minute), which correspond to an etch selectivity (TiSi₂ to Si) of about 200:1. This is based on a silicon etch rate of about 3 angstroms per minute in 180°C concentrated phosphoric acid (*see*, van Gelder et al., "The Etching of Silicon Nitride in Phosphoric Acid with Silicon Dioxide as a Mask", J. Electrochem. Soc., Vol. 114, No. 8, pp. 869-872 (1967)).

Example 9 - Infiltration of etched silicide with polyacrylonitrile (PAN) and creating of thin carbon coating on surfaces

[0099] A binary Si-Cr eutectic alloy product was made by directional solidification in the form of Czochralski-growth processing, and in a manner similar to that of Example 3. Several coupons of the product were obtained. Various ones of the coupons were etched in dilute 10 wt.% HF, and the etch depth was controlled by immersion duration. Some of the coupons were fully etched, removing substantially all of the chromium silicide, leaving a

silicon monolith having pores. Others of the coupons were partially etched, leaving silicon, some chromium silicides, and pores.

[00100] Next, about 5 grams of polyacrylonitrile (PAN) was dissolved in about 100 mL Dimethylformamide (DMF) at a temperature of about 60°C and for a duration of about 4 hours. The etched coupons were then submerged in this PAN-DMF solution, after which a vacuum is created so as to facilitate infiltration of the pores with the PAN-DMF solution. After several hours, the coupons were removed from the PAN-DMF solution, and the coupons were then pyrolyzed in a furnace under an argon atmosphere at about 550°C for about 1 hour. A thin carbon coating is formed on the surfaces coupons, including the surface of the pores. FIGS. 13a-13b are SEMs showing a top view (surface view) and a cross-section view, respectively, of the carbon coated materials. An EDS analysis confirmed the presence of a thin carbon-containing coating. It is believed that the thickness of the film is in the nanometer range, such as a monolayer thickness. Thicker films may be produced by replicating this submersion and pyrolyzation process.

[00101] Similar tests were performed with boiling 85 wt.% phosphoric acid. Similar results were obtained.

Example 10 - Infiltration of etched silicide with SiC

[00102] A binary Si-Cr eutectic alloy product was made by directional solidification in the form of Czochralski-growth processing, and in a manner similar to that of Example 3. Several coupons of the product were obtained. Various ones of the coupons were etched in dilute 10 wt.% HF, and the etch depth was controlled by immersion duration. Some of the coupons were fully etched, removing substantially all of the chromium silicide, leaving a silicon monolith having pores. Others of the coupons were partially etched, leaving silicon, some chromium silicides, and pores.

[00103] The etched coupons were then submerged in a pre-ceramic polymer solution of allylhydridopolycarbosilane (AHPCS) for several hours at room temperature, after which a vacuum is created so as to facilitate infiltration of the pores with the AHPCS solution. The allylhydridopolycarbosilane (SMP-10) was purchased from Starfire LLC. The coupons were then removed from the AHPCS solution, after which the coupons were then pyrolyzed in a furnace under an argon atmosphere by heating to 400°C (holding for 1 hour), and then to 950°C (holding for 1-2 hours). In order to completely fill all pores with AHPCS, several of the above infiltration and pyrolysis (PIP) cycles were executed. FIGS. 12a-12b are SEMs showing a top view (surface view) and a cross-section view, respectively, of the final

materials. The pores are generally filled with SiC (silicon carbide). FIG. 12c is a top view at a lower resolution showing that the SiC also coats the surface of the material. An EDS analysis confirmed the presence of SiC on the surface and in the pores of the coupons. One example of the EDS results for one coupon is provided in Table 4, below. Fewer cycles could be used to only partially fill the pores with a SiC mass.

TABLE 4

Spectrum	C	O	Si
Surface Film 1	45.6	8.0	46.3
Surface Film 2	43.3	8.7	48.0
Surface Film 3	47.1	8.1	44.8
Surface Film 4	49.2	7.8	43.0
Surface Film 5	45.2	7.9	46.9
Average	46.1	8.1	45.8
Std. Dev.	2.2	0.4	2.0

[00104] Similar tests were performed with boiling 85 wt.% phosphoric acid. Similar results were obtained.

[00105] Additional experiments using AHPCS and the above procedure was used, but with the addition of a filling agent, in this case nanocrystalline SiC particles in powder form (<100 nm in particle size), to the AHPCS solution. This AHPCS-particulate mixture was used to coat the surface and infiltrate the pores of several coupons, using the above procedure. Similar results were obtained.

[00106] While various embodiments of the present disclosure have been described in detail, it is apparent that modifications and adaptations of those embodiments will occur to those skilled in the art. However, it is to be expressly understood that such modifications and adaptations are within the spirit and scope of the present disclosure.

CLAIMS

What is claimed is:

1. A method comprising:
 - (a) contacting surfaces of a silicon-silicide product with a fluid;
 - (i) wherein the fluid comprises an acid selected from the group consisting of hydrofluoric acid (HF), phosphoric acid (H₃PO₄) and mixtures thereof;
 - (ii) wherein the silicon-silicide product comprises a first phase comprising silicon and a second phase comprising at least one silicide;
 - (iii) wherein, during the contacting, the fluid contacts both (A) at least some of the first phase comprising the silicon and (B) at least some of the second phase comprising the at least one silicide;
 - (b) concomitant to the contacting step (a), removing at least some of the silicides from the silicon-silicide product via the fluid, wherein the average amount of silicides removed during the removing step is a silicide removal rate (MSi_x-RR);
 - (c) concomitant to the contacting step (b), retaining a majority of the silicon of the silicon-silicide product, wherein the average rate of silicon removal during the retaining step is a silicon removal rate (Si-RR);
wherein the ratio of the silicide removal rate to the silicon removal rate is at least 5.0 (MSi_x-RR / Si-RR $\geq$ 5.0).
2. The method of claim 1, wherein the fluid is a liquid, and wherein the liquid comprises 0.5 - 48 wt. % HF.
3. The method of claim 1, wherein the silicon-silicide product is a silicon-eutectic alloy, wherein the second phase comprising the at least one silicide is dispersed within the first phase, wherein the first phase comprises silicon eutectic.
4. The method of claim 3, wherein, prior to the contacting step, the silicides are in the form of lamella, rods, globes, acicular, disks, flakes, dendrites, interpenetrated, Chinese script and combinations thereof.
5. The method of claim 1, wherein the silicides are chromium silicides of the formula Cr_aSi_b, wherein b is 1 or 2.
6. The method of claim 1, comprising:
 - selecting a silicon-silicide characteristic;
 - producing the silicon-silicide product, wherein the silicon-silicide product realizes the silicon-silicide product characteristic; and

completing the contacting, removing and retaining steps.

7. The method of claim 6, wherein the silicon-silicide characteristic is a pre-etch silicon characteristic.
8. The method of claim 7, wherein the first phase of the silicon-silicide product comprises polysilicon, and wherein the pre-etch silicon characteristic is a grain size of the polysilicon.
9. The method of claim 6, wherein the silicon-silicide characteristic is a pre-etch silicide characteristic.
10. The method of claim 9, wherein the pre-etch silicide characteristic is a pre-etch silicide dimension characteristic.
11. The method of claim 10, wherein the pre-etch silicide dimension characteristic is one of a silicide volume, a silicide spacing, a silicide characteristic length and a silicide aspect ratio.
12. The method of claim 6, wherein the pre-etch silicide characteristic is a silicide type.
13. The method of claim 12, wherein the silicide type is a predetermined amount of monosilicides.
14. The method of claim 12, wherein the silicide type is a predetermined amount of disilicides.
15. The method of claim 1, comprising:

after the contacting step, recovering a selectively-etched silicon-based product derived from the silicon-silicide product.
16. The method of claim 15, comprising:

prior to the recovering step, selecting a selectively-etched product characteristic; and
completing the contacting, removing, retaining and recovering steps;

wherein the selectively-etched silicon based product realizes the selectively-etched product characteristic.
17. The method of claim 16, wherein the selectively-etched product characteristic is at least one of a pre-etch silicide characteristic and a pre-etch silicon characteristic.
18. The method of claim 17, wherein the pre-etch silicide characteristic is at least one of a silicide presence characteristic and a pre-etch silicide dimension characteristic.
19. The method of claim 16, wherein the pre-etch silicon characteristic is at least one of a silicon porosity characteristic and a silicon surface area characteristic.

20. The method of claim 19, wherein the pre-etch silicon characteristic is a silicon porosity characteristic, and wherein the silicon porosity characteristic is one of pore volume and pore size.
21. The method of claim 16, comprising:
selecting a first silicon-silicide characteristic, wherein the first silicon-silicide characteristic corresponds to a first selectively-etched product characteristic; and
producing the silicon-silicide product, wherein the silicon-silicide product realizes the first silicon-silicide product characteristic; and
wherein the selectively-etched silicon based product realizes the first selectively-etched product characteristic.
22. The method of claim 21, wherein the first silicon-silicide characteristic is a pre-etch silicide dimension characteristic, and wherein the first selectively-etched product characteristic is a silicon porosity characteristic, and wherein the selectively-etched silicon based product realizes the silicon porosity characteristic.
23. A product comprising:
a first phase comprising silicon;
a plurality of blind pores dispersed within the first phase;
wherein the plurality of blind pores comprise a proximal open end located at a surface of the product;
wherein the plurality of blind pores comprise a terminal closed end located within the first phase;
a second phase dispersed within the silicon, wherein the second phase comprises a silicide, and wherein the second phase comprises ends adjacent the terminal closed ends of the plurality of blind pores.
24. A product comprising:
a first phase comprising eutectic silicon;
a plurality of pores dispersed within and partially surrounded by the first phase,
wherein the pores are in the shape of a eutectic silicide phase.
25. The product of claim 24, wherein at least some of the plurality of pores are in the shape of a eutectic rod phase.
26. The product of claim 24, wherein at least some of the plurality of pores are in the shape of a eutectic lamella phase.

27. The product of claim 24, wherein at least some of the plurality of pores are in the shape of a eutectic globular phase.

28. The product of claim 24, wherein at least some of the plurality of pores are in the shape of a eutectic acicular phase.

29. The product of claim 24, wherein at least some of the plurality of pores are in the shape of a eutectic flake phase.

30. The product of claim 24, wherein at least some of the plurality of pores are in the shape of a eutectic disk phase.

31. The product of claim 24, wherein at least some of the plurality of pores are in the shape of a eutectic dendrite phase.

32. A method comprising:

(a) contacting surfaces of a silicon-silicide product with a fluid;

(i) wherein the fluid comprises an acid selected from the group consisting of hydrofluoric acid (HF), phosphoric acid (H₃PO₄) and mixtures thereof;

(ii) wherein the silicon-silicide product comprises a first phase comprising silicon and a second phase comprising at least one silicide;

(iii) wherein, during the contacting, the fluid contacts both (A) at least some of the first phase comprising the silicon and (B) at least some of the second phase comprising the at least one silicide;

(b) concomitant to the contacting step (a), removing at least some of the silicides from the silicon-silicide product via the fluid, wherein the average amount of silicides removed during the removing step is a silicide removal rate (MSi_x-RR);

(c) concomitant to the contacting step (b), retaining a majority of the silicon of the silicon-silicide product, wherein the average rate of silicon removal during the retaining step is a silicon removal rate (Si-RR);

wherein the ratio of the silicide removal rate to the silicon removal rate is at least 5.0 (MSi_x-RR / Si-RR ≥ 5.0);

wherein, due to steps (a)-(c) the silicon-silicide product contains pores;

(d) depositing a substance into at least one pore of the silicon-silicide product, thereby at least partially covering a surface of the at least one pore of the silicon-silicide product with the substance.

33. The method of claim 32, wherein the depositing comprises:

depositing a precursor into at least a portion of the at least one pore; and

converting the precursor into the substance.

34. The method of claim 32, wherein, after the depositing, the substance in the form of a film, and wherein the film is located on a surface of the at least one pore.

35. The method of claim 34, wherein, after the depositing step, the film substantially coats all surfaces of the at least one pore.

36. The method of claim 32, wherein, after the depositing, the substance in the form of a mass.

37. The method of claim 36, wherein the at least one pore comprises a pore volume, and wherein, after the depositing step, the mass occupies at least 10% of the pore volume of the at least one pore.

38. The method of claim 37, wherein the mass occupies at least 25% of the pore volume of the at least one pore.

39. The method of claim 37, wherein the mass occupies at least 50% of the pore volume of the at least one pore.

40. The method of claim 37, wherein the mass occupies at least 75% of the pore volume of the at least one pore.

41. The method of claim 37, wherein the mass occupies at least 95% of the pore volume of the at least one pore.

42. The method of claim 37, wherein the mass occupies at least 99% of the pore volume of the at least one pore.

43. The method of claim 32, wherein, after the depositing, the substance at least partially covers outer surfaces of the silicon-silicide product.

44. The method of claim 32, wherein the depositing is a first depositing, wherein the substance is a first substance, and wherein the method comprises:

after the first depositing, second depositing a second substance into the at least one pore of the silicon-silicide product, thereby at least partially covering at least one (a) a surface of the at least one pore of the silicon-silicide product, and (b) the first substance, with the second substance.

45. The method of claim 44, wherein the first substance is a different material than the second substance.

46. The method of claim 44, wherein the first substance is the same material as the second substance.

47. The method of claim 44, wherein the first substance is in the form of a film or a mass, and wherein the second substance is in the form of a film or a mass, wherein the second substance is at least partially located on the first substance.

48. The method of claim 47, wherein the first substance is in the form of a first mass, and wherein the second substance is in the form of a second mass, wherein the second mass is at least partially located on the first mass.

49. The method of claim 47, wherein the first substance is in the form of a first film, and wherein the second substance is in the form of a second film, wherein the second film is at least partially located on the first film.

50. The method of claim 47, wherein one of the first substance and the second substance is in the form of a mass, and wherein the other of the first substance the second substance is in the form of a film.

51. The method of claim 32, wherein the depositing is a first depositing, wherein the substance is a first substance, wherein the at least one pore comprises at least a first pore, and wherein the method comprises:

after the first depositing, second depositing a second substance into a second pore of the silicon-silicide product, thereby at least partially covering a surface of the second pore of the silicon-silicide product with the second substance, wherein the second pore is a different pore than the first pore, and wherein the second pore is free of the first substance.

52. A product comprising:

a first phase comprising silicon;

a plurality of blind pores dispersed within the first phase;

wherein the plurality of blind pores comprise a proximal end located at a surface of the product;

wherein the plurality of blind pores comprise a terminal closed end located within the first phase;

a second phase dispersed within the silicon, wherein the second phase comprises a silicide, and wherein the second phase comprises ends adjacent the terminal closed ends of the plurality of blind pores;

a third phase located within at least some of the plurality of blind pores, wherein the third phase is a different material than the first phase and second phase.

53. The product of claim 52, wherein the third phase is in the form of a film, and wherein the film is located on surfaces of at least some of the plurality of blind pores.

54. The product of claim 52, wherein the third phase is in the form of a film, and wherein the film substantially coats all surfaces of at least one pore of the plurality of blind pores.
55. The product of claim 52, wherein the third phase is in the form of a mass, and wherein the mass occupies at least 10% of a volume of at least one pore of the plurality of blind pores.
56. The product of claim 55, wherein the mass occupies at least 25% of the volume of at least one pore of the plurality of blind pores.
57. The product of claim 55, wherein the mass occupies at least 50% of the volume of at least one pore of the plurality of blind pores.
58. The product of claim 55, wherein the mass occupies at least 75% of the volume of at least one pore of the plurality of blind pores.
59. The product of claim 55, wherein the mass occupies at least 95% of the volume of at least one pore of the plurality of blind pores.
60. The product of claim 55, wherein the mass occupies at least 99% of the volume of at least one pore of the plurality of blind pores.
61. The product of claim 52, wherein the third phase comprises carbon.
62. The product of claim 52, wherein the third phase consists essentially of carbon.
63. The product of claim 52, wherein the third phase comprises silicon carbide.
64. The product of claim 52, wherein the third phase consists essentially of silicon carbide.
65. The product of claim 52, wherein the third phase comprises an electrically conductive material.
66. The product of claim 65, wherein the electrically conductive material is a material selected from the group consisting of metals, conductive metal oxides, conductive nitrides, conductive silicides, conductive polymers, graphite, and combinations thereof.
67. The product of claim 52, wherein the third phase comprises a dielectric.
68. The product of claim 67, wherein the dielectric is selected from the group consisting of ceramics, titanates, apatites, carbides, borides, nitrides, polymers, carbon-based materials, and combinations thereof.
69. The product of claim 52, wherein the third phase comprises a semiconductor.
70. The product of claim 69, wherein the semiconductor is a material selected from the group consisting of silicon, germanium, phosphides, semiconductive silicides, silicon carbide, and combinations thereof.

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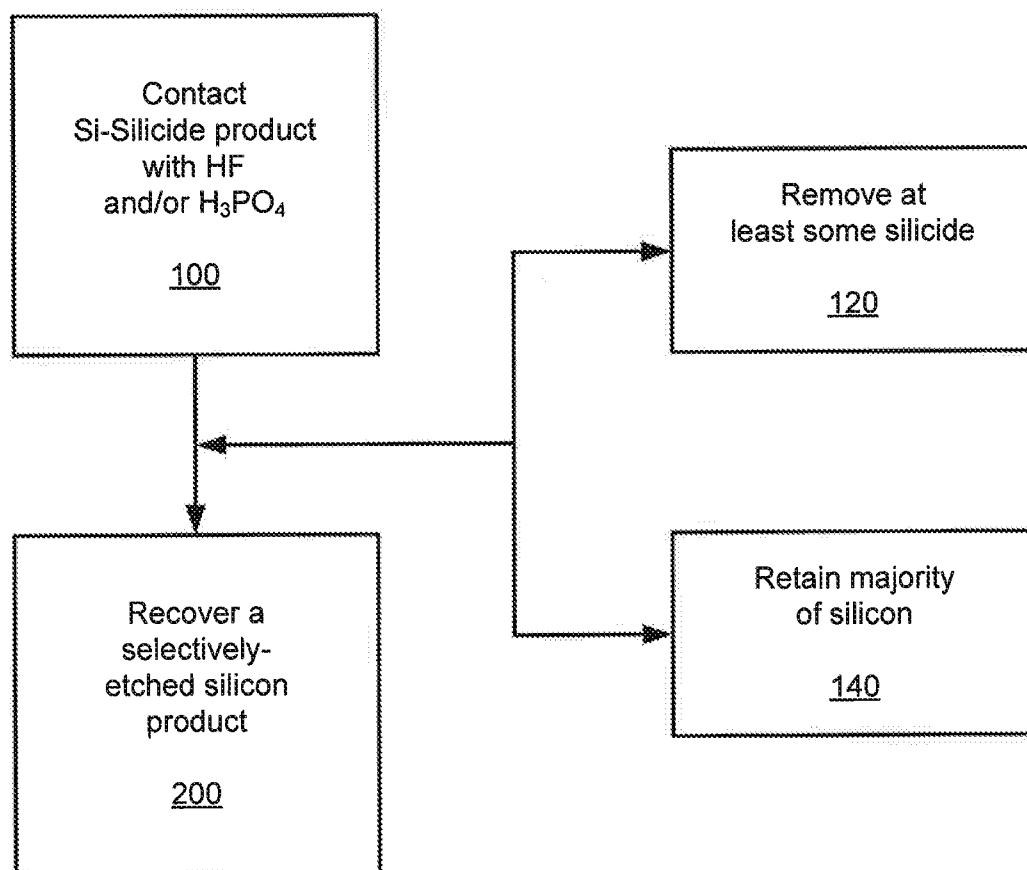


FIG. 1

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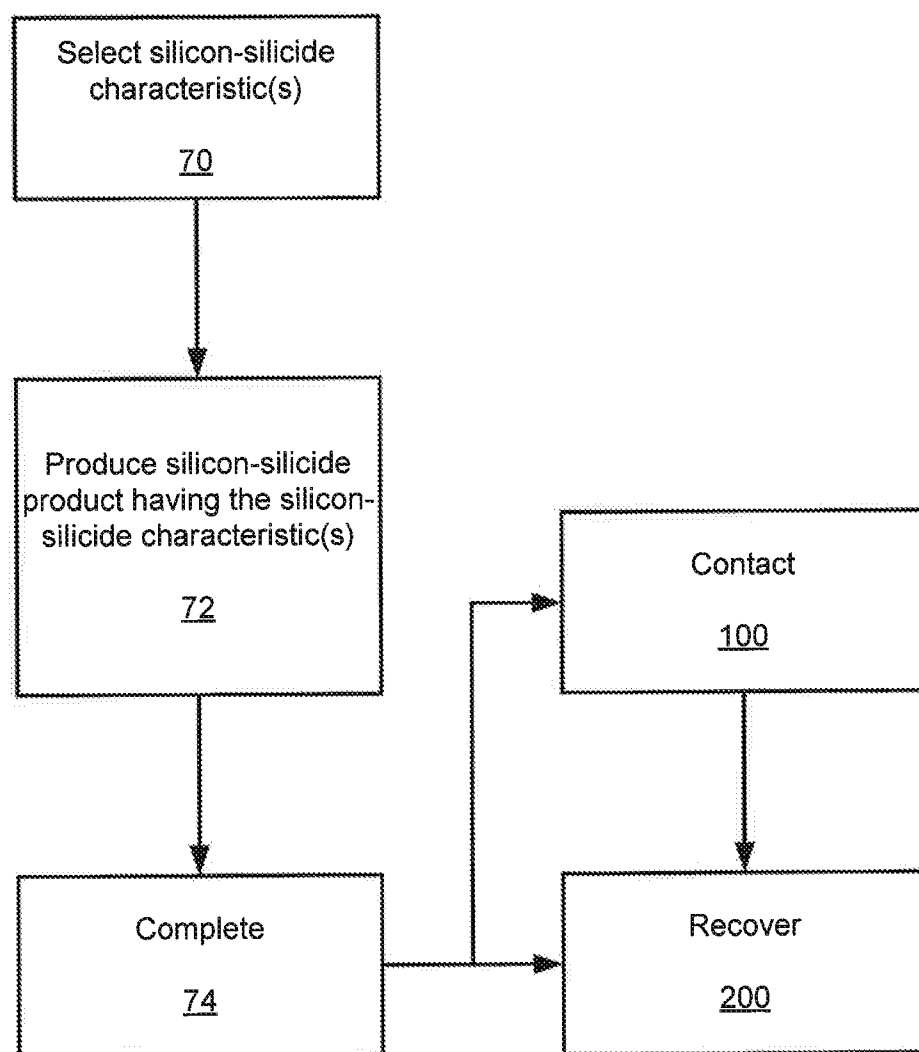


FIG. 2

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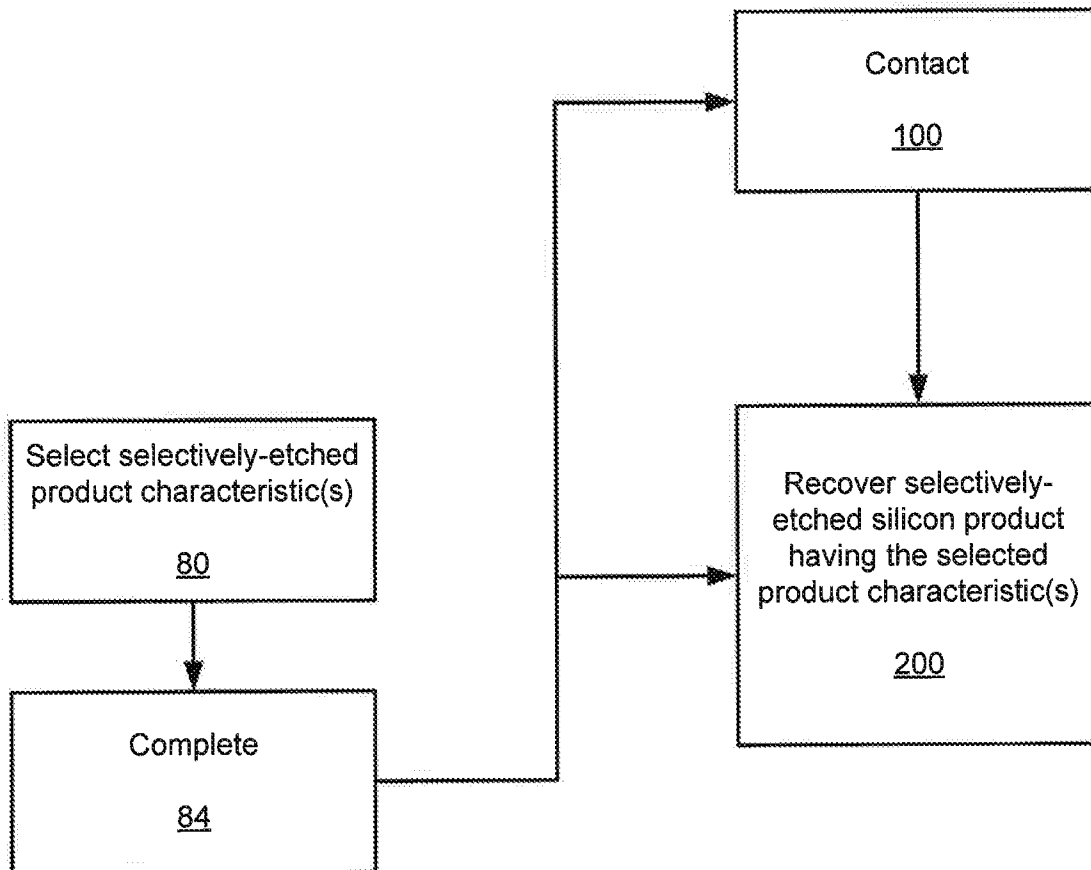


FIG. 3

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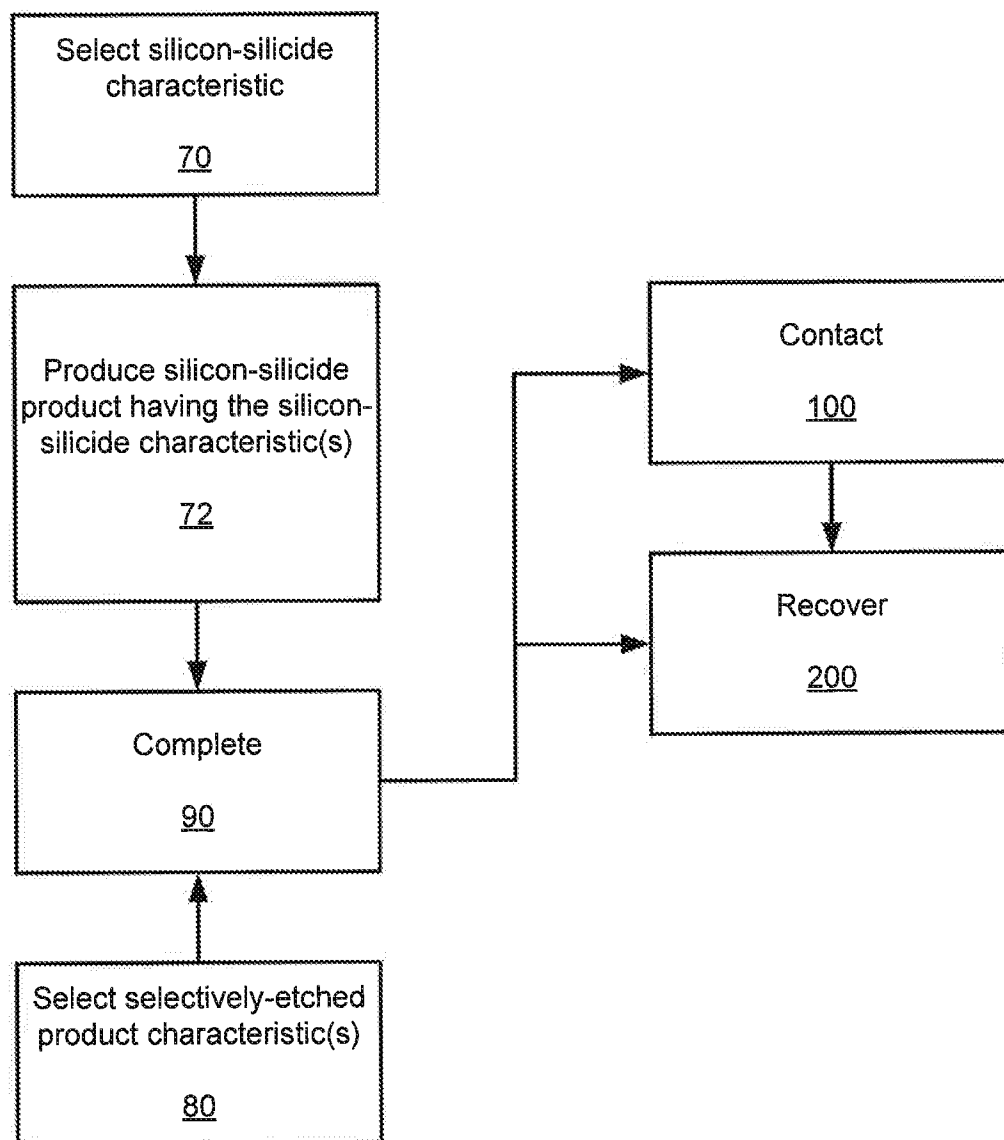


FIG. 4

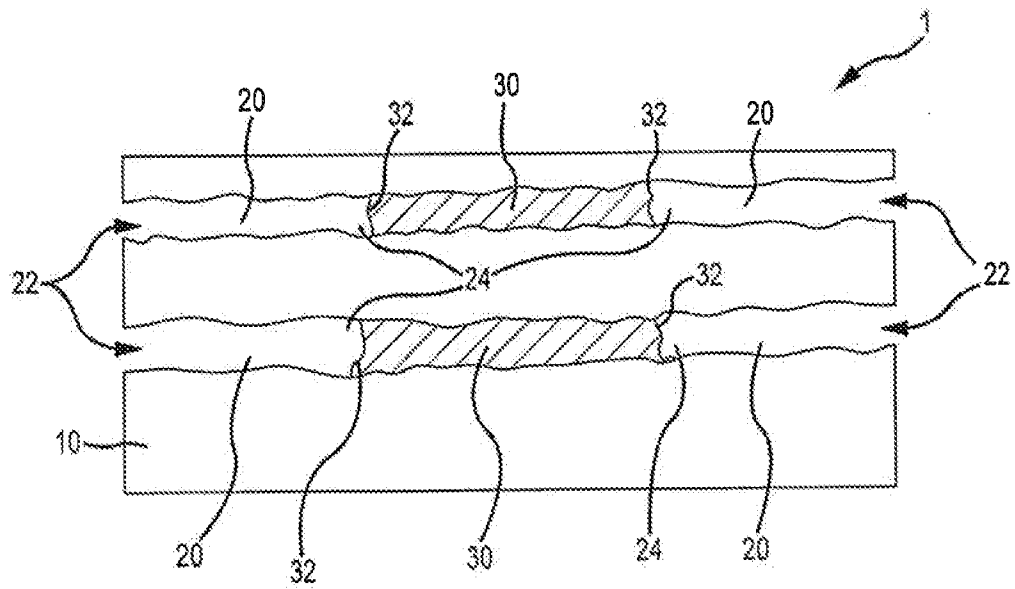
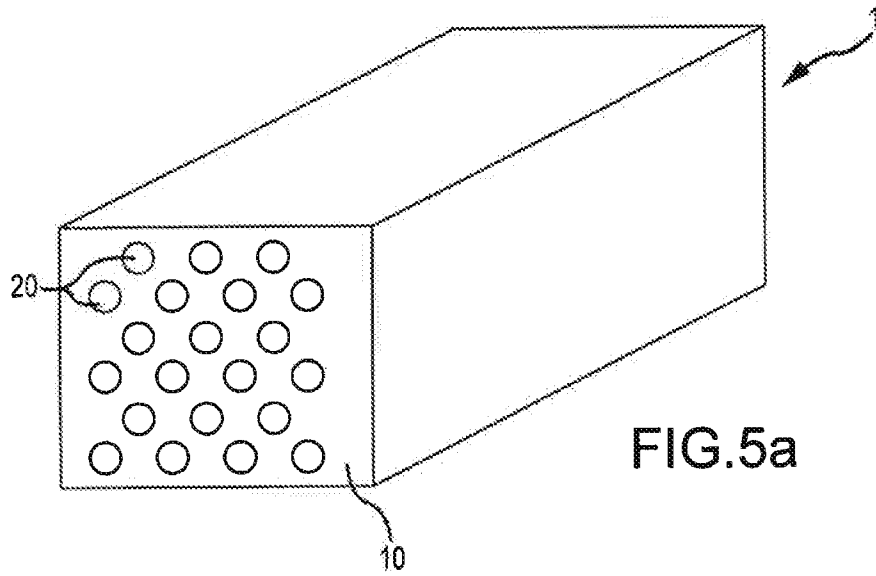


FIG. 5b

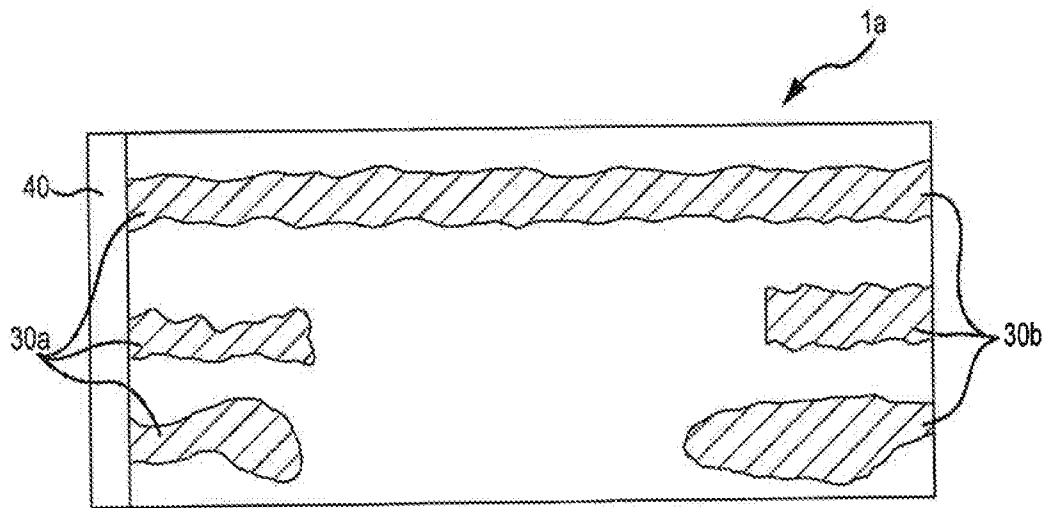


FIG. 6a

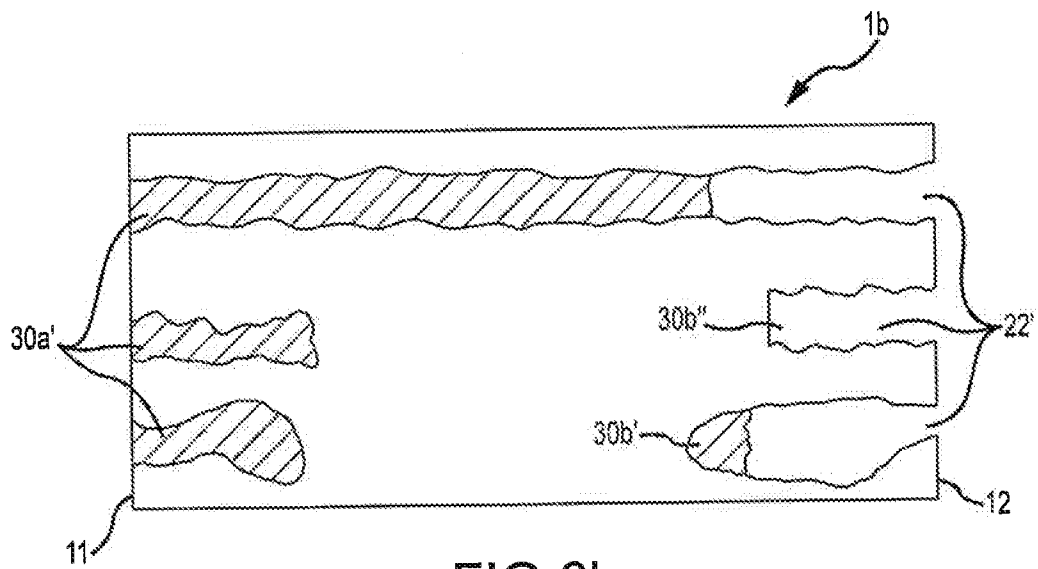


FIG. 6b

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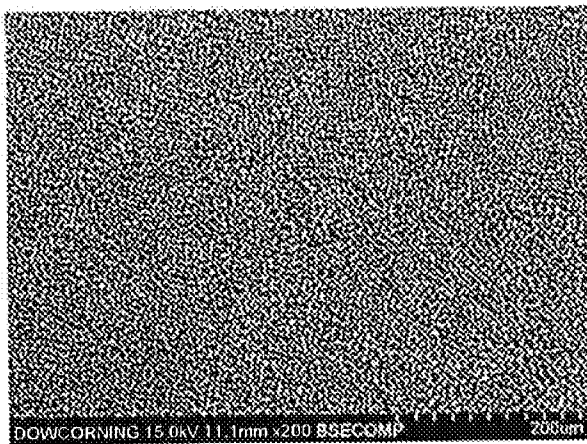


FIG. 7a

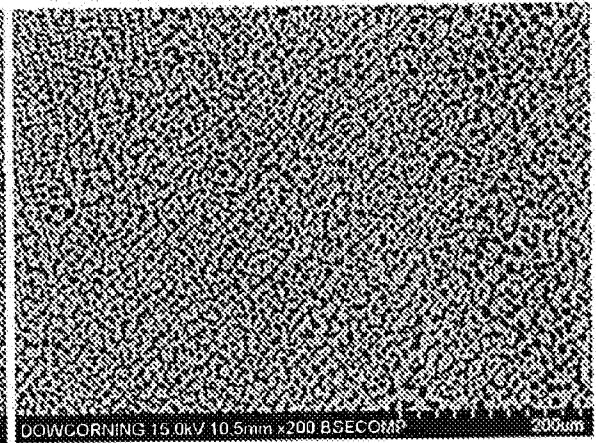


FIG. 7c

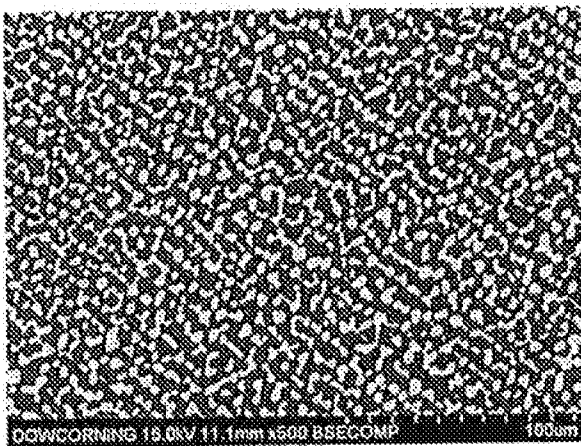


FIG. 7b

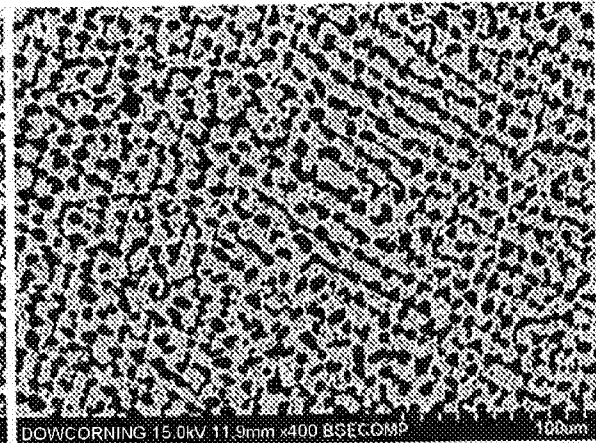


FIG. 7d

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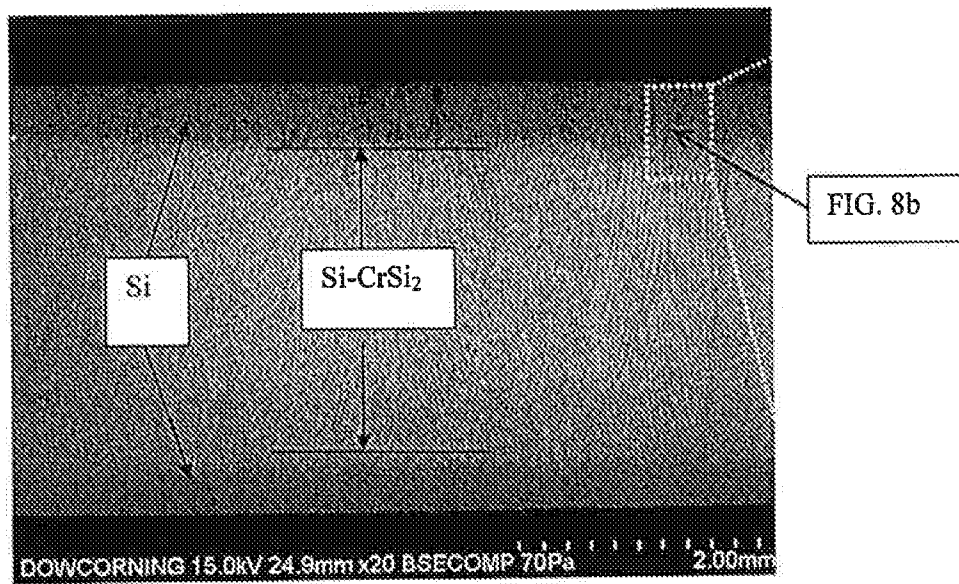


FIG. 8a

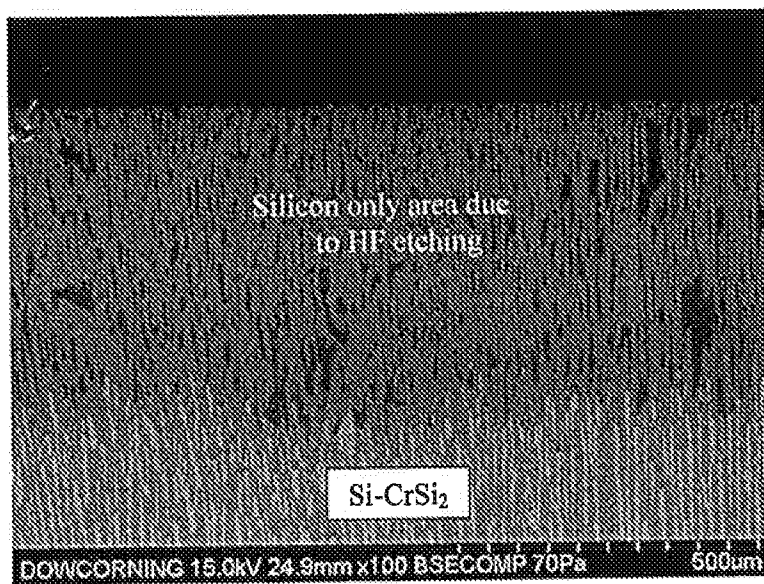


FIG. 8b

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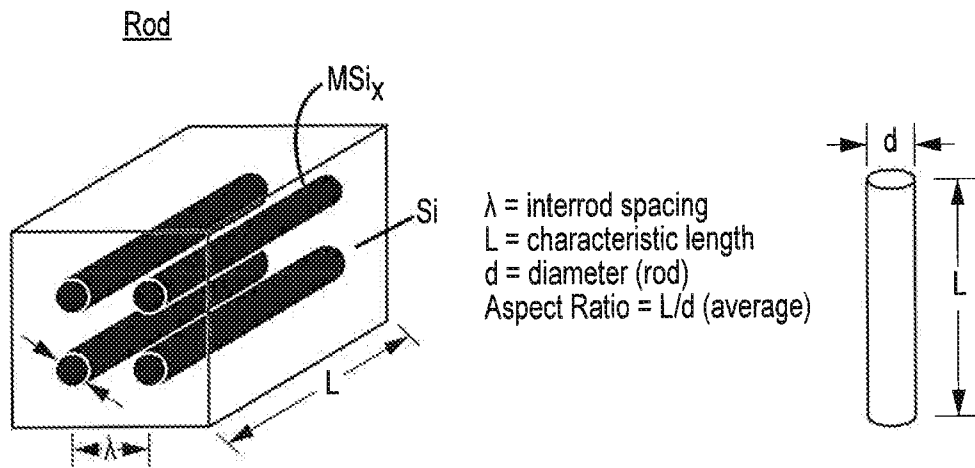


FIG.9a

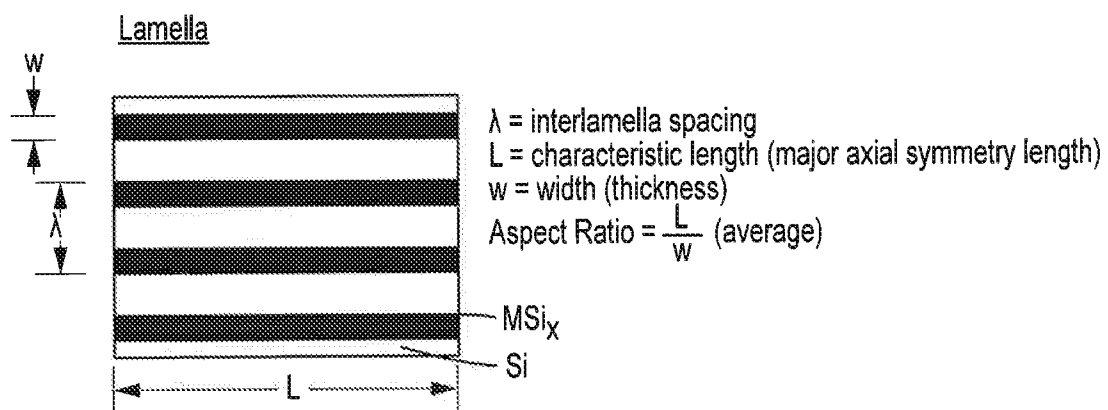


FIG.9b

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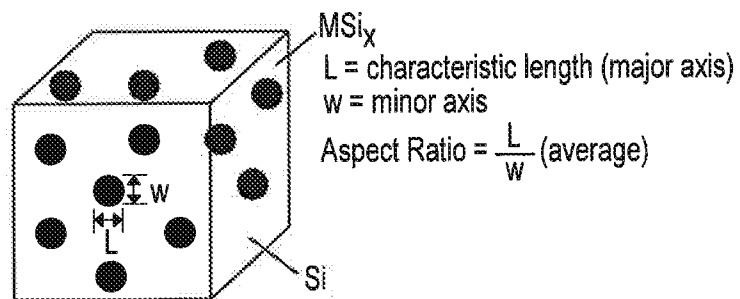
Globular

FIG.9c

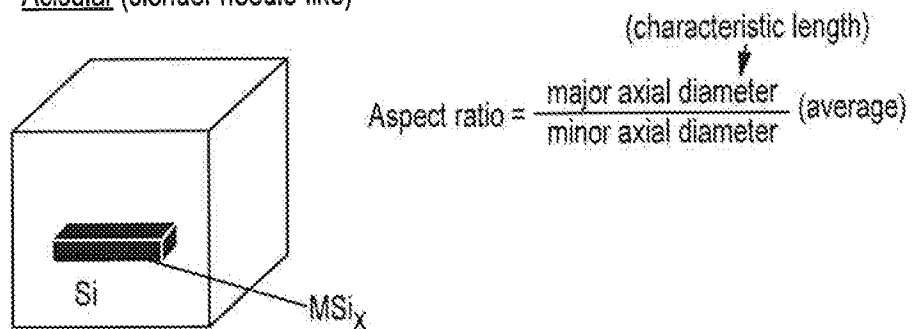
Acicular (slender needle-like)

FIG.9d

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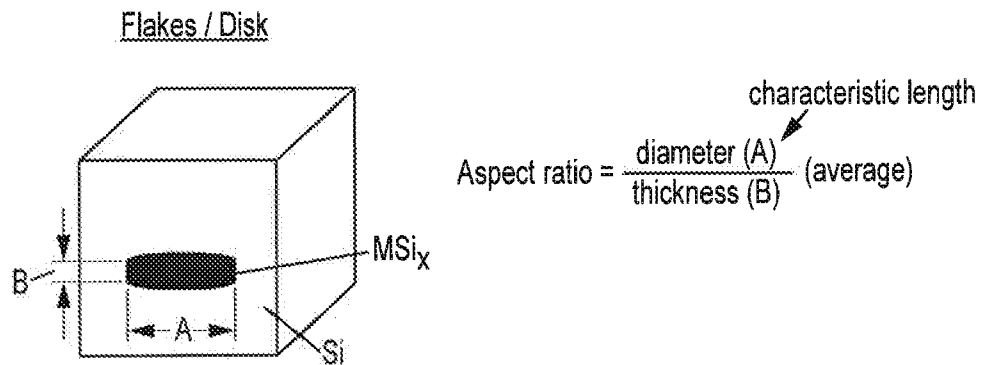


FIG.9e

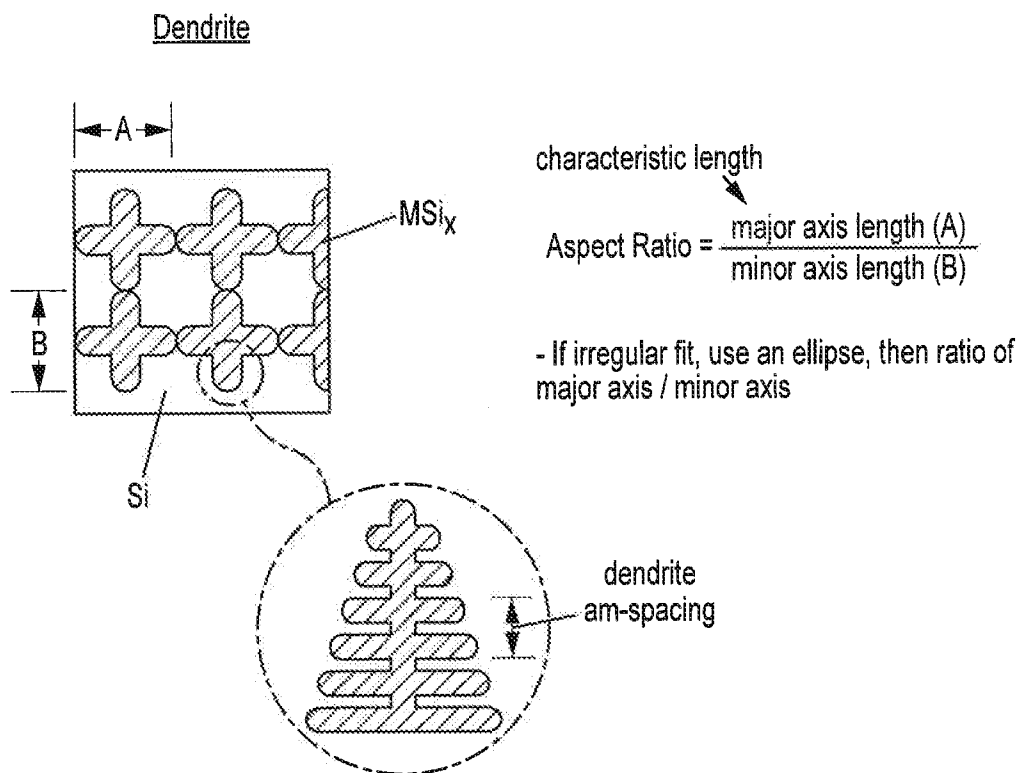


FIG.9f

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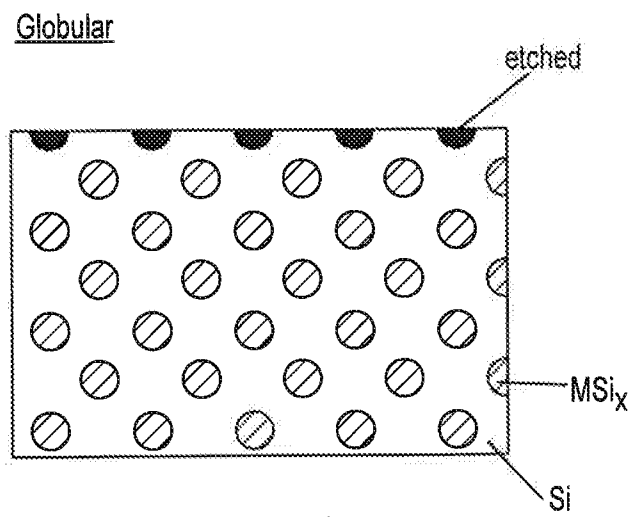


FIG.10a

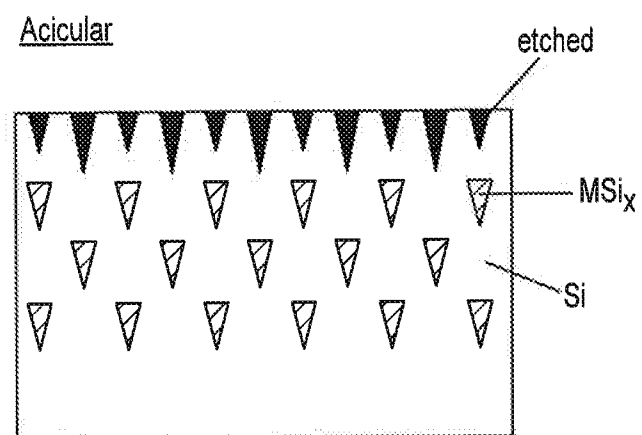


FIG.10b

Interpenetrated / Percolated

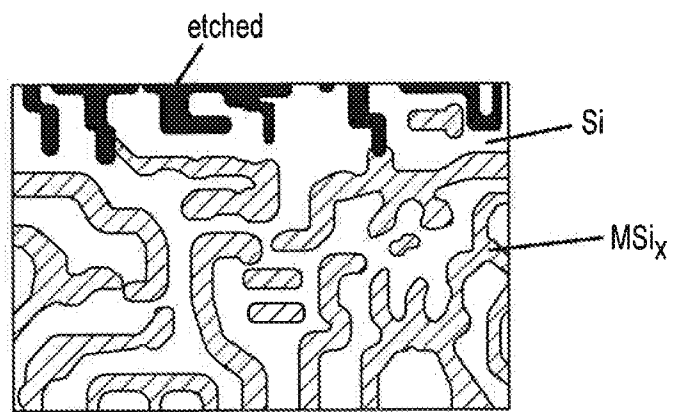


FIG.10c

Dendritic

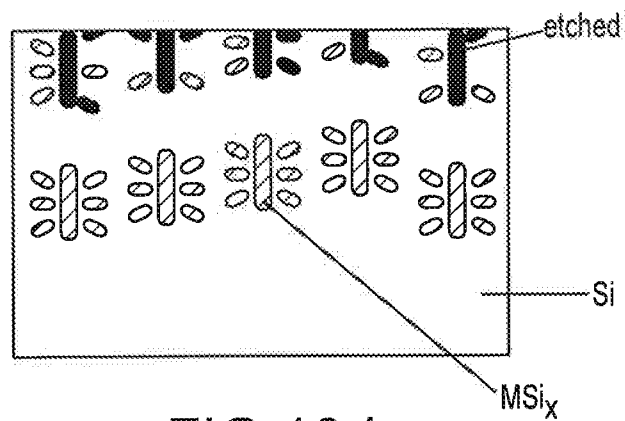


FIG.10d

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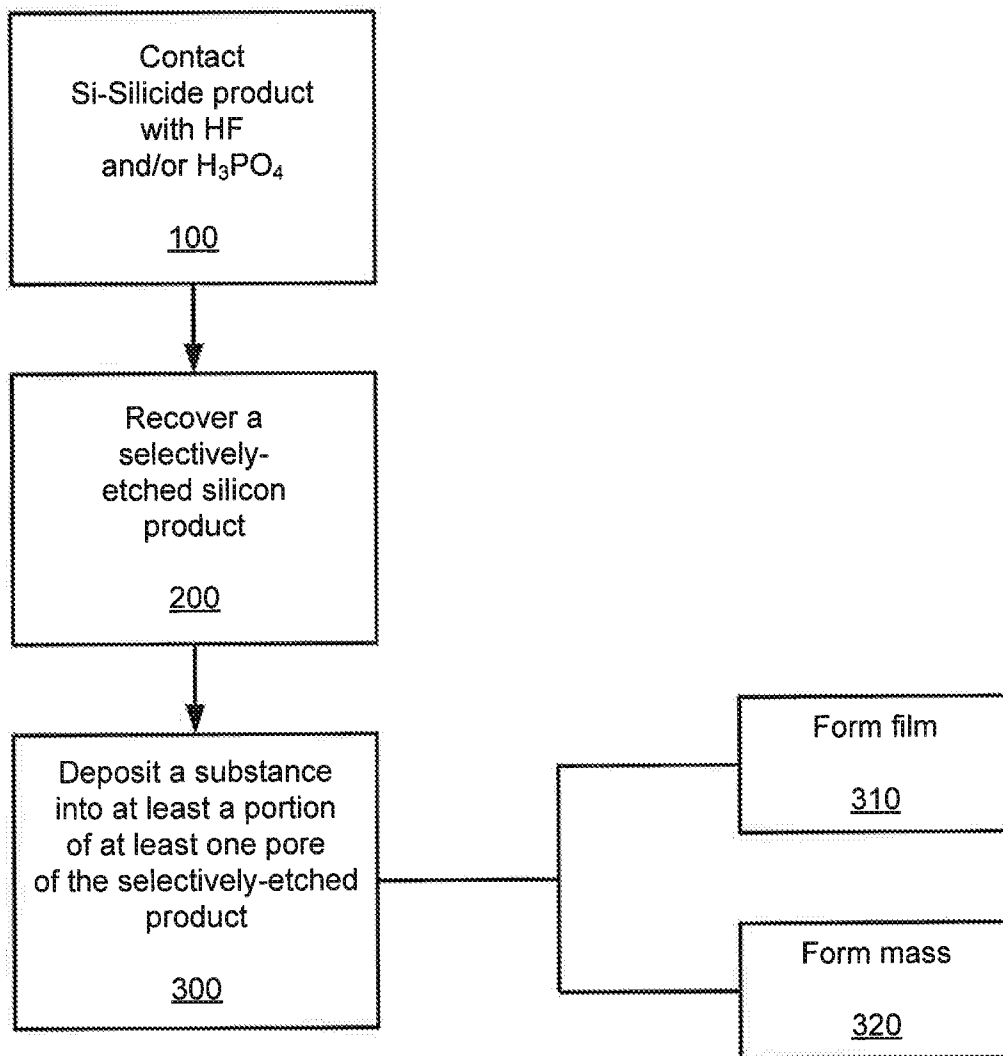


FIG. 11a

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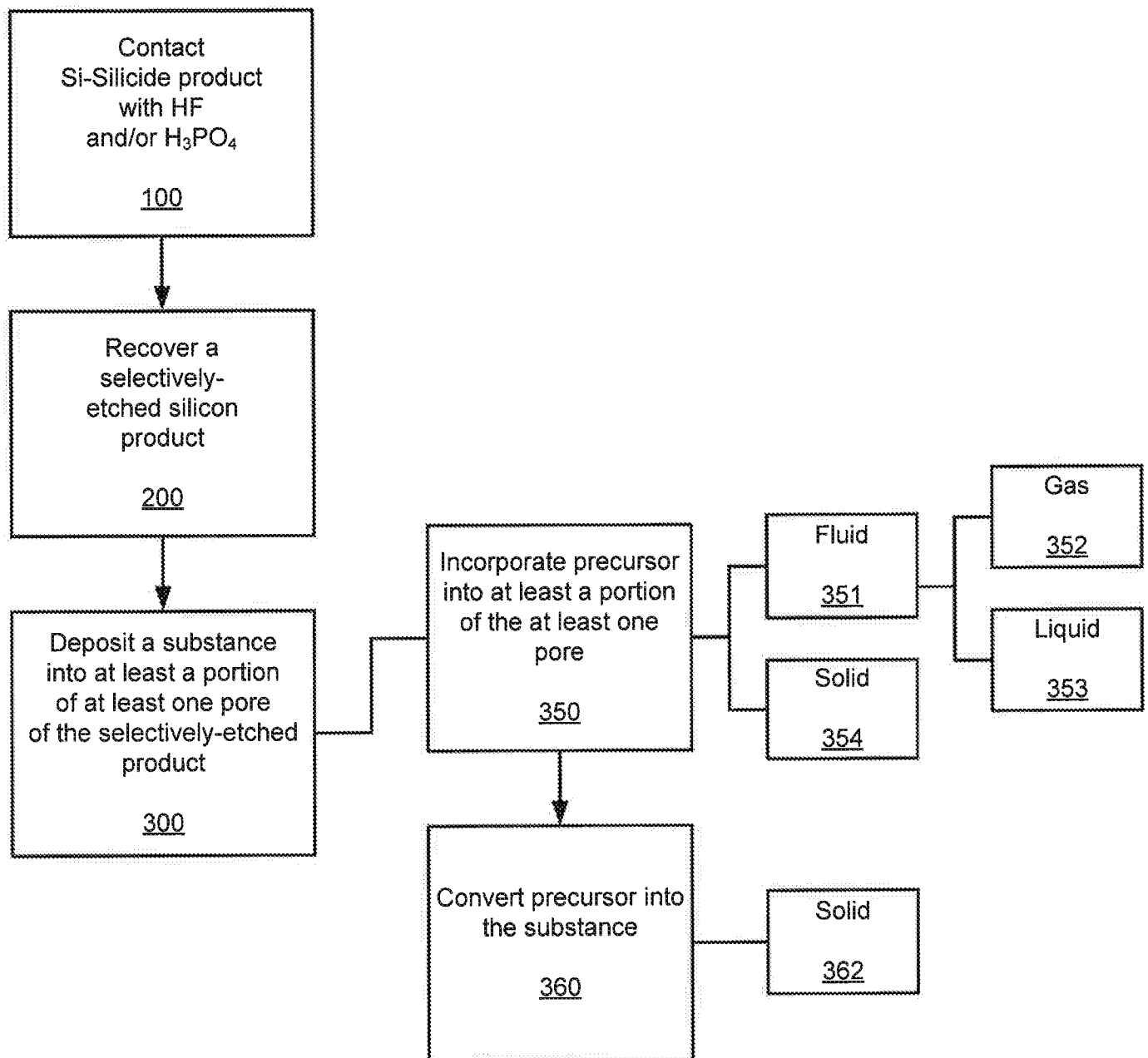


FIG. 11b

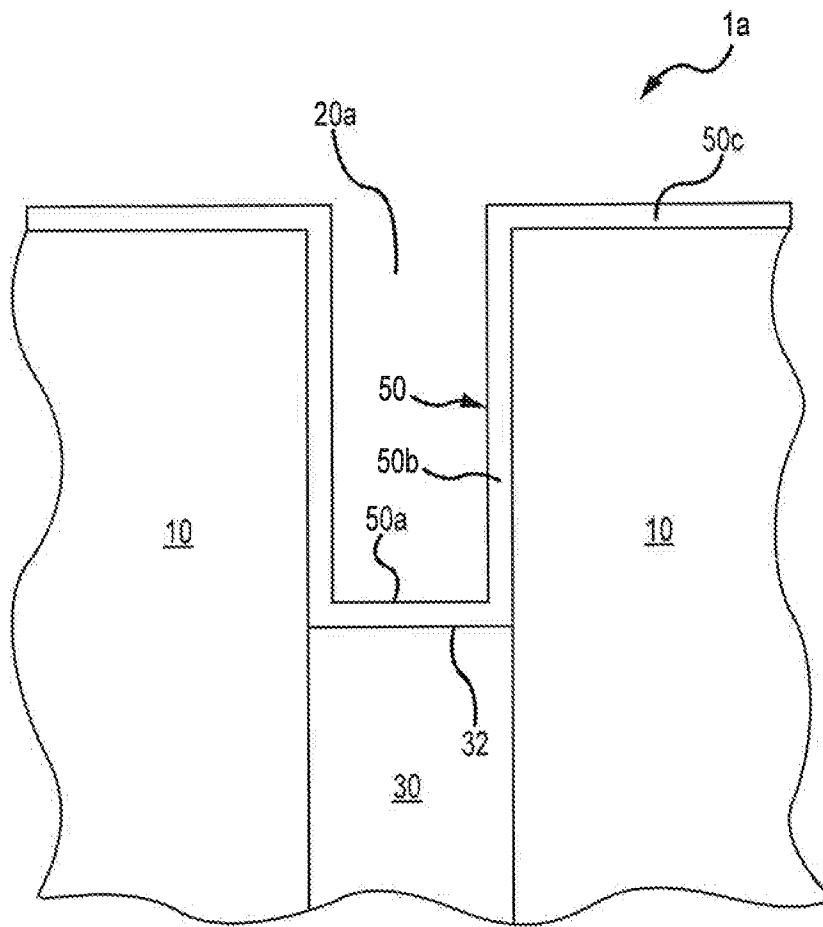


FIG.12A

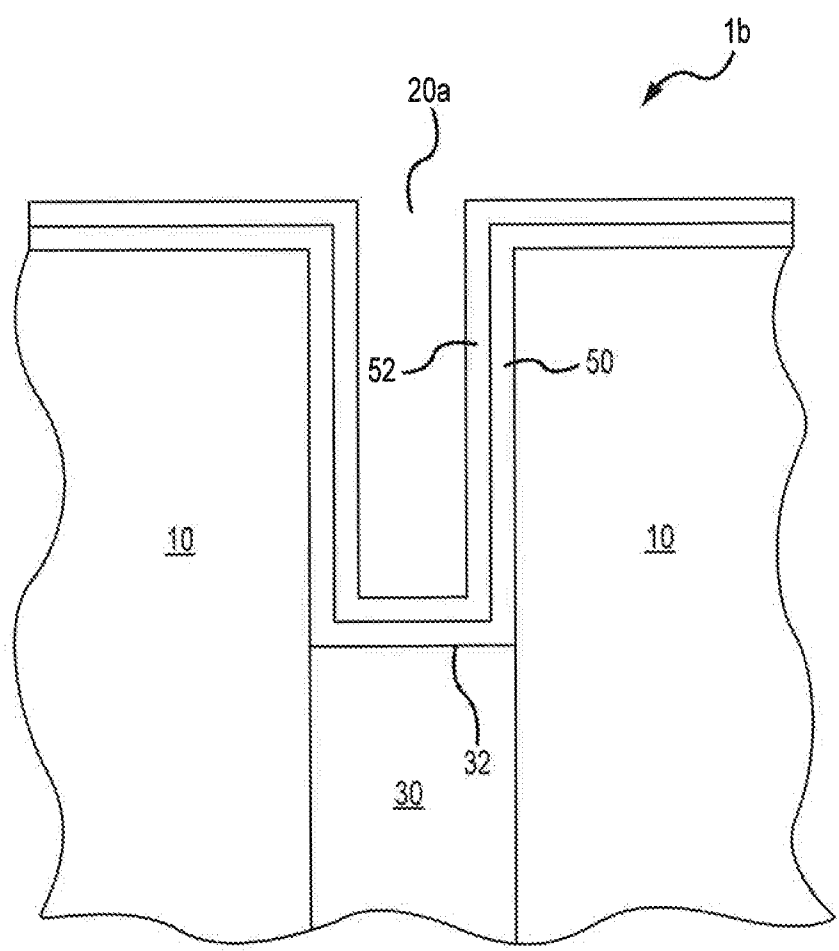


FIG. 12B

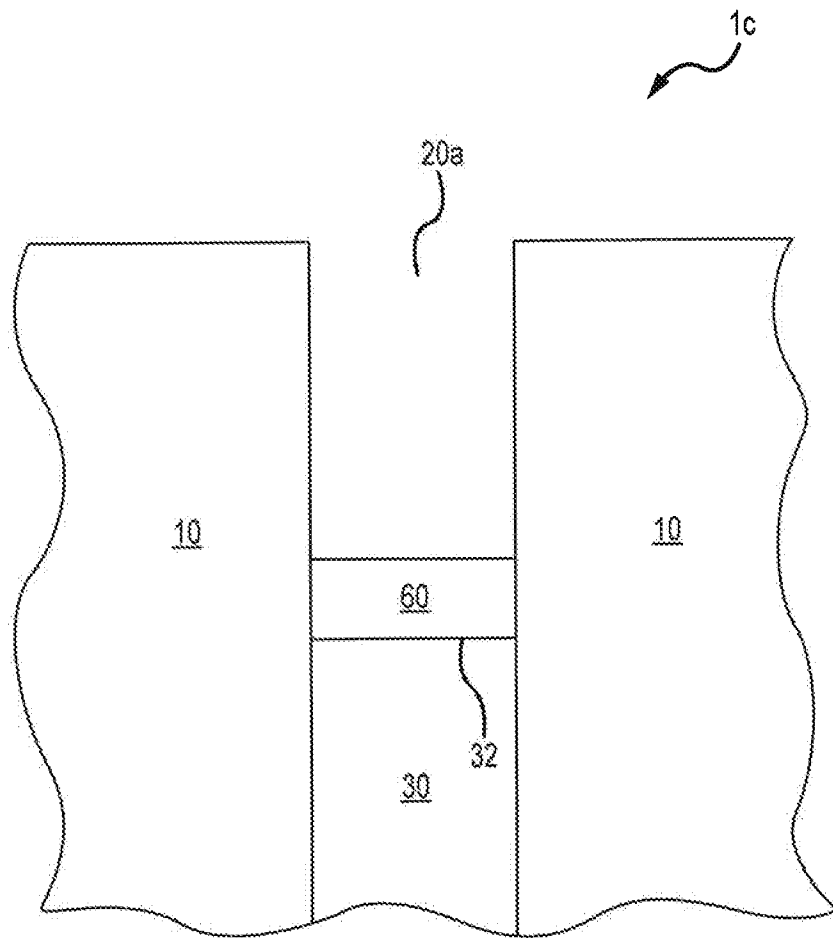


FIG. 12C

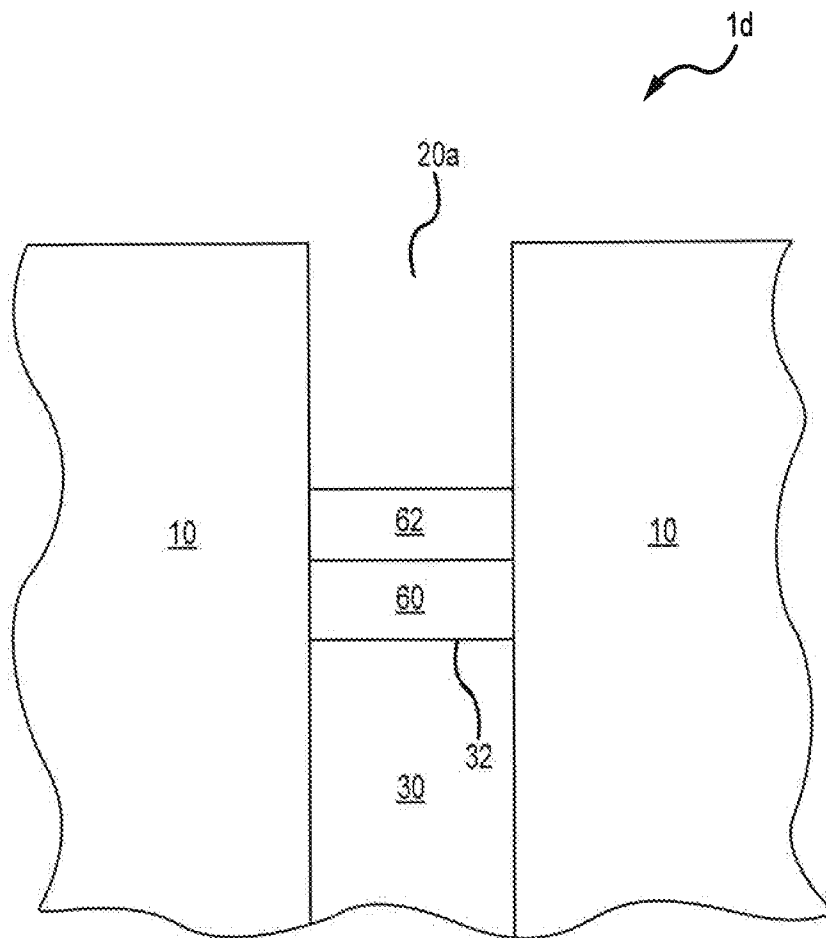
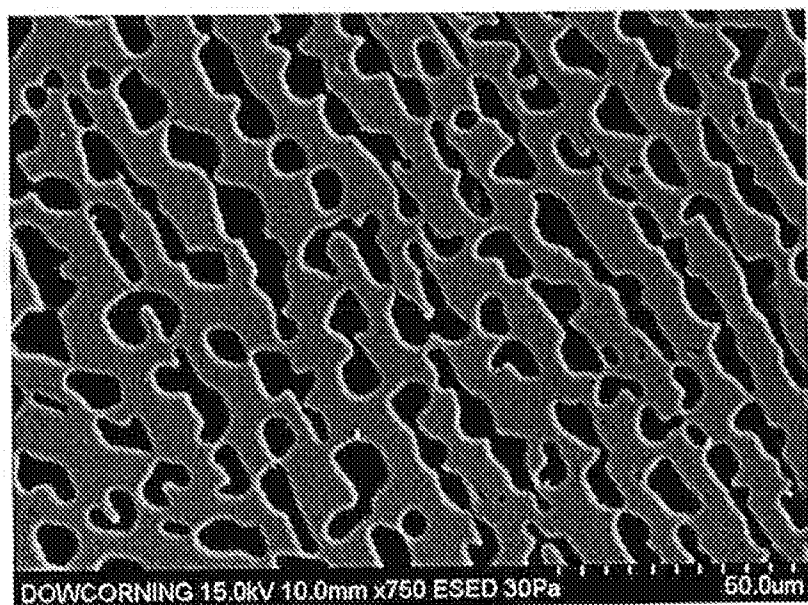
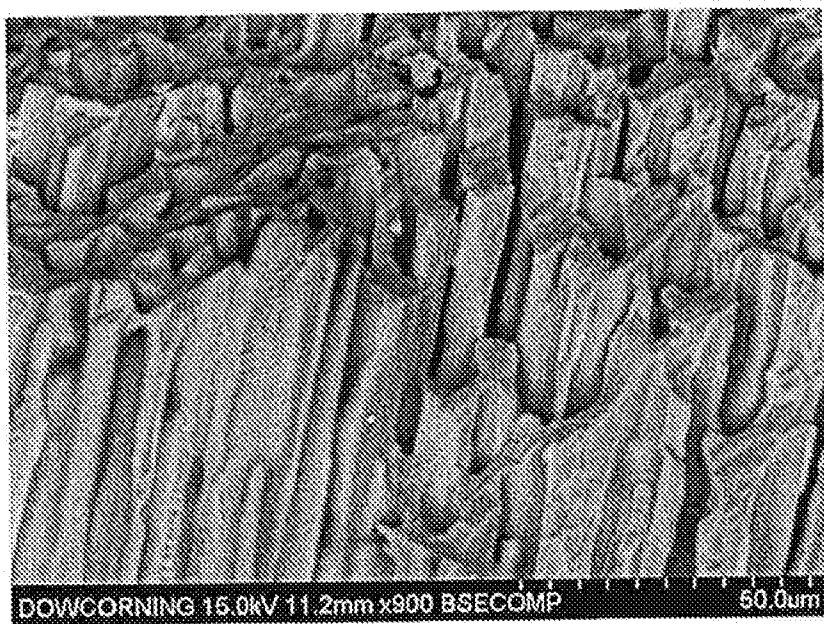


FIG.12D

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**FIG. 13a****FIG. 13b**

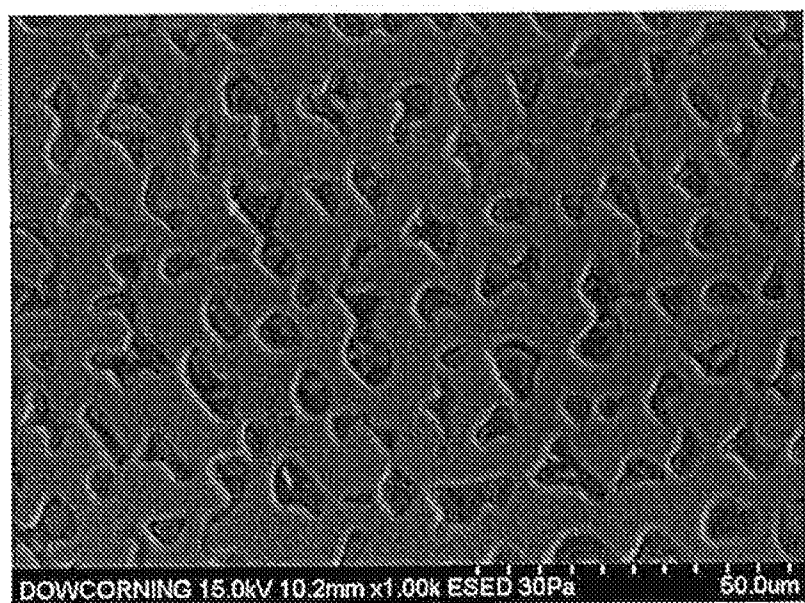


FIG. 14a

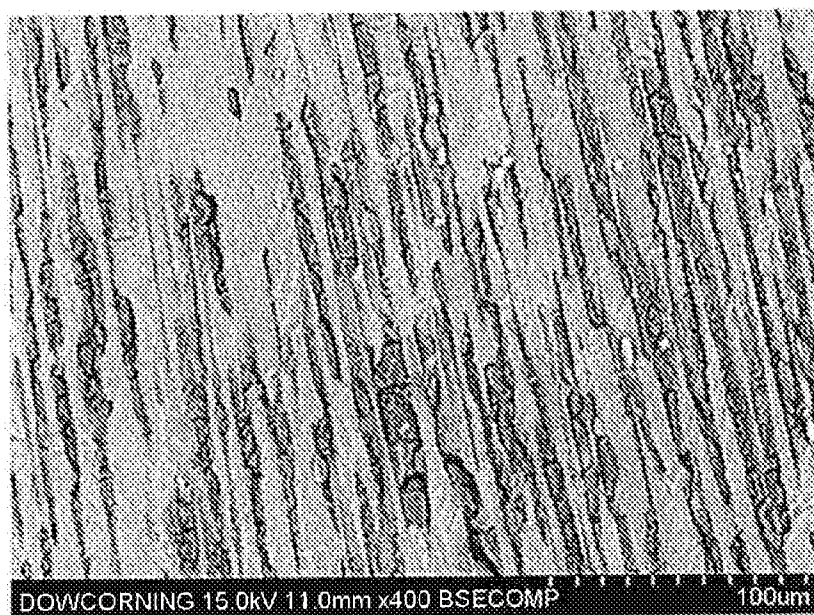


FIG. 14b

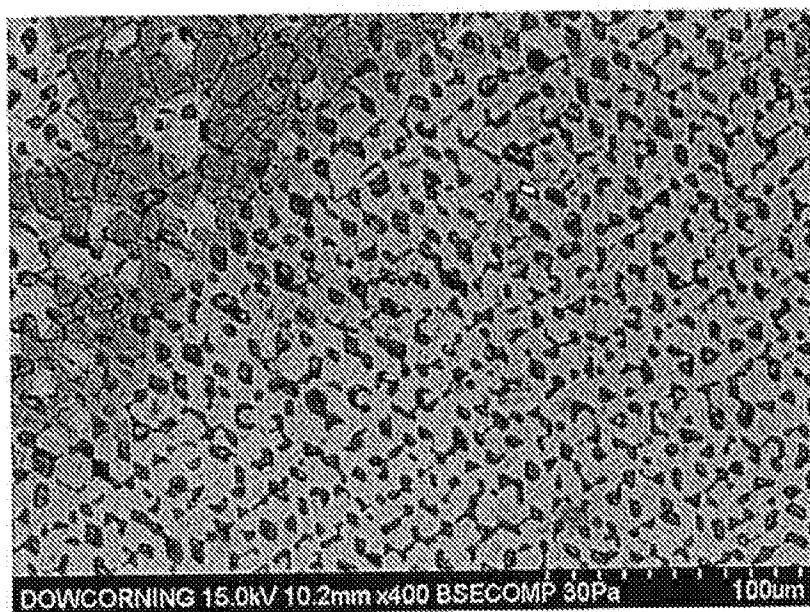


FIG. 14c

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/042703

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L21/3213 C01B33/02
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 C01B

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, CHEM ABS Data, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/214085 A1 (SHEEM KYOU-YOON [KR] ET AL) 28 October 2004 (2004-10-28)	23-31
Y	claims 1-15 paragraphs [0026], [0044], [0045], [0074] - [0081] examples 1-4	1-22, 32-70
Y	US 2003/124779 A1 (SEO HYUN-SIK [KR] ET AL) 3 July 2003 (2003-07-03) claim 1 paragraphs [0019], [0027], [0030] ----- -/-	1-22



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

29 October 2014

Date of mailing of the international search report

11/11/2014

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

Rigondaud, Bernard

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/042703

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SAAD K B ET AL: "AC impedance spectroscopy of porous silicon thin films containing metallic cations", MATERIALS SCIENCE AND ENGINEERING C, ELSEVIER SCIENCE S.A, CH, vol. 28, no. 5-6, 1 July 2008 (2008-07-01), pages 623-627, XP022632911, ISSN: 0928-4931, DOI: 10.1016/J.MSEC.2007.10.052 [retrieved on 2007-10-16] abstract pages 624 and 625: "2. Experimental preparations" -----	1-22, 32-70
A	MIRANDA C R B ET AL: "Nanodiamond infiltration into porous silicon through etching of solid carbon produced at different graphitization temperatures", JOURNAL OF NANOPARTICLE RESEARCH SPRINGER NETHERLANDS NETHERLANDS, vol. 13, no. 9, September 2011 (2011-09), pages 4219-4228, XP002731753, ISSN: 1388-0764 abstract pages 4220 and 4221: "Experimental" -----	1-70
A	MURZINA TATYANA ET AL: "Tunable ferroelectric photonic crystals based on porous silicon templates infiltrated by sodium nitrite", APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS, US, vol. 90, no. 16, 18 April 2007 (2007-04-18), pages 161120-161120, XP012094173, ISSN: 0003-6951, DOI: 10.1063/1.2724928 the whole document -----	1-70
A	US 5 223 081 A (DOAN TRUNG T [US]) 29 June 1993 (1993-06-29) abstract claims 8,13 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/042703

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US 2003124779 A1	03-07-2003	KR 20030056252 A US 2003124779 A1 US 2005167634 A1	04-07-2003 03-07-2003 04-08-2005
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