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(54) **INORGANIC NANOPOROUS MEMBRANES AND METHODS TO FORM SAME**

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(52) **U.S. Cl.** **205/363**

(57) **ABSTRACT**

The invention provides a method of forming an inorganic porous membrane that includes forming an inorganic membrane material on a substrate, forming a porous self-assembled material on the inorganic membrane material, and patterning the membrane material using the porous self-assembled material as a mask.

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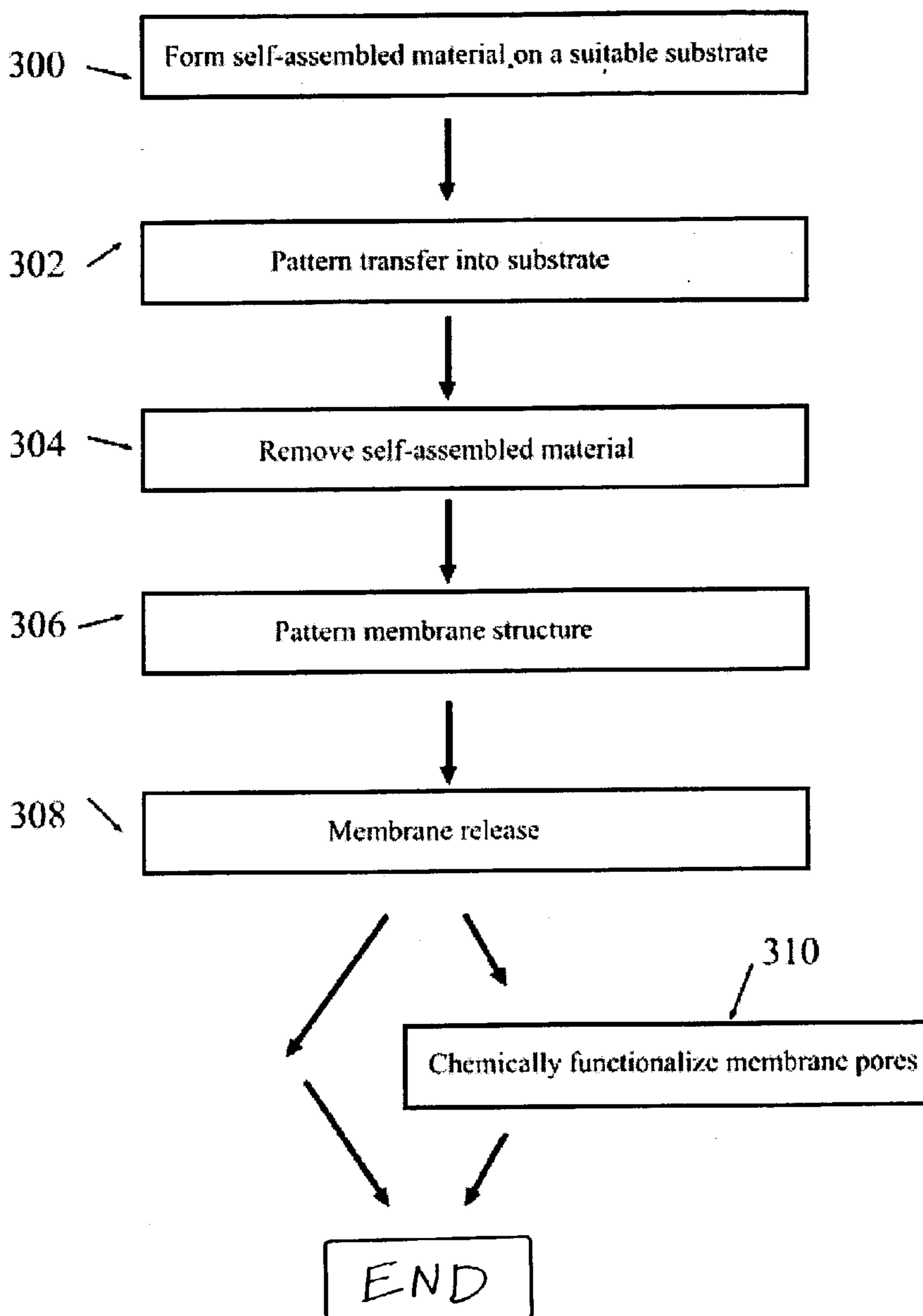
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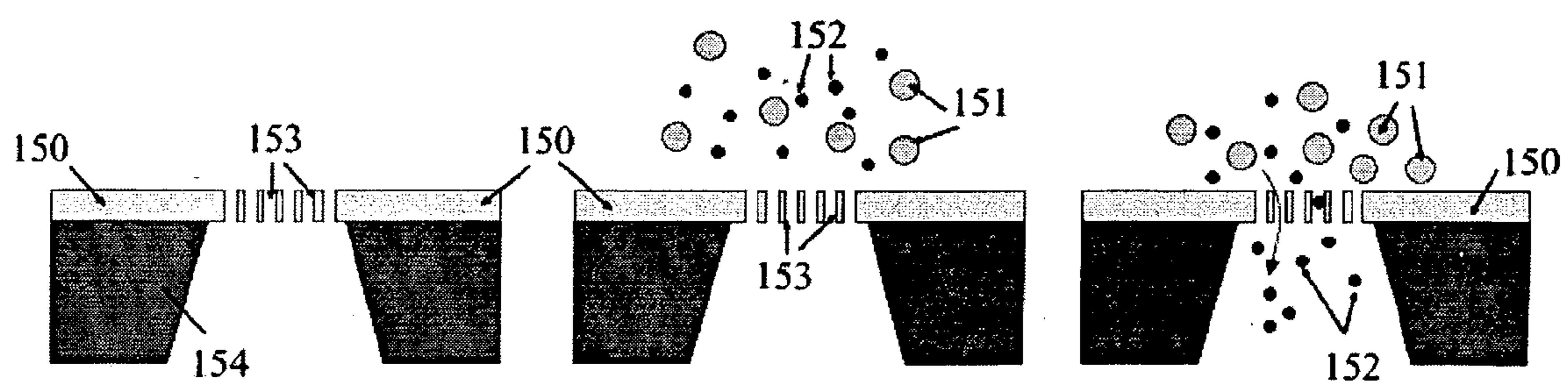


FIGURE 1A

FIGURE 1B

FIGURE 1C

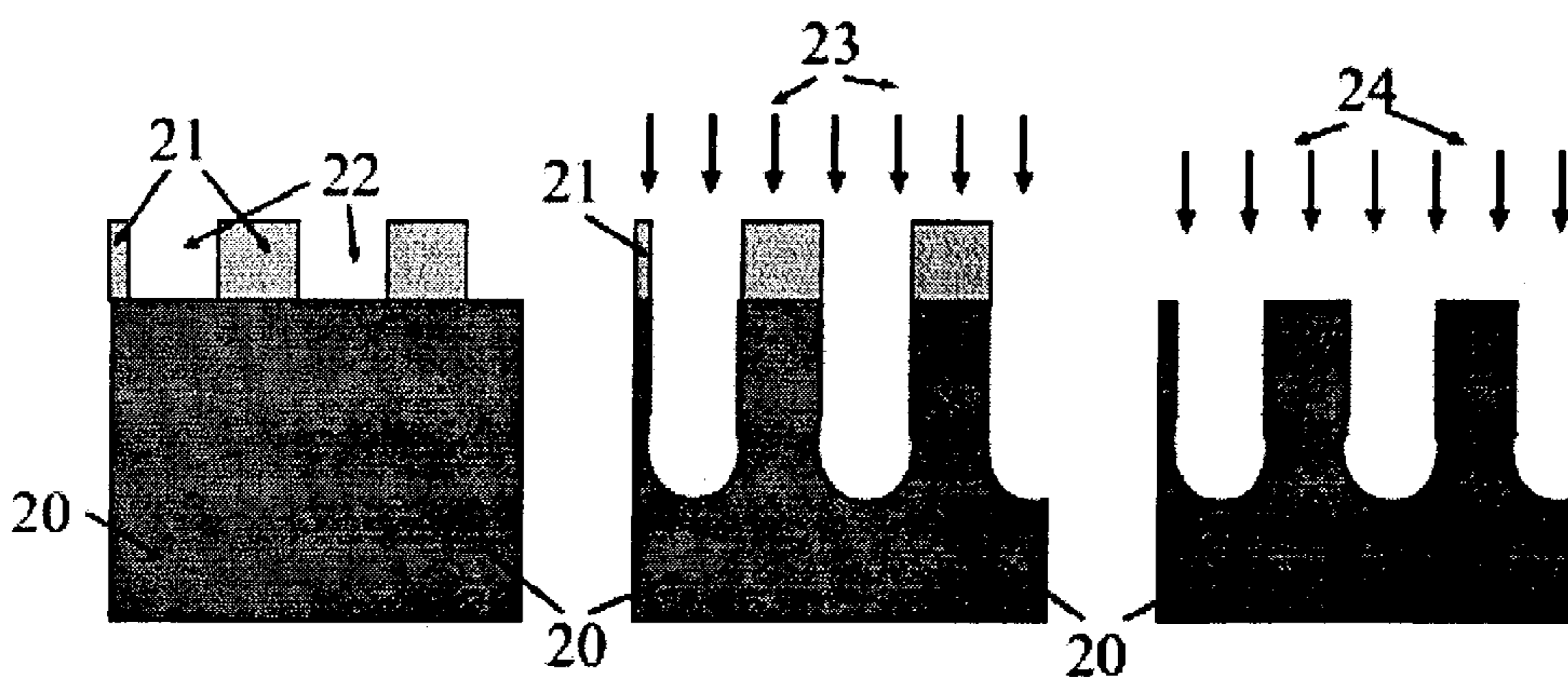


FIGURE 2A

FIGURE 2B

FIGURE 2C

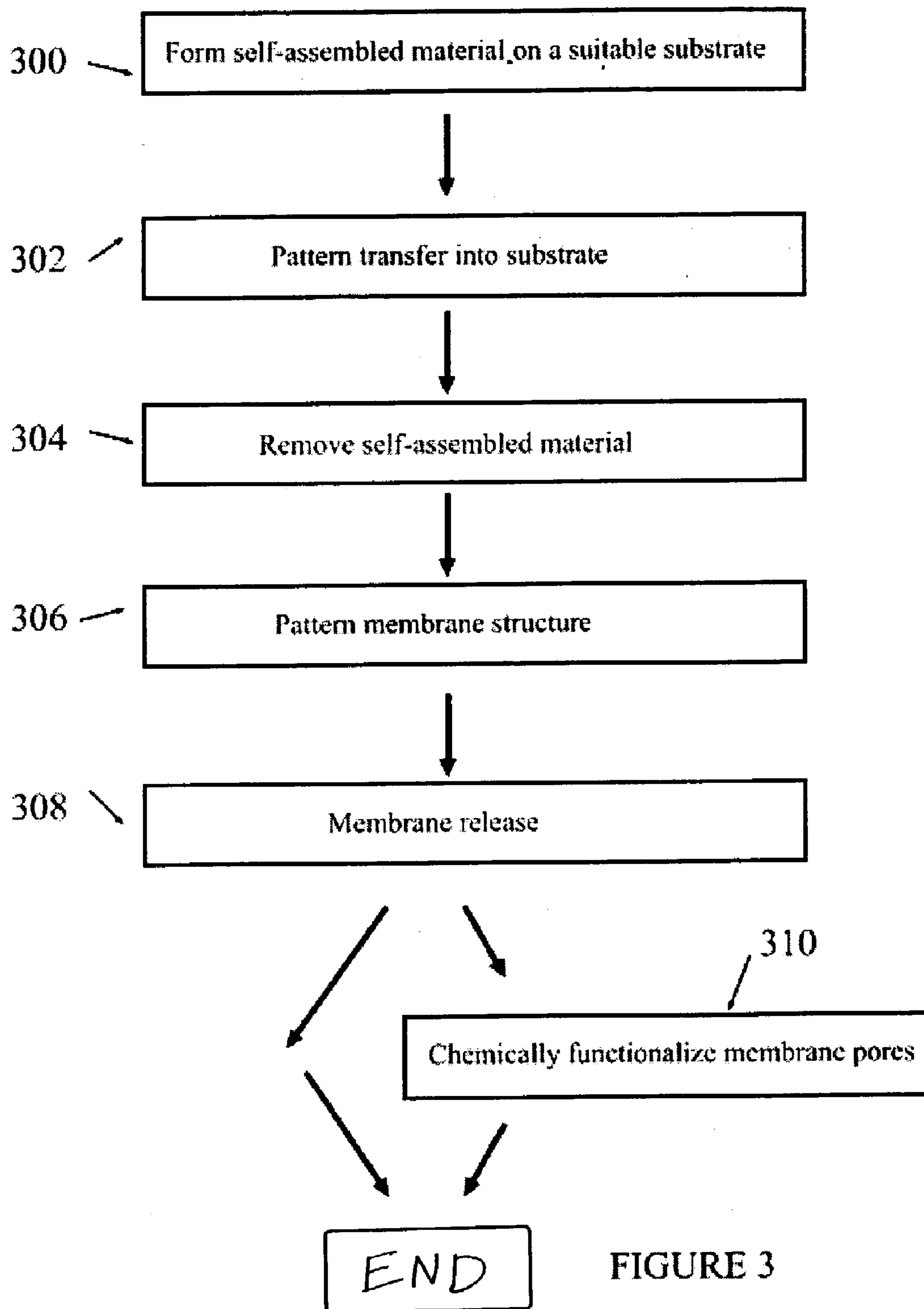


FIGURE 3

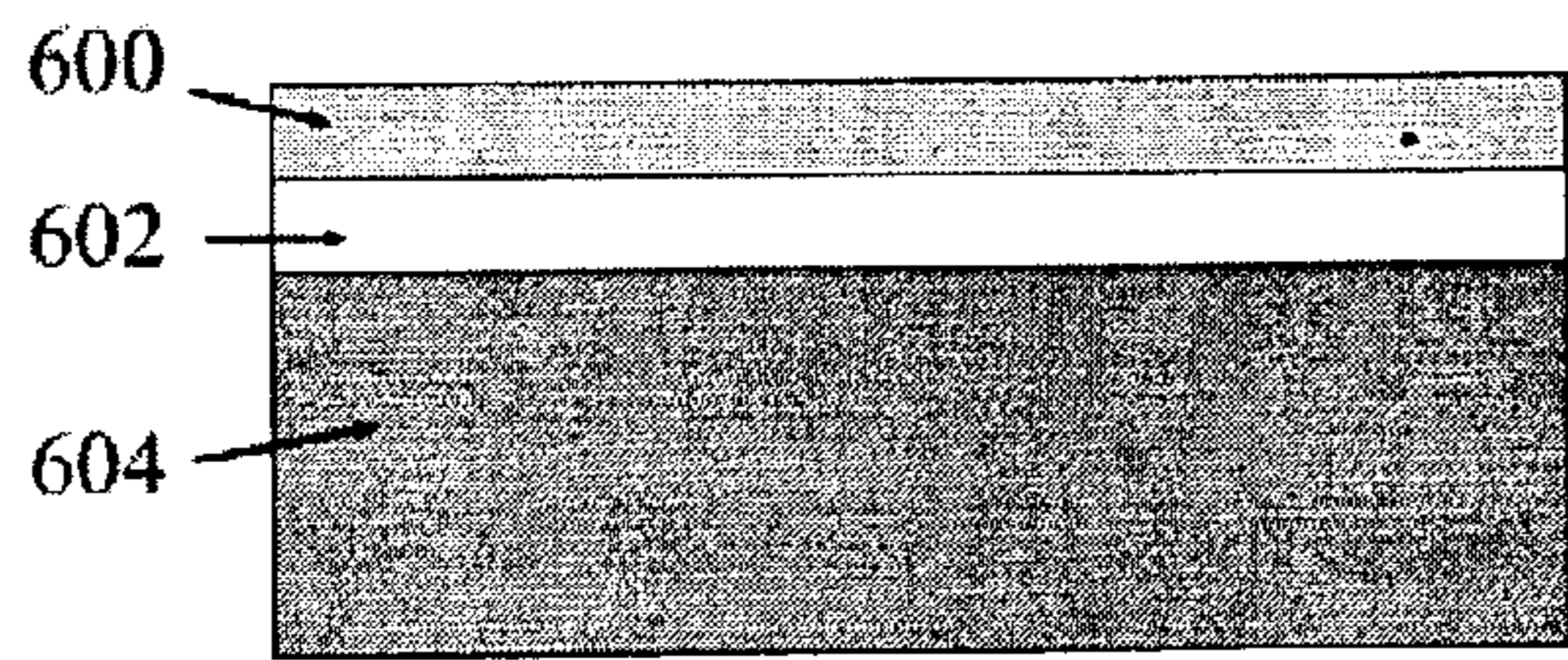


FIGURE 4A

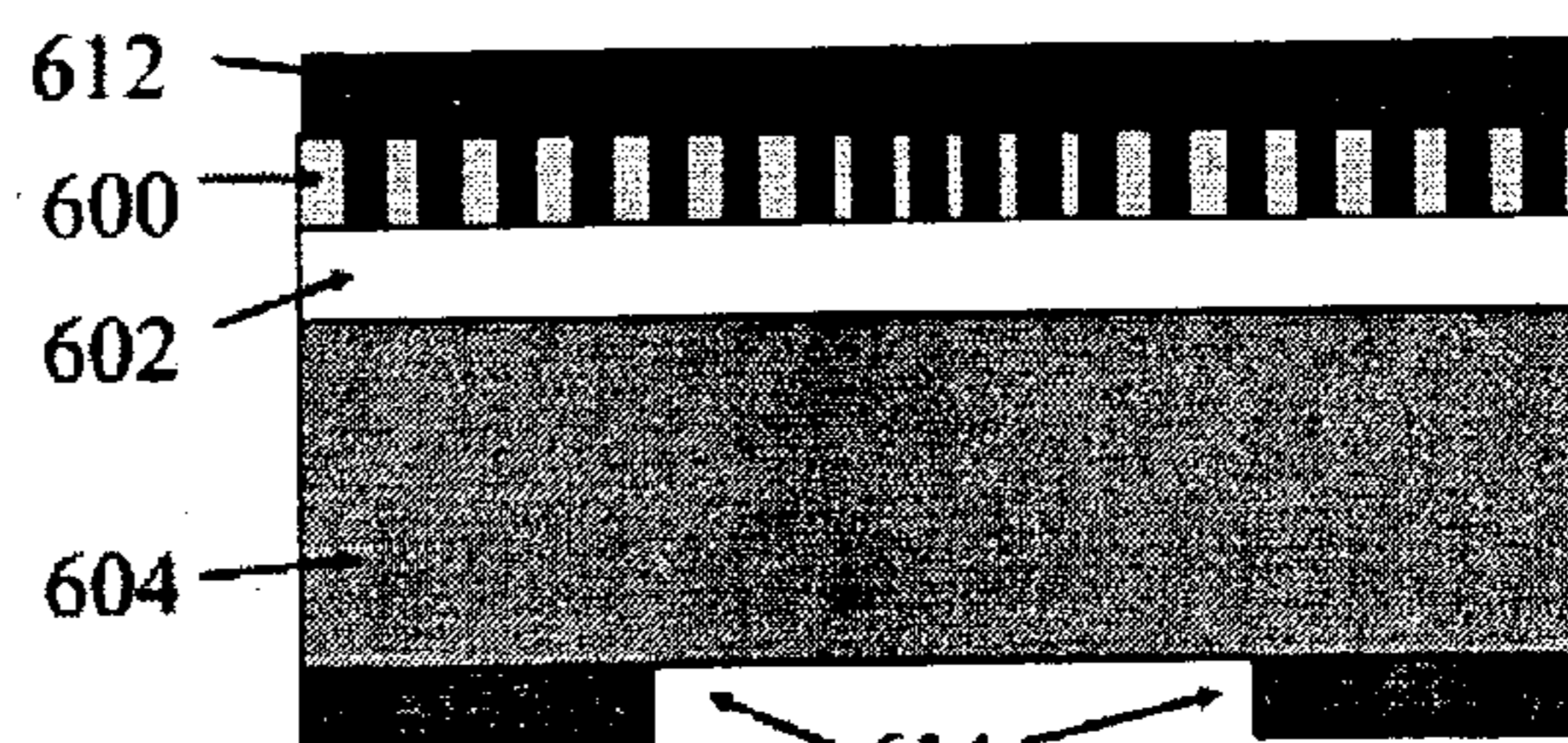


FIGURE 4E

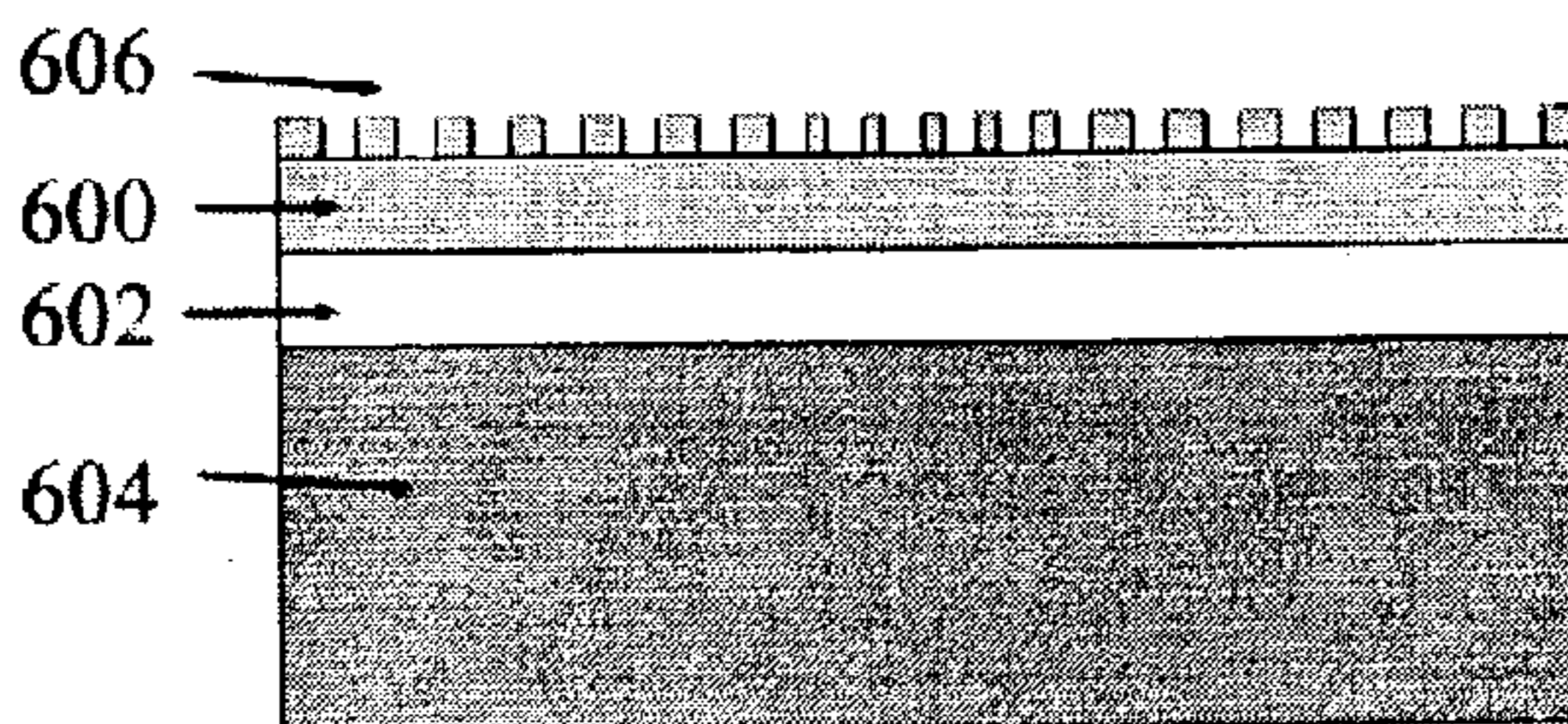


FIGURE 4B

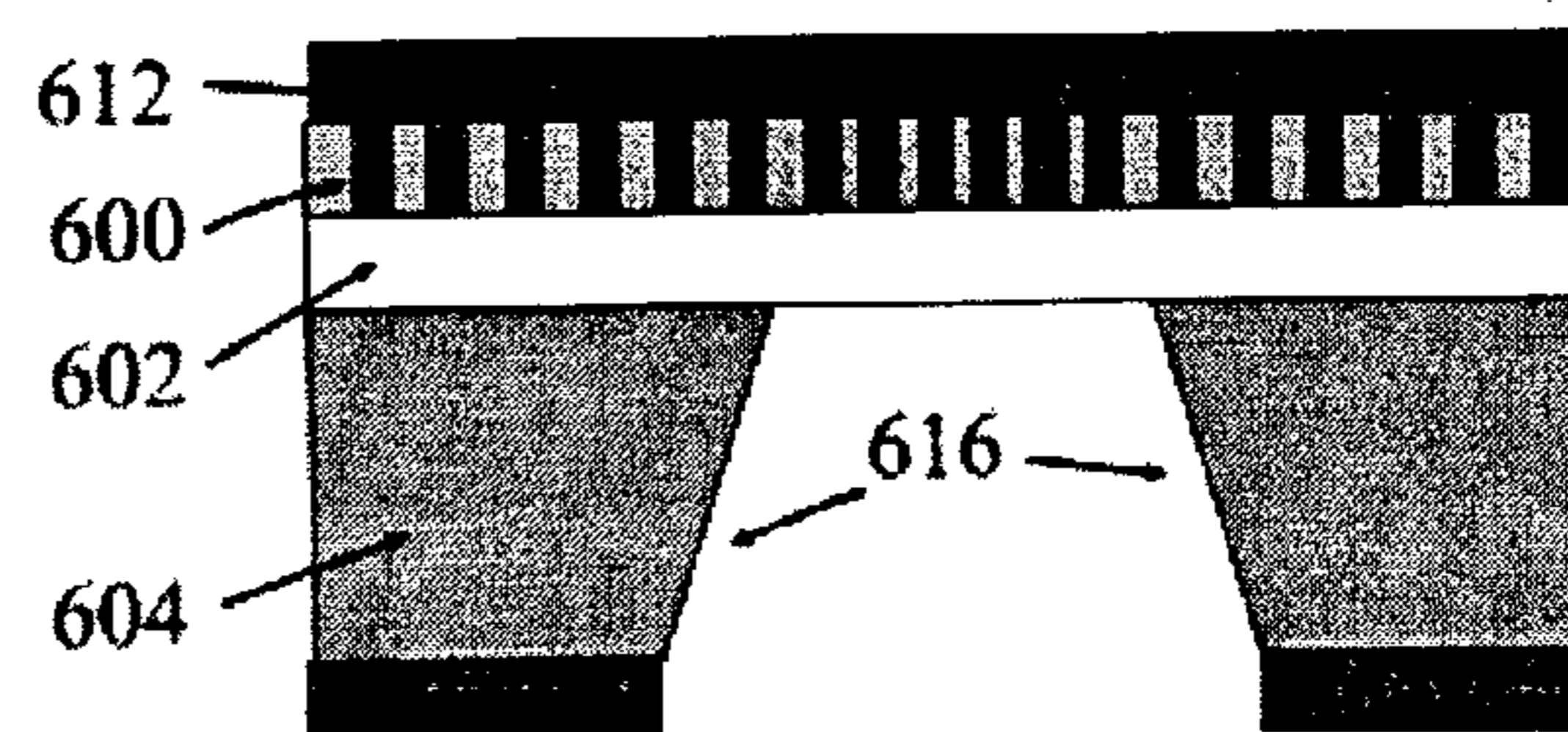


FIGURE 4F

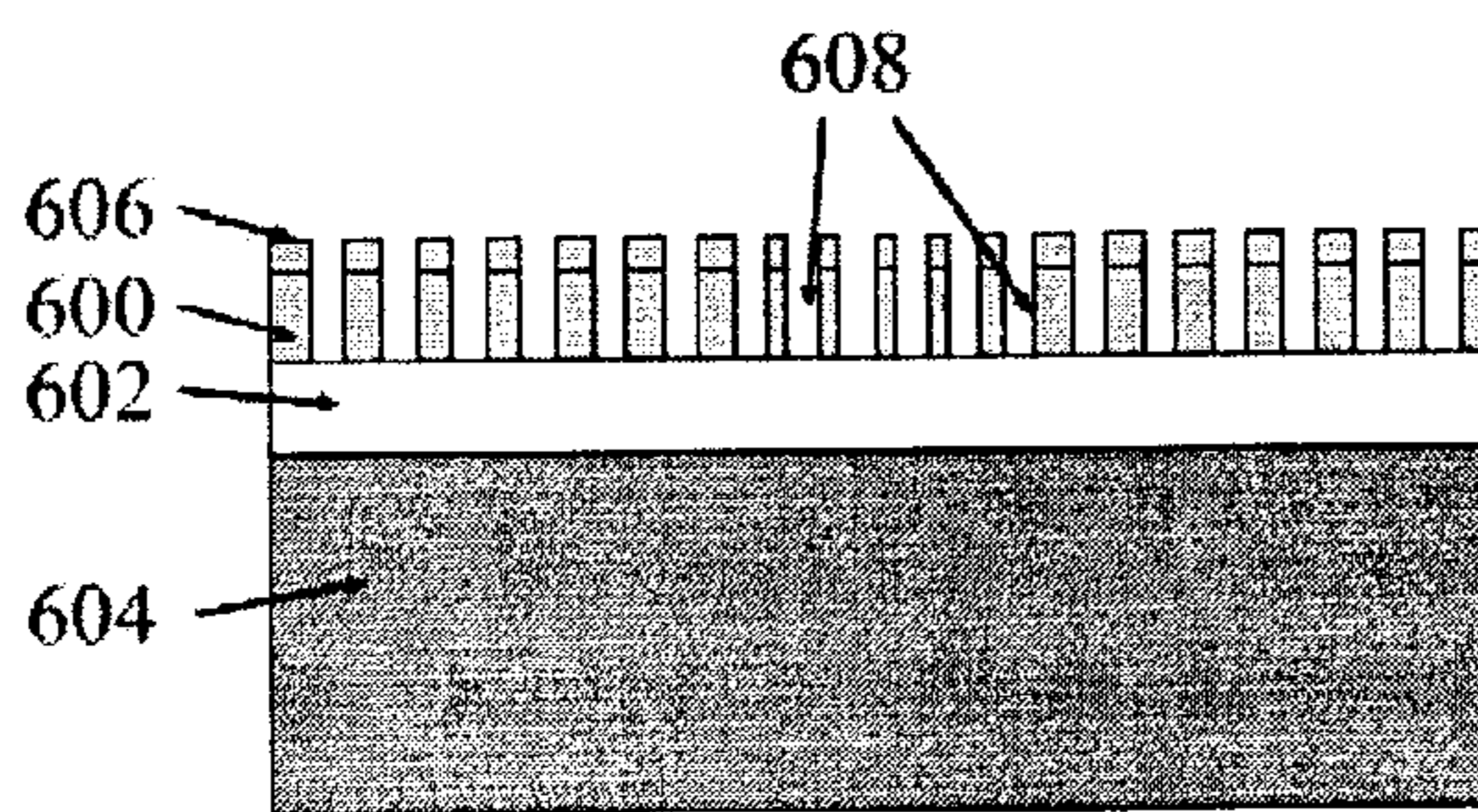


FIGURE 4C

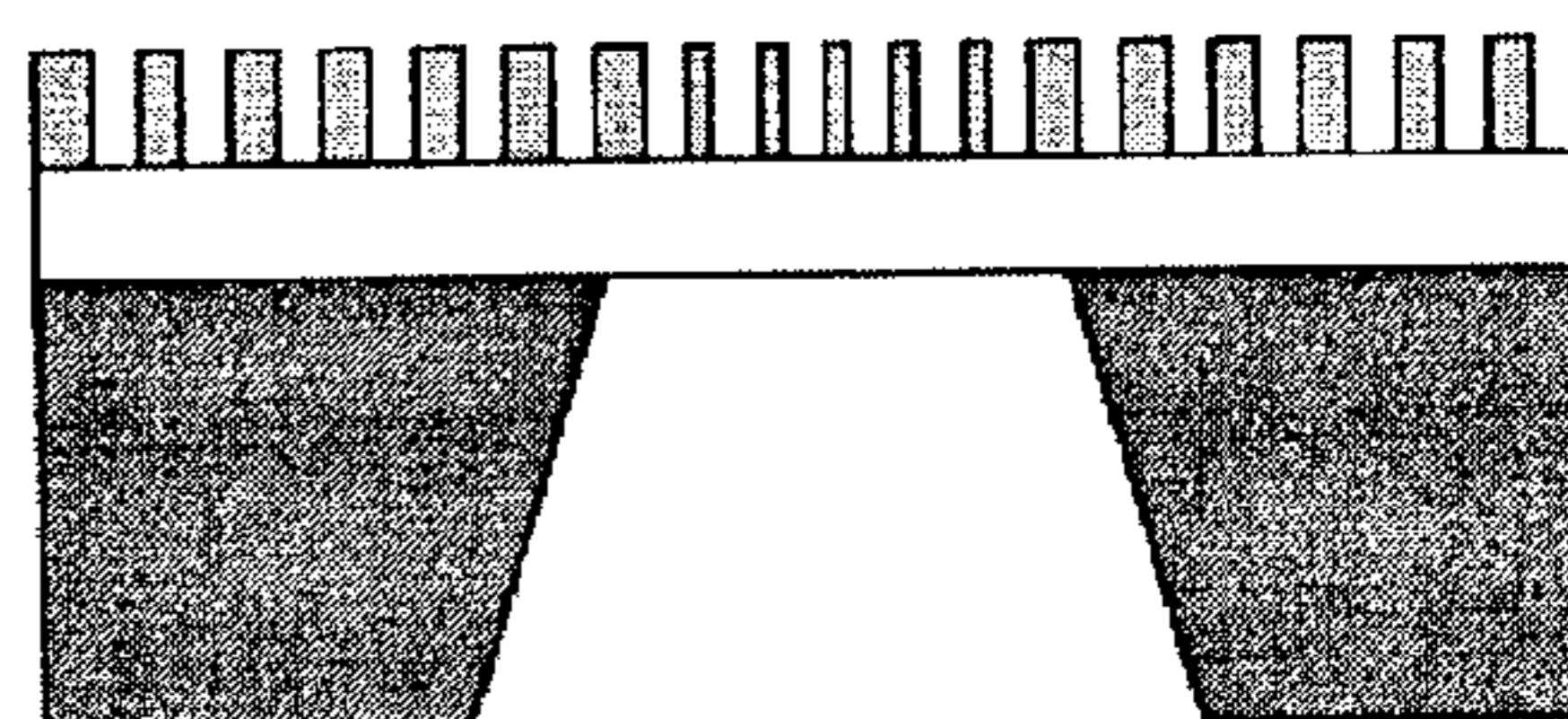


FIGURE 4G

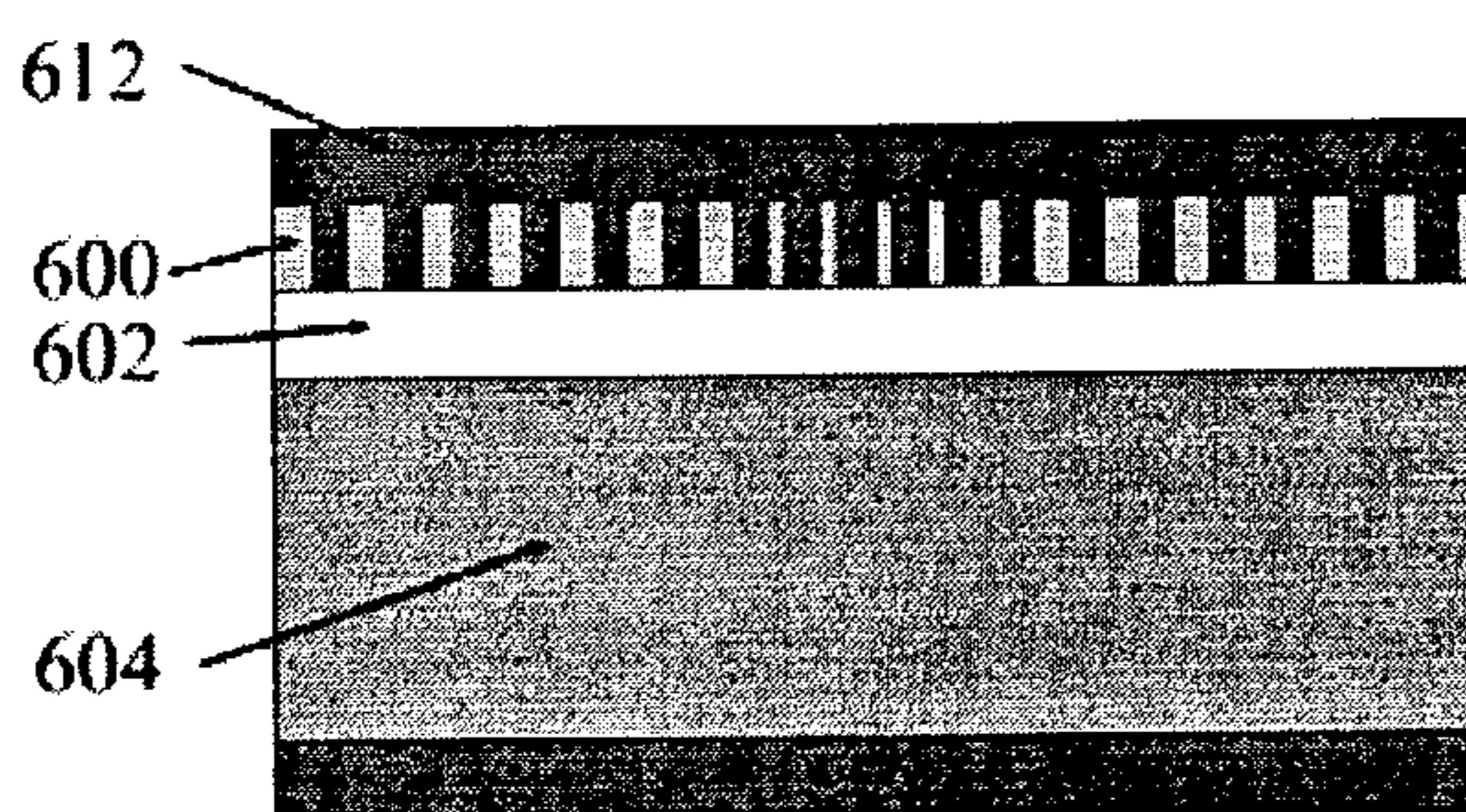


FIGURE 4D

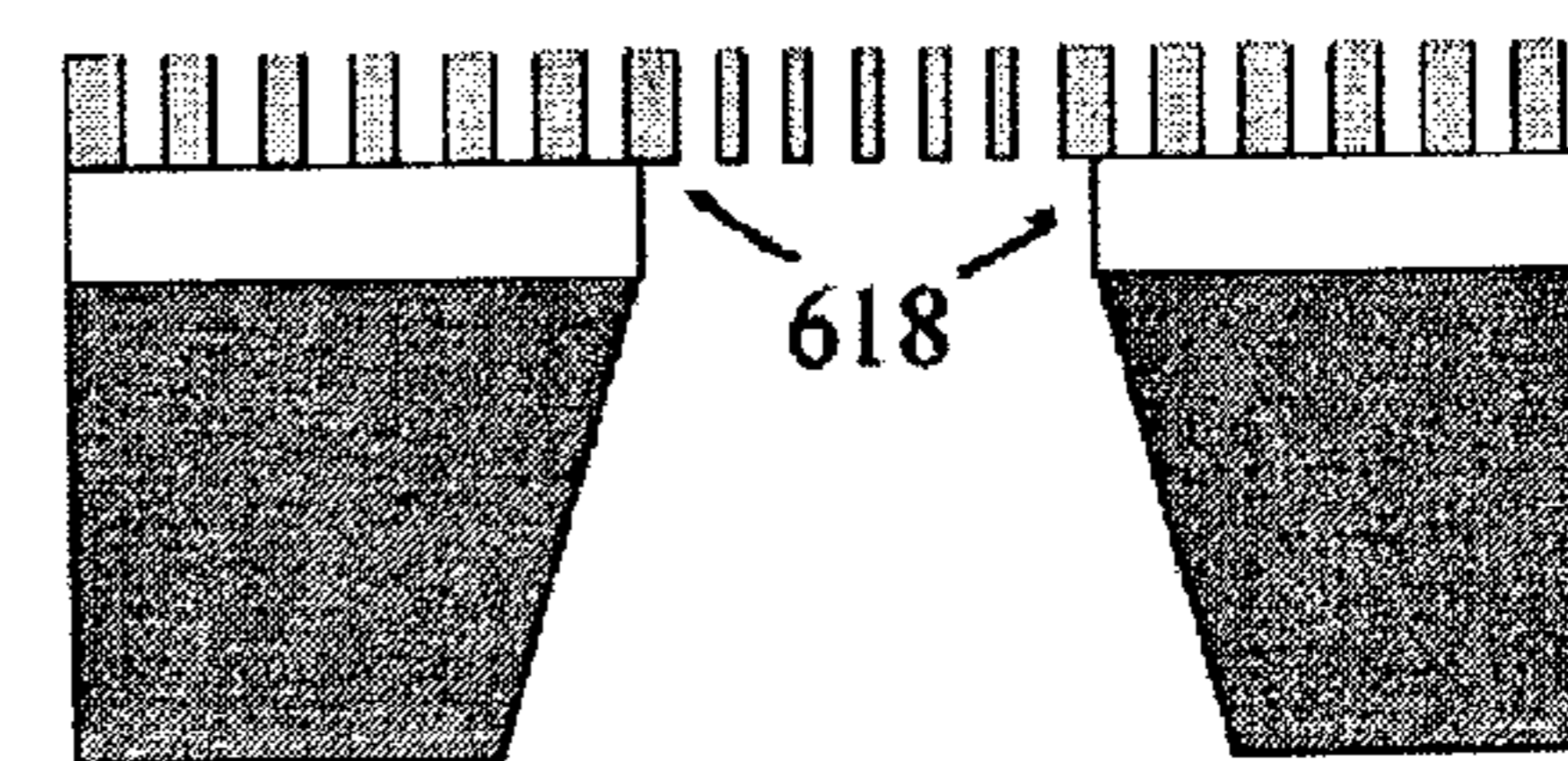


FIGURE 4H

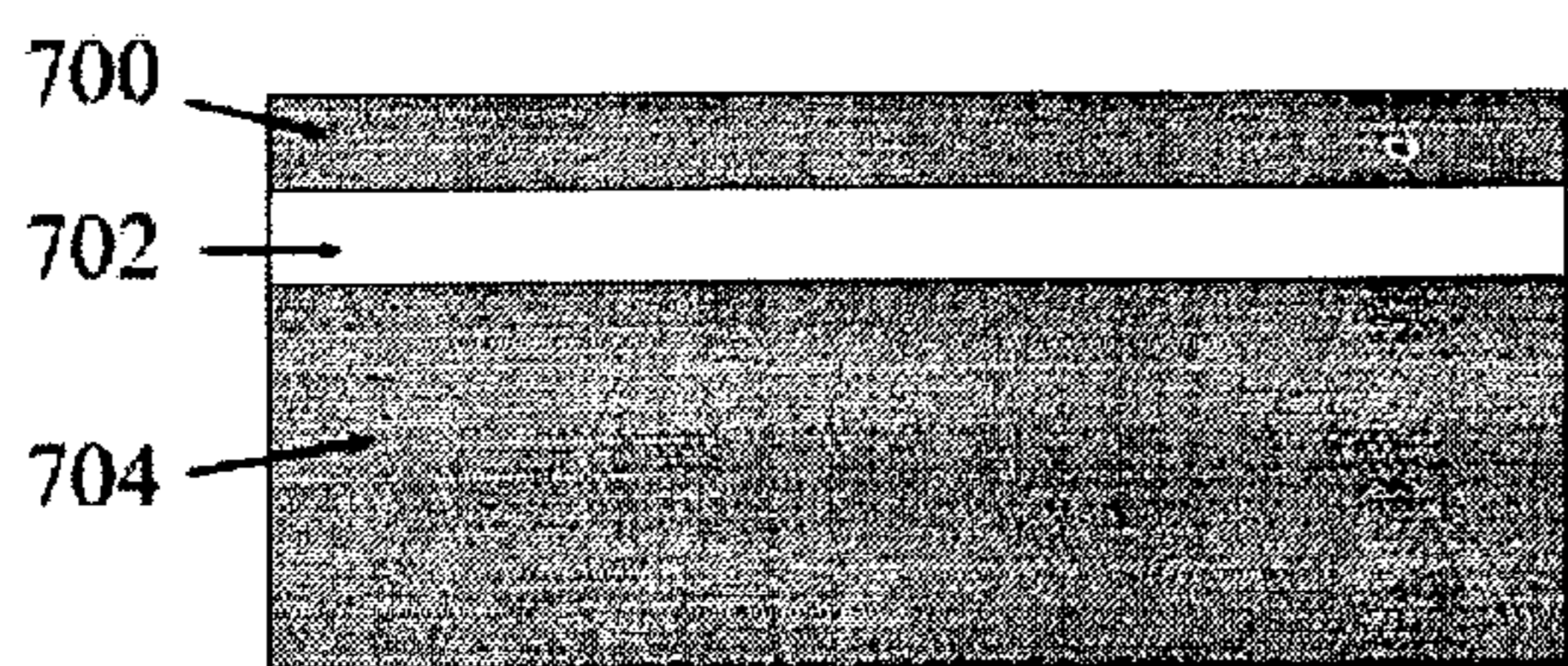


FIGURE 5A

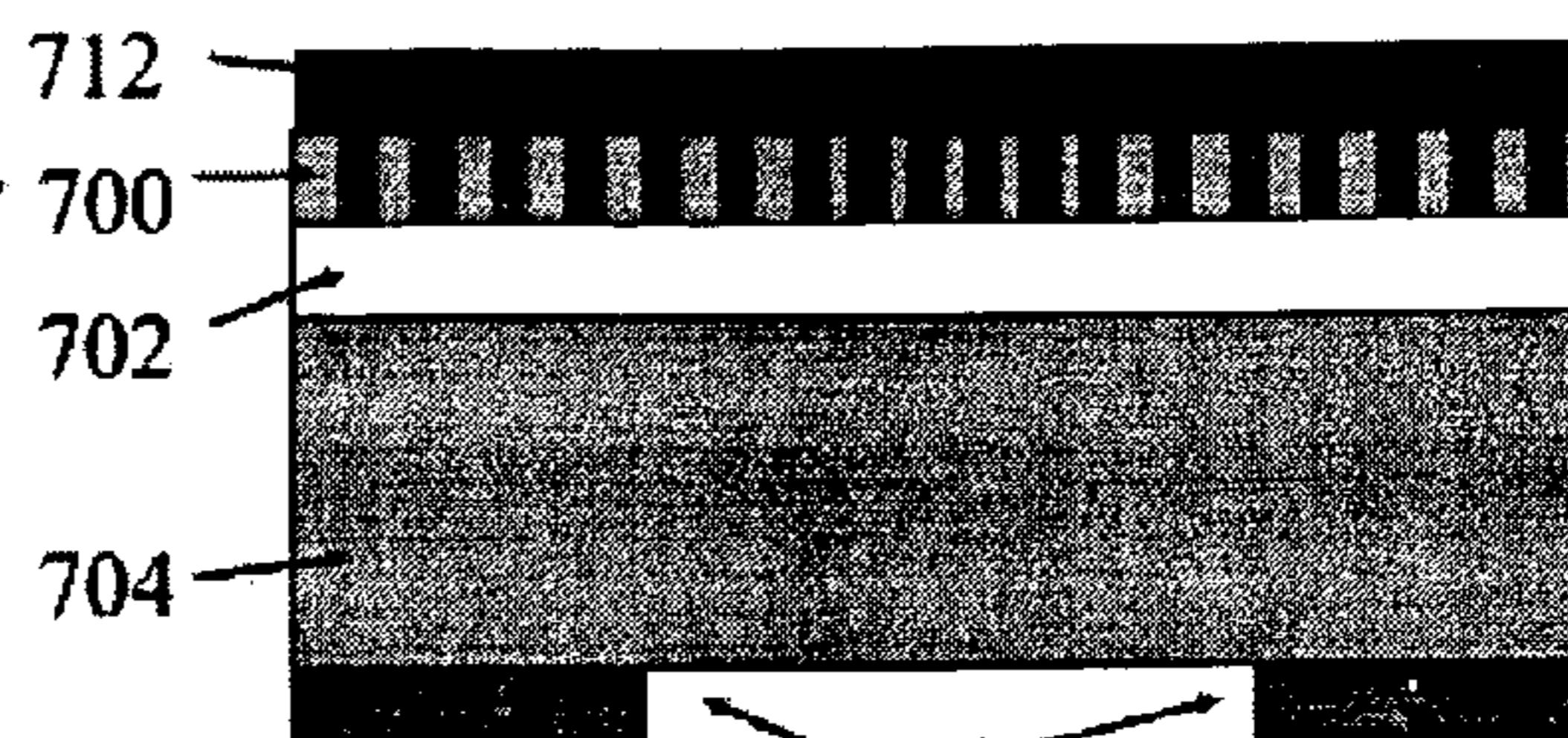


FIGURE 5E

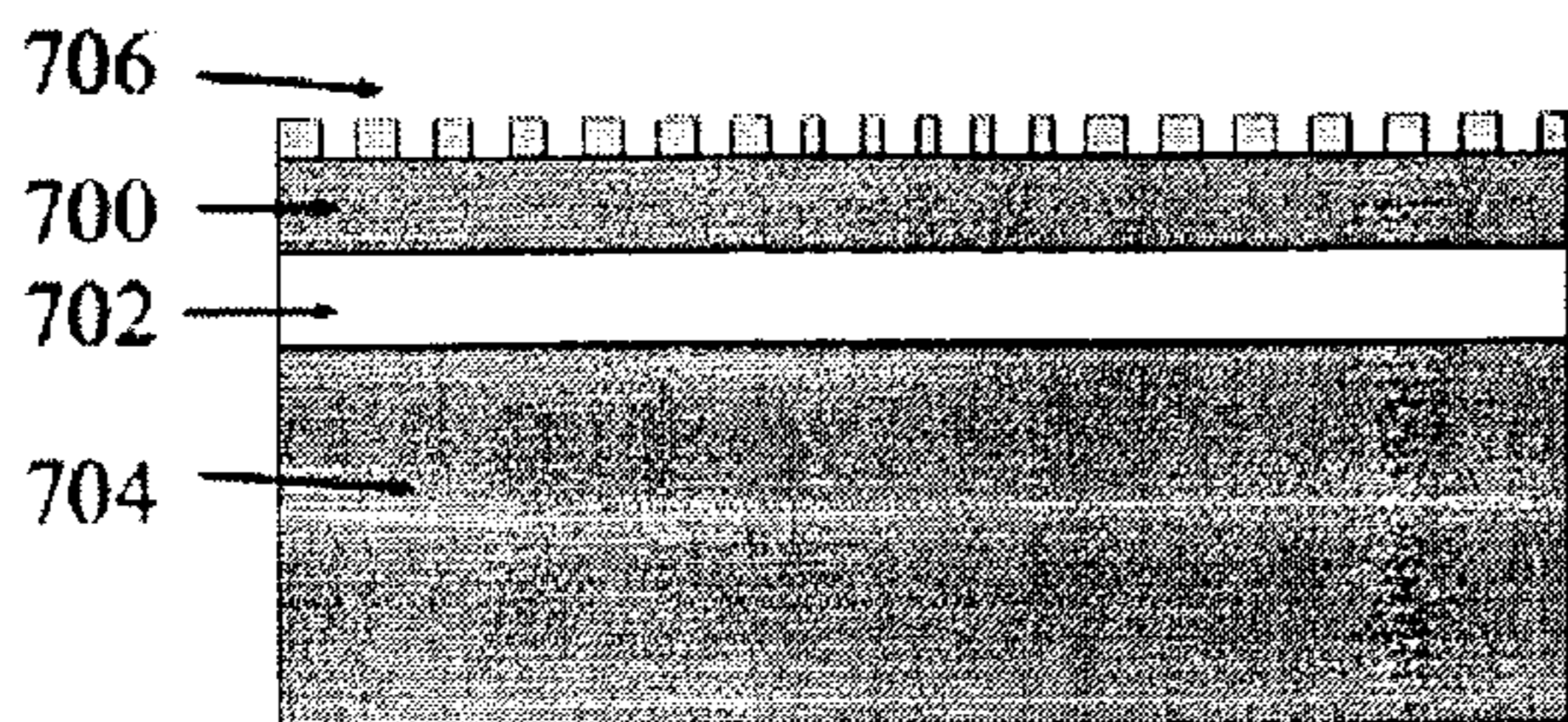


FIGURE 5B

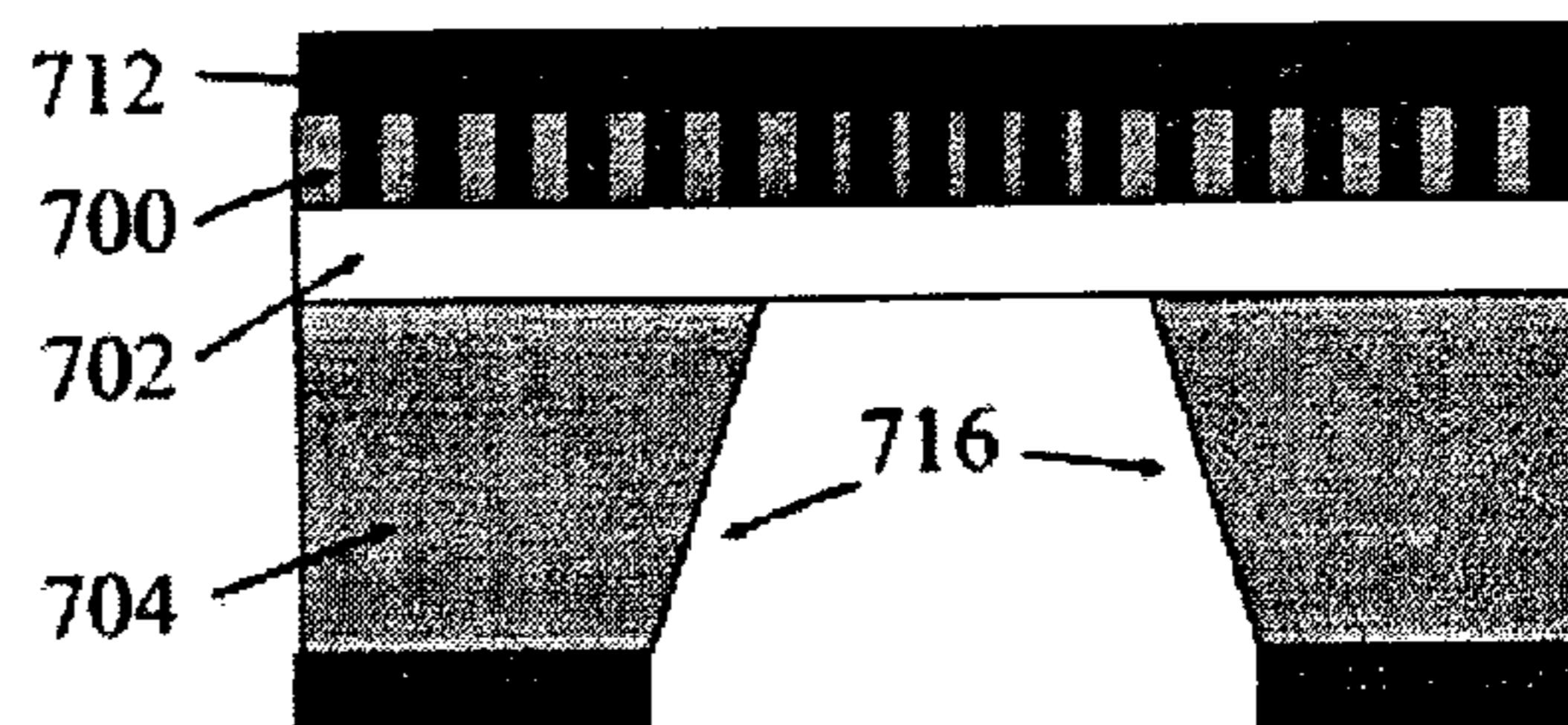


FIGURE 5F

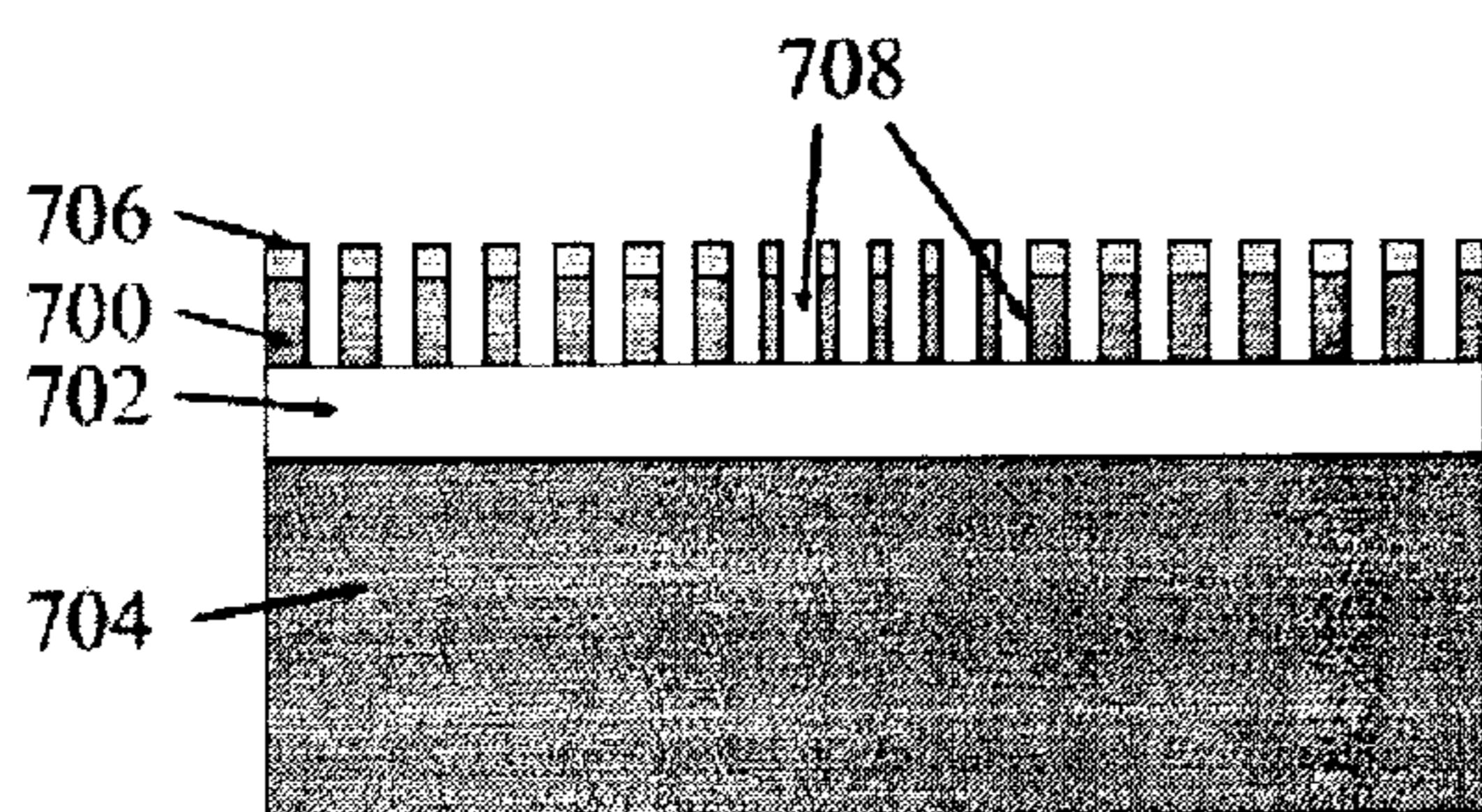


FIGURE 5C

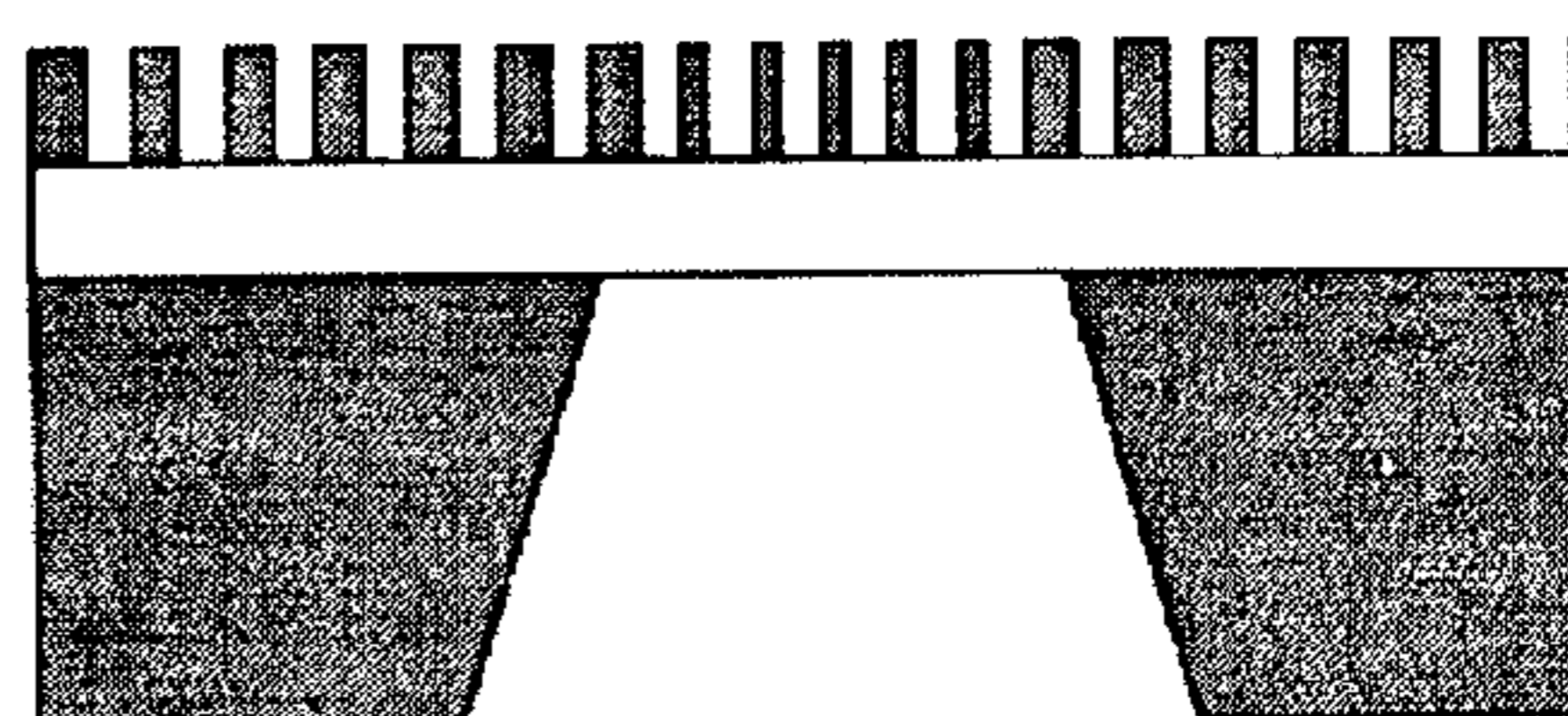


FIGURE 5G

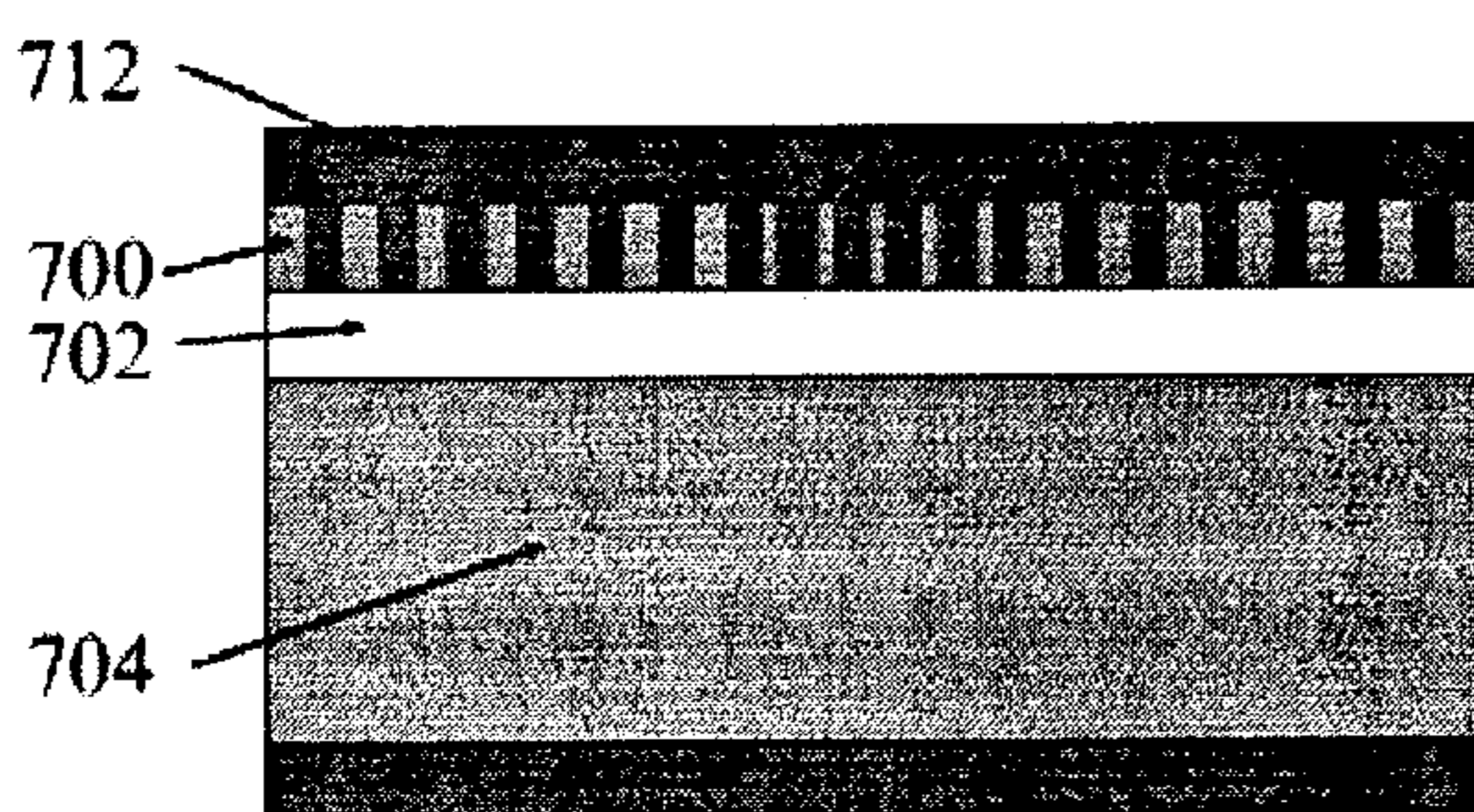


FIGURE 5D

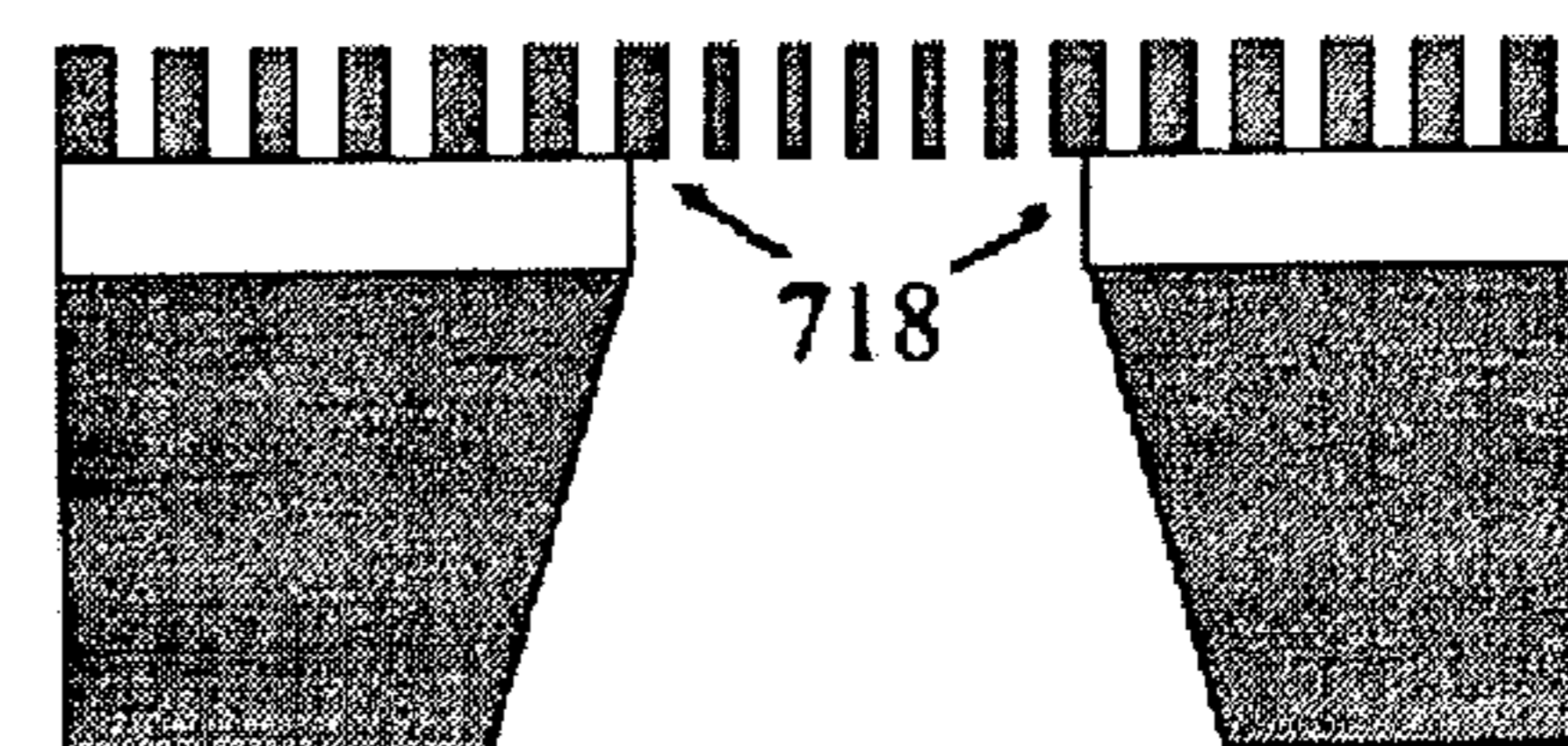


FIGURE 5H

INORGANIC NANOPOROUS MEMBRANES AND METHODS TO FORM SAME

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention generally relates to porous inorganic membranes and more particularly to an improved method for forming inorganic membranes that utilizes a self-assembled material as a sacrificial template material in the fabrication process.

[0003] 2. Description of the Related Art

[0004] Filtration of approximately 5-100 nm sized objects (e.g., molecules, proteins, nanocrystals, viruses) is desirable for biosensors and biomedical applications, among other areas. Several different types of porous membranes are available for use in different types of applications, including polymeric membranes, silicon micromachined membranes, ion-track etched membranes, and anodically-etched membranes.

[0005] Several factors play into a type of membrane's technological suitability. For example, because porous membranes work by allowing objects of a certain size to pass through while excluding anything larger, a relevant figure of merit is a membrane's pore size uniformity. Furthermore, the ability to control and tune pore size during membrane fabrication allows for flexibility in choice of membrane application. High pore densities increase the membrane filter throughput. The porous membrane material itself is important both for compatibility with the material passing through, and also for compatibility with the environment in which the membrane will be used. This issue is particularly relevant for biological applications. Ideally, these types of membrane filters are producible with minimal complexity and low cost, allowing their use as disposable devices.

SUMMARY OF THE INVENTION

[0006] The invention provides a nanoporous membrane structure which utilizes a self assembling material as a sacrificial layer to define the membrane pore size and pore density. As described in more detail below, the nature of self assembling materials is to organize into dense arrays of uniformly-sized domains, and this invention makes use of this material property for inorganic porous membranes. Both pore density and uniformity improve membrane filter operation, as was described above.

[0007] More specifically, the invention provides a method of forming an inorganic porous membrane that includes forming an inorganic membrane material on a substrate, forming a porous self-assembled material on the inorganic membrane material, and patterning the membrane material using the porous self-assembled material as a mask.

[0008] In one embodiment, to form the mask, the invention forming a first material on the membrane material (the first material includes self-assembled particles) and removes the particles to leave pores in the first material. Essentially, the membrane mask comprises a modified multi block copolymer layer, wherein the modified multi block copolymer layer is modified to have one type of block copolymer removed. Openings where the one type of block copolymer

was previously positioned make up the pores in the mask. The invention orients the particles to the plane of the first material before removing them. In this embodiment, the particles can comprise multi block copolymers, which are removed by applying a solvent or applying radiation.

[0009] In alternative embodiments, the porous self-assembled material comprises an anodized alumina film or a layer of chemically synthesizing nanoparticles (interstices between the nanoparticles make pores in the porous self-assembled material).

[0010] The inorganic porous membrane produced comprises a substrate support having a gap. The inorganic film is suspended from the substrate across the gap. The inorganic film comprises an array of pores, where the pores have pore diameters less than 30 nm and pore diameter distributions of less than 20%. The density of the pores is greater than $10^9/\text{cm}^2$.

[0011] By using self assembled materials to define pore dimensions, this invention teaches that it is possible to have regular arrays of close packed pores of less than 30 nm in diameter (with pore size distributions of approximately 10%). Furthermore, because the self assembling material itself may not be suitable for application as a membrane, this invention teaches that the self assembling material is used as a template to pattern an underlying membrane material. In this way, membranes of a wide variety of materials may be formed, each type possessing the characteristics dimensions of the self assembling (template) material. The invention also provides methods for fabricating a nanoporous membrane using a self-assembled material as a template for transferring the nanometer-scale pattern into the underlying material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The invention will be better understood from the following detailed description with reference to the drawings, in which:

[0013] FIGS. 1A-1C are schematic diagrams of a nanoporous membrane structure made using a self assembled material to pattern an underlying membrane material;

[0014] FIGS. 2A-2C illustrate the use of a self assembled material in patterning an underlying material layer;

[0015] FIG. 3 is a flow diagram illustrating a preferred method of the invention.;

[0016] FIGS. 4A-4H are a series of schematics illustrating a preferred method of the invention; and

[0017] FIGS. 5A-5H are a series of schematics illustrating a preferred method of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

[0018] In the invention, a self assembled material is used as a sacrificial layer in creating a nanoporous inorganic membrane, which may be used for molecular filtration or molecular sensing, among other things. FIGS. 1A-1C show schematic diagrams of a nanoporous membrane **150** (formed on a substrate **154**) used in such a capacity, illustrating its use for separating particles (shown schematically as spheres, which could represent molecules of different sizes) of two

different sizes **151**, **152**. More specifically, **FIG. 1B** illustrates particles **151**, **152** together on one side of the porous membrane **150**. **FIG. 1C** illustrates that the membrane filter **150** only allows the smaller particles **152** to pass and keeps the larger particles **151** isolated on one side. In addition, the pores of the membrane **153** may be chemically functionalized in order to permit or exclude particle **151**, **152** passage based on chemical composition.

[0019] As described in more detail below, in the invention a self-assembled material is used as a sacrificial layer to form nanopores on a substrate, which may be formed of silicon or other materials. By using the self-assembled material as a template to pattern the substrate, the invention forms nanoporous membranes of materials which were not a priori porous.

[0020] The membrane pore size, uniformity and density are determined by characteristic dimensions of a self-assembling material. For purposes of this invention, the term "self-assembled material" refers to certain type of materials which under suitable conditions will organize into uniform nanometer-scale domains with a degree of longer-range order. Typically the self-assembled domains arrange themselves into hexagonal lattices, however there are also certain systems which assemble into oblique and square lattices. Typical domain dimensions are less than 50 nm, and can be adjusted down to only a few nm in the proper material system. In these materials, because domain dimensions are a fundamental property of the material, domain size uniformity can have deviations (from the mean) of less than 10%. Examples of self-assembling materials (their use in this application will be described further) are diblock copolymers, uniformly-sized nanocrystals, anodized alumina films, and bacterial cell surface layers (S-layers), among other systems. Self-assembly provides a precise, efficient, and straightforward means for creating nanostructures with dimensions below the resolution limits achievable with conventional techniques, and makes them attractive options for membrane applications. With the domain dimensions achievable using self-assembled materials, this invention provides a route to achieving uniform membrane pore size densities in excess of $10^9/\text{cm}^2$, and up to $10^{12}/\text{cm}^2$.

[0021] In one preferred embodiment of the invention, a diblock copolymer material is used to generate a mask comprising a dense array of nanometer-scale domains. One possible choice of diblock copolymer material is polystyrene-polymethylmethacrylate (PS:PMMA). Through suitable choice of polymer molecular weight and polymer block molecular weight ratio, the diblock copolymer film can be made to self-assemble into a hexagonally packed array of PMMA cylinders in a polystyrene matrix. The PMMA cylinders can be made to orient normal to the plane of the film by, among other known means, spin-coating a dilute polymer solution (polymer diluted in toluene, or other suitable solvent) onto a substrate and annealing the resulting film. The PMMA cylinders can then optionally be removed by exposure to electron-beam or ultraviolet radiation and dissolution in acetic acid or other effective solvent. Depending on choice of polymer molecular weight, the resulting thin film typically has hexagonally packed pores about 20 nanometers in diameter. By controlling the molecular weights and relative ratios of the two polymer blocks, one can control the hole size range from about 2 nanometers up to about 100 nanometers (such as from about 10 to about 50

nanometers), the hole separations from about 2 nanometers up to about 100 nanometers (such as from about 10 to about 50 nanometers). This self-assembly process is simple, cheap, and fast. Also, the pore/domain dimensions can be tailored (in the range of about 10 to >100 nm), with tight distribution of pore sizes determined by a fundamental molecular length scale (the polymer molecular weight).

[0022] Although the above embodiment of the invention uses diblock copolymers composed of polystyrene and polymethylmethacrylate, there are many other types of diblock copolymers which can be used. Some examples of other diblock copolymers include: polyethyleneoxide-polyisoprene, polyethyleneoxide-polybutadiene, polyethyleneoxide-polystyrene, polyethyleneoxide-polymethylmethacrylate, polystyrene-polyvinylpyridine, polystyrene-polyisoprene, polystyrene-polybutadiene, polybutadiene-polyvinylpyridine, and polyisoprene-polymethylmethacrylate. In addition, self-assembled films can be formed of block copolymers containing more than two blocks, such as triblock and multiblock copolymers. Finally, the morphology of the self-assembled diblock copolymer thin film may be adjusted by varying the relative molecular weight ratio of the two polymer blocks composing the diblock copolymers. For ratios greater than about 80:20, the diblock copolymer assembles into a spherical phase. For ratios between about 60:40 and 80:20, the diblock copolymer assembles into a cylindrical phase. For ratios between about 50:50 and 60:40, the film takes on a lamellar phase.

[0023] In a second embodiment of the invention, the self-assembled material is used as a mask material to generate membrane pores comprising anodized alumina. As is well known, anodization of aluminum films under appropriate conditions results in alumina films containing uniformly sized, densely packed ordered pore arrays. Pore size and density can be controlled from about 5 nm to about 300 nm through the anodization conditions (such as anodizing voltage and electrolyte). As with the diblock copolymer material in the embodiment above, the alumina film can be used to template an underlying substrate material and then removed. The templated underlying material will eventually become the porous membrane structure, using the means outlined below.

[0024] In another embodiment of the invention, the self-assembled material used to template the underlying substrate is formed of a single layer of chemically synthesized nanoparticles. Various chemical means exist for producing nanoparticles (of a wide variety of materials) with diameters from about 2 nm to about 20 nm, with diameter distributions of less than 5%. By using nanoparticle which are sufficiently uniform in size, they can be made to assemble on the substrate into ordered hexagonal arrays. The single nanoparticle layer can then be used to template a surface, by using the nanoparticle array interstices as pores. In this embodiment, pore size and spacing of the self-assembled mask are controlled through choice of nanoparticle size.

[0025] Although the foregoing describes three embodiments of self-assembled materials which may be used as sacrificial mask layers to pattern underlying substrates into porous membrane structures, there are many other materials which may be used in this same manner.

[0026] Referring now to FIGS. 2A-2C the process of using a self-assembled material as a template to pattern an under-

lying inorganic substrate (which will eventually become the membrane) is shown. More specifically, **FIG. 2A** illustrates the substrate **20** and the nanoporous self-assembled material **21** containing uniformly-sized pores **22**. Note that the material **21** can be any of the list described above, or another self-assembling material which generates uniformly-sized, densely packed pore arrays at sub-100 nm dimensions. In **FIG. 2B**, an etching process **23** (such as reactive ion etching, chemical etching, or ion beam etching) is used to remove portions of the substrate **20** only in the porous regions of the self-assembled material **21**. The self-assembled material **21** is removed **24** in **FIG. 2C**, leaving behind the nanoporous pattern reproduced in the substrate **20**.

[0027] **FIG. 3** illustrates a flow chart of the inorganic nanoporous membrane fabrication process. In item **300**, a self-assembled material is formed on a substrate. Note that this step includes the entire procedure necessary to form the self-assembled material. In the case of diblock copolymers, this includes any polymer annealing step, and chemical developing. For the case of anodized alumina, this includes aluminum film deposition and appropriate aluminum anodization. For nanoparticle layers, this includes solution deposition and solvent evaporation. Next, in item **302**, the invention transfers the nanometer-scale pattern of the self-assembled material into the underlying substrate (which will eventually form the inorganic membrane). In item **304**, the invention removes the sacrificial self-assembled material. The invention patterns the membrane structures using micromachining techniques (described below) in item **306**. Finally in item **308**, the membrane is released and (in item **310**) the membrane pores are optionally chemically functionalized for specific applications.

[0028] The formation and release of the final membrane structure is done using techniques from micromachining or micro-electrical mechanical systems (MEMS). The following examples (**FIGS. 4A-4H** and **5A-5H**) show possible membrane fabrication sequences, however would be understood by one ordinarily skilled in the art that other self-assembled materials could be used equally. In the first example (shown in **FIGS. 4A-4H**) the final membrane material will be silicon nitride (SiN). The processing begins in **FIG. 4A** by depositing a silicon nitride film **600** on top of a sacrificial oxide **602** on a silicon substrate **604**. The diblock copolymer self-assembly process (described earlier) is performed on the top nitride film **600**, resulting in a nanoporous polymer film **606** formed on top of the silicon nitride **600** (**FIG. 4B**). The porous polymer template pattern is transferred through the full nitride film by, for example, reactive ion etching **608** (**FIG. 4C**). Then, the remaining polymer is stripped away. Next, in **FIG. 4D**, the top of the wafer is protected **612** (for example by polymer resist, silicon dioxide or other material), and the backside of the wafer is patterned **614** by photolithography or other means (**FIG. 4E**) to define the membrane dimensions (multiple membranes can be patterned at once). As shown in **FIGS. 4F and 4G**, the substrate silicon is removed from these membrane openings by etching **616**, using, for example, KOH or TMAH wet etching or plasma etching. Finally, the membrane is released by removing the front-side protection and removing the sacrificial oxide layer **618** (using, for example HF), as shown in **FIG. 4H**. The resulting structure consists of a suspended nitride membrane containing a dense array of nanometer-scale holes/pores (defined by the self-assembled material). The suspended inorganic film can have pore

diameters less than 30 nm the pores in the suspended inorganic film can have pore diameter distributions less than 20%. The density of pores in the suspended inorganic film can be greater than $10^9/\text{cm}^2$ (or even greater than $10^{11}/\text{cm}^2$).

[0029] In a second embodiment (**FIGS. 5A-5H**), the starting substrate is a silicon-on-insulator (SOI) wafer, comprising a silicon film (**700**) on top of silicon dioxide (**702**) on a silicon substrate (**704**) as shown in **FIG. 5A**. The diblock copolymer self-assembly process (described earlier) is performed on the top silicon film **700**, resulting in a nanoporous polymer film **706** formed on top of the silicon **700** (**FIG. 5B**). The porous polymer template pattern is transferred through the full silicon film by, for example, reactive ion etching **708** (**FIG. 5C**). Then, the remaining polymer is stripped away. The remaining membrane processing shown in **FIGS. 5D-5H** (i.e., frontside protection **712**, wafer backside patterning **714**, through-wafer etching **716**, and membrane release **718**) is the same as was described in the previous example. This process yields a suspended silicon membrane containing dense array of nanometer-scale holes.

[0030] Alternatively, the fabrication sequence could be reversed. The backside membrane patterning and etching may be performed first, and then later the diblock copolymer self-assembly and pattern transfer into the membrane material can be completed (for both SiN and SOI membrane fabrication). The inventive nanoporous membrane formed using the self-assembled diblock copolymer template shown above would have utility as a nanofilter for biotechnology/biomedical/biosensors applications.

[0031] By using self assembled materials to define pore dimensions, this invention teaches that it is possible to have regular arrays of close packed pores of less than 30 nm in diameter (with pore size distributions of approximately 10%). Furthermore, because the self assembling material itself may not be suitable for application as a membrane, this invention teaches that the self assembling material is used as a template to pattern an underlying membrane material. In this way, membranes of a wide variety of materials may be formed, each type possessing the characteristics dimensions of the self assembling (template) material. The invention also provides methods for fabricating a nanoporous membrane using a self-assembled material as a template for transferring the nanometer-scale pattern into the underlying material.

[0032] While the invention has been described in terms of preferred embodiments, those skilled in the art will recognize that the invention can be practiced with modification within the spirit and scope of the appended claims.

1. A method of forming an inorganic porous membrane comprising:

forming an inorganic membrane material;

forming a porous self-assembled material on said inorganic membrane material; and

patterning the membrane material using said porous self-assembled material as a mask.

2. The method in claim 1, wherein said forming of said porous self-assembled material comprises:

forming a layer that comprises a material that self-assembles into a structure having pores.

3. The method in claim 2, wherein said forming of said layer further comprises removal of at least one component from said layer.

4. The method in claim 3, wherein said component comprises a multi block copolymer.

5. The method in claim 2, further comprising orienting said pores perpendicular to the plane of said layer.

6. The method in claim 1, wherein said forming of said porous self-assembled material comprises forming an alumina film; and

anodizing said alumina film.

7. The method in claim 6, wherein said anodizing forms a porous alumina film.

8. The method in claim 1, wherein said forming of said porous self-assembled material comprises chemically synthesizing nanoparticles into a layer.

9. The method in claim 8, wherein interstices between said nanoparticles in said layer comprise pores in said porous self-assembled material.

10. The method in claim 1, wherein said forming of said porous self-assembled material comprises:

forming a first material on said membrane material, wherein said first material includes self-assembled particles; and

removing said particles to leave pores in said first material.

11. A method of forming a porous self-assembled mask comprising:

forming a layer that comprises a material that self-assembles into a structure having pores.

12. The method in claim 11, further comprising orienting said pores perpendicular to the plane of said layer.

13. A method of forming a porous self-assembled mask comprising:

forming an alumina film; and

anodizing said alumina film.

14. The method in claim 13, wherein said anodizing forms a porous alumina film.

15. A method of forming a porous self-assembled mask comprising chemically synthesizing nanoparticles into a layer.

16. The method in claim 15, wherein interstices between said nanoparticles in said layer comprise pores in said porous self-assembled mask.

17. A method of forming a porous self-assembled mask comprising:

forming a first material, wherein said first material includes self-assembled particles; and

removing said particles to leave pores in said first material.

18. The method in claim 17, further comprising, before said removing process, orienting said particles perpendicular to the plane of said first material.

19. The method in claim 17, wherein said particles comprise multi block copolymers.

20. An inorganic porous membrane comprising:

a substrate support having a gap; and

an inorganic film suspended from said substrate across said gap, said inorganic film comprising an array of pores,

wherein said pores have pore diameters less than 30 nm, and

wherein said pores have pore diameter distributions of less than 20%.

* * * * *