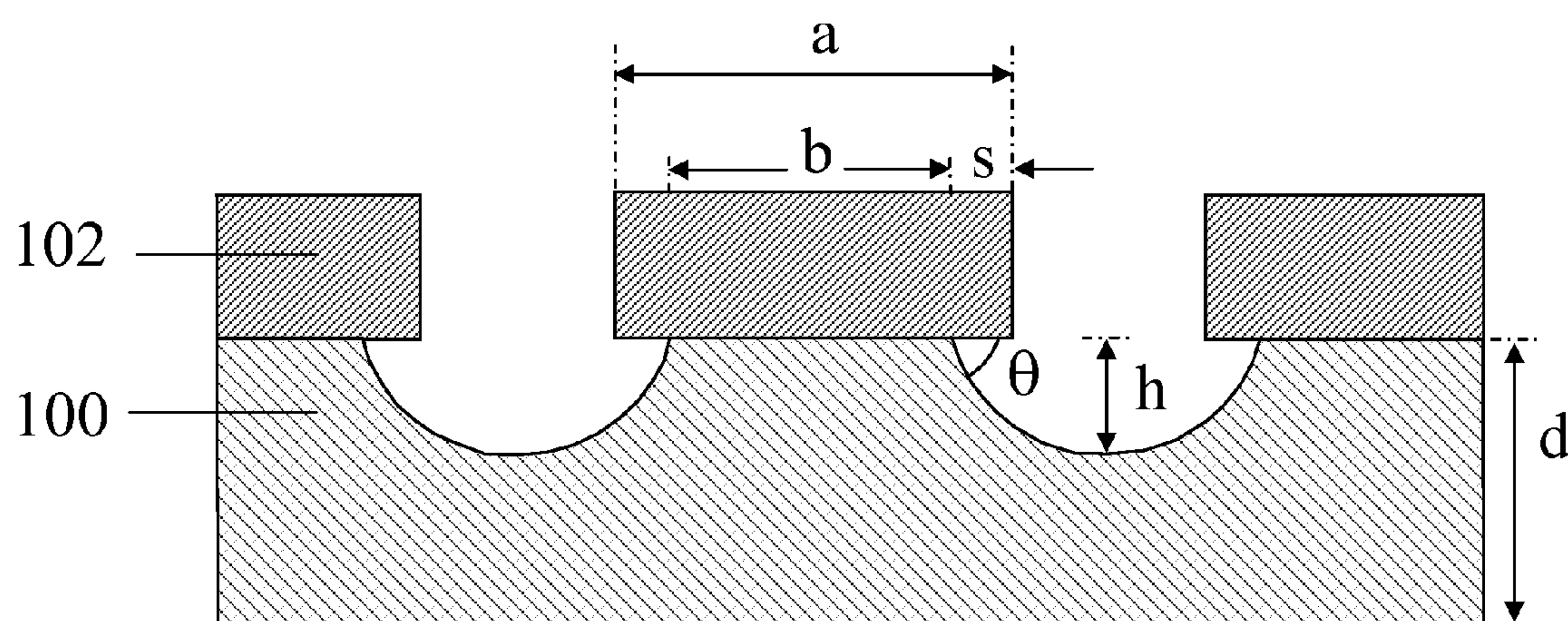


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(19) **United States**(12) **Patent Application Publication**
Taylor et al.(10) **Pub. No.: US 2011/0017608 A1**(43) **Pub. Date: Jan. 27, 2011**(54) **ELECTROCHEMICAL ETCHING AND
POLISHING OF CONDUCTIVE SUBSTRATES**(22) Filed: **Jul. 27, 2010****Related U.S. Application Data**(75) Inventors: **E. Jennings Taylor**, Troy, OH
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OH (US)(60) Provisional application No. 61/228,660, filed on Jul.
27, 2009.**Publication Classification**(51) **Int. Cl.**
C25F 3/02 (2006.01)(52) **U.S. Cl.** **205/666**(57) **ABSTRACT**

A method for electrochemically etching a metal layer through an etch-resist layer pattern using a non-active electrolyte solution is described. The method is particularly useful in fabrication of advanced fuel delivery systems for land-based power generation turbines and aerospace turbine engines; of components for advanced thermal management in aerospace electronic devices and in cooling channels; of stents used in medicine; and of microchannels for sensors, chemical reactors, and dialysis and the like. In one embodiment of the invention the metal layer is copper and the non-active electrolyte solution is a mixture of sodium nitrate and sodium chloride and a pulse electric current is employed to accomplish the electrochemical etching.

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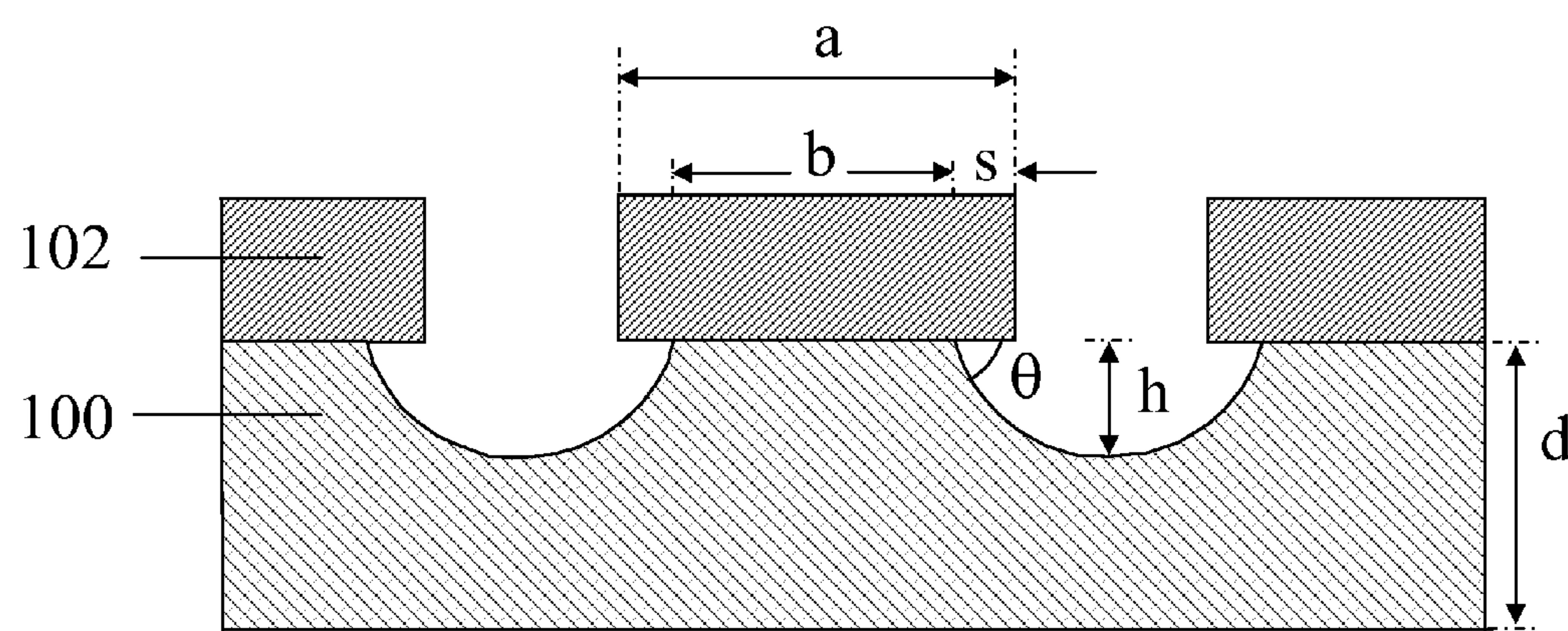


FIG. 1

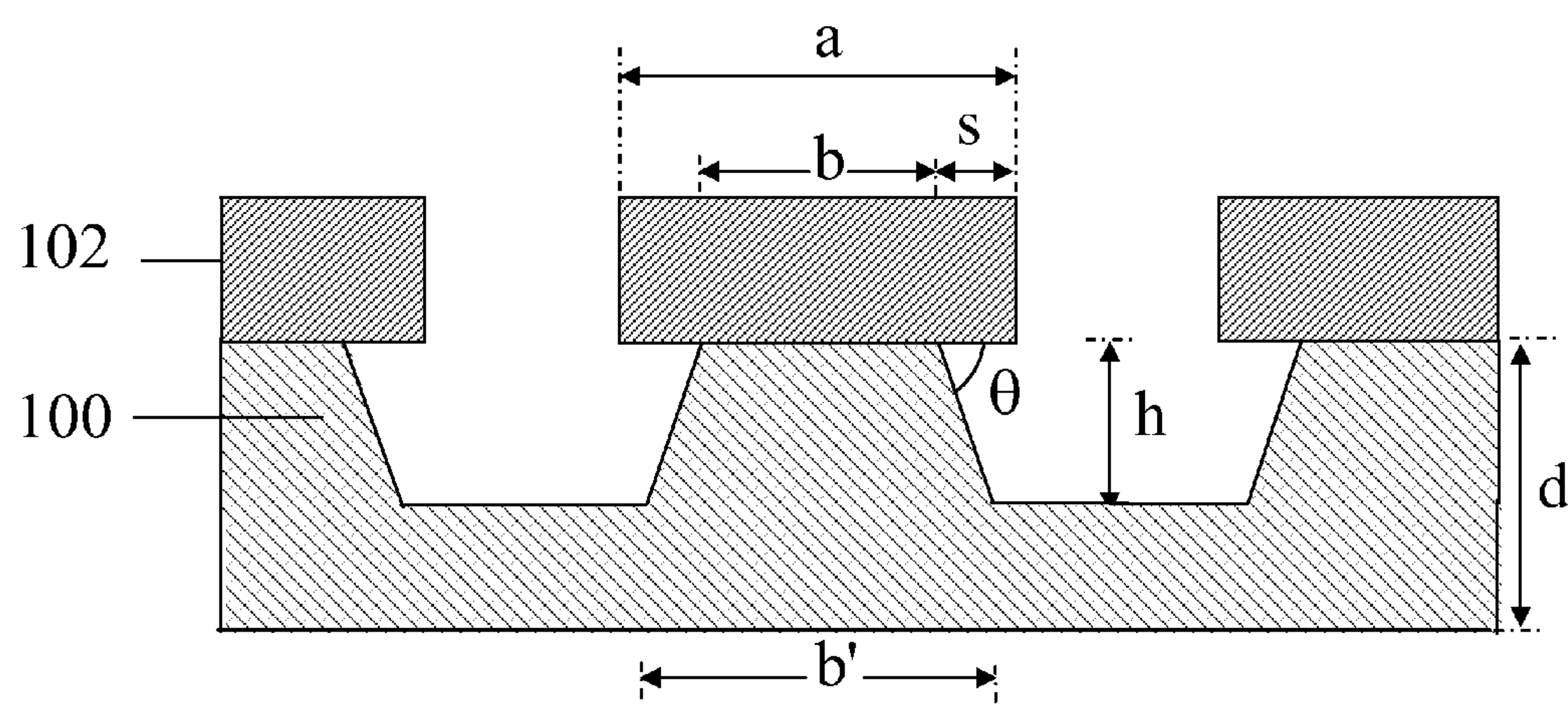
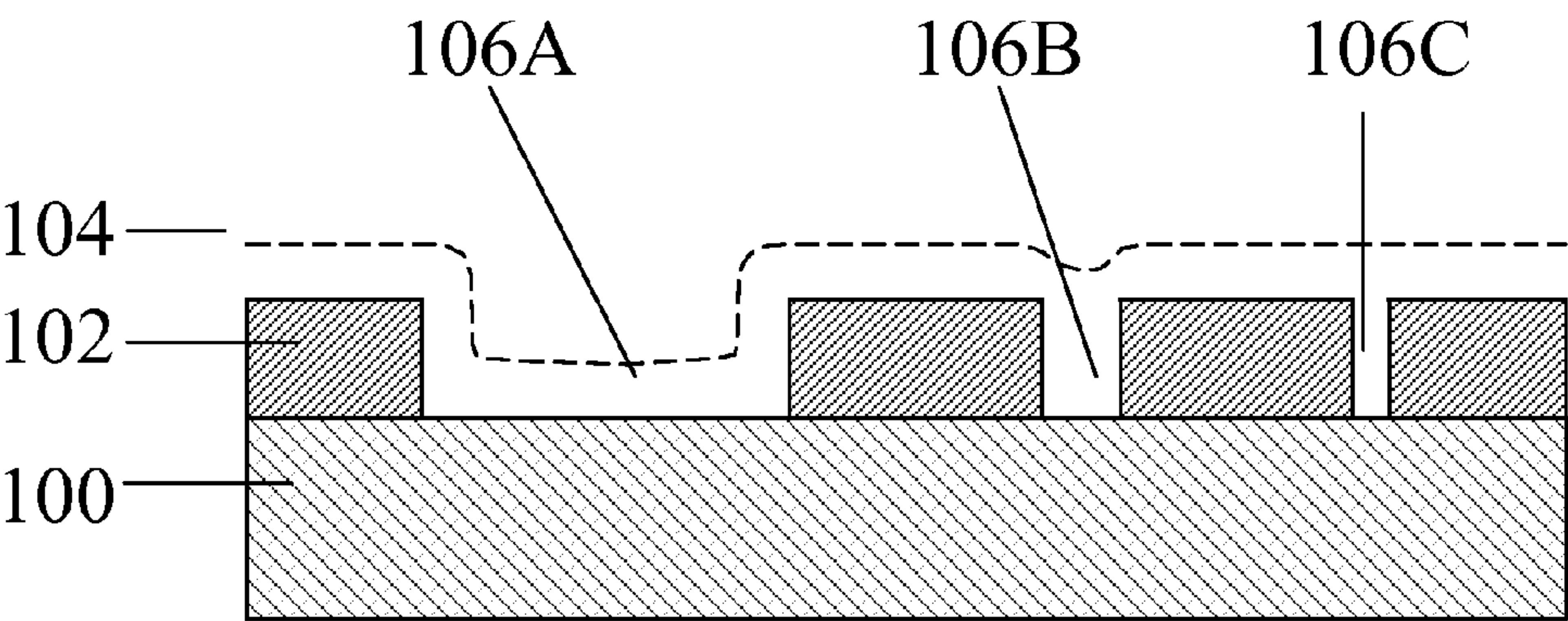
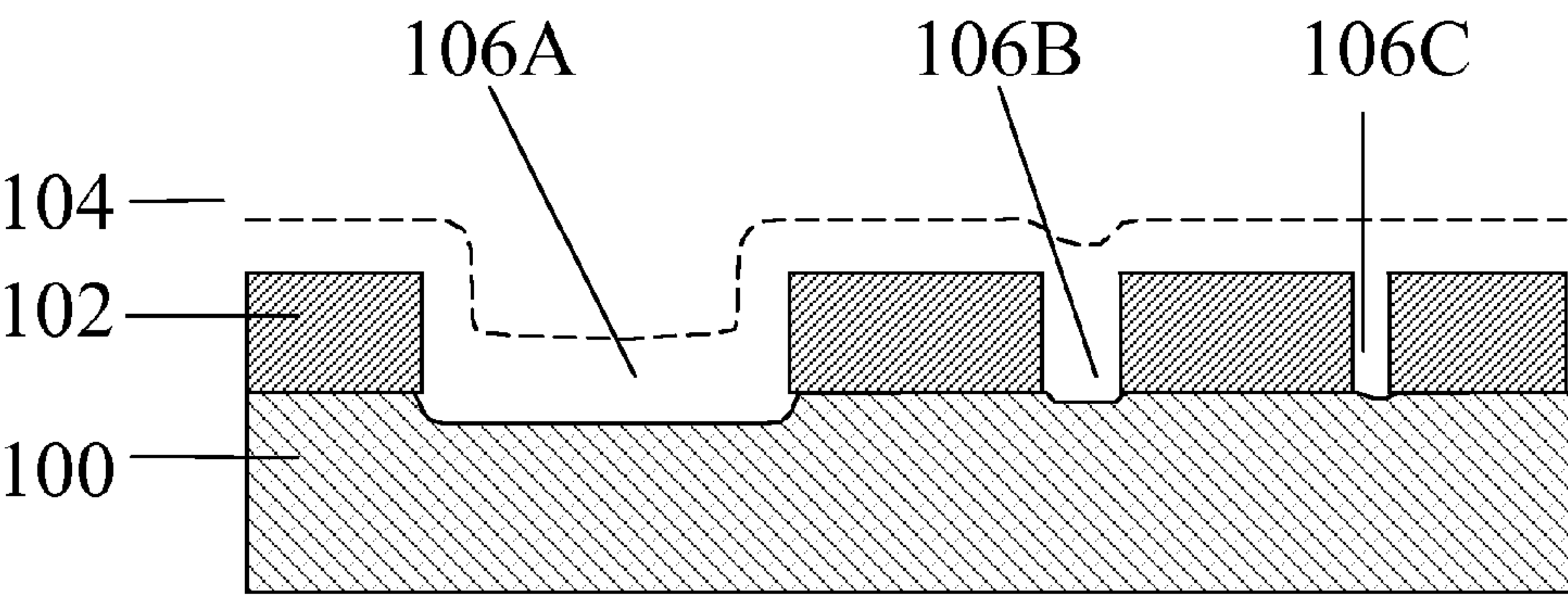


FIG. 2



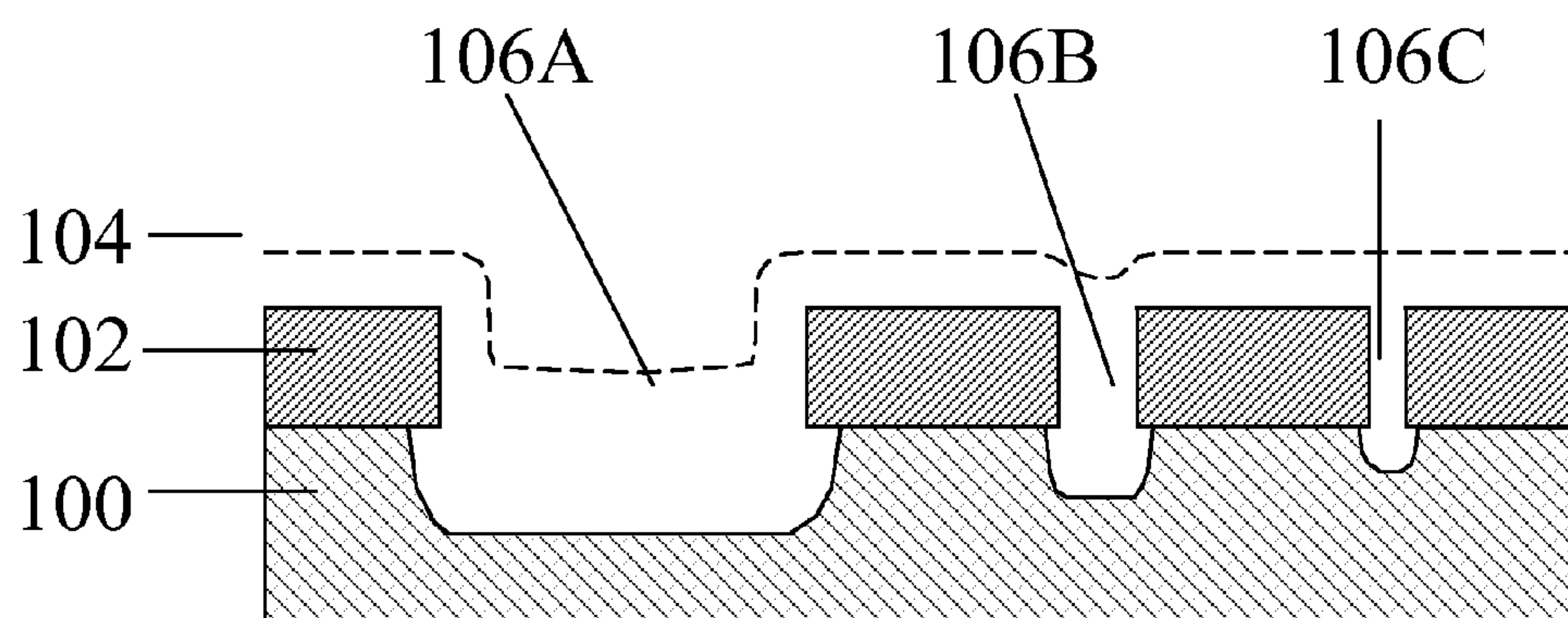
PRIOR ART

FIG. 3A



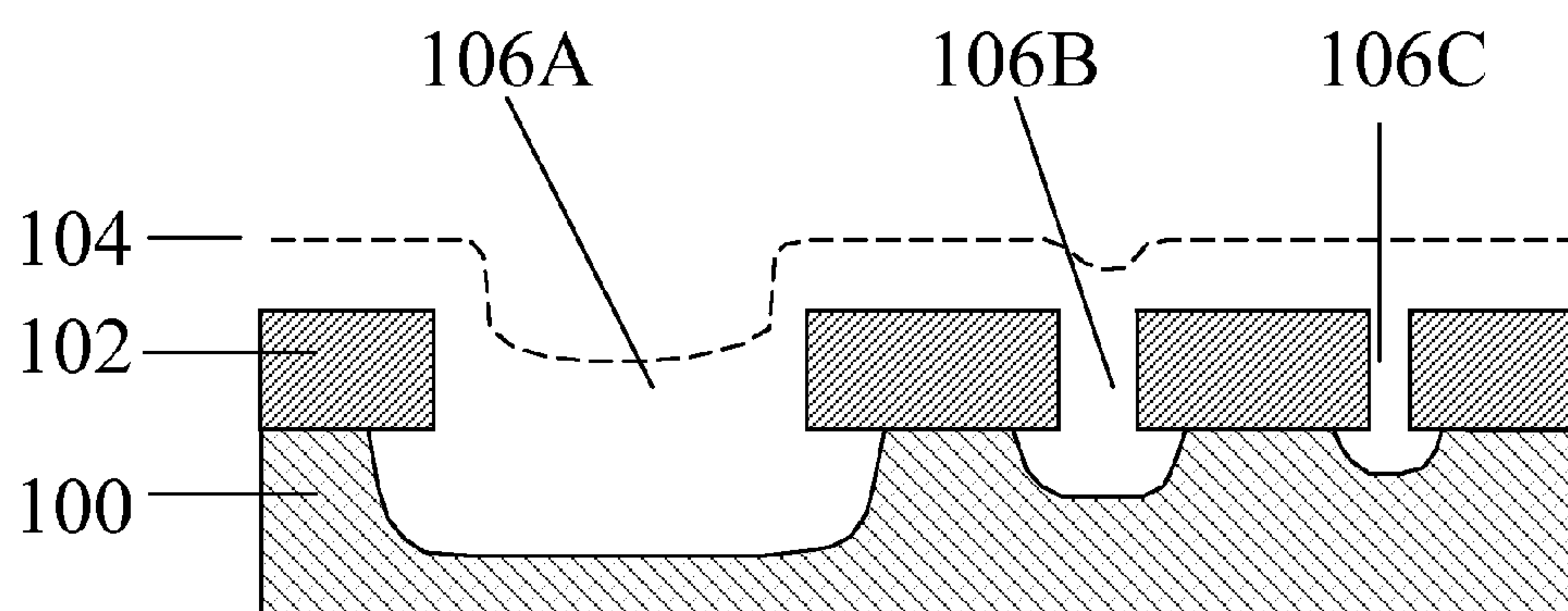
PRIOR ART

FIG. 3B



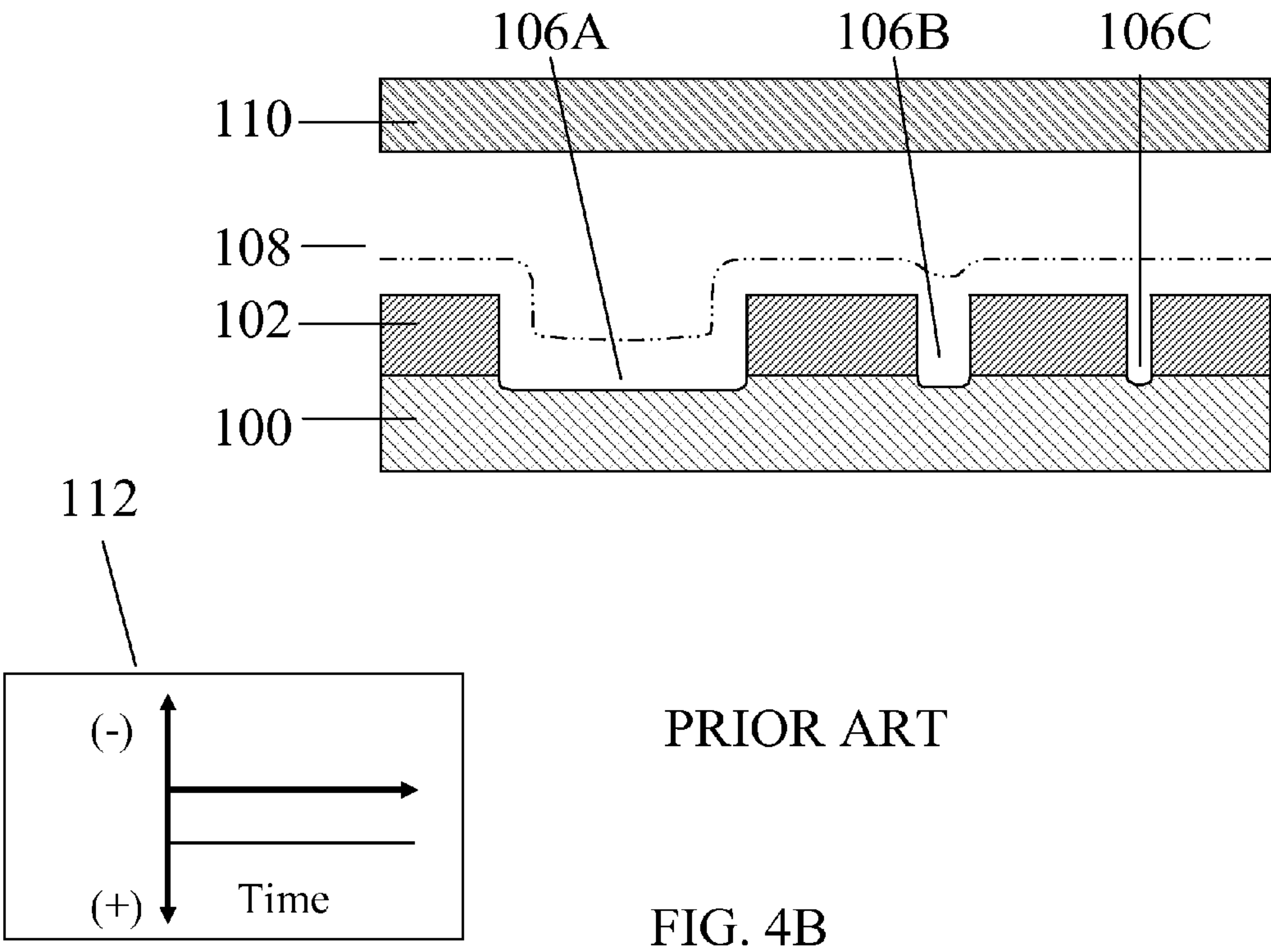
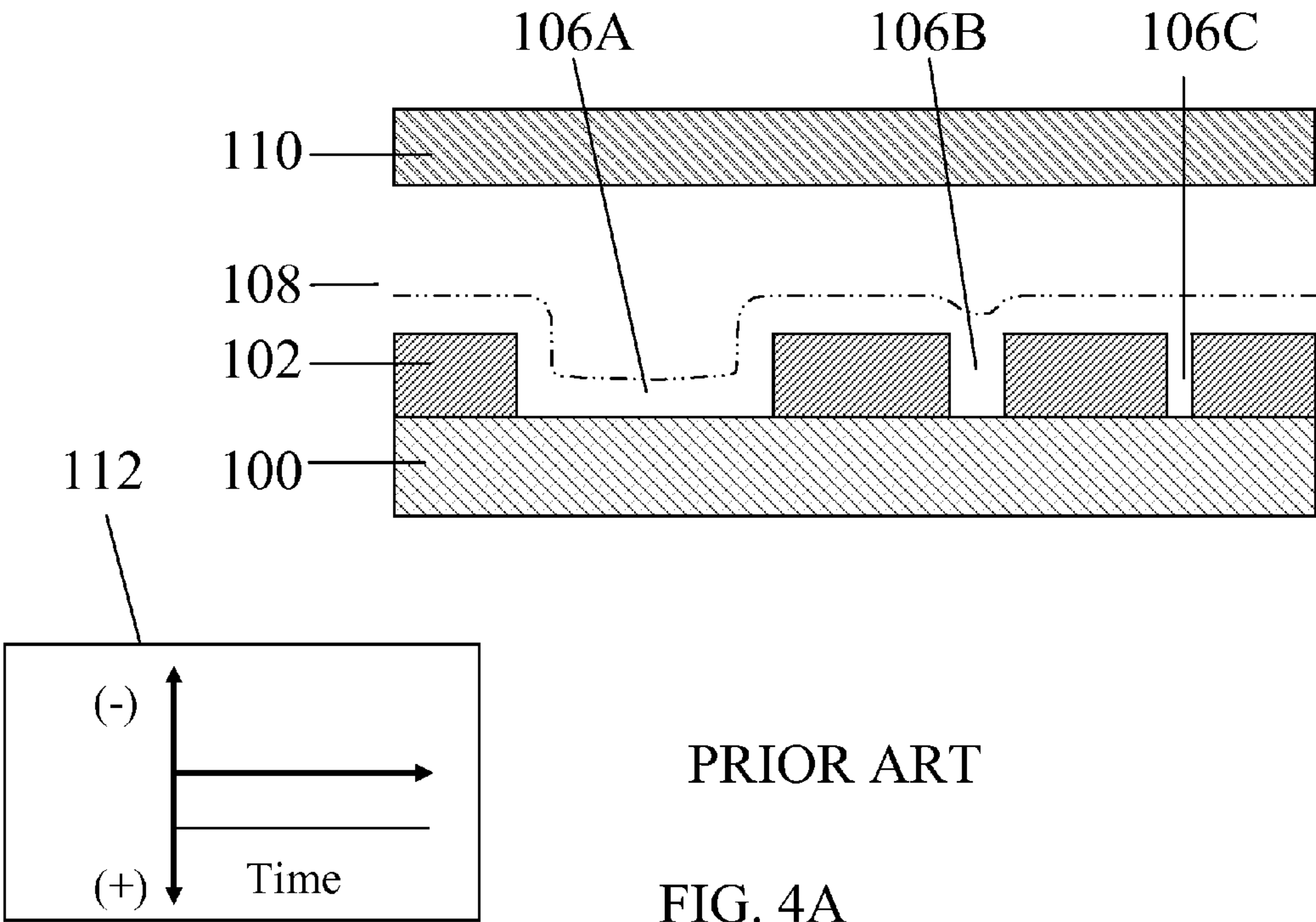
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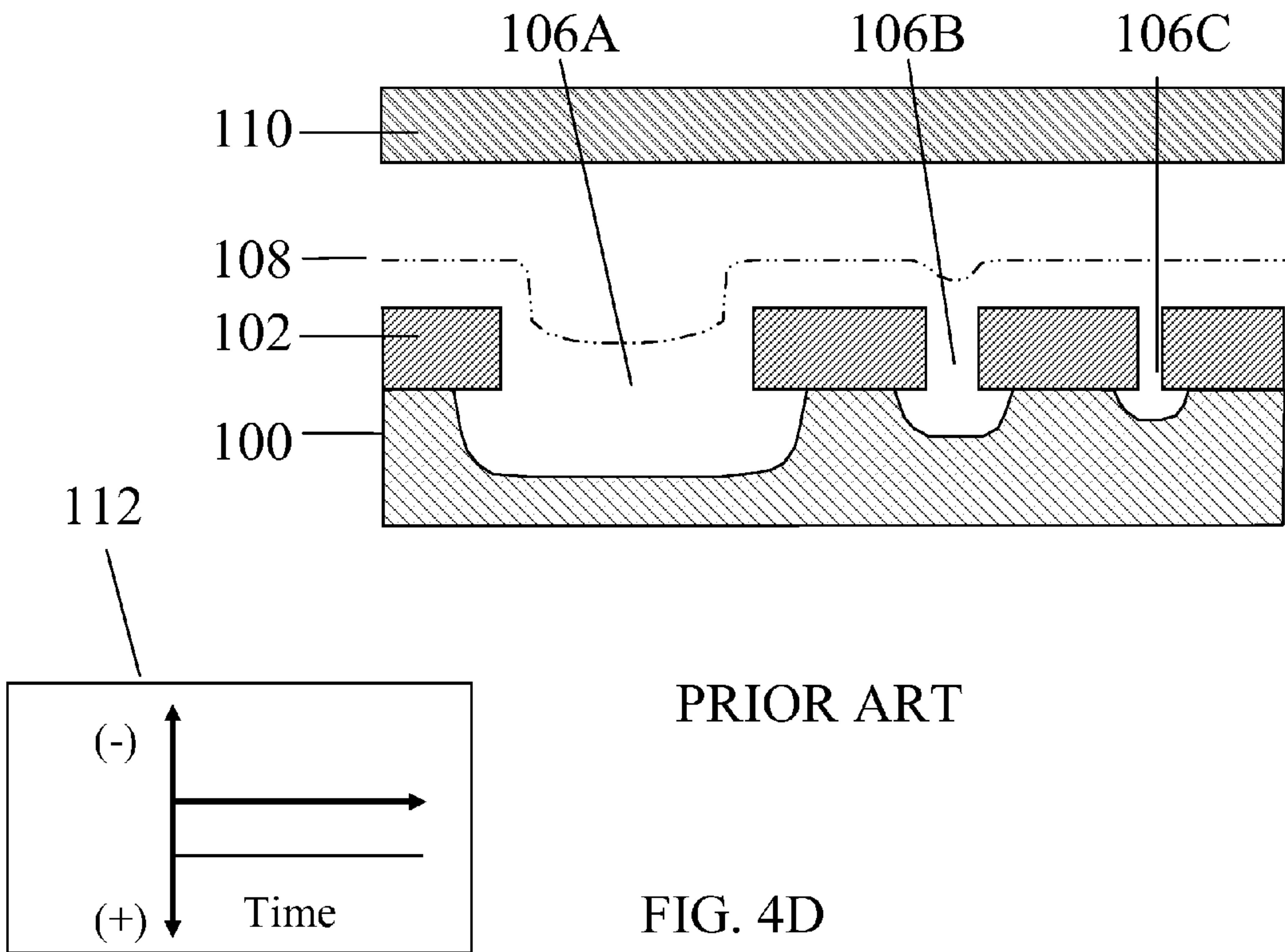
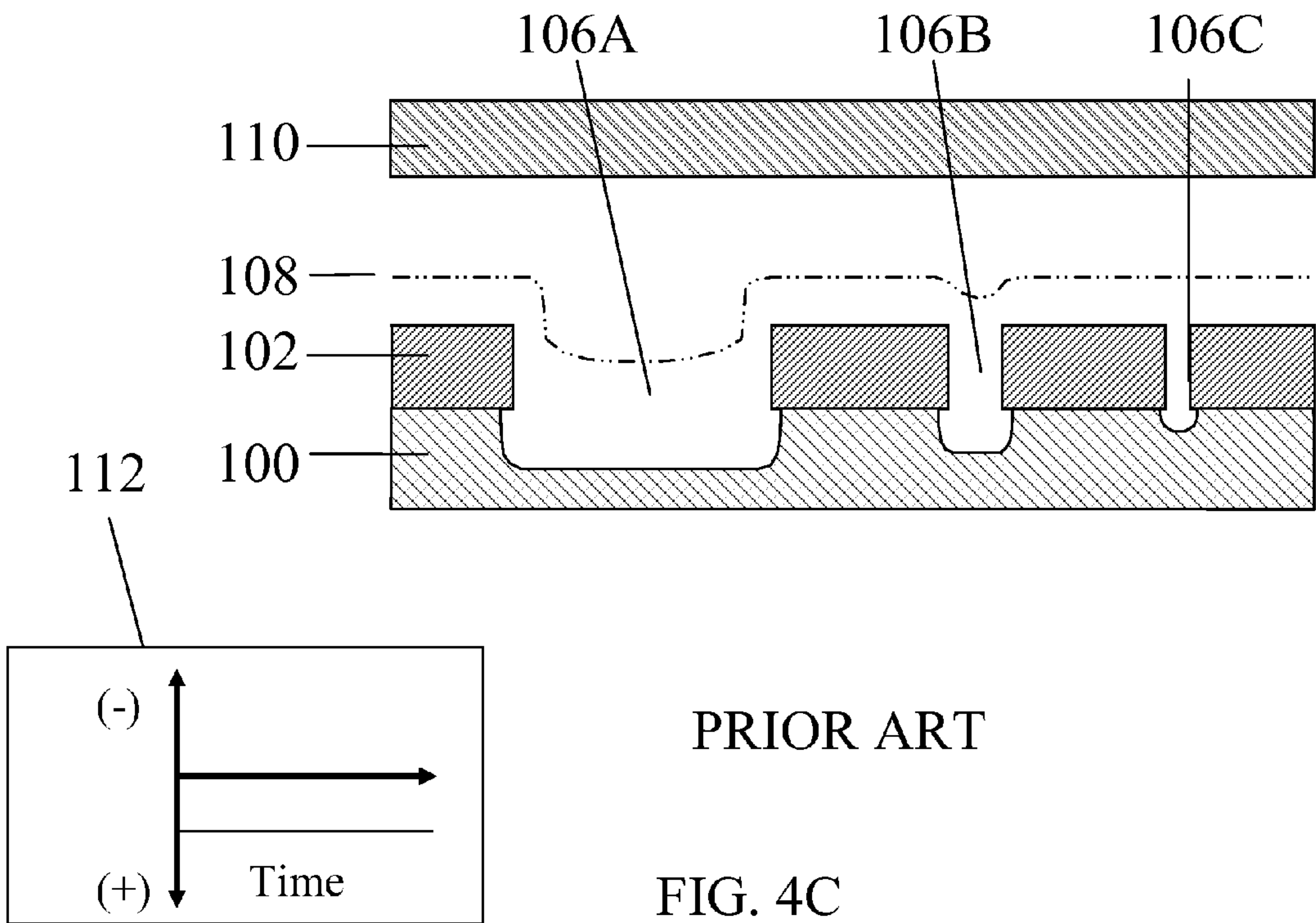
FIG. 3C



PRIOR ART

FIG. 3D





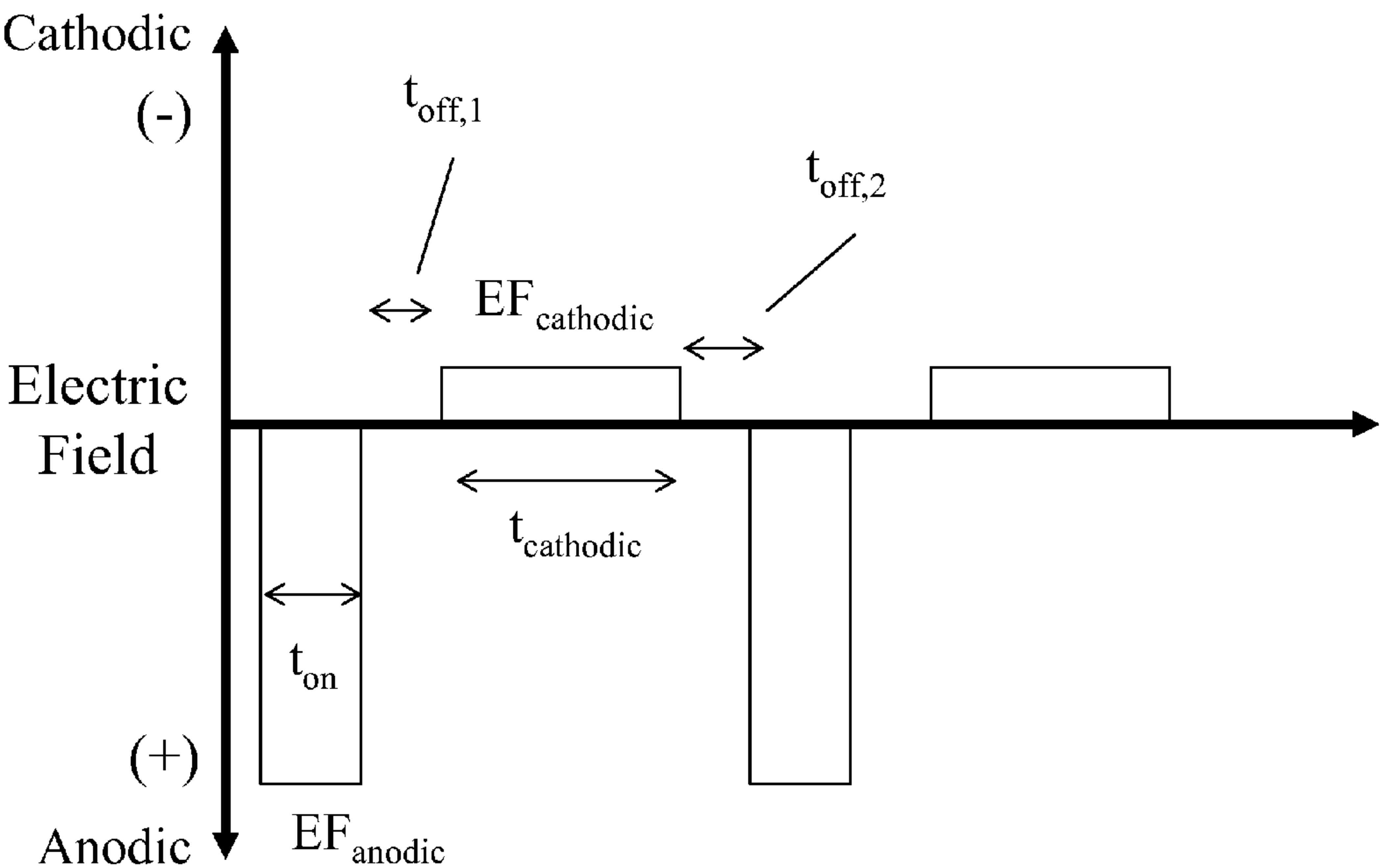


FIG. 5A

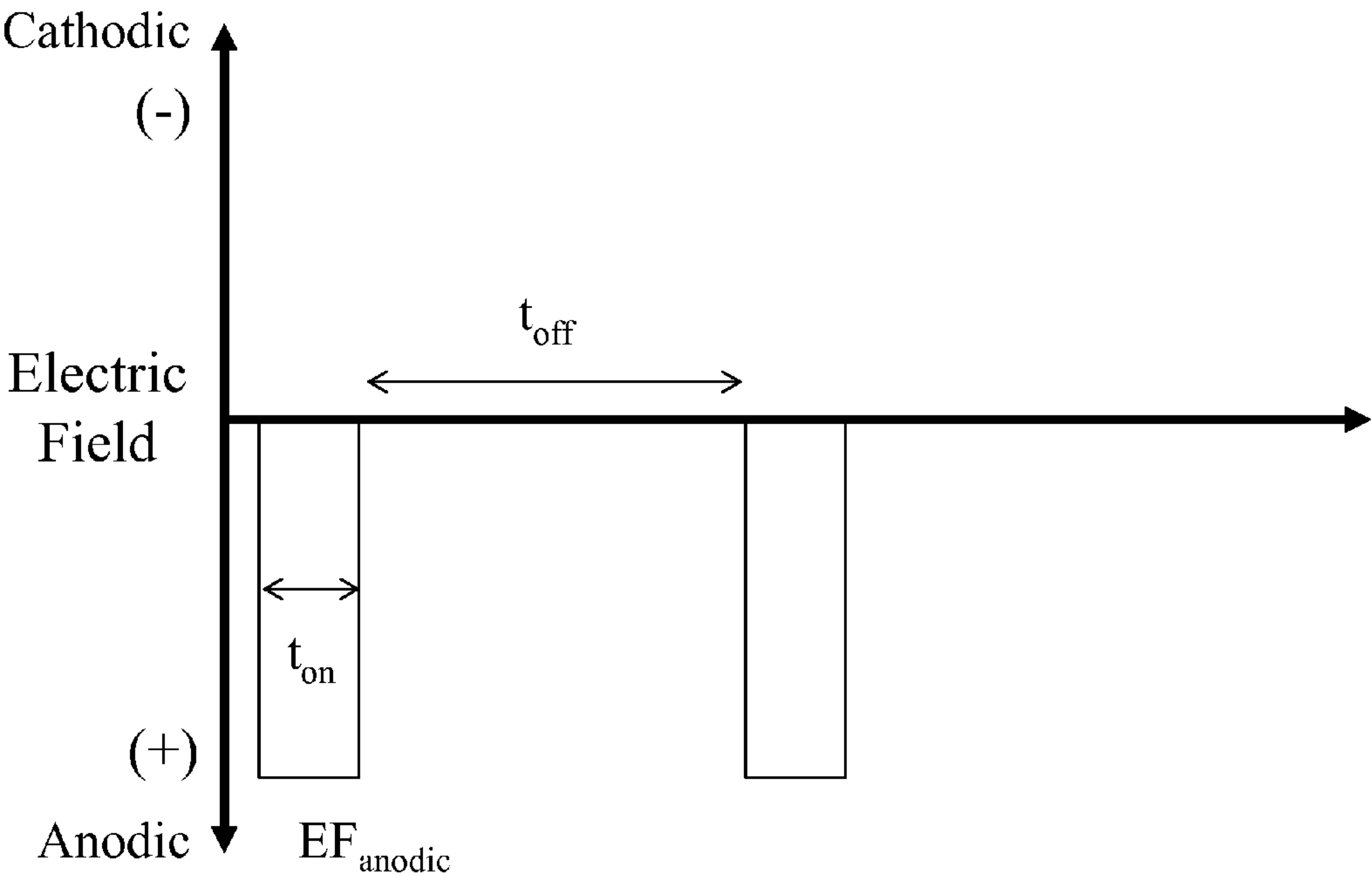
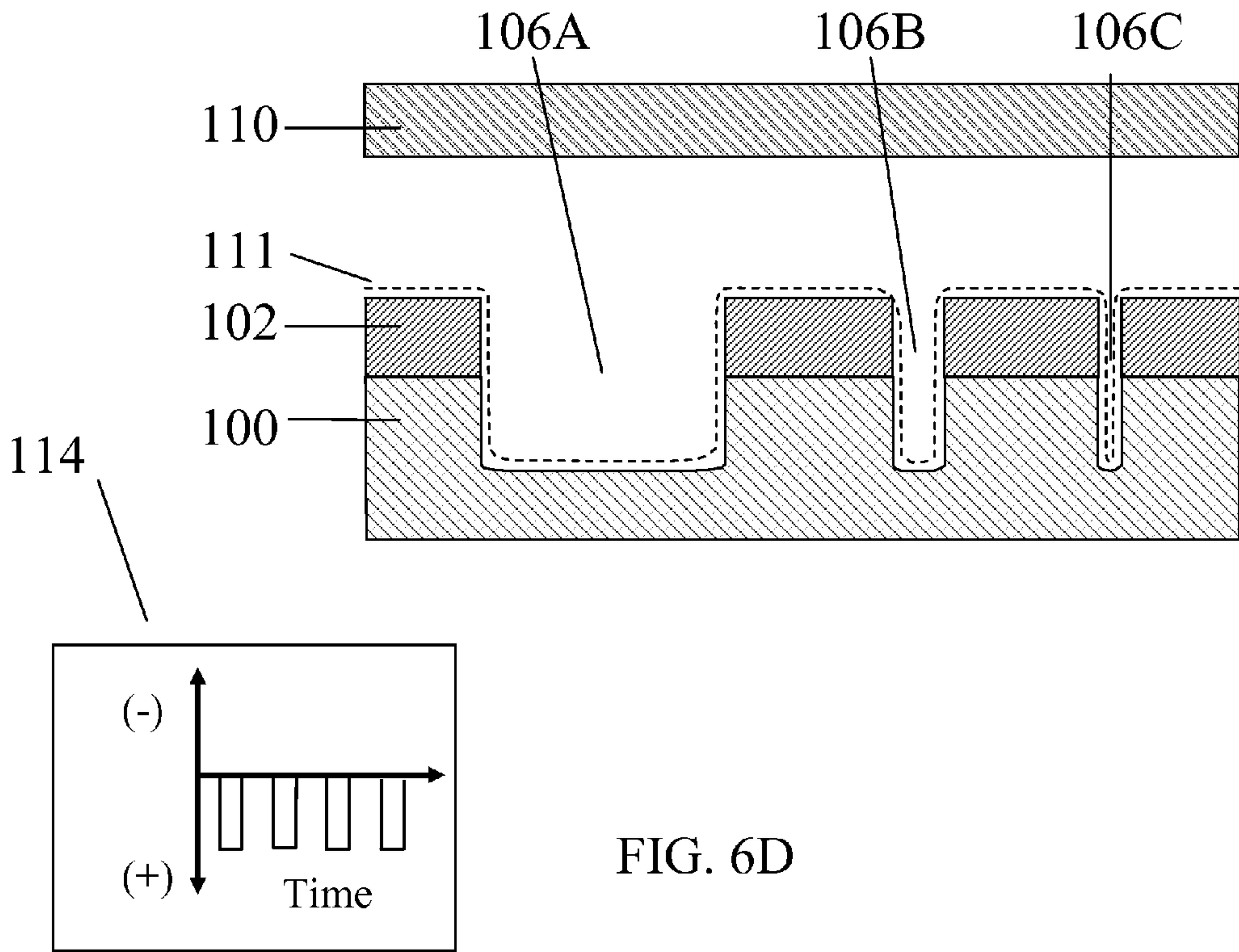
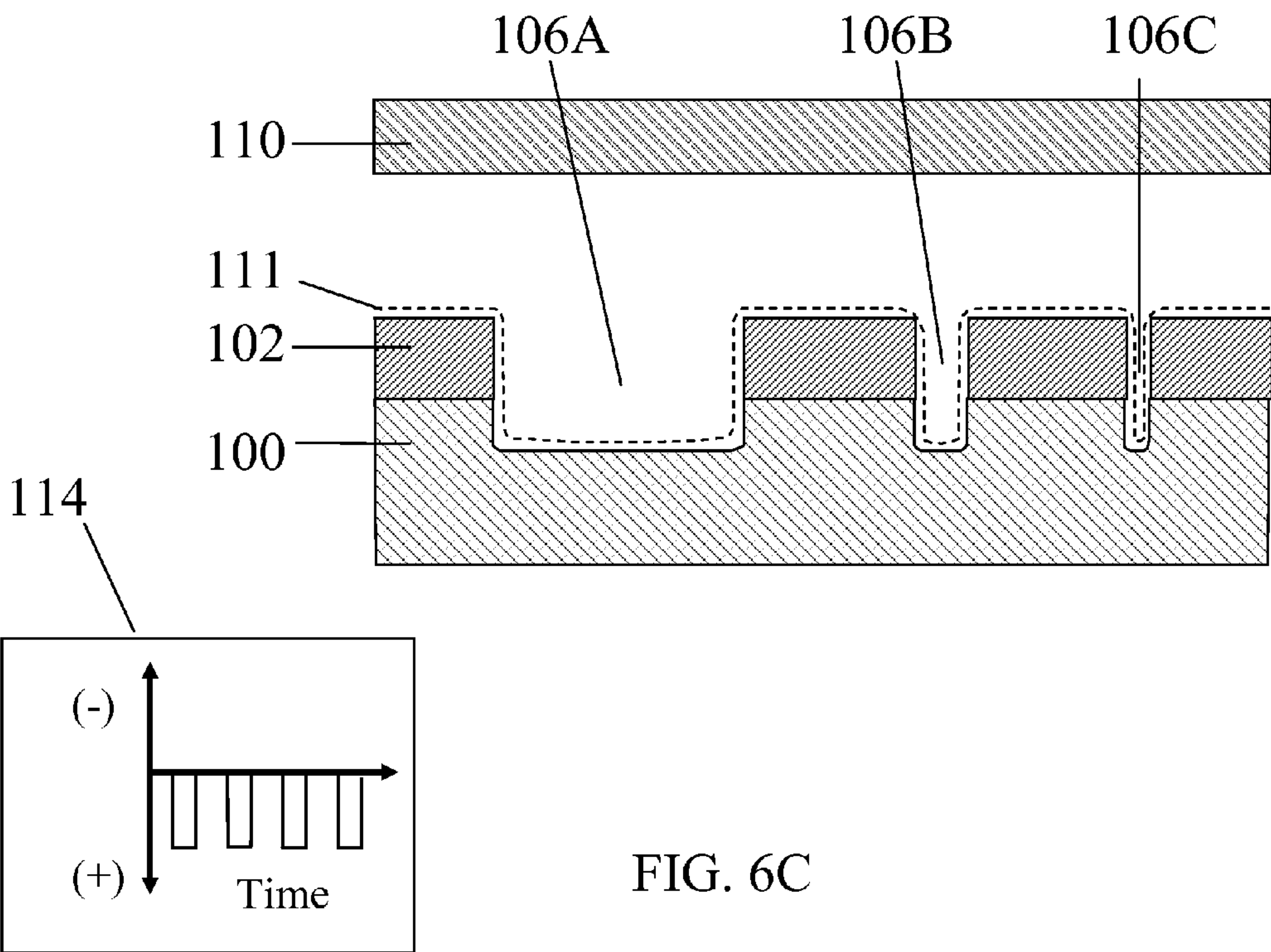


FIG. 5B



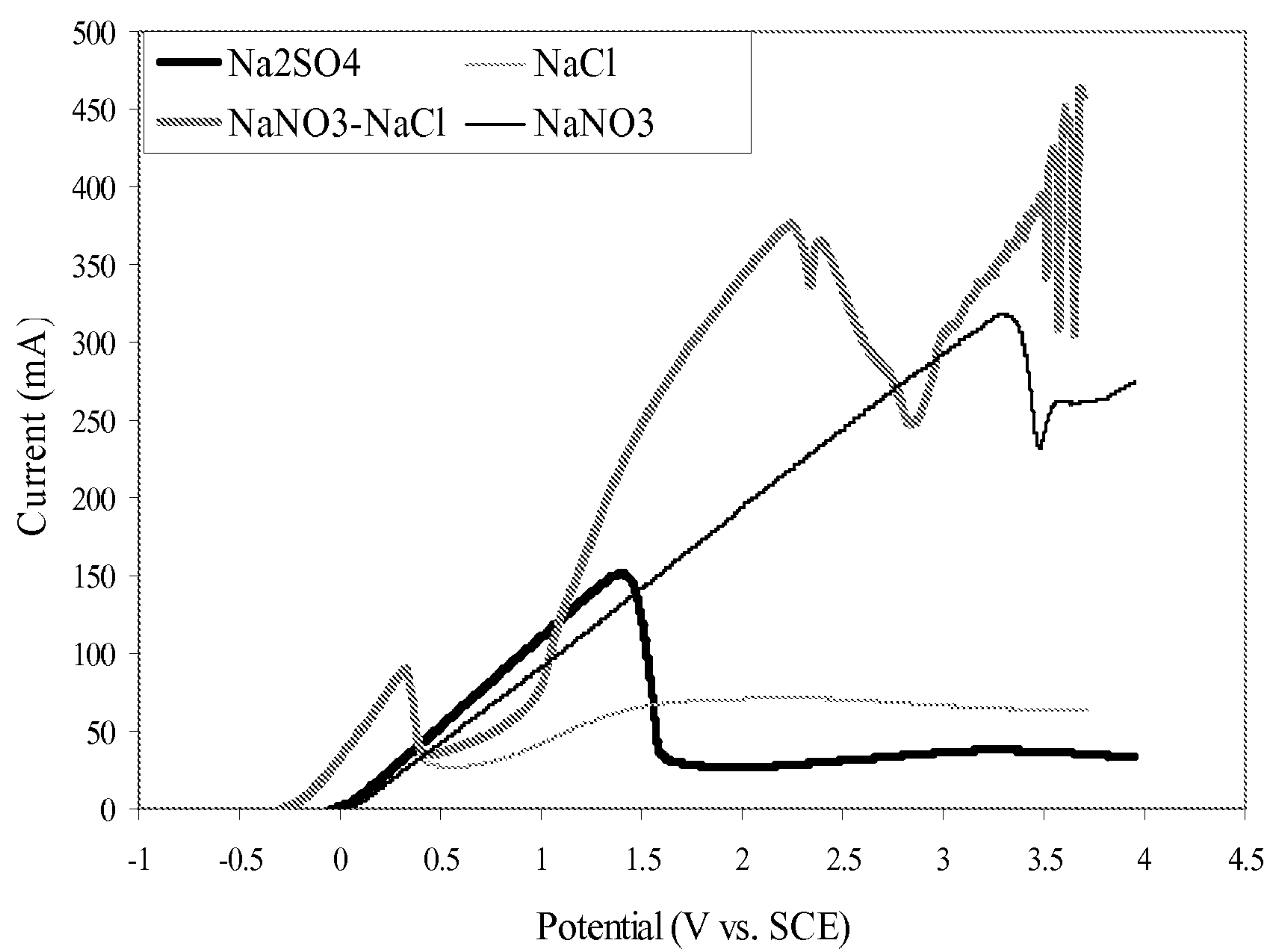


FIG. 7

ELECTROCHEMICAL ETCHING AND POLISHING OF CONDUCTIVE SUBSTRATES

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 61/228,660 filed Jul. 27, 2009, the entire contents of which are hereby incorporated by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with U.S. Government support under U.S. Department of Energy DE-FG02-08ER85112. The U.S. Government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] The present invention relates to the fabrication of parts and devices by a photoelectrolytic machining or an electrolytic through mask etching method.

[0004] One aspect of the present disclosure relates to the fabrication of fuel nozzles.

[0005] Another aspect relates to the formation of cooling channels for thermal management for aerospace components.

[0006] Another aspect relates to the manufacture of stents.

[0007] Another aspect relates to the formation of micro-channel reactors.

[0008] Another aspect relates to the machining of internal fluid flow passageways for modular manifolds for fluid delivery.

[0009] Another aspect relates to the fabrication of thin fluid channels in devices such as dialysis machinery.

BACKGROUND

[0010] This disclosure relates to process improvements for etching and/or polishing metal surfaces by coupling pulsed electric current with conventional through mask etching process or photoelectrolytic machining.

[0011] The turbine engine industry has considerable interest in improved combustion efficiency and low exhaust emission. Towards this end, the industry has devised sophisticated fuel nozzles of increasingly smaller sizes. One previous development of fuel nozzle manufacturing was laminating multiple discs together to form the nozzles. Ideally, each disc has a different opening profile etched either partially or entirely through the disc. When the discs are surface bonded together to form nozzles, their etched profiles form complex fuel and air passages. These advanced passage designs significantly enhance spray characteristics, resulting in a homogeneous mixture of fuel and air and improved combustion and reduced emissions. Due to the operating conditions endured by fuel injectors, the materials of choice range from 440C Stainless Steel (for land based power generation) to nickel- and cobalt-based alloys (for aerospace jet engines).

[0012] In the case of the advanced thermal management for aerospace components, metals are similarly bonded together to enable the manufacture of complex cooling channels in a lightweight, small footprint design while realizing enhanced performance over previous designs. Regardless of the application, the air and fuel passages are extremely sensitive to channel geometry and surface integrity as would be expected for a complex dynamic fluid system. Any losses due to com-

ponent deviation from the intended design result in loss of product quality. Therefore, a robust manufacturing process is required.

[0013] Conventional machining has been used to fabricate small numbers of relatively large nozzles. The more recent trend is towards large numbers of small nozzles. The smaller nozzles deliver smaller droplets of fuel resulting in more complete combustion. This enables better fuel efficiency and less polluting emissions, such as NO_x. The diminutive size required all but eliminates conventional machining for nozzle fabrication, except in cases where other manufacturing processes are not available. In addition, surface roughness requirements and smooth blending of transition points become even more critical as the size scale decreases; neither of these are strong points for conventional machining. The state of the art fabrication technique for stainless steel nozzles is through mask chemical etching. U.S. Pat. No. 5,435,884 discloses the use of through mask chemical etching on metals (preferably stainless steel) polymers and composites in the manufacture of spray nozzles. However, through mask chemical etching is an isotropic process and etches away all of the exposed metal. Consequently, undercutting of the metal under the mask occurs. This undercutting is problematic for small feature sizes and where the requirement for dimensional tolerance is high. Furthermore, conventional through mask chemical etching requires more aggressive etching solutions for more passive alloy formulations.

[0014] In the aerospace turbine engine application, the current materials are high temperature, nickel-based alloys that do not respond to the current chemical etching process due to their highly passive nature. They are currently fabricated using conventional milling, which is difficult due to the mechanical properties of the alloys. The present invention overcomes the limitations associated with the surface passivity, allowing the use of a through mask etching process. In addition, the next generation of fuel atomizers will require the use of even higher temperature alloys, such as cobalt-based alloys. This transition has been delayed because there is currently no suitable manufacturing process for these alloys. Embodiments of the present invention are suited for this application due to its ability to control surface passivity, thereby enabling the next generation of materials.

[0015] For the electronics thermal management application, the aluminum alloy used is not conducive to the current chemical milling or etching process due to its highly passive nature, similarly to nickel-based alloys. Embodiments of the present invention are suited for this application due to its ability to control surface passivity. The present invention will enable the fabrication of features that are smaller than those currently achievable.

[0016] Embodiments of the present invention can also be applied in the milling of microchannels into metal substrates. As described in U.S. Pat. No. 6,989,134 microchannels can be utilized as microreactant chambers for catalytic reactions. Used in this way the microchannels increase the surface area upon which reactions can occur; thereby, maximizing catalysis. Further benefit of microchannels is derived from their short mass and heat transfer distances. In addition, U.S. patent application Ser. No. 10/801,366 disclose that methods of manufacturing thin fluid microchannels can enable the development of portable and more efficient dialysis machinery. Furthermore, microchannels are useful for delivery of minute volumes of solution to chemical detectors capable of microscale sensitivity.

[0017] Embodiments of the present invention also have application in the manufacture of stents. Stents are medical devices implanted within the lumen of a body passageway to support the walls of the lumen. The stent prevents collapse of the lumen and subsequent blockage of fluid flow through the passageway. Stents are particularly useful during angioplastic surgery, which is performed to clear arteries obstructed by plaques. The plaques are formed within the walls of the arteries by the accumulation of cells laden with cholesterol and fatty acids. During the angioplastic procedure, a tiny deflated balloon on the tip of a catheter is inserted into the lumen of an obstructed artery. Upon inflation of the balloon, the plaque is compressed against the walls of the arteries relieving the blockage. However, due to the elasticity of the arteries, once the catheter is removed, the blood vessel would collapse if not for the insertion of tube-shaped stents into the lumen to keep it open.

[0018] Stents commonly are made of a metallic mesh material. Metals selected for stent fabrication are selected due to the metal's ability to resist corrosion and for its mechanical properties, such as flexibility and rigidity. Stents are most commonly fabricated from stainless steel and nickel-titanium (e.g., nitinol) alloys. The mesh-like pattern is usually cut in either a sheet of the metal or a hollow tube of the metal.

[0019] The prior art discloses several methods for machining the mesh pattern into the stents. One method is laser beam machining in which a high-energy beam of light is utilized to cut the mesh pattern into the starting material. Another method disclosed in the prior art involves the use of an electrical discharge in machining out the pattern. However, both laser beam machining and electrode discharge machining lead to the unwanted presence of metal burrs, sharp surfaces, and oxidized metal at the edges of the cuts. These byproducts must be removed in subsequent descaling, electropolishing or manual finishing steps. Unfortunately, these finishing processes are costly, labor-intensive, and are performed with chemicals that may be hazardous to both the environment and the worker.

[0020] U.S. Pat. No. 5,902,475 discloses a third method of stent fabrication, through-mask photochemical etching. In through-mask chemical etching, the metal substrate is overlaid with an etch-resistant mask pre-cut to serve as a template of the etch pattern. The metal substrate can be comprised of stainless steel, platinum, titanium, tantalum, polymers, gold alloys, and gold/platinum alloys, U.S. Pat. No. 6,774,985 discloses that the metal substrate can be overlaid with an etch-resistant, photosensitive layer that upon exposure to light, i.e. ultraviolet (UV) light becomes cross-linked to the metal substrate. The photosensitive material is exposed to the light in a predetermined pattern yielding cross-linked areas of the substrate and unaffected areas that were not exposed to the light. A negative developer is applied that dissolves away the unexposed, photosensitive material while the exposed material remains cross-linked to the metal. Alternatively, the light exposure could be used to deactivate the photosensitive material causing the unexposed material to be left intact and the exposed material to be removed upon chemical treatment. In whichever case, after treatment of the masked metal with a chemical, metal-dissolving agent only the areas cross-linked to the etch-resistant material will remain. This results in stents with the desired mesh pattern.

[0021] Chemical etching is a method well known in the art of metal machining. In this method chemicals are used to dissolve unprotected areas of the metal substrate. Commonly

used chemical etching solutions include alkaline ammonia, hydrogen peroxide-sulfuric acid, cupric chloride, persulfates, ferric chloride, chromic-sulfuric acids, nitric acid and the like. One manner of implementing chemical etching is immersion etching. In immersion etching, the substrate is immersed in a solution that chemically dissolves the exposed metal conductor. However, this method is limited by the need to reintroduce fresh etchant into the etching chamber as reactants in the solution are depleted by the etching process. Consequently, immersion etching was modified into the bubble etching process. Bubble etching involves the introduction of air bubbles into the etchant solution to recirculate the reactants in the solution. However, with bubble etching, non-uniform etching is encountered because of the difficulty of achieving uniform injection of the bubbles into the etchant bath.

[0022] Another variation in the chemical etching process is spray etching. In spray etching, etching solutions are sprayed onto the top and bottom of the work piece, positioned either horizontally or vertically in relation to the spray nozzles. However, spray etching when compared to immersion etching results in less uniform etching because of uneven dispersal of the etchant.

[0023] In all chemical etching processes, anisotropic etching is desired to obtain fine lines and spaces with vertical walls. However, chemical etching is inherently isotropic, etching all areas of the exposed part of the metal layer at the same rate. Consequently, chemical etching proceeds downwards and laterally under the etch-resist layer at the same rate. Therefore it is desirable in the industry to minimize isotropic etching in favor of anisotropic etching.

[0024] Chemical etching uses aggressive, acidic or alkaline chemical etching solutions that pose safety and disposal problems, which contribute significantly to product cost of the etching process. As the metal concentration in the etching solution increases, the performance of the etching process degrades. Therefore, additives are included in the etchant to bind the metal, and the etchant must be either continually regenerated, or dumped to waste treatment. In addition, the choice of chemical etchant is often a compromise between etch rate, metal containing capacity and compatibility with the mask or etch-resist layer. For chemical etching processes, spray etching is preferred over immersion etching, for higher etch rates. Horizontal spray etching is preferred over vertical etching, for better definition of lines and spaces. If very fine patterns and lines are required, the result can be loss of the pattern due to undercut. Due to these limitations, new technologies are required to produce the more demanding etch features.

[0025] Similarly, many contemporary methods of photo-electrochemical etching use similar hazardous chemicals in the etchant bath. U.S. Pat. No. 6,726,829 discloses the use of bath solutions consisting of ferric chloride; potassium cyanide; hydrochloric acid and nitric acid; phosphoric acid and sulfuric acid; sodium hypochlorite; or hydrochloric acid. Because these chemicals are hazardous, workers must take precautionary measures to prevent exposure and steps must be taken to properly dispose of these chemicals after use. This adds extra cost and efforts to the metal etching process. Therefore, there is a need to develop an alternative etchant bath composition that obviates these hazardous chemicals.

[0026] Another etching process widely utilized in metal machining is electrochemical etching in which direct current (DC), or constant current, is used to control metal dissolution.

A DC field is applied between a cathode and the work piece. The cathode may be placed a few millimeters from the work piece to improve the primary current distribution. The cathode and workpiece are submerged in a chemical, metal-dissolving solution resulting in a combination of both electrolytic dissolution and chemical etching of the exposed part of the metal layer. Some commonly used chemical etching solutions include a solution of sulfuric and phosphoric acids and a solution containing ferric chloride.

[0027] The present invention will enhance the reproducibility of the final product by displacing a difficult to control chemical etching process with a robust electrochemical machining process. Chemical etching is driven solely by the chemical reaction between the substrate and etching bath. Electrolytic etching is an etching process driven by an external power source that is controlled by the user. The present invention takes conventional electrolytic etching a step further through the sophisticated application of pulsed electric fields. A key advantage of the present invention is the ability to enhance anisotropic dissolution behavior, thereby increasing the achievable aspect ratio.

SUMMARY OF THE INVENTION

[0028] There is need for a method that can etch features with minimal undercutting and without the use of caustic chemicals in the plating bath in the manufacture of devices having small features, such as stents, fuel nozzles, cooling channels, bipolar plates for fuel cells, and microchannels for sensors, microfluidic devices, chemical reactors, and dialysis. More particularly, embodiments of the invention are useful in forming features that range in size from about 5 to about 1500 microns, e.g., microfluidic channels may range from about 5 to 300 microns, bipolar plates may range from about 500 to 1500 microns and cooling channels range from about 200 to 1500 microns.

[0029] In one embodiment of the present invention, the exposed part of the metal layer, e.g. 440C stainless steel or copper, is electrochemically etched using an electric current in combination with a non-active electrolyte solution. As discussed herein, a “non-active” electrolyte solution is an electrolyte solution that does not provide chemical etching capability (e.g., the ability to electrolessly oxidize the metal forming the surface of the substrate) in the absence of an electric current. Further improvements on the disclosed electrochemical etching process are obtained using pulsed electric currents.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] FIG. 1 illustrates a metal substrate overlayed with an etch-resistant material during the etching process.

[0031] FIG. 2 illustrates a metal substrate overlayed with an etch-resistant material and spacing after completion of the etching process.

[0032] FIG. 3A illustrates the beginning stage of the chemical etching process for forming lines and spaces, as described in the prior art.

[0033] FIG. 3B illustrates an early stage, following the beginning stage, in chemical etching process for forming lines and spaces, as shown in the prior art.

[0034] FIG. 3C illustrates further progression of the chemical etching process for forming lines and spaces, as shown in the prior art.

[0035] FIG. 3D illustrates the completion of the chemical etching process for forming lines and spaces, as shown in the prior art.

[0036] FIG. 4A illustrates the beginning stage of the DC electric current electrolytic-cum-chemical process for forming circuitry lines and spaces, as described in the prior art.

[0037] FIG. 4B illustrates an early stage, following the beginning stage, of the DC electric current electrolytic-cum-chemical process for forming lines and spaces, as described in the prior art.

[0038] FIG. 4C illustrates the further progression of the DC electric current electrolytic-cum-chemical process for forming lines and spaces, as described in the prior art.

[0039] FIG. 4D illustrates the completion of the DC electric current electrolytic-cum-chemical process for forming lines and spaces, as described in the prior art.

[0040] FIG. 5A illustrates the pulse/pulse reverse electric current used in accordance with one method of the present invention.

[0041] FIG. 5B illustrates a preferred embodiment pulse electric current used in accordance with one method of the present invention.

[0042] FIG. 6A illustrates the beginning stage of one embodiment of the present invention, an electrochemical etching process using a PC electric current in a non-active, electrolyte solution, more specifically, an electrolyte solution that does not provide substantial chemical etching capability in the absence of an electric current.

[0043] FIG. 6B illustrates an early stage, following the beginning stage, of one embodiment of the present invention, an electrochemical etching process using a PC electric current in a non-active, electrolyte solution, more specifically, an electrolyte solution that does not provide chemical etching capability in the absence of an electric current.

[0044] FIG. 6C illustrates the further progression of an electrochemical etching process in accordance with one embodiment using a PC electric current in a non-active electrolyte solution, more specifically, an electrolyte solution that does not provide chemical etching capability in the absence of an electric current.

[0045] FIG. 6D illustrates the completion of an electrochemical etching process in accordance with one embodiment using a PC electric current in a non-active electrolyte solution, more specifically, an electrolyte solution that does not provide chemical etching capability in the absence of an electric current.

[0046] FIG. 7 presents a set of polarization curves for electrolytic etching of copper in various electrolytes.

[0047] The descriptions and identification of the items in the figures are tabulated in the following table.

Numeral	Item Description
100	Metal layer
102	Etch-resist layer
104	Hydrodynamic boundary layer
106A	Large width space
106B	Medium width space
106C	Small width space
108	Nernst boundary layer
110	Counter electrode
111	Electrodynamic boundary layer
112	DC electric current
114	Pulsed electric current

-continued

Numeral	Item Description
a	Etch-resist layer width
b	Conductor line width
b'	Maximum conductor line width
s	Undercut width
θ	Undercut angle
h	Metal removal depth
d	Metal layer thickness
EF_{anodic}	Anodic electric current
$EF_{cathodic}$	Cathodic electric current
t_{on}	Anodic on-time
$t_{off,1}$	Off-time before cathodic pulse
$t_{off,2}$	Off-time after cathodic pulse
t_{off}	Off-time
$t_{cathodic}$	Cathodic on-time

DETAILED DESCRIPTION OF THE INVENTION

[0048] The present invention provides a method for etching an exposed part of a metal substrate, specifically for the manufacture of devices having small features, such as fuel nozzles and stents and in the machining of cooling channels for thermal management in aerospace electronics. The method of the invention can be carried out using any suitable electrolytic etching apparatus. That apparatus includes a vessel which houses a counter electrode, which can be formed from any suitable electrode material such as titanium or platinum. In practice, the number of counter electrodes will be selected to facilitate achieving a uniform etching. The work piece to be treated is clamped in the vessel using a chuck in a position in which it is located opposite the counter electrode or counter electrodes. A power supply or rectifier completes a circuit whereby a net anodic electric current is delivered to the work piece, causing electrochemical etching of the exposed part of the metal layer, and a net cathodic electric current is delivered to the counter electrode or counter electrodes. The rectifier may use either voltage control or current control to deliver the electric current, and the rectifier is capable of delivering pulsed electric currents. Preferably, a mechanism is provided to provide uniform flow of electrolyte over the substrate surface during the etching process. The vessel includes an inlet for a supply of electrolyte, which is pumped into and out of the vessel using any convenient pump. Liquid mass flow controllers deliver the electrolyte at flow rates, which are adjusted for the volume of the vessel.

[0049] FIGS. 1 and 2 schematically illustrate features in a metal substrate during and after completion of the etching process, respectively. FIG. 1 illustrates a metal substrate (100) which has a thickness 'd', and an etch-resist layer (102) on top of the metal substrate (100). The etch-resist layer (102) has been processed to produce the desired etch pattern by techniques known to those skilled in the art. The exposed part of the metal substrate (100) is etched through the features in the etch-resist layer (102). Dimension 'a' is the width of the etch-resist layer and represents the desired metal conductor width after removal of the exposed part of the metal layer. Dimension 'b' is the metal conductor width after removal of the exposed part of the metal substrate. Ideally, 'b' and 'a' should be equal. During removal of the exposed part of the metal substrate (100), as the depth of the metal removal proceeds vertically, the sidewalls of the exposed metal conductor tend to etch laterally and produce an undercut beneath the etch-resist, the width of which is referred to as the under-

cut width 's'. It is desired that the undercut width 's' be equal to zero at the completion of the etching process. The undercut angle ' θ ' refers to the angle between the side walls of the metal conductor (100) and the etch-resist layer (102). It is desired that the undercut angle ' θ ' be equal to 90° as well as 's' being zero.

[0050] FIG. 2 illustrates the completion of the etching process depicted in FIG. 1. The degree of lateral undercutting, or side etch, at the completion of the etching process is depicted by the dimension 's'. The maximum conductor width after exposed part of the metal layer removal is 'b'. Ideally, 'b' and 'a' should be equal to 'a'.

[0051] The quality of the etching process is determined by calculating measured parameters, which may include the Undercut (C), Etch Factor, and $\tan \theta$. Although desired values for these parameters are provided below, the present invention is not limited to etching processes capable of providing the desired values.

[0052] Undercut: The degree of undercut (C) is the given by the equation:

$$C=(a-b)/2 \quad (1)$$

The smaller this value, the better the quality of the exposed part of the metal layer removal process. Ideally, $C=0$.

[0053] Etch Factor: If $h < d$, the Etch Factor is calculated from the equation:

$$\text{Etch Factor} = h/s. \quad (2)$$

If $h = d$, the Etch Factor is calculated from the equation:

$$\text{Etch Factor} = h/s = d/s. \quad (3)$$

[0054] The larger the Etch Factor the better the metal removal process.

[0055] Tan θ : Tan θ is calculated from the equation:

$$\tan \theta = h/((b'-b)/2). \quad (4)$$

The larger the value of $\tan \theta$ the better.

[0056] FIGS. 3A-D are schematic illustrations of the prior art chemical etching process for forming lines and spaces. FIG. 3A illustrates a metal substrate (100) and an etch-resist layer (102) on top of the metal substrate (100). The etch-resist layer (102) has been processed to produce the desired etch pattern by techniques known to those skilled in the art.

[0057] Furthermore, FIG. 3A illustrates an etch pattern with varying width spaces (106A, 106B, 106C) in the etch-resist layer (102). The metal substrate (100) is removed by chemical etching through the spaces in the etch-resist layer (102) to produce the desired etch pattern in the metal substrate (102). A diffusion layer exists in the solution. The thickness of this diffusion layer is dependent upon the hydrodynamics in the solution at the workpiece. The diffusion layer is referred to as the hydrodynamic boundary layer (104) and is conformal to the larger spaces (106A) in the etch-resist layer (102), slightly conformal to the medium width spaces (106B) in the etch-resist layer (102), but non-conformal to the smaller spaces (106C) in the etch-resist layer (102). This non-conformal diffusion layer results in hydrodynamic inaccessibility of fresh solution into the smaller spaces (106C) and limits the hydrodynamic accessibility of fresh solution into the medium width spaces (106B). Those skilled in the art recognize the relative nature of a conformal diffusion layer or a non-conformal diffusion layer in terms of the solution hydrodynamics and the actual widths of the spaces in the etch-resist layer.

[0058] FIG. 3B schematically illustrates an early stage, following the beginning stage (FIG. 3A), in the chemical

etching process for forming lines and spaces, as described in the prior art. Removal of metal from the exposed part of the metal substrate (100) is initiated, with more metal removal from the larger spaces (106A, 108B) than from the smaller spaces (106C).

[0059] FIG. 3C schematically illustrates further progression in the chemical etching process for forming lines and spaces, as described in the prior art. Further metal removal from the exposed part of the metal substrate (100) has progressed to approximately half the total depth in the large space (106A), and there is lateral undercutting beneath the etch-resist layer (102). In the smaller spaces (106B, 106C) in the etch-resist layer (102), the metal substrate (100) is not removed as deeply, due to the hydrodynamic inaccessibility of the smaller spaces preventing effective transport of fresh chemical etching solution into those spaces. Furthermore, as the removal of exposed metal from the metal layer (100) proceeds, the diffusion layer (104) becomes less conformal with the large space (106A).

[0060] FIG. 3D schematically illustrates the completion of the chemical etching process for lines and spaces, as described in the prior art. In the large space (106A), the removal of exposed metal from the metal layer (100) has progressed downward. Considerable lateral undercutting has occurred beneath the etch-resist layer (102) in this large space (106A). However, in the medium (106B) and small (106C) spaces, the removal of exposed metal from the metal layer (100) has not progressed downward to the same extent as in the large space (106A) but lateral undercutting beneath the etch-resist layer (102) has occurred.

[0061] If the chemical etching processes were continued in an attempt to etch the metal layer (100) down to the same level for all the spaces (106A, 106B, 106C), the degree of lateral undercutting in the large feature (106A) would continue to increase and the degree of undercutting would be unacceptable. These deleterious effects are exacerbated by the fact that the chemical etching activity cannot be easily terminated.

[0062] FIGS. 4A-D are schematic illustrations of a DC electric current electrolytic dissolution-cum-chemical etching process for forming high density interconnect circuitry lines and spaces, as described in the prior art. FIG. 4A illustrates a metal layer (100) and an etch-resist layer (102) on top of the metal layer (100). The etch-resist layer (102) has been processed to produce the desired etch pattern by techniques known to those skilled in the art.

[0063] Furthermore, FIG. 4A illustrates an etch pattern with varying width spaces (106A, 106B, 106C) in the etch-resist layer (102). The inset of FIG. 4A shows a DC electric current (112) that is maintained between a counter electrode (110) and the metal layer (100), with the metal layer (100) being maintained anodic with respect to the counter electrode (110). The electric current is established by either controlling the voltage of the power supply or by controlling the current of the power supply. The metal layer (100) is removed by the electrolytic dissolution combined with chemical etching through the spaces in the etch-resist layer (102) to produce the desired etch pattern in the metal layer (100). A diffusion layer exists in the solution. The thickness of this layer is dependent upon the hydrodynamics in the solution at the substrate and the electric current. This diffusion layer is called the Nernst boundary layer (108). The thickness of the Nernst boundary layer (δ_{Nernst}) is approximated by the equation:

$$\delta_{Nernst} = (nFD\Delta C)/i_{Limiting} \quad (5)$$

[0064] The other terms in the equation are: 'n' is the number of electrons involved in the electrolytic dissolution of one mole of the metal, 'F' is the Faraday constant, 'D' is the diffusion coefficient of the dissolved metal, ' ΔC ' is the concentration gradient of the dissolved metal from the metal surface/solution interface to the bulk solution, and $i_{Limiting}$ is the limiting current. The Nernst boundary layer (108) is conformal to the larger spaces (106A) in the etch-resist layer (102), slightly conformal to the medium width spaces (106B) in the etch-resist layer (102), but not conformal to the smaller spaces (106C) in the etch-resist layer (102). This lack of conformality results in hydrodynamic inaccessibility of fresh solution into the smaller features (106C). The removal of the exposed metal from the metal layer (100) is caused by the application of the electric current and the action of the chemical etchant. Due to the presence of an active chemical etching solution, the chemical etching process cannot be stopped by simply turning off the applied electric current.

[0065] FIG. 4B schematically illustrates an early stage, following the beginning stage (FIG. 4A) of the DC electric current electrolytic dissolution-cum-chemical etching process as described in the prior art. Removal of metal from the exposed part of the metal layer (100) is initiated with more metal removal from the larger spaces (106A, 106B) than from the smaller spaces (106C). The insets of FIGS. 4A, 4B and 4C show a DC electric field (112) that is maintained between the counter electrode (110) and the metal layer (100), with the metal layer (100) being maintained anodic with respect to the counter electrode (110).

[0066] FIG. 4C schematically illustrates further progression of the DC electric current electrolytic dissolution-cum-chemical etching process for forming high density interconnect circuitry lines and spaces, as described in the prior art. Further metal removal from the exposed part of the metal layer (100) has progressed to approximately half the total depth in the large space (106A), and there is lateral undercutting beneath the etch-resist layer (102). In the smaller spaces (106B, 106C) in the etch-resist layer (102), the metal layer (100) is not removed as deeply, due to the hydrodynamic inaccessibility of the smaller spaces preventing effective transport of fresh chemical etching solution into those spaces. Furthermore, as the removal of exposed metal from the metal layer (100) proceeds, the Nernst boundary layer (107) becomes less conformal with the large space (108A).

[0067] FIG. 4D schematically illustrates the completion of the DC electric current electrolytic dissolution-cum-chemical etching process for etching lines and spaces, as described in the prior art. In the large space (106A), the removal of exposed metal from the metal substrate (100) has progressed downward. Considerable lateral undercutting has occurred beneath the etch-resist layer (102) in this large space (106A). However, in the medium (106B) and small (106C) spaces, the removal of exposed metal from the metal substrate (100) has not progressed downward at the same level as in the large space (106A), and lateral undercutting beneath the etch-resist layer (102) has occurred. If the DC electric current electrolytic dissolution-cum-chemical etching process were continued in an attempt to etch the metal substrate (100) downward to the same extent for all the spaces (106A, 106B, 106C), the degree of lateral undercutting in the large space (106A) would continue to increase and the degree of undercutting would be unacceptable. While the DC electric current provides an additional control variable for establishing a conformal diffusion layer, that is Nernst boundary layer, the degree of control of

the DC electric current electrolytic dissolution-cum-chemical etching process is not sufficient to meet the demands of applications requiring very fine lines and spaces. Furthermore, while turning off the DC electric current will terminate the electrolytic dissolution activity, the chemical etching activity cannot be easily terminated. This further exacerbates the deleterious effects of the combined DC electric current electrolytic dissolution-cum-chemical etching process.

[0068] One embodiment of the present invention comprises an electrochemical etching process using a pulse/pulse reverse electric current in a non-active electrolyte solution, more specifically, an electrolyte solution that does not provide chemical etching capability (e.g., electroless oxidation) in the absence of an electric current. As used herein, the term “non-active electrolyte solution” refers to a solution that would not be practical for using in a chemical etching operation without an electric current because the solution alone does not provide any significant etching within a reasonable time period. A schematic representation of the pulsed current (PC) electric current used in the process of one embodiment of the present invention is illustrated in FIG. 5A. The PC electric current essentially comprises an anodic pulse of amplitude (EF_{anodic}) for a period of on-time (t_{on}) followed by a period without an anodic pulse. Those skilled in the art will recognize that the voltage and current will be proportional under the circumstances of the electrochemical process of the invention. Accordingly the ordinate in FIGS. 5A-B could represent either the voltage or the current. Furthermore, the pulse process need not be rectangular as illustrated. During the period without an anodic pulse, the electric current may be off, or the electric current may be cathodic ($EF_{cathodic}$) for a period of time ($t_{cathodic}$), the latter referred to as a pulse/pulse reverse electric current. In the case of a pulse/pulse reverse electric current with a cathodic pulse ($EF_{cathodic}$), off-times may be interspersed in the pulse/pulse reverse electric current prior to the cathodic pulse ($t_{off,1}$) or after the cathodic pulse ($t_{off,2}$) or both before and after the cathodic pulse. Again, one skilled in the art will recognize that the point in time chosen as the initial point of the pulse train is entirely arbitrary. Either the anodic pulse, the cathodic pulse or any point in the pulse train could be considered as the initial point.

[0069] In accordance with one embodiment of the invention, the electric current is a pulsed (PC) electric current as depicted in FIG. 5B. In accordance with particular aspects of the process, the anodic on-time may range from about 10 microseconds to about 100 milliseconds, preferably about 50 microseconds to about 50 milliseconds, and more preferably from about 100 microseconds to about 10 milliseconds. The off-time or summation of non-anodic on-time may range from about 100 milliseconds to about 10 microseconds, preferably from about 50 milliseconds to about 50 microseconds, and more preferably about 10 milliseconds to about 100 microseconds. In accordance with certain embodiments, the anodic voltage amplitude may range from about 1 to about 20 volts, and more preferably from about 2.5 to about 10 volts. FIGS. 6A-D are schematic illustrations of certain aspects of the present invention. An electrochemical etching process is shown using a PC electric current in a non-active electrolyte solution, more specifically, an electrolyte solution that does not provide chemical etching capability in the absence of an electric current. FIG. 6A illustrates a metal layer (100), e.g., copper, and an etch-resist layer (102) on top of the metal layer

(100). The etch-resist layer (102) has been processed to produce the desired etch pattern by techniques known to those skilled in the art.

[0070] Furthermore, FIG. 6A illustrates an etch pattern with varying width spaces (106A, 106B, 106C) in the etch-resist layer (102). The inset in FIG. 6A (and also in FIGS. 6B, 6C and 6D) illustrates a pulsed (PC) electric current (114) is maintained between a counter electrode (110) and the metal layer (100). The PC electric current (114) is shown to include a series of anodic pulses with off-times interspersed between the anodic pulses. However, the PC electric current may include cathodic pulses interspersed between the anodic pulses, or may include both cathodic pulses and off-times interspersed between the anodic pulses. However the PC electric current is designed, the metal layer (100) maintains a net anodic charge with respect to the counter electrode (110). The PC electric current (114) is established by either controlling the voltage of the power supply or by controlling the current of the power supply. The metal layer (100) is removed by electrochemical dissolution through the spaces in the etch-resist layer (102) to produce the desired etch features in the metal layer (100). The electrolyte is non-active and does not provide chemical etching ability in the absence of the PC electric current. Consequently, the removal of the exposed part of the metal layer (100) stops when the PC electric current is discontinued. In this manner, more precise control of the removal of exposed metal from the metal layer (100) is obtained. A diffusion layer exists in the solution, and the thickness of this layer is dependent upon the hydrodynamics in the solution at the substrate and the PC electric current. The diffusion layer under a PC electric current has been described in greater detail in commonly owned U.S. Pat. No. 6,524,461 issued to Taylor et al. and is approximated as a duplex diffusion layer, as proposed by Ibl, N., et al., *Surface Technology* 6, p. 287 (1978). This duplex diffusion layer includes a stationary outer layer and an inner layer that fluctuates with the PC electric current. The thickness of the entire duplex diffusion layer is still predominately determined by the hydrodynamic conditions. However, the thickness of the inner fluctuating layer is principally determined by the parameters of the PC electric current, for example, on-time, off-time, amplitude and the like. Accordingly, this fluctuating inner diffusion layer may be described as an electrodynamic boundary layer. In FIG. 6A only the electrodynamic boundary layer (111) is shown. The electrodynamic boundary layer thickness ($\delta_{Electrodynamic}$) may be approximated by the following relationship:

$$\delta_{Electrodynamic} \sim (2Dt)^{1/2} \quad (6)$$

The other term in the relationship not previously defined is: ‘t’ is the time of the PC electric current is applied and in the case of an anodic current it is t_{on} and in the case of a cathodic current it is $t_{cathodic}$.

[0071] As evident from the relationship (6) the thickness of the electrodynamic boundary layer is proportional to the square root of the pulse on-time. Accordingly, the electrodynamic boundary layer can be made substantially thinner than the Nernst boundary layer by using short pulse on-times. Consequently, the thickness of the electrodynamic boundary layer may be tuned to the dimension of the spaces in the etch-resist layer (104).

[0072] In FIG. 6A the PC electric current is tuned so that the thickness of the electrodynamic boundary layer (111) is con-

formal to all the spaces in the etch-resist layer, that is large (106A), medium (106B) and small (106C) spaces.

[0073] FIG. 6B schematically illustrates an early stage, following the beginning stage (FIG. 6A) of the electrochemical etching process using a PC electric current in a non-active electrolyte solution. Removal of metal from the exposed part of the metal layer (100) is initiated to an equal depth for all the features (106A, 106B, 106C). Due to the influence of the PC electric current, the electrodynamic boundary layer (111) is conformal to all the large size (106A), medium size (106B) and small size (106C) spaces.

[0074] FIG. 6C schematically illustrates further progression in the electrochemical etching process using a PC electric current in a non-active electrolyte solution. Further metal removal from the exposed part of the metal layer (100) has progressed to approximately half the total depth in all the spaces (106A, 106B, 106C), and there is minimal or no lateral undercutting beneath the etch-resist layer (102). Again, due to the influence of the PC electric current, the electrodynamic boundary layer (111) is conformal to all the large size (106A), medium size (106B) and small size (106C) spaces.

[0075] FIG. 6D schematically illustrates the completion of the electrochemical etching process using a PC electric current in a non-active electrolyte solution. In all the features (106A, 106B, 106C), the metal layer (100) has been etched downward. Minimal or no lateral undercutting has occurred beneath the etch-resist layer (102) in all the large size (106A), medium size (106B) and small size (106C) spaces. Furthermore, while the illustrations in FIG. 6A-D indicate that the PC electric current (114) does not change during the progression from the initial to the completion of the electrochemical etching process, the PC parameters may be adjusted during the process to insure a conformal electrodynamic boundary layer (111) and hence insure a favorable etching profile.

[0076] FIG. 7 is a polarization curve for a copper substrate in Na_2SO_4 , NaCl , NaNO_3 , and $\text{NaNO}_3\text{—NaCl}$. At the low potential, the current rises abruptly as the applied voltage increases owing to the anodic activation of the anode surface. The anodic reaction is controlled by the kinetics of the metal dissolution reaction. However, the metal surface may be rough due to non-uniform dissolution rate on the metal surface. As the applied voltage increases, the metal dissolution process becomes diffusion limited. This appears to facilitate a smooth polished surface and uniform feature profile. Based on FIG. 7, sodium nitrate, sodium chloride and the mixture thereof are useful nonactive electrolytes for etching and polishing a copper substrate.

[0077] While the invention has been described in detail and by reference to specific examples and embodiments, those skilled in the art will recognize that deviations and variations are possible without departing from the scope of the invention as defined by the following claims.

What is claimed is:

1. A method for etching a conductive substrate, comprising:

- (a) providing a conductive substrate with an etch-resist layer pattern deposited on said conductive substrate resulting in spaces defining an exposed part of the conductive substrate;
- (b) providing a counterelectrode;
- (c) interposing a non-active electrolyte solution between and in contact with said conductive substrate and said counterelectrode;

- (d) applying an electric current between said conductive substrate and said counterelectrode and maintaining said conductive substrate predominantly anodic with respect to said counterelectrode; and

- (e) etching said exposed part of the conductive substrate electrochemically thereby forming an etched pattern from said etch-resist layer pattern.

2. The method of claim 1 wherein said conductive substrate is copper, titanium, 440C stainless steel, gold, silver, or nickel.

3. The method of claim 1 wherein said non-active electrolyte solution is an electrolyte solution selected from the group consisting of sodium nitrate, sodium chloride, and a mixture of sodium nitrate and sodium chloride.

4. The method of claim 1 wherein said electric current is a pulse/pulse reverse electric current comprising an anodic on-time and a cathodic on-time.

5. The method of claim 4 wherein said pulse/pulse reverse electric current further comprises an off-time interspersed after said anodic on-time and before said cathodic on-time.

6. The method of claim 4 wherein said pulse/pulse reverse electric current further comprises an off-time interspersed after said cathodic on-time and before said anodic off-time.

7. The method of claim 4 wherein said pulse/pulse reverse electric current further comprises a first off-time interspersed after said anodic on-time and a second off-time interspersed before said cathodic on-time.

8. The method of claim 1 wherein said electric current is a pulsed electric current consisting of an anodic on-time and an off-time.

9. The method of claim 8 wherein said anodic on-time ranges from about 10 microseconds to about 100 milliseconds.

10. The method of claim 8 wherein said anodic on-time ranges from about 50 microseconds to about 50 milliseconds.

11. The method of claim 8 wherein said anodic on-time ranges from about 100 microseconds to about 10 milliseconds.

12. The method of claim 8 wherein said off-time ranges from about 100 milliseconds to about 10 microseconds.

13. The method of claim 8 wherein said off-time ranges from about 50 milliseconds to about 50 microseconds.

14. The method of claim 8 wherein said off-time ranges from about 10 milliseconds to about 100 microseconds.

15. The method of claim 8 wherein said pulsed electric current has an anodic voltage amplitude wherein said anodic voltage amplitude ranges from about 1 to about 20 volts.

16. The method of claim 8 wherein said pulsed electric current has an anodic voltage amplitude wherein said anodic voltage amplitude ranges from about 2.5 to about 10 volts.

17. The method of claims 4 wherein an electrodynamic boundary layer conformal to said spaces in said etch-resist layer pattern is formed.

18. The method of claim 8 wherein an electrodynamic boundary layer conformal to said spaces in said etch-resist layer pattern is formed.

19. A process for removing metal from a metal substrate comprising:

- (a) providing a metal substrate;
- (b) providing a counterelectrode;
- (c) interposing a non-active electrolyte solution between and in contact with said substrate and said counterelectrode; and

(d) applying a pulse/pulse reverse electric current comprising an anodic on-time and a cathodic on-time electric current between said substrate and said counterelectrode and maintaining said substrate predominantly anodic with respect to said counterelectrode thereby removing metal from metal clad substrate and forming an etched pattern.

20. The method of claim **19** wherein said metal is selected from the group consisting of copper, gold, silver, nickel and combinations thereof.

21. The method of claim **20** wherein said electrolyte solution is selected from the group consisting of sodium nitrate, sodium chloride, and mixtures of sodium nitrate and sodium chloride.

22. The method of claim **20** further comprising providing an etch-resist material wherein said etch-resist material covers a portion of the metal substrate thereby forming exposed portions and covered portions of said metal and said exposed portions of said metal are removed.

23. The method of claim **22** wherein said covered portions of said metal are retained and form a pattern on said substrate.

24. A process for forming etch patterns on a metal substrate comprising:

(a) providing a metal substrate having a predetermined pattern of covered metal portions and exposed metal portions;

(b) providing a counterelectrode;

(c) interposing a non-active electrolyte solution between and in contact with said substrate and said counterelectrode; and

(d) applying an electric current between said substrate and said counterelectrode and maintaining said substrate predominantly anodic with respect to said counterelectrode thereby removing the exposed metal portions from the metal substrate to form an etch pattern.

25. The method of claim **24** wherein said metal is selected from the group consisting of copper, gold, silver, nickel and combinations thereof.

26. The method of claim **25** wherein said electrolyte solution is selected from the group consisting of sodium nitrate, sodium chloride, and mixtures of sodium nitrate and sodium chloride.

27. The method of claim **25** wherein said electric current is a pulse/pulse reverse electric current comprising an anodic on-time and a cathodic on-time.

28. The method of claim **1** wherein the electric voltage and current are such that the dissolution of the metal from the surface of the substrate is diffusion limited.

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