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(54) **NANOTUBE STRUCTURES, MATERIALS,
AND METHODS**

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977/842

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(57) **ABSTRACT**

(21) Appl. No.: **12/202,280**

Nanotube structures and methods for forming nanotube structures are disclosed. The methods include forming nanotubes such that they are associated with a surface of a substrate and compressing at least a portion of the nanotubes. In some embodiments, the nanotubes may be dimensionally constrained in one direction while being compressed in another direction. Compressing at least a portion of the nanotubes may comprise stamping an impression into a surface of the nanotubes, at least a portion of which is retained when the stamp is removed. In some embodiments, the nanotubes may be aligned with respect to one another and to the surface of the substrate and may extend in a direction that is, for example, normal to the substrate.

(22) Filed: **Aug. 31, 2008**

Related U.S. Application Data

(63) Continuation-in-part of application No. 11/897,893, filed on Aug. 30, 2007.

(60) Provisional application No. 61/066,647, filed on Feb. 22, 2008, provisional application No. 60/841,266,

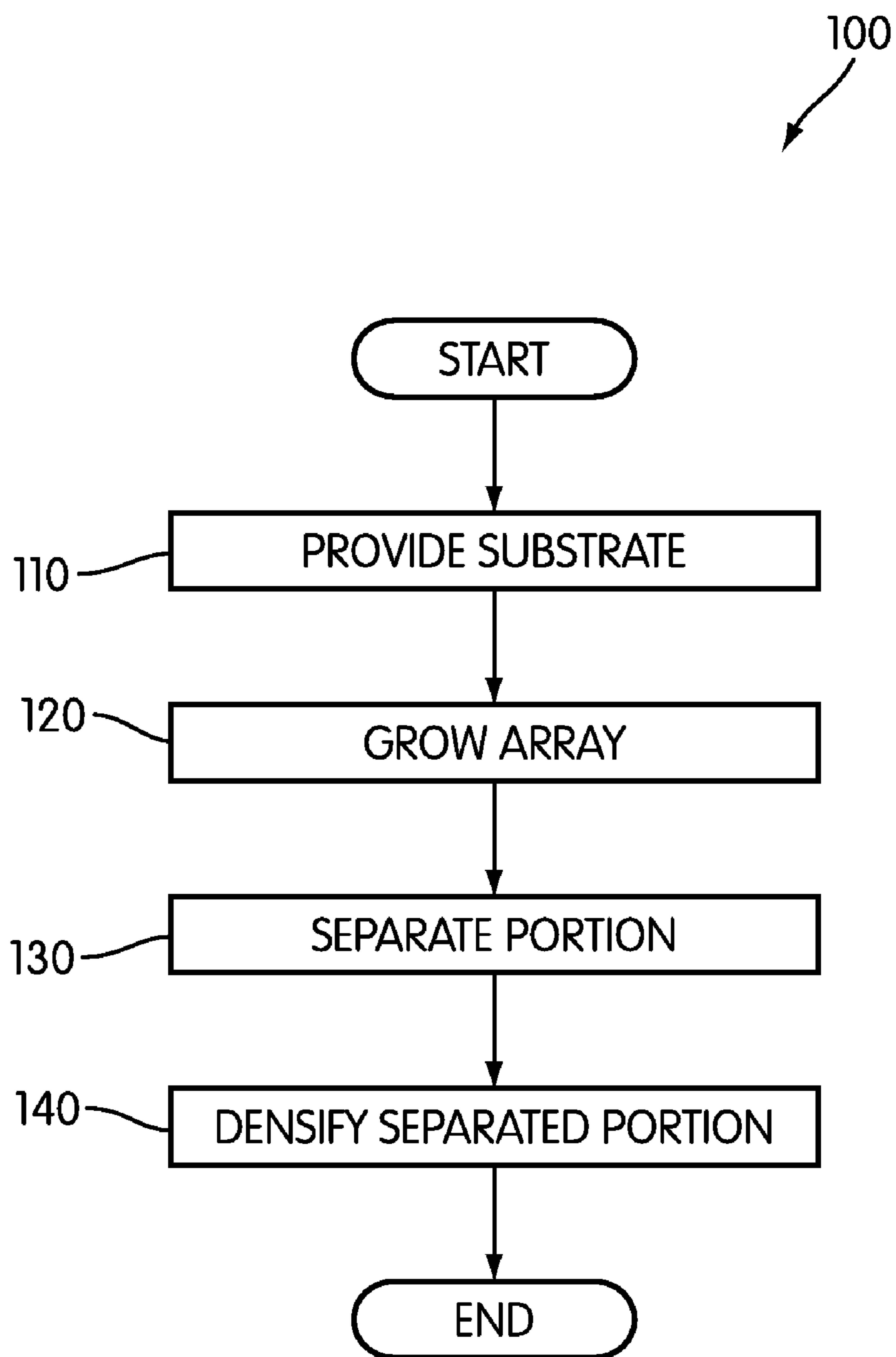


FIG. 1

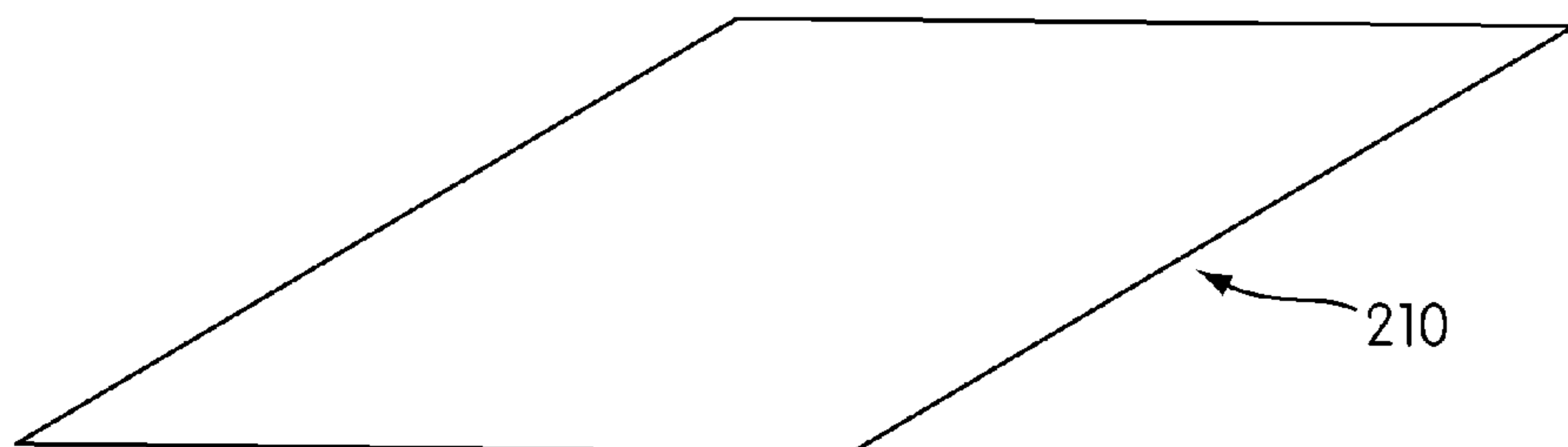


FIG. 2A

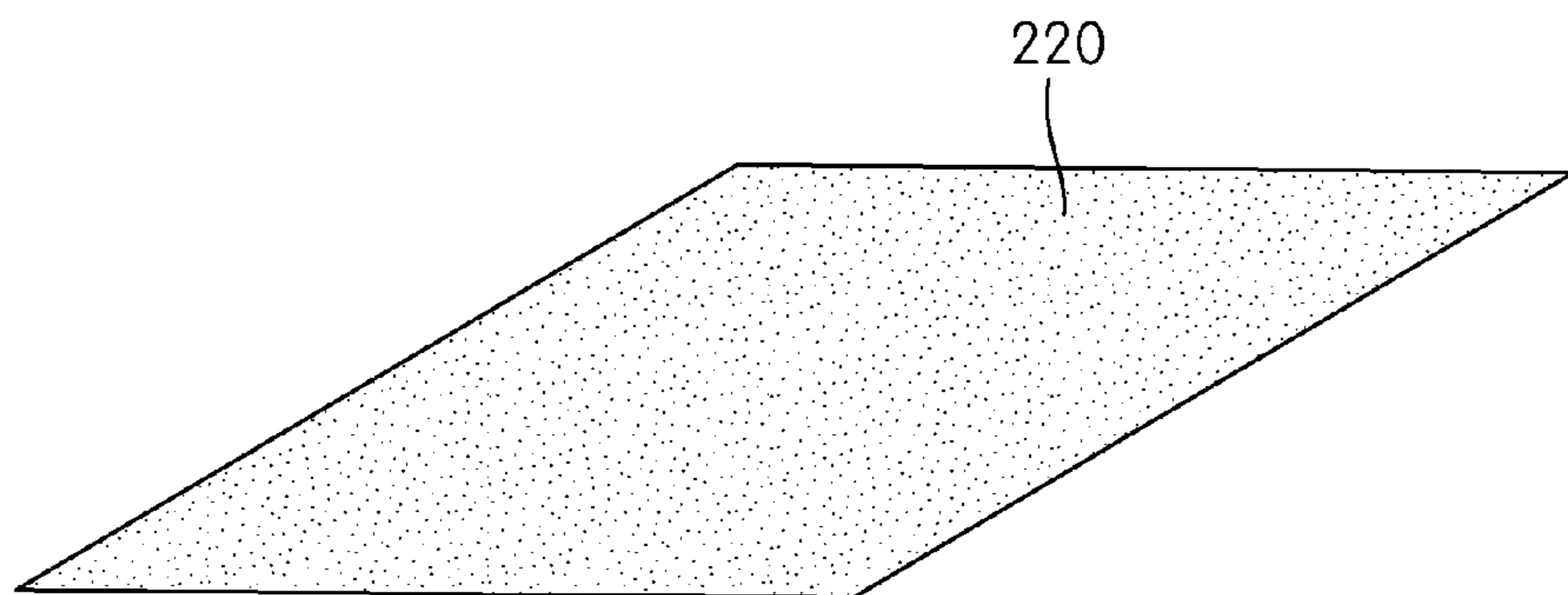


FIG. 2B

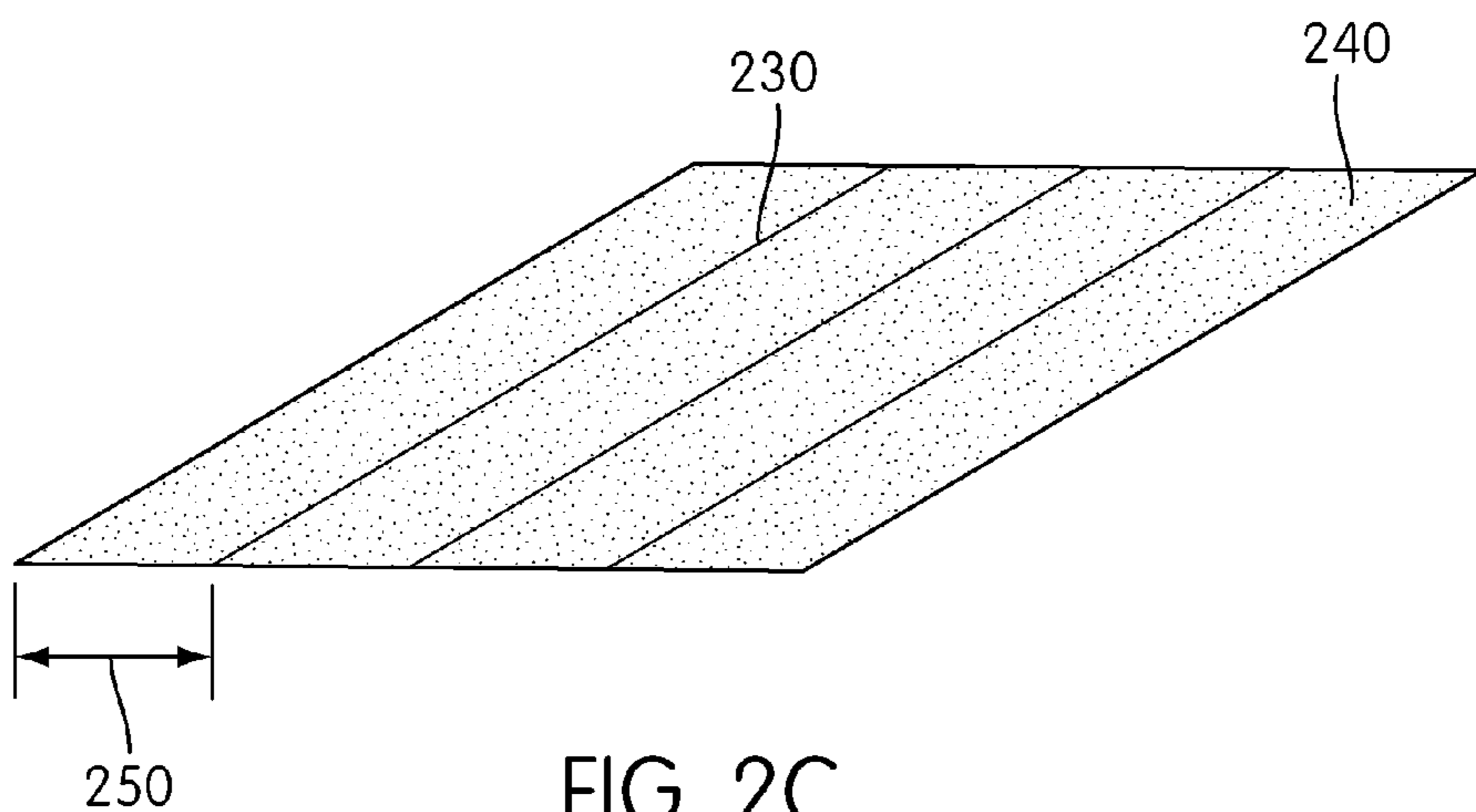


FIG. 2C

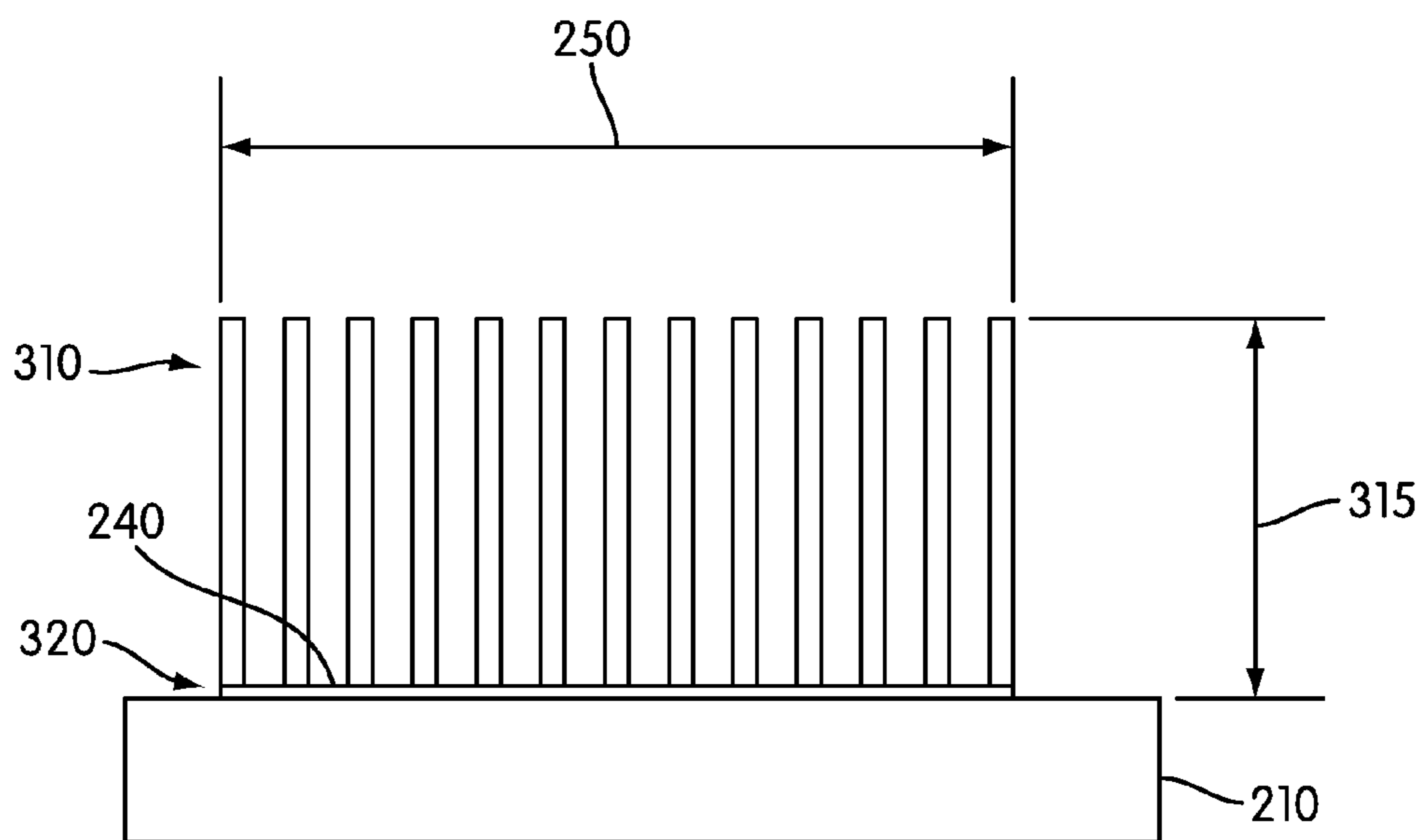


FIG. 3

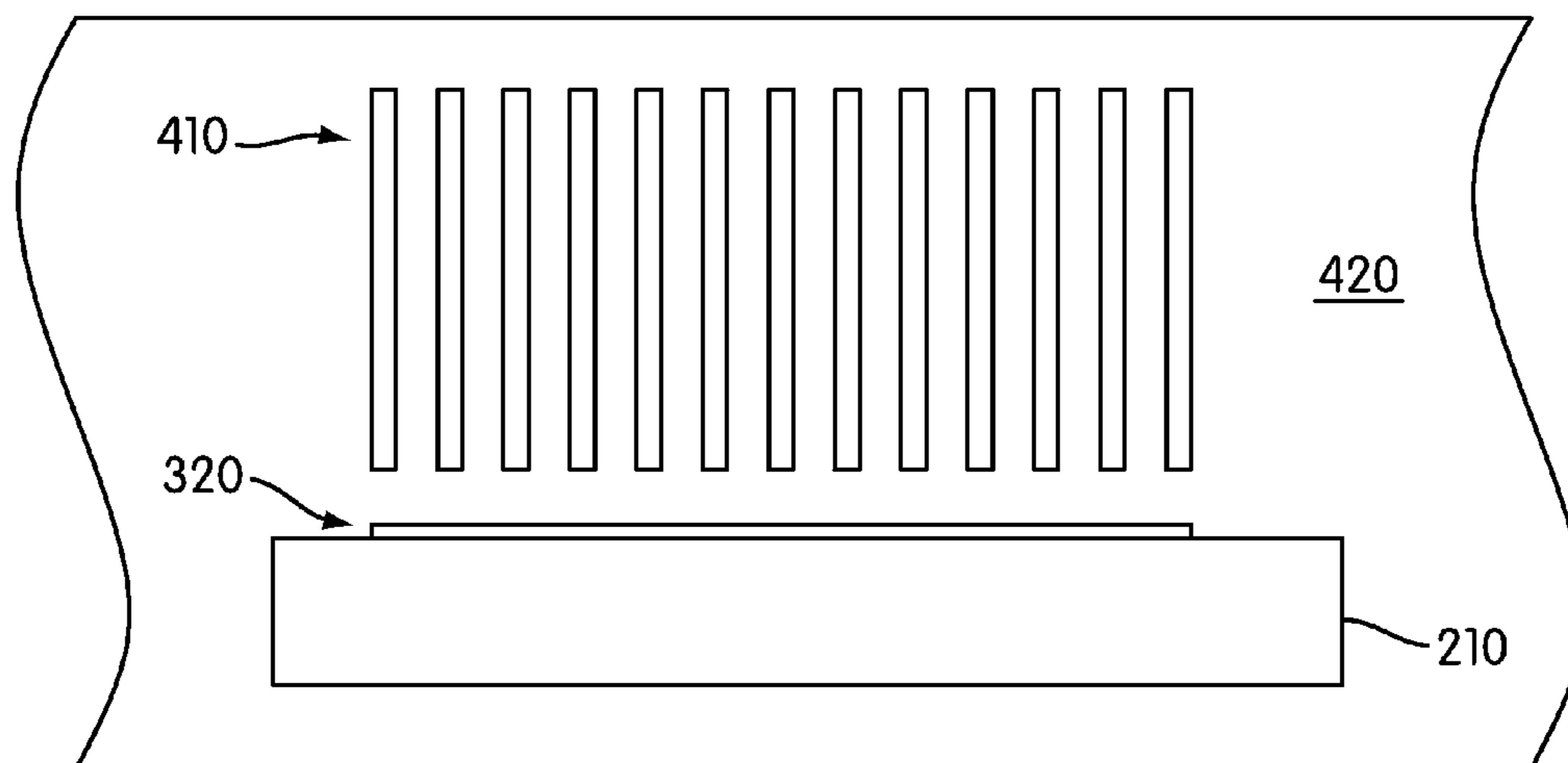


FIG. 4A

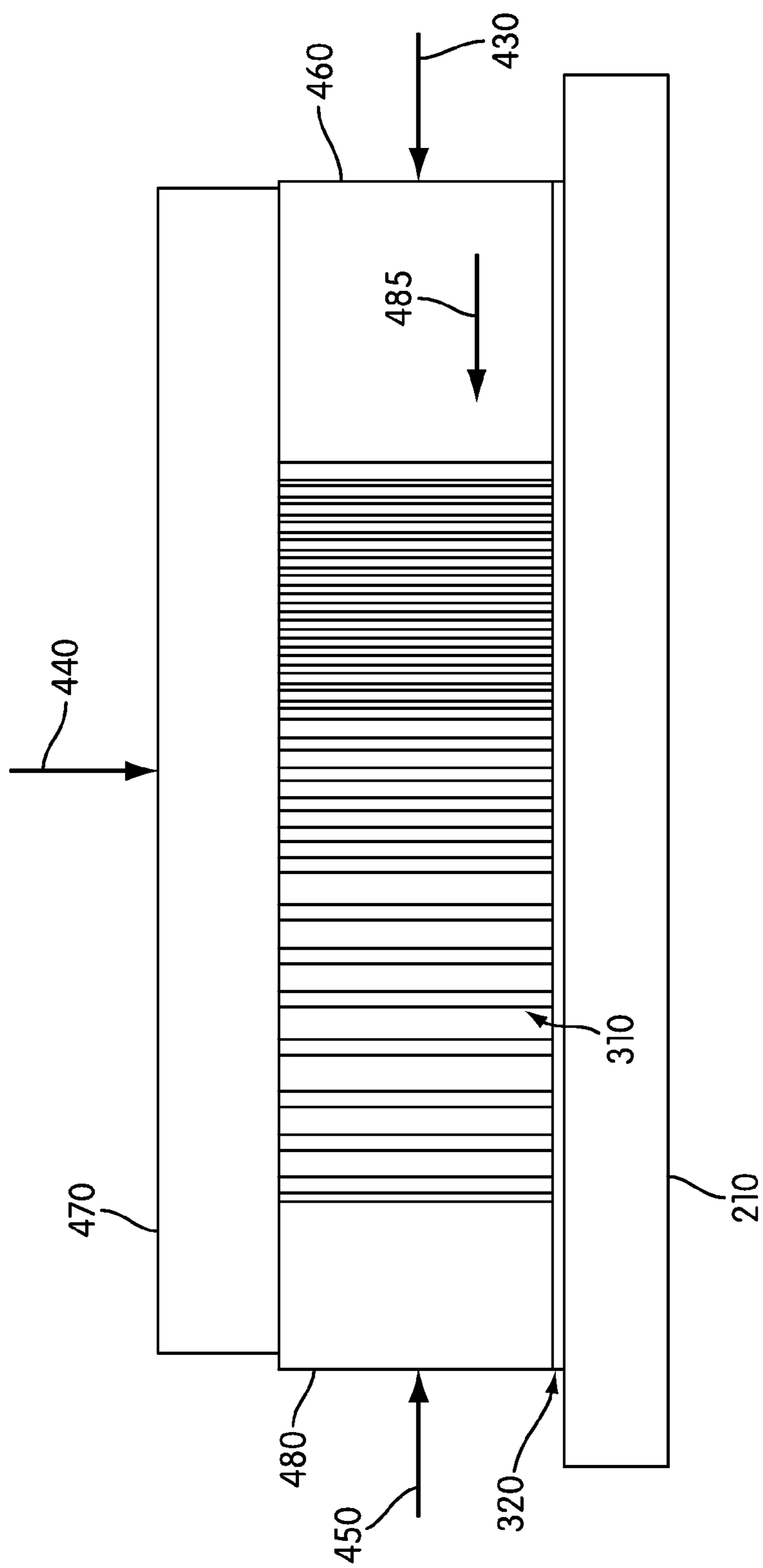
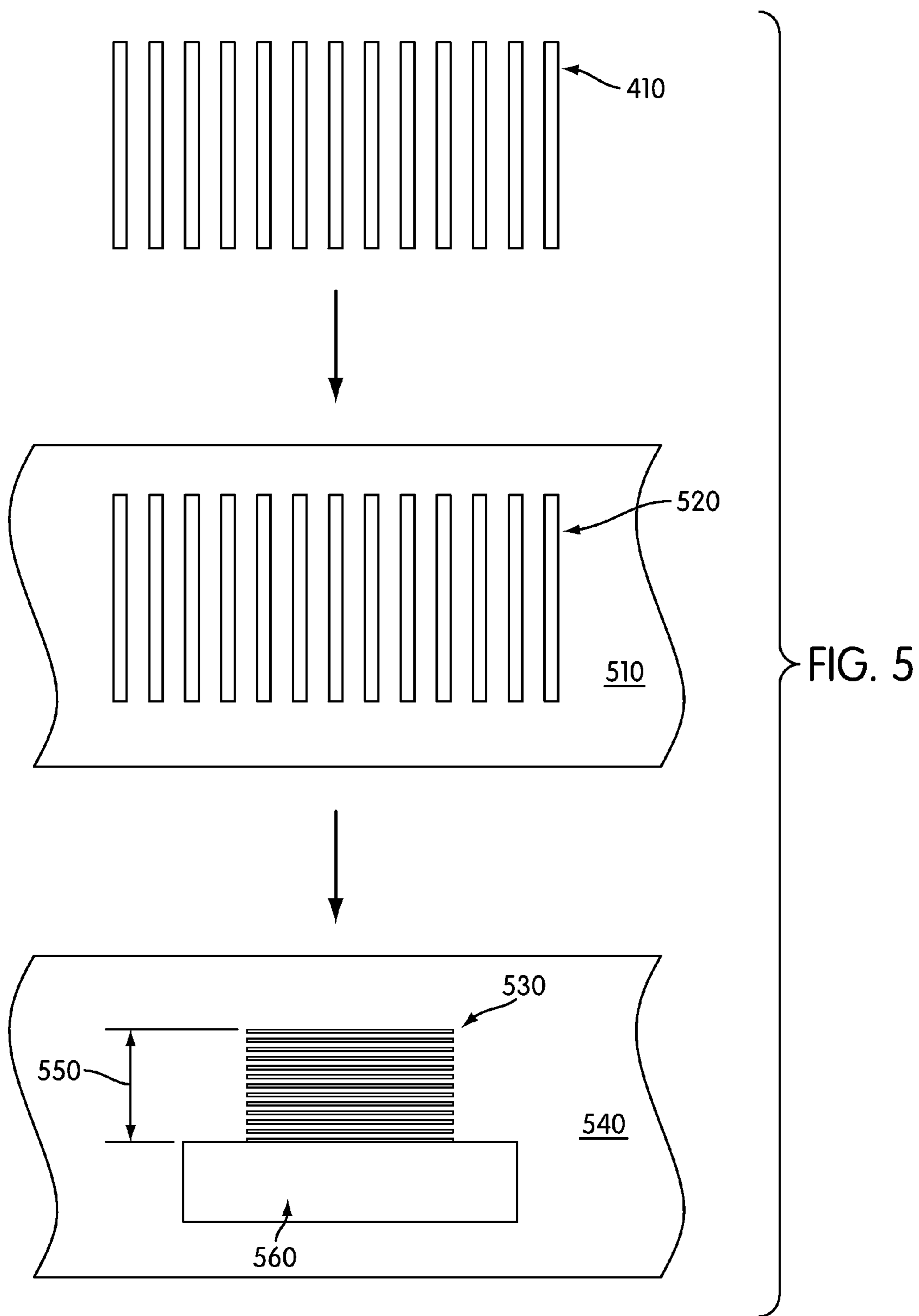
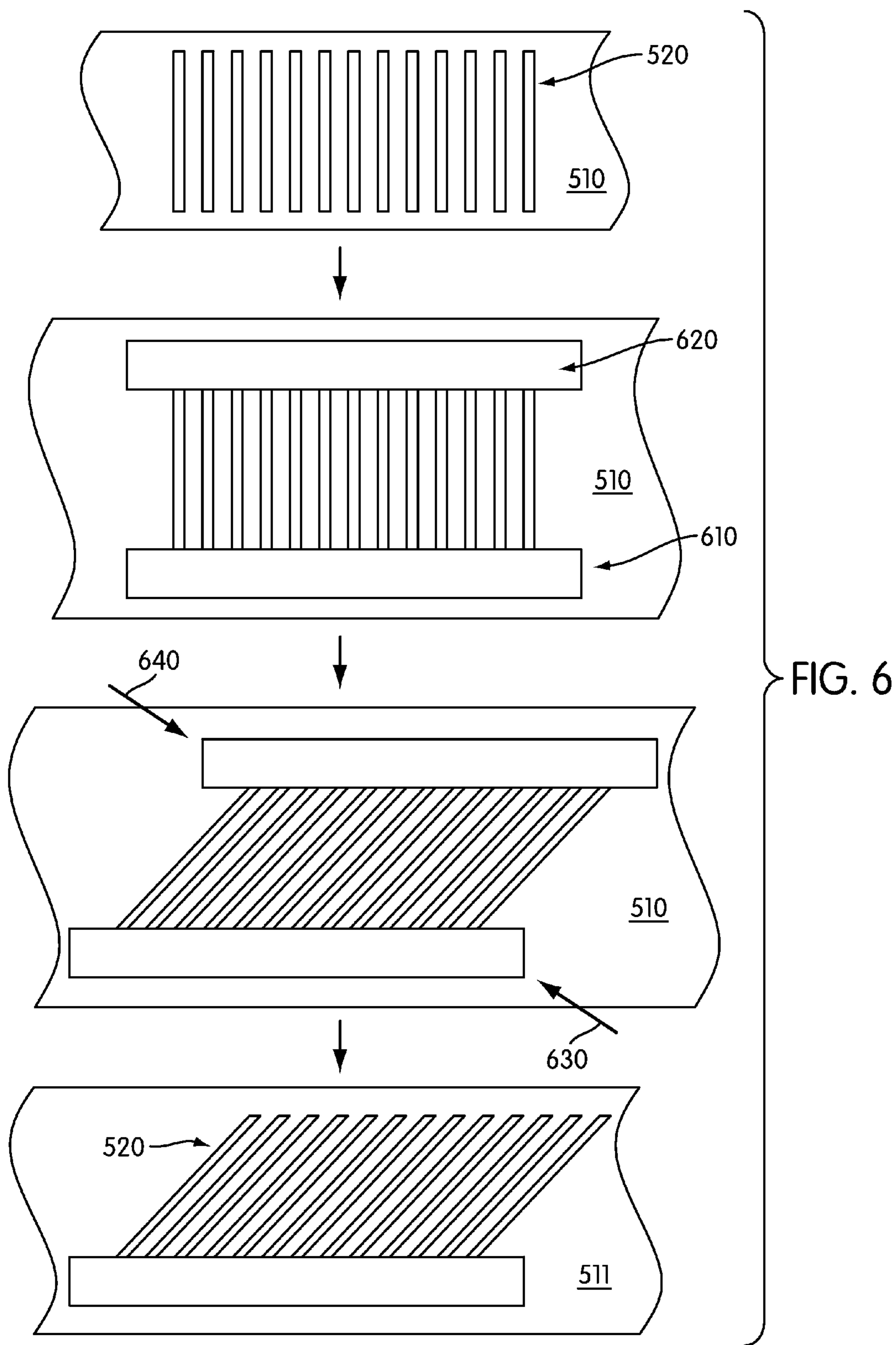


FIG. 4B





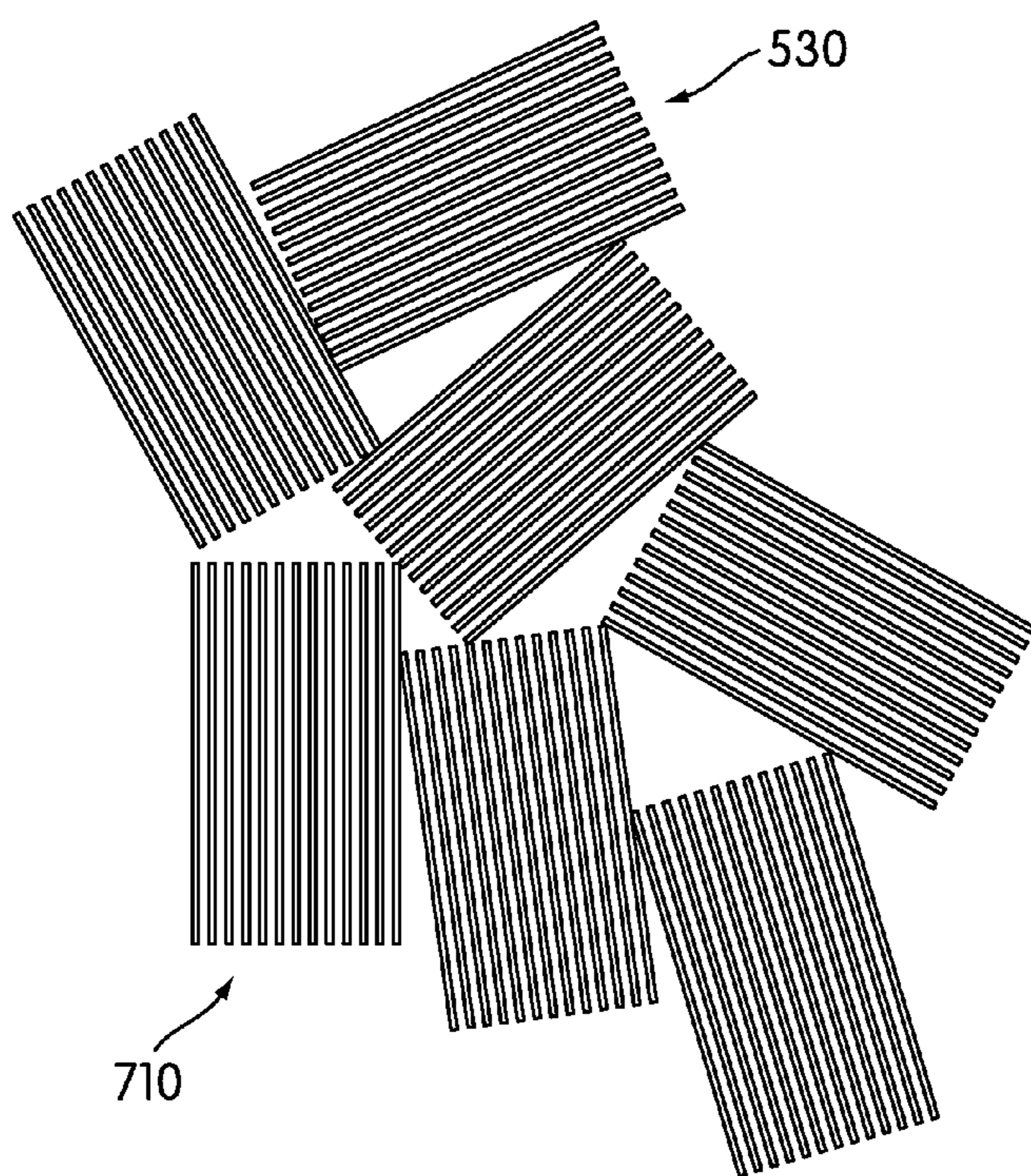


FIG. 7A

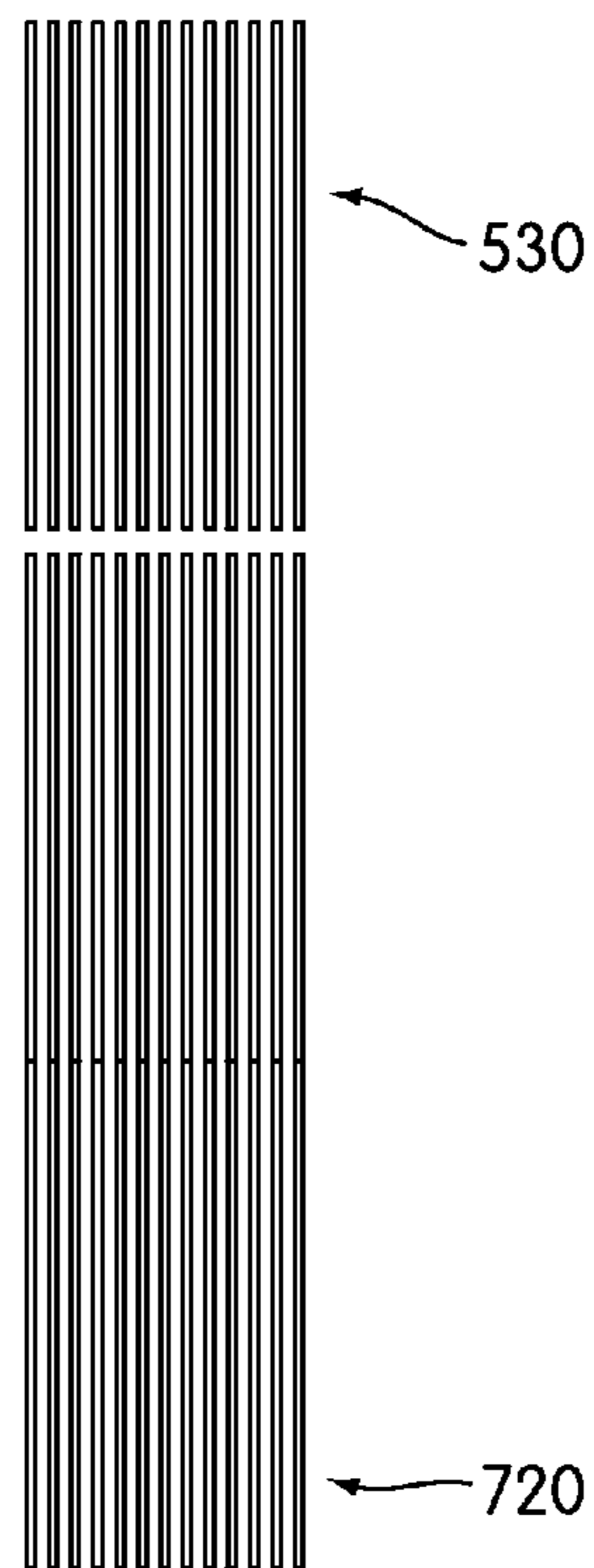


FIG. 7B

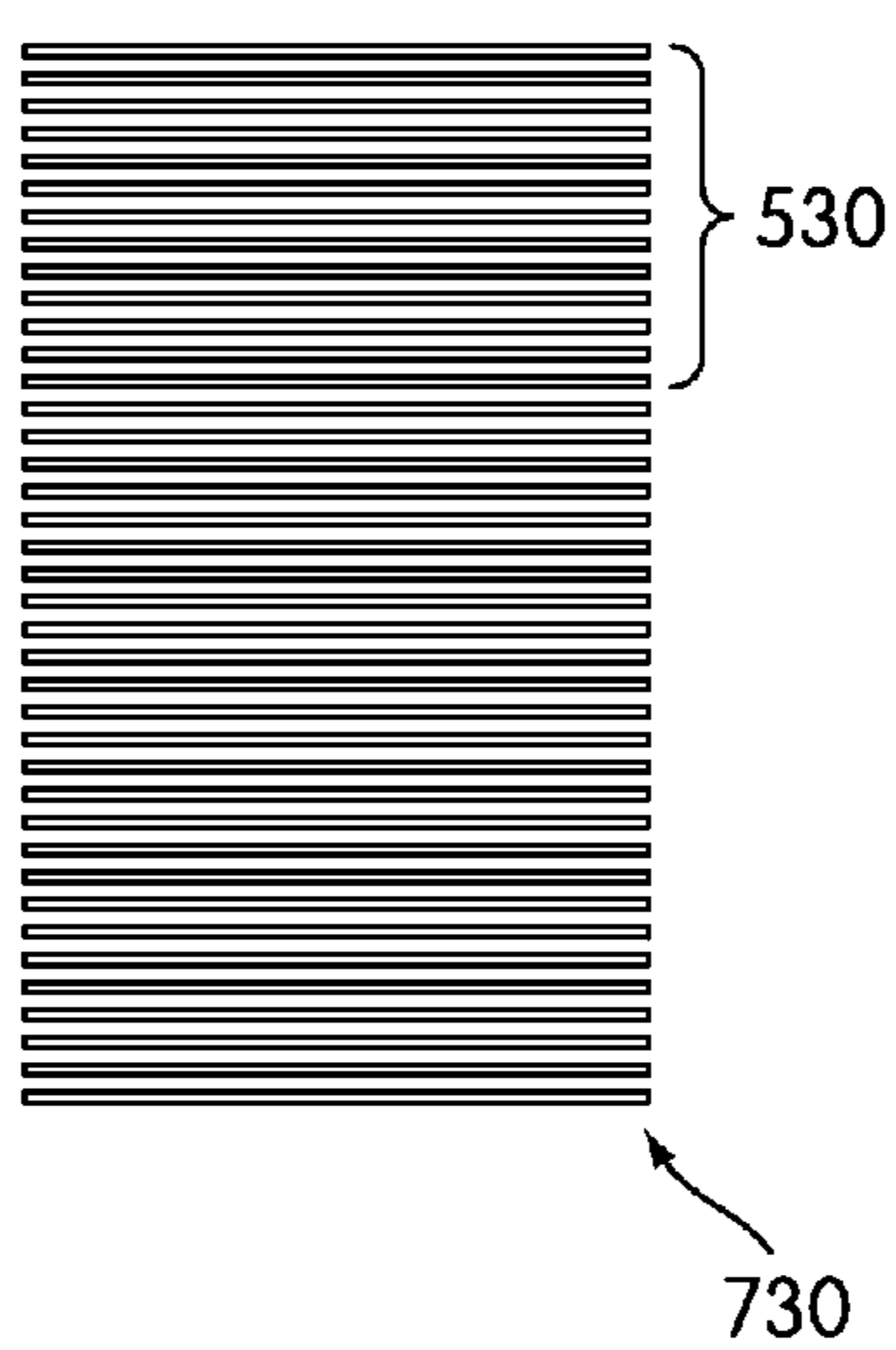


FIG. 7C

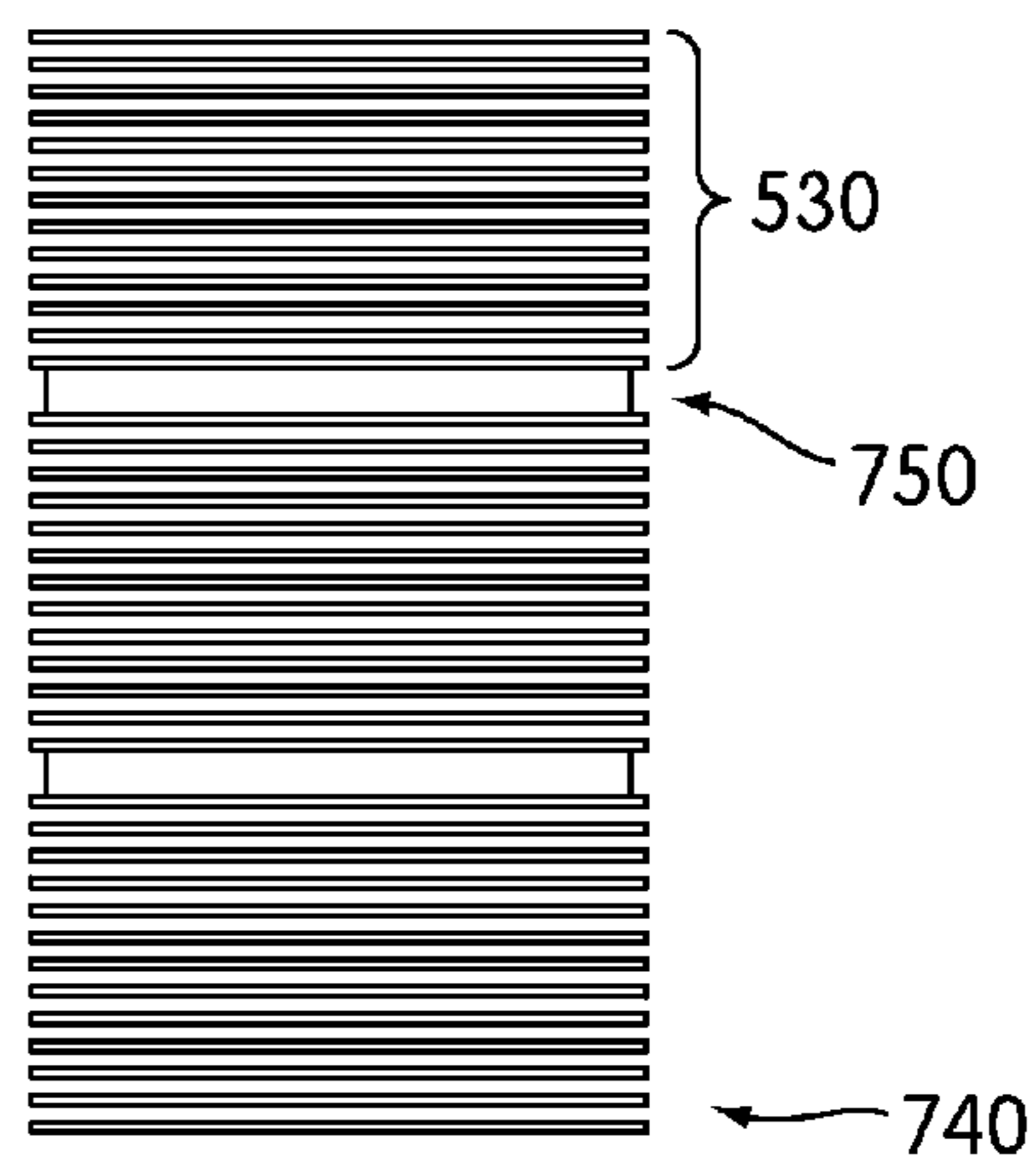


FIG. 7D

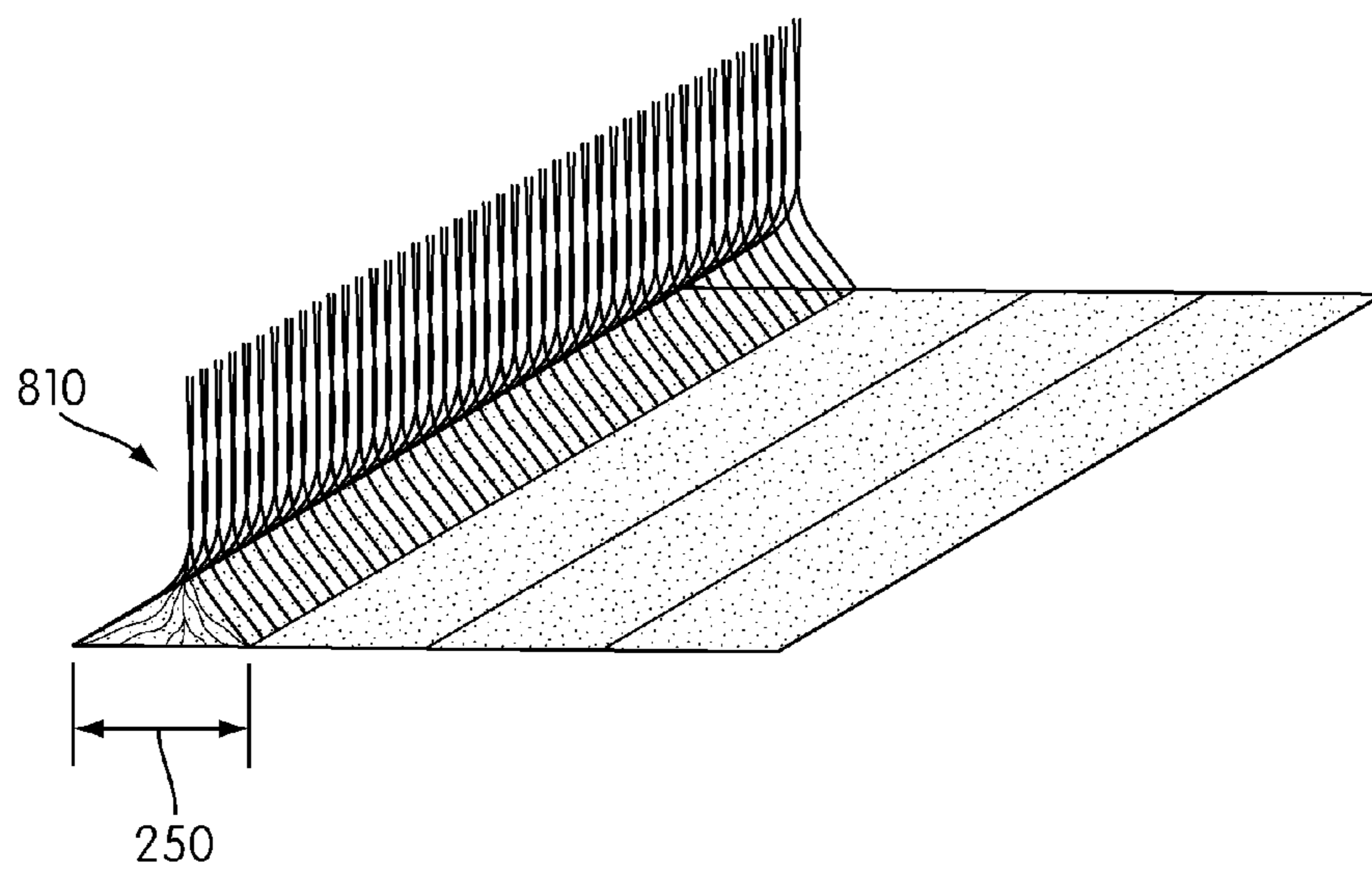


FIG. 8A

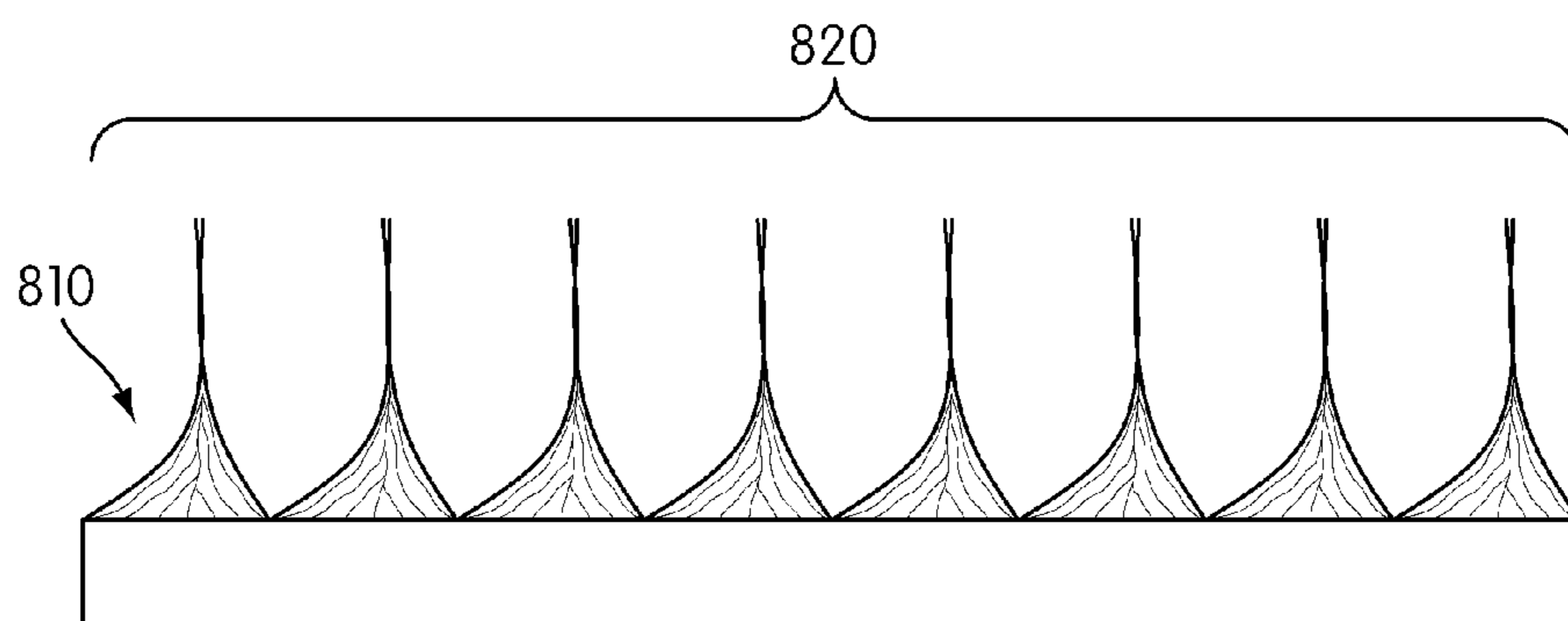


FIG. 8B

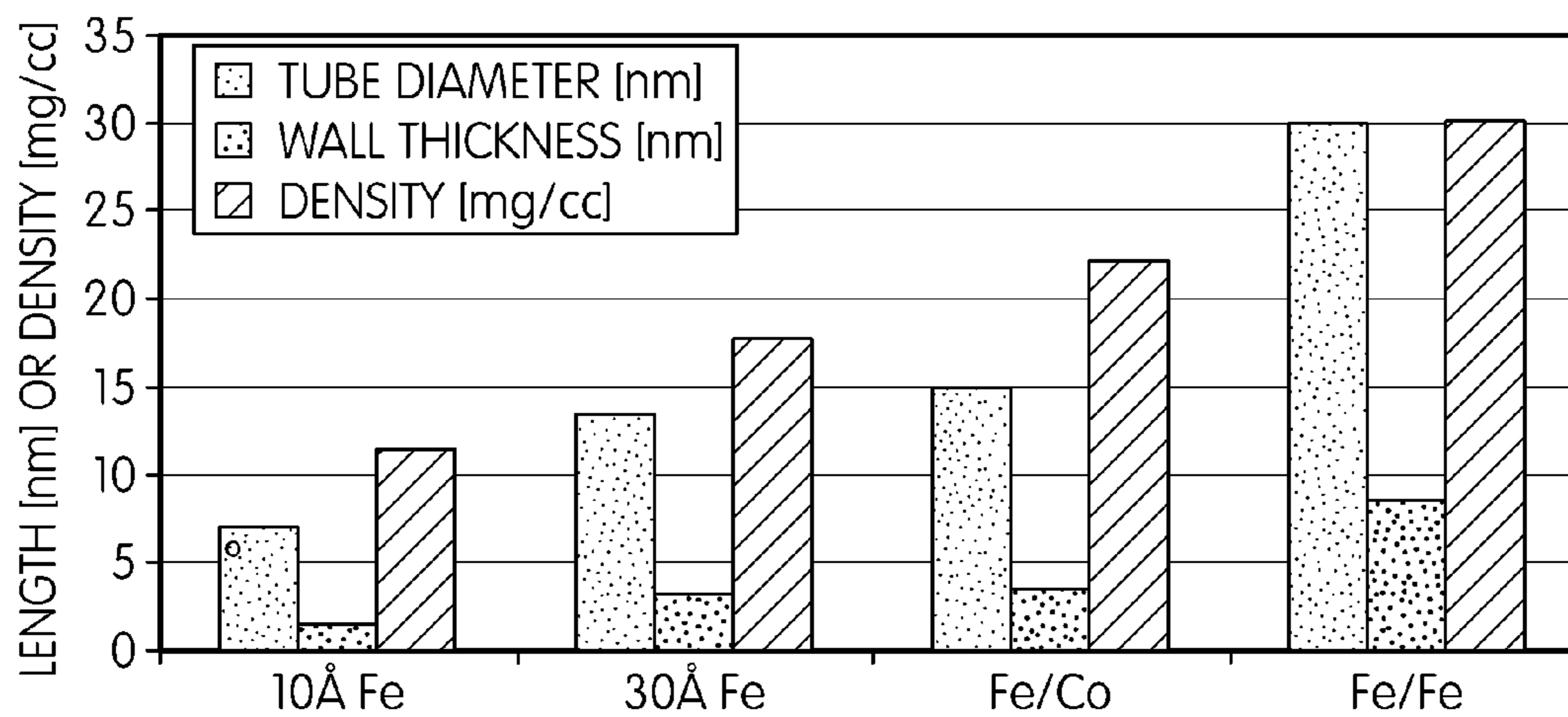


FIG. 9

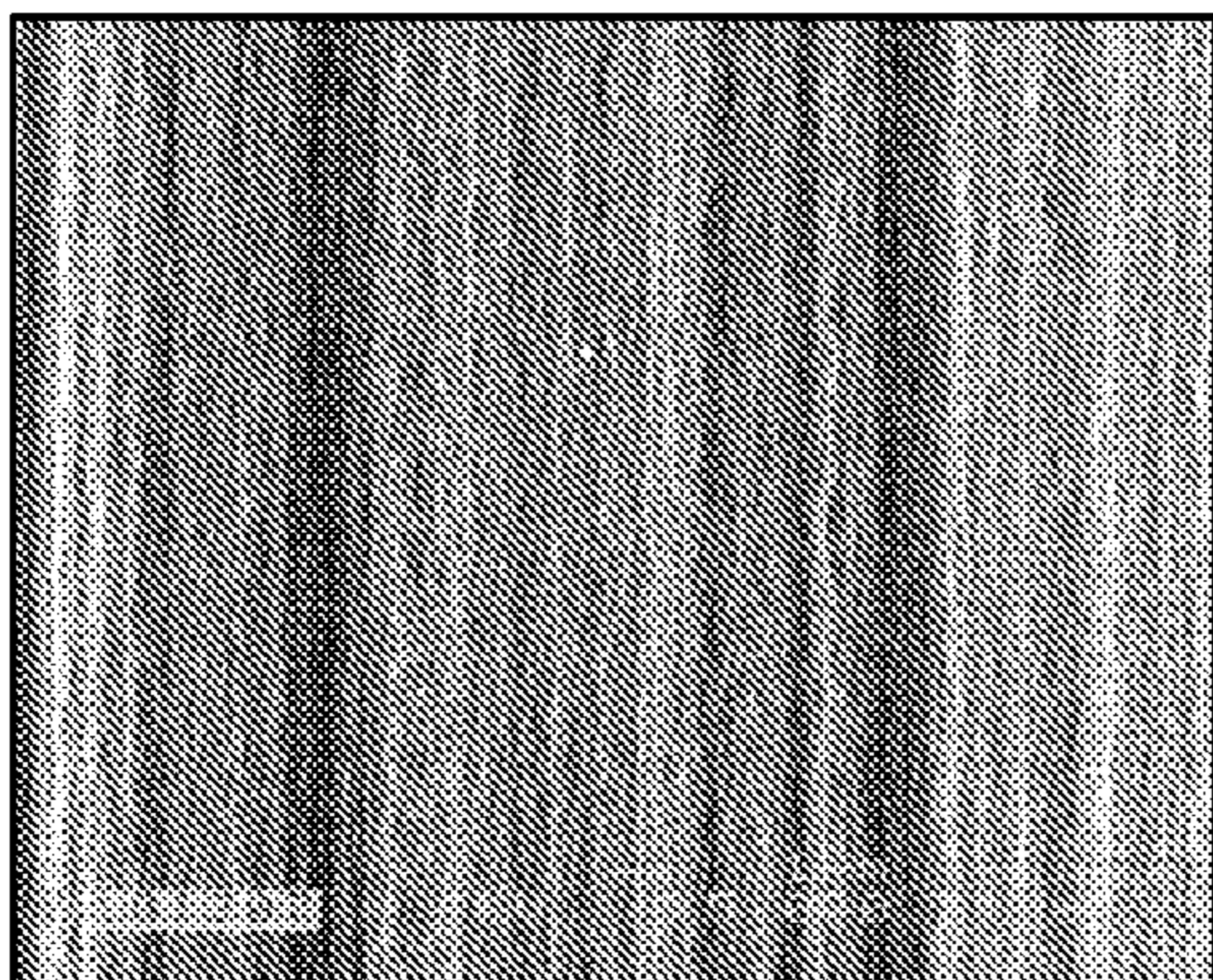


FIG. 10A

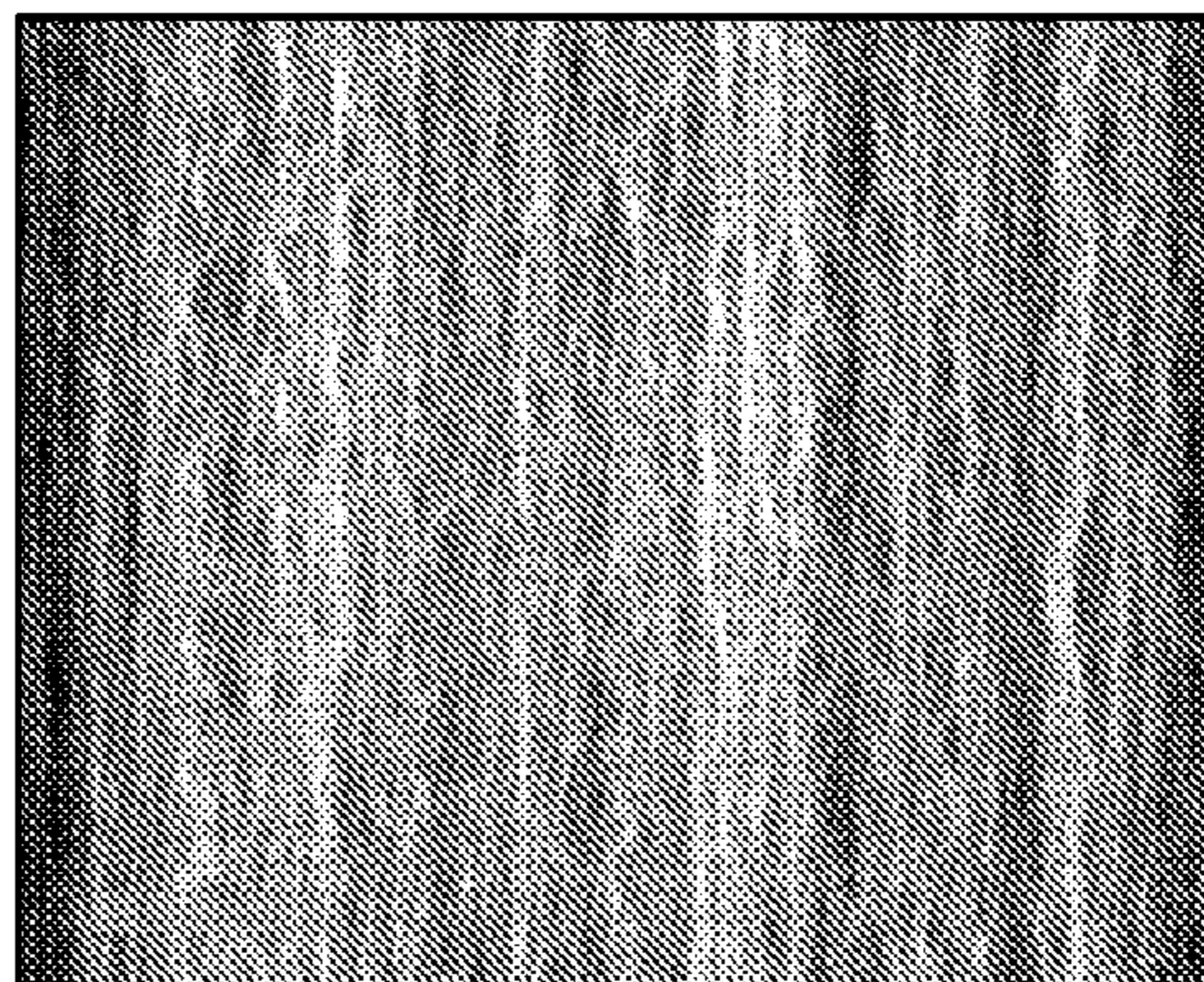


FIG. 10B

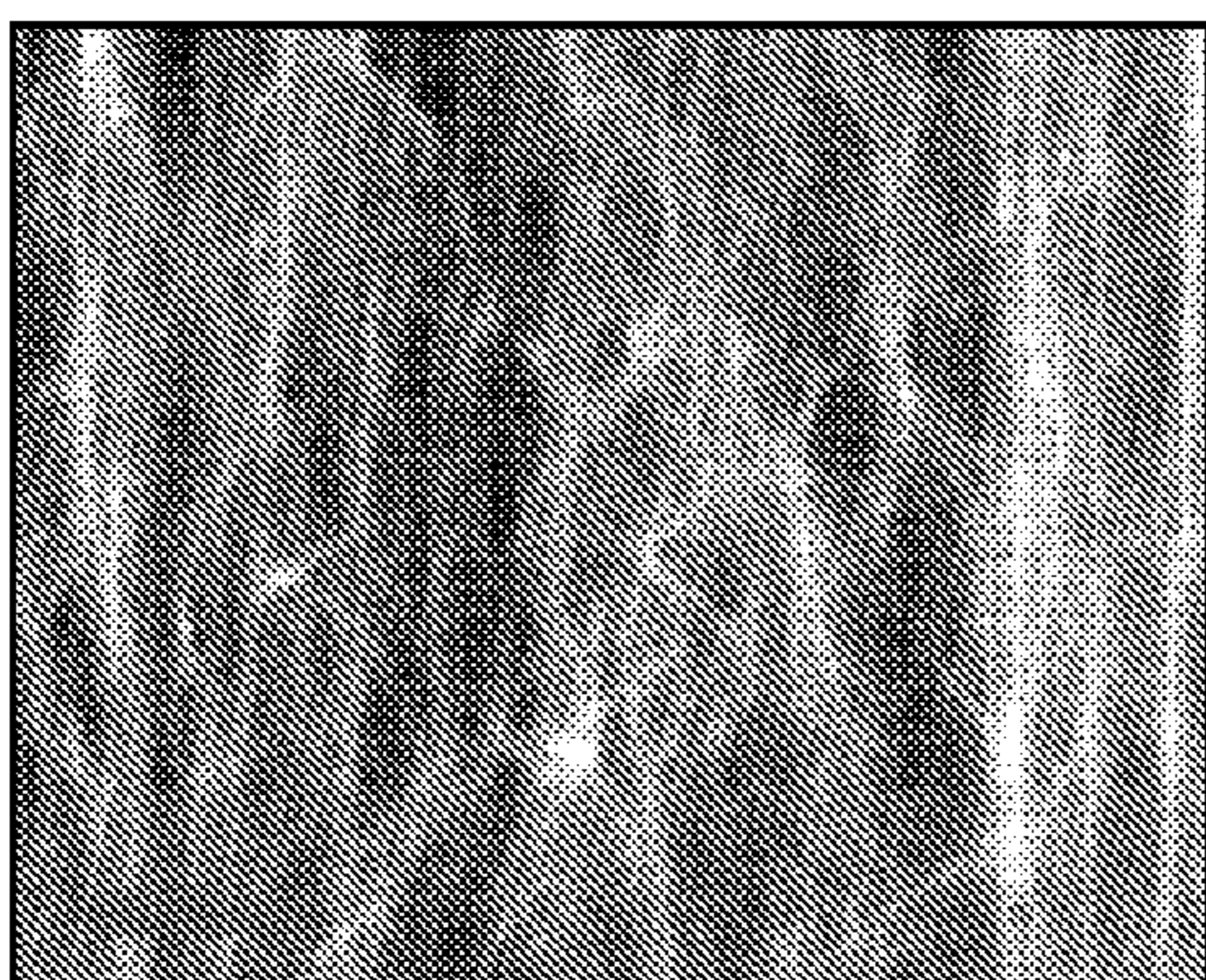


FIG. 10C

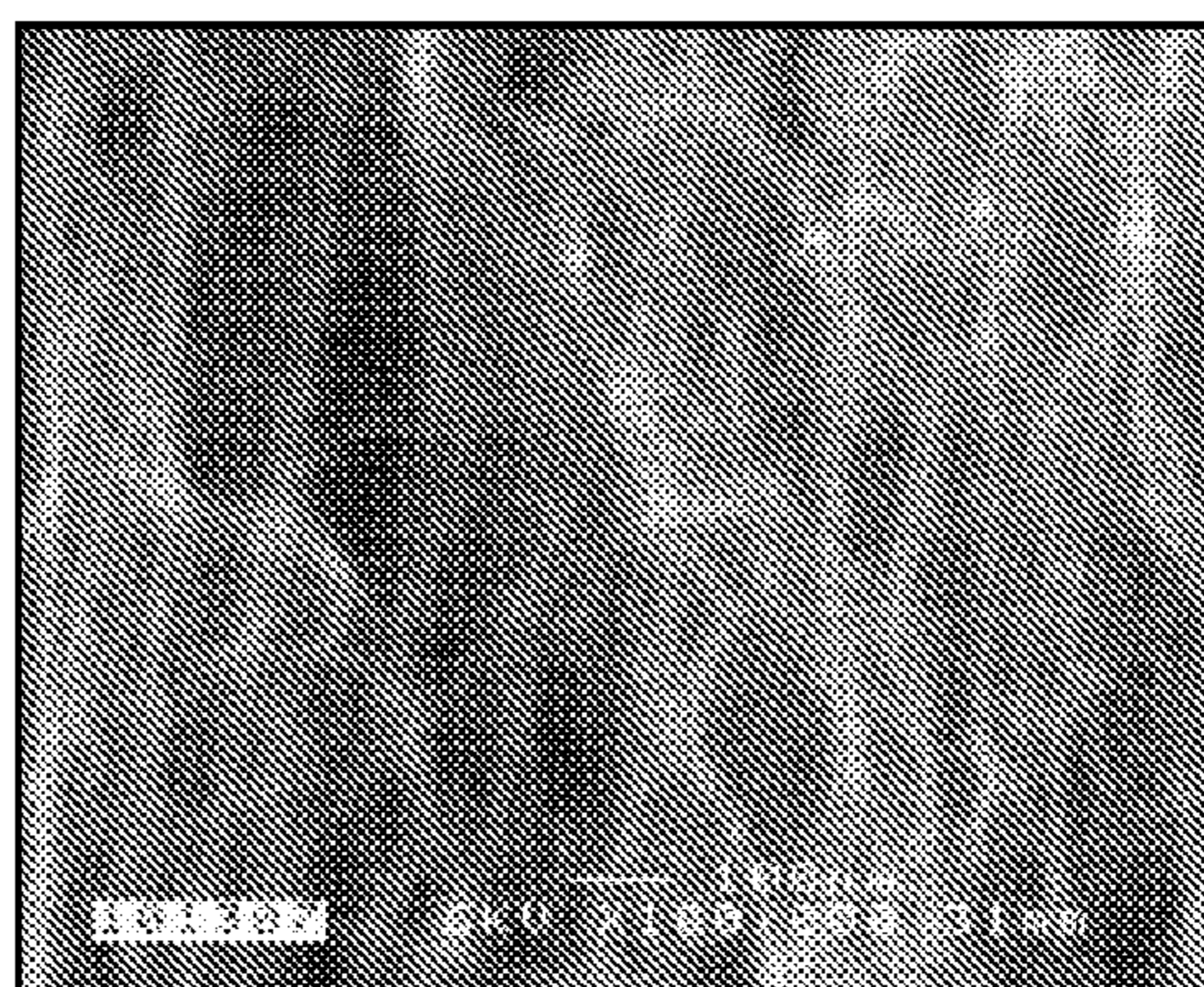


FIG. 10D

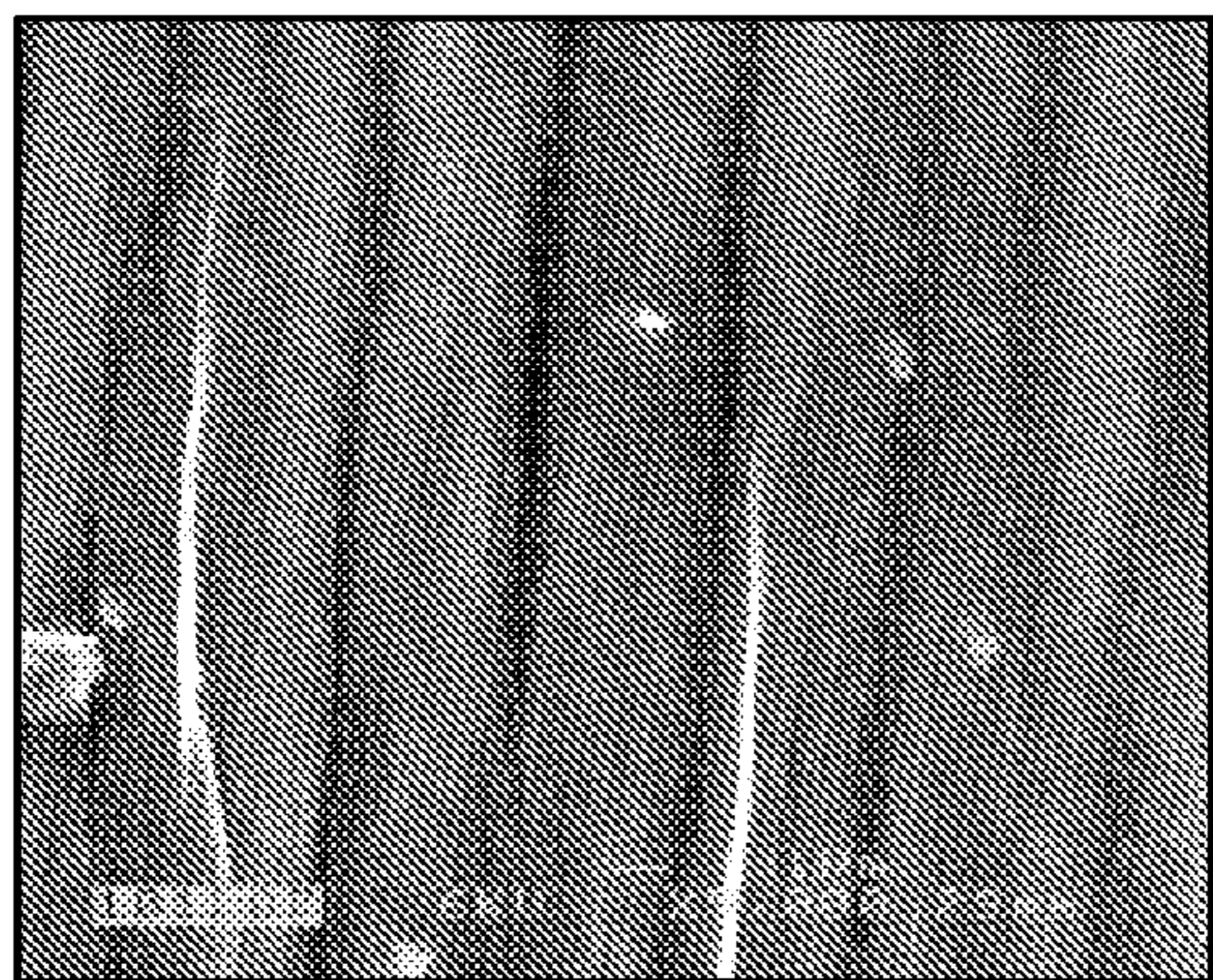


FIG. 11A

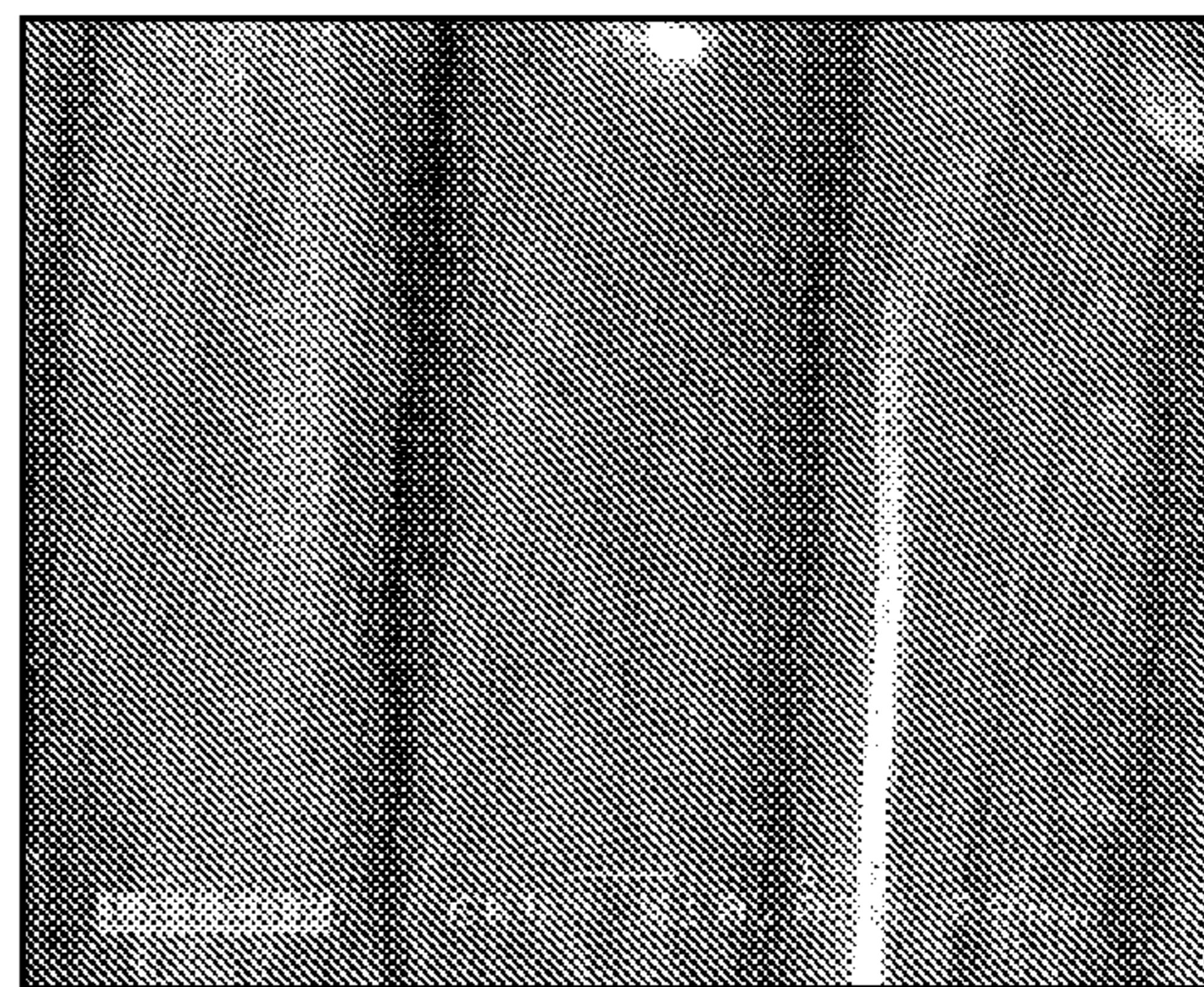


FIG. 11B

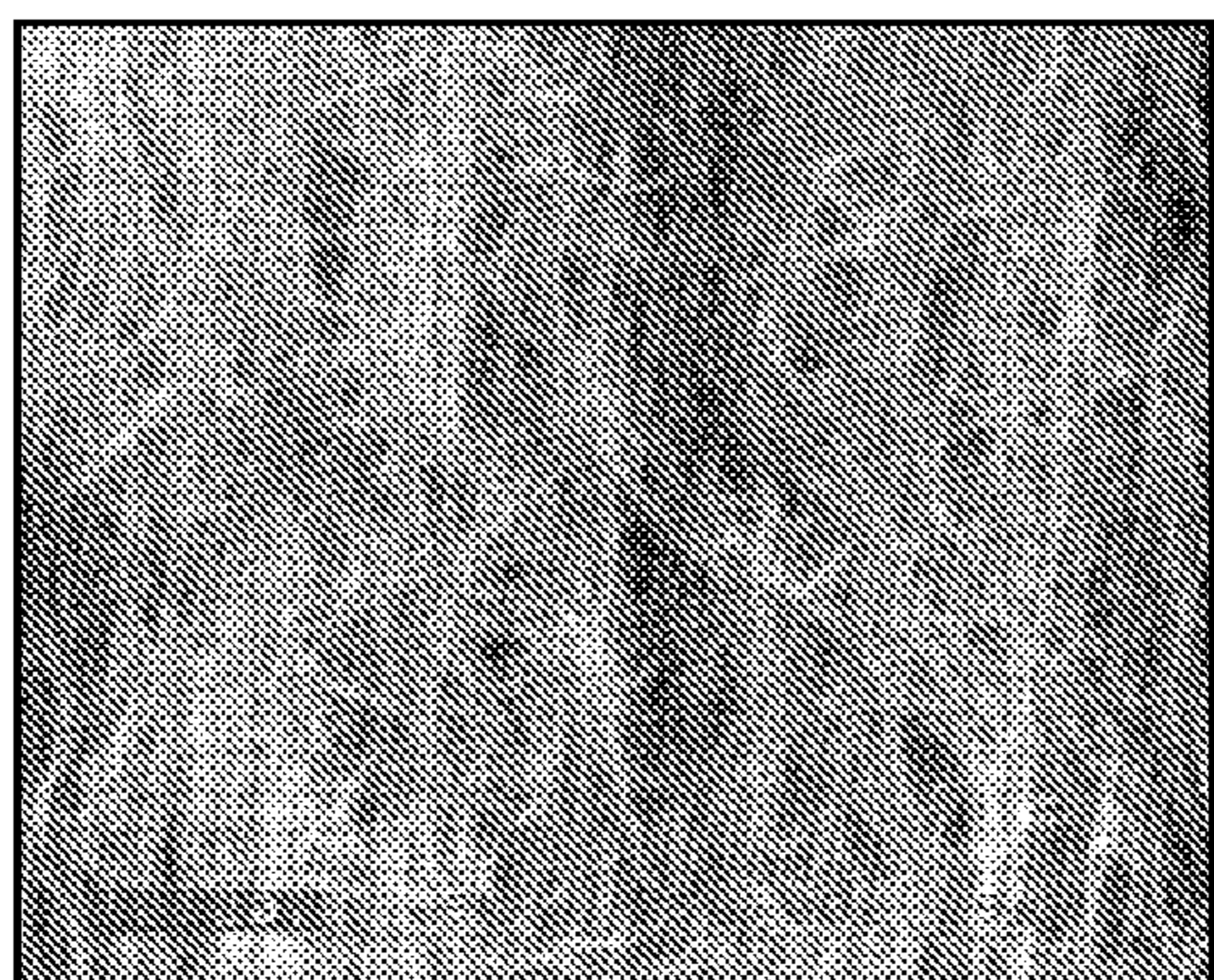


FIG. 11C

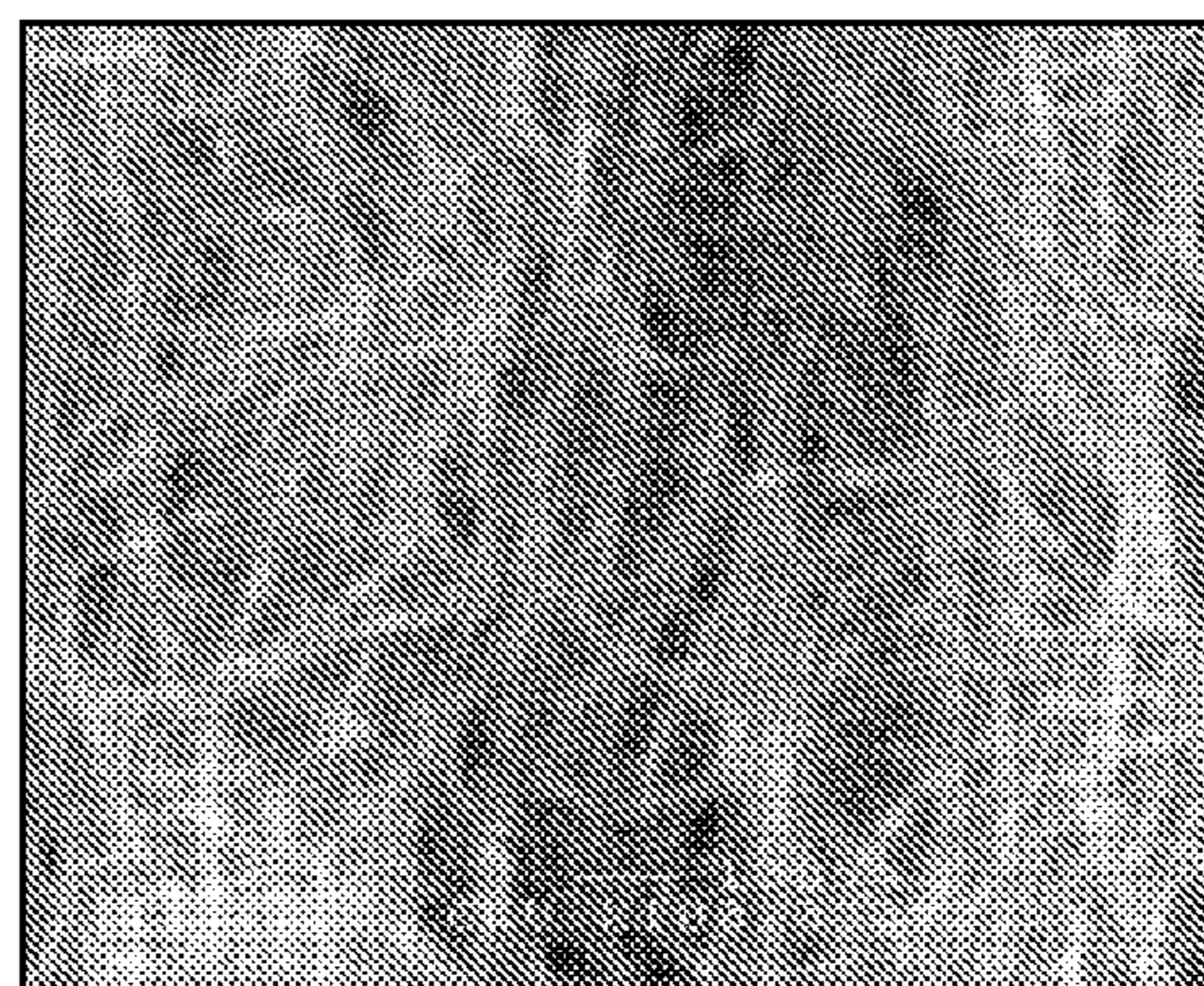


FIG. 11D

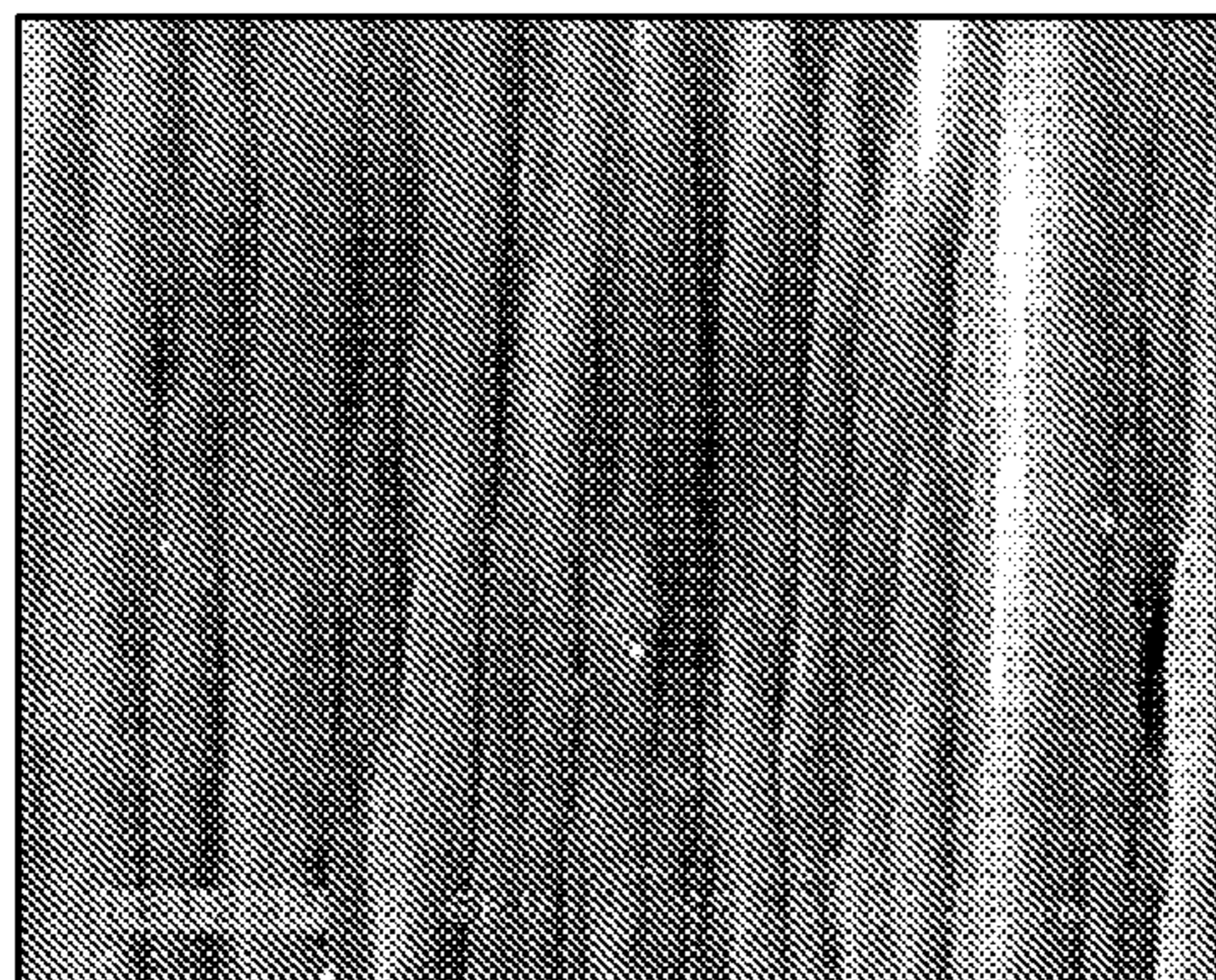


FIG. 12A

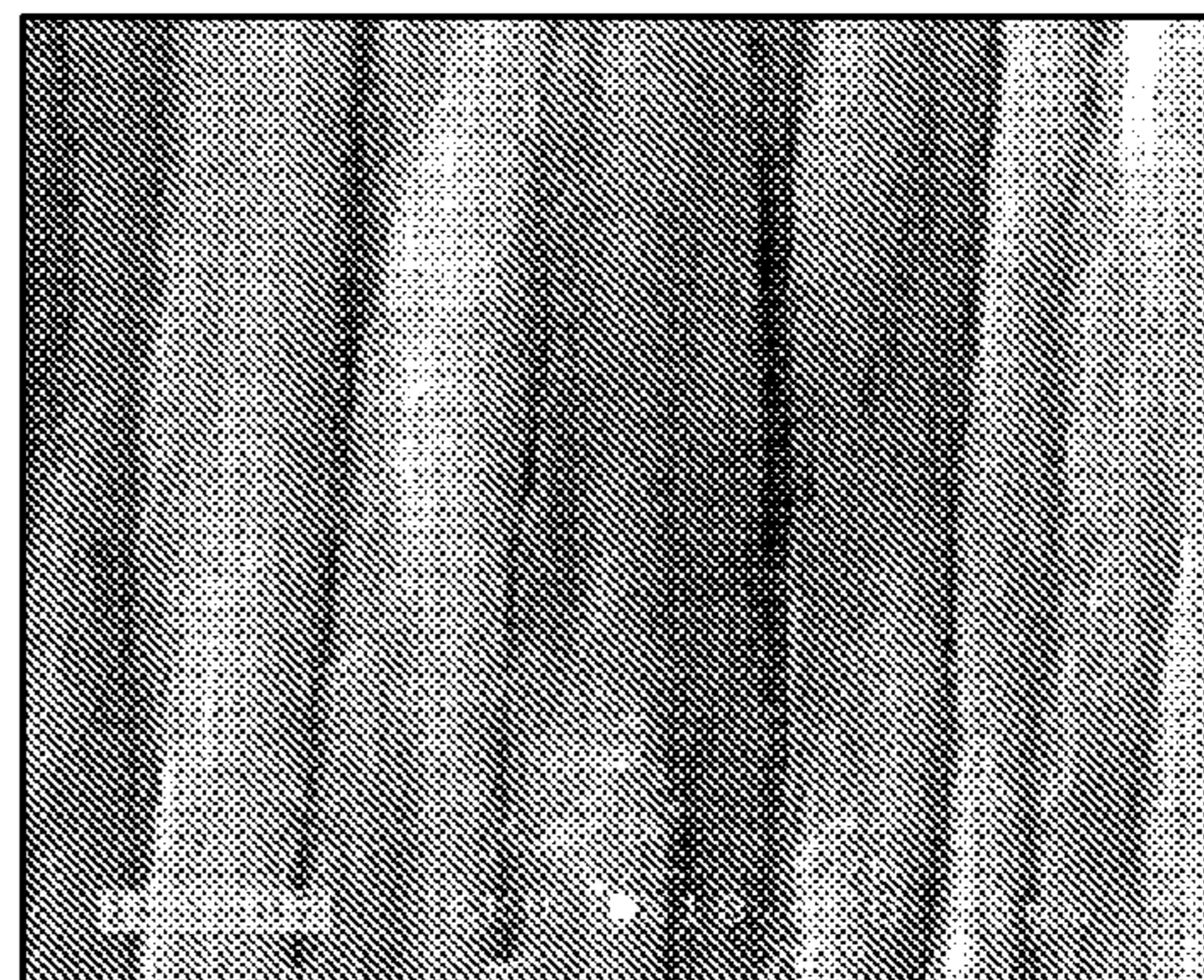


FIG. 12B

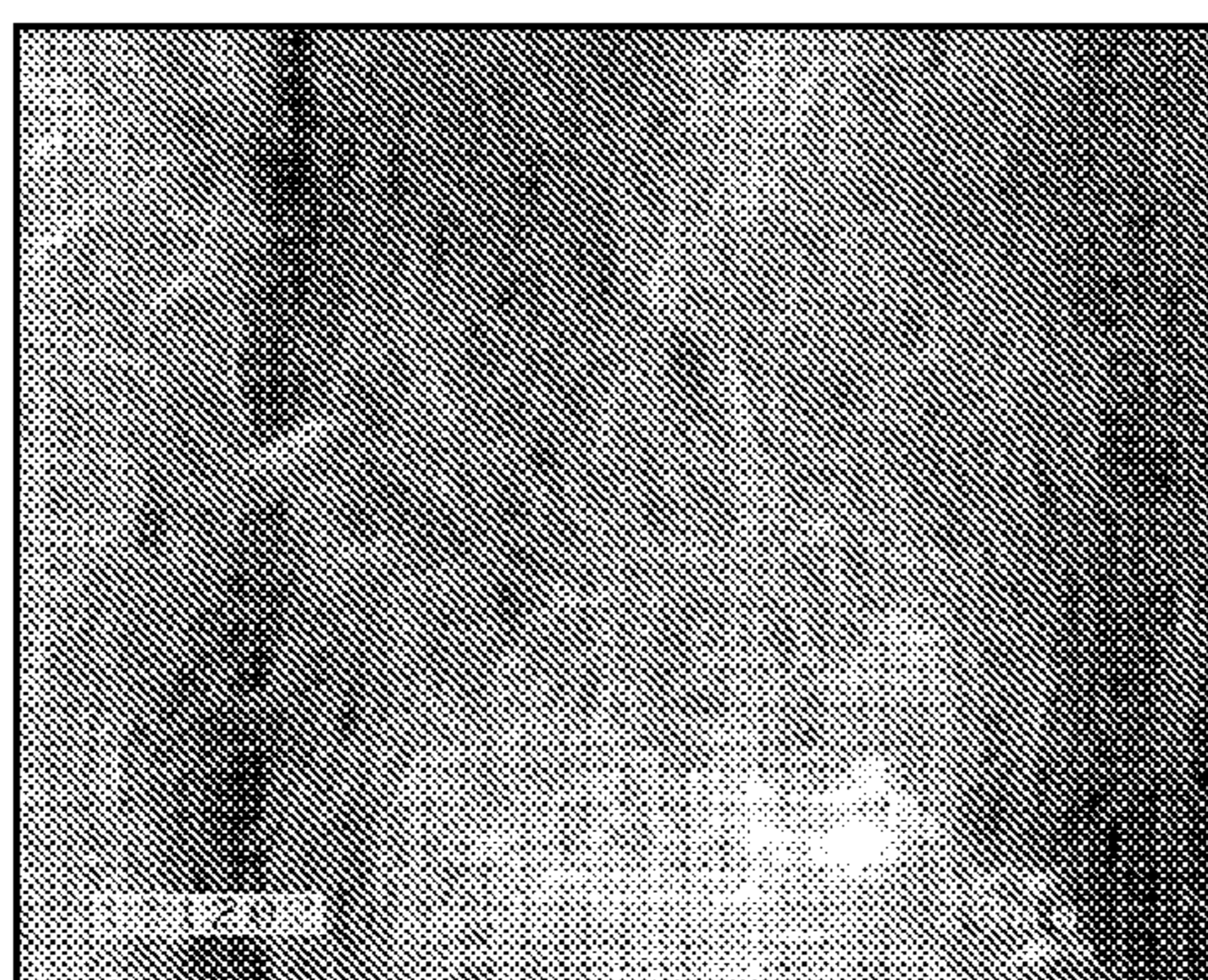


FIG. 12C

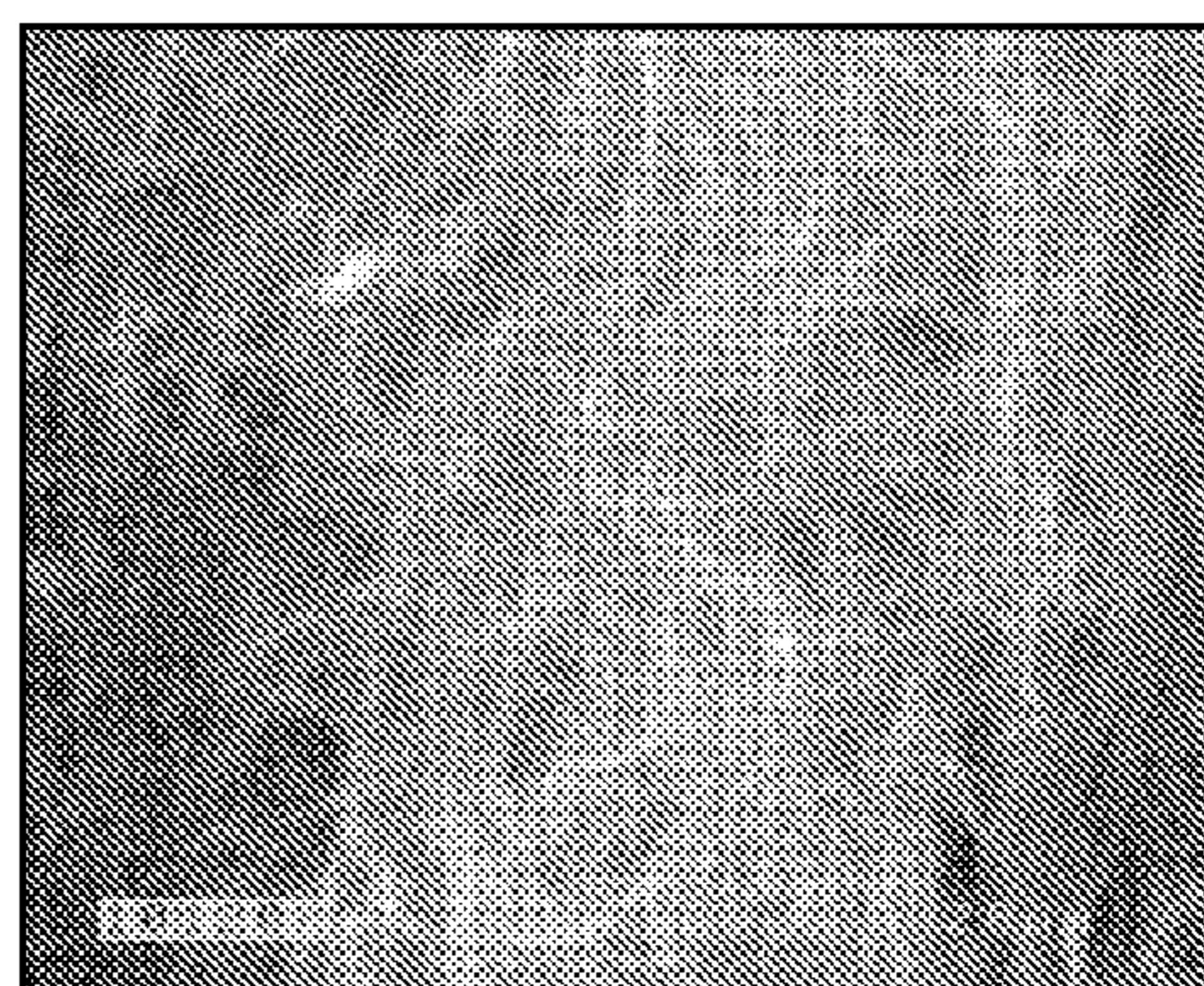


FIG. 12D

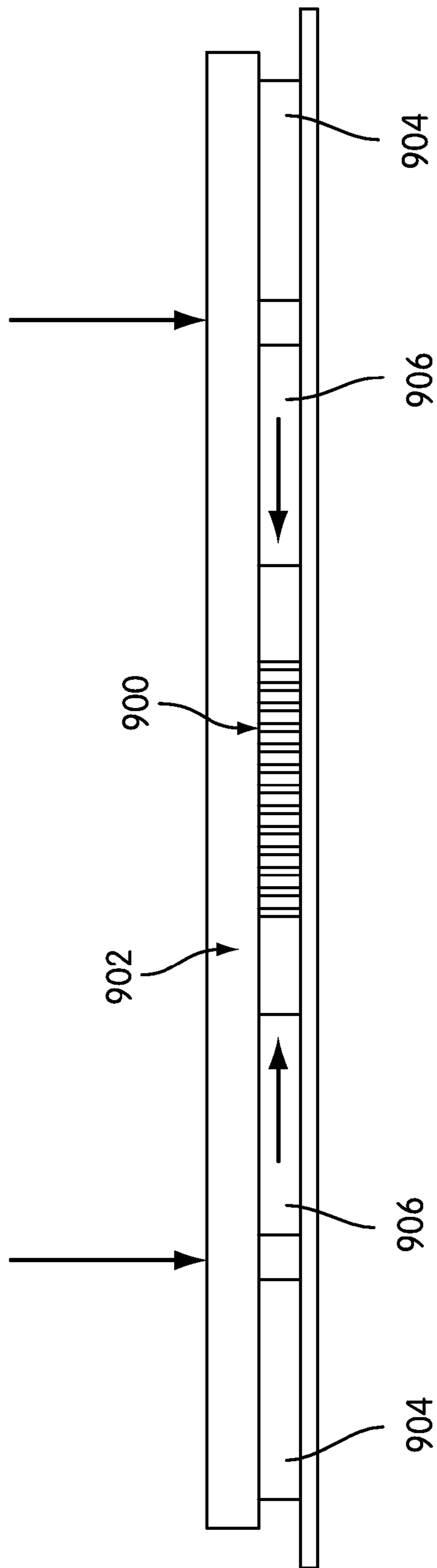


FIG. 13

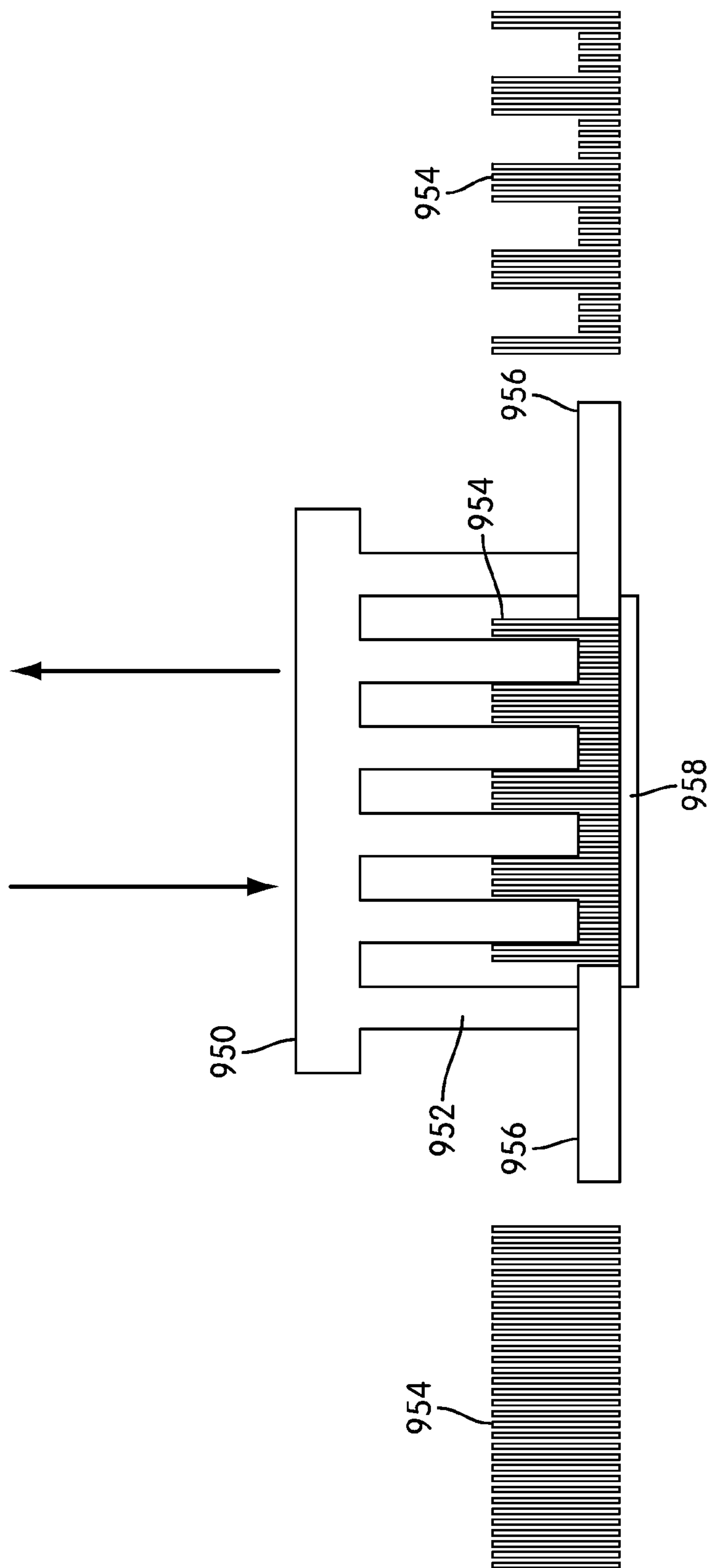


FIG. 14

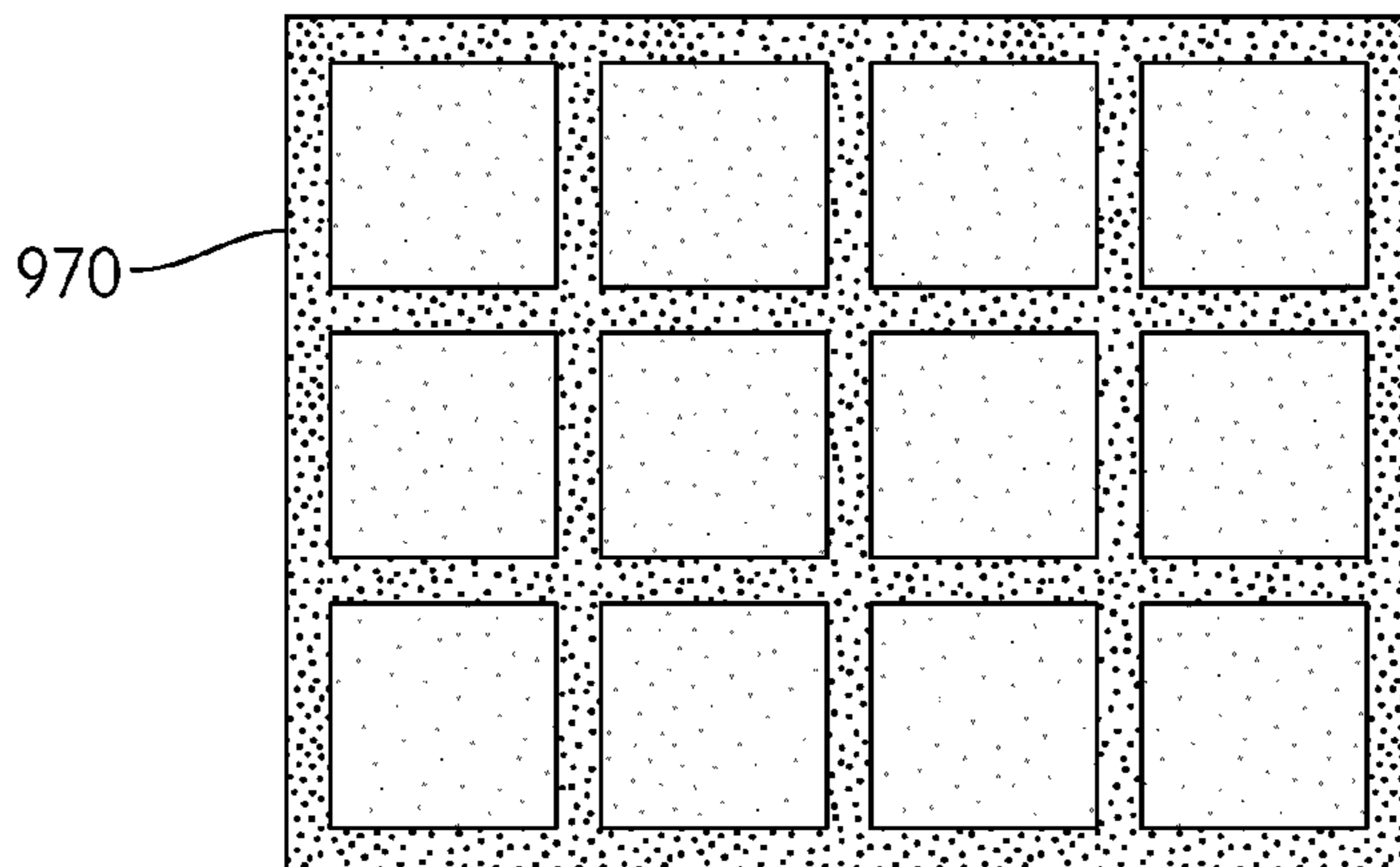


FIG. 15

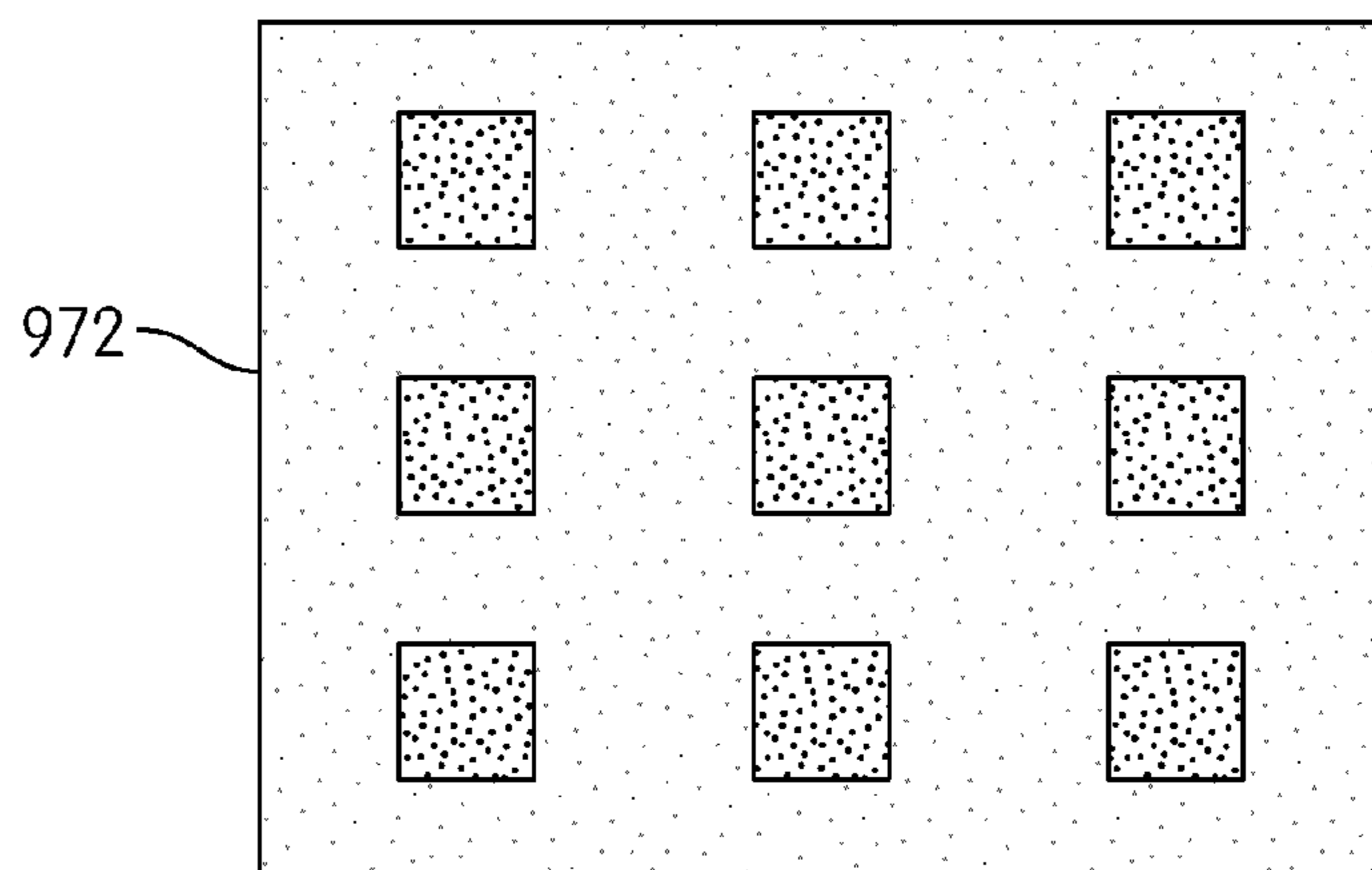


FIG. 16

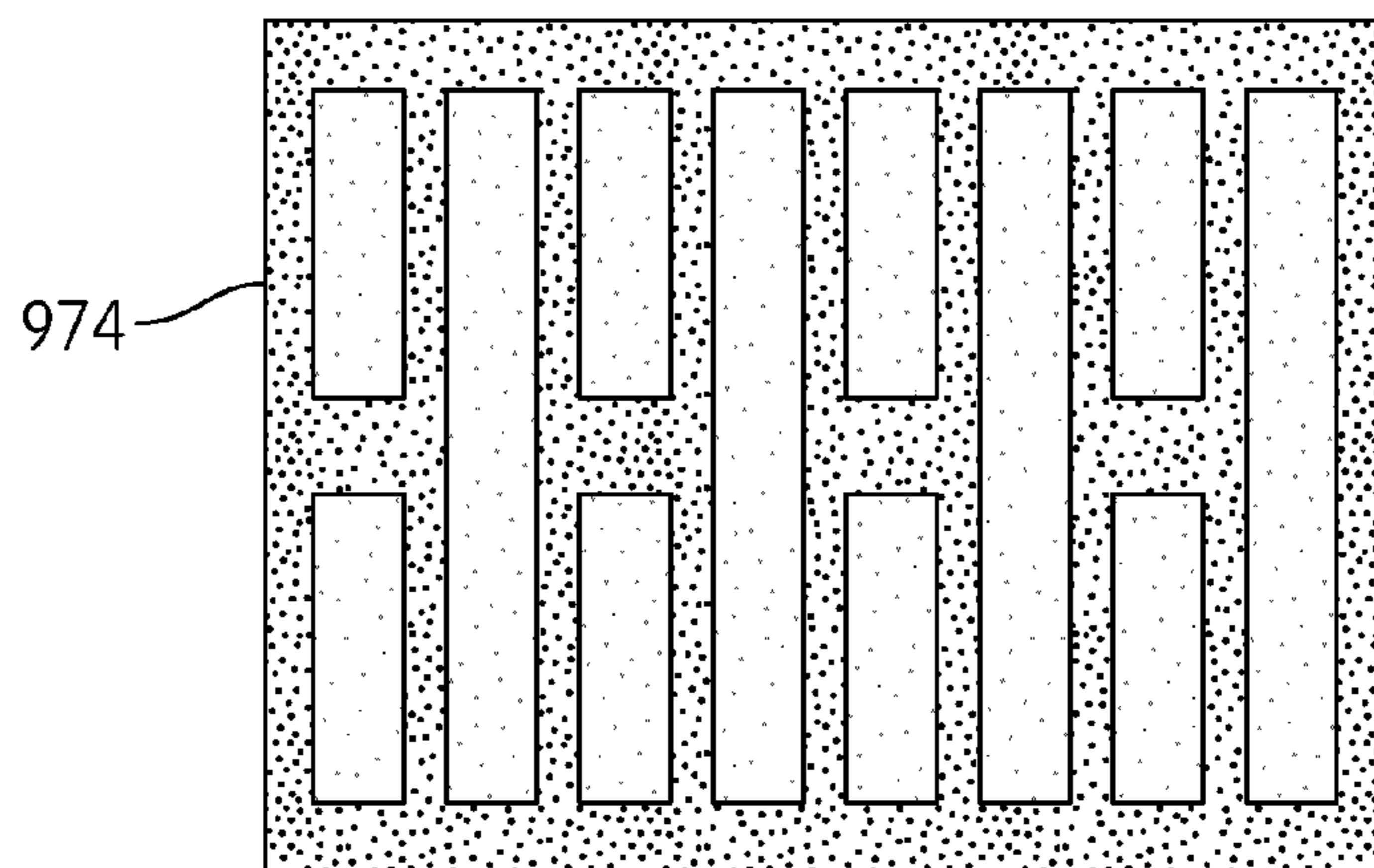


FIG. 17

NANOTUBE STRUCTURES, MATERIALS, AND METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 11/897,893, filed Aug. 30, 2007, which claims priority to, and the benefit of, U.S. Provisional Application Nos. 60/841,266, filed Aug. 30, 2006; 60/876,336, filed Dec. 21, 2006; and 60/923,904, filed Apr. 17, 2007. This application also claims priority to, and the benefit of, U.S. Provisional Patent Application No. 61/066,647, filed Feb. 22, 2008. The entire contents of all of those applications are incorporated by reference herein in their entireties.

STATEMENT REGARDING FEDERALLY FUNDED RESEARCH AND DEVELOPMENT

[0002] This invention was made with United States Government support under SBIR Contract # 0422198 from the National Science Foundation. The United States has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] 1. Field of the Invention

[0004] The invention relates generally to the field of materials science, and more particularly to nanotube structures, materials, and methods.

[0005] 2. Description of Related Art

[0006] By most accounts, synthetic nanotubes have been described in the scientific literature since 1991, see Iijima, "Helical microtubules of graphitic carbon", *Nature*, vol. 354, Nov. 7, 1991. Iijima described the nanotubes as a product of arc-evaporation synthesis of fullerenes. Scientists have since determined that carbon nanotubes have unusual and commercially valuable physical characteristics, and their potential use in many different applications has attracted much attention. For example, single-wall carbon nanotubes have high-current density and low capacitance characteristics.

[0007] Research has shown that single-walled nanotubes have the highest reversible capacity of any carbon material for use in lithium ion batteries. Carbon nanotubes also have applications in a variety of fuel cell components. They have a number of properties, including high surface area and thermal conductivity, which make them useful as electrode catalyst supports in PEM fuel cells. Because of their high electrical conductivity, they may also be used in gas diffusion layers, as well as current collectors. Carbon nanotubes' high strength and toughness-to-weight characteristics may also prove valuable as part of composite components in fuel cells that are deployed in transport applications, where durability is extremely important.

[0008] The unique properties of nanotubes, especially carbon nanotubes, have resulted in attempts to use nanotubes in a variety of different applications. In many of these applications, a body of relatively dense nanotubes is desired. For example, an application using nanotubes to store a chemical or electrical species may have a constraint on the maximum size of the storage container, and the user desires the maximum storage within this volume. Thermal management applications may also require a high density of nanotubes, and these latter applications may also require an aligned body of nanotubes. In these and other applications, a maximum density of nanotubes is desired.

[0009] However, synthesis methods for nanotubes often result in arrays or other sets of nanotubes having a relatively low packing density of nanotubes in the array or set (e.g. for carbon nanotubes, sometimes below 1% of the theoretical density of graphite). For chemical vapor deposition (CVD) growth of nanotubes on a substrate, a low nanotube density may even enhance growth rates by allowing gases to easily pass through the tubes to the tube/substrate interface where growth occurs. Although low densities may be helpful during nanotube formation, many applications require more densely packed nanotubes.

SUMMARY OF THE INVENTION

[0010] One aspect of the invention relates to methods for forming nanotube structures. The methods comprise forming nanotubes such that they are associated with the surface of a substrate and then applying a compressive force to at least a portion of the nanotubes in at least one direction.

[0011] Another aspect of the invention relates to a method for making a nanotube structure. The method comprises forming nanotubes such that they are associated with a surface of a substrate, impressing a stamp having a stamp surface upon at least a portion of the nanotubes to make an impression in at least the portion of the nanotubes, and removing the stamp from the portion of the nanotubes. The portion of the nanotubes retains at least a portion of the impression.

[0012] Yet another aspect of the invention relates to a nanotube structure produced by a process comprising forming nanotubes on a surface of a substrate, and applying a compressive force to at least a portion of the nanotubes to form the nanotube structure. The resulting nanotube structure is denser and smaller in at least one dimension than the nanotubes.

[0013] Other aspects, features, and advantages of the invention will be set forth in the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The invention will be described with respect to the following drawing figures, in which like numerals represent like structures throughout the figures, and in which:

[0015] FIG. 1 is a flowchart generally illustrating a method for forming a freestanding nanotube object according to an exemplary embodiment of the invention;

[0016] FIGS. 2A-2C schematically show exemplary tasks for providing a substrate according to an exemplary embodiment of the invention;

[0017] FIG. 3 schematically shows an array of substantially aligned nanotubes on a surface of a substrate according to an exemplary embodiment of the invention;

[0018] FIG. 4A schematically shows a portion of an array separated from the surface according to an exemplary embodiment of the invention;

[0019] FIG. 4B schematically illustrates a method for mechanically separating and densifying a portion of an array according to an exemplary embodiment of the invention;

[0020] FIG. 5 schematically illustrates a process for densifying an array of nanotubes according to an exemplary embodiment of the invention;

[0021] FIG. 6 schematically illustrates tasks of a method for partially densifying a wet nanotube array prior to drying, according to an exemplary embodiment of the invention;

[0022] FIGS. 7A-7D show examples of assemblages constructed from densified nanotube arrays, according to exemplary embodiments of the invention;

[0023] FIGS. 8A and 8B schematically illustrate another exemplary method for creating an assemblage, according to an exemplary embodiment of the invention;

[0024] FIG. 9 shows a graphical representation of nanotube diameter, nanotube wall thickness, and nanotube density for four exemplary catalysts;

[0025] FIGS. 10A-D are scanning electron microscope images of as-grown vertically aligned nanotubes at magnification levels of 5,000 \times , 10,000 \times , 50,000 \times and 100,000 \times , respectively;

[0026] FIGS. 11A-D are scanning electron microscope images of nanotubes after densification via capillary forces at the same magnification levels as the nanotubes of FIGS. 10A-D;

[0027] FIGS. 12A-D are scanning electron microscope images of nanotubes further compressed with mechanical force at the same magnification levels as the nanotubes of FIGS. 11A-D;

[0028] FIG. 13 is a schematic side elevational view illustrating the application of multiple mechanical forces to a nanotube sample;

[0029] FIG. 14 is a schematic side elevational view illustrating a stamping process on a nanotube sample; and

[0030] FIGS. 15-17 are illustrations of various types of stamps that may be used on nanotubes in embodiments of the invention.

DETAILED DESCRIPTION

[0031] The specification provides methods for forming freestanding objects formed primarily from aligned carbon nanotubes, as well as the objects made by these methods. In these methods, arrays of generally aligned carbon nanotubes are first synthesized and then densified, maintaining the aligned arrangement. The densified arrays can take the form of thin strips which can be joined together, for example by lamination, to form larger objects of arbitrary size. These objects can be further cut or otherwise machined to desired dimensions and shapes.

[0032] FIG. 1 shows a flowchart 100 that provides an overview of an exemplary embodiment of the invention. In a Task 110, a suitable substrate is provided for the growth of nanotubes. In a Task 120, one or more nanotube arrays are grown on the surface of the substrate. Task 130 comprises separating at least a portion of an array from the substrate, and Task 140 comprises densifying the separated portion. In general, the steps of providing the substrate and growing the one or more arrays of nanotubes are performed prior to the steps of separation and densification. In different embodiments, the step of densification follows the step of separation, the step of densification starts before the step of separation is completed, or the two steps are performed simultaneously. In some embodiments, which will be described below in more detail, densification may be performed without first separating the array from the substrate.

[0033] FIGS. 2A-2C illustrate exemplary steps of Task 110 (FIG. 1) of providing the substrate. In FIG. 2A, Substrate 210 is a suitable substrate for the growth of nanotubes. For the purposes of Task 120 (FIG. 1), in which a high temperature process such as chemical vapor deposition (CVD) is used to grow one or more arrays of refractory nanotubes such as carbon nanotubes, Substrate 210 can be composed of a refractory material such as Si, SiO₂, or Al₂O₃. However, nanotubes may be formed by processes other than CVD, and in certain embodiments of the invention, the substrate may comprise a

material selected from the list including silicon; silica; carbon; graphite; diamond; metal; steel; stainless steel; gold; silver; a chalcogenide; polymer; silicone; glass; quartz; ceramic; and, piezoelectric material.

[0034] It will be appreciated that although Substrate 210 is shown in FIGS. 2A-2C as flat, the Substrate 210 is not limited to being flat and may have whatever profile is desired in other embodiments.

[0035] As shown in FIG. 2B, Substrate 210 is provided with an Active Surface 220 on which the one or more arrays of nanotubes will be grown in Task 120. The Active Surface 220 can cover the entire surface of the Substrate 210 as shown, or can be limited to portions of the surface of the Substrate 210, as discussed below in connection with FIG. 2C. Because nanotube growth can be sensitive to the composition and morphology of the Active Surface 220, preparing the Active Surface 220 can optionally include cleaning the surface of the Substrate 210 and/or providing a catalyst layer on the surface of the Substrate 210 to enhance growth. An exemplary cleaning procedure for silicon substrates includes immersion for 10 minutes in a 4:1 bath of H₂SO₄/H₂O₂, maintained at 120° C. The Substrate 210 is then rinsed in water and immersed for 10 minutes in a 5:1:1 bath of H₂O/H₂O₂/HCl, maintained at 90° C. The Substrate 210 is then rinsed in water and immersed for 1 minute in a 50:1 HF:H₂O room temperature bath. The Substrate 210 is then rinsed in water and spun dry.

[0036] Exemplary catalysts for carbon nanotube synthesis are well known and include Fe, Co, Ni, Mo and oxides thereof. In some embodiments, providing the catalyst layer on the surface of the Substrate 210 includes creating small (e.g. <100 nm) catalyst particles on the Active Surface 220. Techniques such as physical vapor deposition (PVD) followed by annealing can be used to create these particles. U.S. Pat. No. 7,235,159 "Methods for Producing and Using Catalytic Substrates for Carbon Nanotube Growth" discloses several methods, and is incorporated by reference herein in its entirety.

[0037] In some aspects that include providing the catalyst layer, the Active Surface 220 is enhanced by forming one or more interfacial layers between the Substrate 210 and the catalyst layer. For example, an interfacial layer can comprise about a 10-150 nm thick Al₂O₃ layer between the catalyst layer and the surface of the Substrate 210. Another interfacial layer can comprise an approximately 500 nm thick SiO₂ layer disposed between the Al₂O₃ layer and the Substrate 210.

[0038] In some aspects, providing the catalyst layer includes depositing a thin layer of a catalyst material on the Substrate 210 through the use of electron beam evaporation followed by annealing the Substrate 210. Exemplary catalysts can comprise Fe, Co, Ni, Mo, Ru and combinations thereof. Suitable thicknesses of the deposited layer are between 0.1 nm and 5 nm, and preferably between 1 nm and 3 nm.

[0039] Providing the catalyst layer, in some embodiments, can comprise sequentially depositing multiple layers of catalyst, optionally with an intermediary processing step between layers to effect a chemical or physical change in the initially deposited layer or layers prior to the deposition of a subsequent layer. Examples of such a multilayer deposition process include depositing a 1 nm Fe layer followed by an anneal and then by depositing another 1 nm Fe layer (1 nm Fe/anneal/1 nm Fe); 1 nm Fe/anneal/1 nm Co; and 1 nm Co/anneal/1 nm Fe. An appropriate anneal may be performed at temperatures between about 600 and 900° C., and more preferably between about 700 and 800° C. For an annealing tube furnace having

a 6" diameter tube, an appropriate ambient comprises 2.5 standard liters per minute of ultra high purity argon, with a ramp rate of 15° C./minute and virtually no dwell time at the desired maximum annealing temperature.

[0040] The Active Surface **220** may optionally be patterned; creating Boundaries **230** that define bounded Regions **240**, as shown in FIG. 2C. A Boundary **230** may be straight, curved, angled, continuous, discontinuous, regular or irregular. Although shown as a line in FIG. 2C, the Boundary **230** can have an appreciable width to separate one Region **240** from the next. An exemplary Region **240** is rectangular, as shown, but is not so limited.

[0041] Nanotube growth on or within a Boundary **230** may be prevented or minimized by not applying a catalyst to the surface of the Substrate **210** on the Boundary **230**. In some aspects, the Substrate **210** can be masked, then subjected to a line of sight deposition technique (e.g. PVD) for deposition of a catalyst. Here, the masked regions do not receive deposited catalyst, while the regions exposed to the catalyst deposition become the Regions **240** that comprise the Active Surface **220**. Contact masks, lithography, and other masking methods can be used to demarcate Boundaries **230**.

[0042] An exemplary photolithography method includes coating a silicon wafer with a 1 μm positive photoresist layer, baking the resist, masking the resist using an appropriate mask, exposing the resist, developing the resist, dissolving the exposed portion (or unexposed, if using a negative resist), and optionally inspecting the wafer. Following catalyst deposition, the remaining resist is lifted off (e.g. via an acetone soak, optionally including surface swabbing) followed by an acetone rinse and an isopropanol rinse, followed by drying in nitrogen.

[0043] For the purposes of this specification, a Region **240** is any contiguous area on the surface of the Substrate **210** where nanotubes are intended to grow in Task **120**. If no Boundaries **230** are present, the entire surface of the Substrate **210** will define a single unbounded Region **240**. If Boundaries **230** are present, multiple discrete Regions **240** will exist on the surface of the Substrate **210**. The number, size, shape and other aspects of each Region **240** may depend on the final application of the nanotubes fabricated thereon. In addition to the methods described above, Boundaries **230** can also be created after the formation of the Active Surface **220** (e.g. by masking followed by etching or ablating, or by targeted ablating of appropriate areas of the Active Surface **220**).

[0044] Each Region **240** of the Active Surface **220** can be characterized by at least one Length **250** that is the smallest lateral dimension of the Region **240**. As will be discussed later, Length **250** may correspond to the smallest lateral dimension of a nanotube array grown on that Region **240**.

[0045] Methods for growing nanotubes, especially carbon nanotubes, are well known. For the purposes of the present invention, growth conditions that yield substantially aligned nanotubes are utilized for Task **120** (FIG. 1). For certain densification processes in Task **140** (FIG. 1), discussed below, in which separation of the nanotubes includes etching, it may be advantageous to choose a "base growth" method for growing the nanotubes (in which the nanotubes grow from the point of attachment to the catalyst) and to choose a catalyst that can be readily etched. Exemplary thermal CVD growth conditions for growing carbon nanotubes in a 1" tube furnace include a temperature in the range of about 700-800° C. Substrates may be initially heated in an inert atmosphere (e.g. argon), then exposed to a deposition atmosphere comprising,

for example, a hydrocarbon component. An exemplary deposition atmosphere includes 0.1 standard liters per minute (SLM) ethylene, 0.4 SLM hydrogen, and water vapor. An appropriate water vapor concentration may be created by bubbling 0.1 SLM of argon through a water bubbler at ambient temperature. Typical growth times are between 5 minutes and 100 minutes.

[0046] FIG. 3 schematically shows an exemplary nanotube array that may be grown according to exemplary embodiments of Task **120** (FIG. 1). As in FIGS. 2A-2C, the Substrate **210** includes a Region **240** having a Length **250**. In Task **120** an Array **310** of nanotubes is grown on the Region **240** to an Array Height **315**. Nanotubes in the Array **310** are connected to the Active Surface **220** at an Interface **320**. It may be advantageous to grow the Array **310** to a sufficient Height **315** that the ratio of the Height **315** to the Length **250** is greater than 1:1. For thermal CVD growth of carbon nanotubes as described herein, 30 minutes of growth at 800° C. can yield an Array **310** having a Height **315** of approximately 1 mm or greater.

[0047] FIG. 4A schematically shows an exemplary result of separating a Portion **410** of the Array **310** from the Substrate **210** after Task **130** (FIG. 1). As shown, the Portion **410** can include the entire Array **310**, while in some aspects the Portion **410** comprises some segment of the Array **310**. For example, it may be advantageous to release all of the Array **310** except for one or more small attached sections at the edges, in order to keep the Array **310** loosely connected to the Substrate **210** for further processing.

[0048] In some embodiments, Task **130** is performed by introducing a suitable Separation Atmosphere **420** to the Substrate **210** and Array **310**, where the Separation Atmosphere **420** is capable of etching the Interface **320** to release the Portion **410** from Substrate **210**. Advantageously, in some embodiments Task **120** of growing the Array **310** and Task **130** of releasing at least the portion **410** of the Array **310** can be performed in the same reaction vessel. For example, the Separation Atmosphere **420** can be introduced into the reaction vessel (e.g., a tube furnace) immediately following the deposition atmosphere. An exemplary Separation Atmosphere **420** includes 0.5 SLM hydrogen and water carried on 0.1 SLM argon bubbled through a water bubbler at ambient temperature.

[0049] FIG. 4B schematically illustrates a method for concurrently separating and densifying a Portion **410** of an Array **310**. In this example, the Portion **410** comprises the entire Array **310** which is subjected to Forces **430**, **440**, and **450** by Blocks **460**, **470**, and **480**, respectively. For example, Force **430** is used to move the Block **460** in the direction **485**, as shown, to mechanically shear the nanotubes of the Array **310** off of the Substrate **210**. As the nanotubes of the Array **310** are separated from the Substrate **210** and densified through compaction against Block **480**, the Force **450** increases against the Array **310**. The Block **470** also exerts the Force **440** against the top of the Array **310** in order to resist buckling of the Array **310** in response to the Forces **430** and **440**. While in the illustrated example the Block **480** is fixed and exerts the Force **450** reactively in response to the compaction of nanotubes against the Block **480**, in some embodiments Blocks **460** and **480** are moved towards one another to compact the Array **310** from both sides.

[0050] FIG. 5 schematically illustrates, for Task **140** (FIG. 1), an exemplary method for densifying a Portion **410** that has been previously separated from the Substrate **210**. In this

method, the Portion **410** is first exposed to a Wetting Environment **510** to create a Wet Portion **520** that is subsequently dried to create a Densified Portion **530**. When allowed to dry, capillary forces between nanotubes in the Wet Portion **520** draw the nanotubes closer together as the drying progresses.

[0051] The Wetting Environment **510** can comprise a wetting fluid and a type of exposure. For instance, the type of exposure can be immersion in the wetting fluid, exposure to a vapor including the wetting fluid, or exposure to a mist of the wetting fluid. A wetting fluid having at least some nonpolarity may be advantageous, and isopropyl alcohol (and solutions thereof) is a suitable example. Other suitable wetting fluids include water, xylene, acetone, methanol, and ethanol. The choice of a wetting fluid may also be partially influenced by desired drying kinetics. Fluids with particularly low vapor pressures may dry too slowly; fluids with particularly high vapor pressures may dry too quickly (at a given drying condition of pressure and temperature).

[0052] One or more surfactants may also be added to the Wetting Environment **510**. Surfactants may increase the wetting of the nanotubes by a particular fluid. Surfactants may also substantially adhere to the nanotubes, and in some cases may create a degree of steric separation between tubes (e.g. surfactant molecules prevent two tubes from approaching closer than a certain distance). In certain aspects, this steric separation may be used to control a final density by maintaining a minimum separation between tubes or groups of tubes. Thus, a desired density may be achieved by balancing the compressive forces of the densification process with repulsive forces between tubes (e.g. by a surfactant), allowing a user to tailor the density to a target application. Certain embodiments may result in nanotube bodies having final mass densities between 2% and 97%, preferably between 5% and 90%, more preferably between 10% and 80%, and still more preferably between 15% and 70%. Sodium dodecylbenzene sulfonate can be a suitable surfactant for creating these steric forces.

[0053] As noted above, Portion **410** can be exposed directly to a liquid, for example, by immersion. In these embodiments the Portion **410** rapidly becomes saturated with the wetting fluid. Portion **410** can also be exposed to a mist or vapor such that the exposure begins gradually and increases until the Portion **410** is sufficiently wet. In some cases, complete saturation of Portion **410** (i.e. substantially filling all intertubular space with the wetting fluid) may not be necessary.

[0054] As shown in FIG. 5, Wet Portion **520** is exposed to a Drying Atmosphere **540** to produce the Densified Portion **530**. Where the wetting fluid is isopropyl alcohol, for example, a Drying Atmosphere **540** comprising air at ambient temperature and pressure can produce the Densified Portion **530** within a few minutes. In some embodiments, drying the Wet Portion **520** results in the Densified Portion **530** having a Length **550** that is smaller than the corresponding Length **250** of the Portion **410** prior to densification. By gently wetting and drying the Portion **410**, alignment of the nanotubes can be preserved to enhance densification, resulting in a Length **550** substantially smaller than the corresponding Length **250** of the Portion **410** prior to densification.

[0055] FIG. 5 shows the Densified Portion **530** disposed on a Drying Substrate **560**, but it will be appreciated that the Drying Substrate **560** is not essential in some embodiments. For example, the Wet Portion **520** can be suspended in the Drying Atmosphere **540** by one end and allowed to densify. In some embodiments, however, it is advantageous to support

and/or mold the Wet Portion **520** while disposed in the Wetting Environment **510** and/or the Drying Atmosphere **540**. For instance, the Wet Portion **520** can be removed from the Wetting Environment **510** using a substrate, form, mandrel, mold or other support, which may also be used to mold, support and/or constrain Wet Portion **520** during the subsequent exposure to the Drying Atmosphere **540**. The orientation of such a support (e.g. Drying Substrate **560**) with respect to a supported portion can be such that the nanotubes are aligned substantially parallel to the support, substantially perpendicular to the support, or in any desired orientation. One or many portions may be supported by a single support, and the degree of alignment or randomness among portions can be tailored to a desired application. Appropriate materials for such a support include fused silica, Teflon® (polytetrafluoroethylene), silicon, and silicone.

[0056] FIG. 5 shows an example in which the support comprises the Drying Substrate **560**. It may be advantageous to fabricate the Drying Substrate **560** from an elastic material (e.g. rubber, latex, or silicone), which allows the Drying Substrate **560** to be stretched. By stretching Drying Substrate **560** prior to contact with the Wet Portion **520**, Wet Portion **520** may be placed or molded onto the stretched Drying Substrate **560**. Subsequently, releasing or relaxing the stretched Drying Substrate **560** during exposure to the Wetting Environment **510** and/or the Drying Atmosphere **540**, or even after drying, will cause the Drying Substrate **560** to contract which may enhance the densification of the portion attached thereto. In some of these embodiments, the Wet Portion **520** is oriented on the Drying Substrate **560** such that the direction of alignment of the nanotubes is normal to the surface of the Drying Substrate **560**, whereas in other embodiments the orientation of the Wet Portion **520** is as shown in FIG. 5.

[0057] FIG. 6 illustrates steps of a method for partially densifying the Wet Portion **520** prior to drying. In this example, Wet Portion **520**, while exposed to Wetting Environment **510**, is disposed between Blocks **610** and **620** as shown. Blocks **610** and **620** are then actuated to apply Forces **630** and **640** to compress and shear the Wet Portion **520**. In this way the nanotubes of the Wet Portion **520** “lay down” with respect to their initial alignment as illustrated while maintaining the substantially parallel alignment that existed prior to the application of Forces **630** and **640**. While the Forces **630** and **640** already include a compressive component, further densification can be achieved by applying additional compression, without the shear component, after the application of Forces **630** and **640**.

[0058] Following the mechanical manipulation shown in FIG. 6, the nanotubes are exposed to the Drying Atmosphere **540**, discussed above, to create the Densified Portion **530**. One or both of Blocks **610** and/or **620** can be removed prior to the exposure to the Drying Atmosphere **540**. Optionally, either or both of the Blocks **610** and **620** can comprise a shaped surface against which the Wet Portion **520** can be molded during the process illustrated by FIG. 6 and/or during the subsequent drying process.

[0059] FIGS. 7A-7D show examples of freestanding assemblages constructed from Densified Portions **530** according to various embodiments. These examples are illustrative, and not meant to be limiting.

[0060] Assemblage **710**, shown in FIG. 7A, comprises multiple Densified Portions **530**, arranged in an ostensibly random fashion. Although FIG. 7A shows the Densified Portions **530** each having a direction of nanotube alignment that is in

the plane of the drawing page, it will be appreciated that the direction of nanotube alignment for the multiple Densified Portions 530 can be randomly oriented in three dimensions as well. In some instances, Assemblage 710 may be constrained within a package such as a can or an envelope. In these embodiments, the multiple Densified Portions 530 can be loosely arranged or packed for greater density. In some cases the package can be the support discussed above with respect to FIG. 5.

[0061] FIG. 7B shows an Assemblage 720 that comprises multiple Densified Portions 530 arranged “end to end” such that the longitudinal direction of the nanotubes (the direction of nanotube alignment) is substantially maintained throughout the Assemblage 720. In some embodiments, the multiple Densified Portions 530 are joined together by a bonding agent such as a glue or an adhesive. Exemplary glues and adhesives include cyanoacrylates and methacrylate esters such as Loctite® formulations 262, 271, 290, 609 and 680.

[0062] FIGS. 7C and 7D show Assemblages 730 and 740, respectively, each comprising multiple Densified Portions 530 arranged such that the longitudinal direction of the nanotubes is substantially parallel for each Densified Portion 530. Assemblages 730 and 740 can be created by stacking Densified Portions 530 as shown. Assemblage 740 further comprises a Bonding Agent 750 such as adhesive or glue, while Assemblage 730 does not.

[0063] Any of the Assemblages 710-740 can additionally be further densified, e.g. by the application of a compressive force. Additionally, any of the Assemblages 710-740 can be trimmed by cutting or machining to a desired dimension or shape. Assemblages 710-740 can also be further joined together to form still larger freestanding structures comprised essentially of only nanotubes. Further still, any of the Assemblages 710-740 can be laminated with layers of other materials. For example, ceramic or metallic layers may be combined with nanotube layers for added stiffness.

[0064] FIGS. 8A and 8B illustrate another exemplary method for creating an assemblage. In FIG. 8A an active surface of a substrate is patterned and used to grow parallel Arrays 810 of generally vertically aligned nanotubes. Here, a Length 250 for each Array 810 is chosen to be about equal to the expected Height 315 of the Arrays 810. The final lateral dimension of the Arrays 810 on the surface (i.e. perpendicular to Length 222 and Height 314) can be made arbitrarily large. While the Arrays 810 are still attached to the active surface, the Arrays 810 can be wetted and dried wet, resulting in a structure as depicted in FIG. 8B, in which the Arrays 810 form Rows 820 of at least partially densified nanotubes. The Rows 820 can be mechanically separated from the substrate and further densified according to the method illustrated with respect to FIG. 4B, for example. The Rows 820 can also be at least partially separated from the substrate by etching prior to mechanical compression as discussed with respect to FIG. 4A.

[0065] Although several aspects of the invention address the densification of an as-grown nanotube array, for some applications it may also be advantageous to increase the densities of the individual nanotubes within an array and/or increase the number of nanotubes per unit area in the as-grown array. The density of each nanotube (essentially a function of the nanotube wall thickness), and the number of nanotubes per unit area in the as-grown array can both be sensitive to several factors including the catalyst composition, distribution on the active surface, and the growth envi-

ronment. FIG. 9 provides a graphical representation of how nanotube diameter, nanotube wall thickness, and nanotube density within an array can vary for four exemplary catalysts.

[0066] As noted above, the invention also includes freestanding objects comprised of aligned and densified nanotubes. In some embodiments, such freestanding objects have a volume of greater than 5 cubic millimeters and comprise at least 10% nanotubes by mass. In further embodiments, a freestanding object can comprise at least 60% nanotubes by mass, and even at least 90% nanotubes by mass. In some of these embodiments, the objects have a density greater than 0.4 grams/cc.

[0067] In some aspects, the invention provides for nanotube structures comprising nanotubes, preferably carbon nanotubes, that have axial and radial directions, and by geometry have different properties in the axial and the radial directions. This property, in some instances, differentiates carbon nanotubes from graphitic sheets that generally do not form tubular structures.

[0068] As described above, the invention provides for growing a network of vertically aligned carbon nanotubes on a substrate which are subsequently made denser through post-processing to form nanotube structures, sometimes referred herein as mesh, meshes, sheet, sheets, film, or films. The invention provides for the use of mechanical force to compress the carbon nanotubes in both parallel and perpendicular directions relative to the carbon nanotube growth direction. Further densification can be achieved through the use of a liquid. Not wishing to be bound by theory, the inventors believe that the liquid draws the carbon nanotubes together through capillary forces.

[0069] FIGS. 10A-D are scanning electron microscope images of as-grown vertically aligned nanotubes at magnification levels of 5,000×, 10,000×, 50,000× and 100,000×, respectively. FIGS. 11A-D are scanning electron microscope images of nanotubes after densification via capillary forces at the same magnification levels as the nanotubes of FIGS. 10A-D, and FIGS. 12A-D are scanning electron microscope images of nanotubes further compressed with mechanical force at the same magnification levels. The density of the carbon nanotubes increased around 16 times after subsequent exposure to liquid, the increased density likely being due to capillary forces. An additional four-fold increase in density was achieved from the application of an additional compressive force after exposure to liquid and the first compressive step. After densification, the sample was about 65% dense.

[0070] As described above, certain aspects of the invention rely, in part, on capillary and mechanical forces to pull together carbon nanotubes in directions generally normal to the length of the tubes (“x-y-compression”). Mechanical pressure can also be applied in a direction parallel to the direction of carbon nanotube growth (“z-compression”).

[0071] In certain embodiments, mechanical force alone, that is, without capillary forces, can produce very dense samples. By way of non-limiting example, pressing an array of nanotubes that is approximately 3 cm² in area and with a height ranging from several hundred micrometers to several millimeters with several tons of force in the z-direction can yield the mesh of the invention in certain circumstances described herein.

[0072] Certain aspects of this description refer to nanotubes as being “vertically aligned.” As used in this description, that term refers to an alignment generally in a direction normal to the substrate on which the nanotubes are grown. It should be

understood that the carbon nanotubes described herein are not necessarily perfectly straight and are generally somewhat twisted and entangled with neighboring carbon nanotubes. Without application of the compressive and capillary forces described herein, the uncompressed nanotube growth process typically produces films that are approximately 1% dense, compared to solid graphite. After compression, such films may retain the original area of the uncompressed sample but are much thinner than their original form. In certain embodiments, the films of the invention range from 20-50 μm in thickness.

[0073] In certain embodiments, compression may be performed without first separating the nanotubes from the substrate. For example, the step of removal prior to compression may be omitted if z-compression is performed while the nanotube array is attached to the substrate. The resulting film may be removed intact. A liquid release agent, for example, a solvent such as isopropyl alcohol, may be applied if the film does not readily separate from the substrate. Use of the liquid often allows the film to be slid off the substrate with little effort. Other release agents may include ethanol, methanol, acetone, xylene, and water. In certain embodiments, a separating implement, for example, a razor blade, may be applied between the outer edge of the film and the substrate to initiate separation of the film from the substrate.

[0074] Mechanical force may be applied in multiple directions simultaneously or sequentially in combination to shape a nanotube structure. As those of skill in the art will realize, when a material is compressed in one direction, the other dimensions of the material may increase. For example, a compressed nanotube film may be far thinner than its uncompressed form, but it may also be considerably longer and wider. For many applications, this dimensional expansion in the uncompressed directions is acceptable, and may even be desired. However, in some embodiments, it may be helpful to constrain the nanotubes (with grips, plates, barriers, etc.) in the uncompressed direction or directions prior to compression so as to maintain particular dimensions. Additionally, constraining the nanotubes in particular directions may prevent the nanotubes from warping out-of-plane during compression.

[0075] For example, FIG. 13 is a schematic side elevational view illustrating the application of mechanical forces in several directions. A nanotube sample 900, which may, for example, be on the order of 1.5 cm \times 2.0 cm, has been detached from its growth substrate in the illustration of FIG. 13. However, in other embodiments, the sample 900 may be attached to its growth substrate. A plate 902 is placed overtop of the sample 900 to distribute force evenly, and force is applied to the plate. However, in FIG. 13, the plate 902 and applied z-direction force is not necessarily intended to permanently compress or deform the sample 900. Instead, at least in the arrangement shown in FIG. 13, the z-direction force is applied at a force level sufficient to constrain the sample 900 and prevent it from warping out of plane as the sample is compressed from the other directions. For a small sample 900 of the dimensions given above, the z-direction force may be on the order of a few hundred grams, for example, supplied by two 200 g weights resting on the plate 902. In order to prevent the plate 902 and its weight from compressing the sample 902, a pair of spacers 904, one on each side of the sample 900, at least partially supports the plate 902. The height of the spacers 904 and the amount of weight on the plate 902 may also be chosen to provide a defined, limited amount of com-

pression. It may be helpful in some embodiments if the plate 902 is generally smooth and planar, although that need not be so, and in some embodiments, which will be described below in more detail, the plate may have a defined shape or profile of its own. As one example, a standard laboratory glass slide may be used as the plate 902 and feeler gages or shim stock of appropriate thicknesses may be used as the spacers 904.

[0076] As is also shown in FIG. 13, a second pair of movable members 906 is positioned inwardly of the spacers 904 and immediately proximate to the sample 902. These movable blocks or members 906, which may have a height that is about the same as the height of the spacers 904, bear against the sample 900 to apply compressive forces in the x-y plane. To apply x-y compressive forces, the movable members 906 are pushed against the sides of the sample 900. The movable members 906 may be driven manually in some embodiments, or they may be part of a load frame that is automatically driven. Although shown as adjacent in FIG. 13, the spacers 904 and movable members 906 may instead be provided adjacent to different faces of the sample 900. The final dimensions of the sample 900 with the arrangement of FIG. 13 will depend on the degree of applied force.

[0077] Force application on a nanotube sample may be controlled by controlling the applied force or by controlling the resulting dimensions of the sample. In many cases, it may be most advantageous simply to decide on the desired final dimensions of the nanotubes and then to apply force until those dimensions are reached. In general, it has been found that compression factors of twenty to twenty-five times the uncompressed dimensions are possible, depending on the density of the uncompressed sample, which may be as little as 1% dense.

[0078] The description above generally relates to compression using planar (i.e., flat) plates and other forms. However, the plates, mandrels, and other forms used to compress nanotubes need not be planar. Instead, forms may be curved or have any desired shape.

[0079] Additionally, compression may be applied selectively over only a portion of the surface of a sample of nanotubes. This can be particularly helpful in creating nanotube structures whose faces have different shapes, or in creating nanotube structures that have greater outer surface area. Various processes may be used in which force is applied selectively over only a portion of a nanotube sample. One particular process that may be used is stamping.

[0080] FIG. 14 illustrates a stamping process. In FIG. 14, a stamp 950 with some surface features 952 is pressed into a nanotube sample 954 to form a pattern in the sample 954. Similar to the arrangement of FIG. 13, spacers 956 may be provided adjacent to the nanotube sample 954 so as to control the depth to which the stamp 950 penetrates or impresses itself upon the nanotube sample 954. Of course, as can be seen from the figure, if the height of the nanotube sample 954 is greater than the height of the stamp 950, some general compression will occur as the stamp 950 is impressed. In the illustration of FIG. 14, the nanotube sample 954 is being impressed with the stamp 950 on its original growth substrate 958. After impressing, the sample 954 may be removed from the substrate 958 by any of the methods described above.

[0081] Stamps can be used to impress various types of patterns into samples 954. FIGS. 15-17 illustrate various stamp patterns that may be used to impress nanotube samples 954. In FIGS. 15-17, the heavily shaded areas represent depressed areas, while the lightly shaded areas represent

raised areas. The pattern of FIG. 15 represents a "pin" stamp 970 with a number of protruding rectilinear "towers." This type of stamp produces a sample with a number of square depressions or holes with a depth that depends on the height of the stamp and the placement of spacers 956, if any. FIG. 16 is a "grid" stamp 972 that is essentially the negative of the "pin" stamp 970. The grid stamp 972 produces a sample with a number of projecting towers. Finally, FIG. 17 illustrates a "slot" stamp 974 that produces a series of slotlike depressions in a nanotube sample 954. It should be understood that although the faces of the stamps 970, 972, 974 that are impressed into the nanotube sample 954 in the illustrated embodiment are flat, stamps according to other embodiments may have contoured or rounded faces or shapes and need not be flat or rectilinear.

[0082] Although essentially any pattern may be impressed into a nanotube sample 954, one consideration when selecting stamp shapes and profiles is the degree to which the stamp may stick to the sample 954 or otherwise prove difficult to remove once an impression has been made. In some embodiments, a stamp like stamp 970 has been found to be more removable than stamps 972, 974 with other profiles. However, the degree of removability of any particular stamp after an impression has been made will depend on the size of the stamp, the density and height of the nanotube sample 954, the amount of compressive force applied and/or the overall amount of compression, among other factors.

[0083] Once a pattern has been impressed into the sample 954, it may or may not be separated from its growth substrate 958. After a pattern has been impressed, the sample 954 may be subjected to coating or deposition of other materials. Certain deposition and coating techniques preferentially add material to the carbon nanotube structure at the exposed surfaces of the carbon nanotube structure. With such techniques, very little material actually penetrates the network of nanotubes, regardless of whether the network is "as-grown" or has been made denser already. Therefore, the increased macroscopic surface area provided by the pattern may be particularly advantageous if the sample 954 is to be subjected to coating or deposition processes that deposit material on the outer surface of the sample 954. If the sample 954 is to be further processed or coated, it may be advantageous to leave the sample 954 on its substrate 958 in order to facilitate further processing.

[0084] The following examples may illustrate certain aspects of the invention.

EXAMPLES

Example 1

Growth of vertically aligned Nanotube Structures

[0085] A four inch single crystal silicon substrate was cleaned by immersion in a 4:1 bath of H_2SO_4/H_2O_2 , maintained at 120° C., for 10 minutes. The substrate was then rinsed in water and immersed in a 5:1:1 bath of $H_2O/H_2O_2/HCl$, maintained at 90° C., for 10 minutes. The substrate was then rinsed in water and immersed in a 50:1 $HF:H_2O$ bath, at room temperature, for 1 minute. The substrate was then rinsed in water and spun dry.

[0086] 500 nm of SiO_2 were thermally grown on the cleaned substrate followed by 20 nm Al_2O_3 deposited by sputtering from an Al_2O_3 target. Straight, 12.5 μm wide boundaries, separating regions to become active surface, were fabricated using lithography, such that each region was

a 1 mm wide strip that traversed the length of the wafer. 1 nm of Fe was then deposited on these regions using electron beam deposition, and then the photoresist mask was lifted off.

[0087] The wafer was then coated with a protective photoresist layer for dicing. The wafer was diced in directions parallel (at 15 mm intervals) and perpendicular (at 20 mm intervals) to the boundaries, such that each die had approximately 14 rectangular regions of active surface, each region being 20 mm (the die length) by 1 mm (as defined by the lithography boundaries). The photoresist was then stripped and the dies were cleaned.

[0088] Arrays of carbon nanotubes were grown in the regions at 800° C. for 30 minutes under conditions previously described. The arrays of nanotubes were separated in-situ, by etching the interface between the nanotubes and the substrate using the etching procedure previously described.

[0089] The density of a representative undensified (as-grown and as-separated) portion of an array was determined by measuring the physical dimensions of the portion using scanning electron microscopy and weighing the sample. As-grown densities were typically 0.01-0.02 g/cc.

[0090] Several portions were exposed to a wetting environment by gently pushing the portions off of the substrate and into an isopropanol bath. The resulting wet portions were captured on a glass cover slip substrate such that the alignment direction of the nanotubes was parallel to the surface of the substrate. The ends of each portion were affixed using a small weight to prevent warping during drying. Each wet portion was allowed to dry at ambient temperature and pressure. Density measurements of 16 portions subsequent to drying resulted in an average density of 0.4 g/cc.

Example 2

Compressing Nanotube Structures

[0091] A sample grown using the procedure of Example 1 is placed in an arbor press (e.g. DEVIN LP-500(TM)) and 1 ton of force applied through a polished stainless steel plate placed on top of the sample. Force is applied in a direction parallel to the growth direction.

[0092] A sample is grown using the procedure of Example 1. To establish an initial height, the sample is first z-pressed with an arbor press using metal spacers. With the spacers still in place, a glass slide is then placed over the film with two 200 g weights over the slide. The spacers are then slid in toward each other and the film is subsequently pressed in the x-direction. Further compression in the z-direction can be performed by changing the spacer heights and using the arbor press.

[0093] While the invention has been described with respect to certain embodiments and examples, the description is intended to be exemplary, instead of limiting. Modifications and changes may be made within the scope of the invention, which is defined by the appended claims.

What is claimed is:

1. A method for making a nanotube structure comprising: forming nanotubes such that they are associated with a surface of a substrate; and applying a compressive force to at least a portion of the nanotubes in at least one direction.
2. The method of claim 1, wherein the nanotubes comprise carbon nanotubes.
3. The method of claim 1, further comprising applying a catalyst onto the surface prior to the nanotube forming.

4. The method of claim 1, wherein the compressive force is applied in a dimension normal or about normal to the substrate surface.

5. The method of claim 1, wherein the compressive force is applied in a direction parallel or about parallel to the substrate surface.

6. The method of claim 5, wherein the compressive force causes at least a portion of the nanotubes to dissociate from the substrate surface.

7. The method of claim 1, wherein the compressive force comprises plurality of compressive forces, each applied from a different direction relative to the substrate surface.

8. The method of claim 1, further comprising dislodging the nanotube structure from the surface using a solvent.

9. The method of claim 1, wherein applying a compressive force to at least a portion of the nanotubes comprises applying the compressive force to substantially the entirety of a surface of the nanotubes.

10. The method of claim 1, further comprising constraining the nanotubes in at least one direction while applying the compressive force in another direction.

11. The method of claim 1, wherein applying the compressive force to at least a portion of the nanotubes comprises applying the compressive force selectively to the nanotubes to create one or more surface features on a surface of the nanotubes.

12. A method for making a nanotube structure comprising:
forming nanotubes such that they are associated with a surface of a substrate;

impressing a stamp having a stamp surface upon at least a portion of the nanotubes to make an impression in at least the portion of the nanotubes; and

removing the stamp from the portion of the nanotubes;
wherein the portion of the nanotubes retains at least a portion of the impression.

13. The method of claim 12, wherein the stamp has one or more surface features, and the impression comprises at least a partial impression of one of the one or more surface features.

14. The method of claim 13, wherein the nanotubes are substantially aligned with respect to one another and with respect to the surface of the substrate.

15. The method of claim 14, wherein the nanotubes extend in a direction essentially normal to the surface of the substrate.

16. The method of claim 12, further comprising, before the impressing, removing at least a portion of the nanotubes from the surface of the substrate.

17. The method of claim 12, wherein the impressing is performed with the nanotubes at least partially attached to the surface.

18. A nanotube structure produced by a process comprising:

forming nanotubes on a surface of a substrate; and
applying a compressive force to at least a portion of the nanotubes to form the nanotube structure;
wherein the nanotube structure is denser and smaller in at least one dimension than the nanotubes.

19. The nanotube structure of claim 18, wherein the nanotube structure is produced by a process further comprising applying a second compressive force in a second direction, and the nanotube structure is denser and smaller in at least two dimensions than the nanotubes.

20. The nanotube structure of claim 18, wherein the nanotube structure comprises two or more connected nanotube structures, each one denser and smaller in at least one dimension than the nanotubes from which it was formed.

21. The nanotube structure of claim 18, wherein the nanotube structure is formed by a process comprising applying a compressive force selectively to portions of the nanotubes, such that the nanotube structure has an impressed or embossed pattern on at least one surface.

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