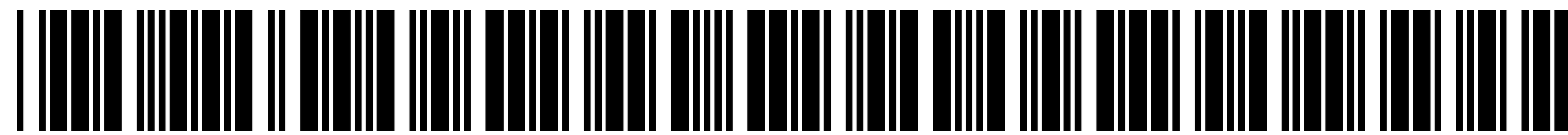

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(54) **METHOD FOR FORMING SOLAR CELL WITH SELECTIVE EMITTERS**

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(30) **Foreign Application Priority Data**

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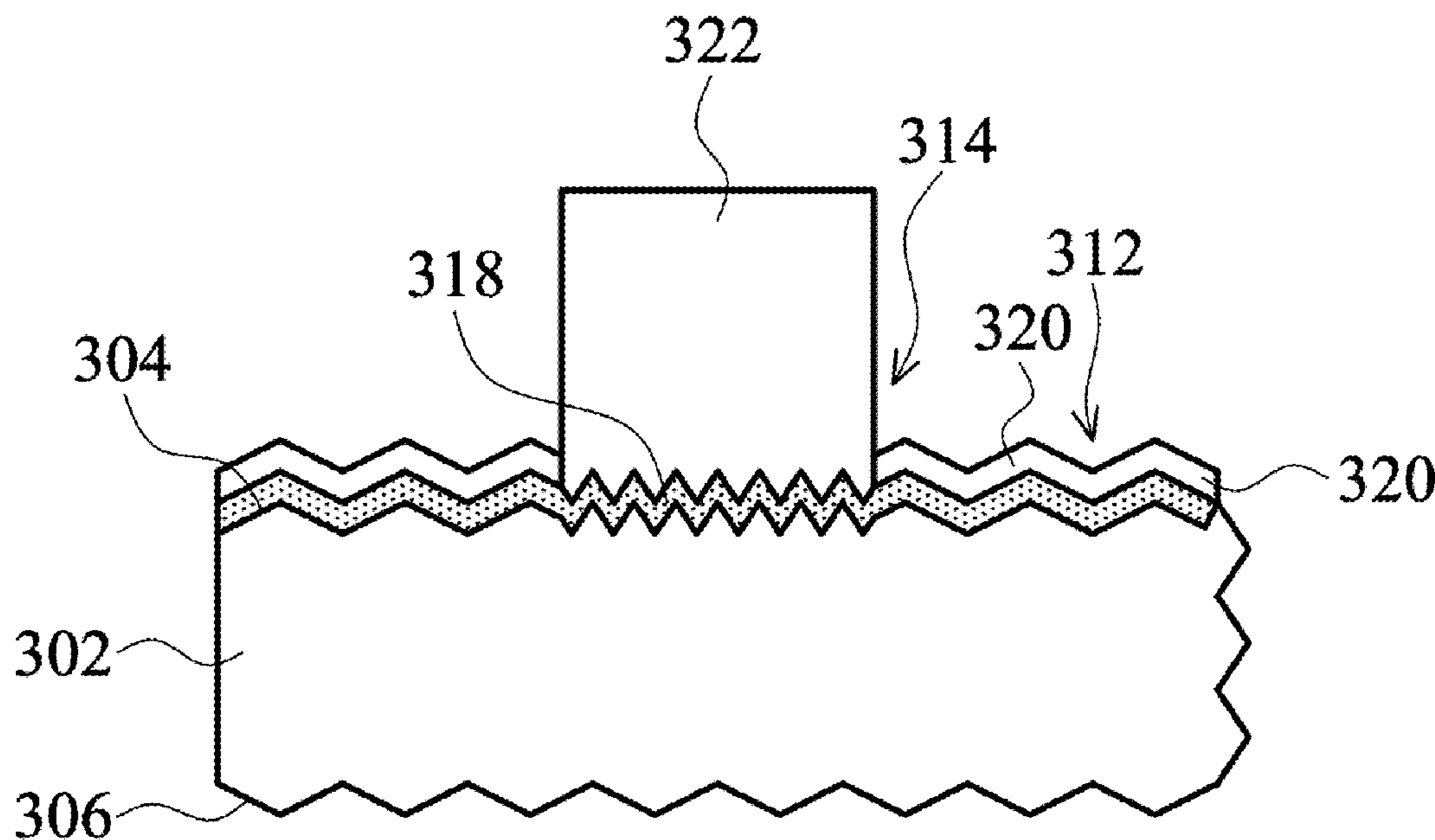
(52) **U.S. Cl.**
CPC ***H01L 31/18*** (2013.01); ***H01L 31/035281*** (2013.01); ***H01L 31/02168*** (2013.01)

(57) **ABSTRACT**

A method for forming a solar cell with selective emitters is provided. The method for forming a solar cell with selective emitters includes providing a substrate; forming a first texture structure on a first surface of the substrate; performing a doping process to the first surface of the substrate to form a first doping region in the substrate; forming a pattered barrier layer in a second region on the first surface of the substrate, wherein another portion of the substrate in a first region is exposed; performing a second texture etching process to etch the first region of the substrate uncovered by the patterned barrier layer; removing the patterned barrier layer; and forming an electrode on the second region of the substrate.



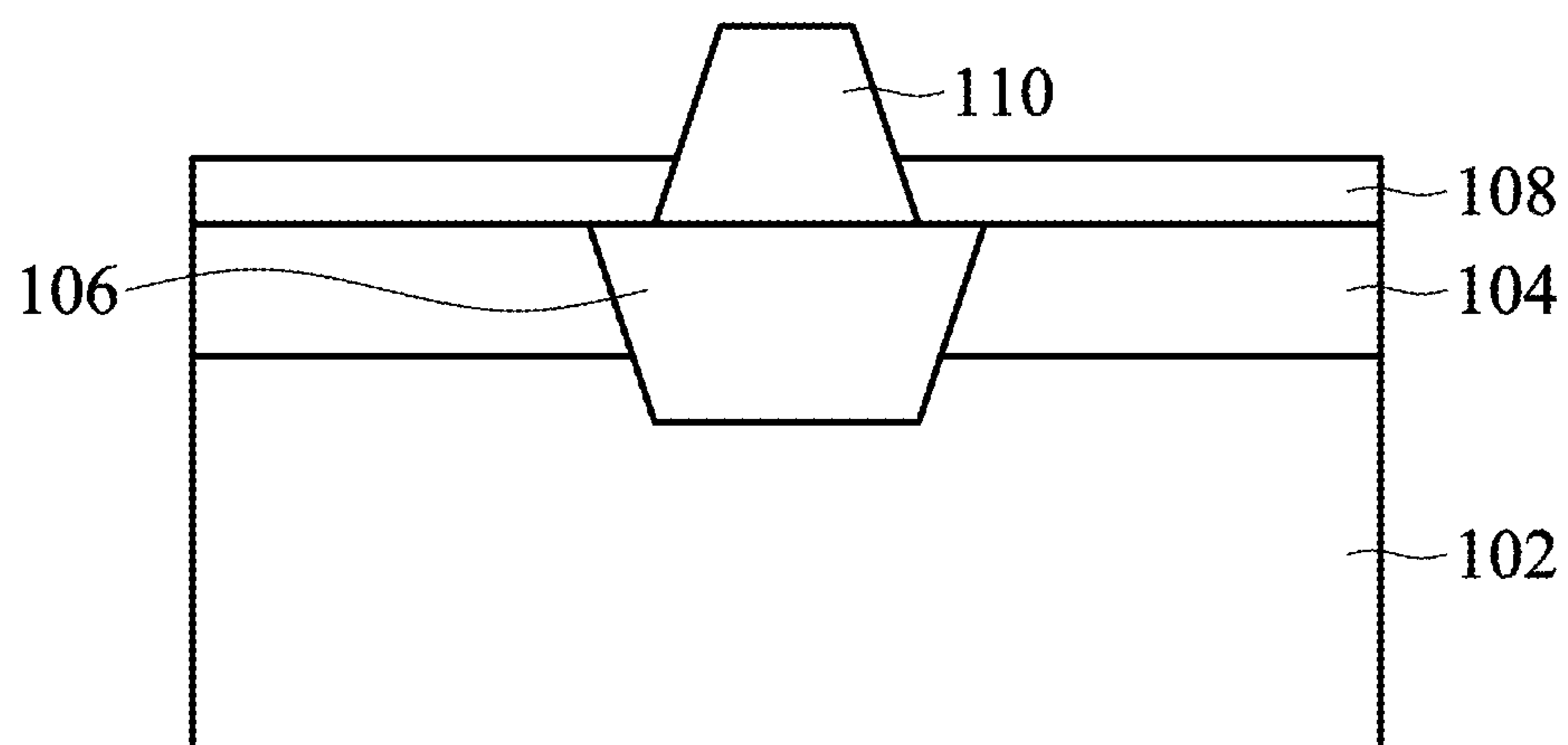


FIG. 1

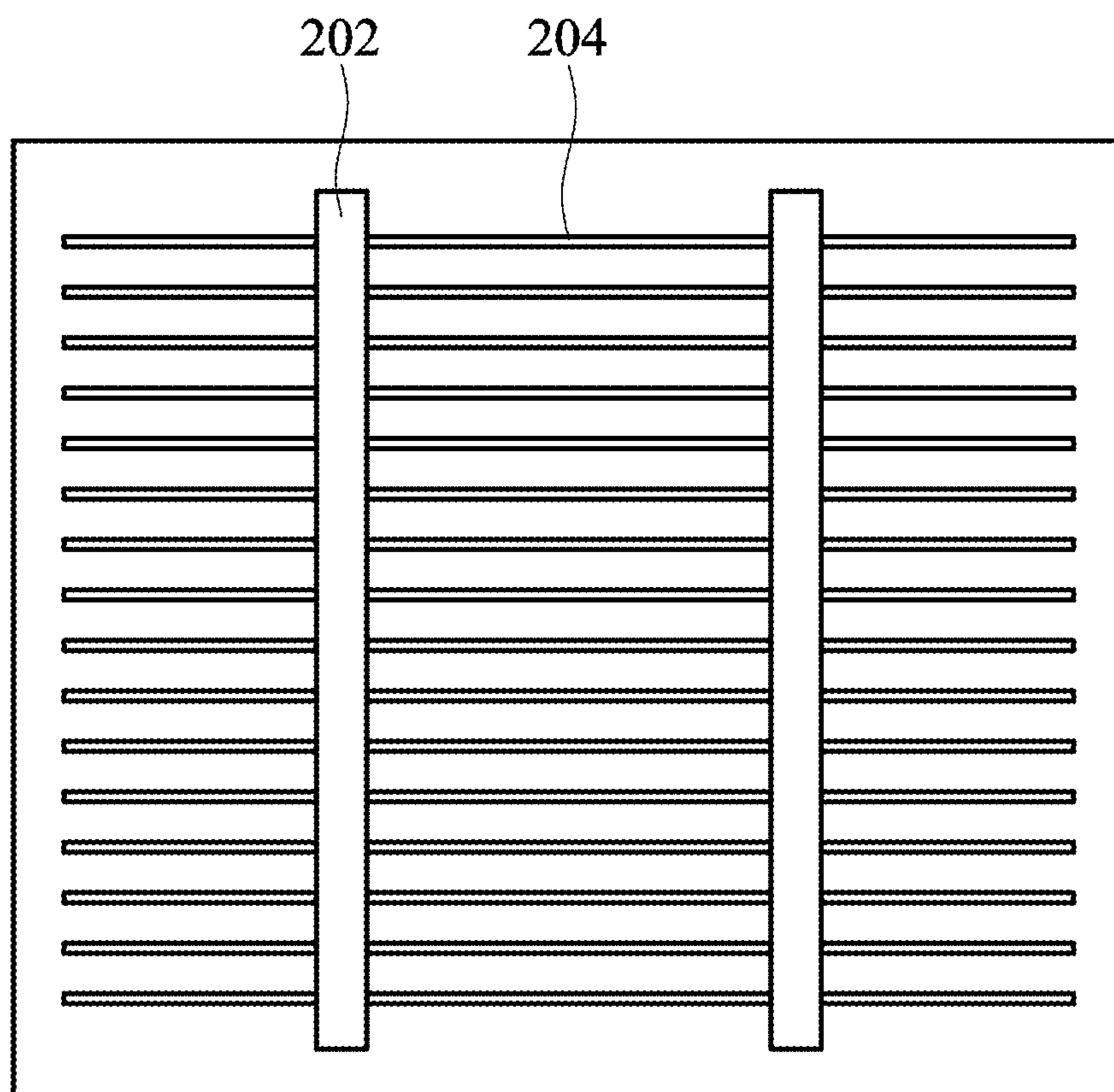


FIG. 2

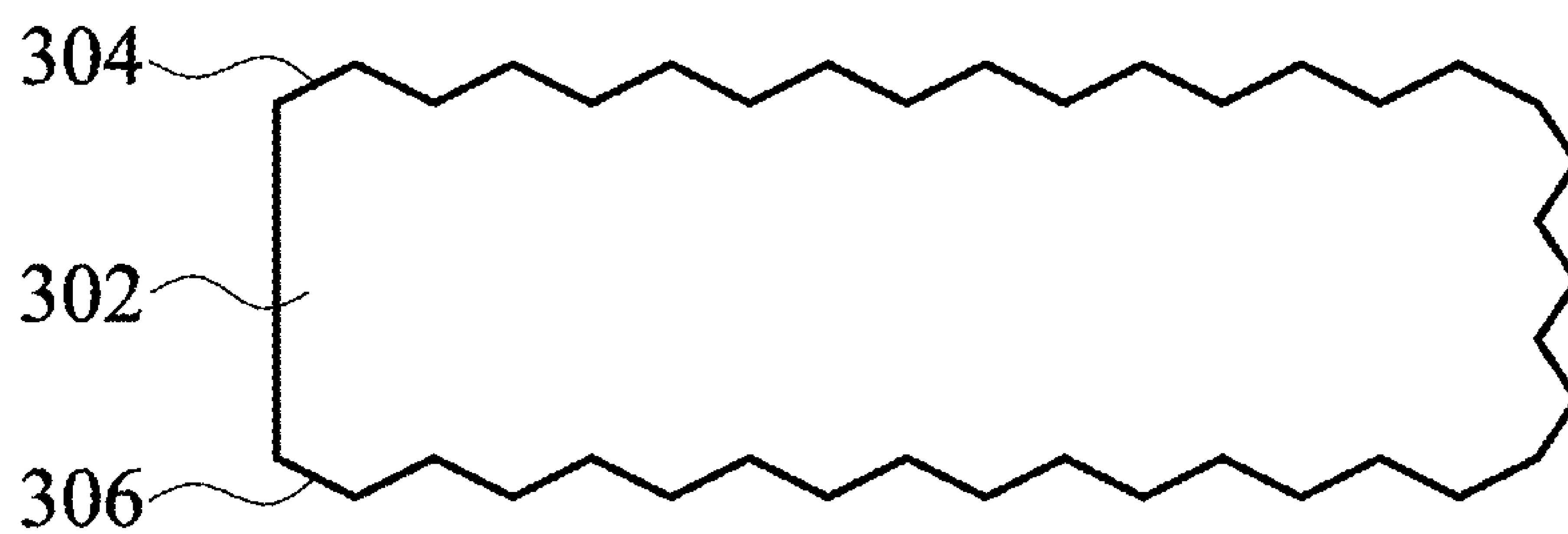


FIG. 3A

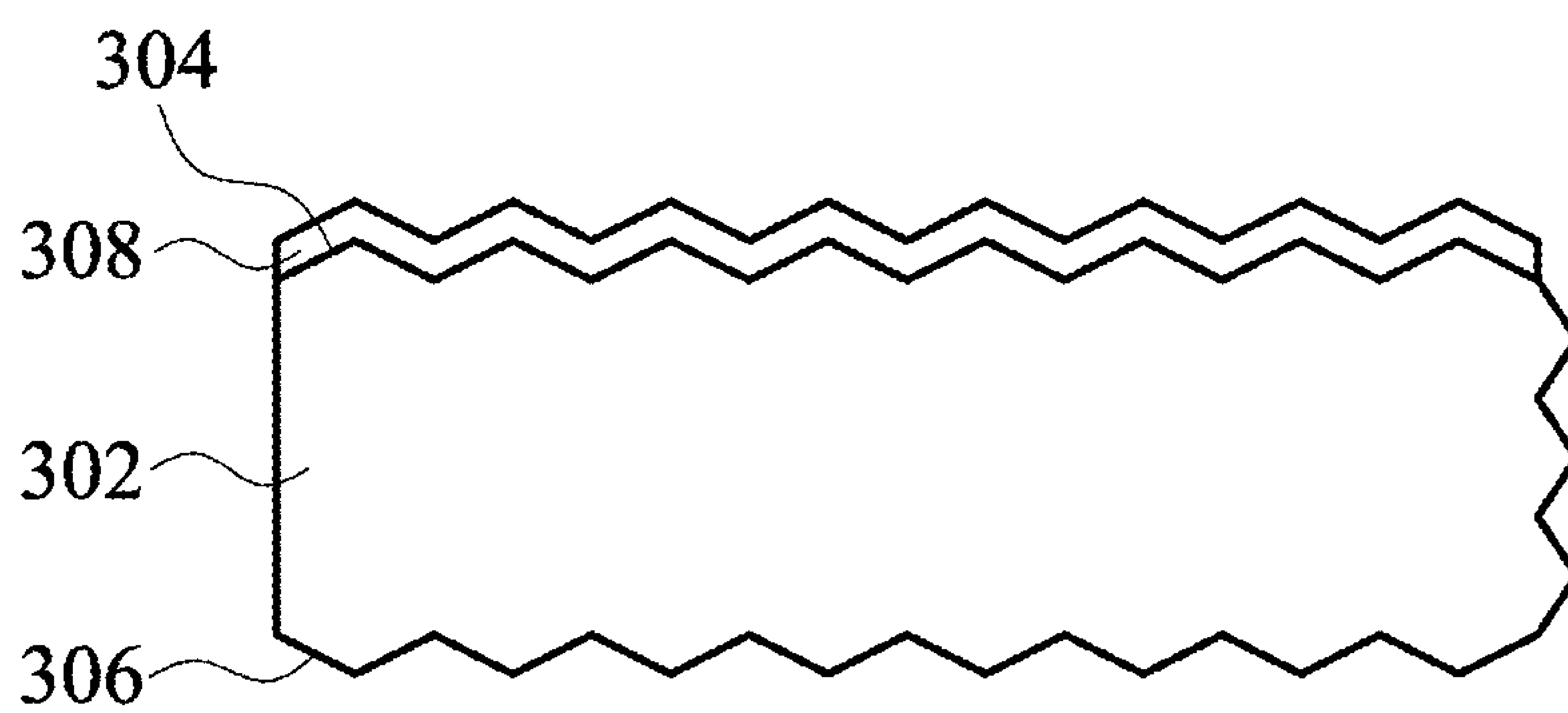


FIG. 3B

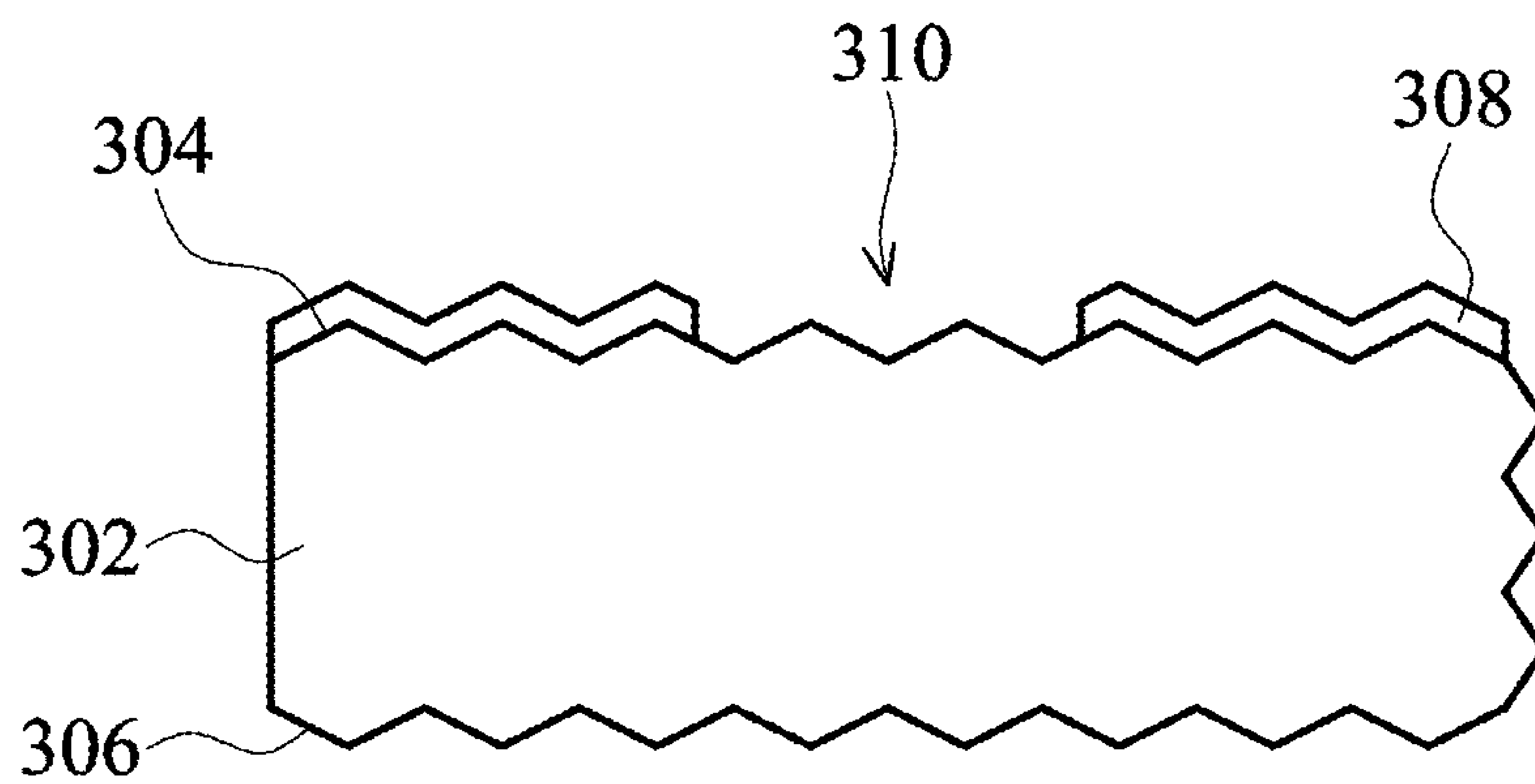


FIG. 3C

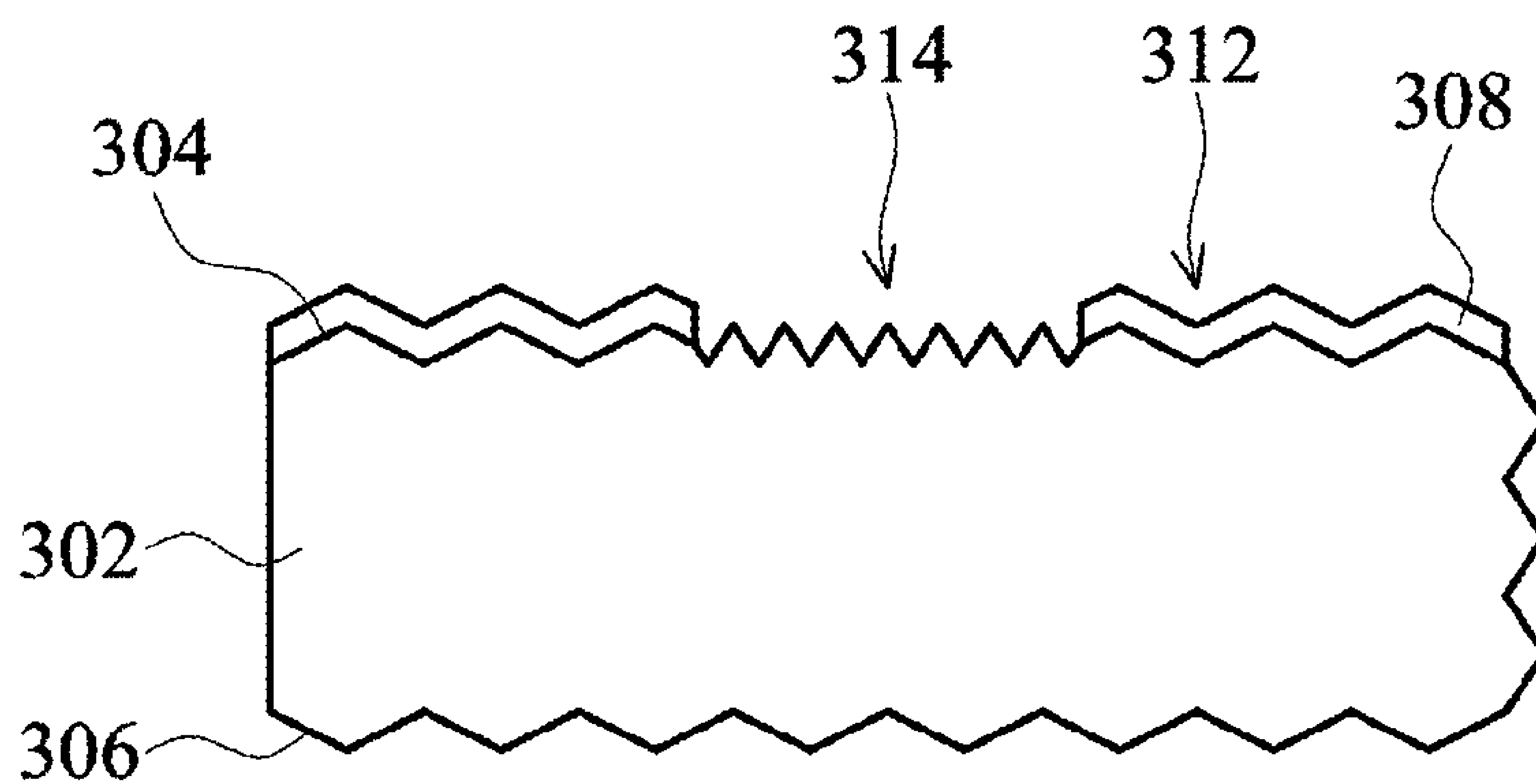


FIG. 3D

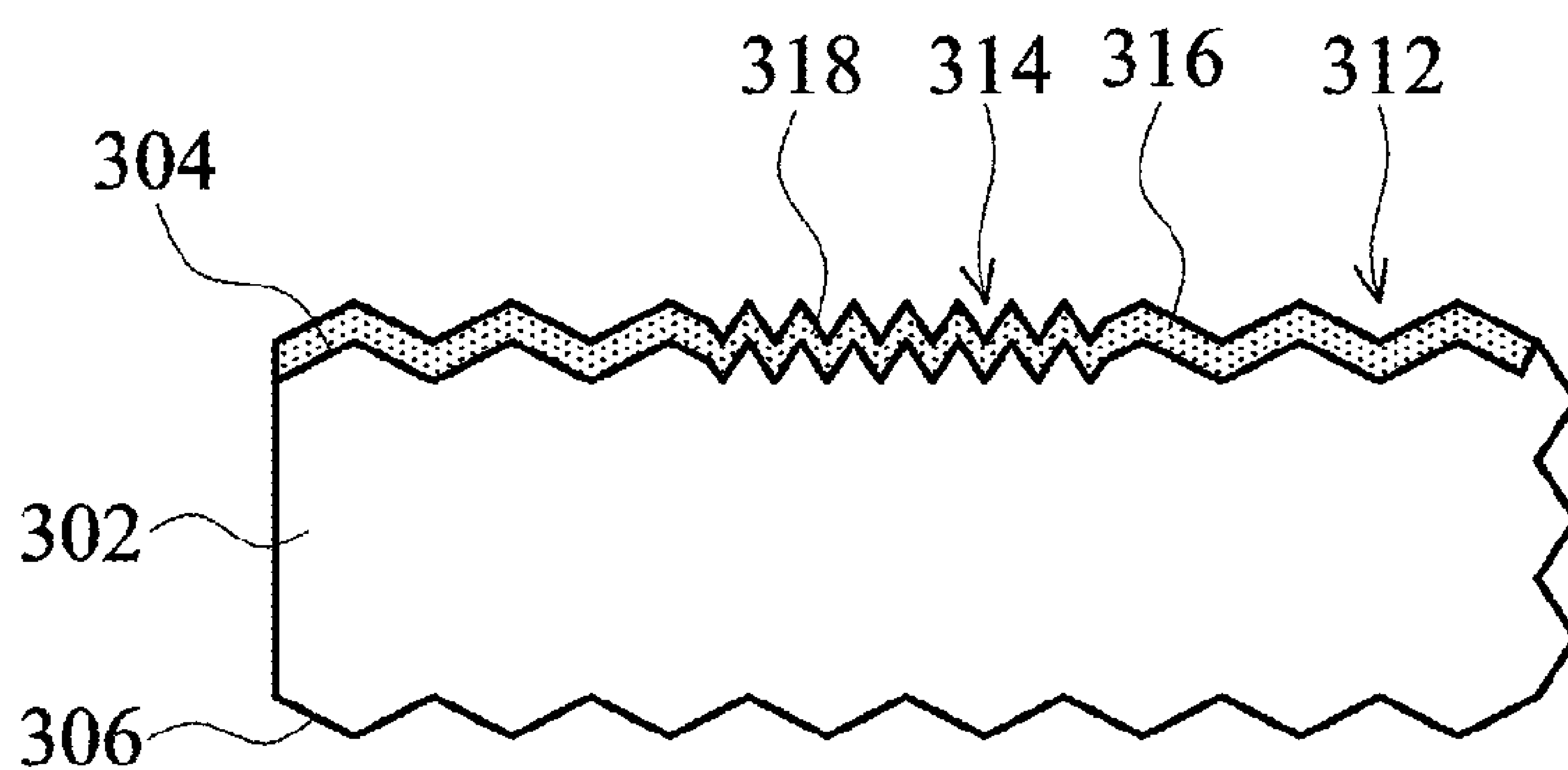


FIG. 3E

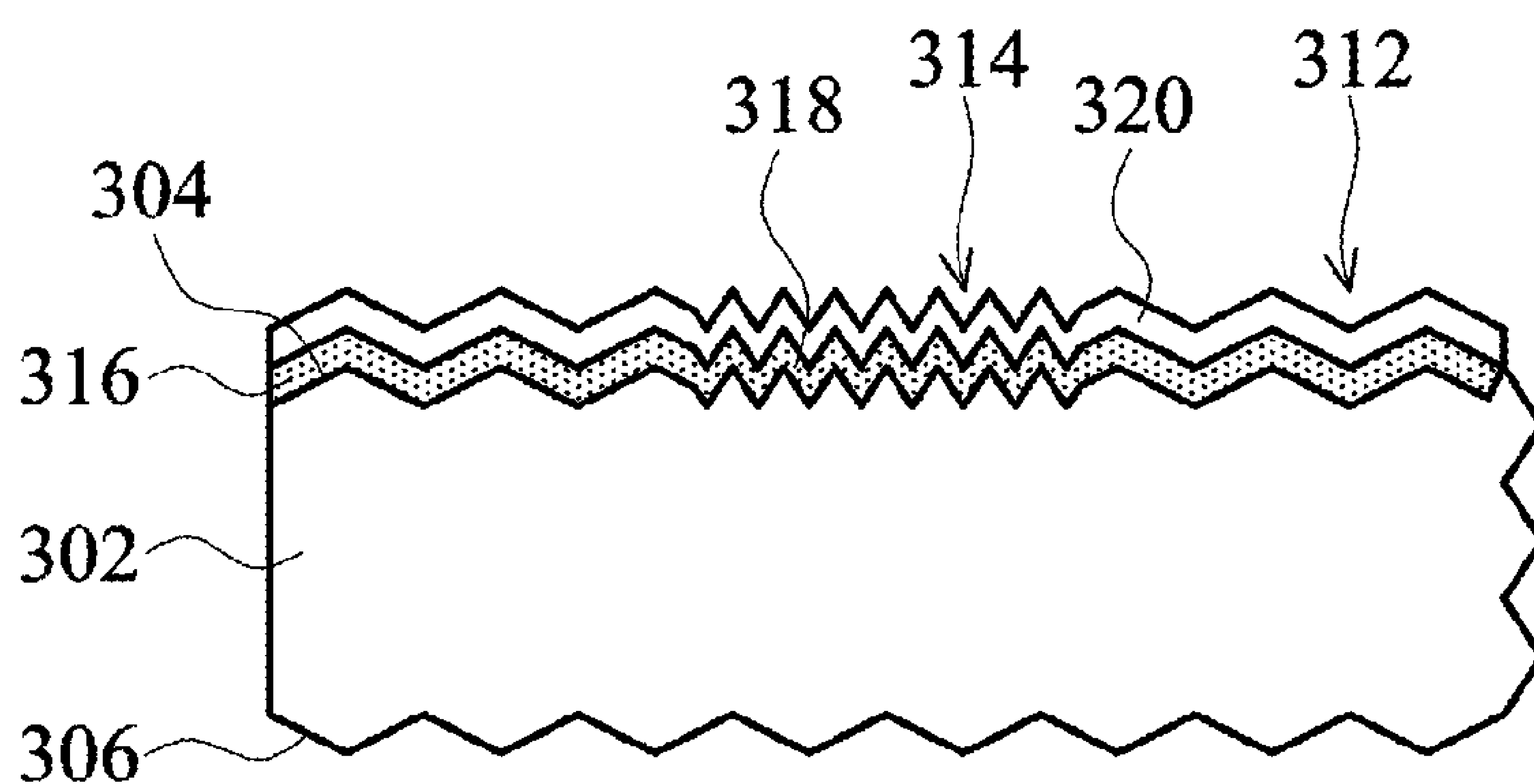


FIG. 3F

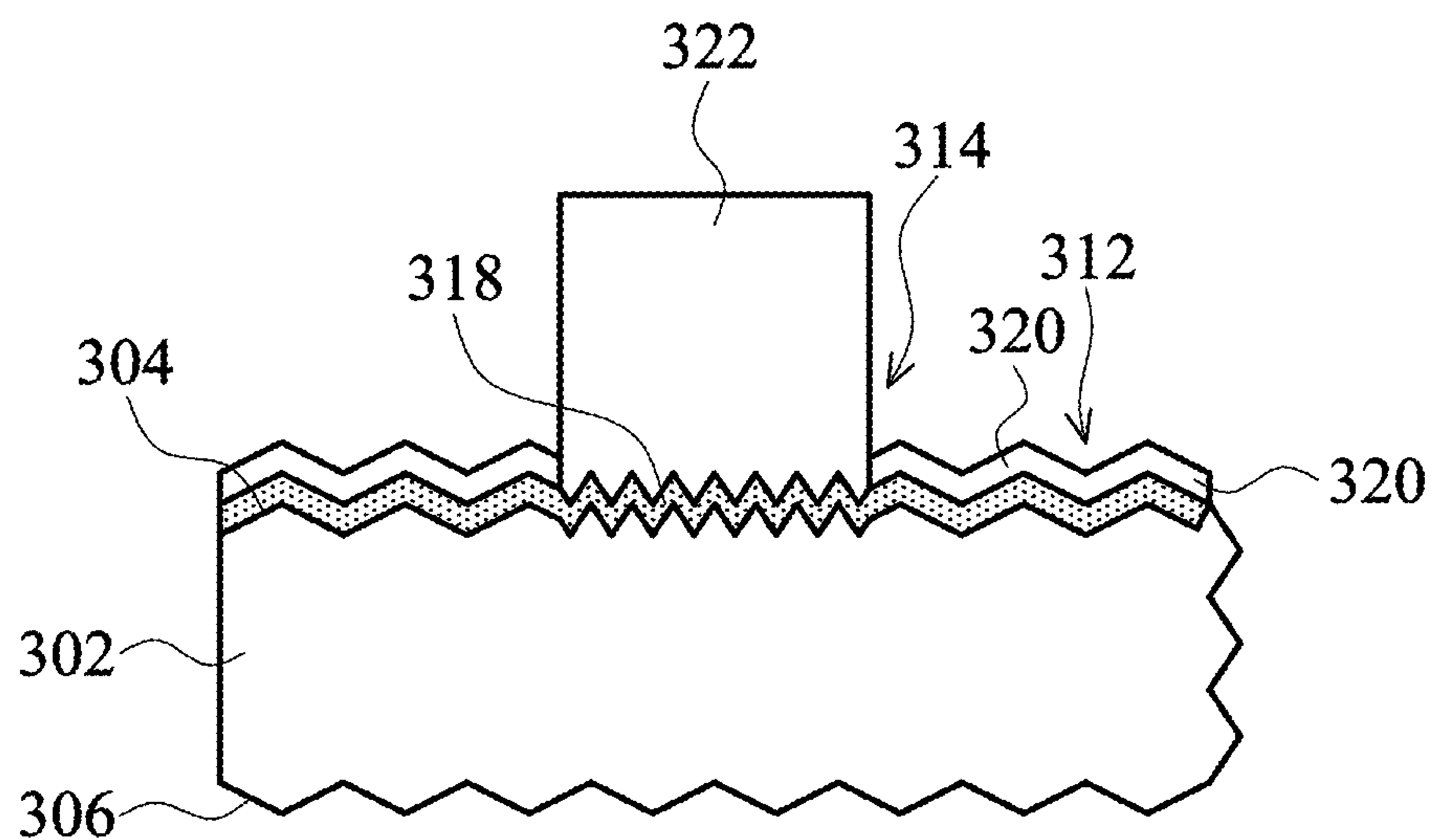


FIG. 3G

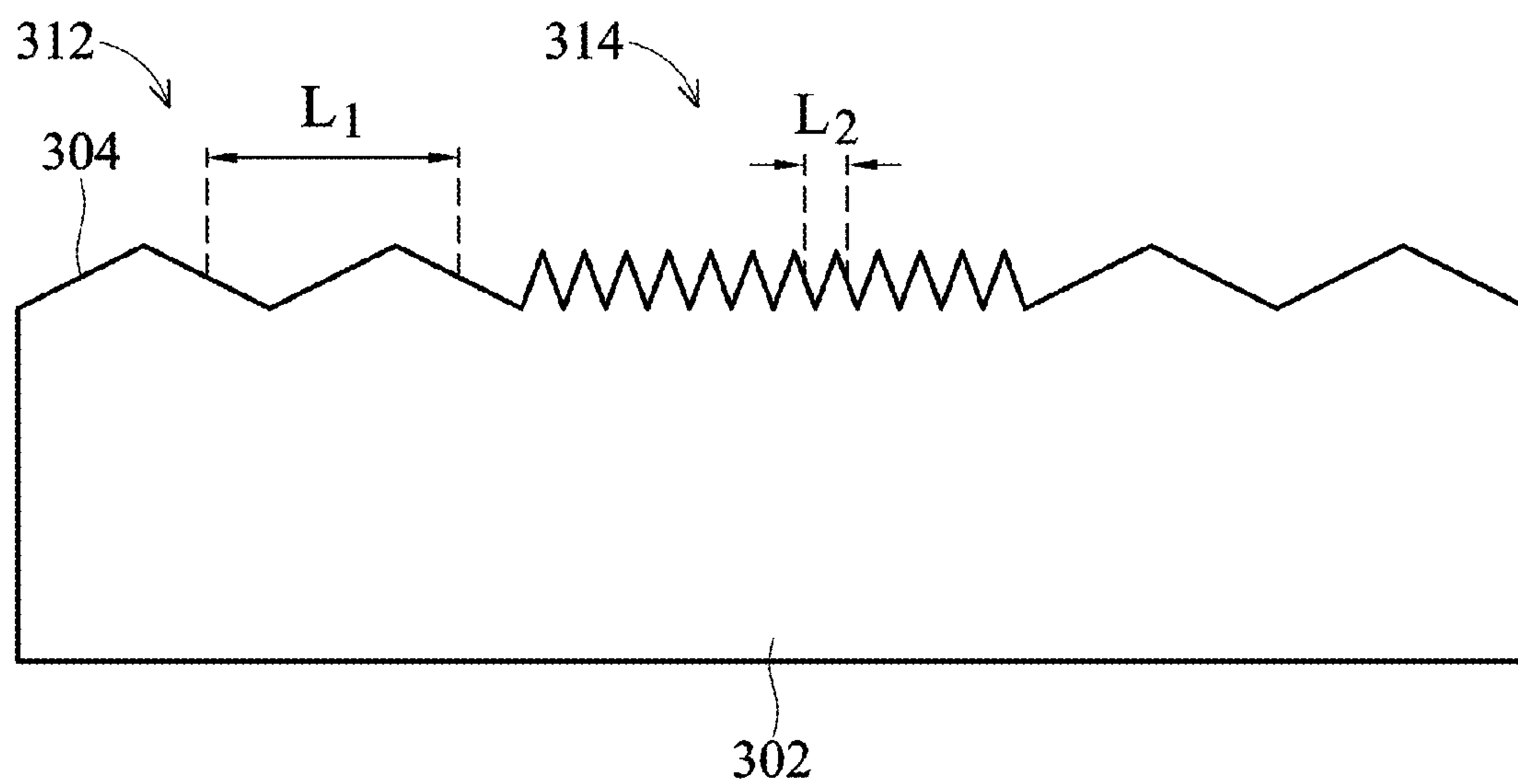


FIG. 4

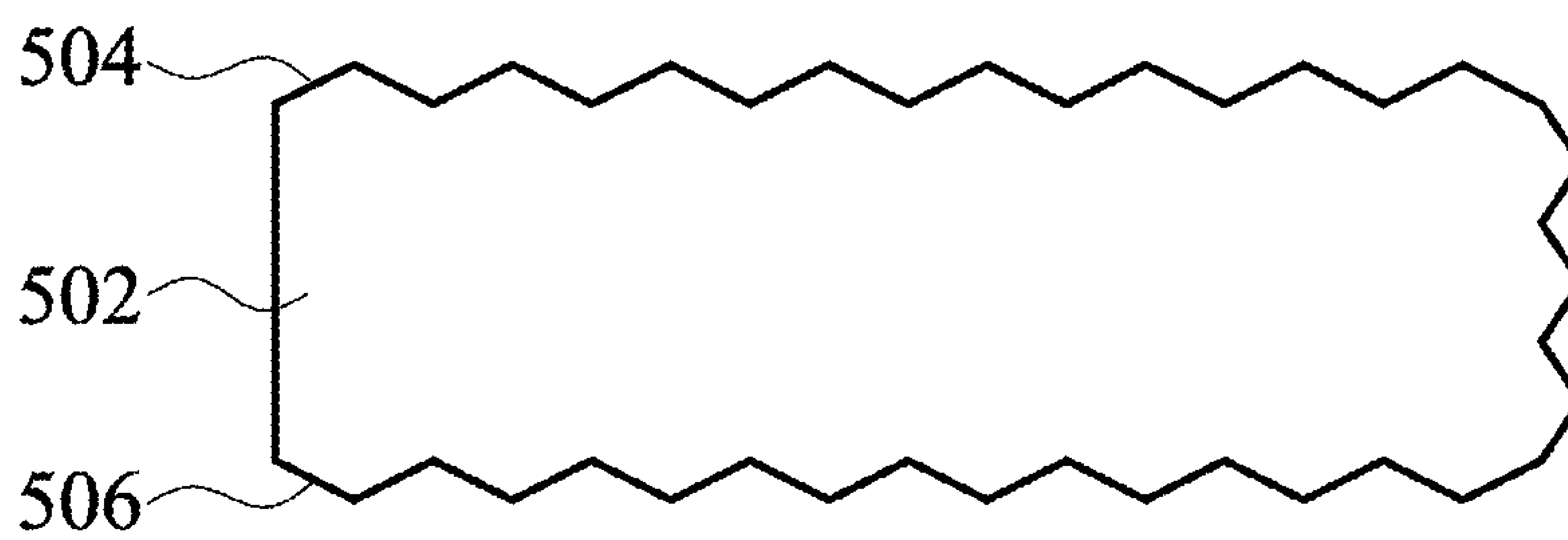


FIG. 5A

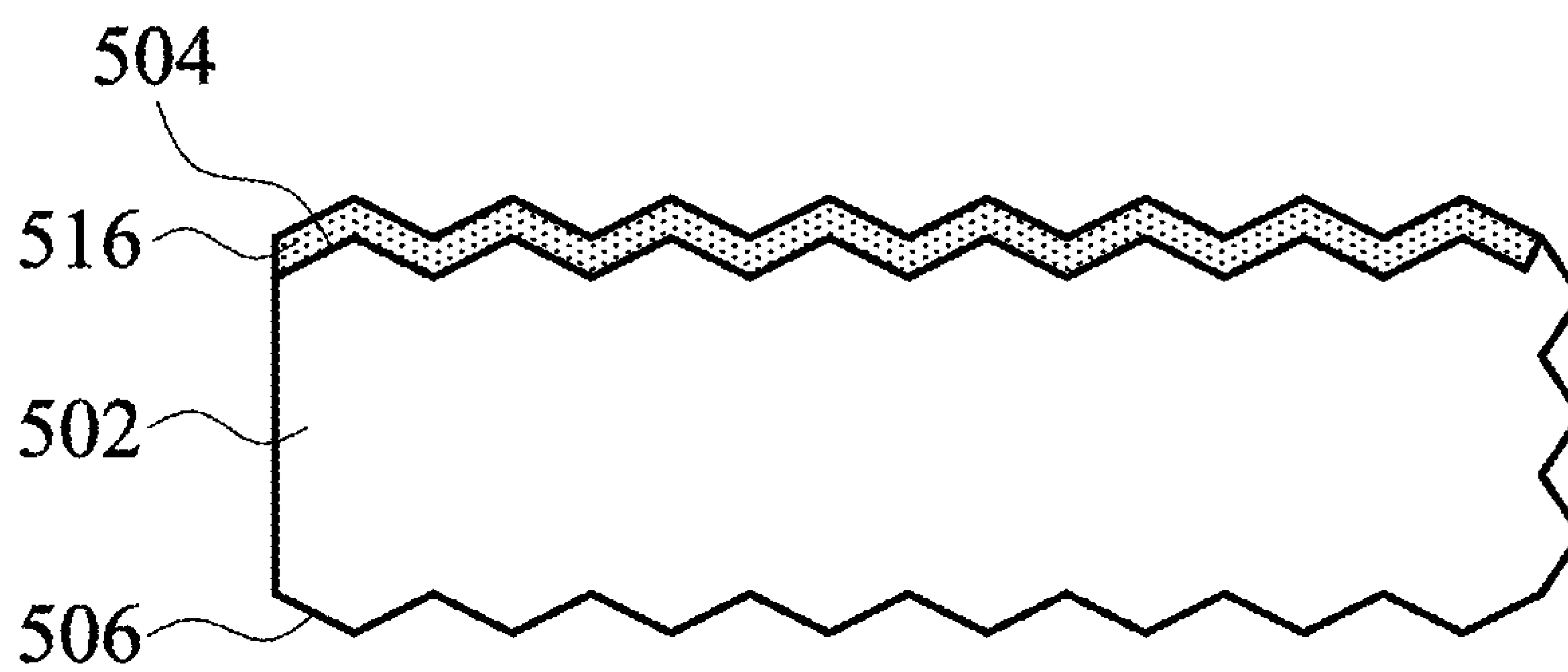


FIG. 5B

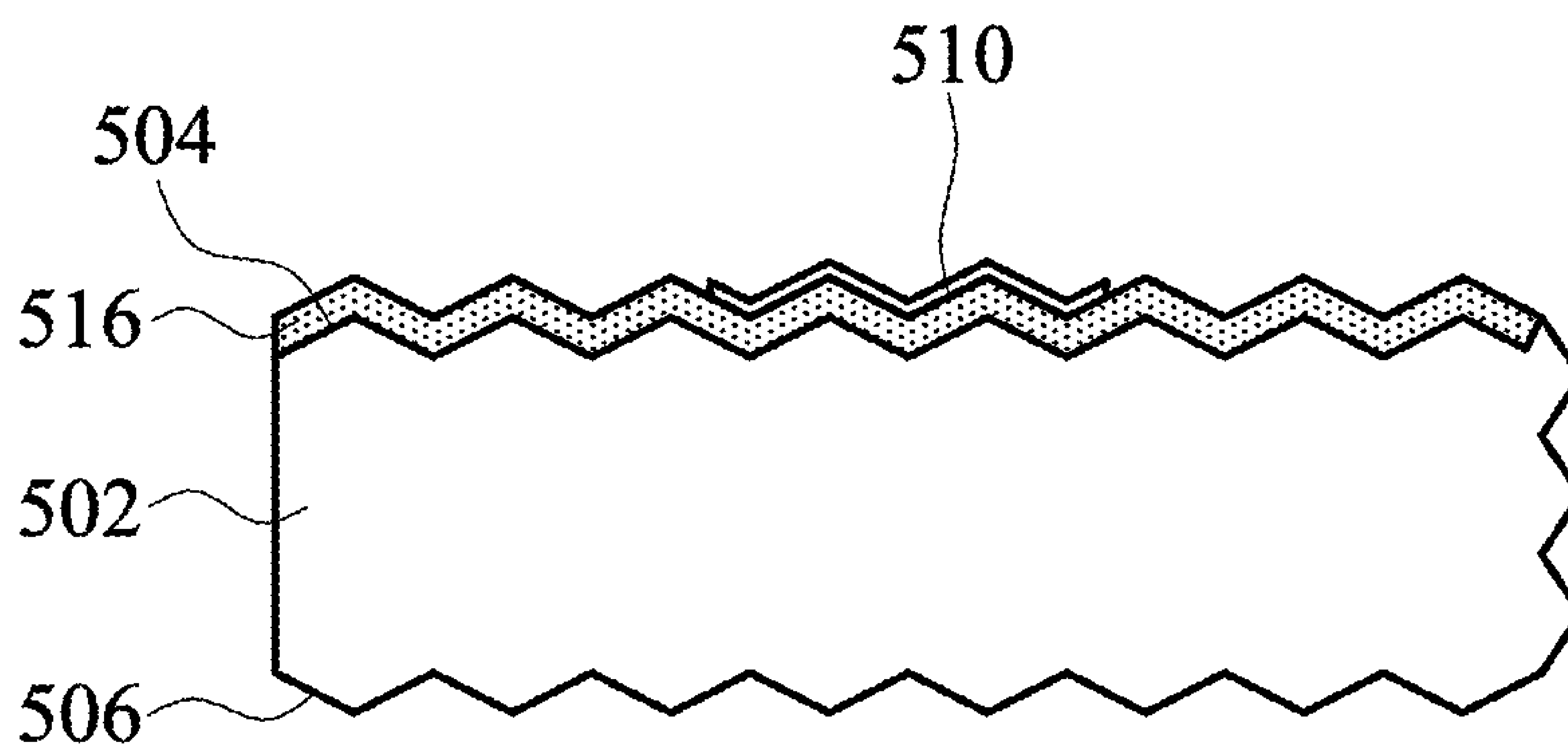


FIG. 5C

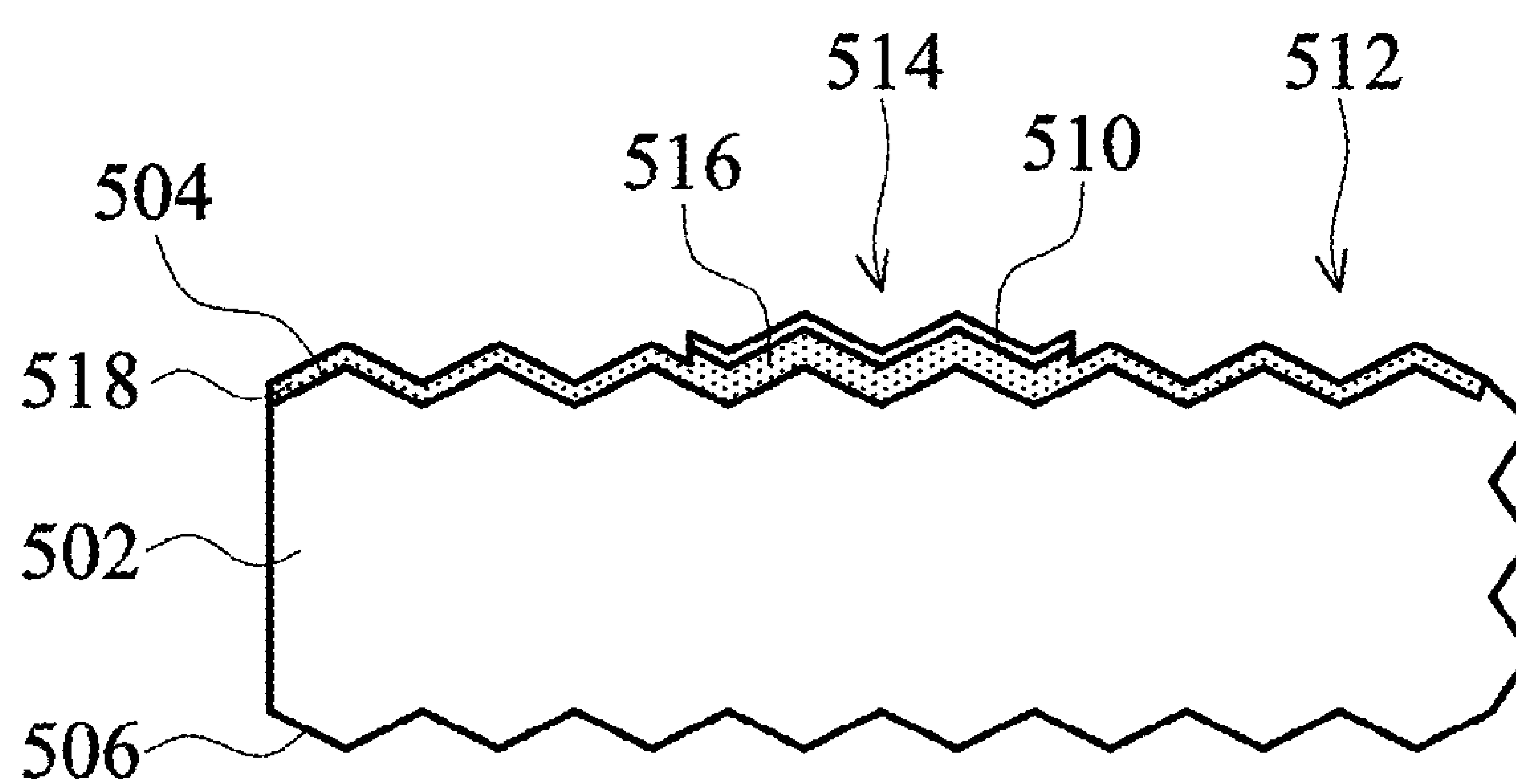


FIG. 5D

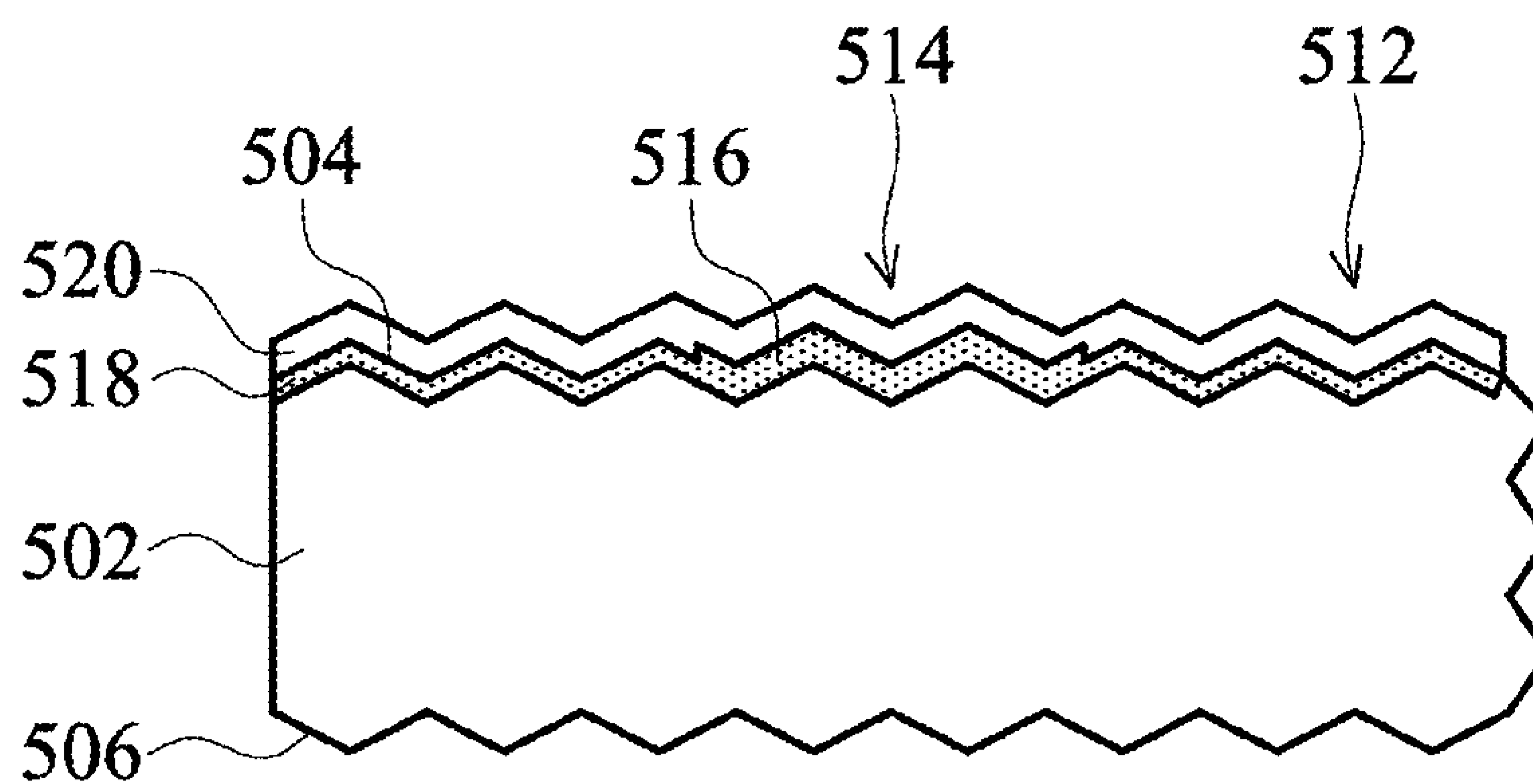


FIG. 5E

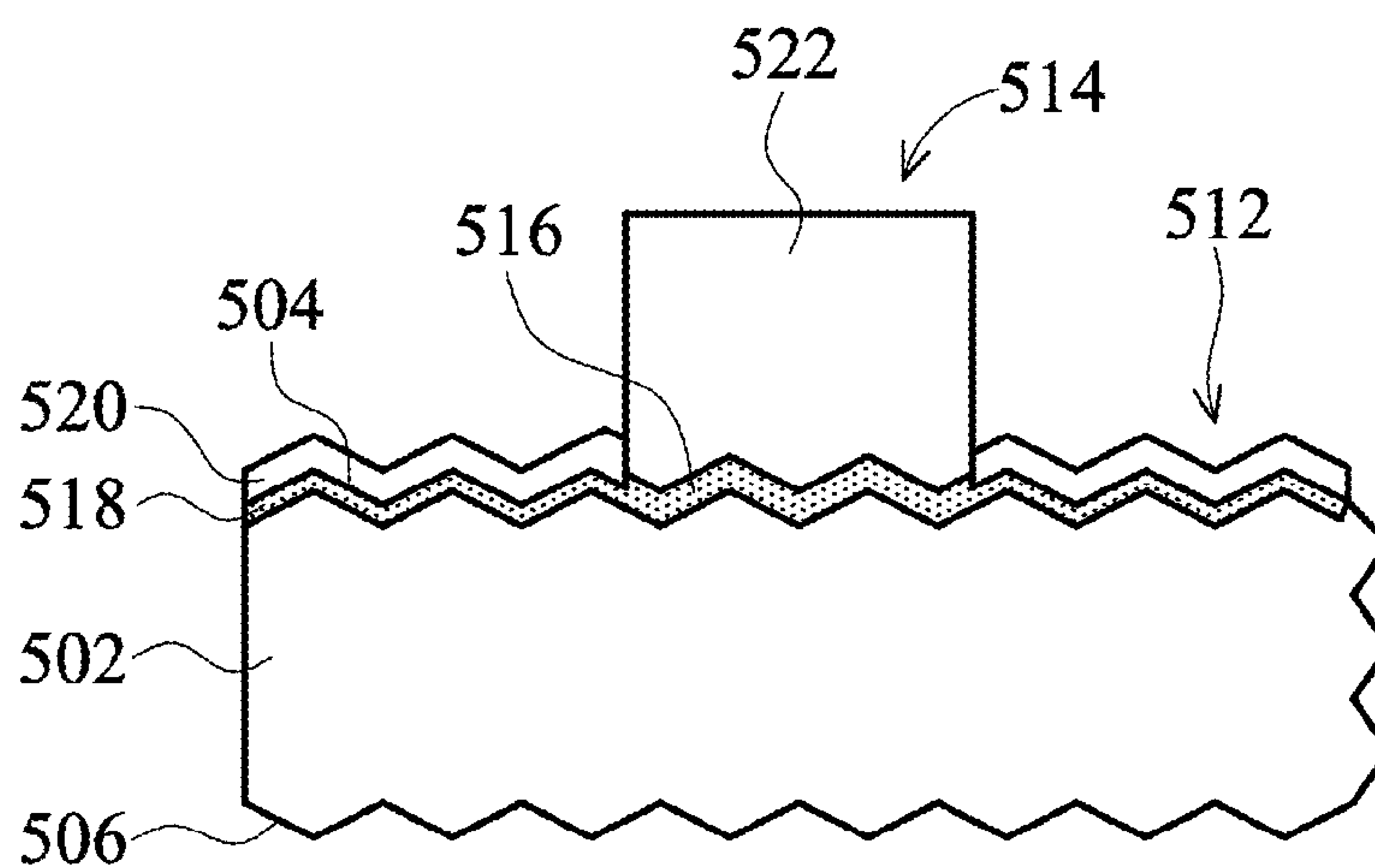


FIG. 5F

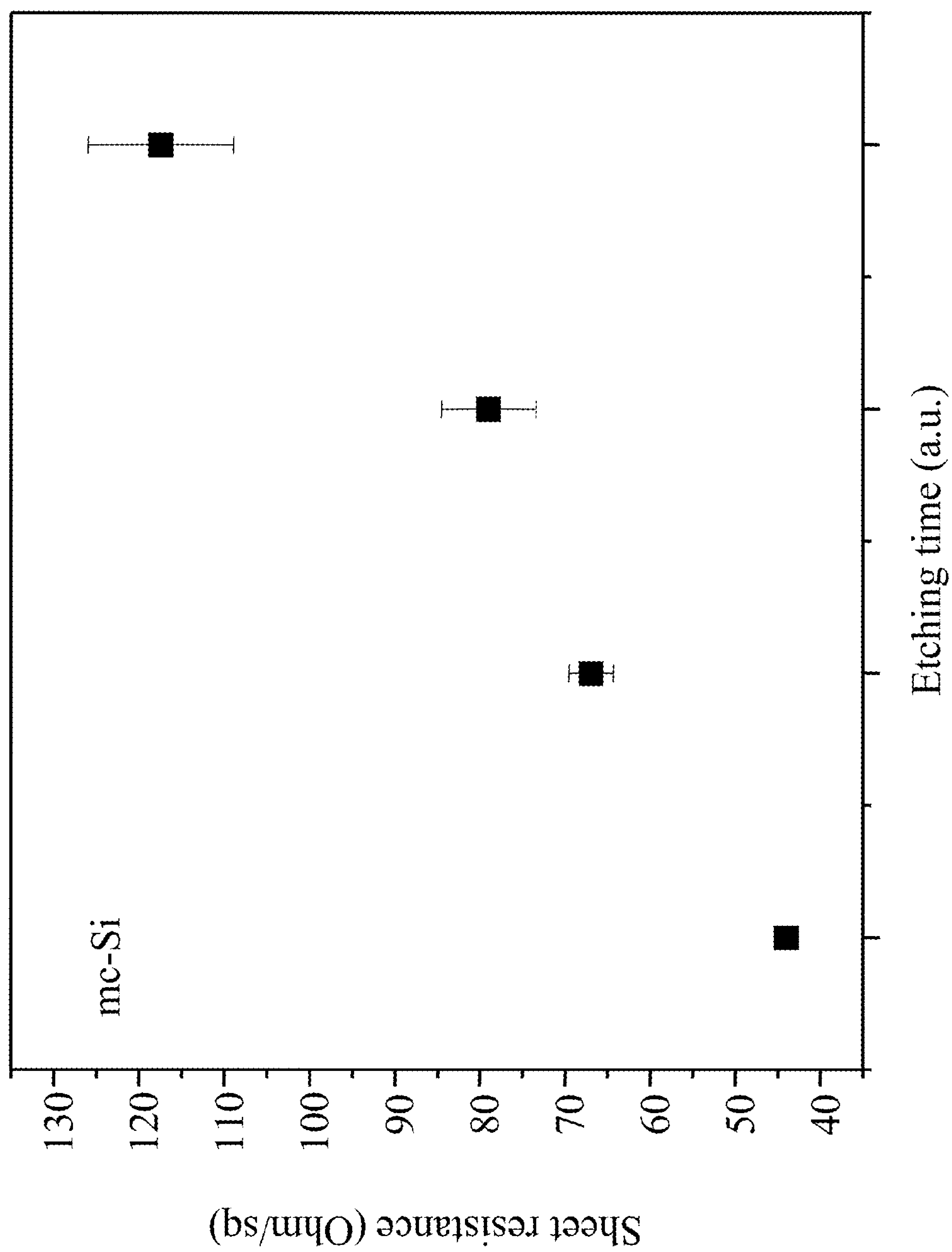


FIG. 6A

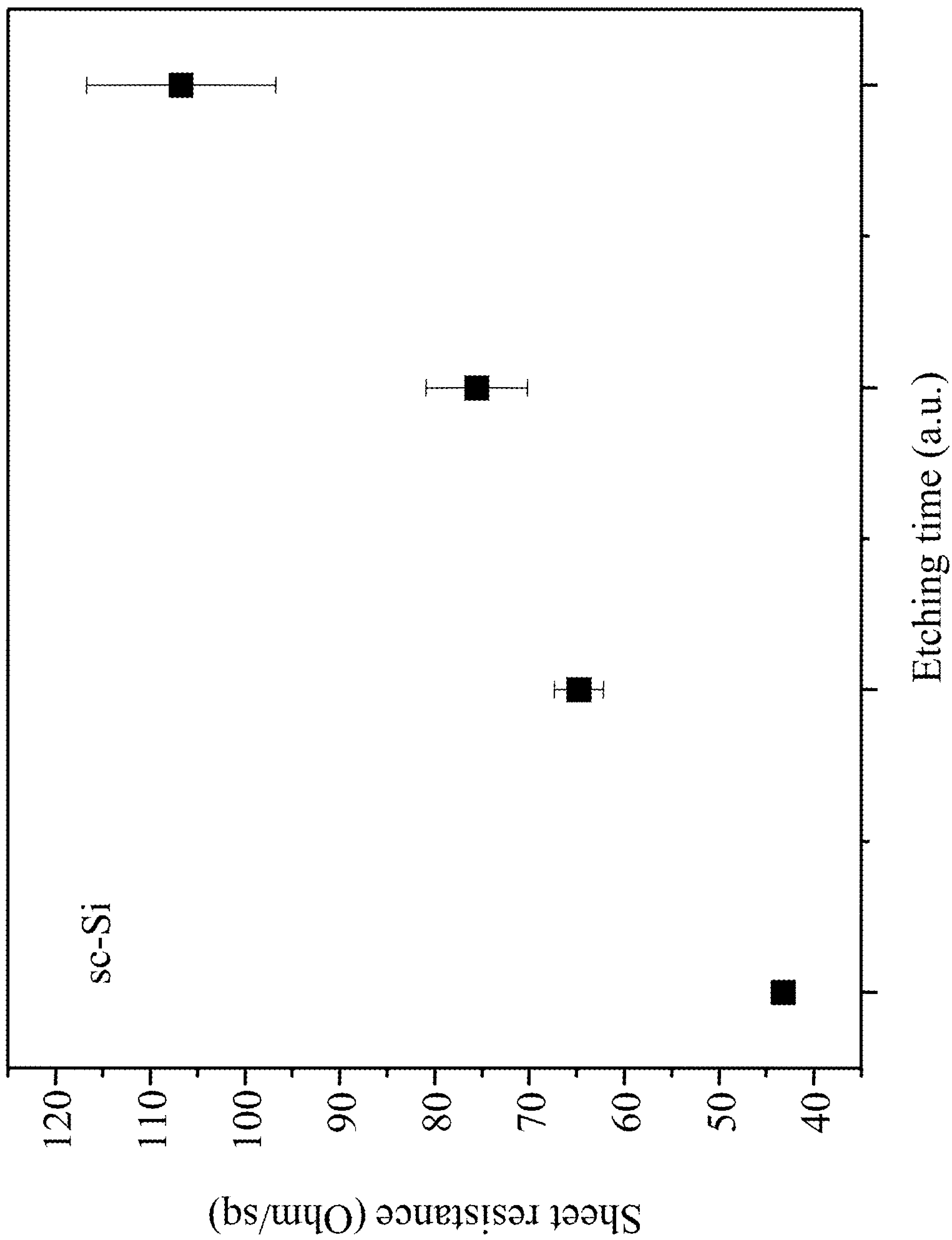


FIG. 6B

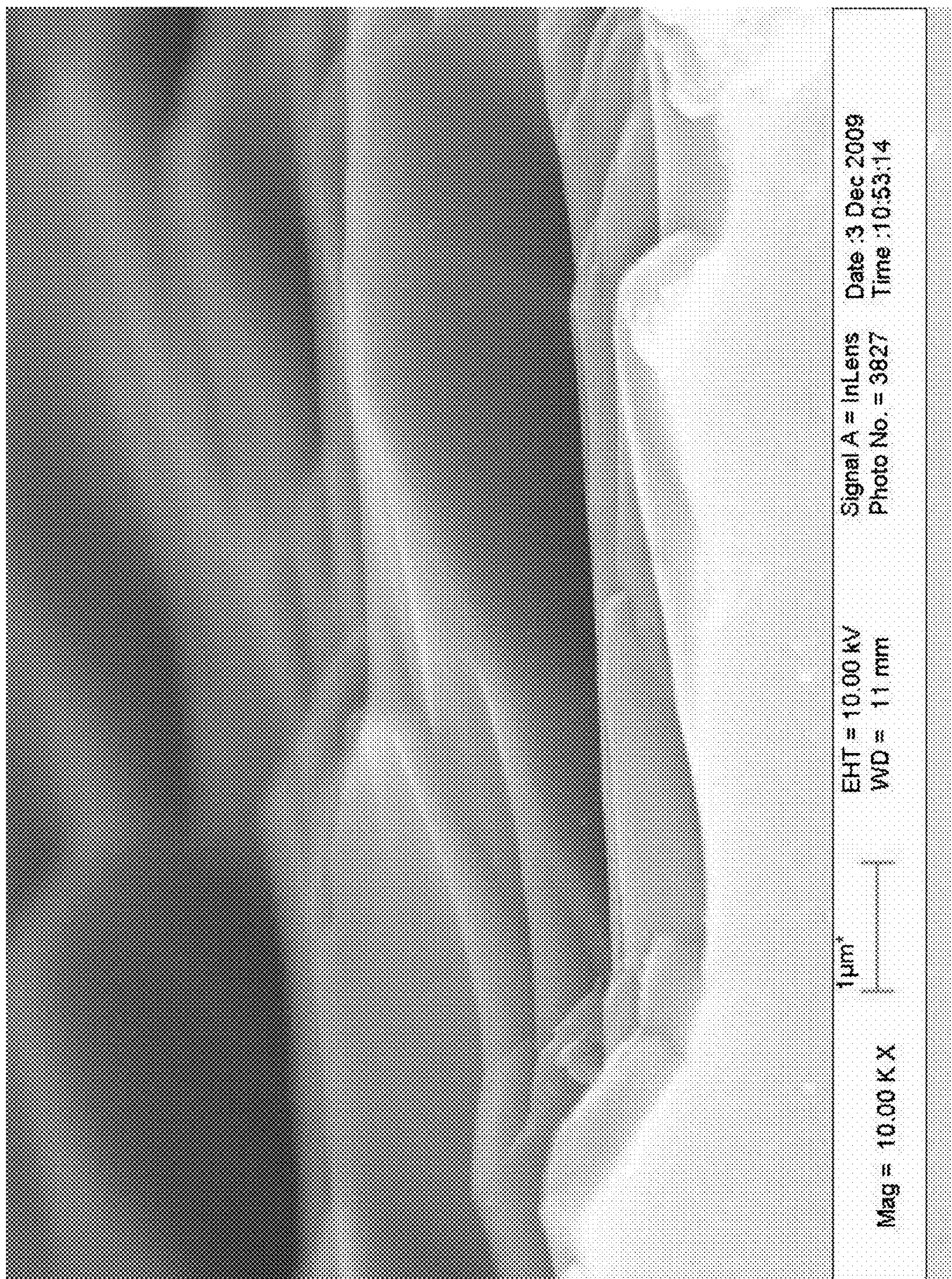


FIG. 7

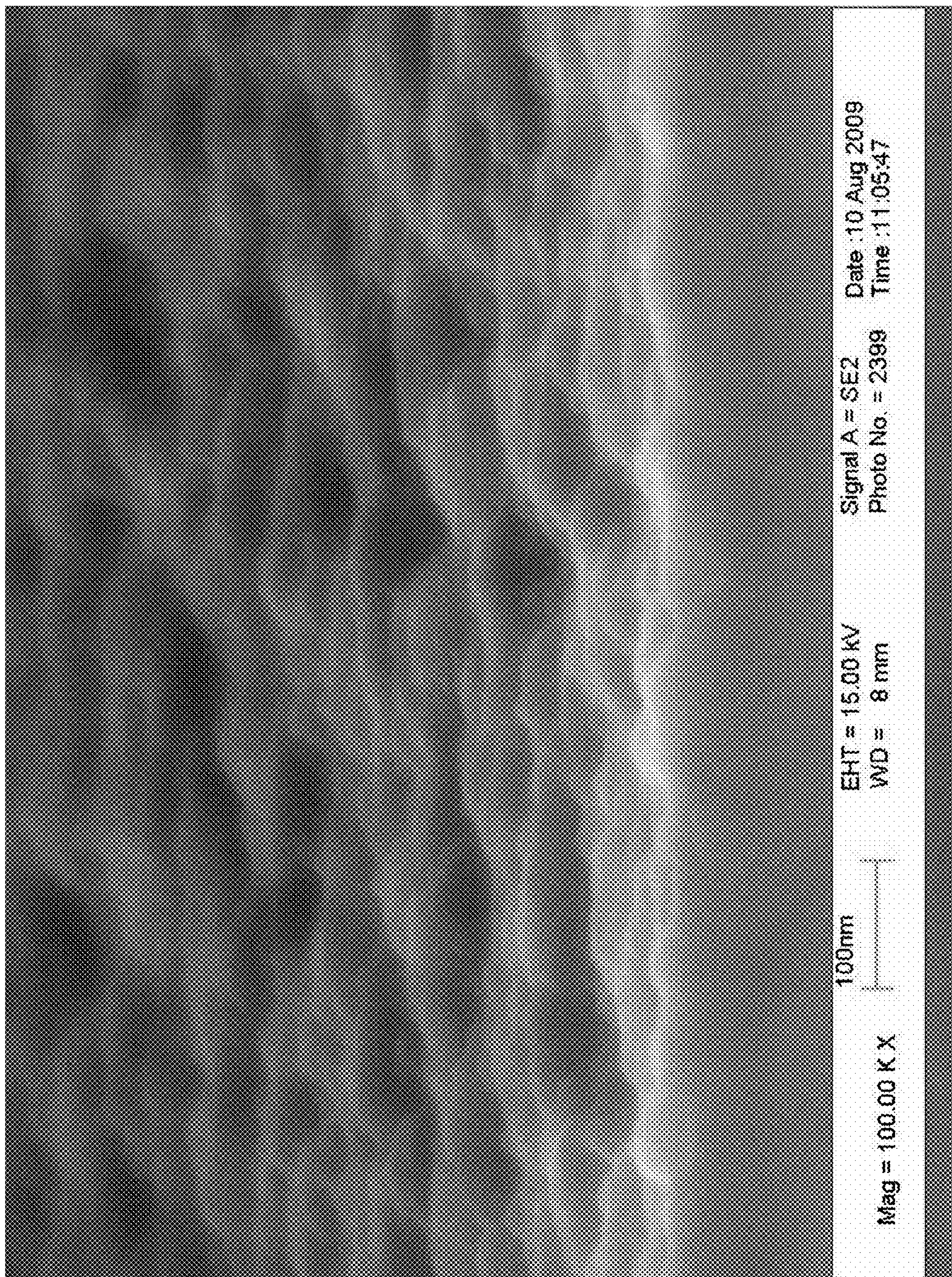
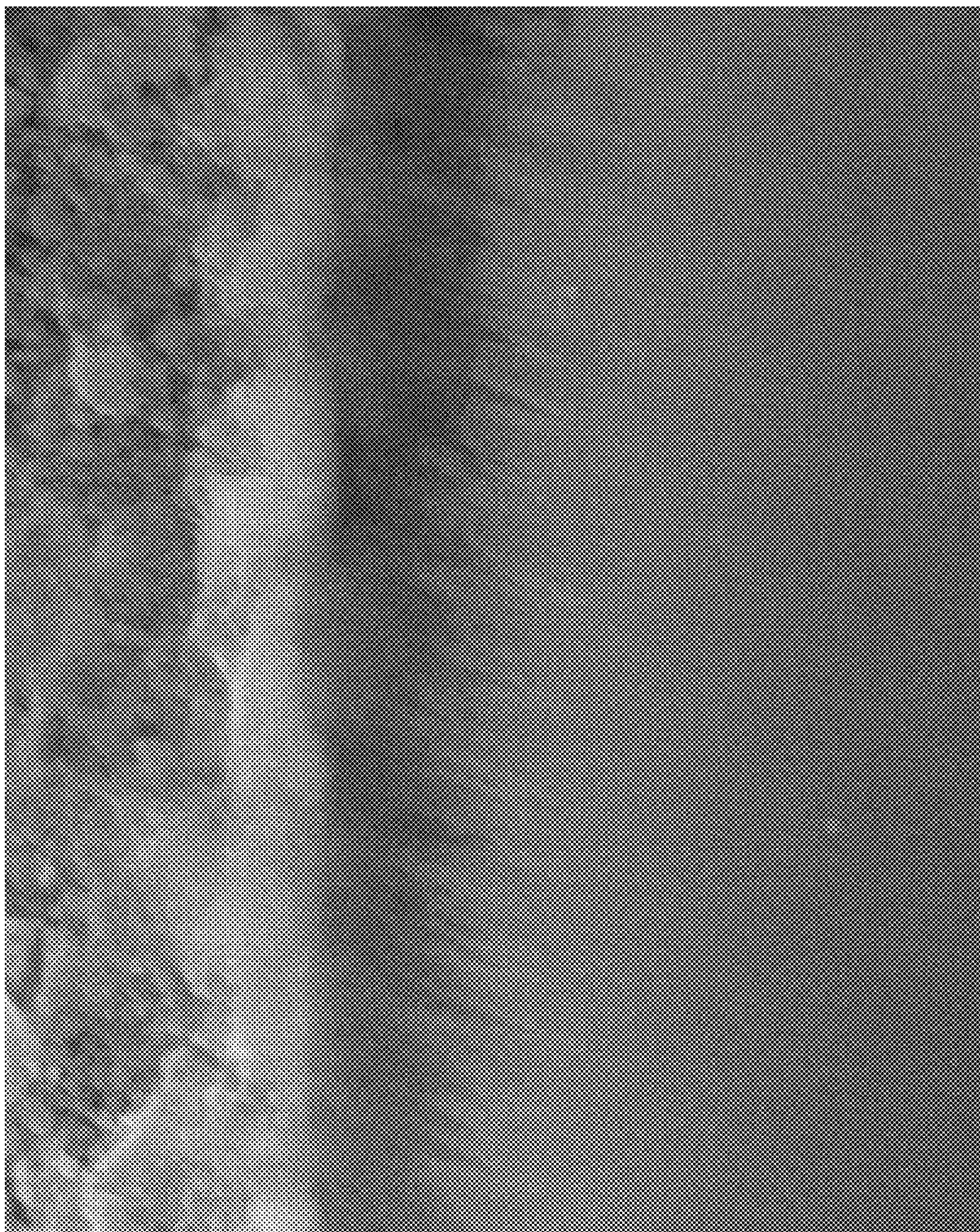


FIG. 8

FIG. 9



METHOD FOR FORMING SOLAR CELL WITH SELECTIVE EMITTERS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority from, and is a divisional application of, U.S. patent application Ser. No. 13/165,670 filed on Jun. 21, 2011, entitled "Method for forming solar cell with selective emitters", which claims the benefit of priority from Taiwan Application No. 099135511, filed on Oct. 19, 2010 and the entirety of which is incorporated by reference herein.

BACKGROUND

[0002] 1. Technical Field

[0003] The disclosure relates generally to a solar cell and fabrication thereof, and more particularly to a solar cell with selective emitters and fabrication thereof.

[0004] 2. Description of the Related Art

[0005] A solar cell with selective emitters has improved conversion efficiency. FIG. **1** is a cross section of a solar cell having a selective emitter. Referring to FIG. **1**, the solar cell having a selective emitter comprises a high concentration doping region **106** in a portion of a substrate **102** under an electrode **110**, a low concentration doping region **104** in the other portion of the substrate **102** outside of the electrode, and an anti-reflective layer **108** on the substrate. The solar cell has a higher open circuit voltage (Voc) and short-circuit current (Isc) than the conventional solar cell having only one doping concentration, since the low doping concentration doping emitter between the electrodes can reduce carrier recombination on the surface of the solar cell and the high concentration doping region under the electrodes can provide good electrode contacts. Therefore, the solar cell with selective emitters has high photoelectric conversion efficiency.

[0006] Since the solar cell with selective emitters has a significant advantage over the conventional solar cell having only one doping concentration, a method for forming a solar cell with selective emitters and fabrication thereof, having a simple process to form high concentration doping regions under the electrodes and low concentration doping regions in the other non-electrode regions is required.

SUMMARY

[0007] The disclosure provides a method for forming a solar cell with selective emitters, comprising, providing a substrate, forming a first texture structure on a first surface of the substrate, forming a barrier layer on the first surface of the substrate, selectively removing a portion of the barrier layer to form an opening exposing the substrate, wherein a portion of the substrate under the barrier layer is a first region and another portion of the substrate under the opening of the barrier layer is a second region, and performing a texture etching process to the second region to form a second texture structure under the opening of the barrier layer, wherein the first texture structure and the second texture structure comprise a plurality of protruding portions and recessing portions, and the distance between neighboring protruding portions of the first texture structure is L_1, the distance between neighboring protruding portions of the second texture structure is L_2, and L_1 is about 2-20 times that of L_2. The method for forming the solar cell with selective emitters further comprises removing the barrier layer, performing a doping process to the first region to form a first doping region and forming a second doping region in the second region of the substrate, and forming an electrode on the second doping region.

[0008] The disclosure further provides a solar cell with selective emitters, comprising a substrate, wherein a first region on a first surface of the substrate has a first texture structure, and a second region on the first surface of the substrate has a second texture structure, and the first texture structure and the second texture structure comprise a plurality of protruding portions and recessing portions, and the distance between neighboring protruding portions of the first texture structure is L_1, the distance between neighboring protruding portions of the second texture structure is L_2, and L_1 is 2-20 times that of L_2, a first doping region under the first region and a second doping under the second doping region, wherein a concentration of the second doping region is higher than that of the first doping region, and an electrode overlies the second region.

[0009] The disclosure yet further provides a method for forming a solar cell with selective emitter, comprising, providing a substrate, forming a first texture structure on a first surface of the substrate, doping the first surface of the substrate to form a first doping region, forming a patterned barrier in a second region on the first surface of the substrate, wherein another portion of the substrate in a first region is exposed, performing an etching process to etch the first region of the substrate uncovered by the patterned barrier layer, and removing the patterned barrier layer, and forming an electrode on the second region of the substrate.

BRIEF DESCRIPTION OF DRAWINGS

[0010] The invention can be more fully understood by reading the subsequent detailed description and examples with references made to the accompanying drawings, wherein,

[0011] FIG. **1** is a cross section of a conventional solar cell having a selective emitter.

[0012] FIG. **2** is a plane view of a solar cell with selective emitter of an embodiment of the invention.

[0013] FIG. **3**A~FIG. **3**G are intermediate cross sections of a solar cell with selective emitter of an embodiment of the invention.

[0014] FIG. **4** is a local enlarged view of FIG. **3**D.

[0015] FIG. **5**A~FIG. **5**F are intermediate cross sections of a solar sell with selective emitters of another embodiment of the invention.

[0016] FIG. **6**A is a diagram of a doped multicrystalline silicon substrate with sheet resistance as a function of the etching time.

[0017] FIG. **6**B is a diagram of a doped single-crystal silicon substrate with sheet resistance as a function of the etching time.

[0018] FIG. **7** is a scanning electron microscope (SEM) picture of a microtexture structure.

[0019] FIG. **8** is a scanning electron microscope (SEM) picture of a second texture structure.

[0020] FIG. **9** is a scanning electron microscope (SEM) picture of an interface between an electrode and the second region of the substrate treated with second texture etching.

DETAILED DESCRIPTION

[0021] It is understood that specific embodiments are provided as examples to teach the broader inventive concept, and

one of ordinary skill in the art can easily apply the teaching of the present disclosure to other methods or apparatus. The following discussion is only used to illustrate the invention, not limit the invention.

[0022] FIG. **2** is a plane view of a solar cell with selective emitter of an embodiment of the invention. Referring to FIG. **2**, a plurality of electrodes **202** extends along a vertical direction, and a plurality of fingers **204** extends along a horizontal direction. The selective emitter of an embodiment of the invention is a structure comprising a high concentration doping region in portions of the substrate under the electrodes **202** and the fingers **204**, and low concentration doping regions in other non-electrode regions. The invention is not limited to the structure above. The selective emitter of another embodiment can comprise high concentration doping regions merely in a portion of the substrate under the electrodes **202** and low concentration doping regions a in other non-electrode regions.

[0023] A method for forming a solar cell having selective emitters is illustrated in accordance with FIG. **3**A~FIG. **3**G. First, referring to FIG. **3**A, a substrate **302** is provided. The substrate can be single-crystal silicon, polysilicon or other suitable semiconductor materials. Next, the substrate **302** is treated with a texturization process to form first texture structures on a first surface **304** and a second surface **306** of the substrate **302**. In order to repair damage to a substrate **302** formed during cutting, a single crystal substrate generally is treated with alkaline etching, such as immersion in a NaOH solution, and a polysilicon substrate is generally treated with acid etching, such as immersion in a $HF:HNO_3:H_2O$ solution. The alkaline etching and acid etching forms first texture structures on surfaces of the substrate **302**.

[0024] Referring to FIG. **3**B, a barrier layer **308** is formed on a first surface **304** of the substrate **302**. In an embodiment of the invention, the barrier layer comprises silicon silicon oxide, silicon nitride or aluminum oxid, and can be formed by plasma enhanced chemical vapor deposition (PECVD). Referring to FIG. **3**C, a portion of the barrier layer **308** at the position predetermined to form electrodes and/or fingers is selectively removed to form openings **310** exposing the substrate. In an embodiment of the invention, the step of selectively removing the barrier layer **308** can be accomplished by laser irradiation or screen printing. Thereafter, referring to FIG. **3**D, a second texture etching process is performed to the portion of the substrate **302** in the opening **310** of the barrier layer **308** to form second texture structures at the region of the substrate **302** predetermined to form electrodes and/or fingers. Therefore, a first surface **304** of the substrate **302** comprises second texture structures at a second region **314** predetermined to form electrodes and/or fingers and first texture structures at a first region **312** outside of the second region **314**. Next, the barrier layer **308** is removed. The barrier layer **308** can be slowly etched during the second texture etching process. The second texture structures and the first texture structures are described in more detail in accordance with FIG. **4** (local enlarged view of FIG. **3**D). Referring to FIG. **4**, the texture structure on the first surface **304** of the substrate **302** in the first region **312** is referred as a first texture structure, and the texture structure on the first surface **304** of the substrate **302** in the second region **314** is referred as a second texture structure. The first texture structure and the second texture structure comprise a plurality of protruding portions and recessing portions, wherein the protruding portions and recessing portions of the second texture structure are more concentrated than the protruding portions and recessing portions of the first texture structure. Specifically, the distance between neighboring protruding portions of the first texture structure is L_1, the distance between neighboring protruding portions of the second texture structure is L_2, and L_1 is about 2-20 times that of L_2. In another embodiment of the invention, L_1 is about 12-15 times that of L_2. In one embodiment of the invention, L_1 is about 1-10 μm . FIG. **7** shows a scanning electron microscope (SEM) picture of a first texture structure. FIG. **8** shows a scanning electron microscope (SEM) picture of a second texture structure. Referring to FIG. **7** and FIG. **8**, the distance between neighboring protruding portions of the first texture structure L_1 is at least larger than two times that of the distance between neighboring protruding portions of the second texture structure L_2.

[0025] In an embodiment of the invention, the second texture etching described comprises the steps as follows. First, an electroless deposition process is performed to form silver particles on a first surface **304** of the substrate **302**, acting as a catalytic agent. Next, a black etching process, such as immersing the substrate in $HF:H_2O_2:H_2O$, is performed. Note that US 20090311821A1 is incorporated by reference to illustrate the details of the second texture etching process. It is also noted that the second texture etching process of the invention is not limited to the etching process described, and any method which can form a second texture structure can be applied in the invention.

[0026] Thereafter, referring to FIG. **3**E, a doping process is performed to form a first doping region **316** in a first region **312** on the first surface **304** of the substrate **302**, and a second doping region **318** in a second region **314** on the first surface **304** of the substrate **302**. In an embodiment of the invention, the doping process uses $POCl_3$ as a doping source. In another embodiment of the invention, the doping process uses boron as a doping source. The difference in sheet resistance between the first doping region **316** and the second doping region **318** is illustrated in accordance with table 1.

TABLE 1

	Sheet resistance (Ω/sq)	Sheet resistance (Ω/sq)	Sheet resistance (Ω/sq)
Target resistance	70	80	100
Reference (first texture structure)	71	81	102
Second texture structure	37	43	85
Difference (Ω/sq)	34	38	17

[0027] The first table shows that the second texture structure on the surface of the substrate **302** has a relatively lower sheet resistance (i.e. higher doping concentration) and the mircotexture structure in the first region **312** on the surface of the substrate **302** has a relatively higher sheet resistance after the phosphorous diffusing process. Accordingly, the doping process can form a second doping region **318** having a relatively high doping concentration at the second region **314** and form a first doping region **316** having a relatively low doping concentration at the first region **312**. It is noted that the embodiment of the invention can form doping regions (first doping region **316** and second doping region **318**) having different doping concentrations during a single doping step. The method of the embodiment of the invention has less process duration and costs than conventional methods of fab-

ricating selective emitters of a solar cell. Next, the phosphorous silicon glass (PSG) on the surface of the substrate **302** is removed.

[0028] Following, referring to FIG. **3**F, an anti-reflective layer **320** is formed on the first surface **304** of the substrate **302**. In an embodiment of the invention, the anti-reflective layer **320** comprises silicon oxide, silicon nitride or aluminum oxid, and can be formed by plasma enhanced chemical vapor deposition (PECVD). Referring to FIG. **3**G, a screen printing and a sintering metallization process are performed to form electrodes **322** contacting the second doping region **318** in the second region **314**. FIG. **9** shows a scanning electron microscope (SEM) picture of an interface between an electrode **322** and the second region **314** of the substrate **302** treated with second texture etching. Last, an edge isolating process is performed by laser irradiation (not shown).

[0029] EXAMPLE 1

[0030] First, a wafer was provided. The wafer was treated with a standard cleaning process wherein a texture structure was formed on a surface of the wafer. A silicon nitride was formed on a surface of the wafer by plasma enhanced chemical vapor deposition (PECVD) to act as a barrier layer. Next, the barrier layer was selectively removed by laser patterning to form openings having similar shapes with a metallization pattern. An immersing alkaline solution process was performed to remove defects on the surface of the wafer caused by laser patterning. A second texture etching process including the following two steps was performed. The first step included performing an electroless treatment, wherein $Na_2S_2O_8$ was used as an oxidizer, and $AgNO_3$, H_2O_2 or NaOH was used as a catalytic agent. The second step included performing selective oxidizing and removing processes by using a solution containing HF and H_2O_2 to form a second texture surface. Both the first and second steps were performed at room temperature, and water based chemistries were used. During the second texture wet chemical treating process, the silicon nitride barrier layer was slowly removed.

[0031] Next, the wafer was cleaned using concentrated HNO_3 and HPM solutions. A single $POCl_3$ diffusing process was performed to form emitter, wherein the standard texture structure had sheet resistance of about 60-80 Ω/sq (for example 70 Ω/sq), and the second texture structure had a sheet resistance of about 15-50 Ω/sq (for example 30 Ω/sq), thereby forming selective emitter. Next, a PECVD process was performed to form a silicon nitride layer, which acted as an anti-reflective layer. A screen printing process was performed to form a silver electrode at the front side and aluminum back surface field (BSF) on the rear side of the substrate. Thereafter, a co-firing step was performed. Lastly, an edge isolating process was performed by laser irradiation. A solar cell with selective emitter formed by the method above was measured, and had a cell efficiency of 16.01%. A comparable example of a solar cell without selective emitter being formed was also measured, and had a cell efficiency of 15.51%. Therefore, the technique of the embodiment indeed increased cell efficiency of the solar cells.

[0032] A method for forming a solar cell having selective emitter of another embodiment of the invention is illustrated in accordance with FIG. **5**A~FIG. **5**F. First, referring to FIG. **5**A, a substrate **502** is provided. The substrate **502** can be made of a single-crystal silicon, polysilicon or other suitable semiconductor materials. Next, the substrate **502** is treated with a texturization process to form first texture structures on a first surface **504** and a second surface **506** thereof. In order to repair damage to a substrate **502** formed during cutting, a single crystal substrate is generally treated with alkaline etching, such as immersion in a NaOH solution, and a polysilicon substrate **502** is generally treated with acid etching, such as immersion in a $HF{:}HNO_3{:}H_2O$ solution. The alkaline etching and acid etching processes form first texture structures on surfaces of the substrate **502**. Referring to FIG. **5**B, a doping process is performed to form a high doping concentration region **516** on a first surface **504** of the substrate **502**. In an embodiment of the invention, the doping process uses $POCl_3$ as a doping source. Next, the phosphorous silicon glass (PSG) on the surface of the substrate **502** is removed. Referring to FIG. **5**C, a patterned barrier layer **510** having similar shapes with the electrode pattern is formed on the first surface **504** of the substrate **502** by, for example screen printing. Thereafter, referring to FIG. **5**D, an etching back process is performed to selectively etch a portion of the substrate **502** surface not covered by patterned barrier layer **510**, thereby forming a low concentration doping region **518** in a first region **512** not covered by the patterned barrier layer **510**, and a high concentration doping region **516** in a second region **514** covered by the patterned barrier layer **510**.

[0033] The mechanism of forming the high concentration doping region and the low concentration doping region is illustrated in accordance with FIG. **6**A and FIG. **6**B. The doping process forms a high concentration doping region on the substrate surface. The deeper the etching of the substrate, the lesser the doping concentration. FIG. **6**A shows a diagram of a doped multicrystalline silicon substrate with sheet resistance as a function of etching time. Referring to FIG. **6**A, the longer the etching time, the higher the sheet resistance of the substrate. That is, when the etching depth is increased, the doping concentration of the substrate is reduced. FIG. **6**B shows a diagram of a doped single-crystal silicon substrate with sheet resistance as a function of etching time. The result shown in FIG. **6**B is similar to that shown in FIG. **6**A. Therefore, the embodiment can form a low concentration doping region **518** in the first region **512** of the substrate **502** uncovered by the patterned barrier layer **510**, while, have the unetched second region **514** covered by the patterned barrier layer **510** not changed from the high concentration doping region **516**, thereby forming selective emitter. In an embodiment of the invention, the etching back process described is accomplished by a second texture etching process. Because the second texture etching process has low etching rate, the etching depth can be precisely controlled. The second texture etching process comprises the steps as follows. First, an electroless deposition process is performed to form silver particles on a first surface **504** of the substrate **502** acting as a catalytic agent. Next, a black etching process, such as immersion in $HF{:}H_2O_2{:}H_2O$, is performed. US 20090311821A1 is incorporated by reference to illustrate the details of the second texture etching process.

[0034] Thereafter, the phosphorous silicon glass (PSG) on the surface of the substrate **502** is removed. Next, referring to FIG. **5**E, an anti-reflective layer **520** is formed on the first surface **504** of the substrate **502**. In an embodiment of the invention, the anti-reflective layer **520** comprises silicon nitride, and can be formed by plasma enhanced chemical vapor deposition (PECVD). Referring to FIG. **5**F, a screen printing and a sintering metallization process are performed to form electrodes **522** contacting the high concentration

doping region **516** in the second region **514**. Last, an edge isolating process is performed by laser irradiation (not shown).

EXAMPLE 2

[0035] First, a wafer was provided. The wafer was treated with a standard cleaning process wherein a texture structure was formed on a surface of the wafer. A single $POCl_3$ diffusing process was performed and the doped substrate surface had a sheet resistance of about 45 Ω/sq. A patterned barrier layer, having similar shapes with an electrode pattern, was formed on the surface of the substrate by screen printing. A portion of the substrate uncovered by the patterned barrier layer was etched by second texture etching. The second texture etching process comprised the two steps as follows. The first step included performing an electroless treatment, wherein $Na_2S_2O_8$ was used as an oxidizer, and $AgNO_3$, H_2O_2 or NaOH was used as a catalytic agent. The second step included performing selective oxidizing and removing processes by using a solution containing HF and H_2O_2 to form second texture structures on the surface of the substrate. The duration of the second-etching back process was about 60 sec, and the etching process substantially removed 50-70 nm of the doping region of the substrate. The etched substrate had high sheet resistance (i.e. lower doping concentration) and the unetched substrate surface had low sheet resistance (i.e. higher doping concentration) on surfaces thereof,. Therefore, selective emitters can be formed. Next, the patterned barrier was removed. Next, a PECVD process was performed to form a silicon nitride layer, which acted as a passivated and anti-reflective layer. A screen printing process was performed to form a silver electrode at the front side of the substrate. Thereafter, a co-firing step was performed. Lastly, an edge isolating process was performed by laser irradiation.

[0036] While the invention has been described by way of example and in terms of the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. It is intended to cover various modifications and similar arrangements (as would be apparent to those skilled in the art). Therefore, the scope of the appended claims should be accorded the broadest interpretation so as to encompass all such modifications and similar arrangements.

What is claimed is:

1. A method for forming a solar cell with selective emitters, comprising:

providing a substrate;

forming a first texture structure on a first surface of the substrate;

performing a doping process to the first surface of the substrate to form a first doping region in the substrate;

forming a pattered barrier layer in a second region on the first surface of the substrate, wherein another portion of the substrate in a first region is exposed;

performing a second texture etching process to etch the first region of the substrate uncovered by the patterned barrier layer;

removing the patterned barrier layer; and

forming an electrode on the second region of the substrate.

2. The method for forming a solar cell with selective emitters as claimed in claim **1**, wherein the second texture etching process treats the substrate surface in the first region to a second doping region, and doping concentration of the second doping region is lower than that of the first doping region.

3. The method for forming a solar cell with selective emitters as claimed in claim **1**, wherein the second texture etching process comprises:

performing an electroless treatment; and

performing selective oxidizing and removing steps.

4. The method for forming a solar cell with selective emitter as claimed in claim **3**, wherein $N_2S_2O_8$ is used as an oxidizer, and $AgNO_3$, H_2O_2 or NaOH are used as catalytic agents in the electroless treatment process and the selective oxidizing products removing steps is performed in a solution containing HF and H_2O_2.

5. The method for forming a solar cell with selective emitter as claimed in claim **1**, further comprising forming an anti-reflective layer on the substrate surface before forming the electrode.

6. The method for forming a solar cell with selective emitter as claimed in claim **5**, wherein the pattered barrier layer and the anti-reflective layer are formed of silicon oxide silicon nitride or aluminum oxide.

7. The method for forming a solar cell with selective emitter as claimed in claim **5**, wherein the anti-reflective layer is formed by plasma enhanced chemical vapor deposition (PECVD).

8. The method for forming a solar cell with selective emitter as claimed in claim **1**, wherein the doping process dopes phosphorous or boron.

9. The method for forming a solar cell with selective emitters as claimed in claim **1**, wherein the second texture etching process treats the substrate surface in the first region to a second doping region, wherein sheet resistance of the first doping region is lower than that of the second doping region.

10. The method for forming a solar cell with selective emitters as claimed in claim **1**, wherein the second texture etching process removes about 50 nm-70 nm of the substrate surface in the first region to form a second doping region.

11. The method for forming a solar cell with selective emitters as claimed in claim **1**, wherein duration of the second texture etching process is about 60 sec.

12. The method for forming a solar cell with selective emitters as claimed in claim **1**, wherein the first texture structure is formed by alkaline etching process.

13. The method for forming a solar cell with selective emitters as claimed in claim **1**, wherein the first texture structure is formed by acid etching process.

14. The solar cell with selective emitters as claimed in claim **1**, wherein the pattered barrier layer is formed by screen printing.

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