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Godet et al.

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(54) **PLASMA POISONING TO ENABLE SELECTIVE DEPOSITION**

(71) Applicant: **APPLIED MATERIALS, INC.**, Santa Clara, CA (US)

(72) Inventors: **Ludovic Godet**, Sunnyvale, CA (US); **Srinivas D. Nemani**, Sunnyvale, CA (US); **Tobin Kaufman-Osborn**, Sunnyvale, CA (US)

(73) Assignee: **Applied Materials, Inc.**, Santa Clara, CA (US)

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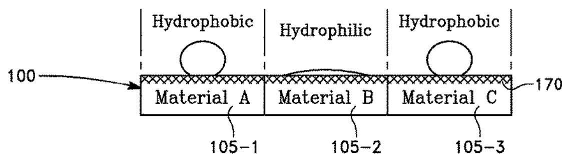
H01L 21/02 (2006.01)
H01L 21/027 (2006.01)
H01L 21/285 (2006.01)
H01L 21/263 (2006.01)

(52) **U.S. Cl.**
CPC ***H01L 21/0262*** (2013.01); ***H01L 21/0228*** (2013.01); ***H01L 21/0274*** (2013.01); ***H01L 21/02315*** (2013.01); ***H01L 21/02658*** (2013.01); ***H01L 21/263*** (2013.01); ***H01L 21/28556*** (2013.01)

(58) **Field of Classification Search**
CPC H01L 21/0262; H01L 21/0228; H01L 21/0274; H01L 21/263; H01L 21/02315; H01L 21/02658; H01L 21/28556
See application file for complete search history.



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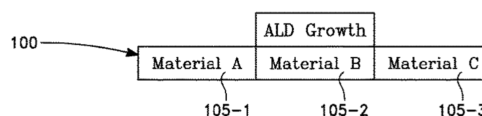
Primary Examiner — Mamadou Diallo
(74) *Attorney, Agent, or Firm* — Fish & Richardson P.C.

(57) **ABSTRACT**

Atomic layer deposition in selected zones of a workpiece surface is accomplished by transforming the surfaces outside the selected zones to a hydrophobic state while the materials in the selected zones remain hydrophilic.

6 Claims, 7 Drawing Sheets



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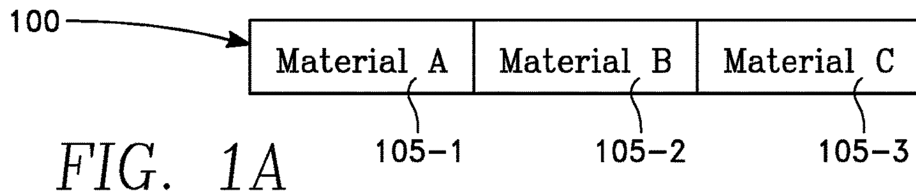


FIG. 1A

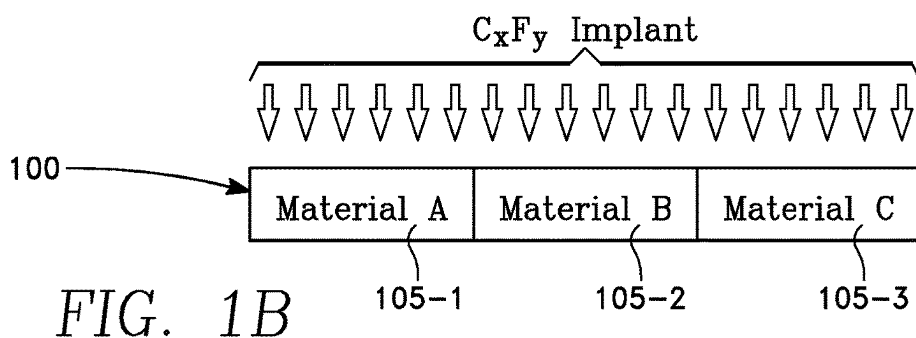


FIG. 1B

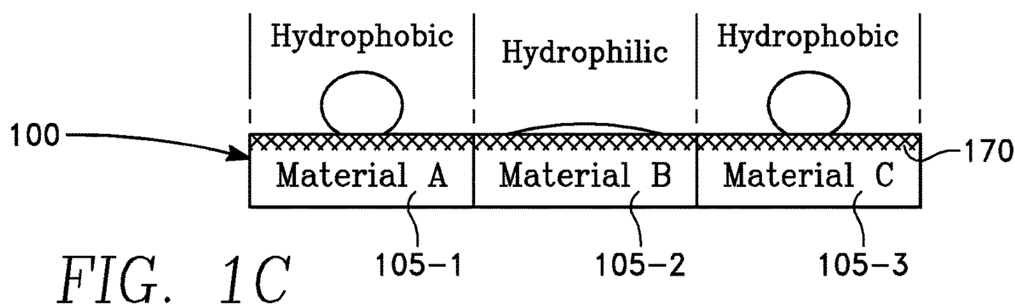


FIG. 1C

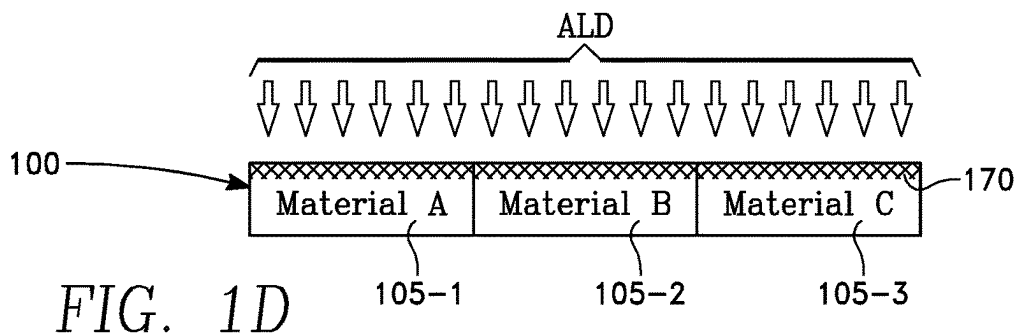


FIG. 1D

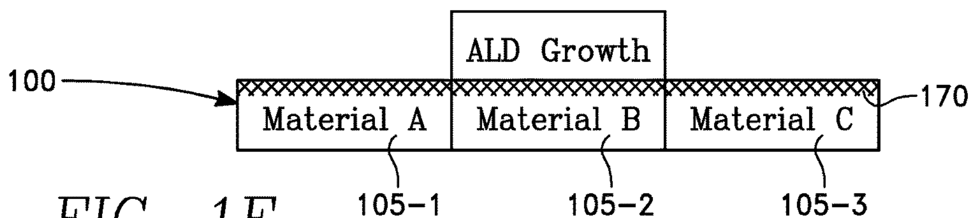


FIG. 1E

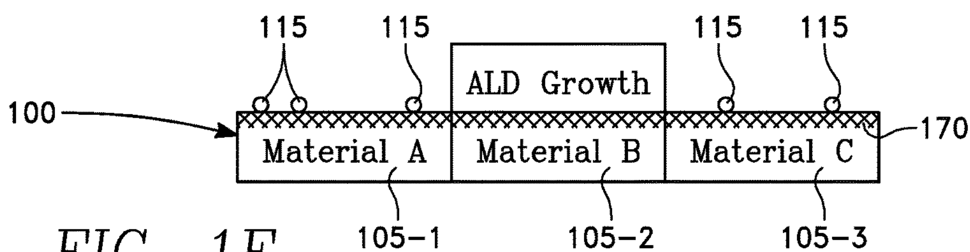


FIG. 1F

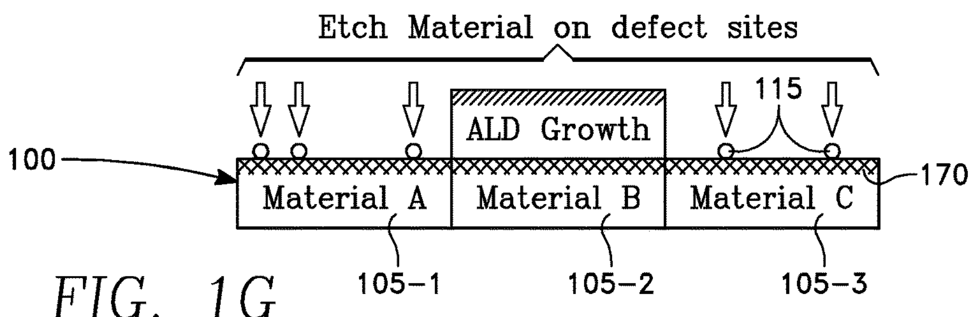


FIG. 1G

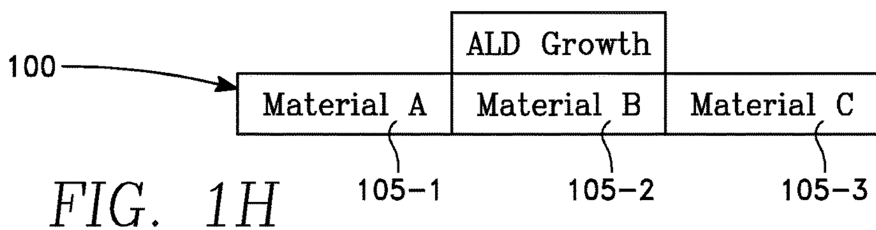


FIG. 1H

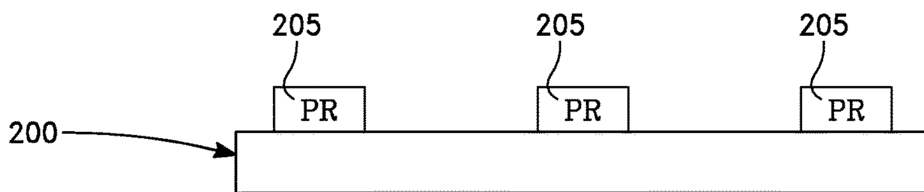


FIG. 2A

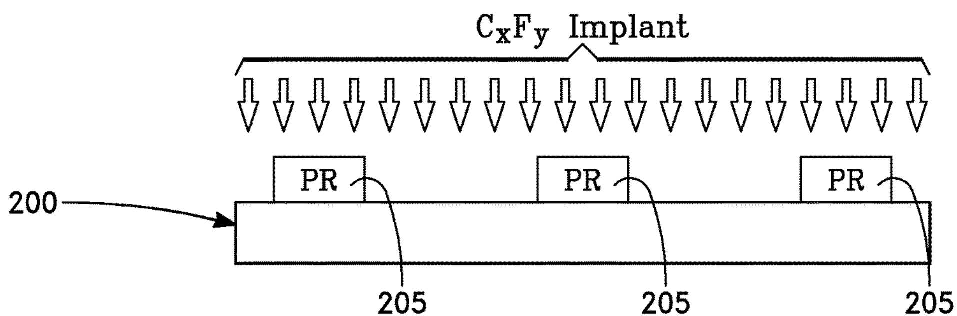


FIG. 2B

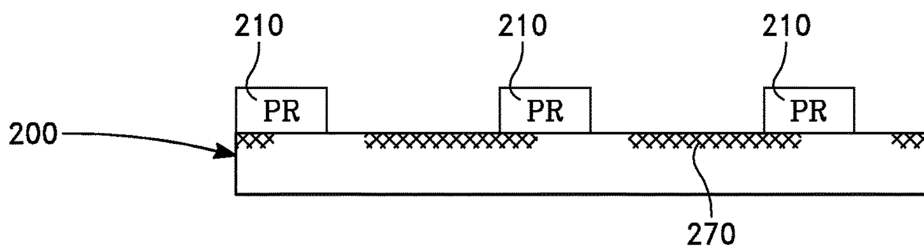


FIG. 2C

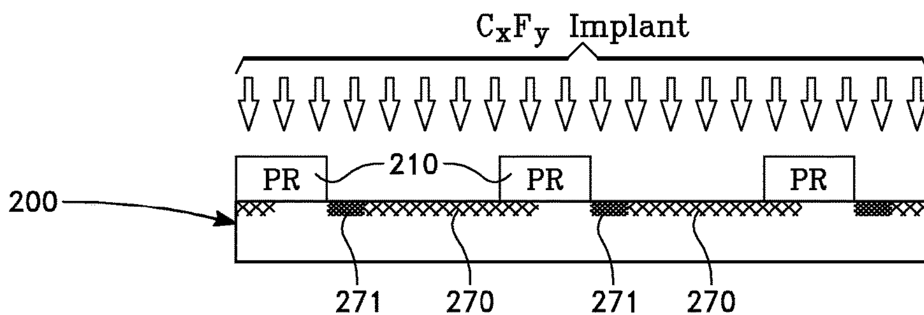
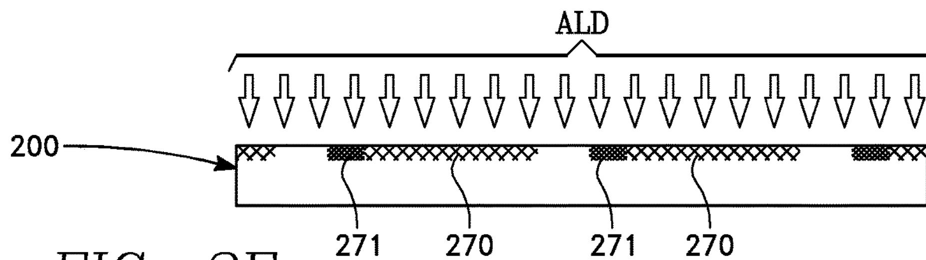


FIG. 2D



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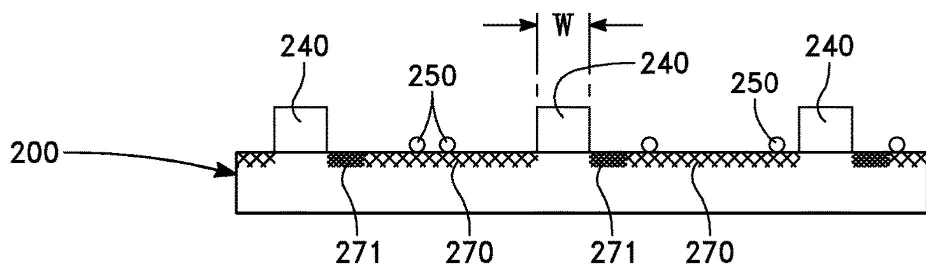

FIG. 2F

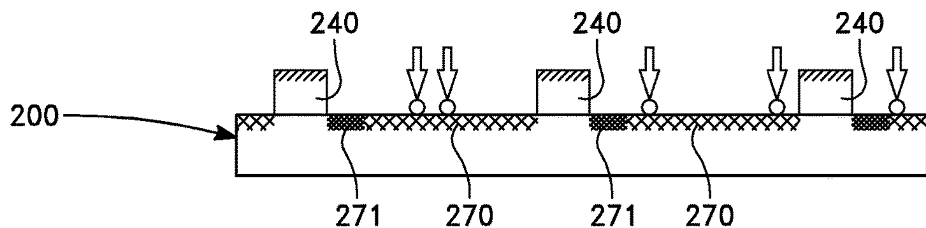

FIG. 2G

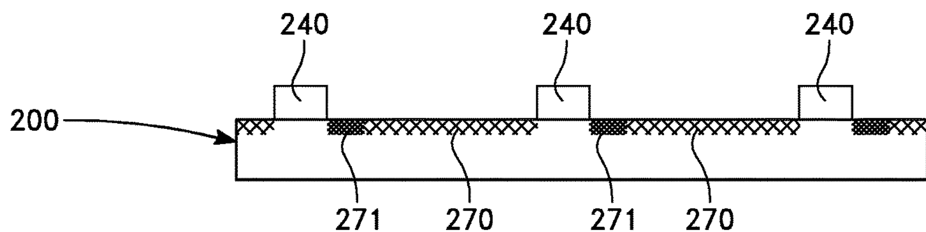

FIG. 2H

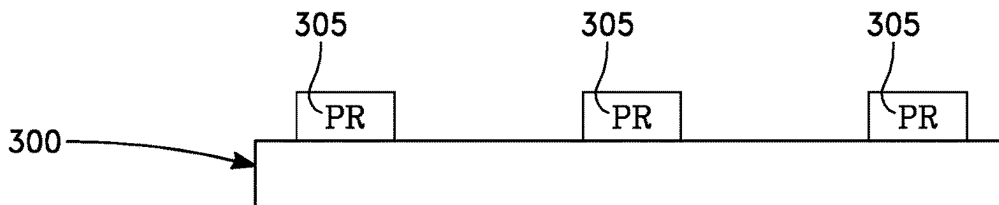

FIG. 3A

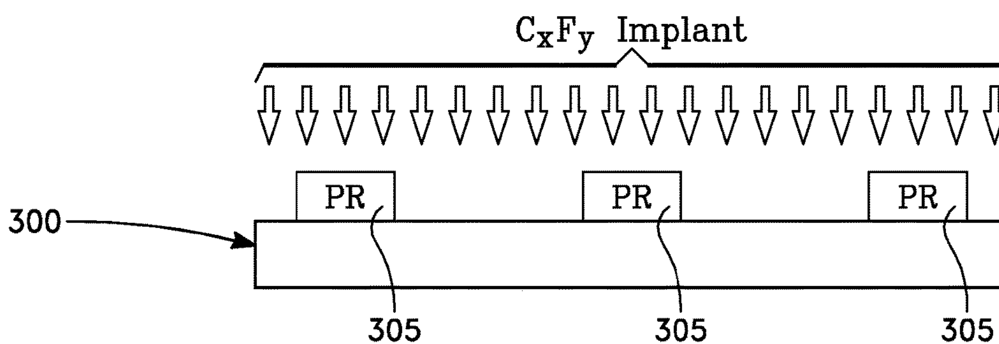

FIG. 3B

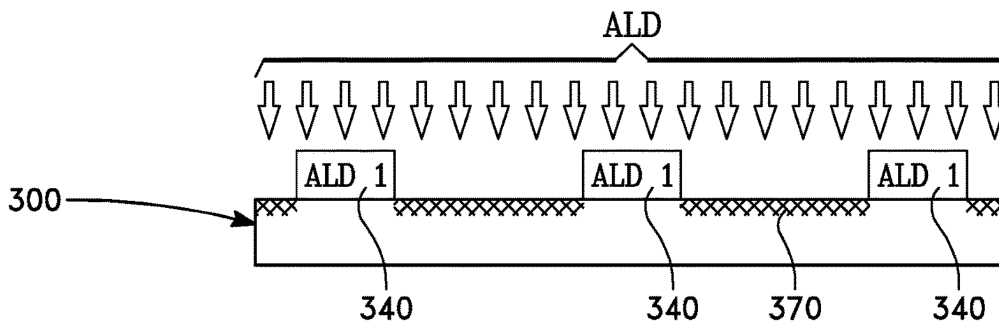

FIG. 3C

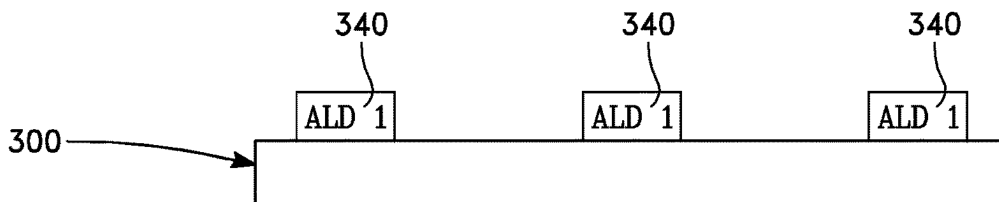

FIG. 3D

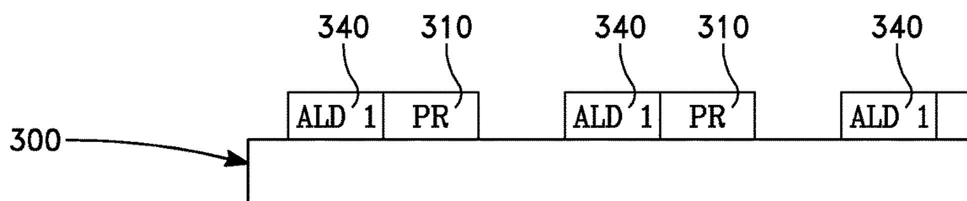

FIG. 3E

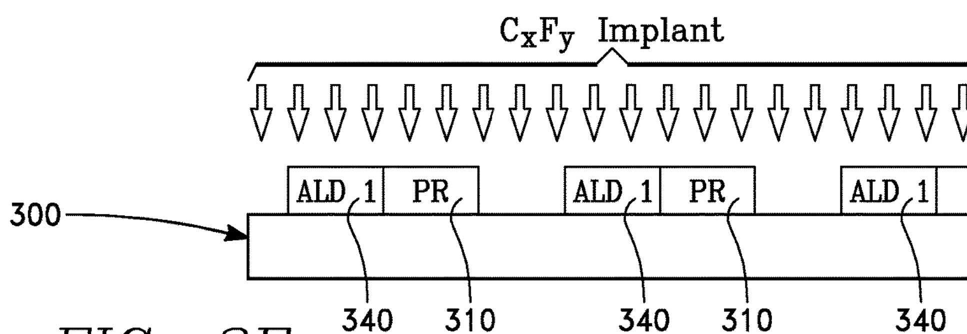

FIG. 3F

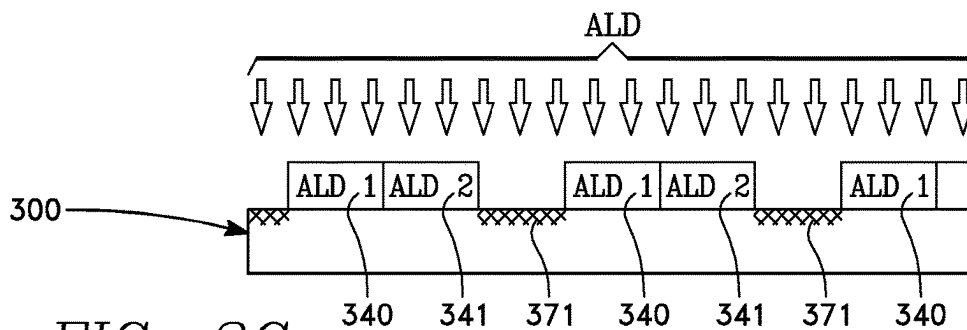

FIG. 3G

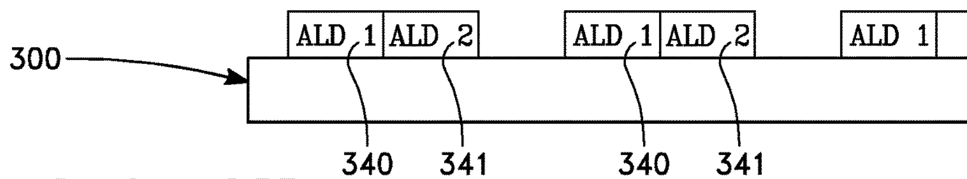

FIG. 3H

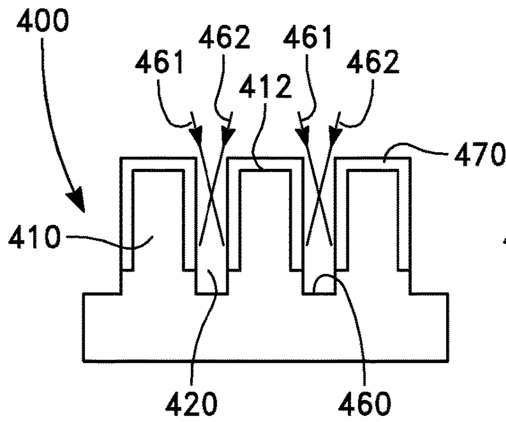

FIG. 4A

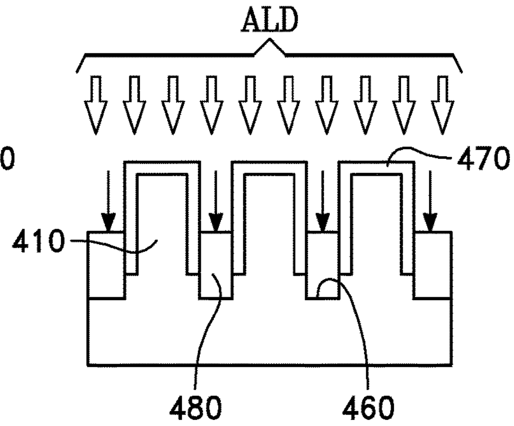

FIG. 4B

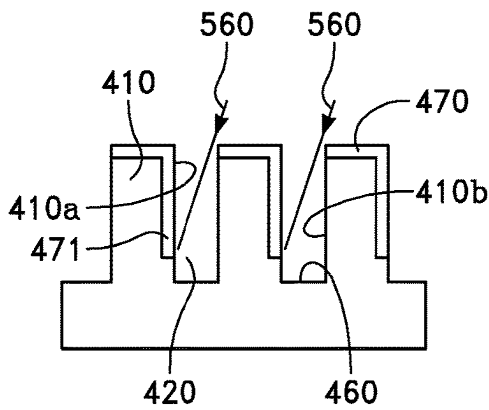

FIG. 5A

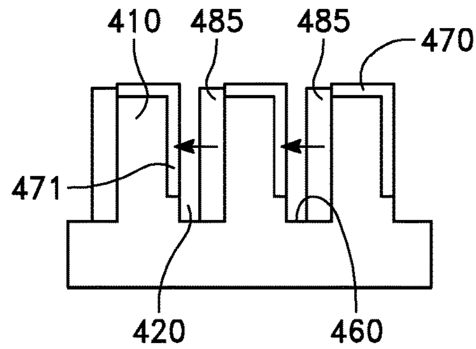

FIG. 5B

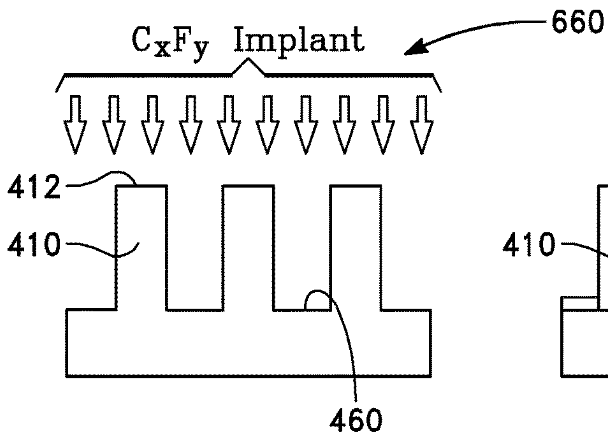

FIG. 6A

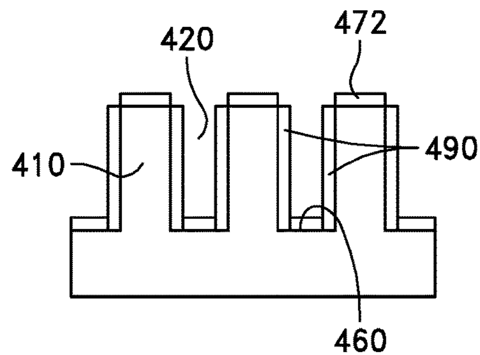

FIG. 6B

PLASMA POISONING TO ENABLE SELECTIVE DEPOSITION

BACKGROUND

Technical Field

The disclosure concerns a method of forming layered structures by atomic layer deposition of materials, in accordance with a predetermined pattern of different materials in an integrated circuit.

Background Discussion

In some fabrication processes for forming integrated circuits, it is desirable to deposit thin films by atomic layer deposition (ALD) in accordance with a predetermined pattern. The pattern defines selective areas on a workpiece surface for deposition by an ALD process, while ALD is prevented in the other areas. Such a process is referred to herein as selective area atomic layer deposition. The problem is how to accurately govern the boundaries of the selective areas.

SUMMARY

A first method of performing atomic layer deposition in selected zones of a workpiece comprises: (a) providing a surface in each of the selected zones of a first material of a first type that is initially hydrophilic and that becomes hydrophobic upon treatment with a fluoro-carbon plasma or fluoro-carbon ion beam; (b) providing a surface of a second material in other zones of the workpiece that remains hydrophilic upon treatment with a fluoro-carbon plasma or fluoro-carbon ion beam; (c) performing a plasma treatment on the workpiece using a plasma derived from a fluoro-carbon species; and (d) performing an atomic layer deposition process on the workpiece, and growing an atomic layer of a growth material on surfaces of the selected zones while generally avoiding growth of an atomic layer of the growth material in the other zones.

In one embodiment, the first material comprises any material that becomes hydrophilic upon treatment with a fluoro-carbon plasma or fluoro-carbon ion beam, such as (but not limited to) for example one of W, Co, SiN, T-oxide, TEOS or Si. In one embodiment, the second material comprises any material that remains hydrophilic upon treatment with a fluoro-carbon plasma or fluoro-carbon ion beam, such as (but not limited to) one of Cu or TiN. In one embodiment, the growth material comprises a metal or an oxide of a metal.

In one embodiment, the method is repeated until a desired thickness of the growth material is reached.

In one embodiment, the method further comprises removing growth material defects in the other zones.

A second method of performing atomic layer deposition in selected zones of a workpiece comprises: (a) depositing a first photolithographic mask on the workpiece comprising first openings corresponding to portions of the selected zones; (b) treating the workpiece by exposure to species derived from a fluoro-carbon plasma; (c) removing the first photolithographic mask; (d) depositing a second photolithographic mask on the workpiece comprising second openings corresponding to remaining portions of the selected zones; (e) treating the workpiece by exposure to species derived from a fluoro-carbon plasma; (f) removing the second photolithographic mask; and (g) performing an atomic layer deposition process.

In one embodiment, the method further comprises removing growth material from areas outside of the selected zones.

In one embodiment, the treating the workpiece comprises forming a fluoro-carbon plasma and exposing the workpiece to the plasma. In one embodiment, the treating the workpiece comprises forming an ion beam from a fluoro-carbon plasma and directing the ion beam to the workpiece.

In one embodiment, the atomic layer deposition process produces a growth material. The growth material may be any material that can be formed by atomic layer deposition such as (but not limited to) metal, a non-metal or a metal oxide.

A third method of performing atomic layer deposition in selected zones of a workpiece comprises: (a) depositing a first photolithographic mask on the workpiece comprising first openings corresponding to portions of the selected zones; (b) treating the workpiece by exposure to species derived from a fluoro-carbon plasma; (c) removing the first photolithographic mask; (d) performing a first atomic layer deposition process on the workpiece; (e) depositing a second photolithographic mask on the workpiece comprising second openings corresponding to remaining portions of the selected zones; (f) treating the workpiece by exposure to species derived from a fluoro-carbon plasma; (g) removing the second photolithographic mask; and (h) performing a second atomic layer deposition process.

In one embodiment, the first and second atomic layer deposition processes deposit different growth materials on the workpiece.

In one embodiment, the treating the workpiece comprises forming a fluoro-carbon plasma and exposing the workpiece to the plasma. In one embodiment, the treating the workpiece by exposure to species derived from a fluoro-carbon plasma comprises forming an ion beam from a fluoro-carbon plasma and directing the ion beam to the workpiece.

In one embodiment, the first and second atomic layer deposition process produce on the workpiece different respective growth materials.

A first method of performing atomic layer deposition in selected zones of a workpiece having 3-dimensional structures on a surface thereof comprising vertical walls separated by trenches, comprises: (a) providing a directional plasma source emitting ions along an ion propagation direction toward the workpiece; (b) orienting the ion propagation direction relative to the vertical walls to enable the vertical walls to mask the selected zones from the ions emitted by the directional plasma source; and (c) performing an atomic layer deposition process on the workpiece.

In one embodiment, the directional plasma source emits ions in two beams tilted relative to the vertical walls through opposing angles and the two beams strike opposing ones of the vertical walls.

In one embodiment, the directional plasma source emits a beam tilted relative to the vertical walls and the beams strikes one of the vertical walls.

In one embodiment, the directional plasma source emits ions in one beam parallel to the vertical walls.

BRIEF DESCRIPTION OF THE DRAWINGS

So that the manner in which the exemplary embodiments of the present invention are attained can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to the embodiments thereof which are illustrated in the appended drawings. It is to be appreciated that certain well known 'processes are not discussed herein in order to not obscure the invention.

FIGS. 1A, 1B, 1C, 1D, 1E, 1F, 1G and 1H depict successive operations of a process performed on a workpiece in accordance with a first embodiment.

FIGS. 2A, 2B, 2C, 2D, 2E, 2F, 2G and 2H depict successive operations of a process performed on a workpiece in accordance with a second embodiment.

FIGS. 3A, 3B, 3C, 3D, 3E, 3F, 3G and 3H depict successive operations of a process performed on a workpiece, in accordance with a third embodiment

FIGS. 4A and 4B depict successive operations of a process performed on a workpiece in accordance with a fourth embodiment.

FIGS. 5A and 5B depict successive operations of a process performed on a workpiece in accordance with a fifth embodiment.

FIGS. 6A and 6B depict successive operations of a process performed on a workpiece in accordance with a fifth embodiment.

To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements and features of one embodiment may be beneficially incorporated in other embodiments without further recitation. It is to be noted, however, that the appended drawings illustrate only exemplary embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

DETAILED DESCRIPTION

Selective ALD formation of a deposited film employs plasma poisoning of the workpiece surface in accordance with a desired pattern. A fluoro-carbon plasma treats selected areas of the workpiece surface to transform those selected areas from a hydrophilic state to a hydrophobic state. Certain ALD processes are enabled on hydrophilic surfaces and disabled on hydrophobic surfaces. In essence, the fluoro-carbon plasma treatment altered (poisoned) the surface to prevent ALD formation of deposited films.

The pattern may be established in various ways. One way (Method I) is to provide a first material only in selective surface areas, the first material being one that becomes hydrophobic upon exposure to a fluoro-carbon. The remaining areas consist of a second material that remains hydrophilic. Another way (Method II) is to provide a material that is hydrophilic unless treated by a fluoro-carbon plasma, in which case it becomes hydrophobic. In this latter case, the desired pattern is realized by masking the selected surface areas during the plasma treatment. This masking may employ photoresist, for example. Yet another way (Method C) is to employ a directional plasma beam so as to exploit 3-dimensional features on the surface to shadow the plasma beam from selected portions of the surface.

FIGS. 1A though 1H depict a first embodiment that employs Method I. FIG. 1A depicts a workpiece surface **100** having two or more zones **105-1** (Material A), **105-2** (Material B), **105-3** (Material C) of different characteristics. In FIG. 1B, the workpiece is subjected to a plasma treatment. The plasma treatment may be carried out by ion implantation of a fluoro-carbon species, or by exposure to an ion beam from a fluoro-carbon plasma (e.g., CF4). The plasma treatment forms a plasma treated surface layer **170**. In the illustrated example, Materials A and C become hydrophobic upon plasma treatment by a fluoro-carbon plasma, while material B remains hydrophilic, as indicated symbolically in FIG. 1C. Next, as depicted in FIG. 1D, an ALD process is performed. The result is depicted in FIG. 1E, in which ALD deposition occurs only on Material B in zone **105-2**. This is because Material B is hydrophilic, while Materials A and C are hydrophobic. FIG. 1F depicts an example in which the operation of FIG. 1D left small ALD deposits **115** in unselected areas. In this case, an ALD clean-up step depicted in FIG. 1G is performed, which removes the unwanted ALD deposits, and the thickness of the ALD deposited film in zone **105-2** is slightly reduced, as depicted in FIG. 1H.

Materials A and C, which become hydrophobic upon exposure to a fluoro-carbon plasma, can be selected from a wide range of materials, such as (but not limited to) W, Co, SiN, T-oxide, TEOS, a nitride, a metal, a metal oxide, a semiconductor or Si. Material B, which remains hydrophilic after exposure to a fluoro-carbon plasma, may be selected from a group of materials including Cu and TiN, for example.

The operations of FIGS. 1A through 1H may be repeated on the workpiece by a number of times until a desired thickness of ALD deposited film is reached. Prior to each repetition, an anneal process may be performed to remove the effects of the plasma treatment. Another way to remove the effect of fluorocarbon plasma treatment is by exposing the surface to another type of plasma such as, for example, an Ar plasma or a N plasma.

FIGS. 2A through 2H depict a process in accordance with a second embodiment. In FIG. 2A, a workpiece surface **200** is patterned by a photoresist layer **205** using photolithography, leaving portions of the workpiece surface **200** exposed. In the next operation, a plasma treatment operation depicted in FIG. 2B, the workpiece surface **200** is exposed to a fluoro-carbon plasma, forming a plasma treated surface layer **270** shown in FIG. 2C. The plasma treated surface layer **270** is formed in areas aligned with openings in the photoresist layer **205**. Then, the photoresist layer **205** is removed and replaced by a new photoresist layer **210**, as depicted in FIG. 2C. The pattern of the new photoresist layer **210** may be slightly shifted relative to the previous photoresist layer **205** (now removed), as shown in FIG. 2C. A second plasma treatment is performed as depicted in FIG. 2D, forming an additional plasma treated surface layer **271** extending beyond the first plasma treated surface layer **270**, as shown in FIG. 2E. The plasma treated surface layers **270** and **271** are hydrophobic while the remainder of the workpiece surface **200** is hydrophilic. The second photoresist layer **210** is removed and an ALD process is performed, as indicated in FIG. 2E. The resulting ALD growth **240** shown in FIG. 2F occurs on the hydrophilic surfaces and has a narrow width W determined by the shift between the first and second photoresist layers **205**, **210**.

FIG. 2G illustrates an example in which defects **250**, such as unwanted ALD growth nodules, are formed. The defects **250** are removed in an etch operation, which decreases the thickness of the ALD growth **240**, as depicted in FIG. 2H.

The process of FIGS. 2A through 2H may be repeated a number of times to increase the thickness of the ALD growth **240**. Prior to each such repeat, an anneal operation may be performed to remove the effects of the previous plasma treatments.

FIGS. 3A through 3H depict a process in accordance with a third embodiment. In FIG. 3A, a workpiece surface **300** is patterned by a photoresist layer **305** using photolithography, leaving portions of the workpiece surface **300** exposed. In the next operation, which is depicted in FIG. 3B, a first plasma treatment is performed by exposing the workpiece surface **300** to a fluoro-carbon plasma. This produces a plasma treated surface layer **370** indicated in FIG. 3C. Then,

the photoresist layer **305** is removed and a first ALD process is performed, as indicated in FIG. **3**C. The resulting ALD growth **340** shown in FIG. **3**C coincides with locations on the workpiece surface **300** not treated by the plasma and which are hydrophilic. Thereafter, the workpiece surface **300** is subjected to an anneal procedure (FIG. **3**D) to remove the effects of the plasma treatment previously performed in FIG. **3**B. This renders the exposed portions of the workpiece surface **300** hydrophilic. Next, as indicated in FIG. **3**E, a second photoresist layer **310** is deposited on the workpiece surface **300** as shown in FIG. **3**E. The pattern of the new photoresist layer **310** may be shifted relative to the previous photoresist layer **305** (now removed), as shown in FIG. **3**E. A second plasma treatment is performed as depicted in FIG. **3**F, which produces a plasma treated surface layer **371** extending beyond the plasma treated surface layer **370**, as indicated in FIG. **3**G. Then the second photoresist layer **310** is removed and a second ALD process is performed, as indicated in FIG. **3**G. This second ALD process results in a second ALD growth layer **341**. The ALD growth layers **340** and **341** may be of the same or different materials, depending upon the ALD processes employed. Next, the workpiece surface **300** is subjected to an anneal procedure (FIG. **3**H) to remove the effects of the fluoro-carbon plasma treatment of FIG. **3**F. Another way to remove the effect of fluorocarbon plasma treatment is by exposing the surface to another type of plasma such as, for example, an Ar plasma or a N plasma.

The foregoing process of FIGS. **3**A through **3**H may be repeated for multi-zone patterning of several or many different materials. The materials may include any material that can be formed by ALD, such as (but not limited to metals, non-metals, nitrides, metal oxides, HfO2, ZrO2, TiO2, SiO2, ZnO, and other similar materials, as some examples.

FIGS. **4**A and **4**B depict a process for ALD in selected areas, by employing shadowing effects of three-dimensional structures on the workpiece surface. In FIG. **4**A, a workpiece **400** has vertical surfaces **410** spaced apart by trenches **420**, the vertical surfaces **410** comprising a hydrophilic material. Selected portions of the vertical surfaces **410** are changed from hydrophilic to hydrophobic by treatment with a directional plasma or plasma beam of a fluoro-carbon species. Also, the vertical surfaces **410** are similarly treated. The plasma treatment forms plasma treated surface layers **470**.

The plasma beam includes two beams **461**, **462**, of respective beam directions tilted through different angles, such as (for example) equal and opposite angles relative to the vertical surfaces **410**. The tilt angle, the width of trench **420** and the depth of the trench **420** are such that the plasma beams **461**, **462** do not reach bottom surface **460** of the trench **420**. The plasma-treated surface layers **470** extend partially toward the bottom surface **460**.

Next, an ALD process is performed as depicted in FIG. **4**B. The growth of ALD material **480** occurs inside the trench **420** starting at the bottom surface **460** and progresses upwardly from the bottom surface **460**. The plasma-treatment changes the exposed surfaces from hydrophilic to hydrophobic, preventing ALD growth on the exposed surfaces.

FIGS. **5**A and **5**B depict a modification of the process of FIGS. **4**A and **4**B. In FIGS. **5**A and **5**B, only a single tilted plasma beam **560** is needed. In FIG. **5**A, only one side (e.g., vertical surface **410***a*) of each vertical feature is exposed to plasma treatment to form a plasma-treated surface layer **471**. The vertical surface **410***b* is untreated and remains hydrophilic. As depicted in FIG. **5**B, an ALD process is performed and produces growth material **485** on the vertical surface **410***b*.

In FIG. **6**A, an untilted (vertical) plasma beam **660** is employed to perform plasma treatment. The result is that only horizontal surfaces (i.e., top surfaces **412** and bottom surfaces **460**) are rendered hydrophobic by the formation of plasma treated surface layer **472**. Next, an ALD process is performed as depicted in FIG. **6**B, depositing an ALD growth material **490** on the vertical surfaces **410** only.

While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is claimed is:

1. A method of performing atomic layer deposition, comprising:

providing in selected zones of a workpiece a first material of a first type that is initially hydrophilic and that becomes hydrophobic upon treatment with a fluoro-carbon plasma or fluoro-carbon ion beam;

providing in other zones of said workpiece a surface of a second material that remains hydrophilic upon treatment with a fluoro-carbon plasma or fluoro-carbon ion beam;

performing a plasma treatment on said workpiece using a plasma derived from a fluoro-carbon species; and

performing an atomic layer deposition process on said workpiece, and growing an atomic layer of a growth material on surfaces of said selected zones while generally avoiding growth of an atomic layer of growth material in said other zones.

2. The method of claim **1** wherein said first material is selected from a group of materials comprising but not limited to W, Co, SiN, T-oxide, TEOS and Si.

3. The method of claim **2** wherein said second material is selected from a second group of materials comprising but not limited to Cu and TiN.

4. The method of claim **1** wherein said growth material comprises any one of a third group of materials comprising but not limited to: a non-metal, a metal, an oxide, a nitride, a semiconductor, HfO2, ZrO2, TiO2, SiO2, ZnO.

5. The method of claim **1** further comprising repeating the operations of claim **1** until a desired thickness of said growth material is reached.

6. The method of claim **1** further comprising removing growth material defects in said other zones.

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