# US Patent & Trademark Office Patent Public Search | Text View

United States Patent

Kind Code

Bate of Patent

Inventor(s)

12396242

August 19, 2025

Liu; Wei-Min et al.

# Nano-structure transistors with air inner spacers and methods forming same

#### Abstract

A method includes forming a stack of layers, which includes a plurality of semiconductor nano structures and a plurality of sacrificial layers. The plurality of semiconductor nano structures and the plurality of sacrificial layers are arranged alternatingly. The method further includes laterally recessing the plurality of sacrificial layers to form lateral recesses, forming inner spacers in the lateral recesses, and epitaxially growing a source/drain region from the plurality of semiconductor nano structures. The source/drain region is spaced apart from the inner spacers by air inner spacers.

Inventors: Liu; Wei-Min (Hsinchu, TW), Wen; Cheng-Yen (Taichung, TW), Su; Li-Li

(Chubei, TW), Li; Chii-Horng (Zhubei, TW), Yeo; Yee-Chia (Hsinchu, TW)

**Applicant: Taiwan Semiconductor Manufacturing Co., Ltd.** (Hsinchu, TW)

Family ID: 1000008764073

Assignee: Taiwan Semiconductor Manufacturing Co., Ltd. (Hsinchu, TW)

Appl. No.: 17/662930

Filed: May 11, 2022

## **Prior Publication Data**

**Document Identifier**US 20230187524 A1

Publication Date
Jun. 15, 2023

# **Related U.S. Application Data**

us-provisional-application US 63289707 20211215

#### **Publication Classification**

Int. Cl.: H10D64/66 (20250101); H01L21/02 (20060101); H01L21/28 (20060101); H10D30/01 (20250101); H10D30/67 (20250101); H10D62/10 (20250101); H10D64/01 (20250101)

U.S. Cl.:

CPC **H10D64/679** (20250101); **H01L21/0259** (20130101); **H01L21/28123** (20130101);

H10D30/031 (20250101); H10D30/6735 (20250101); H10D30/6757 (20250101);

H10D62/118 (20250101); H10D64/018 (20250101);

#### **Field of Classification Search**

**USPC:** None

## **References Cited**

#### U.S. PATENT DOCUMENTS

Patent No.	<b>Issued Date</b>	<b>Patentee Name</b>	U.S. Cl.	CPC
10177227	12/2018	Yoshida et al.	N/A	N/A
11670680	12/2022	Jung et al.	N/A	N/A
11670723	12/2022	Huang et al.	N/A	N/A
2018/0331232	12/2017	Frougier et al.	N/A	N/A
2019/0067441	12/2018	Yang et al.	N/A	N/A
2020/0365692	12/2019	Jung	N/A	H01L 29/0673
2020/0381531	12/2019	Chung et al.	N/A	N/A
2021/0273103	12/2020	Chen et al.	N/A	N/A

#### FOREIGN PATENT DOCUMENTS

Patent No.	<b>Application Date</b>	Country	CPC
20190024535	12/2018	KR	N/A
20190024740	12/2018	KR	N/A
20200132436	12/2019	KR	N/A
20210080308	12/2020	KR	N/A
20210139125	12/2020	KR	N/A

*Primary Examiner:* Ho; Anthony

Attorney, Agent or Firm: Slater Matsil, LLP

# **Background/Summary**

PRIORITY CLAIM AND CROSS-REFERENCE (1) This application claims the benefit of the following provisionally filed U.S. patent application: Application No. 63/289,707, filed on Dec. 15, 2021, and entitled "Nanosheet FETs with Air Inner Spacer," which application is hereby incorporated herein by reference.

#### **BACKGROUND**

(1) In the formation of nano-structure transistors, inner spacers are formed to isolate the epitaxy source/drain regions from gate stacks, which are formed between the stacked nano semiconductor layers. The inner spacers are formed of dielectric materials. The epitaxy regions are grown from the

stacked nano semiconductor layers. In addition, some epitaxy growth may also occur from the inner spacers, resulting in a high density of defects, which adversely affect the performance of integrated circuits.

# **Description**

#### BRIEF DESCRIPTION OF THE DRAWINGS

- (1) Aspects of the present disclosure are best understood from the following detailed description when read with the accompanying figures. It is noted that, in accordance with the standard practice in the industry, various features are not drawn to scale. In fact, the dimensions of the various features may be arbitrarily increased or reduced for clarity of discussion.
- (2) FIGS. **1-4**, **5**A, **5**B, **6**A, **6**B, **7**A, **7**B, **8**A, **8**B, **9**A, **9**B, **9**C, **10**A, **10**B, **11**A, **11**B, **11**C, **12**A, **12**B, **13**A, **13**B, **14**A, and **14**B illustrate the cross-sectional views of intermediate stages in the formation of a Gate All-Around (GAA) transistor including air inner spacers in accordance with some embodiments.
- (3) FIGS. **15** and **16** illustrate the intermediate stages in the growth of epitaxy source/drain regions and the formation of air inner spacers in accordance with some embodiments.
- (4) FIGS. **17**A, **17**B, and **17**C illustrate the sizes of air inner spacers in accordance with some embodiments.
- (5) FIGS. **18** and **19** illustrate the profiles of nano semiconductor structures and dielectric inner spacers in accordance with some embodiments.
- (6) FIGS. **20**A, **20**B, and **20**C illustrate the relative positions of nano semiconductor structures and air inner spacers in accordance with some embodiments.
- (7) FIG. **21** illustrates the sizes of air inner spacers as a function of angles of the air inner spacers in accordance with some embodiments.
- (8) FIG. **22** illustrates the dishing of dielectric inner spacers in accordance with some embodiments.
- (9) FIG. **23** illustrates the sizes of air inner spacers as a function of the dishing of dielectric inner spacers in accordance with some embodiments.
- (10) FIG. **24**A illustrates a perspective view of a FinFET and air inner spacers in accordance with some embodiments
- (11) FIGS. **24**B and **24**C illustrate a perspective view and a cross-sectional view of an air inner spacer in accordance with some embodiments.
- (12) FIGS. **25**A, **25**B, and **25**C illustrate the shapes and sizes of air inner spacers in accordance with some embodiments.
- (13) FIGS. **26** and **27** illustrate the top views of a GAA transistor in accordance with some embodiments.
- (14) FIGS. **28**A, **28**B, **28**C, **28**D, and **28**E illustrate some end profiles of semiconductor nano structures in accordance with some embodiments.
- (15) FIG. **29** illustrates a process flow for forming a GAA transistor having air inner spacers in accordance with some embodiments.

#### **DETAILED DESCRIPTION**

(16) The following disclosure provides many different embodiments, or examples, for implementing different features of the invention. Specific examples of components and arrangements are described below to simplify the present disclosure. These are, of course, merely examples and are not intended to be limiting. For example, the formation of a first feature over or on a second feature in the description that follows may include embodiments in which the first and second features are formed in direct contact, and may also include embodiments in which additional features may be formed between the first and second features, such that the first and second features may not be in direct contact. In addition, the present disclosure may repeat

- reference numerals and/or letters in the various examples. This repetition is for the purpose of simplicity and clarity and does not in itself dictate a relationship between the various embodiments and/or configurations discussed.
- (17) Further, spatially relative terms, such as "underlying," "below," "lower," "overlying," "upper" and the like, may be used herein for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. The spatially relative terms are intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. The apparatus may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein may likewise be interpreted accordingly.
- (18) A Gate All-Around (GAA) transistor having an air inner spacer is provided. The method of forming the GAA transistor is also provided. In accordance with some embodiments, a dielectric inner spacer is formed next to a sacrificial layer. Epitaxy regions are grown from semiconductor layers overlying and underlying the sacrificial layer, and are merged, so that an air inner spacer is formed between the merged epitaxy regions and the dielectric inner spacer. With the air inner spacer being formed, the epitaxy regions have fewer defects, and the performance of the resulting GAA transistor is improved. Embodiments discussed herein are to provide examples to enable making or using the subject matter of this disclosure, and a person having ordinary skill in the art will readily understand modifications that can be made while remaining within contemplated scopes of different embodiments. Throughout the various views and illustrative embodiments, like reference numbers are used to designate like elements. Although method embodiments may be discussed as being performed in a particular order, other method embodiments may be performed in any logical order.
- (19) FIGS. **1-4**, **5**A, **5**B, **6**A, **6**B, **7**A, **7**B, **8**A, **8**B, **9**A, **9**B, **9**C, **10**A, **10**B, **11**A, **11**B, **11**C, **12**A, **12**B, **13**A, **13**B, **14**A, and **14**B illustrate the cross-sectional views of intermediate stages in the formation of a GAA transistor including air inner spacers in accordance with some embodiments of the present disclosure. The corresponding processes are also reflected schematically in the process flow shown in FIG. **29**.
- (20) Referring to FIG. **1**, a perspective view of wafer **10** is shown. Wafer **10** includes a multilayer structure comprising multilayer stack **22** on substrate **20**. In accordance with some embodiments, substrate **20** is a semiconductor substrate, which may be a silicon substrate, a silicon germanium (SiGe) substrate, or the like, while other substrates and/or structures, such as semiconductor-on-insulator (SOI), strained SOI, silicon germanium on insulator, or the like, could be used. Substrate **20** may be doped as a p-type semiconductor, although in other embodiments, it may be doped as an n-type semiconductor.
- (21) In accordance with some embodiments, multilayer stack **22** is formed through a series of deposition processes for depositing alternating materials. The respective process is illustrated as process **202** in the process flow **200** shown in FIG. **29**. In accordance with some embodiments, multilayer stack **22** comprises first layers **22**A formed of a first semiconductor material and second layers **22**B formed of a second semiconductor material different from the first semiconductor material.
- (22) In accordance with some embodiments, the first semiconductor material of a first layer **22**A is or comprises SiGe, Ge, Si, GaAs, InSb, GaSb, InAlAs, InGaAs, GaSbP, GaAsSb, or the like. In accordance with some embodiments, the deposition of first layers **22**A (for example, SiGe) is through epitaxial growth, and the corresponding deposition method may be Vapor-Phase Epitaxy (VPE), Molecular Beam Epitaxy (MBE), Chemical Vapor deposition (CVD), Low Pressure CVD (LPCVD), Atomic Layer Deposition (ALD), Ultra High Vacuum CVD (UHVCVD), Reduced Pressure CVD (RPCVD), or the like. In accordance with some embodiments, the first layer **22**A is formed to a first thickness in the range between about 30 Å and about 300 Å. However, any suitable thickness may be utilized while remaining within the scope of the embodiments.

- (23) Once the first layer **22**A has been deposited over substrate **20**, a second layer **22**B is deposited over the first layer **22**A. In accordance with some embodiments, the second layers **22**B is formed of or comprises a second semiconductor material such as Si, SiGe, Ge, GaAs, InSb, GaSb, InAlAs, InGaAs, GaSbP, GaAsSb, combinations of these, or the like, with the second semiconductor material being different from the first semiconductor material of first layer **22**A. For example, in accordance with some embodiments in which the first layer **22**A is silicon germanium, the second layer **22**B may be formed of silicon, or vice versa. It is appreciated that any suitable combination of materials may be utilized for first layers **22**A and the second layers **22**B.
- (24) In accordance with some embodiments, the second layer 22B is epitaxially grown on the first layer 22A using a deposition technique similar to that is used to form the first layer 22A. In accordance with some embodiments, the second layer 22B is formed to a similar thickness to that of the first layer 22A. The second layer 22B may also be formed to a thickness that is different from the first layer 22A. In accordance with some embodiments, the second layer 22B may be formed to a second thickness in the range between about 10 Å and about 500 Å, for example. (25) Once the second layer 22B has been formed over the first layer 22A, the deposition process is repeated to form the remaining layers in multilayer stack 22, until a desired topmost layer of multilayer stack 22 has been formed. In accordance with some embodiments, first layers 22A have thicknesses the same as or similar to each other, and second layers 22B have thicknesses the same as or similar to each other. First layers 22A may also have the same thicknesses as, or different thicknesses from, that of second layers 22B. In accordance with some embodiments, first layers 22A are removed in the subsequent processes, and are alternatively referred to as sacrificial layers 22A throughout the description. In accordance with alternative embodiments, second layers 22B are sacrificial, and are removed in the subsequent processes.
- (26) In accordance with some embodiments, there are some pad oxide layer(s) and hard mask layer(s) (not shown) formed over multilayer stack **22**. These layers are patterned, and are used for the subsequent patterning of multilayer stack **22**.
- (27) Referring to FIG. **2**, multilayer stack **22** and a portion of the underlying substrate **20** are patterned in an etching process(es), so that trenches **23** are formed. The respective process is illustrated as process **204** in the process flow **200** shown in FIG. **29**. Trenches **23** extend into substrate **20**. The remaining portions of multilayer stacks are referred to as multilayer stacks **22**' hereinafter. Underlying multilayer stacks **22**', some portions of substrate **20** are left, and are referred to as substrate strips **20**' hereinafter. Multilayer stacks **22**' include semiconductor layers **22**A and **22**B. Semiconductor layers **22**A are alternatively referred to as sacrificial layers, and Semiconductor layers **22**B are alternatively referred to as nanostructures hereinafter. The portions of multilayer stacks **22**' and the underlying substrate strips **20**' are collectively referred to as semiconductor strips **24**.
- (28) In above-illustrated embodiments, the GAA transistor structures may be patterned by any suitable method. For example, the structures may be patterned using one or more photolithography processes, including double-patterning or multi-patterning processes. Generally, double-patterning or multi-patterning processes combine photolithography and self-aligned processes, allowing patterns to be created that have, for example, pitches smaller than what is otherwise obtainable using a single, direct photolithography process. For example, in one embodiment, a sacrificial layer is formed over a substrate and patterned using a photolithography process. Spacers are formed alongside the patterned sacrificial layer using a self-aligned process. The sacrificial layer is then removed, and the remaining spacers may then be used to pattern the GAA structure.
- (29) FIG. **3** illustrates the formation of isolation regions **26**, which are also referred to as Shallow Trench Isolation (STI) regions throughout the description. The respective process is illustrated as process **206** in the process flow **200** shown in FIG. **29**. STI regions **26** may include a liner oxide (not shown), which may be a thermal oxide formed through the thermal oxidation of a surface layer of substrate **20**. The liner oxide may also be a deposited silicon oxide layer formed using, for

example, ALD, High-Density Plasma Chemical Vapor Deposition (HDPCVD), CVD, or the like. STI regions 26 may also include a dielectric material over the liner oxide, wherein the dielectric material may be formed using Flowable Chemical Vapor Deposition (FCVD), spin-on coating, HDPCVD, or the like. A planarization process such as a Chemical Mechanical Polish (CMP) process or a mechanical grinding process may then be performed to level the top surface of the dielectric material, and the remaining portions of the dielectric material are STI regions 26. (30) STI regions 26 are then recessed, so that the top portions of semiconductor strips 24 protrude higher than the top surfaces 26T of the remaining portions of STI regions 26 to form protruding fins 28. Protruding fins 28 include multilayer stacks 22' and the top portions of substrate strips 20'. The recessing of STI regions 26 may be performed through a dry etching process, wherein NF.sub.3 and NH.sub.3, for example, are used as the etching gases. During the etching process, plasma may be generated. Argon may also be included. In accordance with alternative embodiments of the present disclosure, the recessing of STI regions 26 is performed through a wet etching process. The etching chemical may include HF, for example.

- (31) Referring to FIG. **4**, dummy gate stacks **30** and gate spacers **38** are formed on the top surfaces and the sidewalls of (protruding) fins 28. The respective process is illustrated as process 208 in the process flow 200 shown in FIG. 29. Dummy gate stacks 30 may include dummy gate dielectrics 32 and dummy gate electrodes **34** over dummy gate dielectrics **32**. Dummy gate dielectrics **32** may be formed by oxidizing the surface portions of protruding fins **28** to form oxide layers, or by depositing a dielectric layer such as a silicon oxide layer. Dummy gate electrodes **34** may be formed, for example, using polysilicon or amorphous silicon, and other materials such as amorphous carbon may also be used. Each of dummy gate stacks 30 may also include one (or a plurality of) hard mask layer **36** over dummy gate electrode **34**. Hard mask layers **36** may be formed of silicon nitride, silicon oxide, silicon carbo-nitride, silicon oxy-carbo nitride, or multilayers thereof. Dummy gate stacks **30** may cross over a single one or a plurality of protruding fins **28** and the STI regions **26** between protruding fins **28**. Dummy gate stacks **30** also have lengthwise directions perpendicular to the lengthwise directions of protruding fins 28. The formation of dummy gate stacks **30** includes forming a dummy gate dielectric layer, depositing a dummy gate electrode layer over the dummy gate dielectric layer, depositing one or more hard mask layers, and then patterning the formed layers through a pattering process(es). (32) Next, gate spacers **38** are formed on the sidewalls of dummy gate stacks **30**. In accordance
- with some embodiments of the present disclosure, gate spacers **38** are formed of a dielectric material such as silicon nitride (SiN), silicon oxide (SiO.sub.2), silicon carbo-nitride (SiCN), silicon oxynitride (SiON), silicon oxy-carbo-nitride (SiOCN), or the like, and may have a single-layer structure or a multilayer structure including a plurality of dielectric layers. The formation process of gate spacers **38** may include depositing one or a plurality of dielectric layers, and then performing an anisotropic etching process(es) on the dielectric layer(s). The remaining portions of the dielectric layer(s) are gate spacers **38**.
- (33) FIGS. **5**A and **5**B illustrate the cross-sectional views of the structure shown in FIG. **4**. FIG. **5**A illustrates the reference cross-section A**1**-A**1** in FIG. **4**, which cross-section cuts through the portions of protruding fins **28** not covered by gate stacks **30** and gate spacers **38**, and is perpendicular to the gate-length direction. Fin spacers **38**, which are on the sidewalls of protruding fins **28**, are also illustrated. FIG. **5**B illustrates the reference cross-section B-B in FIG. **4**, which reference cross-section is parallel to the lengthwise directions of protruding fins **28**. (34) Referring to FIGS. **6**A and **6**B, the portions of protruding fins **28** that are not directly
- underlying dummy gate stacks **30** and gate spacers **38** are recessed through an etching process to form recesses **42**. The respective process is illustrated as process **210** in the process flow **200** shown in FIG. **29**. For example, a dry etch process may be performed using C.sub.2F.sub.6, CF.sub.4, SO.sub.2, the mixture of HBr, Cl.sub.2, and O.sub.2, the mixture of HBr, Cl.sub.2, O.sub.2, and CH.sub.2F.sub.2, or the like to etch multilayer semiconductor stacks **22**′ and the

- underlying substrate strips **20**′. The bottoms of recesses **42** are at least level with, or may be lower than (as shown in FIG. **6**B), the bottoms of multilayer semiconductor stacks **22**′. The etching may be anisotropic, so that the sidewalls of multilayer semiconductor stacks **22**′ facing recesses **42** are vertical and straight, as shown in FIG. **6**B.
- (35) Referring to FIGS. 7A and 7B, sacrificial semiconductor layers 22A are laterally recessed to form lateral recesses **41**, which are recessed from the edges of the respective overlying and underlying nanostructures **22**B. The respective process is illustrated as process **212** in the process flow **200** shown in FIG. **29**. The lateral recessing of sacrificial semiconductor layers **22**A may be achieved through a wet etching process using an etchant that is more selective to the material (for example, silicon germanium (SiGe)) of sacrificial semiconductor layers 22A than the material (for example, silicon (Si)) of the nanostructures **22**B and substrate **20**. For example, in an embodiment in which sacrificial semiconductor layers 22A are formed of silicon germanium and the nanostructures **22**B are formed of silicon, the wet etching process may be performed using an etchant such as hydrochloric acid (HCl). The wet etching process may be performed using a dip process, a spray process, a spin-on process, or the like, and may be performed using any suitable process temperatures (for example, between about 400° C. and about 600° C.) and a suitable process time (for example, between about 100 seconds and about 1,000 seconds). In accordance with alternative embodiments, the lateral recessing of sacrificial semiconductor layers 22A is performed through an isotropic dry etching process or a combination of a dry etching process and a wet etching process. In accordance with some embodiments, the wet etching is prolonged, so that the lateral recessing distance LR**1** is increased.
- (36) FIGS. **8**A and **8**B illustrate the deposition of spacer layer **43**, which is formed of a dielectric material. The material of spacer layer **43** may include Si, O, C, N, or combinations thereof. The respective process is illustrated as process **214** in the process flow **200** shown in FIG. **29**. Spacer layer **43** is deposited as a conformal layer, and has a relatively low k value, which may range from about 3.0 to about 4.5. Accordingly, spacer layer **43** may sometimes be formed as a low-k dielectric layer (when its k value is lower than about 3.8) or a high-k dielectric layer, depending on the formation process. The thickness of spacer layer **43** may be in the range between about 4 nm and about 6 nm. Spacer layer **43** may be a conformal layer, which extends into the lateral recesses **41** (FIG. **7**B).
- (37) Referring to FIGS. **9**A, **9**B, and **9**C, an etching process (also referred to as a spacer trimming process) is performed to trim the portions of spacer layer **43** outside of the lateral recesses **41**, leaving the portions of spacer layer **43** in the lateral recesses **41**. The respective process is illustrated as process **216** in the process flow **200** shown in FIG. **29**. The remaining portions of spacer layer **43** are referred to as (dielectric) inner spacers **44**. FIGS. **9**A and **9**B illustrate the cross-sectional views of the inner spacers **44** in accordance with some embodiments. The etching of spacer layer **43** may be performed through a wet etching process, in which the etching chemical may include H.sub.2SO.sub.4, diluted HF, ammonia solution (NH.sub.4OH, ammonia in water), or the like, or combinations thereof.
- (38) The etching process may be performed until the edges of the inner spacers **44** are laterally recessed from the overlying and underlying nano structures **22**B. For example, referring to FIG. **9**C, the lateral recessing distance LR**2** may be greater than about 5 nm, and may be in the range between about 5 nm and about 10 nm. The increase in the lateral recessing distances LR**1** and LR**2** (FIG. **9**C) may help the formation of air inner spacers in subsequent processes.
- (39) In accordance with some embodiments, after the formation of inner spacers **44**, the sidewall profile of nano structures **22**B is further shaped in an isotropic etching process, an anisotropic etching process, or the combination of an isotropic etching process and an anisotropic etching process. The respective process is illustrated as process **218** in the process flow **200** shown in FIG. **29**. The isotropic etching process may be performed through wet etching or dry etching. When a wet etching process is performed, potassium hydroxide (KOH), tetra methyl ammonium hydroxide

- (TMAH), ethylene di-amine pyro-catechol (EDP), or the like, or combinations thereof may be used. When an anisotropic dry etching process is performed, process gases such as CF.sub.4, CH.sub.3F, HBr, O.sub.2, He, Ar, or the like may be used, with bias power being applied. When an isotropic dry etching process is performed, process gases such as NF.sub.3, Cl.sub.2, H.sub.2, Ar, He, or the like, or combinations thereof may be used.
- (40) FIGS. **28**A through **28**E illustrate some end profiles of nano structures **22**B in accordance with some embodiments after the shaping of the sidewall profile of nano structures **22**B. In FIG. **28**A, the end of nano structure **22**B is rounded and convex. In FIG. **28**B, the end of nano structure **22**B has facets and may form a triangular shape. In FIG. **28**C, the end of nano structure **22**B is rectangular. In FIG. **28**D, the end of nano structure **22**B is concave and has a rectangular profile. In FIG. **28**E, the end of nano structure **22**B is concave, and may be rounded.
- (41) Although the inner sidewalls (contacting sacrificial layers 22A) and the outer sidewalls of the inner spacers 44 are schematically illustrated as being straight in FIG. 9B, the inner sidewalls and the outer sidewalls of the inner spacers 44 may be curved. As an example, FIG. 9C illustrates an amplified view of an embodiment in which the sidewalls of sacrificial layers 22A are concave, outer sidewalls of the inner spacers 44 are concave, and the inner spacers 44 are recessed from the corresponding sidewalls of nano structures 22B. The inner spacers 44 may be used to prevent the damage that may occur to subsequently formed source/drain regions (such as the epitaxial source/drain regions 48), which damage may be caused by subsequent etching processes (FIGS. 13A and 13B) for forming replacement gate structures.
- (42) Referring to FIGS. **10**A and **10**B, epitaxial source/drain regions **48** are formed in recesses **42**. The respective process is illustrated as process **220** in the process flow **200** shown in FIG. **29**. In accordance with some embodiments, the source/drain regions 48 may exert stress on the nanostructures **22**B, which are used as the channels of the corresponding GAA transistors, thereby improving performance. Depending on whether the resulting transistor is a p-type transistor or an n-type transistor, a p-type or an n-type impurity may be in-situ doped with the proceeding of the epitaxy. For example, when the resulting transistor is a p-type Transistor, silicon germanium boron (SiGeB), silicon boron (SiB), or the like may be grown. Conversely, when the resulting transistor is an n-type Transistor, silicon phosphorous (SiP), silicon carbon phosphorous (SiCP), SiAs, or the like, or combinations thereof may be grown. After recesses 42 are filled with epitaxy regions 48, the further epitaxial growth of epitaxy regions **48** causes epitaxy regions **48** to expand horizontally, and facets may be formed. The further growth of epitaxy regions 48 may also cause neighboring epitaxy regions **48** to merge with each other. Voids (air gaps) **49** (FIG. **10**A) may be generated. (43) When the epitaxy regions **48** comprises silicon, the precursors may comprise a siliconcontaining precursor such as a silane, such as monosilane (SiH.sub.4), disilane (Si.sub.2H.sub.6), trisilane (Si.sub.3H.sub.8), trichlorosilane (HCl.sub.3Si), dichlorosilane (H.sub.2SiCl.sub.2), or the like. When the dopant comprises arsenic, the dopant-containing precursor may include arsine (AsH.sub.3) or the like. When the dopant comprises phosphorous, the dopant-containing precursor may be a phosphorous-containing precursor such as diphosphine (P.sub.2H.sub.6), phosphorus trichloride (PCl.sub.3), or the like. The epitaxy temperature may be in the range between about 500° C. and about 800° C. The pressure of the precursors may be in range between about 1 Torr and about 760 Torr.
- (44) FIGS. **15** and **16** illustrate the intermediate stages in the formation of epitaxy regions **48** in accordance with some embodiments. Referring to FIG. **15**, epitaxy regions **48** are selectively grown from semiconductor materials including bulk semiconductor substrate **20** and nano structures **22**B. FIG. **15** schematically illustrates the layer-by-layer growth of epitaxy regions **48**. For example, a first sub-layer **48-1** is grown first, and air inner spacers **46** (which may be filled with air later, or remain as vacuumed) are sealed in the first sub-layer **48-1**. A second sub-layer **48-2** is then grown. FIG. **16** illustrates the further growth of epitaxy regions **48** to a level higher than the top nano structure **22**B.

- (45) In the epitaxy, process conditions are adjusted to form air inner spacers **46**. For example, reducing the wafer temperature in the formation of epitaxy regions **48**, reducing the pressure of precursors, and/or increasing the flow rate of etching gases (such as Cl.sub.2, HCl, or combinations thereof) may result in the increase in height H.sub.EpiV (FIG. **16**), which is the height of the epitaxy regions **48** grown from and contacting inner spacers **44**. The height H**46** of air inner spacer **46** is equal to (H**44**–2\*H.sub.EpiV), with H**44** being the height of inner spacer **44**. When H.sub.EpiV is increased, the height H**46** of air inner spacer **46** is reduced. Conversely, increasing the wafer temperature, increasing the pressure of precursors, and/or reducing the flow rate of etching gases (such as Cl.sub.2, HCl, or combinations thereof) may reduce the H.sub.EpiV value, and accordingly may increase the height H**46** of air inner spacers **46**.
- (46) Furthermore, the lateral recessing distance LR2 also affects whether the air inner spacers 46 can be generated or not, and the sizes of the air inner spacers 46. For example, FIGS. 17A, 17B, and 17C illustrate that with the increase in LR2 from negative value to positive value, the air inner spacers 46 start to appear, and with the increase in lateral recessing distance LR2, the sizes of the air inner spacers 46 increase accordingly. In FIGS. 17A, 17B, and 17C and some subsequent figures, the reference "22A/70" represents that the corresponding regions may be sacrificial layers, and are also the replacement gate regions after sacrificial layers are removed. In the embodiments as shown in FIG. 17A, the lateral recessing distance LR2, which is the recessing of the outer sidewall of inner spacer 44 from the outer sidewall of nano structure 22B, has a negative value, and no air inner spacer is formed. In FIG. 17B, lateral recessing distance LR2 has a small positive value. A small air inner spacer 46 is formed, and its height H46 is smaller than the height H44 of inner spacer 44. In FIG. 17C, lateral recessing distance LR2 has a higher positive value. The height H46 of air inner spacer 46 is equal to the height H44 of inner spacer 44.
- (47) In accordance with some embodiments, the embodiments in FIG. **17**B or **17**C may be adopted, depending on the requirement of the resulting GAA transistor. In addition, by adjusting the recessing distances LR**2**, a first transistor, a second transistor, and a third transistor having the structures as shown in FIGS. **17**A, **17**B, and **17**C, respectively, may be formed in the same die/wafer through different processes, so that the performance of the resulting transistors may be tuned to desirable.
- (48) After the epitaxy process, epitaxy regions **48** may be further implanted with a p-type or an n-type impurity to form source and drain regions, which are also denoted using reference numeral **48**. In accordance with alternative embodiments of the present disclosure, the implantation process is skipped when epitaxy regions **48** are in-situ doped with the p-type or n-type impurity during the epitaxy, and the epitaxy regions **48** are also source/drain regions.
- (49) FIGS. **11**A, **11**B, and **11**C illustrate the cross-sectional views of the structure after the formation of Contact Etch Stop Layer (CESL) **50** and Inter-Layer Dielectric (ILD) **52**. The respective process is illustrated as process **222** in the process flow **200** shown in FIG. **29**. CESL **50** may be formed of silicon oxide, silicon nitride, silicon carbo-nitride, or the like, and may be formed using CVD, ALD, or the like. ILD **52** may include a dielectric material formed using, for example, FCVD, spin-on coating, CVD, or any other suitable deposition method. ILD **52** may be formed of an oxygen-containing dielectric material, which may be a silicon-oxide based material formed using Tetra Ethyl Ortho Silicate (TEOS) as a precursor, Phospho-Silicate Glass (PSG), Boro-Silicate Glass (BSG), Boron-Doped Phospho-Silicate Glass (BPSG), Undoped Silicate Glass (USG), or the like.
- (50) FIGS. **12**A and **12**B through FIGS. **14**A and **14**B illustrate the process for forming replacement gate stacks. In FIGS. **12**A and **12**B, a planarization process such as a CMP process or a mechanical grinding process is performed to level the top surface of ILD **52**. The respective process is illustrated as process **224** in the process flow **200** shown in FIG. **29**. In accordance with some embodiments, the planarization process may remove hard masks **36** to reveal dummy gate electrodes **34**, as shown in Figure s **12**A and **12**B. In accordance with alternative embodiments, the

- planarization process may reveal, and is stopped on, hard masks **36**. In accordance with some embodiments, after the planarization process, the top surfaces of dummy gate electrodes **34** (or hard masks **36**), gate spacers **38**, and ILD **52** are level within process variations.
- (51) Next, dummy gate stacks **30** are replaced with replacement gate stacks. In the replacing process, dummy gate electrodes **34** (and hard masks **36**, if remaining) and dummy gate dielectrics **32** are removed in one or more etching processes, so that recesses **58** are formed, as shown in FIGS. **13**A and **13**B. The respective process is illustrated as process **226** in the process flow **200** shown in FIG. **29**. In accordance with some embodiments, dummy gate electrodes **34** and dummy gate dielectrics **32** are removed through an anisotropic or isotropic dry etch process. For example, the etching process may be performed using reaction gas(es) that selectively etch dummy gate electrodes **34** at a faster rate than ILD **52**.
- (52) Next, sacrificial layers **22**A are removed to extend the recesses **58** between nanostructures **22**B, and the resulting structure is also shown in FIGS. **13**A and **13**B. Sacrificial layers **22**A may be removed by performing an isotropic etching process such as a wet etching process using etchants which are selective to the materials of sacrificial layers **22**A, while nanostructures **22**B, substrate **20**, and STI regions **26** remain un-etched as compared to sacrificial layers **22**A. In accordance with some embodiments in which sacrificial layers **22**A include, for example, SiGe, and nanostructures **22**B include, for example, Si or SiC, TMAH, ammonium hydroxide (NH.sub.4OH), or the like may be used to remove sacrificial layers **22**A.
- (53) In subsequent processes, replacement gate stacks are formed. The respective process is illustrated as process **228** in the process flow **200** shown in FIG. **29**. Referring to FIGS. **14**A and **14**B, gate dielectrics **62** are formed. In accordance with some embodiments, each of gate dielectric **62** includes an interfacial layer and a high-k dielectric layer on the interfacial layer. The interfacial layer may be formed of or comprises silicon oxide, which may be deposited through a conformal deposition process such as ALD or CVD. In accordance with some embodiments, the high-k dielectric layers comprise one or more dielectric layers. For example, the high-k dielectric layer(s) may include a metal oxide or a silicate of hafnium, aluminum, zirconium, lanthanum, manganese, barium, titanium, lead, and combinations thereof.
- (54) Gate electrodes **68** are then formed. In the formation, conductive layers are first formed on the high-k dielectric layer, and fill the remaining portions of recesses **58**. Gate electrodes **68** may include a metal-containing material such as TiN, TaN, TiAl, TiAlC, cobalt, ruthenium, aluminum, tungsten, combinations thereof, and/or multilayers thereof. For example, although single-layer gate electrodes **68** are illustrated in FIGS. **14**A and **14**B, gate electrodes **68** may comprise any number of layers, any number of work function layers, and possibly a filling material. Gate dielectrics **62** and gate electrodes **68** also fill the spaces between adjacent ones of nanostructures **22**B, and fill the spaces between the bottom ones of nanostructures **22**B and the underlying substrate strips **20**′. After the filling of recesses **58**, a planarization process such as a CMP process or a mechanical grinding process is performed to remove the excess portions of the gate dielectrics and the material of gate electrodes **68**, which excess portions are over the top surface of ILD **52**. Gate electrodes **68** and gate dielectrics **62** are collectively referred to as gate stacks **70** of the resulting nano-FETs. GAA transistor **74** is thus formed.
- (55) FIGS. **18** and **19** illustrate air inner spacers **46** in accordance with some embodiments. In FIG. **18**, the outer sidewall of inner spacer **44** exposed to the air inner spacer **46** is curved and concave. In FIG. **19**, the outer sidewall of inner spacer **44** exposed to the air inner spacer **46** is straight. (56) FIGS. **20**A, **20**B, and **20**C illustrate some different relative positions of inner spacers **44** relative to the ends of nano structures **22**B. From FIG. **20**A to FIG. **20**B, the lateral recessing values LR**1** and LR**2** reduce. In FIG. **20**C, the lateral recess LR**2** of inner spacer **44** relative to the end of nano structures **22**B becomes negative, meaning nano structures **22**B are recessed laterally from the respective outer edges of inner spacer **44**.
- (57) FIG. 21 illustrates the ratio H46/L.sub.46-111, which is the ratio of Height H46 of air inner

- spacer **46** to the length L.sub.46-111 (marked in FIG. **19**) of a side **46**SA (FIG. **19**) of air inner spacer **46** when the side **46**SA is in a {**111**} plane of the epitaxy region **48**. The ratio H**46**/L.sub.46-111 is shown in FIG. **21** as a function of angle  $\theta$ , which is also marked in FIG. **19**. In accordance with some embodiments, the height H**46** of air inner spacer **46** may be expressed as H46~(H44–2H.sub.Epiv)/2\*tan  $\theta$
- (58) When angle  $\theta$  is about 45 degrees, the height H46 of air inner spacer 46 may be expressed as ((H44–2H.sub.EpiV)\*sqrt (2))/2. Assuming the height H46 when sidewall 46SA is on the {111} plane is L.sub.46-111, when sidewall 46SA deviates from the {111} plane ( $\theta$  reduces), the height H46 reduces accordingly, and ratio H46/L.sub.46-111 may be shown as in FIG. 21. The volume of air inner spacers 46 may increase with the increase in angle  $\theta$ . In accordance with some embodiments, the angle  $\theta$  is smaller than about 40 degrees, and may be in the range between about 10 degrees and about 40 degrees.
- (59) In FIGS. **18** and **19**, epitaxy regions **48** may be in contact with the respective inner spacers **44** to form interfaces, or may extend to inner spacers **44**, but have no interfaces formed. Clearly, with the increase in the vertical interface, the size of air inner spacer **46** is also reduced. The vertical interface may also be equal to zero, and hence epitaxy regions **48** may extend to overlying and underlying nano structures **22**B.
- (60) FIGS. 22 and 23 illustrate the effect of dishing (concave recessing) of inner spacer 44. FIG. 22 illustrates that the dishing L.sub.dishing is measured from the outmost point of the outer sidewall of inner spacer **44** to the inner most point of the outer sidewall of inner spacer **44**. FIG. **23** illustrates that the lateral length L**46** of air inner spacer **46** is linear to dishing L.sub.dishing. (61) FIG. **24**A illustrates a perspective view of some portions of GAA transistor **74** in accordance with some embodiments. FIG. 24B illustrates a perspective view of one of air inner spacers 46, which forms a tunnel. Air inner spacer **46** has two end points **76**A and **76**B, and middle point **76**C, wherein air inner spacer **46** have widths L**46**-A, L**46**-B, and L**46**-C at end point **76**A, middle point **76**C, and end point **76**B, respectively. End points **76**A and **76**B are also the entrance points of the tunnel of air inner spacer **46**. Epitaxy region **48** accordingly may have higher growth rates at end points **76**A and **76**B than at the middle point **76**C since after air inner spacer **46** is sealed by epitaxy region **48**, the precursors need to flow through the end points **76**A and **76**B in order to reach the middle point **76**C. The end widths L**46**-A and L**46**-C are smaller than middle width L**46**-B. (62) FIG. **24**C schematically illustrates how the widths of air inner spacer **46** change from end point **76**A to end point **76**B. It shows that the middle width L**46**-B may be the greatest, and from middle point **76**C to end points **76**A and **76**B, the widths of air inner spacer **46** reduce gradually. In accordance with some embodiments, ratios L46-A/L46-B and L46-C/L46-B may be in the range between about 0 percent and about 200 percent. When ratios L46-A/L46-B and L46-C/L46-B are equal to zero percent, the corresponding widths L**46**-A and L**46**-C are equal to zero, as represented by the dashed line in FIG. **24**C, which shows that corresponding widths of air inner spacer **46**. When widths L**46**-A and L**46**-C are equal to zero, the corresponding inner spacer is fully sealed by the corresponding inner spacer 44, epitaxy region 48, and possibly the overlying and/or underlying nano structure(s) 22B.
- (63) FIGS. **25**A, **25**B, and **25**C schematically illustrate the cross-sectional views of air inner spacer **46** and inner spacer **44** at end point **76**A, end point **76**B, and end point **76**B, respectively. It is appreciated that at the time the epitaxy region **48** grown from neighboring nano structures **22**B touch each other, middle width L**46**-B may be fixed. With the proceeding of the formation of epitaxy regions **48**, widths L**46**-A and L**46**-C, on the other hand, will become increasingly smaller, and may or may not be reduced to zero when the epitaxy process is ended.
- (64) FIG. **26** illustrates a top view in a horizontal plane crossing nano structure **22**B in accordance with some embodiments. The horizontal plane contains line **26-26** in FIG. **24**A. FIG. **26** illustrates that epitaxy region **48** directly grows from nano structure **22**B, and air inner spacer **46** does not extend into this plane. The example lattice directions **110**>, **100**>, and **110**> of substrate **20** and

epitaxy region **48** are shown in FIG. **26** also.

- (65) FIG. **27** illustrates a top view in a horizontal plane crossing gate stack **70**, inner spacer **44**, and air inner spacer **46** in accordance with some embodiments. The horizontal plane contains line **27-27** in FIG. **24**A. The X-direction and Y-direction as shown in FIG. **27** correspond to the X-directions and Y-directions in FIGS. **4** and **24**A. The example lattice directions <**110**>, <**100**>, and <**110**> are shown in FIG. **27** also. When there are dielectric fins **78** aside of nano structure **22**B, epitaxy region **48** grows to, and are blocked by, dielectric fins **78**, which may be high-k dielectric fins. It is appreciated that dielectric fins **78** are optional, and may be or may not be formed.
- (66) The embodiments of the present disclosure have some advantageous features. By forming air inner spacers, the growth of epitaxy source/drain regions directly from dielectric inner spacers is reduced, and the resulting defects are also reduced. The performance of the GAA transistors is improved. The volume of the epitaxy source/drain regions is also reduced, and the parasitic capacitance of the GAA transistor is accordingly reduced.
- (67) In accordance with some embodiments of the present disclosure, a method comprises forming a stack of layers comprising a plurality of semiconductor nano structures; and a plurality of sacrificial layers, wherein the plurality of semiconductor nano structures and the plurality of sacrificial layers are arranged alternatingly; laterally recessing the plurality of sacrificial layers to form lateral recesses; forming inner spacers in the lateral recesses; and epitaxially growing a source/drain region from the plurality of semiconductor nano structures, wherein the source/drain region is spaced apart from the inner spacers by air inner spacers.
- (68) In an embodiment, the inner spacers have concaved outer sidewalls facing the air inner spacers. In an embodiment, the method further comprises, after the inner spacers are formed, laterally recessing the plurality of semiconductor nano structures. In an embodiment, the air inner spacers extend into the lateral recesses. In an embodiment, the method further comprises, after the source/drain region is grown, removing the plurality of sacrificial layers; and forming a gate stack extending into spaces left by the plurality of sacrificial layers that have been removed. In an embodiment, one of the air inner spacers extend into one of the inner spacers. In an embodiment, the forming the inner spacers comprises depositing a dielectric layer extending into the lateral recesses; and etching the dielectric layer, wherein remaining portions of the dielectric layer form the inner spacers. In an embodiment, one of the air inner spacers has two end portions, and a middle portion wider than the two end portions. In an embodiment, the end portions have a width substantially equal to zero.
- (69) In accordance with some embodiments of the present disclosure, an integrated circuit structure comprises a plurality of semiconductor nano structures, wherein upper ones of the plurality of semiconductor nano structures overlap corresponding lower ones of the plurality of semiconductor nano structures; a gate stack comprising portions separating the plurality of semiconductor nano structures from each other; inner spacers separating the plurality of semiconductor nano structures from each other; and a source/drain region on a side of the plurality of semiconductor nano structures, wherein the source/drain region is spaced apart from the inner spacers by air inner spacers.
- (70) In an embodiment, one of the air inner spacers extends to a space between an overlying one and an underlying one of the plurality of semiconductor nano structures. In an embodiment, one of the air inner spacers is separated from an overlying one or an underlying one of the plurality of semiconductor nano structures by a part of one of the inner spacers and a part of the source/drain region. In an embodiment, in a cross-sectional view of the integrated circuit structure, one of the air inner spacers comprises two straight edges joined with each other. In an embodiment, one of the air inner spacers comprises a first end portion and a second end portion; and a middle portion between, and being wider than, the first end portion and the second end portion. In an embodiment, one of the inner spacers comprises a concave sidewall exposed to one of the air inner spacers. In an embodiment, upper ones of the air inner spacers overlap lower ones of the air inner spacers.

(71) In accordance with some embodiments of the present disclosure, an integrated circuit structure comprises a first semiconductor layer; a second semiconductor layer over and vertically spaced apart from the first semiconductor layer; a dielectric inner spacer between and physically contacting the first semiconductor layer and the second semiconductor layer; a gate stack comprising a portion between and physically contacting the first semiconductor layer and the second semiconductor layer; an air inner spacer; and a semiconductor region, wherein both of the dielectric inner spacer and the semiconductor region are exposed to the air inner spacer. In an embodiment, the air inner spacer comprises an inner portion extending into a space overlapping the first semiconductor layer. In an embodiment, the air inner spacer further comprises an outer portion vertically offset from the first semiconductor layer and the second semiconductor layer. In an embodiment, a first sidewall of the dielectric inner spacer exposed to the air inner spacer is concaved and rounded, and wherein a second sidewall of the semiconductor region exposed to the air inner spacer comprises two straight edges joined to each other.

(72) The foregoing outlines features of several embodiments so that those skilled in the art may better understand the aspects of the present disclosure. Those skilled in the art should appreciate that they may readily use the present disclosure as a basis for designing or modifying other processes and structures for carrying out the same purposes and/or achieving the same advantages of the embodiments introduced herein. Those skilled in the art should also realize that such equivalent constructions do not depart from the spirit and scope of the present disclosure, and that they may make various changes, substitutions, and alterations herein without departing from the spirit and scope of the present disclosure.

# **Claims**

- 1. A method comprising: forming a stack of layers comprising: a plurality of semiconductor nano structures; and a plurality of sacrificial layers, wherein the plurality of semiconductor nano structures and the plurality of sacrificial layers are arranged alternatingly; laterally recessing the plurality of sacrificial layers to form lateral recesses; forming inner spacers in the lateral recesses; after the inner spacers are formed, laterally recessing the plurality of semiconductor nano structures; and epitaxially growing a source/drain region from the plurality of semiconductor nano structures, wherein the source/drain region is spaced apart from the inner spacers by air inner spacers.
- 2. The method of claim 1, wherein the inner spacers have concaved outer sidewalls facing the air inner spacers.
- 3. The method of claim 1, wherein the air inner spacers extend into the lateral recesses.
- 4. The method of claim 1 further comprising: after the source/drain region is grown, removing the plurality of sacrificial layers; and forming a gate stack extending into spaces left by the plurality of sacrificial layers that have been removed.
- 5. The method of claim 1, wherein one of the air inner spacers extends into one of the inner spacers.
- 6. The method of claim 1, wherein the forming the inner spacers comprises: depositing a dielectric layer extending into the lateral recesses; and etching the dielectric layer, wherein remaining portions of the dielectric layer form the inner spacers.
- 7. The method of claim 1, wherein one of the air inner spacers has two end portions, and a middle portion wider than the two end portions.
- 8. The method of claim 7, wherein the end portions have a width substantially equal to zero.
- 9. The method of claim 1, wherein one of the inner spacers is exposed to, and is taller than, a corresponding one of the air inner spacers.
- 10. A method comprising: forming a gate stack, wherein the gate stack comprises portions separating a plurality of semiconductor nano structures from each other, wherein upper ones of the

plurality of semiconductor nano structures overlap corresponding lower ones of the plurality of semiconductor nano structures; forming inner spacers separating the plurality of semiconductor nano structures from each other; and forming a source/drain region aside of the plurality of semiconductor nano structures, wherein air inner spacers are located between the source/drain region and the inner spacers, wherein in a cross-sectional view of the air inner spacers, one of the air inner spacers comprises two straight edges joined to each other.

- 11. The method of claim 10, wherein one of the air inner spacers is formed as extending to a space between an overlying one and an underlying one of the plurality of semiconductor nano structures.
- 12. The method of claim 10, wherein one of the air inner spacers is formed as separated from an overlying one or an underlying one of the plurality of semiconductor nano structures by a part of one of the inner spacers and a part of the source/drain region.
- 13. The method of claim 10, wherein one of the air inner spacers comprises: a first end portion and a second end portion; and a middle portion between, and being wider than, the first end portion and the second end portion.
- 14. The method of claim 10, wherein one of the inner spacers is formed as comprising a concave sidewall exposed to one of the air inner spacers.
- 15. The method of claim 10, wherein upper ones of the air inner spacers are formed as overlapping lower ones of the air inner spacers.
- 16. The method of claim 10, wherein one of the inner spacers is exposed to, and is taller than, a corresponding one of the air inner spacers.
- 17. A method comprising: a dielectric inner spacer between and physically contacting a first semiconductor layer and a second semiconductor layer, wherein the second semiconductor layer is over and vertically spaced apart from the first semiconductor layer; forming a gate stack comprising a portion between and physically contacting the first semiconductor layer and the second semiconductor layer; forming an air inner spacer, wherein a first sidewall of the dielectric inner spacer exposed to the air inner spacer is concaved and rounded; and forming a semiconductor region, wherein both of the dielectric inner spacer and the semiconductor region are exposed to the air inner spacer, wherein a second sidewall of the semiconductor region exposed to the air inner spacer comprises two straight edges joined to each other.
- 18. The method of claim 17, wherein the air inner spacer comprises an inner portion extending into a space overlapping the first semiconductor layer.
- 19. The method of claim 17, wherein the air inner spacer further comprises an outer portion vertically offset from the first semiconductor layer and the second semiconductor layer.

  20. The method of claim 17, wherein the dielectric inner spacer is taller than the air inner spacer.