

STACKED ARRANGEMENT AND METHOD OF FORMING THE SAME**CROSS-REFERENCE TO RELATED APPLICATION**

[0001] This application claims the benefit of priority of Singapore application No. 10202400138Q filed January 17, 2024, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various embodiments of this disclosure may relate to a stacked arrangement. Various embodiments of this disclosure may relate to a method of forming a stacked arrangement.

BACKGROUND

[0003] Platinized silicon is widely used in various applications such as micro-electromechanical systems (MEMS), electrochemical sensors, photovoltaic devices, surface-enhanced Raman spectroscopy (SERS), fuel cells, optical devices and many others. Platinum (Pt) usually serves as bottom electrode for a device when the structure is required to go through harsh processing or application condition, because it is not only highly electrically conductive, but also has excellent thermal and chemical stability, even at high temperatures. The orientation of the platinum (Pt) electrode has a significant impact on the orientation of subsequent layers and thus the device performance. For the widely used silicon-based technologies in industry, platinum (Pt) film is typically not deposited directly on silicon, as platinum (Pt) and silicon (Si) will form platinum silicide, even at low temperatures. Hence, direct growth of platinum is rare, unless the platinum silicide layer is desired. Moreover, the lattice mismatch between platinum (Pt) and silicon (Si) is large (~28 %), whereby the lattice constants of platinum (Pt) and silicon (Si) are 0.392 nm and 0.543 nm, respectively. It is challenging to obtain a highly oriented platinum (Pt) film on silicon (Si) directly. Therefore, a buffer layer such as titanium oxide (TiO_x) is generally required, which influences the orientation of the platinum (Pt) layer. Generally, a commercial platinized silicon wafer has platinum (Pt) film in (111) orientation, as (111) planes are associated with the lowest surface energy. The commercial platinized silicon wafer typically has a silicon (Si)/silicon dioxide (SiO₂)/ titanium oxide (TiO_x)/platinum (Pt)

arrangement, including a silicon wafer of (100) orientation, a ~500 nm thick SiO₂ layer formed by thermal oxidation, a 30 – 40 nm thick TiO_x layer of (200) orientation formed by sputtering and a 100 – 200 nm thick Pt layer of (111) orientation formed by sputtering. Employing a Pt (111) layer may hinder optimization of many functional films on the top of the Pt (111) layer, as these functional films may require to be in the (100) orientation to be optimized. However, it may be difficult to obtain a highly oriented Pt (100) film on silicon, as the lowest energy of the Pt layer is associated with the (111) orientation. As such, Pt layers with (111) orientation may be commonly found. However, highly oriented Pt films with different crystal orientations (over silicon) may be desirable for different device applications.

[0004] Epitaxial Pt (100), Pt (110) and Pt (111) films on some single crystal substrates, such as magnesium oxide (MgO) substrates, e.g., MgO (100), MgO (110), MgO (111) substrates, have been successful. Nonetheless, these single crystals are expensive, and may not be suitable for monolithic integration of electronic circuitry for large scale industry applications.

SUMMARY

[0005] Various embodiments may relate to a stacked arrangement. The stacked arrangement may include a substrate. The stacked arrangement may also include a buffer layer over the substrate, the buffer layer including zirconium nitride (ZrN). The stacked arrangement may further include a metal layer on the buffer layer. A crystal lattice orientation of the metal layer may be substantially in alignment with a crystal lattice orientation of the buffer layer.

[0006] Various embodiments may relate to a method of forming a stacked arrangement. The method may include forming a buffer layer over the substrate, the buffer layer including zirconium nitride (ZrN). The method may also include forming a metal layer on the buffer layer. A crystal lattice orientation of the metal layer may substantially be in alignment with a crystal lattice orientation of the buffer layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

FIG. 1 shows a schematic of a stacked arrangement according to various embodiments.

FIG. 2 shows a schematic of a method of forming a stacked arrangement according to various embodiments.

FIG. 3A shows a cross-sectional schematic view of a stacked arrangement according to various embodiments.

FIG. 3B shows a cross-sectional schematic of a stacked arrangement according to various other embodiments.

FIG. 3C shows (above) a top schematic view of a platinum Pt (100)/ zirconium nitride ZrN (100)/ silicon Si (100) stacked arrangement according to various embodiments; and (below) a schematic side view of the platinum Pt (100)/ zirconium nitride ZrN (100)/ silicon Si (100) stacked arrangement according to various embodiments.

FIG. 3D shows (above) a top schematic view of a platinum Pt (111)/ zirconium nitride ZrN (111)/ silicon Si (111) stacked arrangement according to various embodiments; and (below) a schematic side view of the platinum Pt (111)/ zirconium nitride ZrN (111)/ silicon Si (111) stacked arrangement according to various embodiments.

FIG. 4A shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of zirconium nitride ZrN (100)/silicon Si (100) and platinum Pt (100)/zirconium nitride ZrN (100)/silicon Si (100) stacked arrangements according to various embodiments.

FIG. 4B shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the platinum Pt (100)/zirconium nitride ZrN (100)/silicon Si (100) stacked arrangement according to various embodiments.

FIG. 4C shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride ZrN (100)/silicon Si (100) stacked arrangement according to various embodiments.

FIG. 4D shows a cross-sectional scanning electron microscopy (SEM) image of the platinum Pt (100)/zirconium nitride ZrN (100)/silicon Si (100) stacked arrangement in which the platinum layer with (100) lattice orientation is formed on the ZrN (100) buffer layer according to various embodiments.

FIG. 5A shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of platinum Pt (111)/zirconium nitride ZrN (111)/silicon Si (111) stacked arrangements formed using different nitrogen flow rates according to various embodiments.

FIG. 5B shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the platinum Pt (111)/zirconium nitride ZrN (111)/silicon Si (111) stacked arrangement formed using a nitrogen (N₂) flow rate of 2 sccm according to various embodiments.

FIG. 5C shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the platinum Pt (111)/zirconium nitride ZrN (111)/silicon Si (111) stacked arrangement formed using a nitrogen (N₂) flow rate of 1 sccm according to various embodiments.

FIG. 5D shows a cross-sectional scanning electron microscopy (SEM) image of the platinum Pt (111)/zirconium nitride ZrN (111)/silicon Si (111) stacked arrangement in which the platinum layer with (111) lattice orientation is formed on the ZrN (111) buffer layer according to various embodiments.

FIG. 6A shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of zirconium nitride ZrN buffer layer over silicon Si (100) stacked arrangements with and without the ultrathin zirconium (Zr) layers according to various embodiments.

FIG. 6B shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of stacked arrangements platinum Pt/zirconium nitride ZrN/silicon Si with and without the ultrathin zirconium (Zr) layers according to various embodiments.

FIG. 7A shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of zirconium nitride (ZrN) buffer layers over silicon Si (100) substrate obtained at different growth temperatures according to various embodiments.

FIG. 7B shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of zirconium nitride (ZrN) buffer layers over silicon Si (100) substrate obtained under different pulsed direct current (PDC) powers and operating pressures according to various embodiments.

FIG. 7C shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride (ZrN) layer over Si (100) substrate obtained with a pulsed direct current (PDC) power of 180 W and an operating pressure of 0.95 mTorr during sputtering according to various embodiments.

FIG. 7D shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride (ZrN) layer over Si (100) substrate obtained with a pulsed direct current (PDC) power

of 120 W and an operating pressure of 2.30 mTorr during sputtering according to various embodiments.

FIG. 7E shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride (ZrN) layer over Si (100) substrate obtained with a pulsed direct current (PDC) power of 120 W and an operating pressure of 2.60 mTorr during sputtering according to various embodiments.

FIG. 7F shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride (ZrN) layer over Si (100) substrate obtained with a pulsed direct current (PDC) power of 120 W and an operating pressure of 2.90 mTorr during sputtering according to various embodiments.

FIG. 8 shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of the platinum Pt /zirconium nitride ZrN (100)/silicon Si (100) stacked arrangements formed using varying pulsed direct current (PDC) powers during formation to the platinum layer according to various embodiments.

FIG. 9 shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of platinum Pt layers on different buffer layers of zirconium nitride ZrN and titanium nitride TiN according to various embodiments.

DESCRIPTION

[0008] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0009] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0010] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0011] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance, e.g., within 10% of the specified value.

[0012] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0013] By “comprising” it is meant including, but not limited to, whatever follows the word “comprising”. Thus, use of the term “comprising” indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0014] By “consisting of” it is meant including, and limited to, whatever follows the phrase “consisting of”. Thus, the phrase “consisting of” indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0015] Embodiments described in the context of one of the stacked arrangements are analogously valid for the other stacked arrangements. Similarly, embodiments described in the context of a method are analogously valid for a stacked arrangement, and vice versa.

[0016] Various embodiments may meet the need for metal layers, e.g., platinum layers, with crystal lattices of different orientations (e.g., (100) crystal lattice orientation or (111) crystal lattice orientation) for different applications. Various embodiments may provide a relatively inexpensive means to obtain metal layers (e.g., platinum layers) with crystal lattices of different orientations.

[0017] FIG. 1 shows a schematic of a stacked arrangement according to various embodiments. The stacked arrangement may include a substrate 102. The stacked arrangement may also include a buffer layer 104 over the substrate 102, the buffer layer 104 including zirconium nitride (ZrN). The stacked arrangement may further include a metal layer 106 on the buffer layer 104. A crystal lattice orientation of the metal layer 106 may be substantially in alignment with a crystal lattice orientation of the buffer layer 104.

[0018] In other words, various embodiments may include a buffer layer 104 over a substrate 102, and a metal layer 106 in contact with the buffer layer 104, such that a crystal lattice orientation of the metal layer 106 and a crystal lattice orientation of the buffer layer 104 are substantially the same, i.e., aligned.

[0019] For avoidance of doubt, FIG. 1 seeks to illustrate certain features of the stacked arrangement, and is not intended to limit, for instance, the dimensions (e.g., thickness) of the various features or the size or orientation of the stacked arrangement.

[0020] In various embodiments, the metal layer 106 may be a platinum (Pt) layer. The platinum layer may be a metal layer including substantially, e.g., above 99 atomic percent (at. %) or 99.9 atomic percent (at. %), platinum. In various embodiments, the platinum layer may be 100% platinum. The platinum layer may have a cubic crystal structure.

[0021] The buffer layer 104 may include e.g., above 99 atomic percent (at. %) zirconium nitride or 99.9 atomic percent (at. %) zirconium nitride. In various embodiments, the buffer layer 104 may consist entirely of zirconium nitride. The buffer layer 104 may have a cubic crystal structure.

[0022] In the present context, a crystal lattice orientation of a first layer substantially in alignment with a crystal lattice orientation of a second layer may mean that the crystal lattice orientation of the first layer is in complete alignment with the crystal lattice orientation of the second layer, or varies from the crystal lattice orientation of the second layer by an angle of less than 1° . In various embodiments, the buffer layer 104 may have a highly oriented crystal lattice, and the metal layer 106 may have a highly oriented crystal lattice in alignment with the buffer layer 104, with an orientation coefficient equal to or close to 1, e.g., above 0.98 or 0.99.

[0023] As mentioned above, in various embodiments, a crystal lattice orientation of the metal layer 106 may be substantially in alignment with a crystal lattice orientation of the buffer layer 104 (i.e., the metal layer and the buffer layer may have an orientation coefficient of about 1, i.e., equal to or close to 1, e.g., above 0.98 or 0.99). In various embodiments, a crystal lattice orientation of the metal layer 106 may also be substantially in alignment with a crystal lattice orientation of the substrate 102 (i.e., the metal layer and the substrate may have an orientation coefficient of about 1, i.e., equal to or close to 1, e.g., above 0.98 or 0.99). The crystal lattice orientation of the substrate 102 may determine the crystal lattice orientation of the buffer layer 104, which may in turn determine the crystal lattice orientation of the metal layer 106. For instance, a substrate with a (100)-oriented crystal lattice may result in a buffer layer with a (100)-oriented crystal lattice, which may in turn result in a metal layer with a (100)-oriented crystal lattice (under suitable conditions). Conversely, a substrate with a (111)-oriented crystal lattice may result in a buffer layer with a (111)-oriented crystal lattice, which may in turn result in a metal layer with a (111)-oriented crystal lattice (under suitable conditions).

[0024] In various embodiments, the stacked arrangement may also include a zirconium (Zr) layer having a first surface in contact with the substrate, and a second surface, the second surface opposite the first surface, in contact with the buffer layer. In other words, the zirconium layer may be on the substrate, and the buffer layer may be on the zirconium layer. The zirconium layer may include e.g., above 99 atomic percent (at. %) zirconium or 99.99 atomic percent (at. %) zirconium. In various embodiments, the zirconium layer may be 100% zirconium. The zirconium layer may be an ultra-thin pre-layer. In various embodiments, the zirconium layer may have a thickness of below 2 nm, e.g., a value selected from a range from 0.1 nm to 0.3 nm. The zirconium layer may help to form a highly oriented buffer layer 104, which may in turn result in a highly oriented metal layer 106.

[0025] In various embodiments, the substrate 102 may include or be a (100)-oriented crystal lattice (e.g., a (100)-oriented single crystal silicon (Si) lattice). The buffer layer 104 may include or be a (100)-oriented zirconium nitride crystal lattice. The metal layer 106 may include or be a (100)-oriented crystal lattice.

[0026] In various other embodiments, the substrate 102 may include or be a (111)-oriented crystal lattice (e.g., a (111)-oriented single crystal silicon (Si) lattice). The buffer layer 104 may include or be a (111)-oriented zirconium nitride crystal lattice. The metal layer 106 may include or be a (111)-oriented crystal lattice.

[0027] In various embodiments, the buffer layer 104 may have a thickness of below 500 nm. For instance, the thickness of the buffer layer 104 may be of a value selected from a range from 20 nm to 100 nm.

[0028] In various embodiments, the metal layer 106 may have a thickness below 1000 nm. For instance, the thickness of the metal layer 106 may be of a value selected from a range from 100 nm to 600 nm.

[0029] FIG. 2 shows a schematic of a method of forming a stacked arrangement according to various embodiments. The method may include, in 202, forming a buffer layer over a substrate, the buffer layer including zirconium nitride. The method may also include, in 204, forming a metal layer on the buffer layer. A crystal lattice orientation of the metal layer may substantially be in alignment with a crystal lattice orientation of the buffer layer.

[0030] In other words, the method may include forming a zirconium nitride buffer layer over a substrate, followed by forming a metal layer on the zirconium nitride buffer layer, so

that a crystal lattice orientation of the metal layer and a crystal lattice orientation of the buffer layer are substantially the same, i.e., aligned.

[0031] In various embodiments, the metal layer may be a platinum layer. In various embodiments, the method may also include forming a zirconium layer on the substrate before forming the buffer layer on the zirconium layer. Before the zirconium layer is formed on the substrate, a native oxide (e.g., silicon oxide) of the substrate may be removed. Contaminants may also be removed or reduced from a surface of the substrate, e.g., using a cleaning process.

[0032] In various embodiments, the buffer layer and the zirconium layer may be formed by a sputtering deposition process. The sputtering deposition process may be a pulsed direct current (PDC) sputtering deposition process. The sputtering deposition process may be carried out using a zirconium metal target. The zirconium layer may be formed in an ambient of argon gas, e.g., at a temperature below 530 °C, e.g., 380 °C. The buffer layer (including zirconium nitride) may be formed in an ambient of nitrogen gas and argon gas at a suitable temperature (i.e., growth temperature), e.g., of preferably about 530 °C. In other words, the buffer layer may be formed at a temperature higher than a temperature at which the zirconium layer is formed. Forming the buffer layer at an elevated temperature (e.g., preferably about 530 °C) may help to improve the orientation coefficient of the buffer layer, and may improve a crystallinity of the buffer layer (e.g., of (100) crystal orientation or (111) crystal orientation). In addition, having a suitable flow rate of the nitrogen gas (e.g., of preferably about 2 sccm) during formation of the buffer layer may help to improve a crystallinity of the metal layer (e.g., of (100) crystal orientation or (111) crystal orientation) subsequently formed.

[0033] The metal layer may also be formed by a sputtering deposition process, e.g., a pulsed direct current (PDC) sputtering deposition process. In various embodiments, the metal layer may be formed in an ambient of argon gas, e.g., at a temperature of preferably about 530 °C. In other words, the metal layer may be formed at a temperature higher than a temperature at which the zirconium layer is formed. In various embodiments, the zirconium layer, the buffer layer and/or the metal layer may be formed without breaking vacuum. The substrate may be cooled after the metal layer is formed at any suitable rate, e.g., at a rate of about 10 °C/min.

[0034] In various embodiments, the substrate may include or be a (100)-oriented crystal lattice (e.g., a (100)-oriented single crystal silicon (Si) lattice). The buffer layer may include or be a (100)-oriented zirconium nitride crystal lattice. The metal layer may include or be a (100)-oriented crystal lattice.

[0035] The buffer layer with the (100)-oriented zirconium nitride crystal lattice may be formed under an operating pressure selected from a range from 0.95 mTorr to 2.9 mTorr (e.g., 2.6 mTorr), and a pulsed direct current (DC) power selected from a range from 120 W to 180 W (e.g., 120 W). The above range of operating pressure and pulsed DC power may result in highly oriented buffer layer. As mentioned above, the buffer layer may be formed in an ambient of nitrogen gas and argon gas. In various embodiments, the ratio of the argon gas to the nitrogen gas may be of any suitable ratio, e.g., preferably 9 : 2. The metal layer with the (100)-oriented crystal lattice may be formed under an operating pressure selected from a range from 0.92 mTorr to 1 mTorr (e.g., 1 mTorr), and a pulsed direct current (DC) power of equal to or below 30 W (e.g., 20 W). A lower pulsed DC power may help to obtain a highly oriented metal layer with (100) crystal lattice. The zirconium layer may be formed under an operating pressure selected from a range from 0.8 mTorr to 1 mTorr (e.g., about 0.91 mTorr), and a pulsed direct current (DC) power of below 50 W (e.g., 45 W).

[0036] In various other embodiments, the substrate 102 may include or be a (111)-oriented crystal lattice (e.g., a (111)-oriented single crystal silicon (Si) lattice). The buffer layer 104 may include or be a (111)-oriented zirconium nitride crystal lattice. The metal layer 106 may include or be a (111)-oriented crystal lattice.

[0037] The buffer layer with the (111)-oriented zirconium nitride crystal lattice may be formed under an operating pressure selected from a range from 0.95 mTorr to 2.9 mTorr (e.g., 2.9 mTorr), and a pulsed direct current (DC) power selected from a range from 120 W to 180 W (e.g., 120 W). The above range of operating pressure and pulsed DC power may result in highly oriented buffer layer. As mentioned above, the buffer layer may be formed in an ambient of nitrogen gas and argon gas. In various embodiments, the ratio of the argon gas to the nitrogen gas may be of any suitable ratio, e.g., preferably 11 : 2. The metal layer with the (111)-oriented crystal lattice may be formed under an operating pressure selected from a range from 0.92 mTorr to 1 mTorr (e.g., 1 mTorr), and a pulsed direct current (DC) power of below 30 W (e.g., 20 W). The zirconium layer may be formed under an operating pressure selected from a range from 0.8 mTorr to 1 mTorr (e.g., about 0.91 mTorr), and a pulsed direct current (DC) power of equal to or below 50 W (e.g., 45 W).

[0038] FIG. 3A shows a cross-sectional schematic view of a stacked arrangement according to various embodiments. The stacked arrangement may include a substrate 302, a buffer layer 304 and a platinum layer 306. FIG. 3B shows a cross-sectional schematic of a stacked

arrangement according to various other embodiments. Other than the substrate 302, the buffer layer 304 and the platinum layer 306, the stacked arrangement may also include a zirconium layer 308 between the substrate 302 and the buffer layer 304.

[0039] For avoidance of doubt, FIGS. 3A - B seek to illustrate certain features of various stacked arrangements, and are not intended to limit, for instance, the dimensions (e.g., thickness) of the various features or the size or orientation of the various stacked arrangements.

[0040] The substrate 302 may be a single crystal silicon (Si) substrate with (100) or (111) orientation. The fabrication method may include a two-step process for the deposition of the buffer layer 304 to improve the orientation of the platinum layer 306 by selecting the substrate and growth parameters, such as substrate temperature, gas pressure, gas flow and/or sputtering power.

[0041] The buffer layer 304 of zirconium nitride (ZrN) may have a cubic crystal structure with orientation in accordance with the orientation of the silicon substrate 302, and the platinum layer 306 may have a cubic crystal structure in accordance with the orientation of the buffer layer 304, as shown in FIGS. 3C - D.

[0042] FIG. 3C shows (above) a top schematic view of a platinum Pt (100)/ zirconium nitride ZrN (100)/ silicon Si (100) stacked arrangement according to various embodiments; and (below) a schematic side view of the platinum Pt (100)/ zirconium nitride ZrN (100)/ silicon Si (100) stacked arrangement according to various embodiments. FIG. 3D shows (above) a top schematic view of a platinum Pt (111)/ zirconium nitride ZrN (111)/ silicon Si (111) stacked arrangement according to various embodiments; and (below) a schematic side view of the platinum Pt (111)/ zirconium nitride ZrN (111)/ silicon Si (111) stacked arrangement according to various embodiments.

[0043] Example 1

[0044] To fabricate a stacked arrangement with Pt (100) orientation, a silicon (100) substrate is first cleaned using acetone, ethanol, dilute hydrofluoric acid (HF) (5%), and is subsequently rinsed in de-ionized water to remove the surface contamination and native oxide. Immediately, the cleaned silicon (100) substrate is loaded into a sputtering deposition chamber which is pumped to a base pressure of less than 2×10^{-7} Torr. Next, the substrate is heated up to 380 °C and a layer of ultrathin Zr metal layer having a thickness below 2 nm, preferably $\sim 1 - 3 \text{ \AA}$, is deposited by sputtering as a pre-treatment process step. A pulsed direct current (PDC) of 45 W, 5 kHz, 0.4 μs is used in an argon ambient at pressure $\sim 0.91 \text{ mTorr}$ and argon

flow rate at 9 sccm in the first pre-treatment sputtering process step. Subsequently, this substrate is heated up to 530 °C in an argon-ambient at the same operating pressure of ~0.91 mTorr. This is followed by a second step deposition of ZrN layer of (100)-orientation with a thickness preferably below 500 nm, by PDC sputtering at 2.6 mTorr with argon-nitrogen ambient of argon : nitrogen gas ratio of 9 : 2. The second step PDC sputtering conditions are 120 W, 5 kHz, 0.4 μs, using a zirconium metal target. Without breaking the vacuum, the platinum layer, typically with a thickness below 1000 nm, is deposited at 530 °C using PDC sputtering power of 20 W at 5 kHz, 0.4 μs at 1 mTorr with a platinum metal target in an argon ambient with argon flow rate of 5 sccm. Finally, the substrate is cooled down at a rate of 10 °C/min. FIG. 4A shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of zirconium nitride ZrN (100)/silicon Si (100) and platinum Pt (100)/zirconium nitride ZrN (100)/silicon Si (100) stacked arrangements according to various embodiments. FIG. 4B shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the platinum Pt (100)/zirconium nitride ZrN (100)/silicon Si (100) stacked arrangement according to various embodiments. FIG. 4C shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride ZrN (100)/silicon Si (100) stacked arrangement according to various embodiments. To quantify crystal lattice orientation, an orientation coefficient may be defined as the ratio between the intensity of XRD peak for the lattice planes with the specified orientation over the sum of the XRD intensity for all the planes of the film, as provided in Equation (1):

$$\text{Orientation coefficient} = \frac{\sum I_{Pt(100)} + I_{Pt(200)} + I_{Pt(400)}}{\sum I_{Pt(100)} + I_{Pt(200)} + I_{Pt(400)} + I_{Pt(111)} + I_{Pt(220)} + I_{Pt(kmn)}} \quad (1)$$

wherein k, m and n may be whole numbers such that $I_{Pt(kmn)}$ represent intensity resulting from lattice planes of Pt other than the ones already listed in Equation (1). An orientation coefficient of approximately 100% may be considered as highly crystal lattice oriented layer. In FIG. 4A, there is only one Pt (200) diffraction peak observed for platinum even in log scale, hence the orientation coefficient is approximately 100%, meaning the platinum layer has highly oriented crystal lattice.

[0045] FIG. 4D shows a cross-sectional scanning electron microscopy (SEM) image of the platinum Pt (100)/zirconium nitride ZrN (100)/silicon Si (100) stacked arrangement in which the platinum layer with (100) lattice orientation is formed on the ZrN (100) buffer layer according to various embodiments. The thickness of the platinum layer is about 103 nm and

the thickness of ZrN layer is about 85 nm. A chromium layer (~107 nm) serves as a protection layer to prepare the sample for cross-sectional SEM imaging.

[0046] Example 2

[0047] For the fabrication of stack structure with Pt (111) orientation, a (111)-oriented silicon substrate is cleaned using acetone, ethanol, dilute hydrofluoric acid (HF) (5%) and rinsed in de-ionized water to remove the surface contamination and native oxide. After the silicon substrate is cleaned, first, a ZrN buffer layer is deposited on the silicon by depositing an ultrathin layer of Zr metallic layer of $\sim 1 - 3 \text{ \AA}$ using PDC sputtering at 380°C in argon ambient at pressure of about 0.91 mTorr with argon flow rate of 9 sccm as the first processing step. The second processing step involves heating up to 530°C in same argon ambient, followed by deposition of a single phase ZrN layer at 530°C by PDC sputtering of 120 W, 5 kHz, $0.4 \mu\text{s}$ using a Zr target in an argon-nitrogen ambient of argon : nitrogen gas ratio of 11 : 2 at a pressure of 2.9 mTorr. The total thickness of the obtained ZrN layer is about 51 nm. Next, the platinum layer is deposited using PDC sputtering of 20 W at 5 kHz, $0.4 \mu\text{s}$ at 1 mTorr using a platinum metal target in an argon ambient and then the silicon is cooled down at a rate of $10^\circ\text{C}/\text{min}$. The thickness of the Pt layer is about 105 nm. The nitrogen flow during ZrN growth may affect the crystallinity of the Pt as shown in the XRD spectra.

[0048] FIG. 5A shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of platinum Pt (111)/zirconium nitride ZrN (111)/silicon Si (111) stacked arrangements formed using different nitrogen flow rates according to various embodiments. FIG. 5B shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the platinum Pt (111)/zirconium nitride ZrN (111)/silicon Si (111) stacked arrangement formed using a nitrogen (N_2) flow rate of 2 sccm according to various embodiments. FIG. 5C shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the platinum Pt (111)/zirconium nitride ZrN (111)/silicon Si (111) stacked arrangement formed using a nitrogen (N_2) flow rate of 1 sccm according to various embodiments. A nitrogen flow of 2 sccm gives rise to a sharper Pt (111) peak with full width at half maximum (FWHM) of $\sim 1.301^\circ$ compared to nitrogen flow of 1 sccm with FWHM $\sim 1.430^\circ$, indicating the growth parameters may be critical for the crystallinity of Pt (111). The orientation coefficient for the Pt (111) layer is approximately 100%, meaning the Pt layer has a highly oriented crystal lattice.

[0049] FIG. 5D shows a cross-sectional scanning electron microscopy (SEM) image of the platinum Pt (111)/zirconium nitride ZrN (111)/silicon Si (111) stacked arrangement in which the platinum layer with (111) lattice orientation is formed on the ZrN (111) buffer layer according to various embodiments.

[0050] Example 3

[0051] In this stacked arrangement, the buffer layer includes a highly oriented ZrN (100) layer formed on a single crystal Si (100) substrate by means of sputtering deposition method. There is a two-step process in which an ultrathin Zr metallic layer of $\sim 1 - 3 \text{ \AA}$ -thick is first formed in the first pre-treatment step, followed by forming the ZrN buffer layer in the second processing step. Preferably, the ZrN buffer layer has a thickness of 20 - 90 nm. FIG. 6A shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of zirconium nitride ZrN buffer layer over silicon Si (100) stacked arrangements with and without the ultrathin zirconium (Zr) layers according to various embodiments. FIG. 6A shows that forming the Zr layer in the first pre-treatment step may be crucial for the ZrN buffer layer to achieve high (100) orientation. Without the highly oriented ZrN (100) layer, it may be difficult to obtain the resulting highly oriented Pt (100) layer. The orientation coefficient for the ZrN (100) layer with ultrathin Zr is approximately 100%, while the orientation coefficient for ZrN layer without the ultrathin Zr layer is 42%.

[0052] FIG. 6B shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of stacked arrangements platinum Pt/zirconium nitride ZrN/silicon Si with and without the ultrathin zirconium (Zr) layers according to various embodiments. The Pt layer and the ZrN buffer layer may be formed over (100) Si substrate with and without an intervening Zr layer. In the absence of the ultrathin Zr layer, there may be presence of the ZrN (111) peak and the Pt (220) peak, while the Pt (200) peak may be degraded. The orientation coefficient for the Pt (100) layer with the ultrathin Zr layer is approximately 100% while the orientation coefficient for Pt layer without the ultrathin Zr layer is 80%.

[0053] Example 4

[0054] The growth conditions for the ZrN layer may also be of significance to obtaining lattice orientation. FIG. 7A shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of zirconium

nitride (ZrN) buffer layers over silicon Si (100) substrate obtained at different growth temperatures according to various embodiments. At lower growth temperatures, such as 30 °C, 330 °C, 510 °C, the ZrN layers as obtained are not completely (100) oriented, but show a mixture of ZrN (111) and ZrN (100). When the growth temperature reaches 530 °C, only ZrN (200) is obtained, without ZrN (111) observed. The orientation coefficient for 530 °C-ZrN (100) layer is observed to be approximately 100%, while the orientation coefficient for 510 °C-ZrN layer is 67%, and the orientation coefficients for 330 °C-ZrN layer and 30 °C-ZrN layer are below 50%.

[0055] Other than growth temperature, i.e., the substrate temperature during the sputtering process, the PDC power and/or the operating pressure during the sputtering deposition may affect the crystallinity of ZrN (100) on Si (100) substrate, as shown in FIGS. 7B – F, in which the growth temperature is fixed at 530 °C. The experimental results show that an operating pressure in the range of 0.95 - 2.9 mTorr and power between 120 - 180 W may give rise to highly oriented ZrN (100) layers.

[0056] FIG. 7B shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of zirconium nitride (ZrN) buffer layers over silicon Si (100) substrate obtained under different pulsed direct current (PDC) powers and operating pressures according to various embodiments. FIG. 7C shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride (ZrN) layer over Si (100) substrate obtained with a pulsed direct current (PDC) power of 180 W and an operating pressure of 0.95 mTorr during sputtering according to various embodiments. FIG. 7D shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride (ZrN) layer over Si (100) substrate obtained with a pulsed direct current (PDC) power of 120 W and an operating pressure of 2.30 mTorr during sputtering according to various embodiments. FIG. 7E shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride (ZrN) layer over Si (100) substrate obtained with a pulsed direct current (PDC) power of 120 W and an operating pressure of 2.60 mTorr during sputtering according to various embodiments. FIG. 7F shows the X-ray diffraction (XRD) two-dimensional (2D) frames of the zirconium nitride (ZrN) layer over Si (100) substrate obtained with a pulsed direct current (PDC) power of 120 W and an operating pressure of 2.90 mTorr during sputtering according to various embodiments.

[0057] Example 5

[0058] Due to the lowest surface energy associated with (111) planes, platinum layer has a natural preference to form (111) orientation. Thus, after obtaining a highly oriented ZrN (100) layer as shown in Example 1, control of the Pt growth parameter may be required to obtain Pt (100) layer. FIG. 8 shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of the platinum Pt /zirconium nitride ZrN (100)/silicon Si (100) stacked arrangements formed using varying pulsed direct current (PDC) powers during formation to the platinum layer according to various embodiments. The formation of the platinum layer is carried out at 5 kHz, 0.4 μ s at a temperature of 530° and an operating temperature of 0.92 mTorr. At higher powers (60 W and 120 W), a mixture of Pt (111) and Pt (100) forms, and Pt (111) orientation may be dominant in the Pt layer. However, a highly oriented Pt (100) layer with the orientation coefficient of approximately 100% can be obtained with the PDC at lower powers (30 W and 15 W).

[0059] Example 6

[0060] Various embodiments may relate to a stacked arrangement including a highly oriented (100) ZrN buffer layer formed over a single crystal Si (100) substrate formed by a sputtering deposition method. The buffer layer is fabricated by a two-step process in which an ultrathin Zr metallic layer of $\sim 1 - 3$ Å-thick is first formed in the pre-treatment step, followed by deposition of the ZrN layer in the second processing step. In various embodiments, the ZrN buffer layer may have a thickness of 20 – 90 nm. FIG. 9 shows a plot of intensity (in arbitrary units or a.u.) as a function of angle 2θ (in degrees or deg) illustrating the X-ray diffraction (XRD) spectra of platinum Pt layers on different buffer layers of zirconium nitride ZrN and titanium nitride TiN according to various embodiments. When the TiN buffer layer is used, both Pt (111) peak and Pt (220) peaks are observed. This may show that the (100) ZrN buffer layer is crucial to achieve the highly oriented Pt (100) layer (without other crystal orientations such as Pt (111) and Pt (220)). The orientation coefficient for the Pt layer using TiN buffer layer is 33% while the Pt layer using ZrN is approximately 100%.

[0061] Various embodiments may relate to a stacked arrangement including a highly oriented platinum layer, a highly oriented buffer layer including zirconium nitride, and a silicon substrate. The highly oriented buffer layer may produce the highly oriented platinum layer.

[0062] For instance, the stacked arrangement may be Pt (100)/ZrN (100)/Si (100) or Pt (111)/ZrN (111)/Si (111). Various embodiments may include a two-step sputtering process to form the highly oriented ZrN buffer layer. An ultra-thin Zr film may first be formed on the

silicon substrate. This pre-treatment film may help to promote subsequent ZrN (100) orientation and then Pt (100) orientation, even if Pt film usually has spontaneously preferred (111) orientation. The experimental demonstration of the two-step process has been described herein.

[0063] Various embodiments may also relate to further optimization of the orientation and crystallinity of the resulting ZrN and Pt layers with refined growth parameters, such as substrate temperature, operating pressure, and/or sputtering power.

[0064] The integration of Pt layer with conductive ZrN buffer layer may not substantially affect the overall conductivity of the stack structure, in comparison with other insulating buffer layers.

[0065] The highly lattice-oriented Pt (100) or Pt (111) layer may be able to generate a significant impact on the orientation of subsequent layers and thus the device performance.

[0066] The highly lattice-oriented Pt (100) or Pt (111) film and the ZrN buffer layer may be formed using a sputtering process, which is scalable and may be suitable for mass production and industry application.

[0067] Pt films with controlled crystal lattice orientation may find applications in various devices (such as electrodes) for micro-electromechanical systems (MEMS), piezoelectric devices, optoelectronics devices, ferroelectric random access memories (FeRAMs), electrochemical sensors, photovoltaic devices, surface-enhanced Raman spectroscopy (SERS), and fuel cells.

Claims

1. A stacked arrangement comprising:
 - a substrate;
 - a buffer layer over the substrate, the buffer layer comprising zirconium nitride;
 - and
 - a metal layer on the buffer layer;wherein a crystal lattice orientation of the metal layer is substantially in alignment with a crystal lattice orientation of the buffer layer.
2. The stacked arrangement according to claim 1, further comprising:
 - a zirconium layer having a first surface in contact with the substrate, and a second surface, the second surface opposite the first surface, in contact with the buffer layer.
3. The stacked arrangement according to claim 2,
 - wherein the zirconium layer has a thickness of below 2 nm.
4. The stacked arrangement according to claim 3,
 - wherein the thickness of the zirconium layer is of a value selected from a range from 0.1 nm to 0.3 nm.
5. The stacked arrangement according to any one of claims 1 to 4,
 - wherein a crystal lattice orientation of the metal layer is substantially in alignment with a crystal lattice orientation of the substrate.

6. The stacked arrangement according to claim 5,
wherein the metal layer and the substrate have an orientation coefficient of about 1.
7. The stacked arrangement according to any one of claims 1 to 6,
wherein the substrate comprises a (100)-oriented crystal lattice;
wherein the buffer layer comprises a (100)-oriented zirconium nitride crystal lattice; and
wherein the metal layer comprises a (100)-oriented crystal lattice.
8. The stacked arrangement according to claim 7,
wherein the (100)-oriented crystal lattice is a (100)-oriented single crystal silicon lattice.
9. The stacked arrangement according to any one of claims 1 to 6,
wherein the substrate comprises a (111)-oriented crystal lattice;
wherein the buffer layer comprises a (111)-oriented zirconium nitride crystal lattice; and
wherein the metal layer comprises a (111)-oriented crystal lattice.
10. The stacked arrangement according to claim 9,
wherein the (111)-oriented crystal lattice is a (111)-oriented single crystal silicon lattice.
11. The stacked arrangement according to any one of claims 1 to 10,
wherein the buffer layer has a thickness of below 500 nm.
12. The stacked arrangement according to claim 11,

wherein the thickness of the buffer layer is of a value selected from a range from 20 nm to 100 nm.

13. The stacked arrangement according to any one of claims 1 to 12,
wherein the metal layer has a thickness below 1000 nm.

14. The stacked arrangement according to claim 13,
wherein the thickness of the metal layer is of a value selected from a range from 100 nm to 600 nm.

15. The stacked arrangement according to any one of claims 1 to 14,
wherein the metal layer is a platinum layer.

16. A method of forming a stacked arrangement, the method comprising:
forming a buffer layer over a substrate, the buffer layer comprising zirconium nitride; and
forming a metal layer on the buffer layer;
wherein a crystal lattice orientation of the metal layer is substantially in alignment with a crystal lattice orientation of the buffer layer.

17. The method according to claim 16, the method further comprising:
forming a zirconium layer on the substrate before forming the buffer layer on the zirconium layer.

18. The method according to claim 17,
wherein the buffer layer and the zirconium layer are formed by a sputtering deposition process.

19. The method according to claim 18,
wherein the sputtering deposition process is a pulsed direct current (DC)
sputtering deposition process; and
wherein the sputtering deposition process is carried out using a zirconium
metal target.
20. The method according to claim 19,
wherein the zirconium layer is formed in an ambient of argon gas.
21. The method according to claim 19 or claim 20,
wherein the buffer layer is formed in an ambient of nitrogen gas and argon
gas.
22. The method according to claim 21,
wherein the buffer layer is formed at a temperature equal to or above 530 °C.
23. The method according to any one of claims 16 to 22,
wherein a crystal lattice orientation of the metal layer is substantially in
alignment with a crystal lattice orientation of the substrate.
24. The method according to any one of claims 16 to 23,
wherein the substrate comprises a (100)-oriented crystal lattice;
wherein the buffer layer comprises a (100)-oriented zirconium nitride crystal
lattice; and
wherein the metal layer comprises a (100)-oriented crystal lattice.
25. The method according to claim 24,

wherein the (100)-oriented crystal lattice is a (100)-oriented single crystal silicon lattice.

26. The method according to claim 24 or claim 25,

wherein the buffer layer with the (100)-oriented zirconium nitride crystal lattice is formed under an operating pressure selected from a range from 0.95 mTorr to 2.9 mTorr, and a pulsed direct current (DC) power selected from a range from 120 W to 180 W; and

wherein the metal layer with the (100)-oriented crystal lattice is formed under an operating pressure selected from a range from 0.92 mTorr to 1 mTorr, and a pulsed direct current (DC) power of below 30 W.

27. The method according to any one of claims 16 to 23,

wherein the substrate comprises a (111)-oriented crystal lattice;
wherein the buffer layer comprises a (111)-oriented zirconium nitride crystal lattice; and
wherein the metal layer comprises a (111)-oriented crystal lattice.

28. The method according to claim 27,

wherein the (111)-oriented crystal lattice is a (111)-oriented single crystal silicon lattice.

29. The method according to any one of claims 16 to 28,

wherein the metal layer is a platinum layer.