Method forming preferred orientation-controlled platinum films using nitrogen
Herstellungsverfahren von Platinschichten mit gesteueter bevorzugter Orientierung unter
Verwendung von Stickstoff
Procédé de fabrication de films de platine à orientation préférée contrôlée utilisant de l’azote

Designated Contracting States:
DE FR GB IT NL

Priority:
07.01.1997 KR 9700159
06.05.1997 KR 9717210

Date of publication of application:

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EP-A- 0 518 117
EP-A- 0 697 717


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Description

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from commonly-assigned Republic of Korea Application Serial No. P97-159 (filed January 7, 1997) and No. P97-17210 (filed May 6, 1997).

BACKGROUND OF THE INVENTION

[0002] The present invention relates to a technique for depositing a platinum film, which may be used as a bottom electrode for capacitors of dynamic random access memory (DRAM) cells or of non-volatile memory cells and film sensors. More particularly, the invention relates to a technique for controlling the preferred orientation of the platinum films by depositing the platinum under an atmosphere containing nitrogen as well as an inert gas and then annealing to remove the nitrogen which was introduced during the deposition of the platinum. The present invention also relates to a method of manufacturing semiconductor devices or sensor devices comprising such platinum thin films.

[0003] In order to increase the capacitance of a DRAM cell capacitor to meet the requirements of increasingly high integration of semiconductor memory devices, several approaches (e.g., (i) decreasing the thickness of dielectric material films, (ii) increasing the effective area of the capacitor, and (iii) using materials with high dielectric constant as dielectric oxide films) have been proposed. However, decreasing the thickness of a dielectric material film to less than 100Å (1 Å = 0.1 nm) deteriorates reliability of the semiconductor device due to the Fowler-Nordheim current.

[0004] Increasing the effective area is complicated in its process and incurs high manufacturing cost. Moreover, deposited layers are not uniform and leakage current is generated between the trenches when applied to a laminate-type capacitor and a trench type capacitor, respectively. Thus, these two conventional methods have limitations especially when applied to high density memory cells of higher than 1 Gbit. The third proposed method to use high-dielectric materials is currently being investigated to form capacitors of DRAM cells, which have conventionally used polysilicon as the bottom electrode material. However, such high-dielectric oxide films need to be formed under an oxidation atmosphere and high temperature (higher than 500°C) which may result in problems relating to the polysilicon. For example, if polysilicon is employed as the bottom electrode in a DRAM cell using high-dielectric materials as a capacitor, serious problems may occur due to oxidation of the polysilicon under the high temperature (over 500°C) and oxidation atmosphere during formation of the high-dielectric oxide thin films. For this reason, platinum is being investigated for use in place of polysilicon as an electrode of a DRAM cell employing a high-dielectric oxide, because platinum is stable under high temperature and oxidation atmosphere.

[0005] Moreover, it is well known that the properties of anisotropic crystals depend on their crystallographic orientations. The crystallographic orientations of oxide films formed on bottom electrodes depend on the crystallographic orientation of the bottom electrodes. Therefore, it is believed that controlling the preferred orientation of bottom electrodes is very important in controlling the preferred orientation of oxide films with desirable physical properties.

[0006] High-dielectric/ferroelectric materials are used not only for DRAM cells but also for other electronic devices such as non-volatile ferroelectric memory devices, ferroelectric sensors or actuator devices, etc. Platinum is most favored, in particular, as a bottom electrode of such high-dielectric/ferroelectric devices. The favored high-dielectric and ferroelectric materials are oxides having perovskite structure, bismuth-layered perovskite structure and tungsten-bronze type structure along with ReMnO₃ (Re: rare earth element) and BaMF₄ (M: Mn, Co, Ni, Mg, Zn).

[0007] It is known that a platinum thin film, which is deposited on an insulating oxide layer by the conventional method, generally has a preferred (111) orientation. This is due to the fact that the plane with the minimum surface energy in metals with face centered cubic (FCC) structure is (111) and, considering only the surface energy at the depositing, the film is most stable if oriented toward (111).

[0008] Conventional methods for forming preferred orientation-controlled platinum films which have been suggested have limitations. In order to change the preferred orientation of the platinum film, one such conventional method that has been suggested is forming the platinum film on a single crystal substrate of the materials such as MgO, NaCl, KBr, SrTiO₃, LaAlO₃. However, such a method not only is complicated in its process and incurs high unit costs for single-crystalline substrates but also is incompatible with the state-of-the art in manufacturing silicon-integrated circuits. Other conventional methods have formed orientation-controlled platinum by depositing platinum on a glass substrate not on a silicon wafer, or by using a specially designed sputtering equipment which has an "auxiliary electrode" in order to deposit platinum film on silicon substrates. However, it has been reported that orientation-controlled platinum films deposited on glassy substrates have high resistivity (18 to 30 µΩ·cm) since oxygen, which was introduced during the deposition thereof, has remained within the platinum films even after annealing for 10 days. Therefore, it has been thought to be difficult and impractical to apply this process to real manufacturing practices, due to the very long annealing time. Furthermore, the platinum films formed on a silicon wafer by the conventional methods using sputtering are not dense enough and may have a number of pinholes, pores or hillocks, which may result in device performance problems.
SUMMARY OF THE INVENTION

The present invention provides a method of forming an orientation-controlled platinum film and a platinum film formed thereby, according to specific embodiments. In accordance with other specific embodiments, the present invention also provides a method of manufacturing an electronic device comprising an orientation-controlled platinum film and an electronic device manufactured thereby. In particular, the present invention provides a method of freely controlling a preferred orientation of a platinum film by depositing a platinum film under an atmosphere containing nitrogen, and then annealing so that the preferred orientation of the platinum film becomes (111), (200) and/or (220).

According to a specific embodiment, the present invention provides a method of forming a platinum film on a substrate comprising the steps of depositing a platinum film on the substrate under an atmosphere containing nitrogen together with an inert gas to deposit a platinum film containing a nitrogen component; and annealing the platinum film containing the nitrogen component to substantially remove the nitrogen component from the platinum film, whereby orientation of the platinum film can be controlled by changing at least one of the following parameters: the partial pressure ratio of the nitrogen to the entire total depositing atmosphere gas, the temperature of the substrate during the deposition step and the annealing conditions. The platinum film can be formed through two or more deposition steps, according to specific embodiments.

In accordance with the present invention, the platinum film may be deposited by employing one of the following methods: the direct current or radio frequency (DC/RF) magnetron sputtering, DC/RF sputtering, metal organic chemical vapor deposition, partially ionized beam deposition, vacuum evaporation, laser ablation.

In other embodiments, the method forming a platinum film described above can be applied to a process for manufacturing an electronic device by forming a high-dielectric or ferroelectric oxide film on the platinum film. In this case, for example, the platinum film functions as a bottom electrode. Depending on types of electronic devices to which the film is applied, a functional intermediate film (such as an insulation layer, a conductive plug, an adhesion layer, or a diffusion barrier layer) may be provided between the platinum film and the substrate, according to various specific embodiments. In accordance with other specific embodiments, the present invention provides an electronic device with preferable characteristics which are required for DRAM or non-volatile memory devices.

The present invention along with its features and advantages will now be explained in detail with reference to the attached drawings illustrating preferred embodiments of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1a to 1c are cross-sectional views illustrating the steps of manufacturing an electronic device comprising a platinum thin film formed according to a specific embodiment of the present invention; Fig. 2 is a cross-sectional view illustrating a modification to the method of Figs. 1a to 1c, in which an insulation layer is deposited to electrically separate the substrate from the platinum film, in accordance with another specific embodiment of the present invention; Figs. 3a to 3d are cross-sectional views illustrating the steps of another modification to the method of Figs. 1a to 1c, in accordance with yet another specific embodiment of the present invention; Fig. 4 is a cross-sectional view illustrating a modification to the method of Figs. 3a to 3d, in which an insulation layer is interposed between the substrate and the platinum film, in accordance with still further another specific embodiment of the present invention; Fig. 5a is a schematic cross-sectional view of a high integration DRAM memory device, in accordance with a specific embodiment of the present invention;
A method manufacturing an electronic device comprising a platinum film according to the present invention includes a step of forming a high-dielectric/ferroelectric film on top surface of a platinum film after depositing the platinum film. For example, material used for a functional intermediate film such as an insulating layer, a conductive plug layer, a diffusion barrier layer, or an adhesive or glue layer can be interposed between the platinum film and the substrate. The materials used for a functional intermediate film functioning as an insulating layer include SiO₂, Si₃N₄, BPSG, MgO, CaO, CaF₂, Al₂O₃ or B₂O₃. The materials used for a functional intermediate film functioning as a conductive plug layer include TiN, zirconium nitride, titanium silicide, tantalum silicide, tungsten silicide, molybdenum silicide, nickel silicide, cobalt silicide, tantalum carbide, tantalum boride, polysilicon, germanium, W, Ta, Ti, Mo, TiW, boron carbide, Cu, and the like. The material used for a functional intermediate film which functions as a diffusion barrier layer can be selected from any one of the following groups: ternary component amorphous materials (Ti-Si-N, Ta-B-N, Ti-B-N), conductive nitride (titanium aluminum nitride, Zr nitride, Hf nitride, Y nitride, Se nitride, La nitride, rare earth nitride, N deficient Al nitride, doped Al nitride, Mg nitride, Ca nitride, Sr nitride, Ba nitride, TiN, GaN, Ni nitride, Ta nitride, Co nitride, W nitride), and the like. The materials used for a functional intermediate film used for an adhesion or glue layer include TiN, W, Ta, Ti, Sn, Ru, In, Ir, Os, Rh, and silicide compound (Ni silicide, Co silicide, W silicide).

A method manufacturing an electronic device according to the present invention includes a step of forming a high-dielectric/ferroelectric film on top surface of a platinum film after depositing the platinum film. For example, material used
for the high-dielectric film or the ferroelectric film may be selected from any one of the following groups: a perovskite structure oxide, such as BST(BaTiO3), BST(Ba0.6Sr0.4TiO3), ST(SrTiO3), PT(PbTiO3), PZT(Pb(Zr,Ti)O3), PLT(Pb1-xLa1xTiO3), PLZT((Pb1-yTiy)1-xLax)(ZryTi1−yO3), PMN(Pb(Mn1−xNbx)O3), LiTaO3, KNbO3, K(Ta, Nb)O3, CaTiO3, SrSnO3, NaNbO3, LaAlO3, and YAlO3; a bismuth-layered perovskite structure oxide, such as SrBi2Ta2O9, SrBi2Ti2O7, SrBiTa2O6, SrBi2(Ta0.7Nb0.3)2O9 and Bi2SrTi2O7; a tungsten-bronze type structure oxide such as Sr1-xBax Nb2O6, SrBa0.8Re0.2O3 (R: Cr, Zn, Y), (Pb, Ba)Nb2O6, (K, Sr)Nb2O6, (Pb, K)Nb2O6, Pb2KNb2O7, (K, Li)2LiBO3O15, (K, Na)3Li2Nb2O15, (Yb, Li)2LiBO3O15; ReMnO3 (where Re is a rare-earth element); BaMF4 (where M is Mn, Co, Mg, or Zn); and KMrF3.

Specifically, Figs. 1a to 1c are schematic cross-sectional views illustrating the steps of manufacturing an electronic device comprising a platinum film deposited according to one aspect of the present invention.

Referring to Fig. 1a, a platinum film 104 is deposited on top surface of the substrate 100. The depositing atmosphere contains an inert gas (Ar, Ne, Xe, Kr, etc.) and nitrogen component, and under the temperature range between room temperature and 500°C. Accordingly, a nitrogen component is contained in the platinum film 104. Referring to Fig. 1b, the platinum film 104 formed on the substrate 100 is annealed under the temperature range between 400°C and 1,000°C to remove the nitrogen component from the platinum film 104. This process converts the platinum film 104 into the platinum film 108 which is substantially free from nitrogen component. The platinum film 108 has a high-dielectric/ferroelectric oxide film 112 thereon, as shown Fig. 1c, so that it can be used as a bottom electrode in DRAM cells or non-volatile high-dielectric/ferroelectric memory cells or sensor devices. Though not illustrated in the drawings, electronic devices such as capacitors can be manufactured by forming a top electrode comprising the material identical to that of the bottom electrode, i.e., platinum or other conductive material.

For the embodiment of Figs. 1a to 1c, preferred orientation of the platinum film formed according to the above method can be controlled by at least any one of the following parameters: the partial pressure ratio of the nitrogen component to the entire gas of the platinum film deposition atmosphere, the temperature of the substrate during the deposition step or annealing conditions. According to the present invention, even if any one of conductive plug and/or a diffusion barrier layer is used such as materials mentioned before, oxidation of those can be suppressed by control of annealing temperature, unlike in the case of depositing a platinum film under an atmosphere of oxygen as suggested in earlier patent applications.

Fig. 2 is a block diagram illustrating a modification to the method of Figs. 1a to 1c.
cell with high-dielectric capacitors, which may be fabricated in accordance with the present invention. As seen in Fig. 5a, formed in the DRAM cell region of a substrate 400 is a transistor having a gate electrode 402 and source/drain regions 404. Gate electrode 402, which may be formed with doped or undoped polysilicon, is capped with a sidewall oxide layer 406, and field oxide 408 provides isolation. Also formed in the DRAM cell region is a high-dielectric capacitor. The capacitor includes an upper capacitor cell plate 410, a bottom capacitor storage node 412, and a high dielectric constant material 414 formed between plate 410 and node 412. The capacitor is isolated from the transistor by an insulating layer 418, except through vias through layer 418 which are filled with a polysilicon plug layer 420. Insulating layer 418 may be made of SiO2, BPSG, etc. A diffusion barrier layer 416 is formed between bottom capacitor storage node 412 and polysilicon plug 420. As discussed above, the present invention may be used to deposit orientation-controlled platinum for use as bottom capacitor storage node 412 and/or upper capacitor cell plate 410.

Fig. 5b represents a schematic diagram of an exemplary integrated circuit device, such as a non-volatile ferroelectric memory device, which may also be fabricated in accordance with the present invention. As seen in Fig. 5b, formed in the cell region of a substrate 500 is a transistor having a gate electrode 502 and source/drain regions 504. Also formed in the non-volatile ferroelectric memory device is a ferroelectric capacitor. The capacitor includes a top capacitor electrode 510, a bottom capacitor electrode 512, and a ferroelectric material 514 (e.g., PZT) formed between electrodes 510 and 512. Formed underneath the bottom capacitor electrode 512 is a buffer layer 516 (e.g., TiO2) formed over an insulating layer 518 on substrate 500. As discussed above, the present invention may be used to deposit orientation-controlled platinum for use as bottom capacitor storage node 412 and/or upper capacitor cell plate 410.

Figs. 5a and 5b are merely representative examples of integrated circuit devices which may be fabricated in accordance with specific embodiments of the present invention. Other devices also may be fabricated in accordance with other specific embodiments.

Description of exemplary substrate processing apparatus

In accordance with the present invention, the platinum film may be deposited by employing any one of the following methods: DC/RF magnetron sputtering, DC/RF sputtering, metal organic chemical vapor deposition, partially ionized beam deposition, vacuum evaporation, laser ablation.

Fig. 6 is a simplified diagram illustrating an exemplary substrate processing apparatus, such as a DC sputtering apparatus 600, which may be used in accordance with a specific embodiment of the present invention. In the exemplary sputter deposition system of Fig. 6, a platinum target 602 (a plate of the platinum material that is to be deposited) is connected to a DC power supply 606 (alternatively, in a RF sputtering system, target 602 is connected to a RF power supply) at a negative voltage and 100 Watt to 200 Watt power while a substrate holder 604 facing target 602 is grounded (as seen in the specific embodiment of Fig. 6) or/and heated by a heater under substrate holder 604. In the specific embodiments, platinum target 602 may be a 2 inch (1 inch = 2.54 cm), 4 inch or 6 inch diameter target for a 2 inch, 4 inch or 6 inch diameter substrate, respectively. In the specific embodiments discussed below, a 4 inch diameter was used for target 602 and the substrate. An inert gas, such as argon in the specific embodiment, is flowed through a gas line 608 at a rate controlled by a mass flow controller 610 into the system from an argon source 612. As mentioned earlier, an inert gas can be selected from Ar, Ne, Kr or Xe, in accordance with various specific embodiments. Nitrogen also is flowed from a nitrogen source 614 through gas line 608 at a rate controlled by a mass flow controller 616. In the specific embodiment, valves 618 are also used for inert gas source 612 and nitrogen source 614. In the specific embodiment, the system is typically maintained at a basic pressure on the order of about 10⁻⁶ Torr (1 Torr = 133 Pa) using an exhaust valve 624, to provide a medium in which a glow discharge can be initiated and maintained. When the glow discharge is started, positive ions strike target 602, and target platinum atoms are removed by momentum transfer. When a sliding shutter 620 is adjusted to expose substrate holder 604, these target platinum atoms subsequently condense into a thin platinum film on a substrate 622, which is on substrate holder 604. Target 602 and substrate holder 604 are tilted to each other by about 30° in the specific embodiment. Substrate holder 604 rotates during sputter deposition for obtaining uniform platinum film deposition over substrate 622 at a rotating speed of about 3 revolutions per minute, according to the specific embodiment. Prior to sputter deposition, substrate 622 was loaded using a magnetic bar into system 600 through a load lock chamber (not shown) coupled to the main chamber containing substrate holder 604. During sputter deposition, the total gas pressure within the main chamber of system 600 is controlled to a set value by exhaust valve 624, which is connected to a pumping system (not shown). Exhaust valve 624 also controls the flow of exhaust from system 600. It is noted that no auxiliary electrode is required with the exemplary sputtering deposition system 600 in order to deposit a preferred orientation-controlled platinum film onto substrate 622, which is a silicon substrate in the specific embodiment. For some embodiments, a magnetron gun may also be used to provide DC/RF magnetron sputtering.
Description of exemplary platinum deposition processes

[0039] Exemplary processing conditions and variables for sputter depositing preferred orientation-controlled platinum using an inert gas, such as argon in the specific embodiment, and nitrogen are described as follows. In controlling the preferred orientation of the deposited platinum film, four variables are important: (i) the substrate temperature \(T_S\) which is, more specifically for the specific embodiment, the temperature of the substrate surface during deposition; (ii) the nitrogen content in the gas \((F_{N_2} (\text{in } \%)) = 100 \times (N_2 \text{ partial pressure/total gas pressure})\); (iii) the total gas pressure \((P_{\text{tot}} = \text{inert gas partial pressure} + N_2 \text{ partial pressure})\), which is, more specifically for the specific embodiment, the total gas pressure during film deposition; and (iv) the film deposition rate \((\text{DR (in } \AA/\text{minute)} = \text{film thickness} \div \text{time spent in film deposition})\). These four variables determine many properties of the deposited platinum film, such as preferred orientation, hillock and/or pinhole formation, residual stress in the film, etc. In order to make orientation-controlled, defect-free platinum thin films, each of the four variables preferably should be controlled within some ranges, as discussed generally below.

Deposition conditions for preferred (200) orientation-controlled platinum films

[0040] Figs. 7a to 7d illustrate the relationship between the degree (in %) of preferred (200) orientation in the deposited platinum film and variation of the above-discussed four deposition process variables. In particular, the degree of preferred (200) orientation in the deposited platinum film is defined as follows:

\[
P_{200} = 100 \times \left[ \frac{(I_{200})}{(I_{111} + I_{200} + I_{220})} \right] (\%)
\]

where \(I_{hkl}\) is the X-ray diffraction intensity of the \((hkl)\) plane.

[0041] Fig. 7a illustrates the effect of changing the substrate temperature \(T_S\) on the degree of preferred (200) orientation. For the data shown in Fig. 7a, \(P_{\text{tot}} = 2 \text{ mTorr}\) and \(\text{DR} = 130 \text{ Å/min}\). With low nitrogen content \((F_{N_2} = 10 \%)\), the range of \(T_S\) for obtaining (200) orientation is lower than the range of the case with higher nitrogen content \((F_{N_2} = 40 \%)\), as shown in Fig. 7a. Close to 100% of preferred (200) orientation platinum film is obtained for \(F_{N_2} = 10 \%\) at a substrate temperature of about 300°C; whereas, close to 100% of preferred (200) orientation platinum film is obtained for \(F_{N_2} = 40 \%\) at a substrate temperature of about 400°C.

[0042] Fig. 7b illustrates the effect of changing the nitrogen content \((F_{N_2})\) on the degree of the preferred (200) orientation. For the data shown in Fig. 7b, \(P_{\text{tot}} = 2 \text{ mTorr}\) and \(\text{DR} = 130 \text{ Å/min}\). At a lower \(T_S (300°C)\), the range of nitrogen content for obtaining preferred (200) orien-

tation is lower than that of the case at a higher \(T_S (500°C)\), as shown in Fig. 7b. Almost 100% of preferred (200) orientation platinum film is obtained for nitrogen content of about 10 % when depositing at a substrate temperature of 300°C. In contrast, almost 100% of preferred (200) orientation platinum film is obtained for nitrogen content of about 35% when depositing at a substrate temperature of 500°C.

[0043] Fig. 7c illustrates the effect of changing the total gas pressure \((P_{\text{tot}})\) on the degree of the preferred (200) orientation. For the data shown in Fig. 7c, \(F_{N_2} = 20\%\), \(T_S = 300°C\), and \(\text{DR} = 130 \text{ Å/min}\). As seen in Fig. 7c, total gas pressure should be in the range of about 1.5-3.0 mTorr in order to obtain close to 100% of preferred (200) orientation platinum film.

[0044] Fig. 7d illustrates the effect of deposition rate on the degree of the preferred (200) orientation. For the data shown in Fig. 7d, \(P_{\text{tot}} = 2 \text{ mTorr}\) and \(T_S = 300°C\). With low nitrogen content \((F_{N_2} = 10 \%)\), the range of deposition rates for obtaining preferred (200) orientation platinum film is lower than the range of the case with higher nitrogen content \((F_{N_2} = 40 \%)\), as shown in Fig. 7d. In particular, almost 100% of preferred (200) orientation platinum film is obtained for \(F_{N_2} = 10 \%\) at a deposition rate of about 100Å/min; whereas, close to 100% of preferred (200) orientation platinum film is obtained for \(F_{N_2} = 40 \%\) at a deposition rate of about 200Å/min.

Deposition conditions for preferred (111) orientation-controlled platinum films

[0046] Similar experiments were performed in order to obtain preferred deposition conditions for the preferred (111) orientation-controlled platinum films, except using the degree of preferred (111) orientation in the deposited platinum film defined as follows:

\[
P_{111} = 100 \times \left[ \frac{(I_{111})}{(I_{111} + I_{200} + I_{220})} \right] (\%)
\]

where \(I_{hkl}\) is the X-ray diffraction intensity of the \((hkl)\) plane. Platinum films having the preferred (111) orientation were deposited in experiments to determine preferred conditions. For preferred (111) orientation-controlled platinum films, the preferred ranges for the deposition conditions in the argon and nitrogen deposition atmosphere were found to be as follows: \(T_S\) of about 300°C to about 500°C; \(F_{N_2}\) of about 10-40%; \(P_{\text{tot}}\) of about 1.5-3.0 mTorr; and \(\text{DR}\) of about 80-240 Å/min. Under these processing condition ranges, a pre-
ferred (111) orientation-controlled platinum film that was
defect-free could be achieved. It was noted that the
higher the substrate temperature, the higher the nitro-
gen content that is required. Further, it was seen that if
$P_{tot}$ is too low and the nitrogen content is too high, many
hillocks occur on the preferred (111) orientation-control-
led platinum film. It was also seen that if $P_{tot}$ is too high
and the nitrogen content is too low, many pinholes occur
on the preferred (111) orientation-controlled platinum
film.

[0047] It is noted that the values of these four process
variables may not be universal (i.e., the value of a cer-
tain variable to achieve some property of the film may
vary according to the specific substrate processing ap-
paratus used). For example, these variables may vary
depending on the geometrical factors of chamber vol-
ume, target-substrate distance and other properties,
such as the magnetic field intensity of the magnetron
gun if a magnetron sputtering apparatus is used.

[0048] Besides the importance of the four process
variables during deposition, the annealing conditions
are also important for obtaining preferred orientation-
controlled and defect-free platinum films. In order to re-
move most of the nitrogen from the deposited platinum
film, the annealing temperature range is preferably from
about 400°C to about 1000°C.

**Experimental Results**

[0049] The advantages and effects of the present in-
vention will now be explained in detail with reference to
the examples which illustrate the procedures and condi-
tions of tests performed. Figs. 8a to 8f are graphs il-
lustrating X-ray diffraction (XRD) patterns of platinum
films deposited in accordance with examples 1 to 6. Typ-
ical $\theta$-2$\theta$ scans of the platinum films using Cu K$_\alpha$
radiation in the X-ray diffractometer were performed to find
the grains of the platinum films oriented with specific
planes, as discussed below in the examples. Figs. 8a to
8f show the XRD intensity in arbitrary units (a.u.) in re-
lationship to 2$\theta$ (degrees).

**Example 1**

[0050] An insulating layer of SiO$_2$ was formed on a
silicon substrate. A platinum film was deposited on the
top surface of the insulating layer under an atmosphere
containing nitrogen component.

- Deposition method: DC magnetron sputtering
- Depositing atmosphere: Ar+N$_2$
- Partial pressure ratio of nitrogen to the entire gas
  (argon + nitrogen): 10%
- Substrate temperature: room temperature
- Annealing temperature and duration: 600°C for one
  hour.

[0051] The platinum film according to the conditions
of Example 1 has a mixed (111) and (200) orientation as shown in Fig. 8a.

**Example 2**

[0052] Deposition was performed under the same
conditions as in the Example 1 except that the substrate
temperature was 300°C. The platinum film has a pre-
ferrued (111) orientation as shown in Fig. 8b.

**Example 3**

[0053] Deposition was performed under the same
conditions as in the Example 1 except that the substrate
temperature was 500°C. The platinum film has a pre-
ferrued (111) orientation as shown in Fig. 8c.

**Example 4**

[0054] An insulating layer of SiO$_2$ was formed on a
silicon substrate. Following this, a platinum film was
formed on the top surface of the insulating layer under
an atmosphere containing nitrogen.

- Deposition method: DC magnetron sputtering
- Depositing atmosphere: Ar+N$_2$
- Partial pressure ratio of nitrogen against the entire
gas: 5%
- Substrate temperature: 300°C
- Annealing temperature and duration: 650°C for one
  hour

[0055] The platinum film deposited under the above
conditions has a preferred (111) orientation as shown in
Fig. 8d.

**Example 5**

[0056] Deposition was performed under the same
conditions as in the Example 4 except that the partial
pressure ratio of the nitrogen to the entire depositing at-
mosphere is changed to 20%. The platinum film depos-
ited under the above conditions is shown in Fig. 8e. The
platinum film has a mixed orientation of (111) and (200).

**Example 6**

[0057] An insulating layer of SiO$_2$ was formed on a
silicon wafer, a platinum film of 2000Å thickness was de-
posited on the insulating layer.

- Deposition method: DC magnetron sputtering
- Depositing atmosphere: Ar+N$_2$
- Partial pressure of N$_2$ against the entire gas: 30%
- Substrate temperature: 300°C
- Depositing pressure: 1 mTorr
- Annealing temperature and duration: 600°C for one
  hour
[0058] The platinum film formed in this example has a preferred (220) orientation as shown in Fig. 8f.

[0059] Figs. 9a and 9b are scanning electron microscope micrographs showing a 10,000-times magnified planar view and a 50,000-times magnified cross-sectional view, respectively, of the platinum film deposited by a prior art method. In this prior art method, a platinum film is coated on a titanium glue layer deposited on a SiO2 substrate in an argon atmosphere, and then annealed for one hour at 600°C. Many white spots observed in Fig. 9a are hillocks or protrusions in the platinum film of the prior art. Moreover, it is clearly seen in the cross-sectional view of Fig. 9b that the platinum film of the prior art has a very rough surface as a result of these hillocks. Figs. 9c and 9d are scanning electron microscope micrographs showing 50,000-times magnified planar and cross-sectional views, respectively, of the platinum film deposited by Example 2 according to the present invention. In contrast with the prior art platinum film, the platinum film of a specific embodiment of the present invention appears to be free of hillocks or other defects, as seen in Fig. 9c. Moreover, the cross-sectional view of Fig. 9d demonstrates that the surface of the platinum film is smooth. This example shows that the platinum film deposited by the present invention has no hillocks or any other defects.

[0060] The platinum film formed in the other Examples shows the same results, which are not shown to avoid redundancy. This means that the platinum film formed according to the present invention is orientation-controllable, and has a dense structure showing no hillocks, pores or buckling, unlike the platinum film formed according to the prior art. The platinum films formed in accordance with the present invention show excellent electrical conductivity and the resistivities thereof are lower than 15 µΩ-cm.

[0061] It is clear from the above description that preferred orientations of platinum films can be controlled by varying at least one of the following parameters: the partial pressure ratio of the nitrogen, the temperature of the substrate during the deposition step, and annealing conditions.

[0062] Since orientation of the platinum film is controllable by any one of the following parameters: the partial pressure ratio of the nitrogen to the entire platinum deposition atmosphere, the temperature of the substrate during the deposition step, and annealing conditions; it is possible to form a platinum film having desired characteristics for a particular electronic device which uses the platinum film as a bottom electrode.

[0063] It should be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reviewing the above description. By way of example, the inventions herein have been illustrated primarily with regard to specific examples of platinum process recipes, but they are not so limited. Also, the annealing process performed after the platinum deposition may be performed in-situ, or in a different chamber from the deposition chamber. Those skilled in the art will recognize other equivalent or alternative methods of depositing the orientation-controlled platinum layer while remaining within the scope of the claims of the present invention. The scope of the invention should, therefore, be determined not with reference to the above description, but should instead be determined with reference to the appended claims.

Claims

1. A method of forming a platinum film orientation-controlled to (111), (200), and/or (220), comprising the steps of:

   providing a substrate;

   forming a functional intermediate film on the substrate;

   possibly heating the substrate to a temperature;

   depositing a platinum film on the intermediate layer under an atmosphere containing nitrogen and inert gas, so that the platinum film contains nitrogen; and

   annealing the platinum film to substantially remove the nitrogen contained in the platinum film, wherein orientation of the platinum film is controlled by at least one of: the partial pressure ratio of the nitrogen to the entire gas in the deposition atmosphere, the temperature of the substrate during the deposition step, and annealing conditions.

2. The method of claim 1, wherein the substrate is heated to a temperature of about room temperature to about 500°C.

3. The method of claim 1, wherein the inert gas is selected from the group consisting of argon, neon, krypton and xenon.

4. The method of claim 1, wherein the partial pressure ratio of the nitrogen to the entire depositing atmosphere gas is less than 50%.

5. The method of claim 1, wherein the annealing temperature is about 400°C to 1,000°C.

6. The method of claim 1, wherein the substrate is selected from the group of:

   single component semiconductors such as Si, Ge and C;

   compound semiconductors such as GaAs, InP, Si/Ge and SiC;

   single-crystalline ceramic such as SrTiO3.
LaAlO$_3$, Al$_2$O$_3$, KBr, NaCl, MgO, ZrO$_2$, Si$_3$N$_4$, TiO$_2$, Ta$_2$O$_5$ and AlN; poly-crystalline ceramic such as Si, SrTiO$_3$, LaAlO$_3$, Al$_2$O$_3$, MgO, KBr, NaCl, ZrO$_2$, Si$_3$N$_4$, TiO$_2$, Ta$_2$O$_5$ and AlN; metals such as Au, Ag, Al, Ir, Pt, Cu, Pd, Ru and W; and non-crystalline/glassy materials such as BSG, PSG, BPSG and amorphous Si.

7. The method of claim 1, wherein the deposition of the platinum film is performed by using any one of DC/RF sputtering, DC/RF magnetron sputtering, metal organic chemical vapor deposition, vacuum evaporation, partially ionized beam deposition, laser ablation.

8. The method of claim 1 wherein said method manufactures an electronic device with a bottom electrode comprising the platinum film.

9. The method of claim 8, further comprising a step of forming high-dielectric/ferroelectric film on the platinum film.

10. The method of claim 9, wherein the functional intermediate film is selected from the group consisting of:

- a perovskite structure oxide such as BT (BaTiO$_3$), BST(Ba$_{1-x}$Sr$_x$TiO$_3$), ST(SrTiO$_3$), PT (PbTiO$_3$), PZT(Pb(Zr, Ti)O$_3$), PLT(Pb$_1$,La$_{1-x}$Ti$_x$O$_3$), PLZT(Pb$_{1-x}$La$_x$(Zr,Ti)$_{1-x/4}$O$_3$), PMN (PbMg$_{1/3}$Nb$_{2/3}$O$_3$), KNbO$_3$, LiTaO$_3$, K(Ta, Nb)O$_3$, CaTiO$_3$, SrSnO$_3$, NaNbO$_3$, LaAlO$_3$, and YAlO$_3$; a bismuth-layered perovskite structure oxide such as SrBiNbO$_6$, SrBi$_2$Ti$_2$O$_6$, SrBi$_2$Ta$_2$O$_9$, SrBi$_2$(Ta$_{1-x}$Nb$_x$)$_2$O$_9$ and Bi$_4$Ti$_3$O$_{12}$; a tungsten-bronze type structure oxide such as Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$, (Sr, Ba)$_{0.8}$R$_x$Na$_{0.4}$Nb$_2$O$_6$ (R: Cr, Zn, Y), (Pb, Ba)Nb$_2$O$_6$, (K, Sr)Nb$_2$O$_6$, (Pb, K)Nb$_2$O$_6$, Pb$_2$KNb$_5$O$_{15}$, K$_2$Li$_2$Nb$_5$O$_{15}$ and (K, Na)$_2$Li$_2$Nb$_5$O$_{15}$; ReMnO$_3$ (Re: rare-earth element); BaMF$_4$ (M: Mn, Co, Mg, Zn); and KMF$_3$.

15. The method of claim 9, wherein the high-dielectric or ferroelectric oxide film is selected from the group consisting of:

Patentansprüche

1. Verfahren zur Herstellung einer Platinschicht mit einer auf (110), (200) und/oder (220) gesteuerten Orientierung, umfassend folgende Schritte:

- Bereitstellen eines Substrates;
- Bilden einer funktionellen Zwischenschicht auf dem Substrat;
- eventuell Erwärmen des Substrats auf eine Temperatur;
- Abscheiden einer Platinschicht in einer Atmosphäre, welche Stickstoff und ein Edelgas enthält, so dass die Platinschicht Stickstoff enthält; und

2. Verfahren nach Anspruch 1, wobei das Substrat auf eine Temperatur von ungefähr Raumtemperatur bis ungefähr 500°C erwärmt wird.

14. The method of claim 10, wherein the functional intermediate film is an adhesion layer and is formed from a material selected from the group comprising TiN, W, Ta, Sn, Ru, In, Ir, Os, Rh, silicide compound (Ni silicide, Co silicide, W silicide).

11. The method of claim 10, wherein the functional intermediate film is an insulating layer and is selected from the group consisting of SiO$_2$, Si$_3$N$_4$, BPSG, BSG, PSG, MgO, CaO, CaF$_2$, Al$_2$O$_3$ or B$_2$O$_3$.

12. The method of claim 10, wherein the functional intermediate film is a conductive plug and is formed from a material selected from the group consisting of TiN, zirconium nitride, tantalum silicide, tungsten silicide, molybdenum silicide, nickel silicide, cobalt silicide, tantalum carbide, tantalum boride, polysilicon, germanium, W, Ta, Ti, Mo, TiW, boron carbide, Cu.

13. The method of claim 10, wherein the functional intermediate film is a diffusion barrier layer and is formed from a material selected from the group consisting of ternary component amorphous materials (Ti-Si-N, Ta-B-N, Ti-B-N); conductive nitride (titanium aluminum nitride, Zr nitride, Hf nitride, Y nitride, Se nitride, La nitride and rare earth nitride, N deficient Al nitride, doped Al nitride, Mg nitride, Ca nitride, Sr nitride, Ba nitride, TiN, GaN, Ni nitride, Ta nitride, Co nitride, W nitride).

14. The method of claim 10, wherein the functional intermediate film is an adhesion layer and is formed from a material selected from the group comprising
3. Verfahren nach Anspruch 1, wobei das Edelgas gewählt ist aus der Gruppe bestehend aus Argon, Neon, Krypton und Xenon.

4. Verfahren nach Anspruch 1, wobei das Partialdruckverhältnis von Stickstoff zu dem gesamten Abscheidungsatmosphäregas weniger als 50 % beträgt.

5. Verfahren nach Anspruch 1, wobei die Glühtemperatur ungefähr 400 bis 1000 °C beträgt.

6. Verfahren nach Anspruch 1, wobei das Substrat ausgewählt wird aus der Gruppe:
   - Einkomponentenhalbleiter wie Si, Ge und C;
   - Verbundhalbleiter wie GaAs, InP, Si/Ge und SiC;
   - einkristalline Keramiken wie SrTiO₃, LaAlO₃, Al₂O₃, KBr, NaCl, MgO, ZrO₂, Si₃N₄, TiO₂, Ta₂O₅ und AlN;
   - polykristalline Keramiken wie Si, SrTiO₃, LaAlO₃, Al₂O₃, MgO, KBr, NaCl, ZrO₂, Si₃N₄, TiO₂, Ta₂O₅ und AlN;
   - Metalle wie Au, Ag, Al, Ir, Pt, Cu, Pd, Ru und W; und
   - nichtkristalline/glasmäßige Materialien wie BSG, PSG, BPSG und amorphe Si.

7. Verfahren nach Anspruch 1, wobei das Abscheiden der Platin schicht durchgeführt wird unter Verwen dung eines von DC/RF-Sputtern, DC/RF-Magnetronsputtern, metallisches organisches chemisches Dampfabscheiden, Vakuumverdampfung, teilweise ionisierte Strahlenabscheidung, Laserablation.

8. Verfahren nach Anspruch 1, wobei das Verfahren eine elektronische Vorrichtung mit einer Bodenelektrode umfassend die Platischicht herstellt.


10. Verfahren nach Anspruch 9, wobei die funktionelle Zwischenschicht gewählt ist aus der Gruppe bestehend aus SiO₂, Si₃N₄, BPSG, BSG, PSG, MgO, CaO, CaF₂, Al₂O₃ oder B₂O₃.

11. Verfahren nach Anspruch 9, wobei die stark dielektrische oder ferroelektrische Oxidschicht gewählt ist aus der Gruppe bestehend aus:
   - einem Oxid mit Perovskitstruktur wie BT (BaTiO₃), BST(Ba₁₋ₓSrₓTiO₃), ST(SrTiO₃), PT (PbTiO₃), PZT(Pb(Zr, Ti)O₃), PLT(Pb₁₋ₓLaₓTiO₃), PLZT(Pb₁₋ₓLaₓ(0.52)TiO₃₋₀.₄₈); PMN (PbMg₁/3Nb₂/₃O₃), KNbO₃, LiTaO₃, K(Ta,Nb)O₃, CsTiO₃, SrSnO₃, NaNbO₃, LaAlO₃ und YAlO₃; ein Bismuth-geschichtetes Oxid mit Perovskitstruktur wie SrBi₂Nb₂O₇, SrBi₂Ta₂O₉, SrBi₂(Ta,Nb)₂O₉, und Bi₄Ti₃O₁₂; ein Sturkturoxid vom Wolframbronzetyp wie Sr₁₋ₓBaₓNb₂O₆, Cr, Zn, Y), (Pb, Ba)₂Nb₂O₆, (K, Sr)Nb₂O₆, (Pb, K)₂Nb₂O₆, Pb₃KNb₂O₉, K₂Li₂Nb₂O₅ und (K, Na)₃Li₂Nb₂O₅, K₂LiNb₅O₁₅, ReMnO₃ (E: Element der seltenen Erden); BaMF₄(M: Mn, Co, Mg, Zn); und KMgF₃.


14. Verfahren nach Anspruch 10, wobei die funktionelle Zwischenschicht eine Adhäsionsschicht ist und aus einem Material gebildet ist, gewählt aus der Gruppe umfassend TiN, W, Ta, Ti, Sn, Ru, In, Ir, Os, Rh, Silicidverbindung (Ni-Silicid, Co-Silicid, W-Silicid).

15. Verfahren nach Anspruch 9, wobei die stark dielektrische oder ferroelektrische Oxidschicht gewählt ist aus der Gruppe bestehend aus:
   - einer Oxid mit Perovskitstruktur wie BT (BaTiO₃), BST(Ba₁₋ₓSrₓTiO₃), ST(SrTiO₃), PT (PbTiO₃), PZT(Pb(Zr, Ti)O₃), PLT(Pb₁₋ₓLaₓTiO₃), PLZT(Pb₁₋ₓLaₓ(0.52)TiO₃₋₀.₄₈); PMN (PbMg₁/3Nb₂/₃O₃), KNbO₃, LiTaO₃, K(Ta,Nb)O₃, CsTiO₃, SrSnO₃, NaNbO₃, LaAlO₃ und YAlO₃; ein Bismuth-geschichtetes Oxid mit Perovskitstruktur wie SrBi₂Nb₂O₇, SrBi₂Ta₂O₉, SrBi₂(Ta,Nb)₂O₉, und Bi₄Ti₃O₁₂; ein Sturkturoxid vom Wolframbronzetyp wie Sr₁₋ₓBaₓNb₂O₆, Cr, Zn, Y), (Pb, Ba)₂Nb₂O₆, (K, Sr)Nb₂O₆, (Pb, K)₂Nb₂O₆, Pb₃KNb₂O₉, K₂Li₂Nb₂O₅ und (K, Na)₃Li₂Nb₂O₅, K₂LiNb₅O₁₅, ReMnO₃ (E: Element der seltenen Erden); BaMF₄(M: Mn, Co, Mg, Zn); und KMgF₃.

Revendications

1. Procédé pour former un film de platine ayant une orientation contrôlée (111), (200) et/ou (220), comprenant les étapes qui consistent à:
prévoir un substrat;  
former un film intermédiaire fonctionnel sur le substrat;  
chauffer éventuellement le substrat jusqu'à une certaine température;  
déposer un film de platine sur la couche intermédiaire sous une atmosphère contenant de l'azote et un gaz inerte, afin que le film de platine contienne de l'azote; et  
soumettre le film de platine à un recuit pour éliminer pratiquement tout l'azote contenu dans le film de platine, l'orientation du film de platine étant contrôlée par au moins l'un des moyens constitués par le taux de la pression partielle de l'azote par rapport à l'ensemble du gaz présent dans l'atmosphère de dépôt, la température du substrat au cours de l'étape de dépôt et les conditions de recuit.

2. Procédé selon la revendication 1, dans lequel le substrat est chauffé jusqu'à une température située dans la plage allant d'approximativement la température ambiante à environ 500°C.

3. Procédé selon la revendication 1, dans lequel le gaz inerte est choisi dans le groupe constitué par l'argon, le néon, le krypton et le xénon.

4. Procédé selon la revendication 1, dans lequel le taux de la pression partielle de l'azote par rapport à l'ensemble du gaz de l'atmosphère de dépôt est inférieur à 50%.

5. Procédé selon la revendication 1, dans lequel la température de recuit est d'environ 400°C à 1000°C.

6. Procédé selon la revendication 1, dans lequel le substrat est choisi dans le groupe constitué par :

- des semi-conducteurs à un seul composant, tels que Si, Ge et C;
- des semi-conducteurs composites, tels que GaAs, InP, Si/Ge et SiC;
- des céramiques monocrystallines, telles que SrTiO3, LaAlO3, Al2O3, KBr, NaCl, MgO, ZrO2, Si3N4, TiO2, Ta2O5 et AlN;
- des céramiques polycristallines, telles que SrTiO3, LaAlO3, Si3N4, MgO, KBr, NaCl, ZrO2, Si3N4, TiO2, Ta2O5 et AlN;
- des métaux, tels que Au, Ag, Al, Ir, Pt, Cu, Pd, Ru et W; et
- des matières non cristallines/vitreuses, telles que BSG, PSG, BPSG et Si amorphe.

7. Procédé selon la revendication 1, dans lequel le dépôt du film de platine est réalisé à l'aide de l'un quelconque des procédés de pulvérisation cathodique CC/RF, de pulvérisation cathodique par magnétron CC/RF, de dépôt chimique en phase vapeur de composés organométalliques, d'évaporation sous vide, de dépôt par faisceau partiellement ionisé, et d'ablation au laser.

8. Procédé selon la revendication 1, comprenant la fabrication d'un dispositif électronique comportant une électrode inférieure comprenant le film de platine.

9. Procédé selon la revendication 8, comprenant également l'étape qui consiste à former un film haute-ment diélectrique/ferroélectrique sur le film de platine.

10. Procédé selon la revendication 9, dans lequel le film intermédiaire fonctionnel est choisi dans le groupe constitué par une couche isolante, une couche formant fiche conductrice, une couche d'adhérence et une couche formant barrière de diffusion.

11. Procédé selon la revendication 10, dans lequel le film intermédiaire fonctionnel est une couche isolante et est choisi dans le groupe constitué par SiO2, Si3N4, BPSG, BSG, PSG, MgO, CaO, CaF2, Al2O3 et B2O3.

12. Procédé selon la revendication 10, dans lequel le film intermédiaire fonctionnel est une fiche conductrice et est formé à partir d'une matière choisie dans le groupe constitué par TiN, le nitrure de zirconium, le siliciure de titane, le siliciure de tantale, le siliciure de tungstène, le siliciure de molybènène, le siliciure de nickel, le siliciure de cobalt, le carburde de tantale, le borure de tantale, le polysilicium, le germanium, W, Ta, Ti, Mo, TiW, le carburde de bore et Cu.

13. Procédé selon la revendication 10, dans lequel le film intermédiaire fonctionnel est une couche formant barrière de diffusion et est formé à partir d'une matière choisie dans le groupe constitué par des matières amorphes à composants ternaires (Ti-Si-N, Ta-B-N, Ti-B-N); et des nitrures conducteurs (nitrure d'aluminium et de titane, nitrure de Zr, nitrure de Hf, nitrure de Y, nitrure de Se, nitrure de La et nitrure de terres rares, nitrure de Al déficient en N, nitrure de Al dopé, nitrure de Mg, nitrure de Ca, nitrure de Sr, nitrure de Ba, TiN, GaN, nitrure de Ni, nitrure de Ta, nitrure de Co et nitrure de W).

14. Procédé selon la revendication 10, dans lequel le film intermédiaire fonctionnel est une couche d'adhérence et est formé d'une matière choisie dans le groupe comprenant TiN, W, Ta, Ti, Sn, Ru, In, Ir, Os, Rh, et un composé siliciure (siliciure de Ni, siliciure de Co ou siliciure de W).
15. Procédé selon la revendication 9, dans lequel le film d’oxyde hautement diélectrique ou ferroélectrique est choisi dans le groupe constitué par :

un oxyde à structure perovskite, tel que BT (BaTiO₃), BST(Baₓ₋₁SrₓTiO₃), ST(SrTiO₃), PT (PbTiO₃), PZT(Pb(Zr, Ti)O₃), PLT(Pbₓ₋₁Laₓ₋₁TiO₃), PLZT (Pbₓ₋₁Laₓ₋₁(Zr,yTi₃₋₄)O₉), PMN (PbMg₁₋ₓNb₂O₃), KNbO₃, LiTaO₃, K(Ta, Nb) O₃, CaTiO₃, SrSnO₃, NaNbO₃, LaAlO₃ et YAlO₃; un oxyde à structure perovskite à couche de bismuth, tel que SrBiNbO₉, SrBiₓ⁻₋₂TixO₉, SrBi₁₋₂(Ta,Nbx,y)₂O₆ et Bi₄Ti₃O₁²; un oxyde à structure de type tungstène-bronze, tel que Sr₁₋ₓBaₓNb₂O₆, (Sr, Ba)₀,₈₋ₓ RG₄₋ₓNaₐ₋ₓY₀₋ₓSrₓ₋₁₀₋ₓNb₂O₆ (R: Cr, Zn, Y), (Pb, Ba)Nb₂O₆, (K, Sr)Nb₂O₆, (Pb, K)Nb₂O₆, Pb₂KNb₅O₁₅, K₃Li₂Nb₅O₁₅ et (K, Na)₃Li₂Nb₅O₁₅, K₂LiNb₂O₁₅, ReMnO₃ (Re: élément des terres rares); BaMF₄ (M : Mn, Co, Mg, Zn); et KMgF₃.
Ar\text{(inert gas)} + N_2

Fig. 1a

Annealing

Fig. 1b

Fig. 1c

Fig. 2
Fig. 3a

Fig. 3b

Annealing

Fig. 3c

Fig. 3d