Description

The present invention relates generally to semiconductor substrates having thin films of titanium nitride (TiN) deposited thereon by low pressure chemical vapor deposition (LPCVD) methods, and more particularly, to a process for reducing the chlorine content of such TiN films for lessening the resistivity of such films.

It is well known in the semiconductor industry to use thin films of titanium nitride (TiN) as a barrier-metal for semiconductor devices. Such thin films of TiN can be deposited using chemical vapor deposition (CVD) techniques. As a barrier metal, such thin films of TiN may be deposited over semiconductor contact areas prior to formation of aluminum contact layers to prevent the aluminum connection layer from directly contacting the underlying semiconductor material, which is most typically silicon. Such TiN films provide good step coverage over the surface of the semiconductor substrate, particularly within submicron contacts. Such TiN films also provide low contact resistance to silicide, low leakage, excellent adhesion to the underlying semiconductor substrate, and high thermal stability. Such TiN films also provide good adhesion for subsequent films of tungsten.

In Sherman, "Growth and Properties of LPCVD Titanium Nitride as a Diffusion Barrier for Silicon Device Technology," J. Electrochem. Soc., Vol. 137, No. 6, June 1990, a process is described for depositing thin films of TiN upon a silicon substrate in a single-wafer cold wall reactor using a low pressure CVD (LPCVD) process.

U.S. Patent 4570328 describes a method of producing titanium nitride MOS device gate electrodes. The TiN coating is deposited on a silicon substrate using a chemical vapour deposition (CVD) process in which the silicon substrate is heated and then contacted with a gas mixture comprising ammonia and titanium tetrachloride. The TiN coating thus formed is then annealed, under nitrogen gas, at a temperature of 900 to 1000 °C, in order to decrease the resistivity of the coating.

It is an object of the present invention to provide a process for forming titanium nitride films upon silicon substrates having a decreased sheet resistance.

It is another object of the present invention to provide a process for forming titanium nitride films upon silicon substrates wherein such titanium nitride films have a decreased chlorine content.

It is yet another object of the present invention to provide such a process which can be performed without substantially altering the flow gases or apparatus commonly used to deposit such titanium nitride films.

A process for forming low resistivity titanium nitride films on a silicon substrate by chemical vapour deposition comprises, in accordance with the invention, in combination the steps of:

a) placing a silicon substrate in a reaction chamber, the substrate having a film of titanium nitride deposited on a surface thereof by chemical vapour deposition using $TiCl_4$ gas and at least one other gas reactive therewith, and,

b) passing a gas over the silicon substrate, characterised in that the gas of step b) is a hydrogen-bearing gas that is reactive with chlorine and which, on passage over the substrate, reacts with residual chlorine retained by the deposited titanium nitride film.

Briefly described, and in accordance with the preferred embodiments thereof, the process includes the steps of placing the silicon substrate in a reaction chamber, heating the silicon substrate within the reaction chamber, initially passing both $TiCl_4$ gas and NH_3 gas into the reaction chamber over the silicon substrate to deposit titanium nitride upon a surface of the silicon substrate, and thereafter discontinuing the flow of $TiCl_4$ gas while passing a hydrogen-bearing gas that is reactive with chlorine into the reaction chamber over the silicon substrate to react with and remove residual chlorine atoms retained by the deposited titanium nitride film.

The aforementioned hydrogen-bearing gas is preferably NH_3 gas. In the preferred embodiment the initial flow of NH_3 gas into the reaction chamber is continued over the silicon substrate after the flow of $TiCl_4$ gas is discontinued, allowing hydrogen atoms to react with residual chlorine retained by the deposited titanium nitride film at the end of the titanium nitride growth cycle as a post deposition process. The hydrogen atoms react with the chlorine atoms to form gaseous components that leave the titanium nitride film surface.

The invention will now be further described by way of reference to the accompanying drawing in which:

Fig. 1 is a three-dimensional plot showing sheet resistance of a deposited titanium nitride layer over a range of temperatures and pressures for both a post-deposition argon inert gas anneal and a post-deposition ammonia (NH_3 gas) anneal step.

In a preferred embodiment of the process, titanium nitride films are deposited upon silicon substrates using low pressure chemical vapor deposition (LPCVD) techniques. A silicon wafer is loaded into a reaction chamber, and $TiCl_4$ gas and NH_3 gas are caused to pass over the silicon wafer. The $TiCl_4$ gas and NH_3 gas react to deposit a titanium nitride (TiN) film upon the exposed surface of the silicon wafer.

However, LPCVD TiN films deposited from $TiCl_4$ gas and NH_3 gas incorporate a large amount of chlorine in the film. This chlorine has been found to be concentrated at the grain boundaries and film interfaces. The use of NH_3 gas to react and strip off the remaining unbound chlorine has been found by Applicants to be effective in lowering the chlorine film content. Applicants believe that the hydrogen gas reacts with the chlorine atoms to form HCl gas that is carried off away from the titanium nitride film.

The present process of using NH_3 gas to react and strip off the remaining unbound chlorine is preferably performed insitu at the end of the TiN growth cycle as a post deposition process. The use of NH_3 differs from simple diffusion mechanisms, such as the use of inert gases like argon or nitrogen, which fail to strip off all the available chlorine. For example, in Fig. 1, a plot is shown indicating sheet resistance of the deposited titanium nitride layer over a range of temperatures and pressures for both a post-deposition argon anneal and a post-deposition ammonia (NH_3 gas) anneal step. As shown in Fig. 1, the sheet resistance is continuously lower when the ammonia anneal step is performed as compared with the argon anneal step. Applicants believe that standard post deposition annealing treatments in inert environments merely activate chlorine diffusion through the film; however, this diffusion mechanism does not reactively separate the bound chlorine from the grain boundaries.

The use of an insitu ammonia anneal step accomplishes two objectives. First, the chloride content of the titanium nitride film can be reduced from approximately 2% to 0.7%, which allows the film resistivity to be reduced. Secondly, the sheet resistance uniformity is improved from approximately 8% to 4%.

In practicing the present invention, a single-wafer LPCVD TiN reactor is preferably used. The temperature range within the reactor during the anneal step may be from 600 degrees Centigrade to 700 degrees Centigrade, with the temperature range of 650-680 degrees Centigrade being Preferred. The preferred pressure range within the reactor was 15 Pa to 40 Pa (115 mTorr. to 300 mtorr). Preferred gas flow ranges are 10 sccm for $TiCl_4$ gas and 100 sccm. for the NH_3 gas, wherein the term "sccm" designates standard cubic centimeters per minute. An Argon gas carrier having a flow rate of 30 sccm is added to the $TiCl_4$ gas flow path prior to injection into the reactor to balance the flow through the gas injector manifold of the reaction chamber. The $TiCl_4$ gas and the NH_3 gas are injected through two different sets of injector ports to avoid mixing of such gases within the gas manifold prior to injection into the reaction chamber.

In the preferred embodiment, the deposition of the TiN film was conducted for 60 seconds, followed by an ammonia anneal for 60 seconds. The longer the anneal period, the better the resistivity enhancement. Of course, the period for the ammonia anneal is partly dependent upon the temperature. For anneal temperatures within the range of 650-680 degrees Centigrade, the anneal time period varies between 30-90 seconds. At lower temperatures, a longer anneal period is needed to achieve the same resistivity. Most often, the deposition step and anneal step are performed at the same temperature, though the temperature of the reaction chamber can be quickly raised after the deposition step to lower the anneal time to 30-45 seconds.

It had been theorized by the applicants that merely increasing the percentage of NH_3 gas relative to $TiCl_4$ gas during the deposition phase might reduce the tendency for chlorine atoms to be retained within the titanium nitride film. However, experiments conducted by the applicants failed to show this to be true.

By reducing the titanium nitride film resistivity, one decreases series resistance between the underlying. silicon and the overlying metal connection network. Also, by making the sheet resistance of the titanium nitride film more uniform, one increases the yield of working circuits on a semiconductor wafer, thereby lowering the production cost for such circuits.

If desired, the ammonia anneal post deposition step may be carried out in a process chamber different than the LPCVD reaction process chamber in which the titanium nitride film deposition step is carried out. This approach may be useful when the film deposition step and the post deposition anneal step are carried out in separate process chambers of a cluster tool having a centrally located substrate transport compartment which sequentially transfers the substrate in a controlled oxygen-free vacuum environment to a film deposition LPCVD process chamber, thereafter from the film deposition LPCVD chamber to the post deposition ammonia anneal process chamber, and subsequently from the post deposition ammonia anneal process chamber for further processing, storage in a cassette or the like. The temperature in the separate post anneal process chamber could be the same temperature as in the film deposition LPCVD chamber, or a different temperature, either higher or lower.

Alternatively, the substrate could be removed from the LPCVD process chamber after the film formation step and transported under normal uncontrolled oxygen-containing air atmospheric conditions to a standalone post anneal process chamber which is physically separate from the LPCVD

chamber and not interconnected therewith via an oxygen-free controlled atmosphere and/or vacuum substrate transport compartment. As with the cluster tool configuration described above, the temperature in the standalone post anneal chamber may be different than that in the film forming LPCVD chamber, either higher or lower.

Claims

1. A process for forming low resistivity titanium nitride films on a silicon substrate by chemical vapour deposition comprising in combination the steps of:
   a) placing a silicon substrate in a reaction chamber, the substrate having a film of titanium nitride deposited on a surface thereof by chemical vapour deposition using $TiCl_4$ gas and at least one other gas reactive therewith, and,
   b) passing a gas over the silicon substrate, characterised in that the gas of step b) is a hydrogen-bearing gas that is reactive with chlorine and which, on passage over the substrate, reacts with residual chlorine retained by the deposited titanium nitride film.

2. A process as claimed in Claim 1, wherein the hydrogen-bearing gas is NH_3 gas.

3. A process as claimed in either Claim 1 or Claim 2, wherein the temperature within the reaction chamber during step b) is within the range of 600-700 °C.

4. A process as claimed in any preceding Claim, wherein the temperature within the reaction chamber during step b) lies within the range of 650-680 °C.

5. A process as claimed in any preceding Claim, wherein the pressure within the reaction chamber during step b) lies within the range of 15 Pa and 40 Pa (115 mTorr and 300 mTorr).

6. A process as claimed in any preceding Claim, comprising the further steps prior to step a) of:
   c) placing the silicon substrate in a reaction chamber,
   d) heating the silicon substrate within the reaction chamber,
   e) passing both $TiCl_4$ gas and at least one other gas reactive therewith into the reaction chamber over the silicon substrate to deposit titanium nitride upon a surface of the silicon substrate whereby to form the deposited film of titanium nitride, the deposited film containing chlorine and having a sheet resistivity.

7. A process as claimed in Claim 6, wherein the at least one other gas of step e) is NH_3 gas.

8. A process as claimed in either Claim 6 or Claim 7, including the step of discontinuing the flow of $TiCl_4$ gas after step e).

9. A process as claimed in Claim 8, wherein NH_3 gas is passed into the reaction chamber over the silicon substrate for approximately 30 seconds to 90 seconds after the flow of $TiCl_4$ gas is discontinued.

10. A process as claimed in either Claim 8 or Claim 9 when dependent on Claim 7, wherein the flow of NH_3 gas in step b) comprises a continuation of the flow of NH_3 gas in step e).

11. A process as claimed in any one of Claims 6 to 10, wherein steps a) and b) and steps c) to e) occur in the same process chamber without removal of the substrate therefrom between steps a) and b) and steps c) to e).

12. A process as claimed in Claim 11, wherein the temperature within the chamber during steps b) and e) is substantially the same.

13. A process as claimed in any one of Claims 6 to 10, wherein steps a) and b) and steps c) to e) occur respectively in different process chambers and the substrate is transported between the different process chambers through a transport chamber maintained at a vacuum which interconnects the different process chambers.

14. A process as claimed in Claim 13, wherein the transport chamber is maintained substantially oxygen-free during transport of the substrate between the different process chambers.

15. A process as claimed in any one of Claims 6 to 10, wherein steps a) and b) and steps c) to e) occur respectively in different process chambers and the substrate is transported between the different process chambers in an air atmosphere.

Patentansprüche

1. Verfahren zum Bilden von Titan-Nitrid-Filmen niedrigen spezifischen Widerstandes auf einem Siliziumsubstrat durch chemische Abscheidung aus der Gasphase, die folgenden Schritte in Kombination enthaltend:

* C L M S *

chamber and not interconnected therewith via an oxygen-free controlled atmosphere and/or vacuum substrate transport compartment. As with the cluster tool configuration described above, the temperature in the standalone post anneal chamber may be different than that in the film forming LPCVD chamber, either higher or lower.

Claims

1. A process for forming low resistivity titanium nitride films on a silicon substrate by chemical vapour deposition comprising in combination the steps of:
   a) placing a silicon substrate in a reaction chamber, the substrate having a film of titanium nitride deposited on a surface thereof by chemical vapour deposition using $TiCl_4$ gas and at least one other gas reactive therewith, and,
   b) passing a gas over the silicon substrate, characterised in that the gas of step b) is a hydrogen-bearing gas that is reactive with chlorine and which, on passage over the substrate, reacts with residual chlorine retained by the deposited titanium nitride film.

2. A process as claimed in Claim 1, wherein the hydrogen-bearing gas is NH_3 gas.

3. A process as claimed in either Claim 1 or Claim 2, wherein the temperature within the reaction chamber during step b) is within the range of 600-700 °C.

4. A process as claimed in any preceding Claim, wherein the temperature within the reaction chamber during step b) lies within the range of 650-680 °C.

5. A process as claimed in any preceding Claim, wherein the pressure within the reaction chamber during step b) lies within the range of 15 Pa and 40 Pa (115 mTorr and 300 mTorr).

6. A process as claimed in any preceding Claim, comprising the further steps prior to step a) of:
   c) placing the silicon substrate in a reaction chamber,
   d) heating the silicon substrate within the reaction chamber,
   e) passing both $TiCl_4$ gas and at least one other gas reactive therewith into the reaction chamber over the silicon substrate to deposit titanium nitride upon a surface of the silicon substrate whereby to form the deposited film of titanium nitride, the deposited film containing chlorine and having a sheet resistivity.

7. A process as claimed in Claim 6, wherein the at least one other gas of step e) is NH_3 gas.

8. A process as claimed in either Claim 6 or Claim 7, including the step of discontinuing the flow of $TiCl_4$ gas after step e).

9. A process as claimed in Claim 8, wherein NH_3 gas is passed into the reaction chamber over the silicon substrate for approximately 30 seconds to 90 seconds after the flow of $TiCl_4$ gas is discontinued.

10. A process as claimed in either Claim 8 or Claim 9 when dependent on Claim 7, wherein the flow of NH_3 gas in step b) comprises a continuation of the flow of NH_3 gas in step e).

11. A process as claimed in any one of Claims 6 to 10, wherein steps a) and b) and steps c) to e) occur in the same process chamber without removal of the substrate therefrom between steps a) and b) and steps c) to e).

12. A process as claimed in Claim 11, wherein the temperature within the chamber during steps b) and e) is substantially the same.

13. A process as claimed in any one of Claims 6 to 10, wherein steps a) and b) and steps c) to e) occur respectively in different process chambers and the substrate is transported between the different process chambers through a transport chamber maintained at a vacuum which interconnects the different process chambers.

14. A process as claimed in Claim 13, wherein the transport chamber is maintained substantially oxygen-free during transport of the substrate between the different process chambers.

15. A process as claimed in any one of Claims 6 to 10, wherein steps a) and b) and steps c) to e) occur respectively in different process chambers and the substrate is transported between the different process chambers in an air atmosphere.

Patentansprüche

1. Verfahren zum Bilden von Titan-Nitrid-Filmen niedrigen spezifischen Widerstandes auf einem Siliziumsubstrat durch chemische Abscheidung aus der Gasphase, die folgenden Schritte in Kombination enthaltend:

* C L M S *

a) ein Siliziumsubstrat wird in einer Reaktionskammer angeordnet, wobei das Substrat ein auf der Oberfläche desselben durch chemische Abscheidung aus der Gasphase unter Verwendung von $TiCl_4$-Gas und mindestens einem anderen Gas, welches mit diesem reagiert, aufgetragenen Titan-Nitrid-Film aufweist, und

b) ein Gas wird über das Siliziumsubstrat geschickt,

dadurch gekennzeichnet, daß das Gas aus Schritt b) ein wasserstofftragendes Gas ist, welches mit Chlor reagiert und welches, beim Vorbeistreichen über das Substrat, mit restlichem, durch den aufgetragenen Titan-Nitrid-Film zurückgehaltenem Chlor reagiert.

2. Verfahren nach Anspruch 1, in dem das wasserstofftragende Gas NH_3-Gas ist.

3. Verfahren nach einem der Ansprüche 1 oder 2, in dem die Temperatur innerhalb der Reaktionskammer während des Schrittes b) innerhalb des Bereiches von 600 bis 700 °C liegt.

4. Verfahren nach einem der vorstehenden Ansprüche, in dem die Temperatur innerhalb der Reaktionskammer während des Schrittes b) innerhalb des Bereiches von 650 bis 680 °C liegt.

5. Verfahren nach einem der vorstehenden Ansprüche, in dem der Druck innerhalb der Reaktionskammer während des Schrittes b) innerhalb eines Bereiches von 15 Pa und 40 Pa (115 mTorr und 300 mTorr) liegt.

6. Verfahren nach einem der vorstehenden Ansprüche, die weiteren vor dem Schritt a) liegenden Schritte enthaltend:

c) das Siliziumsubstrat wird in einer Reaktionskammer angeordnet,

d) das Siliziumsubstrat wird innerhalb der Reaktionskammer erhitzt,

e) $TiCl_4$-Gas und mindestens ein weiteres mit diesem reagierendes Gas werden in die Reaktionskammer über das Siliziumsubstrat eingeführt, um Titan-Nitrid auf einer Oberfläche des Siliziumsubstrats abzuscheiden, um den abgeschiedenen Titan-Nitrid-Film zu bilden, wobei der abgeschiedene Film Chlor enthält und einen spezifischen Widerstand pro Fläche aufweist.

7. Verfahren nach Anspruch 6, in dem mindestens ein weiteres Gas des Schrittes e) NH_3-Gas ist.

8. Verfahren nach einem der Ansprüche 6 oder 7, den Schritt einschließend, daß der Fluß von $TiCl_4$-Gas nach dem Schritt e) unterbrochen wird.

9. Verfahren nach Anspruch 8, in dem NH_3-Gas für etwa 30 bis 90 Sekunden, nachdem der Fluß des $TiCl_4$-Gases unterbrochen wurde, über das Siliziumsubstrat in die Reaktionskammer eingeführt wird.

10. Verfahren nach einem der Ansprüche 8 oder 9, soweit abhängig von Anspruch 7, in dem der Fluß des NH_3-Gases im Schritt die Fortsetzung des Flusses von NH_3-Gas im Schritt e) enthält.

11. Verfahren nach einem der Ansprüche 6 bis 10, bei dem die Schritte a) und b) und die Schritte c) bis e) in derselben Prozeßkammer durchgeführt werden, ohne das Substrat aus dieser zwischen den Schritten a) und b) und den Schritten c) bis e) zu entfernen.

12. Verfahren nach Anspruch 11, in dem die Temperatur innerhalb der Kammer während der Schritte b) und e) im wesentlichen die gleiche ist.

13. Verfahren nach einem der Ansprüche 6 bis 10, in dem die Schritte a) und b) und die Schritte c) bis e) jeweils in verschiedenen Prozeßkammern durchgeführt werden und das Substrat zwischen den verschiedenen Prozeßkammern durch eine Transportkammer transportiert wird, welche auf einem Vakuum gehalten wird, welches die verschiedenen Prozeßkammern verbindet.

14. Verfahren nach Anspruch 13, in dem die Transportkammer während des Transports des Substrats zwischen den verschiedenen Prozeßkammern im wesentlichen sauerstoffrei gehalten wird.

15. Verfahren nach einem der Ansprüche 6 bis 10, in dem die Schritte a) und b) und die Schritte c) bis e) jeweils in verschiedenen Prozeßkammern durchgeführt werden und das Substrat zwischen den verschiedenen Prozeßkammern in einer Luftatmosphäre transportiert wird.

Revendications

1. Procédé pour former par dépôt chimique en phase vapeur des films en nitrure de titane à faible resistivité sur un substrat en silicium comprenant les étapes combinées consistant à :

   a) placer le substrat de silicium dans une chambre de réaction, le substrat possédant un film de nitrure de titane déposé sur sa surface par voie chimique en phase vapeur utilisant du gaz TiCL4 avec au moins un autre gaz réactif, et,
   b) répandre un gaz sur le substrat en silicium, caractérisé en ce que le gaz de l'étape b) comporte de l'hydrogène et réagisse au chlore et, en se répandant sur le substrat, réagisse avec les résidus de chlore retenus par le film de nitrure de titane qui y a été déposé.

2. Procédé selon la revendication 1, dans lequel le gaz comportant de l'hydrogène est du NH3.

3. Procédé selon soit la revendication 1 soit la revendication 2, dans lequel la température à l'intérieur de la chambre de réaction pendant l'étape b) est comprise entre 600 et 700 °C.

4. Procédé selon n'importe laquelle des revendications précédentes dans lequel la température à l'intérieur de la chambre de réaction durant l'étape b) est comprise entre 650 et 680 °C.

5. Procédé selon n'importe laquelle des revendications précédentes, dans lequel la pression à l'intérieur de la chambre de réaction durant l'étape b) est comprise ente 15Pa et 40Pa (115 mTorr et 300 mTorr).

6. Procédé selon n'importe laquelle des revendications précédentes comprenant les étapes supplémentaires antérieures à l'étape a) consistant à:

   c) placer le substrat en silicium dans la chambre de réaction,
   d) chauffer le substrat en silicium à l'intérieur de la chambre de réaction,
   e) répandre un gaz TiCL4 avec à la fois au moins un autre gaz de réaction dans la chambre de réaction sur le substrat en silicium pour déposer du nitrure de titane sur sa surface et y former un film de nitrure de titane, ce film déposé contenant du chlore et possédant une résistance par carré.

7. Procédé selon la revendication 6, dans lequel l'autre gaz de l'étape e) est du NH3.

8. Procédé selon soit la revendication 6 soit la revendication 7, comprenant l'étape d'interruption du flux de TiCL4 aprés l'étape e).

9. Procédé selon la revendication 8, dans lequel le gaz NH3 est répandu dans la chambre de réaction sur un substrat en silicium pendant environ 30 à 50 secondes, après interruption du flux de gaz TiCL4.

10. Procédé selon soit la revendication 8 soit la revendication 9 lorsqu'elles dépendent de la revendication 7, dans lequel le flux de gaz NH3 dans l'étape b) se continue dans l'étape e).

11. Procédé selon n'importe laquelle des revendications 6 à 10 dans lequel les étapes a) et b) et c) à e) surviennent dans la même chambre sans que l'on y enlève le substrat entre ces étapes.

12. Procédé selon la revendication 11, dans lequel la température à l'intérieur de la chambre durant les étapes b) et e) est sensiblement la même.

13. Procédé selon n'importe laquelle des revendications 6 à 10, dans lequel les étapes a) et b) et c) à e) interviennent respectivement dans différentes chambres et dans lequel le substrat est transposté entre les différentes chambres au moyen d'une chambre de transport sous vide qui relie les différentes chambres.

14. Procédé selon la revendication 13, dans lequel une chambre de transport est maintenue presque exempte d'oxygène durant le transport du substrat entre les différentes chambres nécessaires au procédé.

15. Procédé selon n'importe laquelle des revendication 6 à 10, dans lequel les étapes a) et b) et c) à e) interviennent respectivement dans les différentes chambres et dans lequel le substrat est transporté entre les différentes chambres sous atmosphère.