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PLASMA TREATMENT TO ENHANCE INORGANIC DIELECTRIC ADHESION TO COPPER

DESCRIPTION

Field of the Invention

The present invention relates to interconnect semiconductor structures and, in particular to a method for improving the adhesion of an inorganic barrier film such as Si_3N_4 to the copper lines or vias of such interconnect structures. The term "interconnect structure" is used broadly herein to include any semiconductor structure which contains copper interconnect metallurgies. Thus, the present invention is applicable for use in damascene structures (single and dual), memory cell capacitors and other wiring applications for logic, memory and input/output applications.

Background of the Invention

In the semiconductor industry, aluminum and aluminum alloys have been used as the traditional interconnect metallurgies. While aluminum-based metallurgies have been the material of choice for use as metal interconnects over the past years, concern now exists

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as to whether aluminum will meet the demands required as circuit density and speeds for semiconductor devices increase. Because of these growing concerns, other materials have been investigated as possible replacements for aluminum-based metallurgies. One highly advantageous material now being considered as a potential replacement for aluminum metallurgies is copper. This is because copper exhibits a lower susceptibility to electromigration failure as compared to aluminum as well as a lower resistivity.

Despite these advantages, copper readily diffuses into the surrounding dielectric material during subsequent processing steps. To inhibit the diffusion of copper, copper interconnects are often times capped with a protective barrier layer. One method of capping involves the use of a conductive barrier layer of tantalum or titanium, in pure or alloy form, along the sidewalls and bottom of the copper interconnection. To cap the upper surface of the copper interconnection, a dielectric material such as silicon nitride, Si_3N_4, is typically employed.

Due to the need for low temperature processing after copper deposition, the silicon nitride layer is

deposited at temperatures below 450°C. Accordingly, silicon nitride deposition is typically performed using plasma enhanced chemical vapor deposition (PECVD) or high density plasma chemical vapor deposition (HDPCVD) wherein the deposition temperature generally ranges from about 200° to about 500°C.

PECVD and HDPCVD silicon nitride has been used for many other applications in semiconductor device manufacturing. However, in using a silicon nitride cap for copper interconnects, conventional PECVD or HDPCVD silicon nitride creates reliability problems. In particular, silicon nitride films deposited using conventional PECVD or HDPCVD processes generally exhibit poor adhesion to the copper surface. For instance, some nitride films delaminate and form blisters over patterned copper lines, particularly during subsequent dielectric depositions, metallization, and chemical-mechanical polishing.

These results are indicative of how the silicon nitride film might adhere to the copper in actual fabrication processes. After being deposited onto copper metallurgy, additional insulating layers generally will be deposited over the silicon nitride

film. However, subsequent deposition of insulating layers onto the nitride film will produce stress which can cause the silicon nitride film to peel from the copper surface. This delamination results in several catastrophic failure mechanisms including: lifting intermetal dielectrics, lifting copper lines, and copper diffusion from uncapped copper lines. Such results are generally seen in dual damascene processing wherein delamination of the silicon nitride RIE stop layer generally occurs during copper chemical mechanical polishing (CMP).

Prior art nitride to copper adhesion requires siliciding the copper surface by reacting it with silicon. This prior art method has two drawbacks: increases the copper sheet resistance due to silicon reacting with copper and diffusion therein; and marginal nitride to copper adhesion due to incomplete or partial copper silicide formation.

In view of the drawbacks mentioned with prior art copper interconnect structures, there is a continued need to develop a new process of facilitating the adhesion of an inorganic barrier film to copper

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surfaces which are present on interconnect semiconductor structures.

Summary of the Invention

One object of the present invention is to provide a method of improving the adhesion of an inorganic deposited barrier film to a copper surface of an interconnect structure.

Another object of the present invention is to provide a method whereby the deposited inorganic barrier film does not delaminate from a copper surface of an interconnect structure during subsequent interconnect processing steps.

A further object of the present invention is to provide a method which can be used in dual damascene processing to improve the adhesion of a Si_3N_4 etch stop layer to copper wiring or copper vias.

These and other objects and advantages can be achieved in the present invention by utilizing a method which includes a step of exposing a layer of copper in an interconnect semiconductor structure to a reducing

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plasma prior to forming an inorganic barrier film on the copper interconnect structure. More specifically, the method of the present invention, which improves the adhesion of an inorganic deposited barrier film on copper surfaces of an interconnect structure, comprises the steps of:

(a) exposing an interconnect semiconductor structure containing at least a layer of copper to a reducing plasma; and

(b) forming an inorganic barrier film on said plasma exposed copper interconnect structure.

In accordance with the method of the present invention, the exposure step, step (a), is carried out in a plasma comprising at least one non-oxidizing gas selected from the group consisting of H_2, N_2, NH_3, noble gases such as He, Ne, Ar, Kr and Xe, and mixtures thereof. It is noted that oxidizing ambients are excluded from the present invention since the may cause the copper present in the interconnect structure to oxidize and weaken the nitride at the copper interface.

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Suitable interconnect structures that are contemplated in the present invention include, but are not limited to: memory cell capacitors including plate capacitors, crown capacitors, stack capacitors and other like capacitors; damascene structures including single and dual; multiple wiring levels containing a plurality of vias and metal lines; and other like interconnect structures.

Brief Description of the Drawings

The sole figure is a cross-sectional view of a typically dual damascene structure which can be employed in the present invention and thus subjected to the plasma exposure step prior to deposition of the inorganic barrier layer.

Detailed Description of the Invention

The present invention, which relates to a method of improving the adhesion of an inorganic deposited barrier film on copper surfaces present in interconnect semiconductor structures, will now be described in greater detail by reference to the sole figure which accompanies this specification. It is

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emphasized that while the present invention illustrates only a dual damascene structure, it is nevertheless applicable for all interconnect semiconductor structures which contain copper metallurgy and use an inorganic deposited barrier film such as SiC or Si_3N_4 as a protective barrier or as an etch stop layer.

Referring to the sole figure present in the application, the sole figure shows a typical dual damascene structure which can be subjected to the method of the present invention. Specifically, the dual damascene structure comprises a lower interconnect level 10 and an upper interconnect level 12. Each level includes a via region 14 and a metal line or wiring region 16. Lower interconnect level 10 includes dielectric 18 having an opening or trench therein that is filled with copper 20. On top of lower interconnect level 10 is an upper interconnect level 12 which includes dielectric 22 having a trench region exposing the copper wiring of the lower interconnect level. The trench region of upper interconnect level 12 is filled with copper 20. Between each interconnect level is an inorganic

barrier layer 24 which serves as a RIE stop layer, a protective barrier layer or both.

The dual damascene structure shown in the figure is fabricated utilizing conventional damascene processing steps well known to those skilled in the art except that before forming barrier layer 24, the interconnect structure is exposed to the method of the present invention which will be described in greater detail hereinbelow.

Dielectric layers 18 and 22 may be the same or different insulative inorganic or organic material. Suitable dielectrics include, but are not limited to: SiO_2, fluorinated SiO_2, Si_3N_4, polyimides, diamond, diamond-like carbon, silicon polymers, paralyne polymers, fluorinated diamond-like carbon and other like dielectric compounds. Of these dielectric materials, it is preferred that layers 18 and 22 be composed of SiO_2. The dielectric layers may be doped or undoped. When doped, the dopant may be boron, fluorine, phosphorus, deutrium, silicon, Ge or another like dopant.

Barrier layer 24 is an inorganic material which serves as a RIE stop layer for the vias or, when present as the outermost layer of the structure, as a protective barrier layer. Suitable materials for barrier layer 24 include, but are not limited to: Si_3N_4, SiC, hydrogenated Si_3N_4 and hydrogenated SiC. Of these materials, it is preferred to use the hydrogenated forms of Si_3N_4 or SiC in the present invention as the barrier layer. An optional RIE stop layer may also be inserted between metal lines 16 and vias 14 (this embodiment is not shown in the drawing).

Barrier layer 24 is formed utilizing conventional vapor deposition techniques including, but not limited to: chemical vapor deposition, low pressure chemical vapor deposition, high pressure chemical vapor deposition, high density plasma chemical vapor deposition, plasma enhanced chemical vapor deposition and other like vapor deposition techniques. Of these deposition techniques, plasma enhanced chemical vapor deposition (PECVD) and high density plasma chemical vapor deposition (HDPCVD) are preferred means for depositing the barrier layer.

It is again emphasized that the dual damascene structure shown in the drawing as well as any of the other contemplated copper interconnect structures are fabricated using techniques well known to those skilled in the art. Since such techniques are well known and are not critical for understanding the present invention, a detailed discussion of the same is not given herein. The only difference in fabricating the interconnect structure of the present invention and prior art interconnect structures is that prior to depositing inorganic barrier layer 24, the copper interconnect structure is subjected to a reducing plasma under the conditions defined hereinbelow.

Specifically, the reducing plasma employed in the present invention is any plasma ambient which is non-oxidizing, i.e. it contains no oxygen atom. Suitable reducing plasmas that can be employed in the present invention include, but are not limited to: H_2, N_2, NH_3 and noble gases. Combinations of two or more of these reducing plasmas such as N_2 and H_2 are also contemplated herein. Of these reducing plasmas, H_2 and NH_3 are highly preferred in the present invention.

The reducing plasma exposure step of the present invention is carried out in a conventional plasma deposition apparatus that is capable of generating a plasma gas. Specifically, the exposure step of the present invention is carried out at a temperature of from about 20° to about 600°C for a time period of from about 1 to about 3600 seconds. Higher exposure times greater than 3600 seconds are also contemplated herein. More preferably, the exposure step of the present invention is carried out at a temperature of from about 360° to about 400°C for a time period of from about 5 to about 30 seconds. Preferably, heating is carried out in the presence of the reducing plasma.

Moreover, the exposure step of the present invention is conducted at a pressure of from about 1 mTorr to about 20 Torr, a power of from about 50 to about 10,000 watts, and a gas flow rate of from about 1 to about 10,000 sccm. The exact conditions are dependent on the type of deposition process utilized in forming the barrier layer. For example, when high density plasma chemical vapor deposition (HDPCVD) is employed, the exposure step of the present invention is carried out at a pressure of from about 3 to about 6 mTorr, a power of from about 1500 to about 3000 watts, and a

gas flow rate of from about 10 to about 50 sccm. On the other hand, when plasma enhanced chemical vapor (PECVD) is to be used, the exposure step of the present invention is carried out at a pressure of from about 2 to about 8 Torr, a power of from about 150 to about 400 watts and a gas flow rate of from about 100 to about 2000 sccm.

It is noted that immediately after the exposure step and without breaking the vacuum, the inorganic barrier layer is formed thereon utilizing any of the above mentioned deposition techniques. The method of the present invention, particularly the reducing plasma exposure step, provides a copper interconnect structure wherein the inorganic barrier layer has improved adhesion to the copper wire or via with no increase in resistance than heretofore obtained with prior art processes. Thus, since the adhesion is improved utilizing the method of the present invention, the copper interconnect structure thus formed does not exhibit any delamination problems that are normally encountered by prior art interconnect structures during subsequent processing steps such as chemical mechanical polishing. Moreover, the interconnect structures produced using the method of

the present invention exhibit little or no increase in their resistance.

The following example is given to illustrate the scope of the present invention. Because this example is given for illustrative purposes only the invention embodied therein should not be limited thereto.

EXAMPLE

A series of experiments were performed on 200 mm Si wafers containing copper lines damascened into SiO_2 in order to demonstrate the improved adhesion between an inorganic vapor deposition barrier layer and copper wiring which was obtained utilizing the method of the present invention. Specifically, dual damascene structures were prepared utilizing standard damascene processing conditions except that prior to depositing Si_3N_4 onto the copper wire of the dual damascene structures, the surfaces were treated utilizing different techniques including no treatment (CE1); treatment in an oxidizing plasma gas ambient (CE2); or treatment in a reducing plasma in accordance with the method of the present invention. After treatment, Si_3N_4 deposition, intermetal deposition and dual damascene copper wire/via fabrication each structure was optically examined for delamination. The results of these experiments are summarized in Table 1 below wherein substantially little or no delamination is reported as good, i.e. the adhesion was improved, and the term "poor" denotes substantially no adhesion. It was also observed that the copper surfaces became more reflective as the nitride adhesion improved.

The above results clearly illustrate that improved adhesion of Si_3N_4 barrier layer to copper can be obtained by utilizing the reducing plasma exposure step of the present invention. In comparative examples (CE1 and CE2) adhesion was poor and delamination of the Si_3N_4 deposited film was observed.

Table 1

PreSi_3N_4 treatment	Pressure	rf power (W)	electrodes	Temperature (°C)	Si_3N_4 adhesion as deposited	Si_3N_4 adhesion post-CMP	434 nm reflectivity
None (CE1)	-	-	-	-	poor	poor	0.50
PECVD NH_3	5 Torr	300	1 cm parallel plate	250	good	marginal to good	0.58
PECVD NH_3	5 Torr	300	1 cm parallel plate	400	good	marginal to good	0.58
PECVD N_2	5 Torr	300	1 cm parallel plate	250	good	poor	not measured
PECVD N_2O+N_2 (1:1) (CE2)	5 Torr	300	1 cm parallel plate	250	poor	poor	not measured
HDPCVD N_2+H_2	5 mTorr	2000	inductively coupled	375	good	good	0.55
HDPCVD H_2	5 mTorr	2000	inductively coupled	375	good	good	0.63
HDPCVD N_2	5 mTorr	2000	inductively coupled	375	good	good	0.59

HDPCVD NH_3	5 mTorr	2000	inductively coupled	375	good	poor	0.53

While this invention has been particularly shown and described with respect to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made without departing from the spirit and scope of the present invention.

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CLAIMS

Having thus described our invention what we claim as new and desire to secure by the Letters Patent is:

1. A method of facilitating the adhesion of an inorganic barrier film formed on a copper interconnect structure, said method comprising the steps of:

(a) exposing an interconnect semiconductor structure containing at least a layer of copper to a reducing plasma; and

(b) forming an inorganic barrier film on said exposed copper interconnect structure

2. The method of Claim 1 wherein said exposure step is carried out in a non-oxidizing plasma ambient selected from the group consisting of H_2, N_2, NH_3, noble gases and mixtures thereof.

3. The method of Claim 2 wherein said non-oxidizing plasma ambient is H_2.

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4. The method of Claim 2 wherein said non-oxidizing plasma ambient is NH_3.

5. The method of Claim 1 wherein said exposure step is carried out at a temperature of from about 20° to about 600°C for a time period of from about 1 to about 3600 seconds or higher.

6. The method of Claim 5 wherein said exposure step is carried out at a temperature of from about 360° to about 400°C for a time period of from about 5 to about 30 seconds.

7. The method of Claim 1 wherein said exposure step is conducted at a pressure of from about 1 mTorr to about 20 Torr, a power of from about 50 to about 10,000 watts, and a gas flow rate of from about 1 to about 10,000 sccm.

8. The method of Claim 1 wherein said exposure step is carried out by high density plasma chemical vapor deposition at a pressure of from about 3 to about 6 mTorr, a power of from about 1500 to about 3000 watts, and a gas flow rate of from about 10 to about 50 sccm.

9. The method of Claim 1 wherein said exposure step is carried out by plasma enhanced chemical vapor deposition at a pressure of from about 2 to about 8 Torr, a power of from about 150 to 400 watts and a gas flow rate of from about 100 to about 2000 sccm.

10. The method of Claim 1 wherein said copper interconnect structure is a capacitor structure, a damascene structure or multiple wiring levels containing a plurality of vias and metal lines.

11. The method of Claim 10 wherein said copper interconnect structure is a single or dual damascene structure containing copper lines and vias.

12. The method of Claim 1 wherein said inorganic barrier film is formed in-situ utilizing a deposition process selected from the group consisting of chemical vapor deposition, low pressure chemical vapor deposition, plasma enhanced chemical vapor deposition and high density plasma chemical vapor deposition.

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13. The method of Claim 12 wherein said inorganic barrier film is formed in-situ by plasma enhanced chemical vapor deposition or high density plasma chemical vapor deposition.

14. The method of Claim 1 wherein said inorganic barrier film is composed of Si_3N_4, SiC, hydrogenated Si_3N_4 or hydrogenated SiC.

15. The method of Claim 14 wherein said inorganic barrier film is hydrogenated Si_3N_4 or hydrogenated SiC.

16. The method of Claim 1 wherein said interconnect structure includes a dielectric material selected from the group consisting of SiO_2, fluorinated SiO_2, Si_3N_4, polyimides, diamond, diamond-like carbon, silicon polymers, paralyne polymers and fluorinated diamond-like carbon.

17. The method of Claim 16 wherein said dielectric material is SiO_2.

18. The method of Claim 1 wherein said layer of Cu is formed inside a trench.