Tungsten Nitride Deposition by Thermal Chemical Vapor Deposition as Barrier Metal for Cu Interconnection

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A CVD-WN film is deposited as a barrier metal for copper interconnection using thermal CVD (Chemical Vapor Deposition) of WF₆/NH₃/SiH₄ gases. Deposition of CVD-WN film with a resistivity of less than 300 μΩ·cm at a temperature of 400°C or less has been realized for the first time in the world. The deposited WN film is proved to be excellent in barrier properties and able to prevent Cu diffusion even with the film thickness of 6 nm as well. It is also proved that the CVD film is superior to a sputtered barrier metal in coverage and ECD (Electro-chemical deposition) filling properties. XPS analysis showed that adhesion of the CVD film to low-k materials is deteriorated by the existence of F at the interface between the WN film and low-k. Chemical surface pretreatment for low-k materials proves to restrain the pile-up of F at the interface and improve adhesion.

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1. Introduction

Sputtered metal films are generally used as a barrier metal for Cu interconnection nowadays. However, it is pointed out that with rapid shrinkage of devices, sputtered films have a limit because they are short of sidewall coverage in a hole, resulting in insufficient filling properties by electrochemical plating. As a matter of course, a CVD barrier metal is expected to take their places because it is superior in step coverage. In fact, TiN-CVD film using TiCl₄ and MO (Metal-organic) precursor has been used as the barrier metal of W-CVD in mass production line. However, it is also true that there is no CVD film existing as the barrier metal for Cu interconnection that replaces sputtered films in performance. Though TiN, TiSiN, WN, WSiN and TaN films have been developed as CVD barrier metals so far, a film that meets all of resistivity, barrier properties and adhesion has not been achieved yet.

As for a CVD film, especially the materials containing Ti or Ta, since the source material is metal organic compound, impurities such as carbon is contained in a deposited film. This makes it difficult to reduce resistivity and achieve adhesion to the insulator. Also, traditionally, a W film, whose main source material is WF₆, is deposited by thermal CVD or plasma CVD. However, in the former, resistivity is high and in the latter, though resistivity is reduced, coverage is poor and the tremendous particle is produced due to plasma reaction, which is a long way to realization of a best film.

When it comes to consider what material is promising as a CVD barrier layer, the material containing W has some advantages as follows:

- Gases that have been used so far for mass production, such as WF₆ and NH₃ are usable as materials and this makes cost low.
- Since a WN film itself does not react with Cu and is superior in barrier properties.
- In CMP (Chemical Mechanical Polish) process, the WN film can be etched by a Cu slurry in one step, unlike Ta materials. As a result, running cost in mass production is largely reduced.

We have developed WN film deposition technology taking the following points into consideration:

- Since plasma CVD-WN film, as mentioned above, has disadvantages of poor coverage and lots of particles produced, thermal CVD should be used.
- Considering low-k dielectric films, deposition temperature is limited to 400°C or below.
- As a film deposited by conventional thermal CVD has high resistivity, thermal CVD which can reduce the resistivity should be developed.

Consequently, the use of source gases of WF₆/NH₃/SiH₄ has achieved success in deposition of WN film with a resistivity of less than 300 μΩ·cm at a deposition temperature of 385°C for the first time in the world. This paper will report on this deposition technology, film properties, filling properties by electrochemical plating and so on.

2. Experimental

The source gases used are WF₆, NH₃, SiH₄ and Ar. Figure 1 illustrates a cross section of the CVD chamber that was used. WF₆/Ar and SiH₄ are introduced through separate shower nozzles on the top of the deposition chamber. NH₃ is introduced through ring nozzle placed near the wafer stage. This is because mixing WF₆ and NH₃ is liable to produce powder like a complex and therefore, these gases are separated as much as possible to restrain the production of particles. Wafer temperature is 385°C and deposition pressure is 40 Pa. The deposition rate at this time is about 40 nm/min.

In order to prevent WF₆ from aggregating on the walls of the chamber, the entire chamber is heated at a temperature of 70°C. The film deposited on the parts in the chamber was cleaned up by using a plasma of F₂ gas.

LTS (Long Throw Sputter) Cu is used for a Cu seed layer to evaluate filling by means of electrochemical plating. The WN-CVD chamber and LTS Cu chamber are incorporated in
a system (ULVAC CERIUS Zi-1000N) that is capable of in-line processing, together with a pretreatment chamber which is used prior to WN film deposition and these processes are all done in a vacuum.

3. Result

3.1 WN film of “WF_6 + NH_3” system

Figure 2 shows the resistivity of a WN film deposited by using WF_6 and NH_3 alone. It represents the dependence on the deposition temperature. The resistivity shows a minimum value at about 350°C, which is about 3000 µΩ·cm. Even if other process parameters such as flow rate and pressure are changed, resistivity is not very largely reduced though it shows a slight change and the value is an order of 1000 µΩ·cm. The XRD spectrum and AES spectrum of the WN film deposited in this way are shown in Figs. 3(a) and (b), respectively. The result of XRD shows that a deposited WN film has the crystallinity of W_2N and that of AES also proves that the W/N ratio is about 2.0. It is clear from these two results that in the source gas using WF_6 and NH_3, no matter how much deposition parameters may be changed, W/N ratio is only 2.0 when a crystal film with minimal resistivity is deposited. The relation between W/N composition ratio and resistivity as to a sputtered WN film is shown in Fig. 4. Increasing N_2 in sputtering conditions forms a N-rich film and this suggests that a W-rich film must be formed to obtain a low-resistivity film. Especially, the W/N ratio must be above 4.0 in order to form a film of 300 µΩ·cm or less. This means that a W-rich composition has to be required to realize a low-resistivity film even in the CVD film.

3.2 Effect of adding SiH_4

As mentioned above, in a thermal equilibrium condition using WF_6 and NH_3, it is impossible to deposit a film whose W/N ratio is above 2.0. Generally, it is known that a W film is deposited by reducing WF_6 with SiH_4 in W-CVD process, and it is expected that the reactions that produce W_2N and W compete each other by adding SiH_4 to the source gas of WF_6 and NH_3, resulting in deposition of a W-rich film. Figure 5 shows the change of resistivity with addition of SiH_4 to WF_6 and NH_3. Obviously, adding SiH_4 reduces resistivity. Figure 5 also shows the W/N ratio measured by AES together, in which as the resistivity decreases, the W/N ratio increases. The XRD spectrum of these films is shown in Fig. 6. When the W/N ratio is as small as 2.8, a film with the texture of W_2N is deposited. However, as the W/N ratio becomes larger, the crystallinity is deteriorated and an amorphous-like film appears. This result shows quite the same behavior as with the sputtered film shown in Fig. 4. It is clear that the W/N ratio must be increased to reduce resistivity and the crystallinity is broken as the W/N ratio becomes larger.

Figure 7 shows the dependence of sheet resistance on deposition temperature in the source gas added with SiH_4. When deposition temperature becomes below 370°C, sheet resistance increases rapidly. Figure 8 shows the dependence of sheet resistance on NH_3 flow rate. As NH_3 increases, the sheet resistance increases. This shows that reactions between WF_6 and NH_3 and between WF_6 and SiH_4 are competing. Especially, sheet resistance decreases with the rise of de-
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3.3 Step coverage of WN film

Figure 9 shows the step coverage of a WN film. As aspect ratio (A/R) becomes higher, step coverage is deteriorated. However, when A/R is 6.0, about 60% of step coverage is obtained, which does not practically impose any problem. Step coverage, not added with SiH₄, is achieved nearly 100%. This suggests that though WF₆ and NH₃ adsorbing on the substrate react into surface reaction mode in the source gas of WF₆ and NH₃, adding SiH₄ induces gas phase reaction mode, leading to deterioration of step coverage.

According to the calculation by means of the molecular orbital method, the following reactions are supposed to occur first in the source gas of WF₆/NH₃/SiH₄:

\[ \text{WF}_6 + \text{NH}_3 \rightarrow \text{WF}_5 \text{NH}_2 + \text{HF} \]  \hspace{1cm} (1)

\[ \text{WF}_6 + \text{SiH}_4 \rightarrow \text{WHF}_5 + \text{SiHF}_3 \]  \hspace{1cm} (2)

WHF₅ produced in formula (2) reacts like WHF₅ + WHF₅ \rightarrow F₂ + W + WF₅ + H₂ and produces W–W bonding, while WF₅ (NH₂) produced in formula (1) does not react easily like...
WF₅(NH₂) + WF₅(NH₂) → F₅W–NH–WF₅ + NH₃ and does not produce W–N–W bonding from such a gas phase reaction. W–N–W bonding is rather possibly produced on the substrate surface, which implies that the source gas of WF₆ and NH₃ alone produces a WN film excellent in step coverage. On the other hand, as temperature rises higher, the gas phase reaction in formula (2) is more promoted to produce W–W bonding, leading to deterioration of step coverage.

### 3.4 Barrier properties of WN film
One of measures to determine if barrier layer performance is good or bad depends on barrier properties against Cu diffusion into the insulator. Barrier properties are evaluated as...
shown in Fig. 10. First, a WN film is deposited on patterned amorphous Si(a-Si) trench and then Cu is sputtered on it. Then it is annealed in a vacuum at a temperature of 450°C for 4 h. If the barrier layer does not have barrier properties, Cu is diffused in the barrier layer and reacts with Si to produce CuSi.3) It is found in our experiment that the silicidation reaction of Cu with Si is almost saturated during the annealing for 2 h at 450°C. Therefore, the annealing condition for 4 h at 450°C which is the same as the 2 h annealing was adopted as the evaluation condition of the barrier performance.

Figure 11 shows TEM images of cross section of trench patterns after being annealed. The result of CVD-TiN film being used as a barrier layer is also shown for the reference. It is found that since CVD-TiN film has no barrier properties, Cu and Si react to produce CuSi. (black mass). On the contrary, in CVD-WN film of even 6 nm, Cu and Si do not react and a-Si remains as it is.

Figure 12 shows how barrier properties change with respect to the W/N composition ratio of CVD-WN film. The photos are taken from the above of trench patterns shown in Fig. 11 by an optical microscope. The area that looks black is where barrier properties are broken and CuSi is produced. When the W/N ratio is as small as 2.3, the degree of barrier breakage is weak but observed on the entire surface of the wafer. As the W/N ratio is larger, barrier properties are more improved and
a film whose W/N ratio is 5.1 does not see any barrier breakage. However, when the W/N ratio is further increased up to 6.4, the breakage comes to be partly observed on the entire wafer. This result shows that the resistivity can be reduced by adding SiH$_4$, but too much W-rich film will deteriorate barrier properties in CVD-WN film.

3.5 Adhesion

Whether CVD barrier metals can be practically used in mass production or not depends on the presence or absence of adhesion to dielectric films, especially low-k materials. It is important how adhesion of CVD barrier metal film can be achieved to various low-k materials. The simplest way to evaluate adhesion is to scratch the surface of a wafer and to check the peeling of the barrier film from a dielectric film with a stick tape. Figure 13 shows the illustration of the evaluation method. After depositing a WN film on dielectric films, Cu is sputtered on a WN film with 500 nm thickness. Then, it is scratched with a diamond cutter to make a tape check test. 9 areas on the entire wafer surface are checked. No peeling at any point is marked as a score of 4 and peeling at all points as a score of zero. If no point is peeled, it amounts to a score of 36 (= 9 x 4) and if all points are peeled, it amounts to a score of zero. The reason that Cu is sputtered to 500 nm is based on the proof that compared to deposition of a plating film of 1 µm, it achieves nearly the same result. Also, it is proved that a film which has got a score of 36 in this test does not peel even if a plating film of 1 µm is deposited and then CMP process is done. This test method evaluates adhesion with ease without plating or CMP processing.

Figure 14 shows the result of adhesion measured in this way. The dielectric layer is of Si-contained low-k material. Adhesion comparison is made between a dielectric film for which no surface pretreatment is done, a dielectric film which is etched by Ar sputtering and a dielectric film for which chemical gas (NH chemical) plasma treatment is done. In the case of the dielectric film with no surface pretreatment
prior to WN film deposition, WN film proves to have no adhesion to the dielectric film. The dielectric film with Ar plasma treatment improves adhesion, though not completely achieved, compared to the no treated one. Further, in the case of the dielectric film with chemical plasma treatment, WN shows perfect adhesion to the dielectric film without peeling.

To investigate this cause, the interface between the dielectric film and the WN film is examined by XPS, which is shown in Fig. 15. It is checked if there is any difference in bonding condition near the interface, focusing on Si, O, N and F. As a result, [Si 2p] and [N 1s] do not show any difference between surface pretreatments of the dielectric film, while F is largely piled up at the interface between the low-k film and the WN film in case that surface pretreatment is not done. Ar plasma treatment reduces the pile-up of F a little and chemical plasma pretreatment reduces the F concentration to almost the detectable level or below. For [O 1s], W–O bonding is shown in both Ar plasma and the chemical treatments. It is inferred that in case of no surface pretreatment, F produced from WF₆ bonds to dielectric film on the surface to produce SiF or OF bonding, while in cases of Ar sputter and chemical plasma treatments being done, the dangling bond
may be formed on the dielectric surface, leading to the formation of W–O bond. In addition, in the case of the chemical treatment, the surface of the dielectric film may be terminated with N and H and fails to bond to F. It seems critical to improve the surface of low-k materials so that F does not remain on the surface as much as possible to improve adhesion of CVD-WN film.

3.6 Filling properties by plating

One of advantages of a CVD barrier metal is to be superior to a sputtered barrier metal in filling properties by plating. Figure 16 shows SEM photos, in which a CVD-WN film of 10 nm is deposited and then LTS-Cu film of 80 nm and 120 nm are deposited over it, followed by the electrochemical plating. The hole is 0.18 µm in diameter and 1.0 µm deep. At 80 nm Cu seed layer, the film thickness of the side wall is short and a void is observed near the hole bottom, while complete filling is observed at 120 nm Cu seed layer. Normally, the use of sputtered barrier metals can not achieve such a perfect filling. It is clear that conformal deposition of CVD film largely extends the margin of filling by plating.

4. Conclusion

The use of thermal CVD of WF<sub>6</sub>/NH<sub>3</sub>/SiH<sub>4</sub> system has achieved success in deposition of CVD-WN film with a resistivity of less than 300 µΩ·cm at a temperature of 400°C or less. It is proved that adding SiH<sub>4</sub> reduces the resistivity and changes the crystal structure to amorphous. Such a film is superior in barrier properties and able to prevent Cu diffusion even if film thickness is about 6 nm. Adhesion of CVD barrier metal layers to dielectric films is the most critical element in Cu interconnection. The W/N film has no adhesion to a dielectric film for which no surface pretreatment is done. However, doing surface treatment for dielectric films achieves such adhesion that no peeling occurs even in CMP processes. It is inferred that the chemical treatment to the dielectric film prevents the element such as F, which deteriorate adhesion, from bonding to the interface.

It is found that CVD barrier layers, because of having conformal coverage, are considerably improved in filling performance by plating, compared to the use of sputtered barrier metals.

Evaluation of electric characteristics of Cu interconnection using CVD barrier metals is now going on. From the fact that CVD barrier metal layers have interconnection resistance reduced compared to sputtered films, a conformal thin CVD film has a great advantage for future Cu interconnection.

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REFERENCES