The novel precleaning treatment for selective tungsten chemical vapor deposition

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Abstract

The new solutions, hydroxylamine sulfate $[(NH_2OH)_2H_2SO_4]$ combined with $CuSO_4$, for cleaning Al via were investigated. It is found that the cleaning capability of hydroxylamine sulfate combined with $CuSO_4$ is better than that of hydroxylamine sulfate. Low via resistance of electrical test structure is obtained if the via is cleaned by this new cleaning solution. The hydroxylamine sulfate can efficiently remove Al_3O_2 and leave the clean Al on the surface of via. Then, the Cu ion in this new solution will immediately react with clean Al and form a copper passivating layer on the surface of via. The copper is more stable than aluminum in the environment and hard to be oxidized. Therefore, hydroxylamine sulfate combined with $CuSO_4$ can provide excellent cleaning capability for aluminum via holes. Also, the clean surface on the bottom of via is helpful for tungsten nucleation in via during CVD-W deposition. Therefore, a low via resistance and good selectivity of tungsten plug are obtained when the Al via is precleaned with this new solution. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In ultralarge scale integration (ULSI) technology, the multilevel interconnection is a key process. It is difficult to clean the bottom of via holes in the multilevel interconnection. If the bottom is not very clean, the performance and yield of IC will be degraded. Selective tungsten chemical vapor deposition (CVD-W) is one of the most attractive techniques for filling deep submicron via holes for ULSI applications [1–3]. Control of the deposition selectivity is essential for the successful selective CVD-W. The deposition selectivity of CVD-W is very sensitive to the condition of the via hole bottoms. If the bottoms are not clean, the local loss of selectivity called 'creep-up' [4] will occur during the subsequent selective CVD-W. Creep-up is a phenomenon where tungsten growth starts not only from the bottoms but also from the sidewalls of via holes. Conventionally, the in-situ plasma sputtering [5–7] and reactive ion etching (RIE) have been employed extensively to remove the native metal oxide prior to tungsten deposition. During the plasma etching, however, the outsputtered aluminum oxide and aluminum atoms can redeposit on the sidewalls of via and on the surface of dielectric layer, where

tungsten nucleation is induced, resulting in creep-up and selectivity loss during the subsequent selective CVD-W. In this work, we developed a simple and efficient precleaning solution, hydroxylamine sulfate $((NH_2OH)_2H_2SO_4)$ mixed with $CuSO_4$, to remove Al native oxide in the Al via. Electrical characterization measurements have been performed to evaluate the effect of this solution.

2. Experimental

Aluminum alloy (Al–0.5%Cu) and antireflection layer (ARL) of TiN were sputter-deposited sequentially on thermally oxidized silicon wafer. The sample with TiN/AlCu bilayer was patterned by Cl_2/BCl_3-based RIE and subsequently covered with a dielectric layer of 1000 nm PECVD oxide. Via holes were patterned using the conventional photolithographic and dry etching technique.

Prior to the deposition of selective CVD-W, the wafers were treated with various precleaning processes for removing the metal oxide on the bottoms of Al via. In this experiment, four types of samples were prepared. Sample A was treated with in-situ BCl_3 plasma precleaning in the CVD system. In this work, the predeposition plasma cleaning was conducted with a RF power of around 50 W, a BCl_3 flow-rate of 100 sccm, and a chamber pressure of 6 mTorr. A post plasma-etching annealing at 370°C for 180 s was

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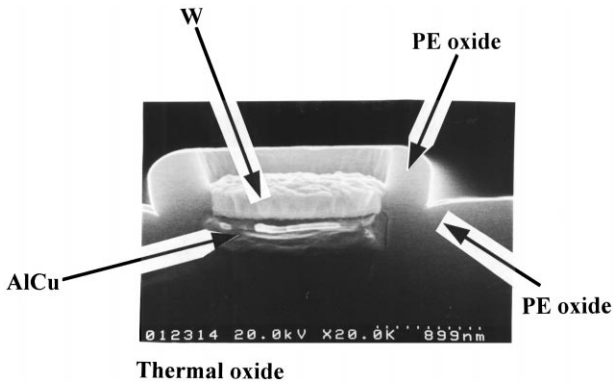*E-mail address:* tcchang@hdl.gov.tw (T.C. Chang)

Fig. 1. SEM cross-section images of W deposition in via holes.

performed to eliminate such by-products as $AlCl_3$ from the aluminum surface. The wafers were then transferred from the plasma-etching chamber to the deposition chamber without exposing to atmosphere. The base pressure of the CVD chamber was 10^{-6} Torr.

Sample B was dipped in diluted solution of hydroxylamine sulfate with a concentration of 0.1 M for 1 min at a temperature of 50°C.

Sample C was treated with two-step cleaning. First, the wafers were dipped in diluted solution of hydroxylamine

sulfate with a concentration of 0.1 M for 1 min at a temperature of 50°C. Secondly, the wafers were sequentially dipped in 0.1 M $CuSO_4$ solution for 1 min at 60°C.

Sample D was dipped in mixed solution of 0.1 M hydroxylamine sulfate and 0.1 M $CuSO_4$ for 1 min at a temperature of 50°C. Then, samples B, C and D were sequentially loaded to the load-lock cold-wall CVD-W system within 5 min and selective CVD-W was deposited. In this work, the typical process conditions for the selective CVD-W were as follows: substrate temperature 300°C, total gas pressure 100 mTorr, WF_6 flow-rate 20 sccm, SiH_4 flow-rate 6 sccm, H_2 carrier gas flow-rate 1000 sccm, and growth time 150 s.

The cross-section images of the W-plugs were obtained with a scanning electron microscope (SEM) as shown in Fig. 1. After the selective tungsten plug deposition, metal II(Ti/TiN/AlCu/TiN) were deposited on the substrate to a thickness of 900 nm. Then, all samples were patterned by RIE to obtain the upper metal strips for the electrode of electrical measurement. The cross-section of the via structure was shown in Fig. 2. Finally, via resistance of AlCu/W/AlCu structure was measured by the four-terminal Kelvin structure as shown in Fig. 3.
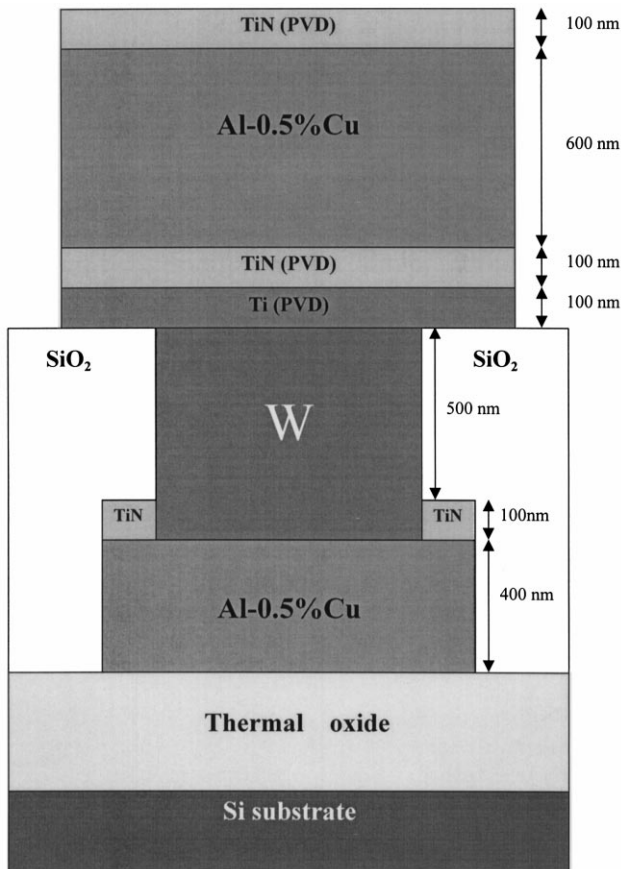

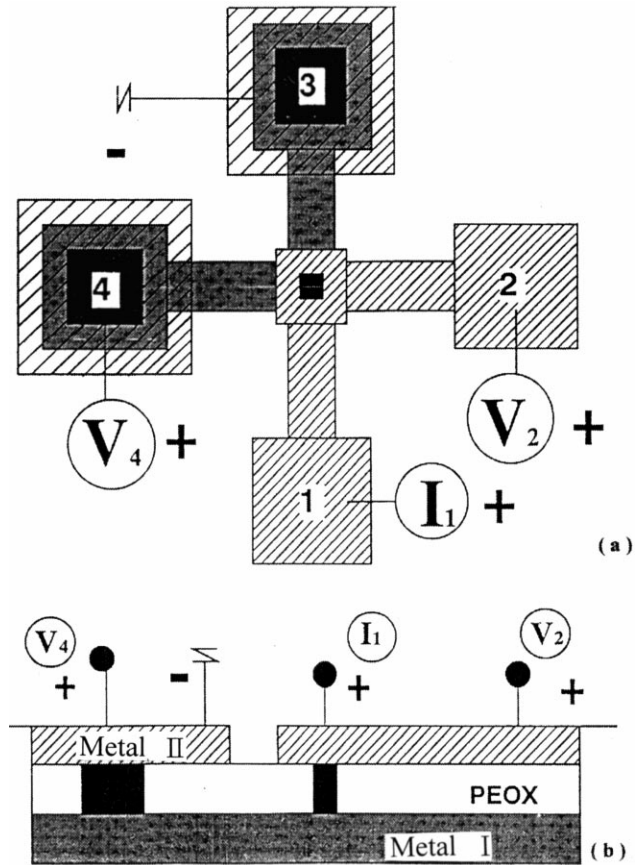Fig. 2. Cross-section diagram of AlCu/W/AlCu via hole.

Fig. 3. The structure of 'four-terminal Kelvin structure'. (a) Top view; (b) Cross-section.

3. Results and discussion

Fig. 4 shows the SEM cross-section images of W deposition in Al via holes with various precleanings. In Fig. 4a, there were only a little tungsten islands deposited in the Al via when the Al via was only precleaned by the deionized water (DI water) rinse. It is shown that tungsten can not be easily deposited on the Al via because aluminum oxide on the surface blocks the nucleation of tungsten. With BCl_3 plasma etching for 60 s, creep-up and selectivity loss of CVD-W deposition was observed, as shown in Fig. 4b. The result is thought to be due to outsputtered aluminum oxide and aluminum atoms induced tungsten nucleation on the sidewall of via and the surface of the dielectric layer. However, the selectivity of CVD-W can be significantly improved by cleaning the via in a hydroxylamine sulfate solution, as shown in Fig. 4c.

For the electrical characterization, via resistance of AlCu/W/AlCu was measured using a four-terminal Kelvin structure. Fig. 5 shows the measured specific via resistance of
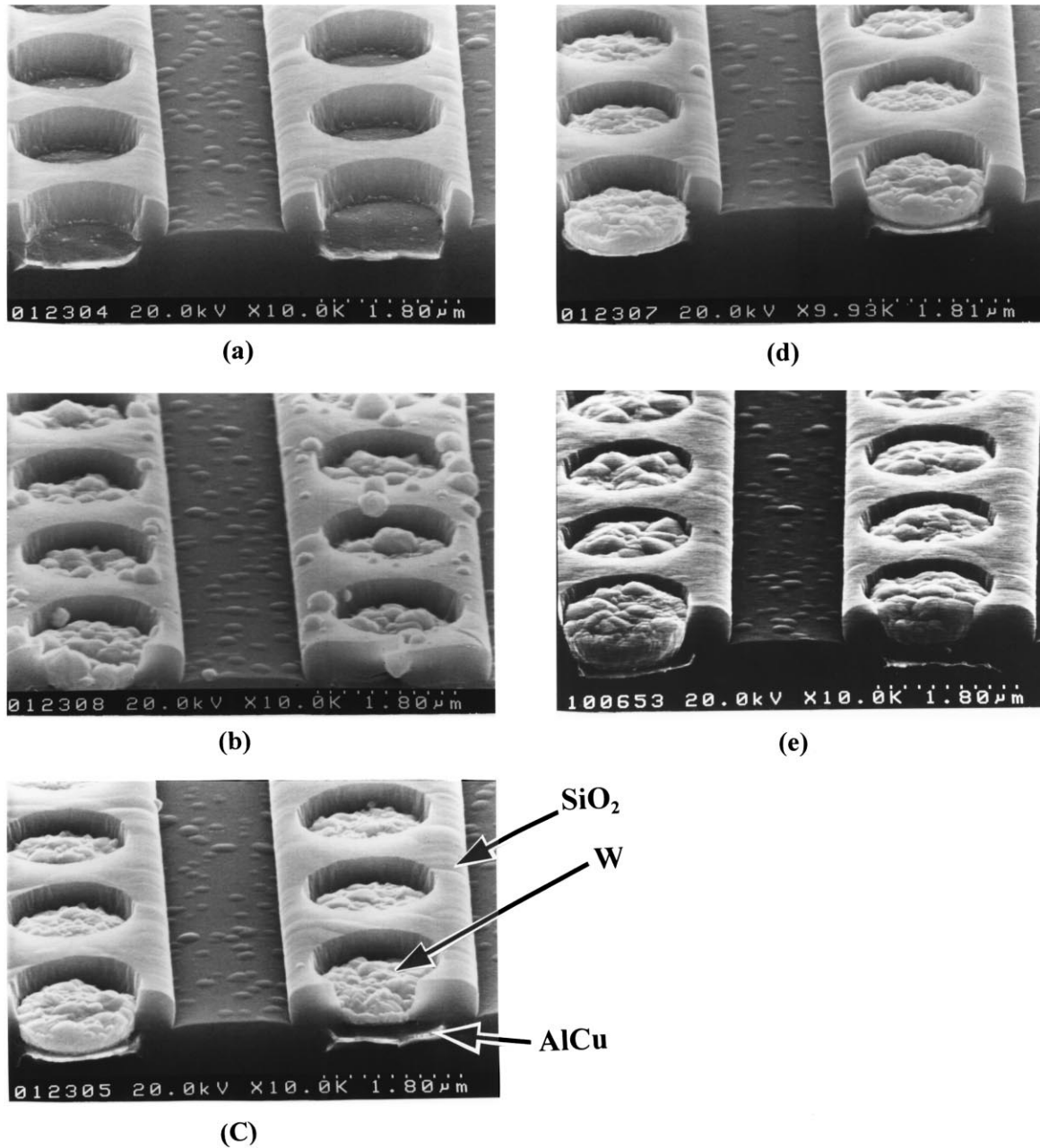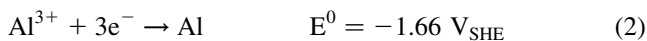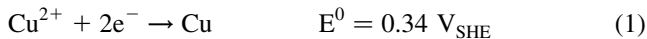

Fig. 4. SEM cross-section images of W deposition in via holes with the various precleanings. (a) Deionized water rinse, (No W deposition); (b) sample A with 50W BCl_3 plasma etching,(loss of CVD-W selectivity); (c) sample B with diluted hydroxylamine sulfate wet etching,(good selectivity); (d) sample C was treated with two-step cleaning (good selectivity); (e) sample D with dipped in mixed solution of 0.1 M hydroxylamine sulfate and 0.1 M $CuSO_4$ for 1 min at 50°C (good selectivity, optima condition).

samples A–E. Compared with the sample only pre-cleaned by DI water, the specific via resistances of sample A and sample B are much lower than that of DI water pre-cleaned sample. The specific via resistances for the sample B is slightly higher than that of sample A. It is presumably due to the reoxidation of the aluminum surface during the short period of time when sample B was exposed to the ambient air before loading into the tungsten deposition chamber. To resolve this issue, we developed the new cleaning solution, hydroxylamine sulfate $[(NH_2OH)_2H_2SO_4]$ combined with $CuSO_4$. Hydroxylamine sulfate is capable of dissolving aluminum oxide (Al_2O_3) and leave the fresh Al surface on the bottom of via. A previous paper has demonstrated the clean effect of hydroxylamine sulfate on Al via [8]. Consequently, the native aluminum oxide can be completely removed and fresh underlying aluminum would be exposed. The copper ion contributed from $CuSO_4$ will react with clean aluminum and then form a very thin elemental copper layer on the bottoms of via according to the following reactions [9].

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^0 = 0.34 \ V_{SHE} \qquad (1)$$

$$Al^{3+} + 3e^- \rightarrow Al \qquad E^0 = -1.66 \ V_{SHE} \qquad (2)$$

where E^0 is the half-cell reduction potential in volts with respect to the standard hydrogen electrode (V_{SHE}). Combining Eqs. (1) and (2) to complete the full redox reaction, as follows

$$3Cu^{2+} + 2Al \rightarrow 3Cu + 2Al^{3+} \qquad \Delta E^0 = 2.0 \ V \quad (3)$$
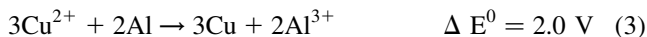
where the reaction is expected to be spontaneous owing to its negative free energy. Finally, a DI water rinse is necessary for removing the by-products of this redox reaction.

To observe the SEM cross-section images of samples B and C, good selectivity of CVD-W could be obtained. It is shown in Fig. 4c,d. In addition, the specific via resistance of sample C is slightly lower than those of samples A and B. It is presumed that little copper ions reacted with partial area of clean aluminum surface to form a very thin elemental copper layer on the parts of bottom of via. So the specific via resistance of sample C is slightly lower then samples A and B.

The two-step cleaning process is as follows: Step I: the wafers were dipped in 0.1 M diluted solution of hydroxylamine sulfate for 1 min at 50°C. Step II: the wafers were sequentially dipped in 0.1 M $CuSO_4$ solution for 1 min at 60°C. It is found that Al_2O_3 could be removed by hydroxylamine sulfate. During the short period of transferring from step I to step II, however, sample C was exposed to the ambient air. Slight reoxidation of the aluminum surface would be still occurred before copper layer passivation. This induces that the via resistance of sample C is not much lower than that of sample B.

Hydroxylamine sulfate mixed with $CuSO_4$ could be used to reduce the chance of fresh aluminum surface exposed to the ambient air. Once Al_2O_3 was removed by hydroxyla-

mine sulfate, the copper ions would immediately react with clean aluminum and then form a very thin elemental copper layer on the bottoms of via. This copper layer would prevent the fresh aluminum surface from reoxidation.

Fig. 4d,e shows the SEM cross-section images of samples C and D at 50°C precleaning temperature. In our experiment, it is found that 50°C precleaning temperature is the optimum condition. From Fig. 4d,e, the image of W deposition in Al via of sample D is smoother than that of sample C and good selectivity of tungsten plug is obtained also. In addition, the via resistance of sample D is the minimum one, as shown in Fig. 5. The reason is that copper can passivate the clean Al surface as well as copper is more stable and harder to be oxidized than aluminum as exposed in the environment. Therefore, a low via resistance and good selectivity of tungsten plug is obtained when the Al via is precleaned with this new cleaning solution.

4. Conclusions

In this work, the effects of a new precleaning solution were investigated. For conventional precleaning BCl_3-based plasma-etches, it is found that creep-up and selectivity loss resulted from the outsputtered aluminum oxide and/or aluminum atoms redeposited on the sidewall of via as well as on the surface of the SiO_2. However, excellent selective CVD-W can be obtained by using the hydroxylamine sulfate mixed with $CuSO_4$ to clean the Al via holes. This precleaning solution not only removes the metal oxide at the bottom of aluminum via, but also in-situ forms a very thin copper passivation layer on the Al surface to prevent aluminum surface reoxidation during the time of loading into the W deposition chamber. A low via resistance and good selec-
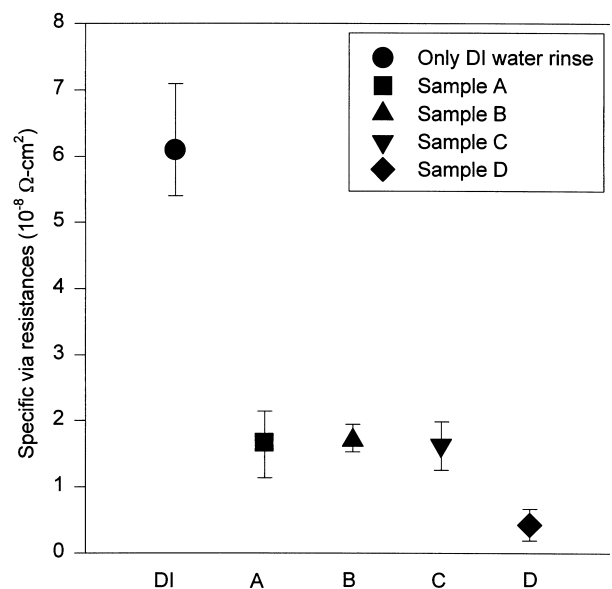
Fig. 5. The specific via resistances of samples A–D, respectively, as compared with the sample only pre-cleaned by DI water.

tivity of tungsten plug can be obtained as the via is cleaned by this new solution. Thus, signal propagation time delay can be significantly reduced due to the low via resistance. Therefore, high performance in electrical characteristics can be achieved.

Acknowledgements

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