

## Suppression of Al/W Reaction in Al/W Layered Interconnects by W Surface Treatment before Al Deposition

Yusuke Harada, Yuhki Itoh, and Hiroshi Onoda

VLSI Research and Development Center, OKI Electric Industry Co., Ltd.  
550-1, Higashi-asakawa, Hachioji, Tokyo 193, Japan

The effect of W surface treatment on suppression of Al/W reaction in Al/W layered structure has been studied. CVD-W film and sputtered Al film were deposited using cluster system without air exposure. Before Al deposition, silane (SiH<sub>4</sub>) gas was introduced onto the W film in the same reactor. After 500°C annealing for 90 min, Al/W reaction of sample with the SiH<sub>4</sub> treatment was greatly suppressed compared with that of the sample without the SiH<sub>4</sub> treatment. The W surface analysis indicates that W surface has adsorbed Si and/or SiF<sub>x</sub> due to the SiH<sub>4</sub> treatment. Adsorbed Si and/or SiF<sub>x</sub> on the W films are expected to retard Al/W reaction during annealing.

### I. Introduction

As dimension of LSI has shrunk, the aspect ratio (defined as the ratio of depth to diameter) of contact holes has increased. Recently, the blanket tungsten (W) Chemical Vapor Deposition (CVD) method has been applied to not only contact plug but also interconnects because low-pressure (LP) CVD method has better step coverage than the conventional sputtering method<sup>1,2</sup>. In addition, blanket CVD-W films have been used for VLSI's interconnects because of high reliability<sup>3</sup>. However, when the widths of interconnects are narrower, the resistance of the W interconnect is too high for high speed LSI to be used. Aluminum(Al)/CVD-W layered interconnect is one of attractive choices for future structure due to low resistance and high reliability. However, reaction between Al and W, which occurs during annealing processes, results in the resistance increase. In this study, suppression of Al/W reaction by W surface treatment has been investigated using the cluster system which combines sputtering and CVD processes. This system made it possible to obtain a precise control at the surface and interface of layered films. Al/W reaction was successfully suppressed by W surface treatment before Al deposition in the same vacuum of the cluster system.

### II. Experimental

In this experiment, a TiN/BPSG/Si structure was employed as the substrate using 6 inch Si wafer. The TiN film is used as an adhesion layer for the blanket CVD-W film. The CVD-W (250 nm) films were deposited on the samples by hydrogen (H<sub>2</sub>) reduction of tungsten hexafluoride (WF<sub>6</sub>) using a cold-wall, single-wafer, LPCVD chamber equipped with a load-lock and an Al sputtering module. Deposition condition was used in the region of WF<sub>6</sub> surface reaction to obtain good step

coverage for WCVD. After the W deposition, the silane (SiH<sub>4</sub>) gas was introduced onto the W film in the same chamber. Partial pressure of SiH<sub>4</sub> was 26 mtorr. We will abbreviate this to "SiH<sub>4</sub> treatment" here. The SiH<sub>4</sub> treatment time varied from 0 to 90 sec. Then, the AlSiCu(300 nm) film was deposited on the W film using DC magnetron sputtering without air exposure. After Al/W/TiN/BPSG/Si structures were formed, the samples were annealed in a nitrogen gas ambient at 500°C. The sheet resistance of Al/W layered structure was then measured by four-point probe method. The Al/W interdiffusion was analyzed by Rutherford backscattering spectrometry (RBS) using 1.5MeV He ions. The W surface was evaluated by X-ray photoelectron spectroscopy (XPS).

### III. Results and Discussion

Sheet resistance of Al/W/TiN/BPSG structures with and without SiH<sub>4</sub> treatment for 30 sec as a function of 500°C annealing time is shown in Fig.1. Both samples show little change in sheet resistance within 30 min. After annealing for 90 min, however, whereas the sheet resistance of the sample with SiH<sub>4</sub> treatment has a little increase, that of the sample without SiH<sub>4</sub> treatment increases sharply. Figure 2 shows sheet resistance of Al/W/TiN/BPSG structures after 500°C annealing for 90 min as a function of the SiH<sub>4</sub> treatment time. The sheet resistance of the sample without the SiH<sub>4</sub> treatment (0 sec) became higher than that of the other samples. However, sheet resistance of the samples with the SiH<sub>4</sub> treatment did not depend on the SiH<sub>4</sub> treatment time. This result indicates that the SiH<sub>4</sub> treatment for only 10 sec, affects thermal stability on Al/W layered structure. Figure 3 shows the RBS spectra of Al/W/TiN/BPSG structures with and without SiH<sub>4</sub> treatment. The W diffusion into Al occurs in both structures after 500°C annealing. In the sample without SiH<sub>4</sub> treatment, it is evident from

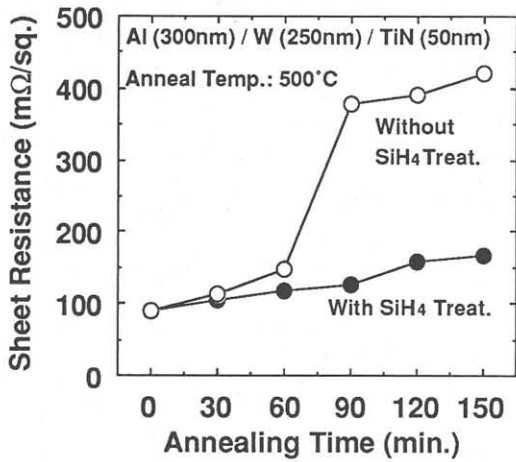


Fig. 1 Sheet resistance of Al/W/TiN/BPSG structures with and without SiH<sub>4</sub> treatment as a function of 500°C annealing time

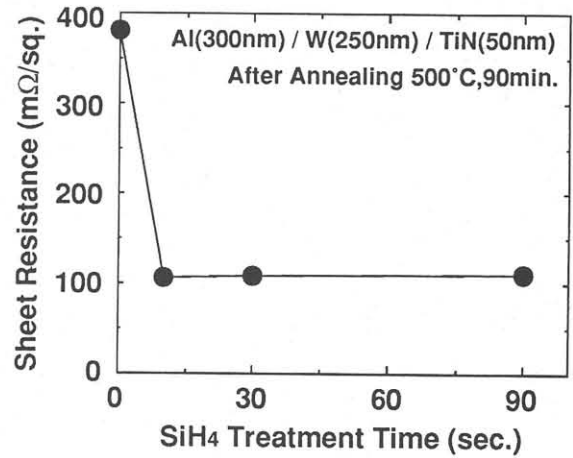


Fig. 2 Sheet resistance of Al/W/TiN/BPSG structures after 500°C annealing for 90 min as a function of SiH<sub>4</sub> treatment time

the leading edge of the W spectrum that W reaches the Al surface after 90 min. Moreover, TiN side of W spectrum is broad because Al surface becomes rough due to Al/W reaction. However, in the sample with SiH<sub>4</sub> treatment, a little amount of W diffuse in Al layer even after annealing for 90 min. Besides, X-ray diffraction measurement indicates that WAl<sub>12</sub> peak intensity of the sample without SiH<sub>4</sub> treatment is higher than that of sample with SiH<sub>4</sub> treatment. As a result, difference of Al/W reaction is found to cause the sheet resistance difference.

The characteristics of the SiH<sub>4</sub> treatment were examined to consider this phenomenon. Figure 4 shows HF signals in the WCVD reactor measured by Q-mass spectrometer as a function of exhaust time after W film deposition. The WCVD process produces lots of reaction by-products such as fluorine species for example WF<sub>x</sub> and HF. In the case using SiH<sub>4</sub> treatment, the HF intensity decreases to background level immediately after starting to exhaust. On the other hand, in the case without SiH<sub>4</sub> treatment, the HF intensity does not reach to background level even after exhaust for 300 sec. Therefore, it is conjectured that almost all fluorine species are removed in the reactor during SiH<sub>4</sub> treatment process. In other word, it seems that the SiH<sub>4</sub> treatment also affects removal of the fluorine species on the CVD-W film.

In order to study change of the W surface during SiH<sub>4</sub> treatment, the CVD-W film surface was evaluated by XPS. Figure 5 shows XPS spectra of the W films with and without SiH<sub>4</sub> treatment. In the case of the sample with SiH<sub>4</sub> treatment, Si-Si, Si-F bonds were observed at CVD-W surface. However, in the case of the sample without SiH<sub>4</sub> treatment, these were not observed. W-F bond peaks were not observed from even the sample without SiH<sub>4</sub> treatment. It is reported that W-F bonds were observed at surface of W film which was exposed to WF<sub>6</sub> by in-situ XPS measurement<sup>4)</sup>. In our experiment, because the samples were exposed to air for XPS measurements, the surface of W film without SiH<sub>4</sub> treatment was not only oxidized by air, but also adsorbed WF<sub>x</sub> and fluorine species probably were easily annihilated. Therefore, these results suggest possibility that adsorbed WF<sub>x</sub> and fluorine species on the CVD-W surface change to Si and SiF<sub>x</sub> by SiH<sub>4</sub> treatment. Because SiH<sub>4</sub> treat-

ment for only 10 sec affects thermal stability on Al/W structure (Fig.2), Si and/or SiF<sub>x</sub> seem to be adsorbed on the W surface. As a results, adsorbed Si and/or SiF<sub>x</sub> on the W films are expected to retard Al/W reaction at 500°C annealing.

#### IV. Conclusion

The effect of W surface treatment on suppression of Al/W reaction in Al/W layered structure has been studied. After 500°C annealing for 90 min, Al/W reaction of sample with the SiH<sub>4</sub> treatment was greatly suppressed compared with that of the sample without the SiH<sub>4</sub> treatment. The suppression of Al/W reaction does not depend on SiH<sub>4</sub> treatment time. The W surface analysis indicates that W surface has adsorbed Si and/or SiF<sub>x</sub> due to SiH<sub>4</sub> treatment. As a result, adsorbed Si and/or SiF<sub>x</sub> on the W films are expected to retard Al/W reaction at 500°C annealing.

#### Acknowledgments

The authors would like to thank M.Kinoshita for the estimation of the W surface by XPS, and K.Tai for her help.

#### References

- 1) C.Caanta, W.Cote, J.Cronin, K.Holland, P.I.Lee, and T.Wright, Tech. Dig. International Electron Device Meeting,(1987)209.
- 2) D.Moy, M.Schadt, C-K.Hu, F.Kaufman, A.K.Ray, N.Mazzeo, E.Baran, and D.J.Pearson, Proc. of VLSI Multilevel Interconnection Conf., p26, IEEE, Santa Clara, CA, June 12-13(1989).
- 3) S.Roehl, L.Camilletti, W.Cote, D.Cote, E.Eckstein, K.H.Froehner, P.I.Lee, D.Restaino, G.Roeska, V.Vynorius, S.Wolff, and B.Vollmer, Proc. of VLSI Multilevel Interconnection Conf., p22, IEEE, Santa Clara, CA, June 9-10(1992).
- 4) M.L.Yu, and B.N.Eldridge, J. Vac. Sci. Technol., A7, 625(1989).

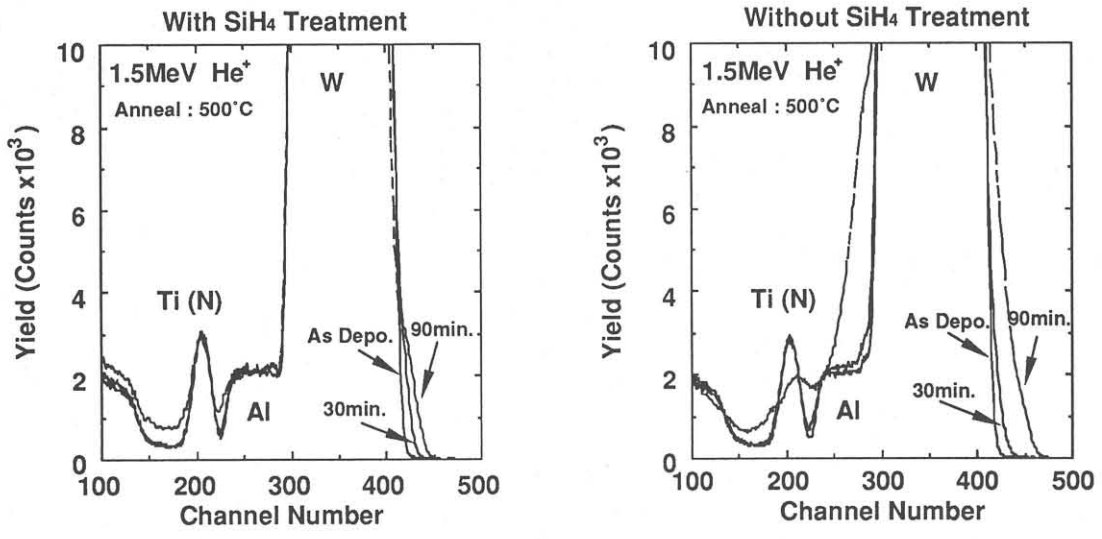


Fig. 3 RBS spectra of Al(300nm)/W(250nm)/TiN(50nm) structures with and without SiH<sub>4</sub> treatment.

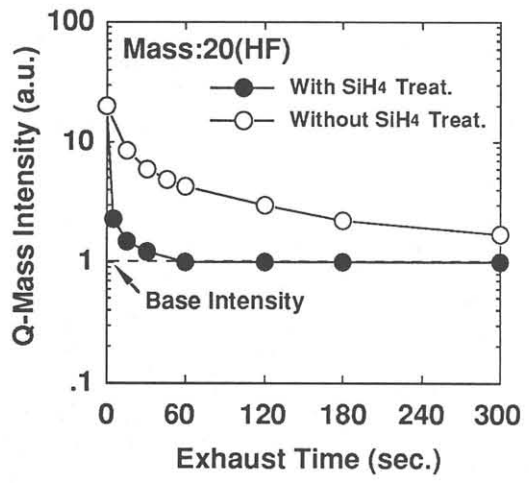


Fig. 4 HF signals in the WCVD reactor measured by Q-mass spectrometer with and without SiH<sub>4</sub> treatment as a function of exhaust time after W film deposition.

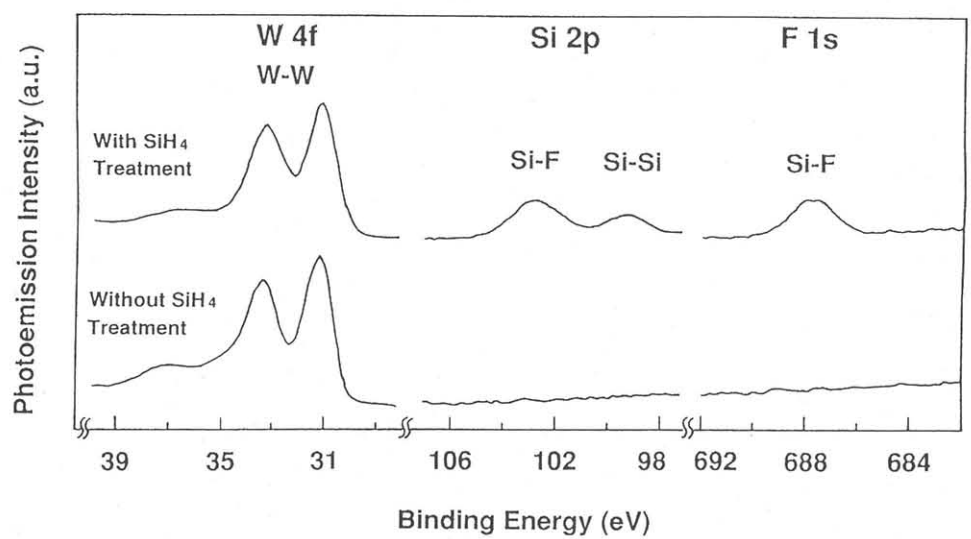


Fig. 5 XPS spectra of W films with and without SiH<sub>4</sub> treatment