Relation between Surface Oxide Growth of Thin TaN Film and Cu Displacement Plating

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1.Introduction

Electroless plating of Cu is a promising method for seed layer deposition prior to Cu electroplating for ULSI interconnections. Recently we found that when the surface of TaN was wet etched to remove a surface oxygen-rich layer, the electroless plated Cu could deposit on the surface without any Pd catalysis adsorption [1,2]. However, the electroless plated copper did not deposited on the surfaces of TaN layers without etching pretreatment. This suggests an existence of surface oxide prohibits displacement plating of Cu. This paper investigated native oxide growth of TaN film deposited at different conditions, and its relationship to the seedless displacement plating of Cu.

2. Experimentals

We deposited TaN films by reactive sputtering of Ta in Ar / N_2 mixture. The Ar partial pressure of 3 mTorr was kept constant and the N_2 partial pressure varied between 0 to 1.0 mTorr. The REDOX (reduction oxidation) potentials of the barrier layers in electroless copper plating solution were measured by two electrodes method using Ag/AgCl as a reference electrode. The main compositions of electroless copper plating solution were glyoxylic acid, TMAH, EDTA, and copper-sulfate.

Fig.1 shows the XPS spectra of TaN films 10 minutes or 5 days after the sputtering. The peaks at 24.4 eV and 26.7 eV are attributed to the peaks of Ta-N for $4f_{7/2}$ and $4f_{5/2}$, respectively. The intensity of TaN peaks were decreased after 5 days, that suggested oxidation of TaN. The atomic ratio of O/Ta on the surface of TaN layer with time is shown in Fig.2. The O/Ta ratio increased with the time when nitrogen partial pressure was 0.1 or 0.3 mTorr, while it did not increase when the nitrogen partial pressure was 1 mTorr .

The REDOX potentials of TaN layers deposited with the various nitrogen partial is shown in Fig.3. In all cases, the potentials of TaN layers are lower than that of copper (-0.01V), which means that the displacement plating of Cu is able to carry out. The potential decreased with addition of N_2 at first, then increased with further increase in the N_2 partial pressure. The Cu film on TaN has a good adhesion strength and damascene interconnection was formed by electroless plating only.

The cross-sectional TEM micrograph of single damascene Cu interconnection formed by the displacement electroless plating on TaN is shown in Fig. 4. The electrical resistivity was 2.1 μΩcm.

3.Conclusions

TaN films deposited with the reactive sputtering of Ar/N_2 showed a good oxidation resistance when N_2 partial pressure was high enough. By this condition, electroless Cu can deposit on a very thin TaN layer, which suggests electroless plating is possible to use practically for ultra fine ULSI interconnections.

References

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[2] Z. Wang, T. Ida, H. Sawa, H. Sakaue, S. Shingubara and T. Takahagi, Electrochem. Sold State Lett., accepted for publication

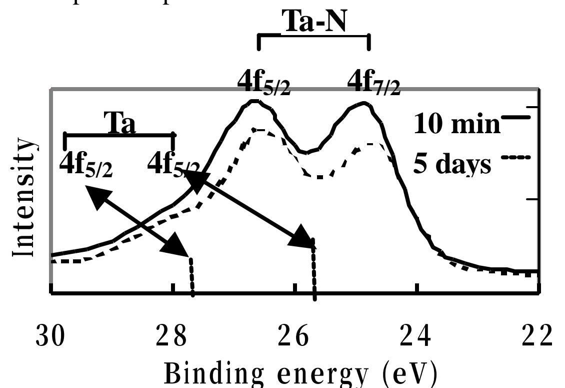

Fig.1. XPS spectra of Ta_{4f} for TaN film sputtered in N_2 partial pressure of 0.5 mTorr.

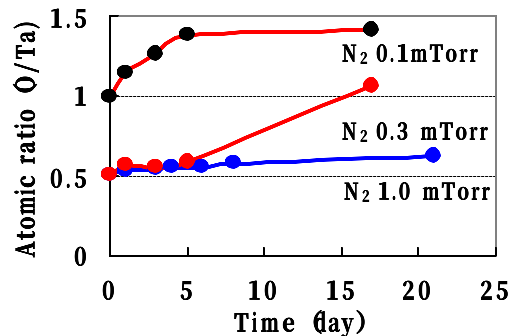

Fig.2 The atomic ratio of O/Ta on the surface of TaN layers with time

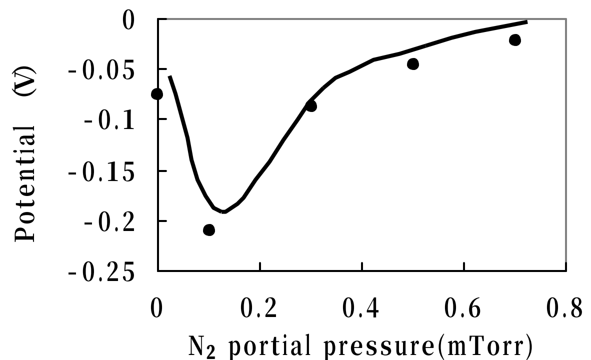

Fig. 3. The relationship of redox potential for TaN films with N_2 partial pressure at 25°C in electroless Cu plating solution

Fig.4. The cross-sectional TEM image of damascene Cu interconnection formed by electroless plating of Cu initiated by displacement reaction on TaN.