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Influence of Surface Oxide of Sputtered TaN Film on Displacement Plating of Cu

Zenglin Wang, Hiroyuki Sakaue, Shoso Shingubara and Talayuki Takahagi

Graduate School of Advanced Science of Matter, Hiroshima University

1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

Phone: + 81-824-24-7683 Fax: + 81-824-22-7195 E-mail: wangzl@hiroshima-u.ac.jp

1.Introduction

Copper (Cu) acts as the main material for global as well as local interconnects in ULSIs [1]. Tantalum nitride (TaN) is promising as a diffusion barrier against Cu because of its good thermal stability at an elevated temperature [2]. The present copper interconnections are fabricated by the electroplating process, in which a sputtered Cu seed layer is necessary. Because the sputtering technology is inherently poor in step coverage, discontinuity of the sputtered Cu seed layer at side walls of fine via holes results in void. Copper electroless plating, which does not need any sputtered seed layer, is an efficient way to fill high aspect ratio holes[3]. 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. However, the electroless plated copper did not deposited on the surfaces of TaN barrier layers without etching pretreatment [3,4]. the thickness of barrier layer becomeS more and more thin (about ~5nm), then electroless plated Cu could not deposit on TaN when it is completely oxidized. Hence , it is necessary to find the sputter conditions by which TaN layer is stable in air. and the electroless plated Cu can be deposited on it.

2. Experimentals

TaN films were deposited by reactive sputtering of Ta in a nitrogen / argon mixture. The base pressure prior to sputtering was 8×10^{-8} Torr. The argon partial pressure of 3×10^{-3} Torr was kept constant and the nitrogen partial pressure varied systematically between 0 to 1×10^{-3} Torr. X-ray Photoelectron Spectroscopy (XPS) measurements were performed using a JPS90-MXV spectrometer. The REDOX (reduction oxidation) potentials of the barrier layers in electroless copper plating solution were measured by two electrodes method (Ag/AgCl as a reference electrode) and the change of the working electrode (substrate) potential against time was recorded. The main compositions of electroless copper plating solution were glyoxylic acid as a reducing agent. TMAH as a pH controller, EDTA, and copper-sulfate, etc. [4]

3. Results and discussions

With the reactive sputtering, under the condition of the argon partial pressure of 3×10^{-3} Torr and the nitrogen partial pressure from 0 to 1×10^{-3} Torr, The Ta and TaN layer were deposited on the surface of SiO_2/Si substrate. When the nitrogen partial pressure was zero, the Ta layer was obtained, which was very quick to be oxidized in air. Fig.1 shows the XPS spectra of Ta film just after the sputtering. The peaks at 21.25eV and 23.35 are attributed to the peaks of Ta metal for $4f_{7/2}$ and $4f_{5/2}$., and the peaks at 26.09 and 28.09 are attributed to the peaks of Ta oxidant for $4f_{7/2}$ and $4f_{5/2}$. The atomic rate of O/Ta on the surface of Ta layer with time is shown in Fig.2. It is clear that the surface of Ta layer is very easy to be oxidized in air and the atomic rate of O/Ta increased with time. For the TaN layer, when nitrogen partial pressure was varied from 0.1 to 1.0 mTorr, the atomic ratio of O/Ta on the surface of TaN layer with time was shown in Fig.3. From the Fig.3, it could be found that the atomic rate of O/Ta on the surface of Ta layer also increased with the time when nitrogen partial pressure was 0.1 or 0.3 mTorr. When the nitrogen partial pressure was higher than 0.5 mTorr, the atomic rate of O/Ta on the surface of TaN layer did not increase with time, which means that when surface of TaN layer was exposed in air, a layer of TaN layer with a depth of about 11Å was oxidized to produce Ta oxidant on the surface of TaN and protect from the TaN from being oxidized. The REDOX potentials of TaN layers deposited with the nitrogen partial pressure of 0.1, 0.5 and 0.5 mTorr in electroless copper plating solution were measured, and the change of the REDOX potentials with time was shown in Fig.4. The initial potentials of TaN layers are lower than that of copper (-0.01V) at the same conditions, which means that the displacement plating between TaN and Cu^{2+} is able to carry out. The potential of TaN layer increased with the increase of the nitrogen partial pressure, which suggests the displacement plating reaction becomes more difficult when nitrogen partial pressure increases.

When TaN layer was etched with $HF:HNO_3:H_2O$ = 1:1:4 (v:v) solution at room temperature for 2 min, and then immersed into the electroless copper plating solution with bath temperature of 72°C for 25 min, the electroless plated copper was deposited on the surface. The cross-sectional TEM micrograph of single

damascene Cu interconnection formed by the displacement electroless plating only is shown in Fig. 5. The measured electrical resistivity is about 2.1 μΩcm.

Conclusions

TaN layers were deposited. with variation of the nitrogen partial pressure in the reactive sputtering conditions. XPS spectra for the surface of TaN layer showed that when the nitrogen partial pressure was higher than 0.5 mTorr, surface oxidized layer of TaN was limited within about 11Å. The REDOX potentials of TaN films in the electroless Cu plating solution were lower than that of copper, which suggested the displacement plating was able to carry out. We succeeded in deposition of Cu by electroless displacement plating on the surface of TaN film. Further study concerning to a relationship between the performance of displacement plating and TaN sputtering conditions are in progress.

References

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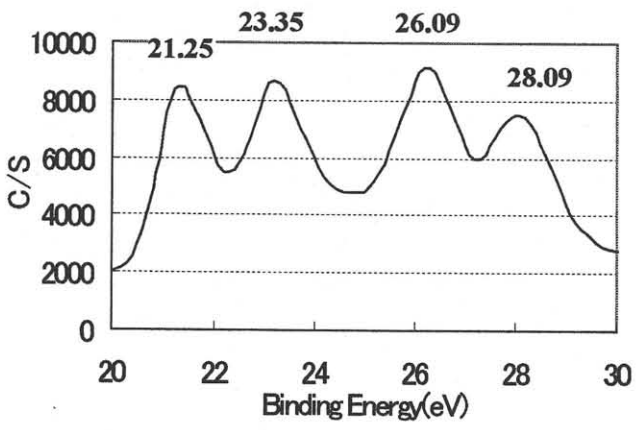

Fig.1 The XPS spectra of Ta4f of Ta film.

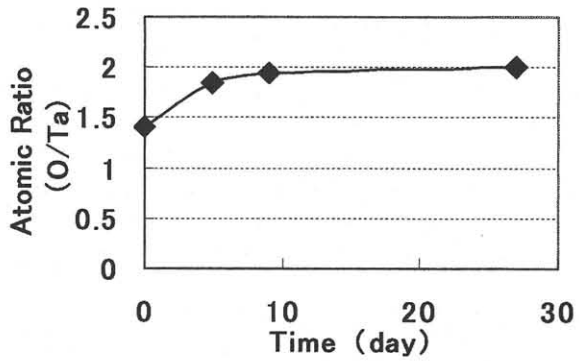

Fig.2 The atomic rate of O/Ta on the surface of Ta layer with time

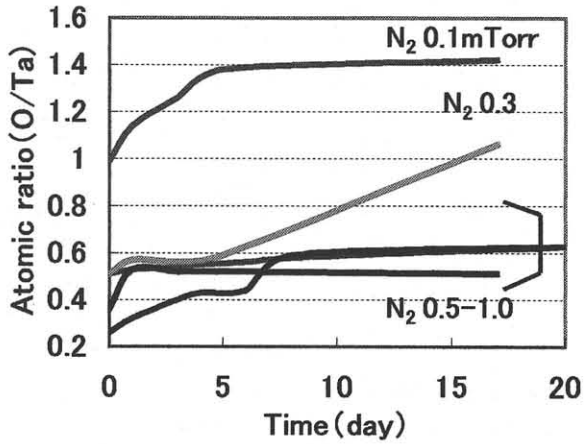

Fig.3 The atomic rate of O/Ta on the surface of TaN layers with time

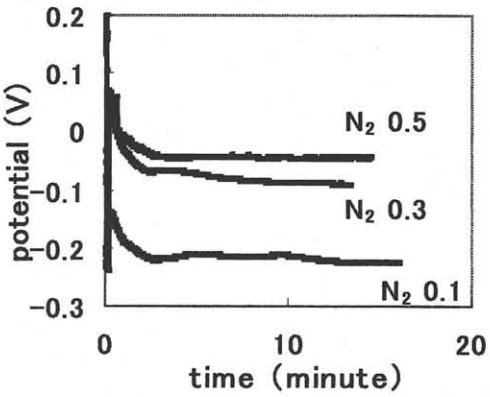

Fig.4 Time dependence of REDOX potential of various TaN film in the Cu electroless plating solution. 20°C. The REDOX potential of Cu is –0.01V.

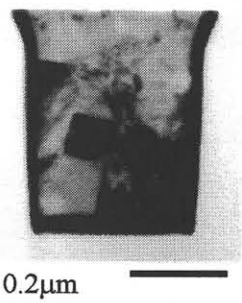

Fig.5 Cross-sectional TEM micrograph of Cu damascene interconnect on TaN formed by the displacement plating only.