Cu Thin Film Fabrication by H_2 Addition Sputtering and Electroplating

Masahiro Ooka and Shin Yokoyama

Research Center for Nanodevices and Systems, Hiroshima University,
1-4-2 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan
Phone: +81-82-424-6265 Fax: +81-82-424-3499 E-mail: ooka@sxsys.hiroshima-u.ac.jp

1. Introduction

Recently, Cu is widely used in ULSI for metal interconnection. The merits of Cu are (1) resistivity of Cu (1.7 μΩ·cm) is lower than that of Al or Al alloys and (2) higher resistance to electromigration [1]. There are many deposition techniques for Cu film on Si wafer. The popular techniques for filling trenches or vias are metal organic chemical vapor deposition, electroplating and electroless plating. Today, Cu electroplating is most popular technique. A conformal and conductive seed layers are necessary for Cu electroplating. The seed layer is generally deposited by sputtering.

Oh *et al.* reported the effects of plasma H_2 pretreatment and also the combined effects of plasma H_2 pretreatment and rapid thermal annealing of the Cu seed layers [2]. The plasma H_2 treatment can remove carbon and oxygen contaminants from the Cu seed layer giving more Cu atoms free for electroplating. We think that H_2 adding is effective for coverage to sub-micron hole in metal sputtering.

In this paper, we study the effect of H_2 adding to Cu sputtering.

2. Experiment

DC magnetron sputtering system we used is schematically shown in Fig. 1. The source DC voltage was set to 500 V. Pressure is 5 mTorr. Plasma source gas was Ar or mixture of Ar and H_2.

Cu surface was measured by atomic force microscope (AFM) and X-ray diffraction (XRD). AFM image shows roughness of Cu surface. And XRD spectra show Cu orientation and grain size.

And next, we tried Cu electroplating. The electroplated Cu films were grown on the sputtered Cu layers (650nm). The electrolyte was composed of Cu sulfate (200 g/l), sulfuric acid (27 cm^3/l), polyethylene glycol (1.3 g/l), and chloride ions (1000 ppm). The solution temperature was 25°C.

3. Results and Discussions

3.1 Effect of H_2 adding on the top Cu surface

A 300 nm thick thermal SiO_2 layer was grown on the Si wafers and then a TiN film was sputtered with the thickness of 30 nm. Finally, Cu was sputtered with the thickness of 650 nm on it. The plasma source gas is the mixture of H_2 (0 - 60%) and Ar.

Cu surface condition was observed using AFM. The AFM images are shown in Fig. 2. Average roughness tends to decrease by H_2 addition. Power spectrum calculated from AFM line profiles (Fig. 3) using fast Fourier transform (FFT) was shown in Fig. 4. The ratio of the high wave number component (4-8 μm^{-1}) with respective to low wave number component (1–3 μm^{-1}) increases by the H_2 addition. It is suggested that Cu surface becomes much smoother by H_2 adding (see Ra in Fig. 2).

Next, crystalinity of sputtered Cu film was investigated by XRD (Fig. 5). All the measured Cu films are almost (111) oriented. However, very small amount of (200) peaks are observed. Figure 6 shows (111) and (200) orientation peaks. All peaks decrease with increasing H_2 adding. However, (200) peaks more rapidly decreases than (111) peak intensity. This means that the more preferred orientation (to (111)) Cu film can be obtained by H_2 adding. This mechanism is unclear at this model.

3.2 Effect of H_2 adding to electric property

Resistivity of sputtered Cu films was measured using van der Pauw method [3]. Table I shows the Cu resistivity. The resistivity tends to decrease with increasing adding H_2. And Cu film, which was grown and stored in atmospheric ambient for 3 months, has very high resistivity. In our opinion, Cu surface was oxidized.

In case of H_2 adding, hydrogen-termination may occur on the surface of deposited Cu. And also O atoms on Cu surface may be scavenged by H radicals (see Fig. 7). H_2 adding causes the Cu surface smooth and suppresses oxidation. Suppression of Cu oxidation also contributes to suppression of the increase of resistivity.

3.3 Cu electroplating

Electroplated Cu was deposited on sputtered Cu seed layer. The deposition rate tends to increase with plating current (see Fig. 8(a)). About 300nm thick electroplated Cu films were deposited and their surface roughness was measured by AFM. Figure 8(b) shows a relation between the roughness and film thickness. The roughness seems to depend on Cu film thickness and not depend on plating current.

Next, the electroplated Cu on sputtered Cu (using Ar or Ar/H_2 mixture plasma) layer is compared (5mA/cm^2). It is found that the electroplated Cu surface roughness is not dependent on Cu seed layer, i.e., H_2 adding during sputtering deposition of seed layer does not affect the final surface roughness.

4. Conclusions

By addition of H_2 to Ar plasma in Cu sputtering, it is found that the surface becomes smooth and the resistivity tends to decrease with increasing the amount of H_2. However, we found that Cu surface roughness becomes same after electroplating of 300 nm.

References

[1] J. Musil *et. al.*: Czch. J. Phys. **45** (1995) 249.
[2] J. Oh *et al.*: Jpn. J. Appl. Phys. **40** (2001) 5294.
[3] L. J. van der Pauw: Philips Research Reports **13** (1958) 1.

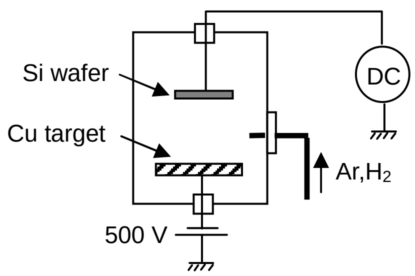


Fig. 1 Schematic diagram of magnetron sputtering apparatus.

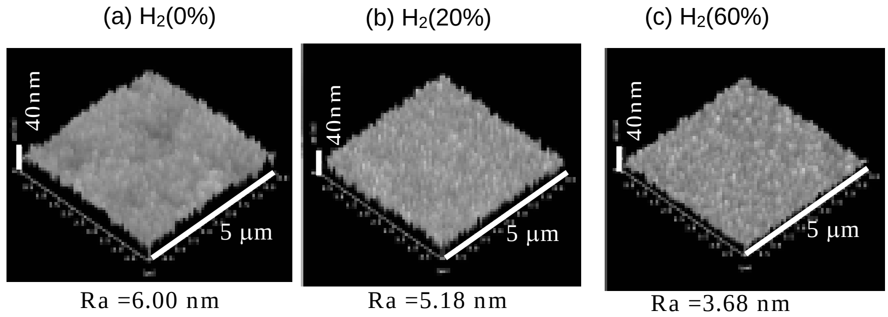


Fig.2 AFM images of Cu film sputtered Ar/H_2 mixture of (a) H_2 (0%) (b) H_2 (20%) and (c) H_2 (60%).

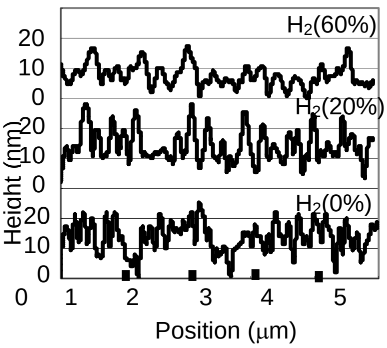


Fig.3 Line profiles of Cu films sputtered in H_2 (0%), H_2 (20%) and H_2 (60%) / Ar.

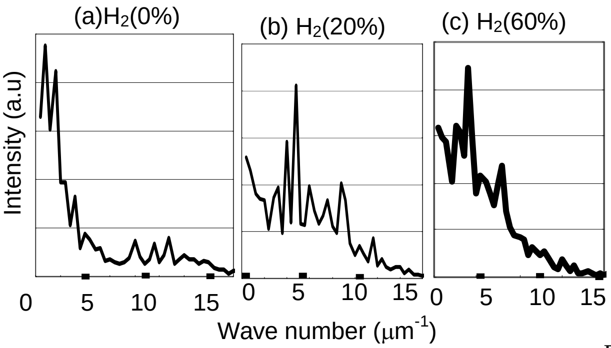


Fig.4 Power spectrum by FFT of Cu films sputtered at (a) H_2 (0%), (b) H_2 (20%) and (c) H_2 (60%).

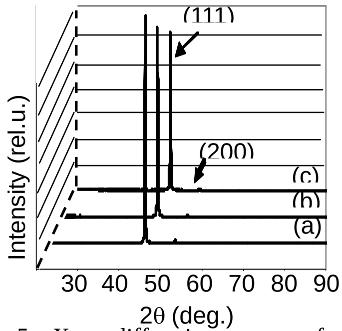


Fig.5 X-ray diffraction patterns of the Cu films sputtered at (a) H_2 (0%), (b) H_2 (20%), and (c) H_2 (60%).

Table I Resistivity of Cu films sputtered at H_2 (0%), H_2 (10%), H_2 (40%) and stored for 3 months.

	H_2 (0%)	H_2 (10%)	H_2 (40%)	H_2 (0 – 60 %) Stored for 3months
R (μΩ·cm)	1.83 1.98	1.77 1.79	1.68 1.76	~20

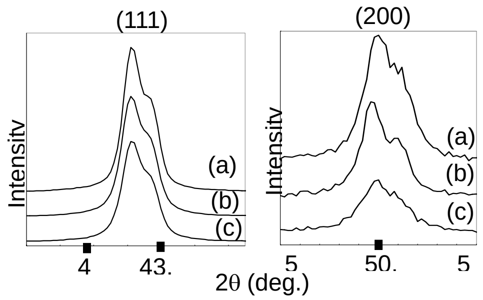


Fig.6 (111) and (200) orientation peaks for X-ray diffraction patterns of the Cu films sputtered in Ar (a), H_2 (20%)/Ar (b), and H_2 (60%)/Ar (c)

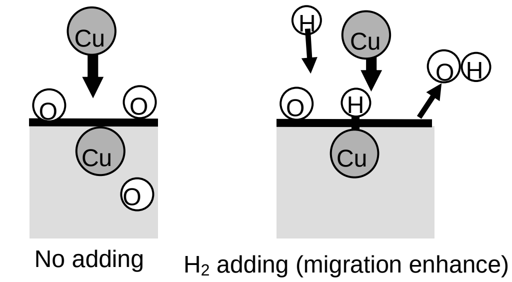


Fig. 7 Mechanism of H_2 adding effect.

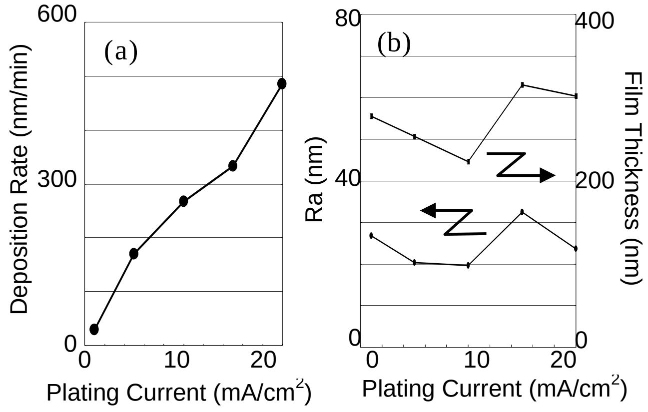


Fig. 8 Effects of plating current on the deposition rate of Cu films (a), deposition rate and roughness (b).

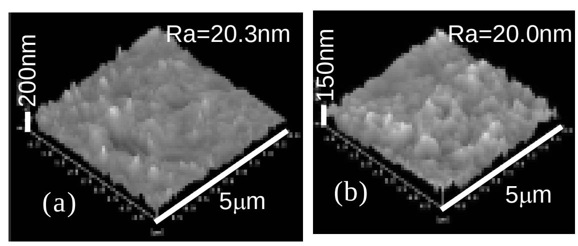


Fig. 9 AFM images of electroplated Cu film. Cu seed layer is sputtered at (a) H_2 (0%) and (b) H_2 (40%).

21st Century COE Program
Fourth Hiroshima International Workshop on Nanoelectronics for Tera-Bit Information Processing

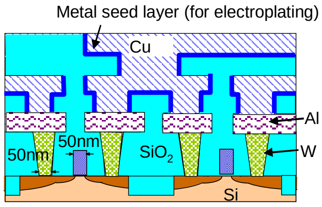
Cu Thin Film Fabrication by H_2 Addition Sputtering and Electroplating

M.Ooka and S.Yokoyama

Introduction

The popular techniques for filling trenches or vias
- metal organic chemical vapor deposition
- **electroplating**
- electroless plating

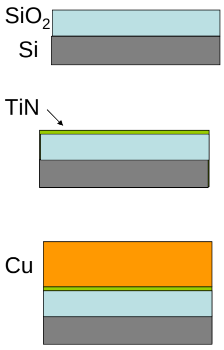
A conformal and conductive seed layers are necessary for Cu electroplating.



We found that H_2 addition sputtering can make sooth Cu layer.

We study the effect of H_2 addition sputtering to Cu electroplating.

Process Flow

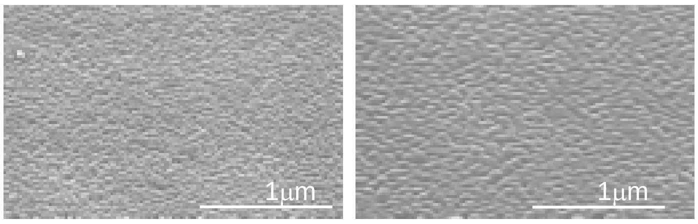


- Thermal SiO_2 : 300nm

TiN film is sputtered (30nm)

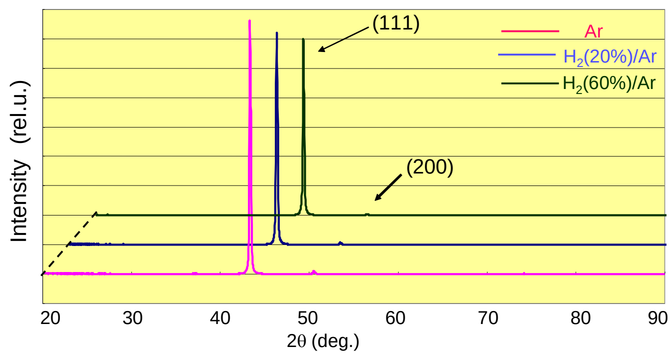
Cu deposition : 650nm
(DC magnetron sputtering • 500V • 5mTorr)
• Gas:H_2(0%〜60%)/Ar

SEM photographs of sputtered Cu surface



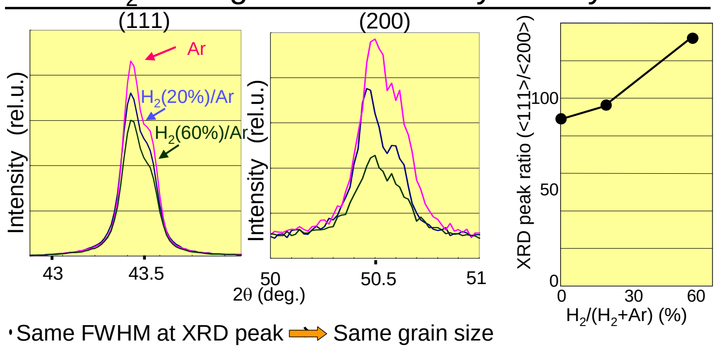
H_2 addition to Cu sputtering influences Cu surface roughness

XRD patterns of sputtered Cu surface



All the measured Cu films are almost (111) oriented.

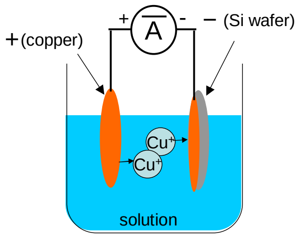
H_2 adding effect on Cu crystalinity



- Same FWHM at XRD peak ⇨ Same grain size
- All XRD peak is decreased ⇨ Crystalinity degraded
- (111)/(200) peak ratio increased ⇨ Adding H_2 tend to make (111) plane

Experimental

Electroplating by $CuSO_4$



Contents of electroplating solution

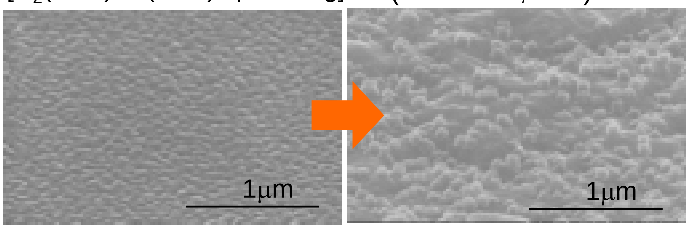
	600cm³
$CuSO_4$	120g
H_2SO_4	16cm³
HCl	0.1cm³
PEG	0.8g
Atmosphere	Air
Temperature	25℃

(PEG: polyethylene glycol)

SEM photographs of electroplated Cu surface

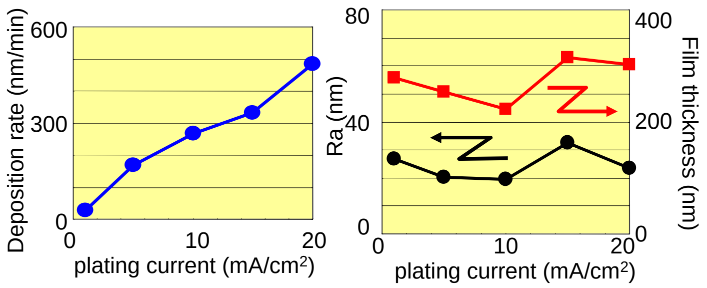
Before electroplating [H_2(10%)/Ar(90%) sputtering]

After electroplating (50mA/cm², 2min)



After electroplating : Cu surface becomes rough.
→The electroplated Cu preferably grows on top of protrusion of sputtered Cu surface.

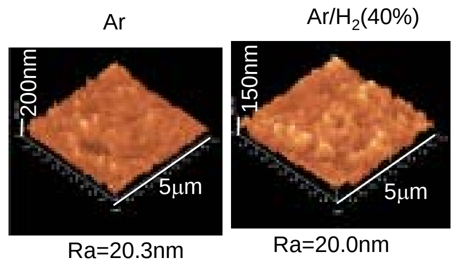
Effect of plating current



• Deposition rate depends on plating current.
• The roughness depend on Cu film thickness and not depend on plating current.

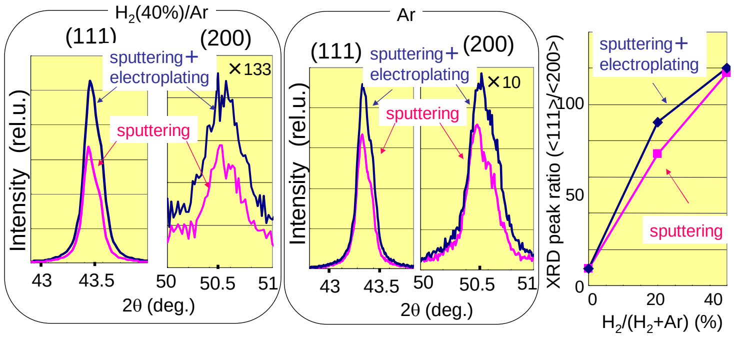
AFM images of electroplated Cu

Condition：5mA/cm², 300nm deposition



• Surface roughness become similar.
• H_2 adding during sputtering deposition of seed layer does not affect the final surface roughness.

Comparison of XRD peak on electroplating



※ Sputtered Cu : 200nm thick

• Orientation of electroplated Cu depend on orientation of Cu seed layer.
→H_2 addition sputtering can be controlled orientation of electroplated Cu.

Conclusion

• We deposited the electroplated Cu on H_2 addition sputtered Cu.

• H_2 adding during sputtering deposition of seed layer does not affect the electroplated surface roughness.

• Orientation of electroplated Cu depend on orientation of Cu seed layer, and H_2 addition sputtering can be controlled orientation of electroplated Cu.