Synergistic Effects of Copper Plating Additives & Filter Type for Coil Plating in Write Heads

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The coils in write heads for disk drives are made of electroplated copper. These can be plated from acid copper baths with proprietary additives. Recently, plating studies done for damascene copper interconnects have shed light on specific chemicals used in copper plating additives. A Hull cell study of three copper additives has been done to assess their applicability for plating copper coils. The three additives studied were polyethylene glycol, Janus Green B and 3-mercapto-propane-sulfonic acid. These coils were also plated in the same acid copper bath in presence of a proprietary additive. A large offset was found between the test sites and the coils plated thickness. This phenomenon was related to polyethersulfone filter and was reduced by changing the filter to the inert polypropylene one. An attempt is made to explain these phenomena.

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Part I. Copper Plating with Superfilling Additives

It is well known that organic additives and contaminants can affect electroplated copper appearance and properties. In this paper we present data on plating from copper baths with "superfilling" additives and on the effect of filter contaminants on plating uniformity.

The introduction in 1997 of electroplated copper as an interconnect metal on semiconductor devices has spurred the publication of numerous studies of copper electroplating baths which possess the property of superfilling. The types of additives used in these baths are mentioned in a review article of the process¹.

One set of additives that have been studied by a few authors²⁻⁴ is chloride, polyethylene glycol (PEG), Janus Green B and 3-mercapto-propane-sulfonic acid (MPSA). We have chosen this set of additives for our study.

A Hull Cell was used for the initial investigation. The cell had an approximate volume of 267 ml. Brass plates were used as the cathode substrates which were 100.4 mm long, 76.9 mm wide and 0.44 mm thick. The electroplating solution used for the experiments is shown in Table 1.

Chemical	Concentration	Units
Copper Sulfate Pentahydrate	117	g/l
Sodium Chloride	83	mg/l
Sulfuric Acid, 96%	110	ml/l
Janus Green B	25-100	mg/l
PEG	1000-2000	mg/l
MPSA	25-100	mg/l

Table 1. Electroplating Bath Composition

A current of 2.0 amperes was passed through the cell for a period of 120 seconds for each sample. Table 2 (below) shows the experimental matrix which was used along with the Hull Cell result.

Test #	PEG (mg/l)	MPSA (mg/l)	Janus Green B (mg/l)	Brightness Range (Amps/sq. ft.)
1	0	0	0	2
2	1000	0	0	8
3	0	25	0	0
4	0	0	25	2
5	2000	0	0	8
6	0	50	0	0
7	0	0	50	2
8	1000	50	0	2
9	1000	0	50	2
10	1000	50	50	60
12	1000	50	100	55
13	1000	100	50	60
14	1000	100	100	80
15	1000	25	100	50
16	1000	75	50	95
17	1000	100	25	70
18	2000	50	50	55
19	2000	100	50	95
20	2000	50	100	60
21	2000	100	100	95
22	2000	25	25	45
23	2000	50	25	95
24	2000	75	50	60

Table 2. Matrix of Experiments

The brightness range is reported as the maximum current density where bright plating was obtained. It can be seen that the best results were obtained for a baths containing a ratio of MPSA:Janus Green B of about 1.5-2.0. The higher PEG concentration of 2000 mg/l produced three out of four of the highest current density results.

The effect of PEG molecular weight was also investigated in the range of 1500 to 6000 molecular weight. This parameter did not have a strong effect on the brightness range.

Conclusions

1. All three additives must be present in solution to produce bright plating with an extended current density range.

PEG concentrations of 2000 mg/l with a ratio of MPSA: Janus Green B of about 1.5 2.0 produce the best results.

Part II. Effects of Filter Contamination on Copper Electroplating

Uniformity

Acid copper baths are used in plating copper coils and studs for thin film magnetic head recording. The bath chemistry used in this study is shown below in Table 3.

Chemical	Concentration	Units
Copper Sulfate Pentahydrate	117	g/l
Hydrochloric acid	83	mg/l
Sulfuric Acid, 96%	60	PPM
Proprietary additive	3	ml/l

Table 3. Electroplating Bath Composition

The bath reservoir was connected to a plating cell where the copper anode was placed horizontally, facing upward. The cathode was placed horizontally, facing downward, 1 inch from the anode. The electrical contact to the 6 inch round wafers was made from the back of the electrically conductive AlTiC substrate. In this study the bath circulation was kept constant at 1.7 l/min through a 0.2 um filter. Also, a paddle agitator oscillated back and forth close the surface of the wafer at constant speed of 30 RPM.

Two types of filters were evaluated:

- 1. An electronic grade, 0.2 µm polyethersulfone (PES) membrane filter (hydrophilic).
- An electronic grade, 0.2 μm polypropylene (PP) membrane filter (hydrophobic).
 The bath temperature was kept constant at 25° C. The current density was also constant at 14 ma/cm². The wafer to thief current ratio was 1:1.4. The plating time was 4 to 5 min.

Experiments

Patterned wafers were plated in two copper acid baths using polyethersulfone and polypropylene filters respectively. After copper coil plating, the photoresist was stripped in NMP solvent and

the coil thickness was measured with a profilometer. The measurements were performed on rectangular test sites (dimensions: $80 \times 70 \ \mu$ m). Cross-sections were made by focussed ion beam (FIB) milling on the actual device to measure and compare the coil turn thickness to test site thicknesses. The total plated coil area is only 3% of the entire wafer area. The thickness measurements were compared from both baths (polyethersulfone and polypropylene filters).

Results and Discussion

In order to evaluate the quality of the electroplated copper, the resistivity and etch rate was measured for copper films plated from both baths. The etch rate test is an indication of how much organic matter has been incorporated into the electroplated copper. A higher etch rate correlates to a higher incorporation of organic material. The etch rate test is done as follows:

- 1. Electroplate copper into a resist mask.
- 2. Strip the resist.
- 3. Measure the thickness by profilometry
- 4. Etch for 14 seconds in an ammonium persulfate etch bath at a basic pH.
- 5. Measure the thickness by profilometry.
- 6. Calculate the etch rate in Å/sec.

The results are shown in Table 4.

Material	PES	PP
Resistivity (µohm-cm)	1.8	1.8
Etch Rate (Å/sec)	128	116

Table 4. Sheet resistance and plated film etch rate

These results indicate no significant difference between PES and PP filters on the resistance and etch rate of the copper plated films.

Thickness uniformity of plated coils in PES and PP filters as measured on test sites by profilometry and from FIB cross sections on both test sites and coil devices are shown below in Table 5.

Thickness offset	Polypropylene filter	Polysulfone filter
FIB narrow width - Tencor test site	0.17 µm	0.38 µm
FIB wide width - Tencor test site	0.21 µm	0.31 µm
FIB narrow width - FIB wide width	-0.04 µm	0.08 µm

Table 5: Thickness measurements of copper plated coils in PP and PES filters

Conclusions

Wafers plated in bath with polypropylene filter:

- 1. Show a minimum thickness offset between the profilometry test site and the coil turns as compared to the bath with a polysulfone filter.
- 2. The thickness difference between the wider pitch coil turns and the profilometry test site for the bath with a polypropylene filter was also reduced as compared to the bath with a polysulfone filter .
- 3. The bath with polypropylene filter showed narrow width coils which were thinner than the wider width coils. The opposite is the case for the bath with a polysulfone filter were the narrow width coils are thicker than wider width coils.

Part III. FTIR Analysis of plating solution with polyethersulfone filter

It seemed clear from the above discussion that the PES filters were leaching organic residues into the plating bath. In order to verify this an FTIR study was done.

The plating solution was solvent extracted, the solvent evaporated, the residue washed with an aqueous solution, and the residue sample from the filter media transferred to an infrared transparent substrate (single crystal silicon) for transmittance mode FTIR analysis utilizing a BioRad FTS6000 FTIR system coupled to a UMA 500 FTIR microscope. The FTIR spectra for reference areas were collected on adjacent clear areas. Infrared spectra were then collected at 8 cm⁻¹ resolution with 1024 scans coadded together prior to Fourier Transformation.

Results

The infrared spectrum of the solvent blank residue (Spectrum 02091101(1)) exhibits no significant infrared absorption bands.

The infrared spectrum of the bad plating bath extract residue (Spectrum 02091102(3)) exhibits O-H stretching absorption bands (3745 cm⁻¹), C-H bending absorption bands (1585, 1485, 1415, and 1323 cm⁻¹), C-O stretching absorption bands (1296, 1238, 1149, 1103, and 1014 cm⁻¹), and C-H OOP bending absorption bands (833 cm⁻¹). This material exhibits a spectrum very similar to a polysulfone resin.

The infrared spectrum of a polysulfone resin standard (Spectrum 02091101(2)) exhibits C-H stretching absorption bands (3086, 2974, 2958, and 2889 cm⁻¹), C-H bending absorption bands (1585, 1485, 1415, and 1323 cm⁻¹), C-O stretching absorption bands (1296, 1238, 1149, 1103, and 1014 cm⁻¹), and C-H OOP bending absorption bands (833 cm⁻¹).



Figure 1. Solvent blank FTIR spectrum.



Figure 2. FTIR spectrum of a sample from an acid copper sulfate bath using a polyethersulfone membrane filter.



Figure 3. FTIR spectrum of a sample of polysulfone resin.

Conclusion

A comparison of Figures 2 and 3 shows that polysulfone residues are present in the bath when polyethersulfone membrane filters are used. This proves that the polyethersulfone filters are leaching out organic materials containing polysulfone resin or fragments thereof. Polyethersulfone (PES) is a polymer which contains repeating molecular units of the form⁵: -O-benzene ring-SO₂-. It is probable therefore, that the organic compound appearing in the plating bath is diphenyl sulfone or some similar derivative.

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