COLORIMETRICALLY CONTROLLED COPPER ETCHING

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INTRODUCTION

Copper is playing an increasingly critical role in the manufacture of electronic components from circuit boards to semiconductor devices. In addition to attractive physical and electrical properties, copper is easily manipulated in the manufacturing environment. Advances in copper technology have led to applications such as transistor wiring for integrated circuits and copper damascene processes for BEOL technology. Copper's high power density and short signal delay time are supporting the shrinking size of electronics packaging while copper pillars are working to reduce heat generation and power consumption.[1]

Etchant technology needs to keep pace with modern manufacturing requirements. Copper etching is a well-known process typically involving hazardous chemicals. For example, solutions of sodium or ammonium peroxydisulfate afford good compatibility with positive and negative photoresists but are oxidizing hazards with limited shelf life.[2] Cupric chloride solutions, on the other hand, are effective etchants but offer reduced compatibility with positive photoresists.[3] Strong acids such as nitric and sulfuric acid or aqua regia are difficult to control and are incompatible with many materials. Solutions of ferric chloride and hydrochloric acid represent the most common copper etching chemistry, but their drawbacks include undercutting, corrosivity, and lack of sub-micron definition.[2,4] Table 1 lists copper etching chemistries with their advantages and disadvantages.

TABLE 1. COMPARISON OF COPPER ETCHANT CHEMISTRIES

CHEMISTRY	ADVANTAGES	DISADVANTAGES
Ferric Chloride/Hydrochloric Acid	Fast Etching Photoresist Compatibility	Corrosive Poor Etch Control Undercut Problems
Sulfuric Acid/Potassium Dichromate[4,5]	Effective Etchant	Toxic
Sodium/Ammonium Peroxydisulfate	Colorless Good Compatibility	Limited Shelf Life Oxidizing Hazard
Cupric Chloride	Controllable Etching	Poor Photoresist Compatibility
Aqua Regia (Nitric Acid and Hydrochloric Acid)	Fast Etching	Poor Compatibility Poor Etch Control
Copper Etchant 49-1 (Citric Acid)	Controllable Etching Excellent Compatibility Readily Monitored Etch Process Non-Hazardous	

These etchant chemistries do not produce easily monitored reactions with copper or facile means to determine when the etch capacity has been reached. A citric acid chemistry recently introduced by Transene Company, Copper Etchant 49-1 offers the advantages of broad compatibility with photoresist and other metals, easily controlled etching, and a readily monitored etch process in a non-hazardous liquid form. Basic colorimetry can be used to determine the remaining lifetime of the etch bath as well as the amount of copper etched.

EXPERIMENTAL

Copper Etchant 49-1, pH 5.63, was added to a 4 liter quartz etch tank equipped with a magnetic stir bar and mounted on a Corning PC-353 stirrer set at 400 RPM. Copper coupons measuring 40 cm^2 were added to the solution with stirring.

Solution pH was measured using a Thermo-Orion 410A+ pH meter. Colorimetric measurements were conducted using a Hitachi U-2000 spectrophotometer scanning the range 400 nm – 1,100 nm with an absorbance range of 0 to 3.00.

During the process, the etchant changed from a clear, colorless solution to a light blue solution to a dark blue solution with an absorbance peak centered at 741-743 nm. A final change to green marked the end of the bath life. Comparisons were made of the amount of copper etched vs. time and absorbance.

RESULTS AND DISCUSSION

The results of the experiment show a strong correlation among etch time, spectrophotometric absorbance, and thickness of copper etched. Table 2 summarizes the correlation of these trends. Figure 1 provides a graphical depiction of time vs. absorbance.

TABLE 2. ETCH TIME VS. ABSORBANCE AND THICKNESS ETCHED

ETCH TIME (minutes)	ABSORBANCE AT 741-743 nm	THICKNESS OF COPPER ETCHED (microns)
15	0.126	1.1
45	0.222	3.4
90	0.341	3.9
120	0.430	4.5
150	0.542	5.0

It can be seen from Table 1 that the etch rate is constant through approximately 90 minutes of etch time or until the absorbance value reaches 0.34. At higher absorbance readings, the etch rate begins to slow. This result is expected: as the solution becomes more and more saturated with copper ions the solution’s effectiveness weakens. During etching, copper is oxidized to the +2 oxidation state, forming copper(II) citrate pentahydrate. Over time, the concentration of citric acid in the solution decreases which makes it more difficult to solublize additional copper.

Figure 2 depicts example graphs of the absorbance spectrum. While the peak is centered just above 740 nm, there is a broad absorbance band stretching from 580 nm to 980 nm. The breadth of the peak does not change with time, but the area under the peak expands. Visually, these results can be observed by the color change to light blue through dark blue until the end point is reached and the color shifts to green (Figure 3). At the end point, the absorbance peak shifts to slightly lower wavelength, 734-737 nm.

CONCLUSION

A citric acid chemistry allows for accurate monitoring of copper etching using spectrophotometry. Baseline results specific to a process can be obtained easily and provide the framework for predicting the etch rate of the solution at various stages of its lifetime. Most etchants depend only on time measurements which may vary depending on the particular lot of etchant, variations in the process, or operator error, but Copper Etchant 49-1 provides the user with a method of determining the etch speed and remaining capacity of the etch bath at any point in its lifetime.

[1]Arthur Keigler, Bill Wu, Zhen Wu, *Semiconductor Manufacturing*, August 2006, Vol. 7, Issue 8, pp. 38-41.

[2]Kirt Williams, Kishan Gupta, and Matthew Wasilik, *J. Microelectromechanical Systems*, December 2003, Vol. 12, No. 6, pp. 761-778.

[3]*Printed Circuit Fabrication*, August 1987, Vol. 10, No. 8, pp. 36-40.

[4]Michael Kohler, *Etching in Microsystem Technology*, Wiley-VCH, New York, 1999, pp. 229-230..

[5]Gunter Petzow, *Metallographic Etching*, American Society for Metals, 1978, pp. 58-61.

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