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BDX-613-1012

SOLUTION CONTROL FOR HYBRID MICROCIRCUIT ETCHING

October 1973

Bendix Corporation
Kansas City, Missouri

MASTER

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**SOLUTION CONTROL FOR
HYBRID MICROCIRCUIT ETCHING**

Published October 1973

**Project Leader:
L. L. Lantz
Department 814**

Technological Spinoff Report

Contract Number AT(29-1)-613 USAEC

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BDX-613-1012, UNCLASSIFIED Technological Spinoff Report, Published
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Prepared by L. L. Lantz, D/814

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THE BENDIX CORPORATION

KANSAS CITY DIVISION

KANSAS CITY, MISSOURI

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Atomic Energy Commission

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Photoresist developing solutions and metal etchant solutions used in hybrid microcircuit production gradually decline in effectiveness. Monitoring procedures have been developed for these solutions. A determination of the composition of Shipley AZ Photoresist Developer and an evaluation of the parameters affecting its developing quality indicated that the best method of monitoring the solution was to measure the solution color, which darkens with use.

The method used for monitoring iodine in the gold etchant, titration with sodium triosulfate, was checked for accuracy against a second analytical procedure. The results proved the titration method to be satisfactory. The etch rate of the solution was found to be dependent on the gold concentration. Measurements of solution density versus gold concentration showed that this was an effective way to monitor the gold concentration.

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DISCUSSION

SCOPE AND PURPOSE

The objective of this work was to develop monitoring methods for solutions used in hybrid microcircuit etching. An evaluation of the effect of solution parameters on etch rate was used to establish monitoring procedures. Bendix Kansas City uses the monitoring procedures to determine when etch solutions must be replenished or replaced.

ACTIVITY

The solutions used in hybrid microcircuit etching are photoresist developer, gold etchant, chromium etchant, and tantalum nitride etchant. Methods have been developed to monitor the photoresist developer and the gold etchant. Monitoring methods for the chromium etchant are being developed and work on the tantalum nitride etchant will follow.

The etch rates of the solutions decrease with use. In all cases, decreasing concentrations of solution components involved in the etching process contributed to the declining etch rate. It is also possible for increasing concentrations of the products of the etching process to depress the etch rate. The problem was to determine which solution components affected the etch rate and to what extent, and to select the best methods for monitoring these components.

Photoresist Developer

Using titrimetry, atomic absorption spectrophotometry, and specific chemical tests, the identity and concentrations of the components of Shipley AZ Photoresist Developer were determined to be 0.7 molar sodium ions (Na^+), 0.14 molar orthophosphate ions (PO_4^{3-} plus HPO_4^{2-}), and 0.21 molar metasilicate ions (SiO_3^{2-}). The solution pH measured 12.5, which has a corresponding hydroxide ion concentration of 0.032 molar. The solution may be prepared by dissolving the appropriate amounts of Na_3PO_4 , Na_2HPO_4 , and Na_2SiO_3 in water.

Titrimetry experiments revealed that the developer solution has a large buffering capacity. The orthophosphate and metasilicate ions act as buffers to keep the pH from changing rapidly. Experience indicated that the pH of the solution did not change significantly during its useful life and would not be satisfactory for monitoring the solution. A determination of the decreasing buffer capacity of the solution by titration would not be satisfactory because

of possible interferences from products of the developing process and from the solution color which darkens with use.

Since the developer solution does darken with use, the solution color was evaluated as a possible monitoring parameter. Spectrophotometric measurements of absorbance versus wavelength of used developer solutions are shown in Figure 1.

Figure 1. Absorbance Versus Wavelength

Sample A was from a solution being discarded because of deterioration of developing quality. Sample B had been used for a short time and Sample C was a 1:3 dilution of B using fresh developer solution. The data shows that the change in absorbance during the life of the solution could be used to effectively monitor the developer.

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Normally, the wavelength at a maximum is used for absorbance measurements. However, for Sample A (Figure 1), which was the deteriorated solution, the maximum is off scale. Two solutions to the problem were to use a shorter light path of less than 1 cm or a different wavelength for the absorbance measurements. A disadvantage of using a shorter light path is that continuous monitoring is more difficult because of the problem of continuous circulation of solution through the smaller absorbance cell. If the wavelength used corresponds to a sloping part of the absorbance-wavelength curve, a larger error will result

from a small error in setting the wavelength. However, this can be minimized by using a spectrophotometer with fixed wavelengths. A wavelength between 400 and 450 nm should be used, because this wavelength range makes a wider portion of the absorbance scale usable.

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Gold Etchant

The gold etch solutions experience a gradual decline in etch rate with use, even when the etching compound (iodine) is replenished regularly. The gold etchant used in hybrid microcircuit production is a solution of iodine and potassium iodide. A 1-Normal iodine concentration has been chosen for the etchant solutions. The etch rate of the solutions is drastically affected by changes in the iodine concentration, which must be closely controlled. The procedure now used to determine the iodine concentration is to titrate the iodine with sodium thiosulfate. An investigation of the iodine analysis was conducted, since errors in the iodine analysis could result in the etch rate decline. Also, the iodine analysis was important during studies of other solution parameters because the iodine concentration had to be held constant at 1-Normal.

A second iodine analysis procedure was used to check the thiosulfate titration method. The procedure involved solvent extraction of the iodine with toluene followed by measurement of the iodine concentration with a visible spectrophotometer. An atomic absorption analysis of gold in the aqueous layer before and after extraction with toluene showed that no gold was extracted with the iodine. This shows that the procedure is free of interference from gold. Four samples of etchant containing gold were analyzed by both the sodium thiosulfate method and the extraction absorbance method (Table 1). The agreement between the two methods is very good indicating no interference is involved in the thiosulfate titration method. The titration method is preferred since it is simpler and quicker.

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Possible metal contaminants other than gold in the gold etchant are chromium, silver, copper, and iron. Chromium is the material deposited under the gold. Silver, copper, and iron have been determined by spark source mass spectroscopy and emission spectroscopy to be the major metal contaminants in the gold wire purchased from one vendor.

An atomic absorption analysis of a used etch solution indicated that if chromium was present, it was in concentrations less than 1 ppm. Iron was

detected by dispersive X-ray analysis of material which crystallized from some used etchant. The gold wire is a possible source of the iron. No silver or copper was detected. However, silver and copper form insoluble compounds with iodide ions and the metal ions would probably not be in concentrations high enough to be determined by the dispersive X-ray technique. The concentrations of these metals are so small that their affect on the etch rate can be considered negligible.

Table 2. Etch Rate Versus Gold Concentration

Iodine Concentration Normality	Gold Concentration (g/cm ³)	Etch Rate		Percent Change in Etch Rate
		(g/min)	(μg/s)	
1.005	0	0.0228	(380)	0
1.001	0.0059	0.0211	(352)	-7.4
1.005	0.0109	0.0194	(323)	-15.0
1.006	0.0141	0.0173	(288)	-24.2
0.999	0.0179	0.0143	(238)	-37.4
1.009	0.0223	0.0099	(165)	-56.6
0.998	0.0278	0.0055	(92)	-75.8

Some solution densities of etchant containing gold were measured to determine if this parameter would be satisfactory for monitoring the gold concentration. The density of two etchant solutions was determined by weighing measured volumes of the solution at 25 ±1°C (Table 3).

Table 3. Densities of Some Used Gold Etch Solutions

Iodine Normality	Gold Concentration	Density
1.004	0	1.236 g/cm ³
0.998	0.0278 g/cm ³	1.302 g/cm ³

Figure 3. Etch Rate Versus Gold Concentration

These two solutions represent the terminal conditions studied in the etch rate experiment. It is probable that only the lower half of the gold concentrations in this range would be encountered in practical experience, since the higher gold concentrations are undesirable because of reduced etch rate and solutions would be adjusted before reaching that point. This leaves a density range of 0.033 g/cm³ (1.236 to 1.269 g/cm³). If the solution temperature is very closely controlled, it will be possible to determine the gold concentrations by measuring the solution density with a precision hydrometer having the narrow density range given above. The density measurements must be made after adjusting the iodine concentration to 1-Normal.

The density cut-off point must be determined during the etching process. This should be done initially by choosing an arbitrary density cut-off point: 1.270 g/cm³ is recommended. If, during processing, incomplete etching occurs before the density cut-off point is reached, the density cut-off point must be changed in the direction of lower density. If the etching process is still satisfactory when the arbitrary density cut-off is reached, the density cut-off point must be changed to a higher density. The cut-off point is adjusted until it corresponds to the point at which etching becomes unsatisfactory.

Figure 4. Percent Change in Etch Rate Versus Gold Concentration

The surface tensions of some etchant solutions were measured by the capillary rise method in order to determine if the wetting properties of the solutions are important factors in the etch rate (See Table 4). The variations in the surface tensions are very small and cannot be significant factors in the etch rate.

ACCOMPLISHMENTS

The composition of Shipley AZ Photoresist Developer was determined. The quantitative relationship between the etch rate and the gold concentration of gold etchant was also determined. Monitoring methods have been established for photoresist developer and gold etchant. These methods will be used to determine when microcircuit processing solutions must be replenished and discarded.

Table 4. Surface Tension of Some Gold Etch Solutions

Solution	Surface Tension (dynes/cm) (μ N/cm)
Unused Etchant 1-N I_2	67.85 (678.5)
Unused Electrotec* Solution	68.79 (687.9)
Used Etchant 0.7-N I_2 0.0275 g/cm ³ Gold	67.25 (672.5)
*Electrotec, Incorporated, Garland, Texas	

FUTURE WORK

Development of monitoring methods for chromium etchant is in progress and work on tantalum nitride etchant will follow.

BDX-613-1012

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Technological Spinoff Report

L. L. Lantz, Project Leader

Published October 1973

Prepared for the
United States Atomic Energy Commission
Under Contract Number AT(29-1)-613 USAEC

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KANSAS CITY, MISSOURI

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