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CHEMICAL CHARACTERIZATION OF A MIXED (ORTHOPHOSPHORIC/POLYPHOSPHORIC) ACID ALUMINUM ETCHANT

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CHEMICAL CHARACTERIZATION OF A MIXED (ORTHOPHOSPHORIC/POLYPHOSPHORIC) ACID ALUMINUM ETCHANT

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Sensitivity of an orthophosphoric acid, a polyphosphoric acid, and an iron (III) chloride etchant to variations in process conditions was examined to determine the potential production application of the etchant system in the photolithographic fabrication of pure aluminum circuits. The effects of changes in temperature, orthophosphoric acid concentration, polyphosphoric acid concentration, iron (III) chloride concentration, and dissolved aluminum concentration on etched circuit quality and etch rate were examined. The etchant system allows reasonable variation in preparation and circuit processing without drastically affecting the etched circuit quality. Control of the etchant can be maintained over a broad range of temperatures and compositions.

In print and etch production of precision patterns in thick metal films, a fundamental understanding of the chemical etchant is required to achieve process optimization and process control.

In the printed circuit industry, chemical etching has long been the accepted method for producing precision patterns in metal films. Etching, in conjunction with present photolithographic technique, affords submicron line resolution.[1] Despite the trend to additive "lift-off" techniques for the production of circuit patterns as the pattern dimension order of magnitude approaches the grain size, chemical etching remains an important method of pattern production.

For etching of pure aluminum circuits, there are many etchant formulations available. For example, more than 80 etchant formulations are reported in the literature for the etching of pure aluminum roll foil circuits.[2] In a preliminary investigation, 80 such formulations were evaluated on the basis of a reasonable etch rate, uniformly good pattern definition, and positive photoresist compatibility. A later work reports on a spray etchant that gave edge definition variation of ± 1.27 μm.[3] This formulation was acceptable but further development was required to find a formulation that would give more predictable results, reduce dependence on operator skill and experience, and increase the use life of the etchant.

Since May 1977, an immersion etchant[4] having a composition of 75 percent (v/v) orthophosphoric acid, 25 percent polyphosphoric acid (v/v) and 20 g/L iron (III) chloride has been used at Bendix to etch pure aluminum circuits. This etchant gives good edge definition and is stable over a relatively long period. No circuit etched in this formulation has been rejected on the basis of etch quality.

The intent of this investigation was to characterize the sensitivity of aluminum etch rate and pattern definition to variations in orthophosphoric acid concentration, polyphosphoric acid concentration, temperature, iron (III) chloride concentration, and dissolved aluminum concentration and to correlate the resulting etch quality to these process variables.

With such an understanding of the etchant, appropriate process controls can be prepared to establish production readiness of the etchant.

EXPERIMENTAL METHOD

In all cases, 250 mL of freshly prepared mixed acids were placed in a 750 mL beaker. The solution was brought to the desired temperature, then the desired weight of iron (III) chloride was dissolved in the mixed acids. After dissolution of iron (III) chloride, the etch bath temperature was stabilized at the desired temperature, and an aluminum on Kapton (Du Pont) sample mounted in a specially made polypropylene holder was immersed in the mechanically agitated bath. The sample was positioned with the plane of the sample normal to the etchant flow (Figure 1).

The etch rates were determined from the etch time and sample aluminum thickness. The etch end point was determined visually. Aluminum thickness was determined from beta backscatter measurements[5] made on the material from which the samples were punched. Samples were prepared from 127 μm thick Kapton on which 11 μm of 99.999 percent aluminum had been deposited on physical vapor deposition (PVD).

Each PVD aluminum on Kapton sample was punched to a 1.346 cm diameter. In all cases except where noted, the samples were prepared from Kapton coated with PVD aluminum on which photoresist pattern had been developed. The pattern consisted of a 860 μm wide line positioned in the approximate center of the 1.42 cm^2 sample area.

In the determination of the effect of various anionic and cationic environments, the various salts were dissolved in 25 mL of freshly prepared 75 percent orthophosphoric, 25 percent polyphosphoric acid etchant at 60°C. Dissolved salt concentrations were approximately 0.05M.

The definition and reduction from the photoresist pattern line width was used to describe etch quality. To quantify line width reduction, the photoresist pattern width before etching and the circuit line pattern width after etching were measured with a closed circuit television system (CCTV) at 75X. Light micrographs (50X) were taken of the samples before and after etching. Scanning electron micrographs (700X) were taken of samples having good pattern definition or line width reduction with a scanning electron microscope (SEM). Samples for SEM work were coated with a gold-palladium film.

A constant temperature bath was used to maintain etch bath temperature to $\pm 0.5°C$. Heavy paraffin oil was used as a bath fluid. The 250 mL volume of etchant was agitated mechanically at a constant speed (250 rpm) with a 5 cm diameter impeller.

Etchant solutions were prepared from polyphosphoric acid [$H_2PO_4(PO_3H)_nPO_3H_2$, 83 to 86 percent P_2O_5], orthophosphoric acid (H_3PO_4) of reagent grade, and reagent grade iron (III) chloride ($FeCl_3 \cdot 6\,H_2O$).

For atomic absorption spectrophotometry of the etchant solutions, 1000 ppm aluminum sulfate and iron (III) chloride standard solutions were diluted to 2 to 50 ppm range with purified water.

All experiments were performed in a laminar flow clean room environment operating at 21°C, 35 percent relative humidity and with a room air particle count not exceeding 350 particles per liter (ppL) of a size 0.5 μm and larger, or 2.3 ppL of a size 5.0 μm and larger.

RESULTS

An excellent characteristic of the etchant formulation (orthophosphoric acid, polyphosphoric acid, iron (III) chloride) is its stability and the reproducibility of test results. In earlier experiments with standard hydrochloric, nitric and phosphoric acid etchants, such reproducibility was rare, making analytical characterization difficult.

Effect of Temperature

Although the mechanism of the etching reaction is hitherto unreported, it is desirable to know how the etch rate changes during the etch. In one test, the sample aluminum weight loss was monitored over the duration of the etch period. The rate of etching of aluminum was found to be constant during the etch period, and a linear relationship was exhibited between the sample weight loss and elapsed time (Figure 2).

The temperature dependence of the etch rate is Arrhenius in nature.

The activation energy of the etching is estimated from the plot and is about 8 kcal/mol (Figure 3). It is interesting to note that reported activation energies for the dissolution of aluminum under alkaline conditions range from 7.5 to 11 kcal/mol.[6,7]

Effect of Iron (III) Chloride

Though the presence of iron (III) chloride is not necessary for the bath to etch, the etch rate and etch quality are sensitive to iron (III) chloride concentration.

At 60 and 70°C there is a range of between 10 and 20 g/L in which increasing iron (III) chloride concentration is associated with increasing etch rate, as exhibited in Figures 4 and 5. The data indicate (Figures 4 through 6) that the etch rate is not sensitive to iron (III) chloride concentrations lower than 10 g/L. This indication may require further substantiation. At 50°C this range of insensitivity covers iron (III) chloride concentration of 10 to 40 g/L for all but the highest orthophosphoric acid concentrations. At higher temperatures and with iron (III) chloride concentration of between 20 and 40 g/L, the etch rate becomes relatively insensitive to iron (III) chloride concentration.

Iron (III) chloride has a significant effect on etch quality (Figures 7 through 9). Generally, iron (III) chloride concentrations greater than 20 g/L gave poor edges and line width reductions greater than 50 µm. Of the conditions studied, 10 g/L iron (III) chloride gave both good edge definition and line width reduction from the resist image of 10 to 25 µm.

Effect of Orthophosphoric Acid Concentration

Within the range studied, the relationship between etch rate and the concentration of orthophosphoric acid is one of direct proportionality (Figures 10 through 12). While the indicated relationship between orthophosphoric acid concentration and aluminum etch rate at constant temperature is clear, the relationship between orthophosphoric acid and line width reduction is not as conclusive (Figures 7 through 9). At higher temperatures (Figure 9), the data seem to suggest that the general effect of increasing orthophosphoric acid concentration is to decrease the line width reduction.

Orthophosphoric acid concentration of between 75 and 95 percent gives line width reduction from the resist image of 10 to 25 µm and an edge profile free of footing (Figure 13).

Effect of Bath Age

The effect of bath age on etch rate was evaluated by comparing the etch rate of pure aluminum in etchant samples that have been aged 30 days

(1) with iron (III) chloride added before aging,

(2) with iron (III) chloride added after aging, but before the sample was etched,

with that of pure aluminum etched in a freshly prepared etchant. The etch rate of pure aluminum in an etchant sample of the aged mixed acid in which iron (III) chloride had been added before etching did not differ significantly from the etch rate of pure aluminum in a freshly prepared bath. However, the etch rate of pure aluminum in a sample of aged mixed acid, to which iron (III) chloride had been added before aging, was 20 percent lower than the etch rate of pure aluminum in a freshly prepared bath.

Effect of Dissolved Aluminum Concentration

To test the effect of dissolved aluminum concentration on etch rate, several samples of PVD aluminum on Kapton were successively etched in one 250 mL bath, giving a final aluminum concentration of 0.0231 g/L. No significant change in etch rate from sample to sample was observed with all values within 3 percent of the mean value (Table 1). Based on this data, an initial catalytic effect of aluminum on etch rate is not indicated.

In another test, samples of PVD aluminum on Kapton were successively etched in one 250 mL bath. Pure aluminum wire of the same purity was dissolved in the bath to vary the dissolved aluminum concentration of the bath from 1 to 5 g/L. About a 4 percent decrease in etch rate was observed for every 1 g/L increase in dissolved aluminum concentration (Figure 14). It is also noted that dissolved aluminum accumulation in the bath does not significantly affect the quality of pattern definition within the product concentrations investigated.

From other tests dissolved aluminum corresponding to 6 g/L remains in homogeneous phase in the etchant. However, dissolved aluminum corresponding to 6 to 8 g/L produces a heterogeneous phase solution (precipitate formation). Dissolved aluminum concentrations of 8 g/L and above could not be obtained.

It was concluded that aluminum dissolved in the etchant does not appear to have an initial catalytic effect on etch rate. However, between 1 and 5 g/L dissolved aluminum concentration in the etchant there is a steady decrease in etch rate. Within the range investigated, the accumulated etch products do not have a significant effect on the quality of pattern definition.

Effect of Salts

The effect of iron (III) salts and transitional metal salts closely related to iron on etch rate and edge definition are listed (Table 2). Iron (III) sulfate and iron (III) phosphate give edge definition and etch rate comparable or superior to iron (III) chloride.

Methods to Determine Aluminum and Total Iron Concentration in Etchant

An analytical method for aluminum and total iron determination was developed to monitor variations in bath composition. The analytical method uses the etchant directly without prior chemical separation for the analysis. In a typical analysis, a 0.200 mL (200 λ) portion of an etch solution is diluted to a 100 mL volume with purified water. The resulting solution is analyzed for the two elements in an atomic absorption spectrophotometer using a hollow cathode lamp and a nitrous oxide/acetylene flame.

The accuracy of the method for the determination of aluminum was established by calibrating the absorbance of a series of synthesized etchant solutions consisting of varying concentrations of dissolved aluminum. Each synthesized solution represents a different ratio of dissolved aluminum to phosphate background. These synthesized solutions were compared to standard aluminum sulfate solutions in the range 2 to 50 ppm aluminum ion concentration and complete agreement in absorbance was found. For similar calibration in the case of total iron, there is a ± 3 percent agreement between synthesized solutions and iron (III) chloride standards. The absorbance of the aluminum free etchant is identical to that of deionized water. The detection limit of the method is 2 ppm.

An atomic absorption spectrophotometric method can be used as a rapid and simple quantitative analytical method for the determination of dissolved aluminum and total iron of the bath.

SUMMARY

It has been established that an etchant formulation of 75 to 95 percent (v/v) orthophosphoric acid, 25 to 5 percent (v/v) polyphosphoric acid, 10 g/L iron (III) chloride at 60 to 70°C is a potential production etchant for photolithographic fabrication of pure aluminum circuits.

The sensitivity of aluminum etch rate and circuit pattern definition to variations in the orthophosphoric acid concentration, polyphosphoric acid concentration, iron (III) chloride concentration, dissolved aluminum concentration, and temperature was characterized. Because the etchant system allows reasonable variation in etchant preparation and circuit processing without drastically affecting line width reduction and pattern definition, adequate process control can be maintained with a conventional temperature controller and a monitor of dissolved aluminum concentration. A rapid and reliable atomic absorption spectrophotometric method to monitor dissolved aluminum concentration was developed.

ILLUSTRATIONS

TABLE

Number

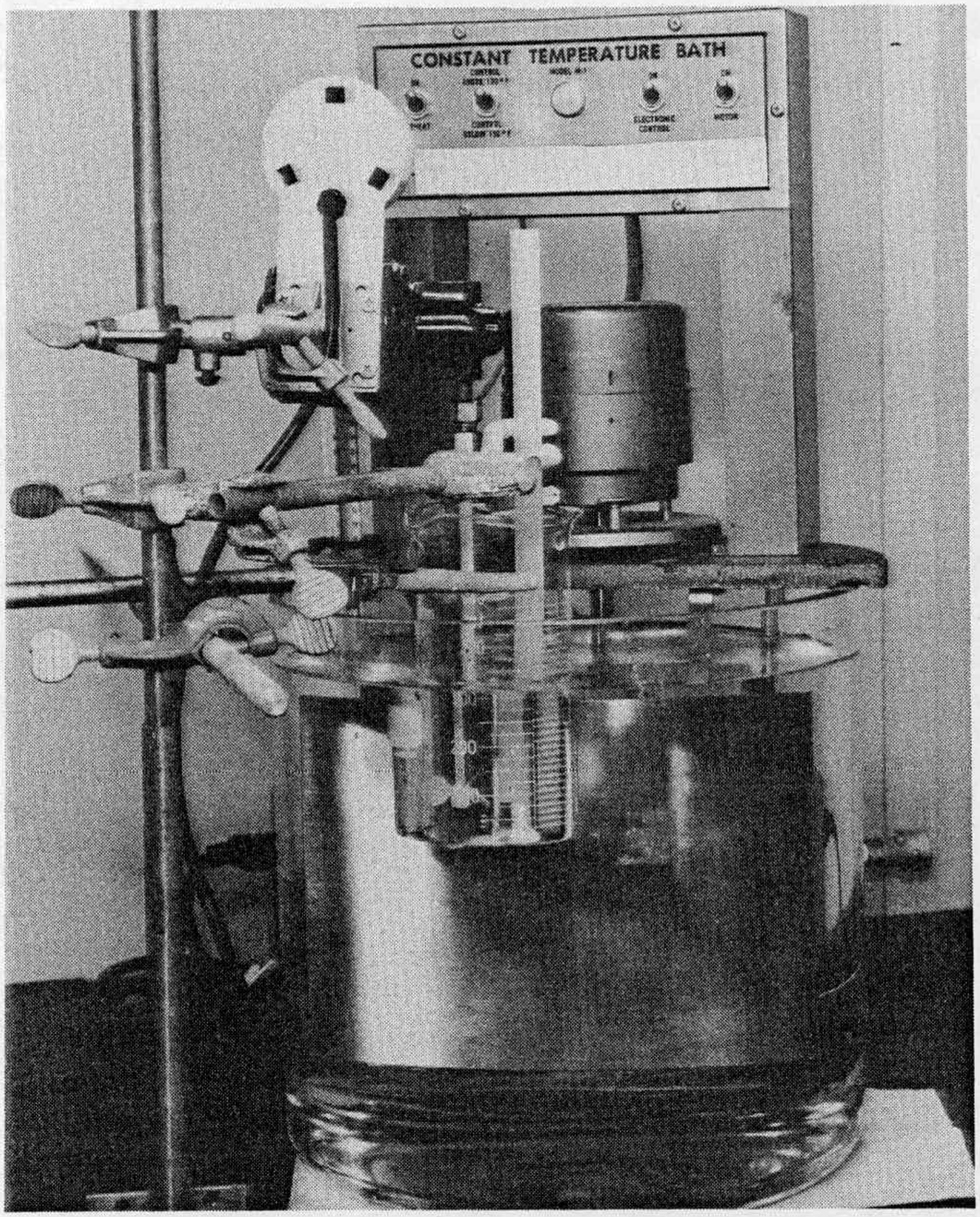

Figure 1. Experimental Apparatus

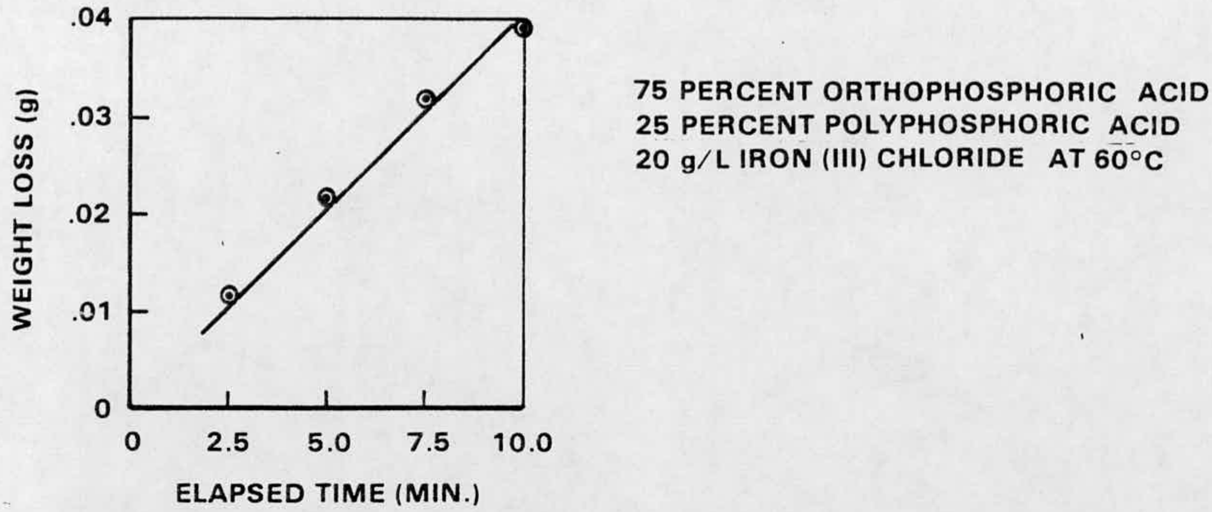

Figure 2. Weight Loss Versus Elapsed Time for Etching of Pure Aluminum

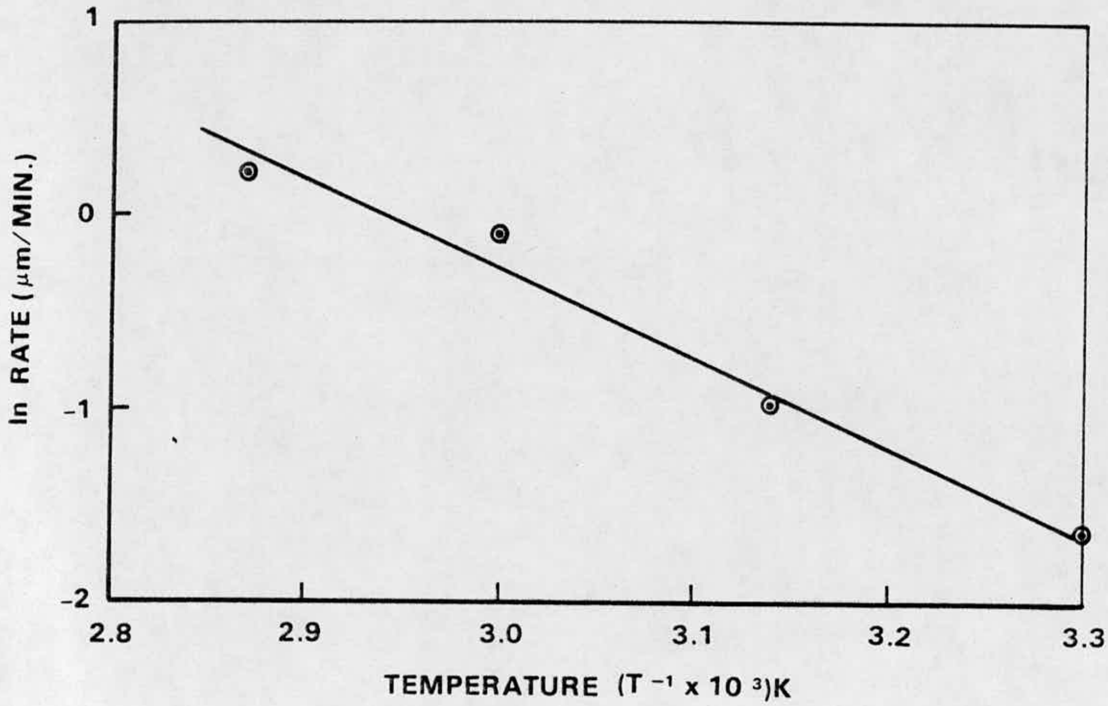

Figure 3. Natural Logarithm of Etch Rate Versus Inverse Absolute Temperature for Etching of Pure Aluminum in 75 Percent Orthophosphoric Acid, 25 Percent Polyphosphoric Acid, and 20 g/L Iron (III) Chloride

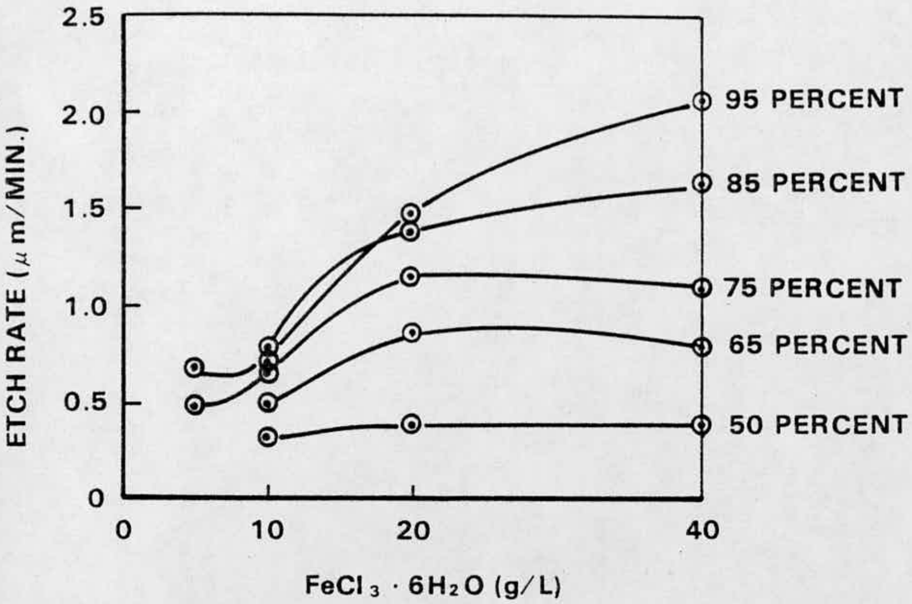

Figure 4. Etch Rate Versus Iron (III) Chloride Concentration for Pure Aluminum Etched in 50, 65, 75, 85, 95 Percent (v/v) Orthophosphoric Acid at 60°C

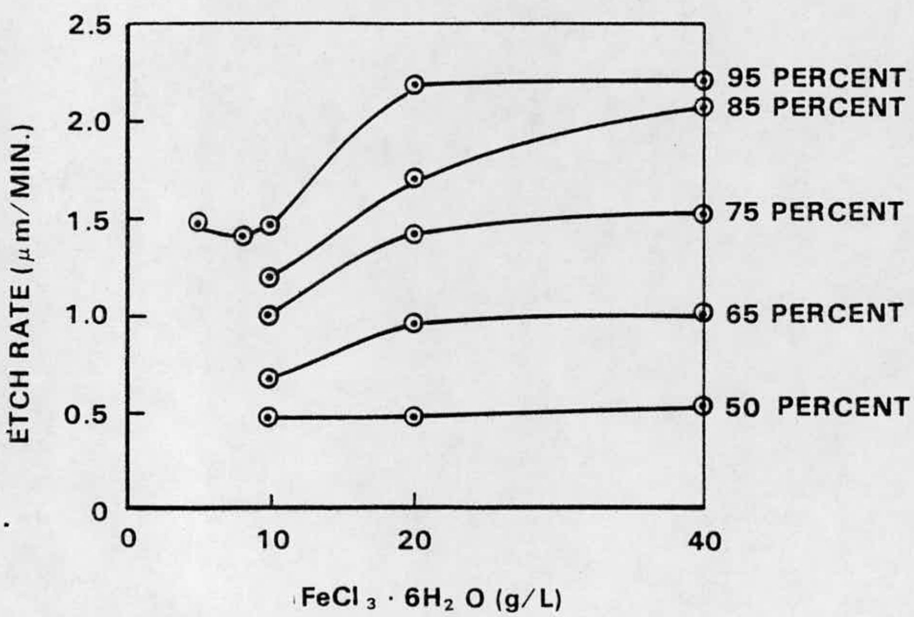

Figure 5. Etch Rate Versus Iron (III) Chloride Concentration for Pure Aluminum Etched in 50, 65, 75, 85, 95 Percent (v/v) Orthophosphoric Acid at 70°C

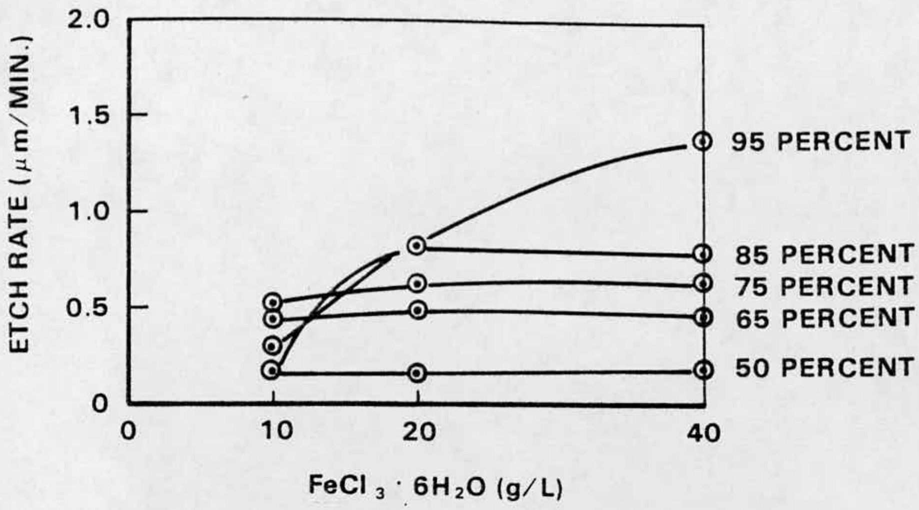

Figure 6. Etch Rate Versus Iron (III) Chloride Concentration for Pure Aluminum Etched in 50, 65, 75, 85, 95 Percent (v/v) Orthophosphoric Acid at 50°C

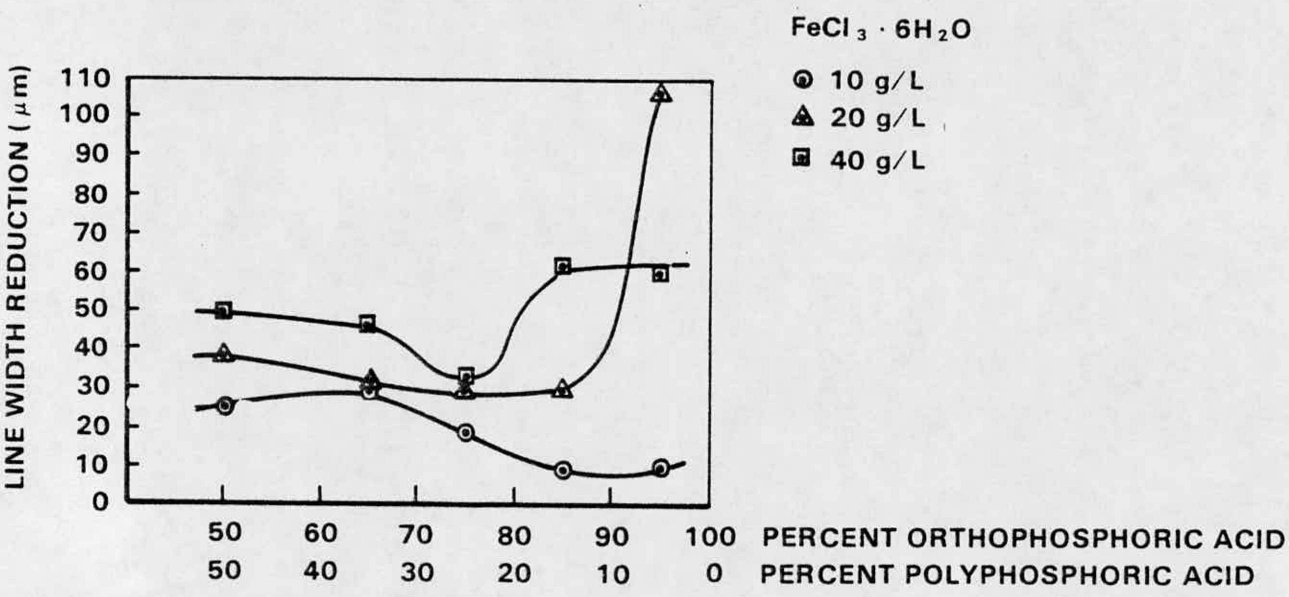

Figure 7. Line Width Reduction Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 50°C

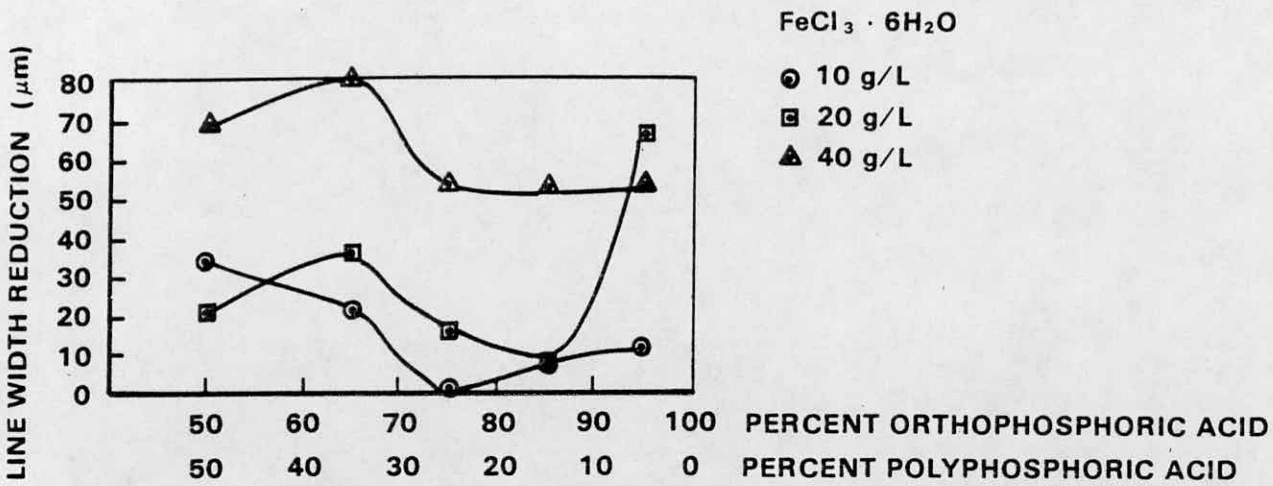

Figure 8. Line Width Reduction Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 60°C

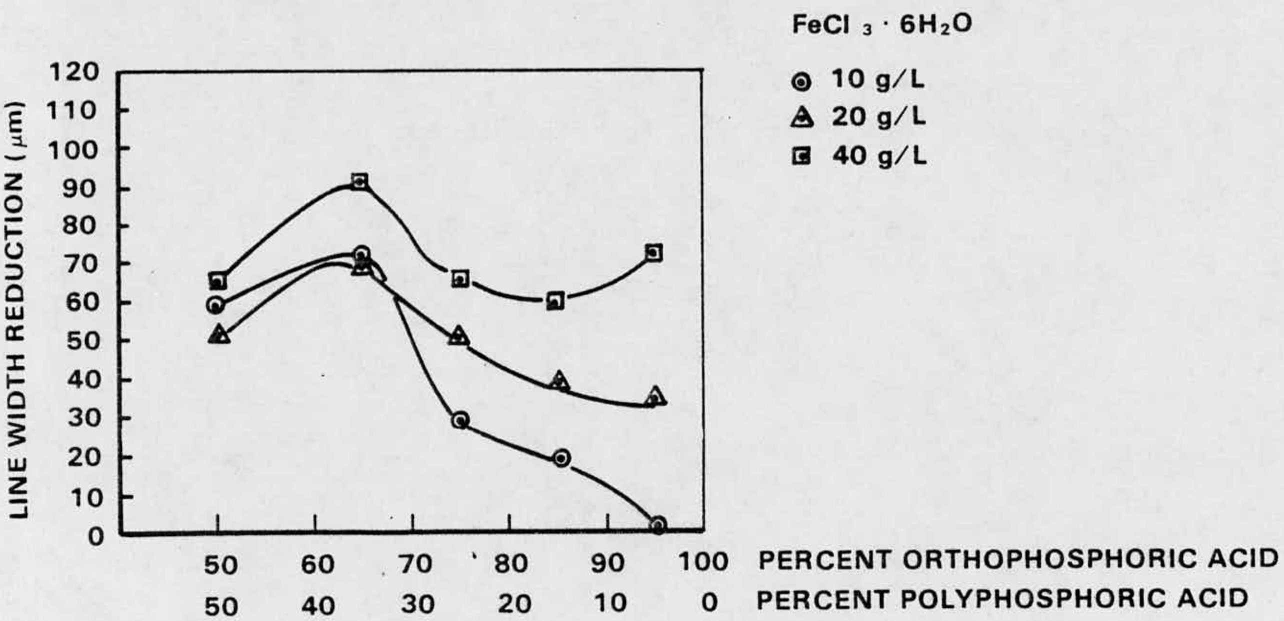

Figure 9. Line Width Reduction Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 70°C

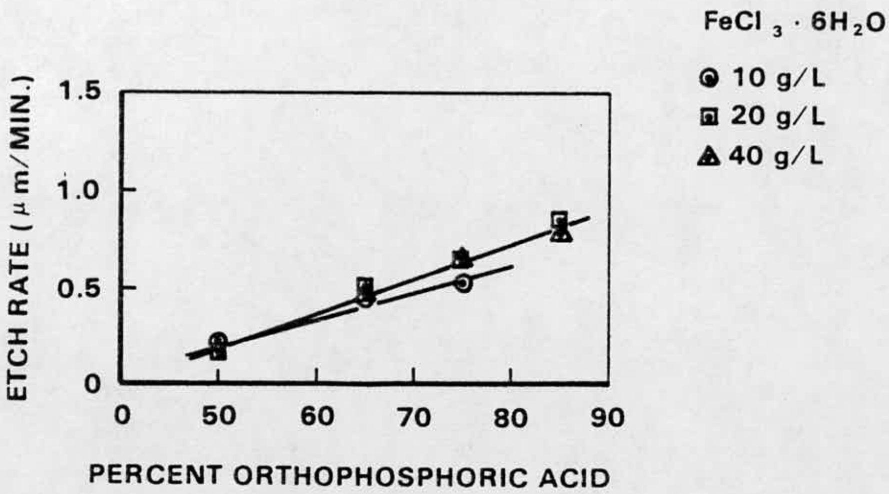

Figure 10. Etch Rate Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 50°C

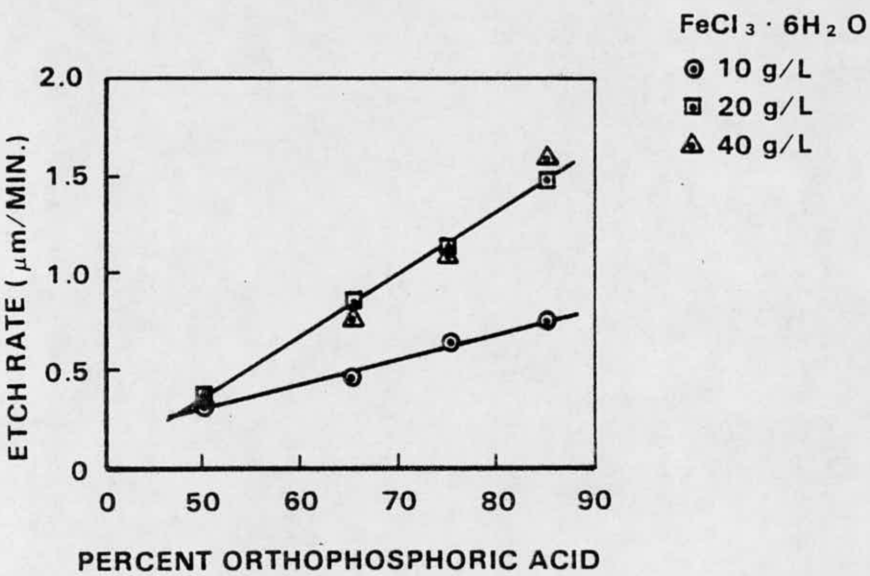

Figure 11. Etch Rate Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 60°C

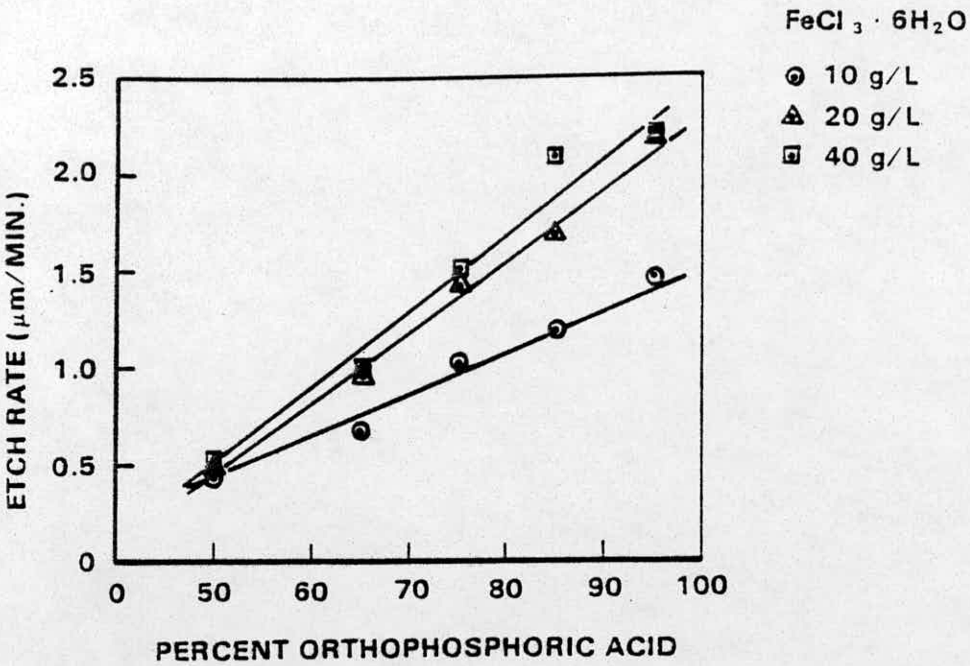

Figure 12. Etch Rate Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 70°C

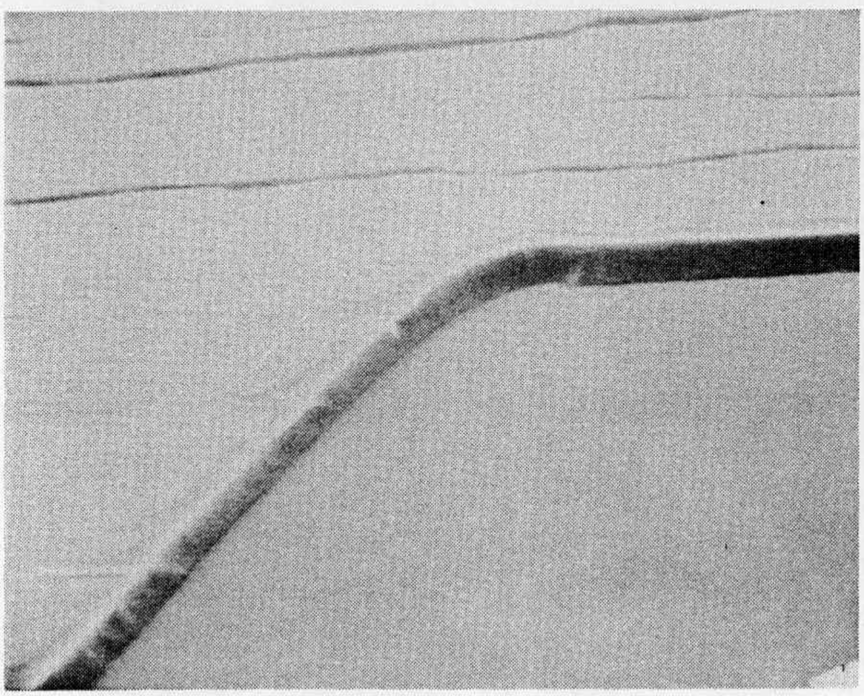

Figure 13. Sample Edge Profile at 700X (Polaroid)

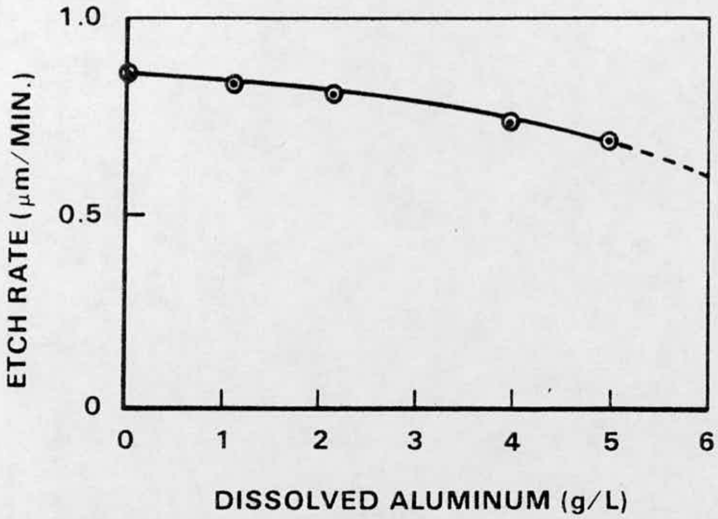

Figure 14. Etch Rate Versus Dissolved Aluminum for Etching of Pure Aluminum in 75 Percent Orthophosphoric Acid, 25 Percent Polyphosphoric Acid, and 20 g/L Iron (III) Chloride at 60°C

Table 1. Relationship Between Dissolved Aluminum and Rate of Aluminum Dissolution at Low Aluminum Concentrations

Dissolved Aluminum (g/L)	Etch Rate* (μm/min)
0.0000	1.42
0.0039	1.36
0.0077	1.33
0.0116	1.34
0.0154	1.42
0.0192	1.38
0.0231	1.36

*In 95 percent (v/v) orthophosphoric acid, 5 percent (v/v) polyphosphoric acid, 10 g/L iron (III) chloride at 70°C.

Table 2. Effect of Salt on Etch Rate and Edge Definition.

Salt	Formula	Solubility	Relative Etch Rate	Edge Definition
Iron (III) chloride	$FeCl_3 \cdot 6H_2O$	Soluble	1.00	Good
Iron (III) fluoride	$FeF_3 \cdot 3H_2O$	Some Solub.	1.61	Rough edges
Iron (III) bromide	$FeBr_3$	Soluble	0.70	Fair
Iron (III) sulfate	$Fe_2(SO_4)_3 \cdot xH_2O$	Soluble	0.67	Good
Iron (III) nitrate	$Fe(NO_3) \cdot 9H_2O$	Soluble	0.81	Footing
Iron (III) phosphate	$FePO_4 \cdot 18H_2O$	Soluble	0.91	Good +
Cobalt (II) chloride	$CoCl_2 \cdot 6H_2O$	Some Solub.	1.05	Poor
Cobalt (II) sulfate	$CoSO_4 \cdot 7H_2O$	Some Solub.	0.73	Fair
Manganese (II) chloride	$MnCl_2 \cdot 4H_2O$	Slight Solub.	0.72	Fair
Nickel (II) chloride	$NiCl_2$	Slight Solub.	0.84	Poor
No salt added			0.74	Rough

Approximate salt concentration 0.05M
Etchant 75 percent ortho, 25 percent poly at 60°C

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Dr. Htain Win, staff engineer, is a coordinator for process solution analysis and control for plating and etching in the Material Evaluations Department. His BS degree (Honors) in chemistry is from the University of Rangoon, Burma; his MS degree in analytical chemistry is from the University of Wisconsin, Madison; his PhD degree in organic chemistry is from the State University of New York at Buffalo. Dr. Win formerly worked for the Union of Burma Applied Research Institute as head of the Department of Standards; at National Aniline Division, Buffalo plant, as a research chemist; and at Pennsylvania State University, Hazleton Campus, as an assistant professor of chemistry.

Terry J. Morin, engineer, is engaged in development activity for hybrid microcircuits. His BS degree (cum laude) in chemical engineering is from Kansas State University, Manhattan. He is involved in developmental activity associated with photolithographic fabrication.