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ALUMINUM ETCHANT CONTROL STUDY

PDO 6984694, Topical Report

W. H. Knopf, Project Leader

Project Team:
J. W. Chesney

Internal Distribution August 1973

Prepared for the
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**Kansas City
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ALUMINUM ETCHANT CONTROL STUDY

BDX-613-955, UNCLASSIFIED Topical Report, Internal Distribution August 1973

Prepared by W. H. Knopf, D/812, under PDO 6984694

Study of the ferric chloride-phosphoric acid-water solution used for etching precision patterns in aluminum foil has resulted in reliable analysis procedures for detecting solution depletions. Replenishment of the etchant on a regular basis using specified guidelines has been shown to increase its effective life and produce more consistent quality than previous attempts at solution control.

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THE BENDIX CORPORATION

KANSAS CITY DIVISION

KANSAS CITY, MISSOURI

A prime contractor for the
Atomic Energy Commission
Contract Number AT(29-1)-613 USAEC

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SUMMARY

Investigation of the aluminum etchant used at Bendix was necessary to control the quality of etched parts over long periods of time. Very thin aluminum foil patterns precisely etched in a solution of phosphoric acid, ferric chloride, and water must meet size and consistency standards. The primary problem with the etchant is that composition variations caused by evaporation and depletion change the etch quality unpredictably.

To solve the problem of composition variation, a study was initiated to determine a reliable method of analyzing the etchant. When the analysis procedure was finalized, a control program was to be established in which the etchant composition would remain as close to a fixed value as possible. After trying various analytical techniques, a method was developed which accurately measures the total iron, ferrous iron, and acid concentrations. Total iron is quantitatively detected with the use of polarograph; the ferrous iron and acid concentrations are determined by separate titrations. Controls were set up which call for solution analysis at about 2-week intervals. Phosphoric acid, ferric chloride, and water are added as needed to produce the desired concentrations.

The control procedures have been followed since January 1973 on a solution made up in November 1972. As a result of these controls, the quality of finished parts has been kept more consistent than in the past. The effective life of the etchant has been lengthened, perhaps indefinitely, by the replenishment program.

DISCUSSION

SCOPE AND PURPOSE

The etch quality of thin aluminum circuits deteriorates when a given batch of etch solution is used beyond approximately 100 hours. The previous practice of replacing the complete batch after 100 hours was both expensive and time consuming. A study was initiated to establish etchant solution characteristics which vary as the resultant etch quality varies and could economically be monitored and adjusted. The reported work was accomplished between August, 1972, and January, 1973.

PRIOR WORK

Previously, no control system was used for the aluminum etchant, but additions were made by trial and error at times to improve etch quality. No work has been reported on etchant analysis and replenishment.

ACTIVITY

Fabrication of precision pattern electric circuit parts involves etching the precision patterns in thin aluminum foil. For very close tolerance parts, the aluminum is generally 0.00045 inch (0.0114 mm) thick and bonded to a nonconducting 0.005-inch-thick (0.13 mm) substrate. The areas over which etching is not desired are protected by a coating of photo resist, a light sensitive material which can be selectively removed by exposure to light. Etching is accomplished by spraying a solution of five parts-by-volume 85-percent phosphoric acid (H_3PO_4), five parts water (H_2O), and one part Rapid Circuit Etch (RCE)*, a proprietary etchant containing ferric chloride ($FeCl_3$), over the aluminum surface at 40°C.

The same etchant composition has been in use for many years because no better etchant was known and because it met the needs at that time. Investigation is beginning, however, on different etchant compositions in hopes of improvement to meet the increasing need for greater precision. In the meantime, it is necessary to improve the present etchant to obtain the best performance possible.

The problem inherent with this etchant, as with any, is that its composition changes with usage and evaporation, causing differences in etch results over

*Philip A. Hunt Chemical Corporation, Palisades Park, New Jersey.

the etchant's life. Without knowledge of what changes are taking place in the solution, its performance cannot be predicted or effectively controlled. For this reason analysis procedures were established and a program of replenishment was instated to retain a fairly constant composition.

Etchant Analysis

The ability to analyze the etchant is the preliminary step in establishing quality controls for the etching process. At any time, the etch solution contains various concentrations of acid, aluminum, and iron in both the +2 (ferrous) and +3 (ferric) valence states. The ferric iron in conjunction with the acid produces the etching action on aluminum. For the etchant to produce consistent results, the balance of iron to acid and water must remain relatively stable.

Iron Concentration Analysis

First attempts at analyzing the iron concentrations in solution with phosphoric acid and water produced inaccurate results because of some assumptions which were made. It was assumed for a close approximation that the total iron concentration stays constant throughout the solution's life and only the ferric and ferrous iron vary in relation to each other, ferrous being produced from ferric as aluminum is etched. The iron concentration in RCE is about 200 kg/m³; when diluted 10 to 1 with H₃PO₄ and H₂O, iron concentration drops to 18 kg/m³. If a known volume of etchant is titrated with potassium dichromate, using p-diphenylaminesulfonic acid as indicator, ferrous iron content can be determined. Ferric content is the difference between total and ferrous iron.

It was desirable that the error in total iron concentration caused by water evaporation be corrected since, without measuring the amount of evaporation, the magnitude of error was not known. Because of the nature of the solution, probably due to an iron-phosphorous complex, problems were encountered in conventional analytical methods for either total iron or ferric iron. Attempts to reduce ferric iron to ferrous with such agents as stannous chloride and sulfur dioxide were unsuccessful because complete reduction could not be achieved. If this were possible, titration of the resulting ferrous iron with potassium dichromate would give total iron. Colorimetric determination was not useful, because the procedures were either too lengthy or impossible in the presence of phosphorous. A method using a polarograph was developed which determines total iron concentration; titration is used to determine ferrous iron, and ferric iron is the difference between the two.

A polarograph measures the dc current between two electrodes placed in a solution, called the supporting electrolyte, containing a sample

of the material to be analyzed. Many different supporting electrolytes are used to analyze for various substances and the method for choosing one suited for the substance needing analysis is largely a matter of trial and error. The supporting electrolyte for the etch solution contains 0.1 molar potassium hydroxide and 0.3 molar triethanolamine. As the potential difference between the electrodes changes, the current is recorded versus applied voltage, and a curve (Figure 1) representing the flow of ions is drawn. At a characteristic voltage, approximately -1.0V for iron, the diffusion current of the iron ions increases rapidly until -1.25V is reached and it levels off again. Comparison of the current jumps between -1.0 and -1.25V for a known and unknown solution gives the total iron concentration in the unknown. Using this method of analysis, total iron in a solution has been measured as high as 25 kg/m^3 when it would have previously been assumed to be 18 kg/m^3 .

Figure 1. Sample Polarogram

Acidity Analysis

The acidity (concentration of H_3O^+) of the etch solution is responsible for much of the etching action. Part of the acidity is furnished by the phosphoric acid and the remainder by the iron in RCE, according to the following chemical equations.

As aluminum is added to the solution, it is etched by H_3O^+ and Fe^{+3} by the following equations.

Acidity is checked by titrating a diluted etchant sample with sodium hydroxide to a pH of 2.5. At pH values higher than 2.5, a precipitate forms and the acidity reading is not accurate. Knowing the normality of the sodium hydroxide and the volume titrated, the depletion of acid can be calculated in kiloequivalents per cubic meter (keq/m^3).

Replenishment of Etchant

Replenishment of the etch solution is necessary to minimize differences in etching over the solution's life. The values of iron and acid concentrations from the solution analysis determine the additions that are needed to bring the etchant back into the proper operation range. At approximately 2-week intervals, an analysis is made and etchant components added for replenishment. When the concentration of ferrous iron reaches about one-half that of total iron, etch rates decrease and quality suffers so that some spent solution must be dumped and newly-made etchant added. It is thought that the etchant may last indefinitely using this method; at any rate, its life is extended.

The procedures for replenishment involve measuring the total volume of etchant in the etch machine, with a calibrated depth scale, and calculating the total iron content and acid depletion. Additions of phosphoric acid, water, and RCE are then made to correct for evaporation and depletion. A typical analysis may give, for example, $19.5 \text{ kg}/\text{m}^3$ iron, $5.5 \text{ kg}/\text{m}^3$ ferrous iron, an acidity of $4.95 \text{ keq}/\text{m}^3$ and a volume of 0.110 m^3 . The desired composition is $18.0 \text{ kg}/\text{m}^3$ iron, $5.50 \text{ keq}/\text{m}^3$ acid, and a volume of 0.132 m^3 , with ferrous content less than half the total iron concentration. The additions to return the composition to normal are then calculated.

Iron

Present iron condition: $0.110 \text{ m}^3 \text{ etchant} \times 19.5 \text{ kg/m}^3 \text{ iron} = 2.14 \text{ kg iron in etchant}$

Desired iron condition: $0.132 \text{ m}^3 \text{ etchant} \times 18.0 \text{ kg/m}^3 \text{ iron} = 2.38 \text{ kg iron in etchant}$

Total iron needed $= 2.38 - 2.14 = 0.24 \text{ kg}$

RCE contains approximately 200 kg/m^3 iron; therefore, the volume of RCE needed is $0.24/200 = 0.0012 \text{ m}^3$.

Acidity

Present acid condition: $0.110 \text{ m}^3 \text{ etchant} \times 4.95 \text{ keq/m}^3 \text{ acid} = 0.545 \text{ keq acid in etchant}$

Desired acid condition: $0.132 \text{ m}^3 \text{ etchant} \times 5.50 \text{ keq/m}^3 \text{ acid} = 0.725 \text{ keq acid in etchant}$

Phosphoric acid contains 14.6 keq/m^3 . The volume of phosphoric acid needed is $0.180/14.6 = 0.0123 \text{ m}^3$.

Water

The rest of the makeup is water, and the additions so far have been 0.0012 m^3 RCE and 0.0123 m^3 phosphoric acid, which totals 0.0135 m^3 . The total addition has to be $0.132 - 0.110 = 0.022 \text{ m}^3$. The amount of water needed is $0.022 - 0.0135 = 0.0085 \text{ m}^3$.

Benefits of Replenishment

The benefits of the replenishment procedures are apparent in a comparison of etchant performance before and after replenishment. A pattern approximately 0.006 inch (0.15 mm) wide was photographed at $150\times$ with resist still present. Figure 2 was etched in January, 1973, before replenishment took place on the same day. Edge appearance is somewhat ragged and etching of the aluminum beneath the resist, called undercut, is fairly great. The sample in Figure 3 was etched after additions had been made to return the composition to normal, and the decreased raggedness and undercut is readily apparent. Pictures such as these are taken before and after all replenishment cycles to check the etch quality.

Figure 2. Etch Quality Before Replenishment, 150X

Figure 3. Etch Quality After Replenishment, 150X

ACCOMPLISHMENTS

Analysis methods have been established which accurately measure depletion of etch components, and controls have been set up to determine changes and additions needed to correct depletions. Over the 5 months since initiating the analysis and replenishment procedure, the quality of finished parts has been acceptable and consistent. As an added benefit there is less down time; additions can be made quickly to return the etch results to normal, instead of having to completely dump and replace the solution.

FUTURE WORK

Using the information obtained from this investigation, some work will be directed toward an automated method of analysis and replenishment of the etch solution to keep a constant control over it. Work is in progress on the investigation of new etchants to replace the current mixture, with the basic goals of

improving slope, undercut, and edge roughness. A method will also be sought to minimize the differences in techniques among operators to increase etching consistency as much as possible.