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Research Article

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A New Quick Sieve Method for Etchant Evaluation and UBM Cu Undercut Improvement

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Abstract

In this study, we have developed a new method that can be used for quick evaluation and testing for metal etchants in the semiconductor package process. With this new method, we can obtain the performance index of the etchant in the shortest time (for example, for the metal etching rate and undercut), so that the formula of the etchant can be quickly determined. In other words, if we use a test material with the same structure as the actual product, this new method can also evaluate whether the etchant formula has potential side effects on the product, for example, whether the etchant will have the galvanic effect on the structure; or whether the etchant may be corrosive to other metals in the actual product; or whether the etchant is aggressive to the PI material used in the actual product. By designing the test according to the structure of the actual product, relevant information on side effects can be obtained with this new method. This new verification method can also be used in the development of new etchant formulations. For example, in this paper, we use this approach to adjust an etchant additive formulation to address the under-etching problem of a commercially available copper etchant (phosphoric acid/hydrogen peroxide). Based on real-world validation, breakthrough results can be achieved in only 3% of the time of traditional validation methods. This new validation method is proven to significantly reduce test time and increase the efficiency of new etchant development and validation.

Keywords: UBM, Cu etchant, UBM etching, Copper pillar bump, RDL, FOSIP

Introduction

Generally, manufacturers of etching chemicals do not know the actual situation of how etchants are used in customer production lines. Even if users provide relevant operating recipes, the etchant maker still cannot catch the full picture to set up a perfect specification that satisfies the requirement of the etchant. This is because many engineers who use etching solutions do not know what a complete etching solution requirement specification is; therefore, the development process of etching solutions is mostly carried out in a try-and-error manner, so the maker of etchant needs to spend a lot of the development time and cost for new etchant research, for users, it is also the verification engineers to invest a lot of time and costs in evaluating and testing new etchant formulations.

In the traditional evaluation of etchant formulations, there are three basic items to be tested:

a) Etching rate

b) Undercut

c) Side effect

Examples of side effects include the ability of the etchant to corrode other metals or other organic or inorganic materials in the process.

Since the metal undercut occurs under the bump or trace in the etching test, cross-sectioning or FIB (focused ion beam) [1] is usually required after the etching test to obtain the metal undercut data. Cross-sectioning not only requires a lot of operating time but also incurs high operating costs. In addition, to test the etchant formulation, wafers with traces or bumps of the target metal must be prepared as test samples. The preparation of such test sam-

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ples is inherently time-consuming and costly. Figure 1 shows the cross-section of the bump with UBM undercut after the etching test.

Figure 2 compares the cross-sections obtained by the traditional manual method and by FIB. It is evident that the undercut with ultra-thin metal films is not easily observed in traditional manual cross-sections. It is often necessary to use more accurate Cross section technology such as FIB Figure 2b for better observation. However, using FIB to get the data and results you want means more time and money spent on analysis (Figures 1,2).

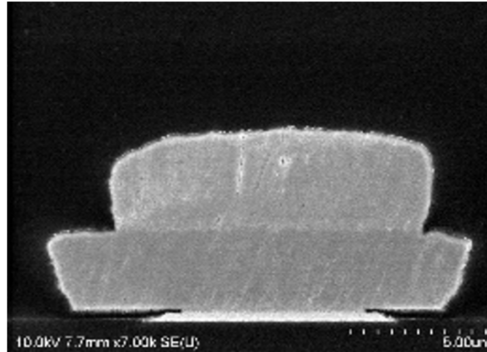


Figure 1: UBM undercut survey by traditional manual cross section.

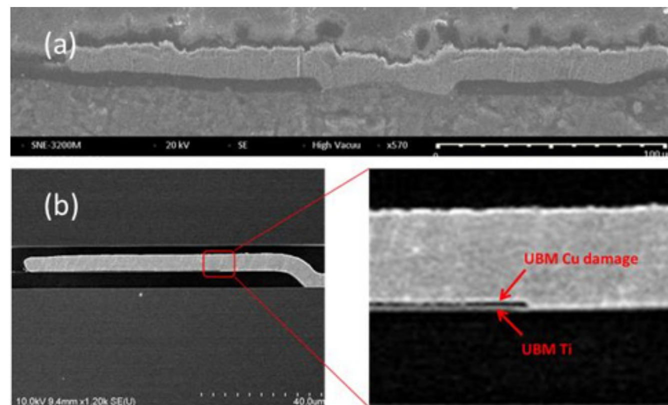


Figure 2: UBM undercut survey by traditional manual cross section.

The results show that FIB has high resolution making it easy to detect UBM copper cuts that are difficult to detect in manual cross-sections. It is clear from Figure 2b that the UBM copper undercutting under nickel is very severe. Such a severe undercut effect is caused by a typical galvanic effect [2,3]. Such results cannot be obtained with traditional etch solution evaluation methods. Typically, it is only after a particular product made using an etchant develops unusual functionality or a large number of integrated circuits made using an etchant are scrapped, that engineers begin to focus on and investigate the true cause of the anomaly. However, such a troubleshooting process is too late and too costly. Therefore, the new test method in this study offers hope not only for accelerating the development of new etchant solutions but also for avoiding the huge cost loss caused by similar side effect problems. The results show that FIB has high resolution making it easy to detect UBM copper cuts that are difficult to detect in manual cross-sections.

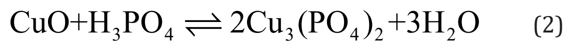
Material and Methods

Cu Etchants Comparison

According to the etching reaction principle, the copper etchants commonly used in the semiconductor packaging market can be divided into three categories. The first category is H_2O_2-based etchants [4,5]; the second category is NH3-based etchants; and the third category is metal oxide-based copper etchants.

The etching principle of a hydrogen peroxide-based Cu etching agent is to etch copper by oxidation and substitution dissolution, and its etching reaction equation is shown in Equation (1), Equation (2), and Equation (3) [6].

$$Cu + H_2O_2 \rightleftharpoons CuO + H_2O \quad (1)$$



$$CuO+H_3PO_4 \rightleftharpoons 2Cu_3(PO_4)_2+3H_2O \quad (2)$$

$$CuO+H_2SO_4 \rightleftharpoons CuSO_4+H_2O \quad (3)$$

In addition, some H_2O_2-based copper etchant manufacturers add special chelating reagents that they claim significantly improve etch rate stability and reduce undercut. Figure 3 is an illustration of the etching mechanism of hydrogen peroxide-based etchants with chelating compounds (Figure 3).

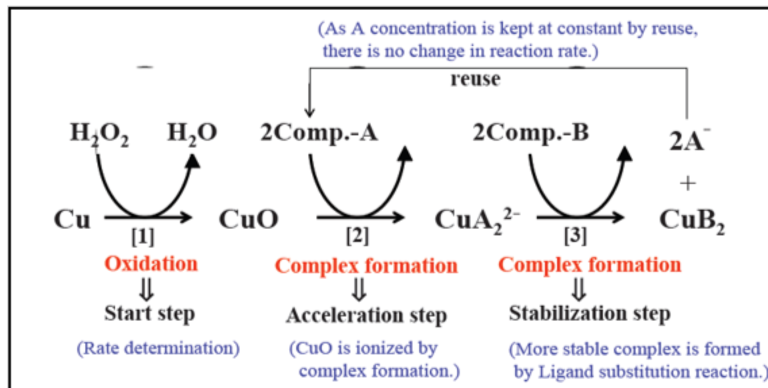
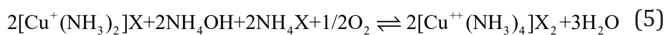


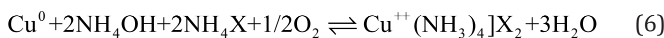
Figure 3: The reaction mechanism of H_2O_2-based etchants with chelating agent compounds.

The reaction mechanism of the second category, the NH3-based etchants, is shown in the following reaction equations, where Equation (4) is the main etching equation, Equation (5) is the reagent regeneration reaction, and Equation (6) is the overall reaction [7].

$$Cu^0+[Cu^{++}(NH_3)_4]X_2 \rightleftharpoons 2[Cu^+(NH_3)_2]X \quad (4)$$



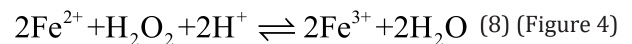
$$2[Cu^+(NH_3)_2]X+2NH_4OH+2NH_4X+1/2O_2 \rightleftharpoons 2[Cu^{++}(NH_3)_4]X_2+3H_2O \quad (5)$$



$$Cu^0+2NH_4OH+2NH_4X+1/2O_2 \rightleftharpoons Cu^{++}(NH_3)_4]X_2+3H_2O \quad (6)$$

From Equation (4), Equation (5), and Equation (6), it can be seen that NH_3 forms complexes with copper, and as a result, the etching reaction mechanism is similar to that of Figure 3. The copper etchant of the third category uses metal with higher activity than copper as an oxidizing agent to oxidize and etch the copper surface. As shown in Equation (7), the oxidized etchant can be removed by a stronger oxidant such as H2O2 to restore the activity of the etchant, and this reaction is shown in Equation (8) [8,9].

$$Fe^{3+}+Cu \rightleftharpoons Fe^{2+}+Cu^{2+} \quad (7)$$



$$2Fe^{2+}+H_2O_2+2H^+ \rightleftharpoons 2Fe^{3+}+2H_2O \quad (8)$$ (Figure 4)

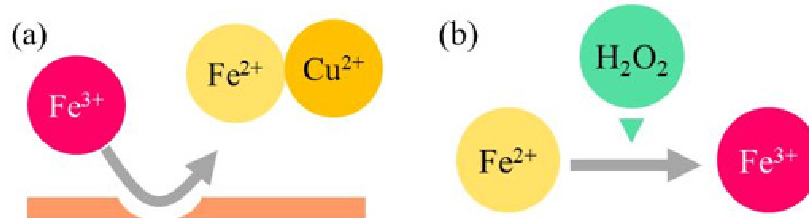


Figure 4: Cu etching mechanism by metal oxidant.

a) A metal with higher activity than copper I used as an oxidant to oxidize and etch the Cu surface.

b) The oxidized etchant can be removed by a stronger oxidant such as H_2O_2 to restore the activity of the etchant.

As shown in the reaction mechanism diagram in Figure 4, trivalent iron ions react with the copper metal surface to form divalent iron ions and divalent copper ions, which are dissolved in the solution, allowing the copper metal surface to be smoothly etched [10]. When the ferrous ions in the etchant are depleted, the etchant becomes less active, so a stronger oxidizer must be used to oxidize the ferrous ions to ferric ions. According to the literature, the most commonly used strong oxidant to restore etchant is hydrogen peroxide (H_2O_2). In addition, these copper etching solutions generally contain halogenated elements (e.g., Cl-), which is of great concern to the semiconductor packaging industry due to product reliability issues. Halogen-free has become a new standard in the semiconductor packaging industry, and as a result, the use of this type of copper etchant in semiconductor packaging processes is now becoming rare.

Material Preparation for The New Test Method

Test sample preparation for the new etchant test method utilizes common UBM sputtering and a photo mask process. The test sample preparation process is shown in Figure 5. After one photo mask exposure and curing using standard UBM sputtering and the PI used in the process, the sample is ready. As shown in Figure 5, the metal intended for etch testing is finally exposed to the open window of the PI and can then be tested for etchant (Figure 5).

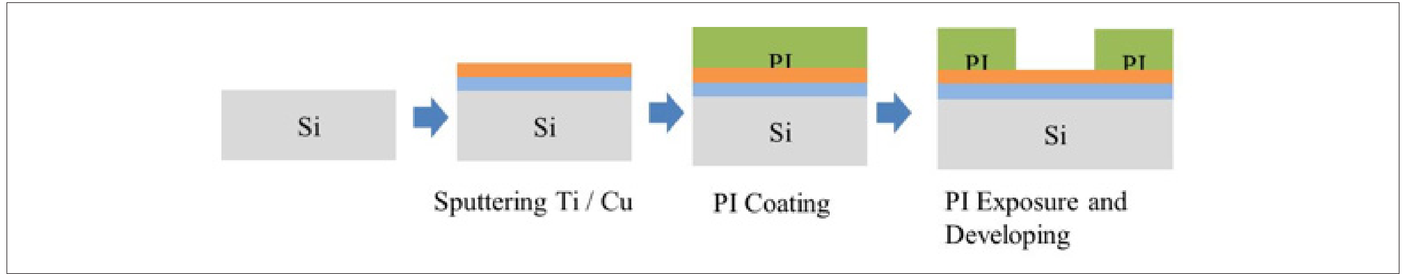


Figure 5: The sample preparation process for the new etching test method, the preparation for the Cu etching test is shown as an example.

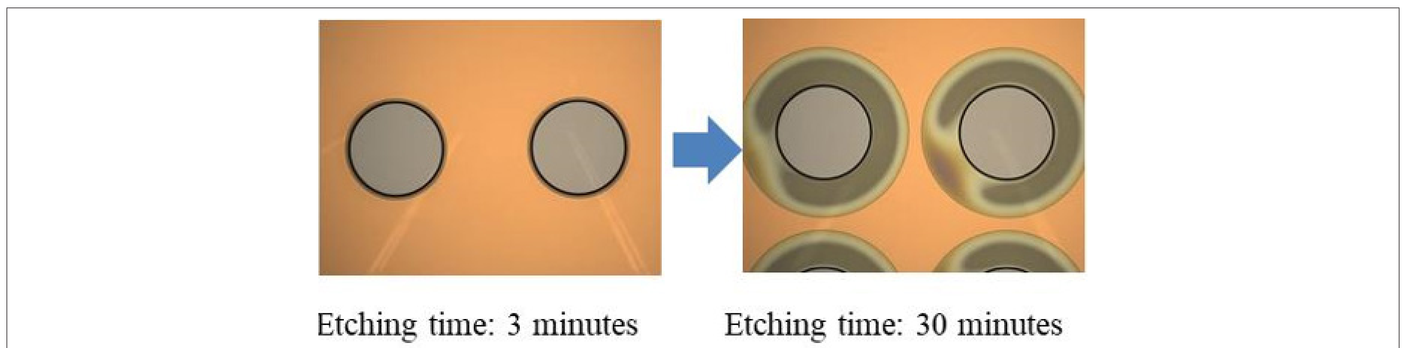


Figure 6: H_2O_2-based Cu etchant was tested by the new etching method. The result shows the degree of undercut at different etching times.

An etch test using such a test sample yields the results shown in Figure 6. Figure 6 shows the result of testing with H_2O_2-base Cu etchant (Figure 6).

If we ignore the cost and focus on the average time required at each station, we can get the result as shown in Figure 7. Using the traditional analysis method, it takes about 16.6days/sample from the preparation of the test sample to the final data collection and analysis. If the more expensive FIB is used is the undercut analysis, it takes about 16.1days/1 sample for all analysis processes. In contrast, if the new method of this paper is used, the time from the preparation of the test sample to the completion of data collection is only 8.2days/sample. The new method can save more than 50% of the time from an entire process (Figure 7).

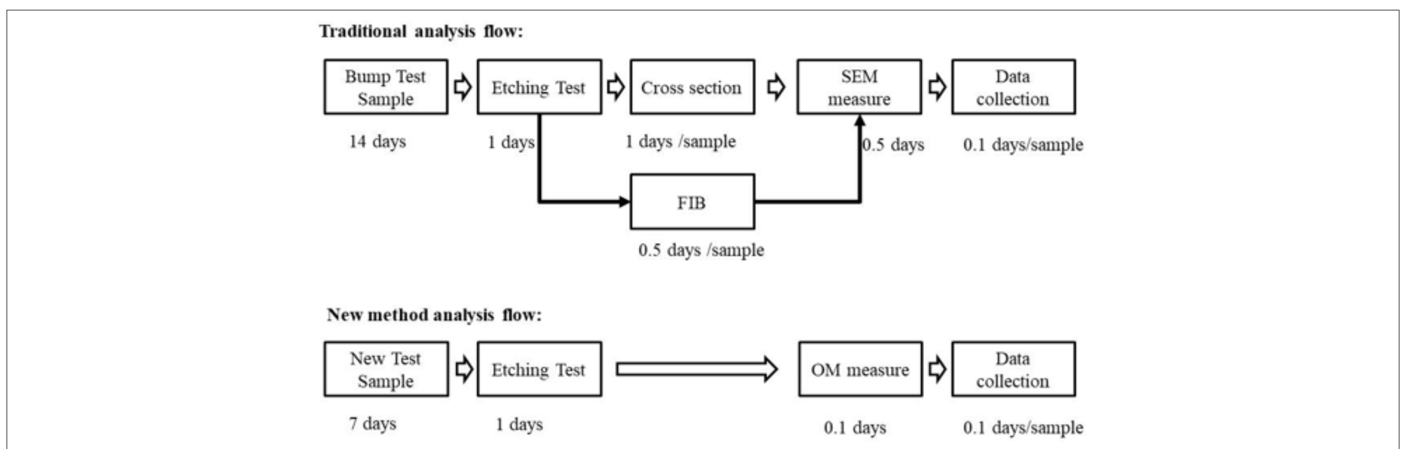


Figure 7: A comparison of analysis methods shows that the new etching test method saves a lot of time and money, thus improving the efficiency of new etchant development.

Galvanic Corrosion and Test Sample Design

Galvanic corrosion is a local form of corrosion that is limited to the contact zone. The intensity of corrosion decreases rapidly with increasing distance, even by a few centimeters, from the point of contact between the two metals. This decrease is greater when the electrolyte is a poor conductor.

This type of corrosion is so localized due to the nature of electricity. Electrical current flows according to a path as linear as possible. Since galvanic corrosion tends to develop at depth, it is not uncommon that galvanic corrosion perforates parts several millimeters thick [11-13] (Figure 8).

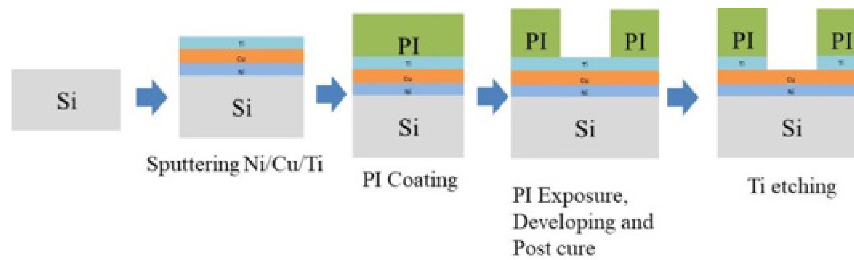


Figure 8: The structure of the test sample is for galvanic corrosion testing of Cu etchants.

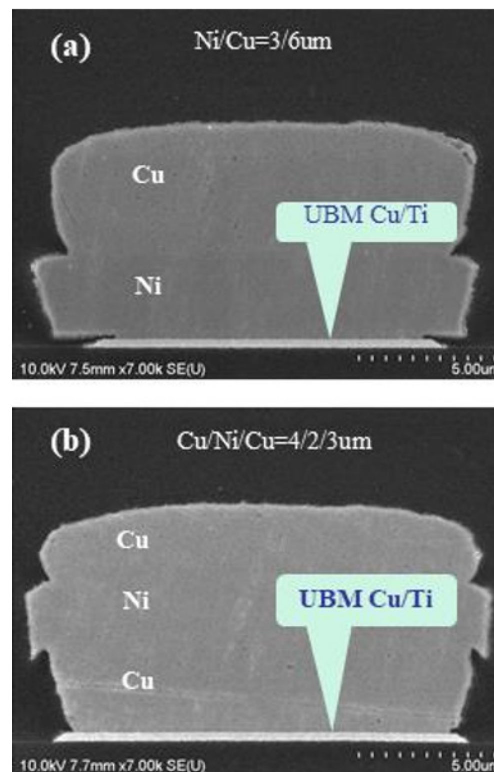


Figure 9: Comparison of galvanic corrosion effects for different copper thicknesses.

According to the principle of galvanic corrosion and our practical experience, we designed the structure in Figure 8 as a galvanic corrosion test specimen for the new Cu etching agent. The thickness of the copper was 2000A with reference to the result in Figure 2(b). In addition, as known from the literature and from the results in Figure 9, the galvanic effect is significantly weakened as the thickness of the copper increases.

The results in Figure 9 clearly show that the galvanic corrosion effect mainly depends on the copper thickness between the metals Ni and Ti. When the copper thickness is as thin as the nanometer scale, the galvanic corrosion effect becomes more pronounced, with the result that the degree of undercutting is more severe. As the thickness of the copper metal increases to the micron level, the galvanic corrosion effect becomes virtually ineffective, and the degree of undercutting is determined solely by the etching time [14-16] (Figure 9).

Result and Discussion

In the data of Figure 7, if we ignore the preparation time of the test specimens and compare only the actual test etch times of a sufficient number of test specimens for statistical analysis, we obtain the results shown in Figure 10, which is a comparison table of the data for 25 test specimens. In Figure 10 shows that the new etchant test method takes only 3% of the time compared to the traditional test method (Figure 10).

The new analysis method reduces the testing time by about 97%. In other words, the results obtained in 3 days with the new method would have taken 3 months with the traditional method (Figure 11).

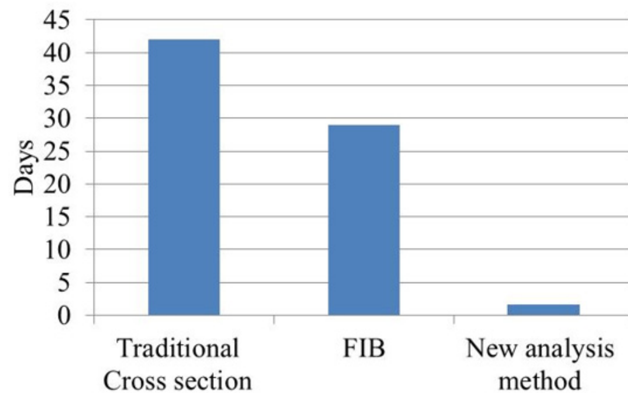


Figure 10: The result of process time comparison by different analysis methods which are based on 25 test samples.

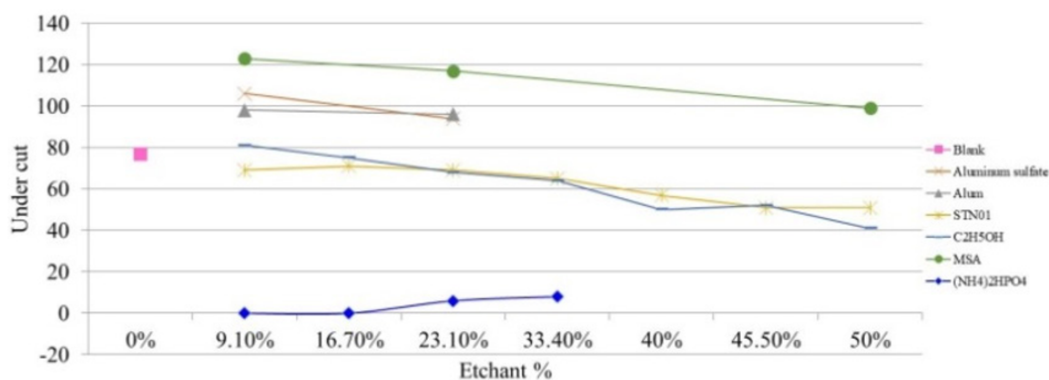


Figure 11: The effects of additives. Ammonium phosphate is the best additive and significantly reduces undercutting.

Figure 11 shows the test results of using the new test method to screen and select additives that are effective in reducing undercut. The test was conducted with a total of 25samples. The results show that the addition of an appropriate amount of diammonium phosphate to the phosphoric acid/hydrogen peroxide-based copper etchant has a very significant inhibitory effect on copper undercutting [17].

The Additives Used for the Testing Can be Divided into the Following Categories

The first type of additive has a surfactant function, such as Methane Sulfonic Acid (MSA) [18]. Since the copper etchant used in the test is phosphoric acid/hydrogen peroxide based, MSA, which belongs to the sulfuric acid system, could not inhibit the undercut, but leads to an accelerated undercut problem in the phosphoric acid system. Under such a condition, the surfactant property of MSA actually promotes etchant attack on Cu undercut instead of inhibiting free hydrogen ions.

The second type of additive is inorganic salts. In general, the purpose of adding inorganic salts is to slow down the etching rate through ionic effects [19]. In this test, inorganic salts such as sulfates were added to the copper etch solution, but the results showed that sulfates had almost no effect and actually increased the degree of the undercut.

The third type of additive is neutral organic alcohol. As mentioned in the literature, the addition of organic alcohol additives significantly alters the polarity of the etching solution when added at more than 50% of the solvent. As the polarity changed by the solvent changed, the ability of the etchant to dissociate decreases, causing a decrease in the etching rate [20-22]. If organic alcohol has polar adsorption on the metal surface, the degree of undercutting

is also further reduced. The test results of this study showed that when the concentration of organic alcohols reached a critical point (the percentage where it became the main solvent), its inhibitory effect on undercutting can be clearly detected. From the data in Figure 11, it can be seen that organic alcohol additives have the effect of inhibiting undercut, with an estimated degree of improvement of around 40~50%. In addition, STN01, which is used as a metal oxide stripper in industry, was selected for the same test in this study and was found to have a comparable profile to organic alcohols.

The fourth type of additive is the inorganic salts which are used in combination with the phosphoric acid/hydrogen peroxide-base copper etchant. Ammonium phosphate was chosen as an additive because it reacts with phosphoric acid to form a weak acid and create a buffer solution that maintains a stable pH range, thereby controlling the etching rate of the copper etchant and therefore the degree of undercutting. The reaction of phosphate and phosphoric acid also limits the ability of phosphoric acid to release free hydrogen ions. Free hydrogen ions in the hydrogen peroxide-based etchant are the main attack initiators that cause the metal to be corroded. Therefore, by controlling the amount of free hydrogen ions, the rate of copper dissolution can be effectively controlled, which also effectively reduces the degree of undercutting.

Figure 11 shows that, after adding an appropriate amount of ammonium phosphate salt, the Cu UBM with a thickness of 2000angstroms can be removed in 5minutes. To enhance the effects, we extended the etch test time to 30minutes (about a 6-fold increase) but found that there were virtually no undercut problems after the test, and the attack by the TiW UBM was effectively suppressed. This demonstrates that adding an appropriate amount of ammonium phosphate to the phosphoric acid/hydrogen peroxide-based copper etchant can indeed effectively alleviate the problem of the RDL trace or bump's undercut.

Figure 12 compares SEM images from etching tests using phosphoric acid/hydrogen peroxide etchant alone Figure 12a and a new etchant with ammonium hydrogen phosphate additive Figure 12b. The results show that the etching solution without diammonium hydrogen phosphate additive has a significant erosion effect on Cu bumps and traces, and also causes significant erosion on TiW UBM. In contrast, the new etchant with the diammonium hydrogen phosphate additive had a significant protective effect on copper bumps and traces, and the erosion of TiW was also significantly improved (Figure 12).

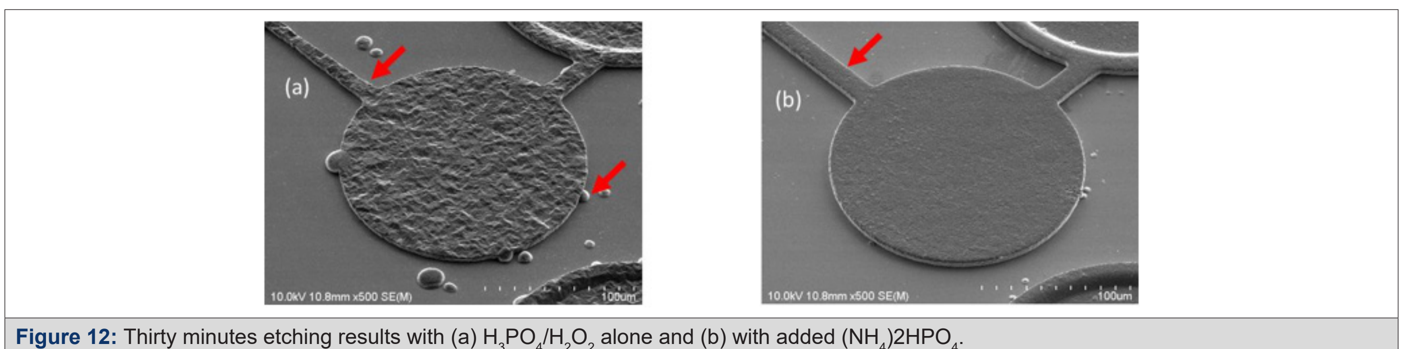


Figure 12: Thirty minutes etching results with (a) H_3PO_4/H_2O_2 alone and (b) with added $(NH_4)2HPO_4$.

Since the additive is diammonium hydrogen phosphate, and phosphate ions and ammonium ions will be dissociated simultaneously in the etching solution, it is inferred that the reaction mechanism of this etching should be the same as the reaction of Equation (4), Equation (5), and Equation (6).

Diammonium hydrogen phosphate mixed with phosphoric acid will create a buffer solution [23,24] with a pH value of around 6.25. Because of the weak acidity of the buffer solution, the etching rate on copper is only about 25% of that of the phosphoric acid/hydrogen peroxide etchant alone, and the attack on the surface of the copper metal is also significantly reduced, as shown in the SEM photo in Figure 12b. As shown in Figure 12a, there are obvious tip bumps around the Cu bump pad, which are formed after the significant attack of TiW by the Cu etchant.

Conclusion

In this research, a new method for etchant verification in the semiconductor package etching process was developed. The test results show that this new method can significantly improve the efficiency of the verification of new etchants. Our research shows that the results achieved in one day with the new method take up to 30 days with the traditional method. The new method can save up to 90% of the cost compared to the conventional method, the main difference being that the new method saves a lot of cross-section work.

This test method, combined with the experimental design of the structural adjustment, can also be an effective tool to evaluate the influence of the new solution on galvanic corrosion. This method allows the experimental design to be adjusted according to the actual conditions of the product and can achieve simulated validation similar to the testing of real products. This new validation method was used to screen phosphoric acid/hydrogen peroxide-based copper etchant additives. It was found that when ethanol and STN01 (a metal oxide stripper) were added at concentrations greater than 50% of the solvent, copper UBM undercutting was significantly improved, with improvements ranging from approximately 40-50%.

In phosphoric acid/hydrogen peroxide-based copper etch solutions, the addition of sulfuric acid series inorganic salts does not provide the same protection or etch inhibition as sulfuric acid series etch solutions.

For additives that reduce surface tension, the results show that they do not reduce the degree of undercutting, but rather increase the risk of undercutting.

Our results show that the addition of diammonium hydrogen phosphate into the phosphoric acid/ hydrogen peroxide-based copper etchant significantly reduces the copper etching rate. However, using this new formulation of copper etches provides excellent protection for copper bumps and traces with little to no copper UBM undercutting. Such a result would be very beneficial to the semiconductor packaging industry as circuit design moves to finer pitch circuit design where any undercutting would limit the development of such designs.

Data Availability

Data will be made available on request.

Funding

Not applicable.

Credit Authorship Contribution Statement

Chen Yu Wang: Data curation, Formal analysis, Investigation, Methodology, Writing original draft.

Teh-Hua Tsai: Methodology, review & editing.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Blauner Patricia G (1992) Focused Ion Beams: A Tool for Repair and Restructuring: Focused Ion Beam Process, Japanese Journal of Applied Physics. JJAP series 5: 309-315.
2. Guang Ling Song (2010) Potential and current distributions of one-dimensional galvanic corrosion systems, Corrosion Science 52(2): 455-480.
3. John W Oldfield (1988) Electrochemical Theory of Galvanic Corrosion, American Society for Testing and Materials. Philadelphia pp. 5-22.
4. Antonopoulos IA, Karantonis A (2017) Electrochemistry of copper in methanolic solutions: Anodic oxidation and fabrication of hydrophobic surfaces. Electrochimica Acta 240: 195-202.
5. Luo Shengwei, Weng Huizhu (2022) Heat-treatment effect on the wettability of a copper mesh surface from superhydrophilic to hydrophobic, Dissertation of the Department of Mechanical Engineering, Chung Yuan University.
6. Li Chin Chiang (2007) Discussion on the influence of different parameters and methods on microetching performance of sulfuric acid/hydrogen peroxide. Dissertation of the Institute of Chemical Engineering. Taipei University of Technology pp.1-62.
7. Xu JF, Ji W, Shen Z X, Tang SH, Ye XR, et al. (1999) Preparation and Characterization of CuO Nanocrystals. J Solid State Chem 147(2): 516-519.
8. WU Pei Chang, CHEN Jing, Chen Liang (2012) PCB acid etching mechanism, technological parameters and troubleshooting. Printed Circuit Information pp.2.
9. Chun Chien Kuo (2004) The Study of Copper Etching in Acid Solutions. National Taiwan University Chemical Engineering.
10. Liu Yihong, Zhang Zhongwei, Wei Huiwen, Hu Zhuochun (1995) Scientific Experiment Design of Photosensitive Circuit Board, Science Education Monthly Issue pp.293.
11. Branko N Popov (2015) Galvanic Corrosion. in Corrosion Engineering.
12. HP Hack (2016) Galvanic Corrosion,in Reference Module in Materials Science and Materials Engineering.
13. HP Hack (2010) Corrosion in Liquids, Corrosion Evaluation. in Shreir's Corrosion.
14. A Atrens, GL Song (2011) Numerical modelling of galvanic corrosion of magnesium (Mg) alloys. in Corrosion of Magnesium Alloys.
15. The Hue Tsai, Chen Yu Wang (2023) A study of ammonium bifluoride as an Agent for Cleaning Silicon Contamination in the wafer dicing process Appl Sci 13(9): 5294.
16. The Hue Tsai, Chen Yu Wang (2023) Metal Corrosion Protect in Ammonium Bifluoride-Base Cleaning Agent for Si Contaminants. Aspects in Mining & Mineral Science 11(4): 1286-1291.
17. John R Van Wazer (1958) Phosphorus and Its Compounds - Volume I: Chemistry. New York: Interscience Publishers, Inc pp.503.
18. Balaji R, Pushpavanam Malathy (2003) Methanesulphonic acid in electroplating related metal finishing industries. Transactions of the Imf 81(5): 154-158.
19. International Union of Pure and Applied Chemistry (2005) Nomenclature of Inorganic Chemistry (IUPAC Recommendations. Cambridge (UK) ISBN 0-85404-438-8.
20. March Jerry (1985) Advanced Organic Chemistry, Reactions, Mechanisms and Structure, third Edition, John Wiley & Sons. ISBN 0-471-85472-7.
21. Reichardt C (1991) Solvents and solvent effects in organic chemistry. 2nd (Edn.,). VCH, New York, USA.
22. Szu Chen Chem (2005) Quantum Chemical studies of Dissociation and Rearrangement of o-Nitrotoluene and of Solvent Effects of 9-Fluorenone, National Chiao Tung university.
23. Medicago AB (2010) Phosphate buffered saline specification sheet.
24. Dulbecco R, M VOGT (1954) Plaque formation and isolation of pure lines with poliomyelitis viruses. In: J Exp Med 99(2): 167-182.