

## SURFACE IONIZATION EFFECT OF MIXED GAS Ar+H<sub>2</sub> PLASMA ON ROUGHENED AND NON-ROUGHENED BARE Cu LEADFRAME

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### ABSTRACT

The surface ionization effect of Ar+H<sub>2</sub> plasma chemistry was evaluated and compared with conventional pure Ar strip plasma on both roughened and non-roughened bare Cu leadframe through optical high magnification inspection, Auger Electron Spectroscopy (AES), contact angle measurement through sessile drop technique, optical surface profiling and Scanning Electron Microscopy (SEM) to investigate the difference in oxide removal in preventing occurrence of pad delamination and leakage current. Based on the results, both optical inspection and AES showed evident oxide layer removal formed on top of the non-roughened bare Cu surface when mixed gas plasma is used but is deemed inappropriate on leadframes applied with roughening treatment such as brown oxide as it removes all layers of intermediate Cu oxides. On the other hand, there is no significant difference on wettability and roughness measured on leadframes treated with pure Ar and Ar+H<sub>2</sub> indicating that additional percentage (%) H<sub>2</sub> does not increase the wettability nor do further roughening on the Cu surface. Lastly, Ar+H<sub>2</sub> showed no evidence of Cu interfacial delamination nor current leakage failure indicating no occurrence of material redeposition and effective removal of brittle oxide layers.

### 1. 0 INTRODUCTION

High power applications have driven the package assembly to design devices into more robust packaging at lower manufacturing cost that could survive stringent reliability tests with no consequent failures such as delamination. For molded packages, the industry slowly shift to non-plated bare Cu leadframes for higher mold adhesion as the organic compound has higher affinity to Cu surfaces. However, the risk of oxide formation on top surface is deemed detrimental especially when exposed to series of heat processes along with material staging time in an uncontrolled environment. Plasma treatment prior mold has been introduced as dry method for isotropic and homogenous cleaning of surface impurities on metal surfaces. Different plasma chemistries are being utilized for different applications on device

packaging with varying surface alteration effect. Plasma cleaning has two different mechanisms – through physical sputtering and through chemical reaction. Pure Ar plasma are widely used for surface activation and has prominent sputtering effect which causes micro to submicron surface roughening. However, material redeposition of etched particles from the topmost layer is commonly encountered which causes performance failure such as leakage current. The pure Ar plasma composition could also not completely remove the unwanted oxide layers since inert Ar ion species are highly unreactive and thus has a less effective surface cleaning.

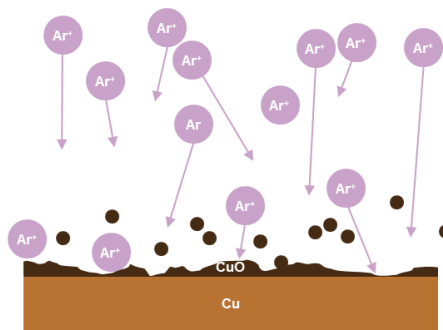


Fig. 1. 100% Ar plasma cleaning mechanism on a CuO layer growth on top of Cu metal.

On the other hand, the mixed gas plasma chemistry with a certain percent amount of Hydrogen introduces minimal to no surface alteration as the primary reactive Hydrogen radicals react with organic layers producing volatile hydrides byproduct during chemical reaction with oxides thus cleaning the surface and exposing the base metal<sup>1</sup>.

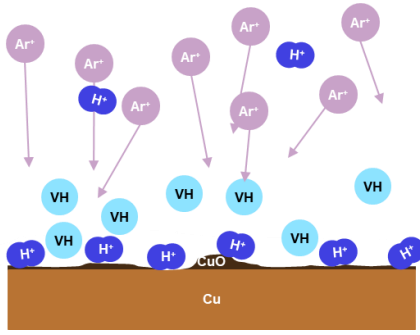


Fig. 2. Mixed gas Ar+H<sub>2</sub> plasma cleaning mechanism on a CuO layer growth on top of Cu metal.

The study focused on surface characterization of non-roughened and oxidation-roughened bare Cu leadframes in response of 95:5 Ar+H<sub>2</sub> strip plasma to assess the effectiveness and define optimized parameters for efficient oxide surface cleaning of mixed gas plasma chemistry in response to 0-hour and post reliability mold-to-Cu surface interface delamination and test performance.

## 2.0 REVIEW OF RELATED WORK

Conventional pure Ar plasma are widely and long been used in package assembly for surface cleaning of metallic surfaces to remove unwanted elements introduced from supplier down to frontline processes. Among two mechanisms know for plasma cleaning, the pure Ar utilizes physical sputtering alone through bombardment of positively charged Ar ions onto the surface of the substrate or leadframe placed on charged plates. The electrode plates on the plasma vacuum system are usually negatively charged to attract the positively charged Ar ions resulting to momentum transfer through elastic collisions on particles residing on the surface of the leadframe and is eventually ejected out through purging<sup>1,3</sup>. The advantage would be no byproducts or other species are generated during cleaning and would not induce nor introduce any possible oxidation on the surface. However, the risk of material redeposition could bring damaging issues on the package performance such as leakage current failures due to shorting by metallic particles. Cleaning mechanism may also be less efficient due to non-uniform etching especially for thick oxide layers. As such, most industries shift to mixed gas plasma chemistry for less risk of surface sputtering and enhanced surface cleaning at higher rate.

Several studies have been reported on the effectiveness of mixed gas plasma against pure inert chemistry. Lee et al.<sup>4</sup> varied the plasma chemistry to O<sub>2</sub>, Ar and Ar+H<sub>2</sub> and claimed that O<sub>2</sub> plasma has the most effective surface cleaning among the three based on contact angle and AES followed by Ar+H<sub>2</sub>. The sputtering mechanism of O<sub>2</sub>, however, is evident to a certain extent if parameters are unoptimized resulting to

surface modification which may or may not improve the adhesion to encapsulant material. In bare Cu surfaces, O<sub>2</sub> environment is projected to trigger oxide layer formation and hence not considered for such type of leadframe surfaces. Meanwhile, the Ar+H<sub>2</sub> could deliver surface cleaning and surface adhesion improvement with less to no risk of surface etching or any other surface alterations. Lee et al<sup>5</sup> reported that 95:5 Ar+H<sub>2</sub> could significantly remove the oxide layers on top of the Cu base material based on the visual color change from violet and red-orange color obtained from high temperature exposure to natural Cu color. Other studies also claim that Ar+H<sub>2</sub> indeed relies on chemical reaction of hydrogen and hydroxyl radicals reacting with metal oxides at higher rate<sup>6-8</sup>. Through such reaction, Cu oxide layers are uniformly removed on top of unreacted Cu thus removing the weak Cu oxide intermediates as most of delamination occurs between Cu-Cu<sub>2</sub>O or Cu<sub>2</sub>O-CuO<sup>9</sup>.

## 3.0 METHODOLOGY

The study is divided into two parts – surface characterization of non-roughened and oxidation-roughened bare Cu leadframes exposed to pure Ar and Ar+H<sub>2</sub> strip plasma and reliability testing of molded plasma-treated leadframe strips to check for delamination on mold-to-Cu interface and impact on product test performance. The surface cleaning, wettability, surface alteration and surface composition of different types of leadframe in response to pure Ar and mixed gas Ar+H<sub>2</sub> plasma chemistry were assessed through visual inspection using high magnification scope, contact angle measurement using sessile drop technique, roughness measurement using optical profilometer and SEM-EDX respectively. The plasma chemistry was varied to pure Ar and mixed gas 95:5 Ar+H<sub>2</sub>, and two levels (high and low) for plasma power and exposure time. The strips underwent standard process flow of the package outline carrier and the oxidation growth after each respective heat exposure were observed through visual inspection. The impact of plasma on wettability and surface roughness were also measured by measuring the contact angle and roughness of the bare Cu surface before and after plasma treatment. Material redeposition and oxidation level post plasma treatment were assessed on each type of leadframe through SEM-EDX. Lastly, all strips were molded and subjected to thermal cycling and high temperature storage test to check for mold-to-Cu delamination with all test performance parameters monitored for any potential leakage.

## 4.0 RESULTS AND DISCUSSION

### 4.1 Surface Characterization

The surface oxidation effect of both pure and mixed gas strip plasma on both non-roughened and oxidation-roughened leadframe are shown Fig. 3.

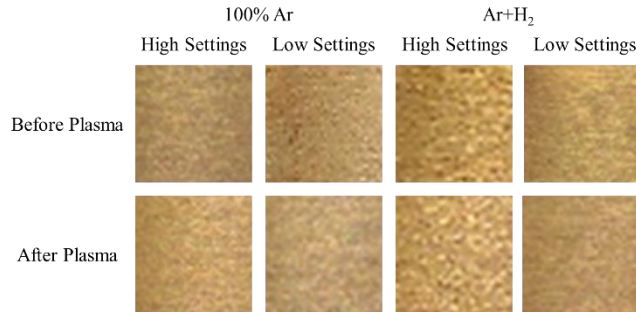


Fig. 3. Optical images of non-roughened bare Cu leadframes before and after plasma treatment at varying plasma chemistry and parameter.

Optical images under 10x magnification showed no visible change on color of bare Cu before and plasma treatment regardless of plasma chemistry and settings. The added H<sub>2</sub> on existing plasma chemistry did not trigger any oxidation during plasma treatment but the surface cleaning mechanism was not evident as no oxidation layer was formed on top of the Cu prior plasma treatment. To assess the difference on the surface cleaning mechanism of pure Ar and Ar+H<sub>2</sub>, strips were exposed to 250°C for 10 minutes to trigger severe oxidation on the surface. The strips were then plasma treated using the same set of parameters.

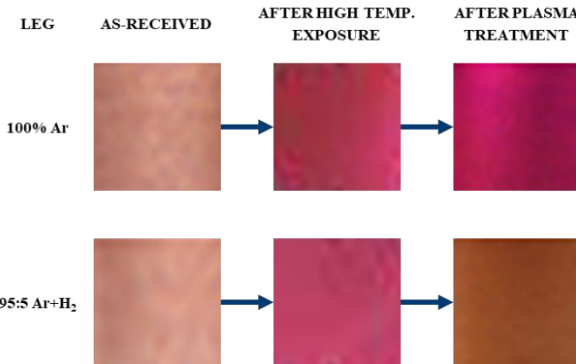


Fig. 4. High magnification images of non-roughened Cu leadframe strips exposed to high temperature and after plasma treatment.

Results showed that CuO and other derivatives are formed on the surface based on reddish brown to violet color upon exposure to high temperature. However, leadframe strips plasma treated using 100% Ar showed no significant changes on color indicating that the oxide layer was not removed. On the other hand, strips with the same level of oxidation plasma treated using mixed gas Ar+H<sub>2</sub> plasma showed color change

from reddish brown and violet to deep brown indicative of exposed unreacted base Cu metal. The visual color change supports the claim that the added percent amount of hydrogen on the plasma composition primarily introduces surface cleaning mechanism to remove the topmost formed brittle oxide layer<sup>1</sup>.

To prove the cleaning mechanism of Ar+H<sub>2</sub>, Auger Electron Spectroscopy (AES) was performed from top surface down to 60nm etch depth at 5nm increment on non-roughened leadframe exposed to low level of heat.

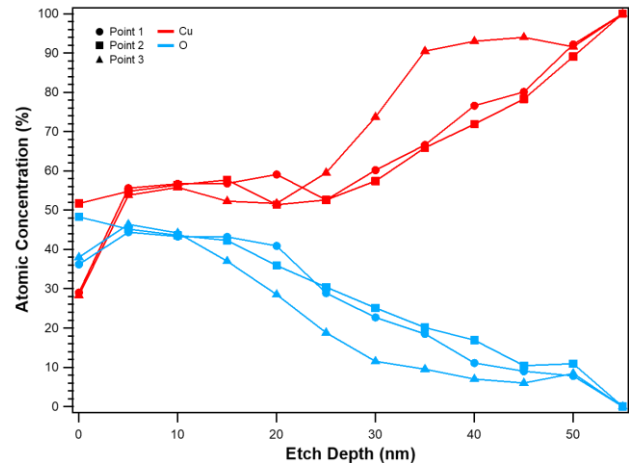


Fig. 5. Atomic concentration of detected Cu and O from surface level down to 60nm depth at 5nm etch increment.

Consistent in three trials, CuO is evident on surface up to 15nm based on derived empirical formula from the obtained atomic concentration and confirmed through corresponding binding energy. Cu<sub>2</sub>O is dominant on 25nm depth and is also present on 15-20nm depth from surface but may be in small amounts. The results exhibit air/CuO (0-15nm)/Cu<sub>2</sub>O (15-50nm)/Cu oxide layer structure<sup>2</sup> with 15nm oxidized Cu thickness. CuO is thicker compared with the two other samples due to further oxidation of Cu<sub>2</sub>O to CuO triggered by higher process temperature. The concentrations of detected oxide layers were examined after subjecting the samples to Ar+H<sub>2</sub> plasma treatment and were compared on earlier AES results.

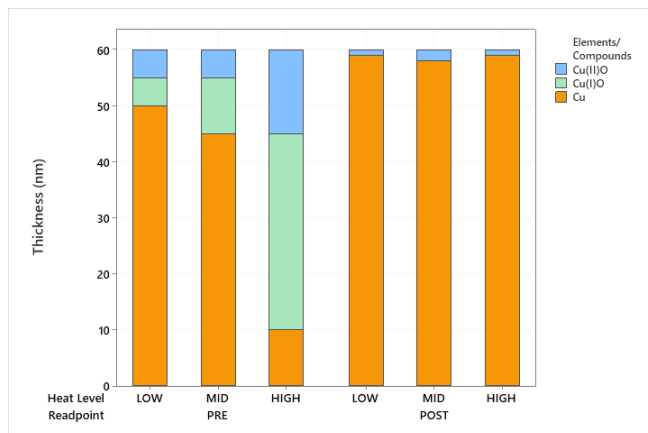


Fig. 6. Thickness of detected Cu and intermediate oxide layers of Cu pre and post plasma treatment using Ar+H<sub>2</sub>.

Approximately 50nm of Cu oxide layers were detected on Cu leadframe when exposed to high process temperature and were maintained at most 2% after plasma treatment using Ar+H<sub>2</sub>. The 2% may be attributed to native oxides on the surface and may indicate that the oxidation induced by heat exposures to assembly process can be effectively removed by Ar+H<sub>2</sub> plasma.

The effect of varying plasma parameter on the degree of Ar+H<sub>2</sub> on surface cleaning was also investigated using roughened Cu leadframe strips and is shown in Fig 7.

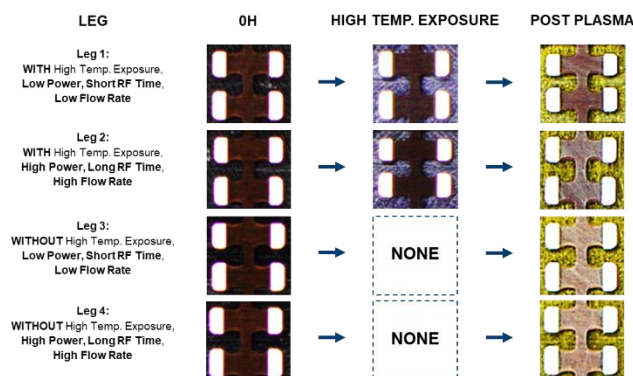


Fig. 7. High magnification images of roughened Cu leadframe strips exposed to high temperature and after plasma treatment at varying plasma parameters.

The high magnification images suggest that increasing the plasma power, exposure time and gas flow rate of Ar+H<sub>2</sub> plasma would remove thicker oxide layer formed on top of the Cu surface. However, such plasma chemistry even at optimum settings could only remove certain levels of oxidation or oxide layer thickness based on images obtained comparing strips exposed and unexposed to high temperature. The results also imply that plasma cleaning is not applicable for roughened Cu surfaces as such process would eradicate roughening treatment which is intentionally fabricated on

topmost layer for improved adhesion of mold compound. The highly reactive hydrogen ions readily react with metal oxides deposited on the surface at a higher rate causing uniform surface cleaning as observed post plasma images<sup>7</sup>.

Using in-house contact angle goniometer through sessile drop technique (Fig. 8), the wettability impact of 100% Ar versus 95:5 Ar+H<sub>2</sub> plasma on bare Cu surface were assessed and compared.

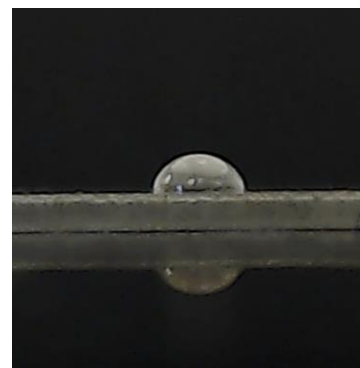


Fig. 8. Goniometer setup for contact angle measurement through sessile drop technique using deionized H<sub>2</sub>O drop calibrated by a reciprocating pump.

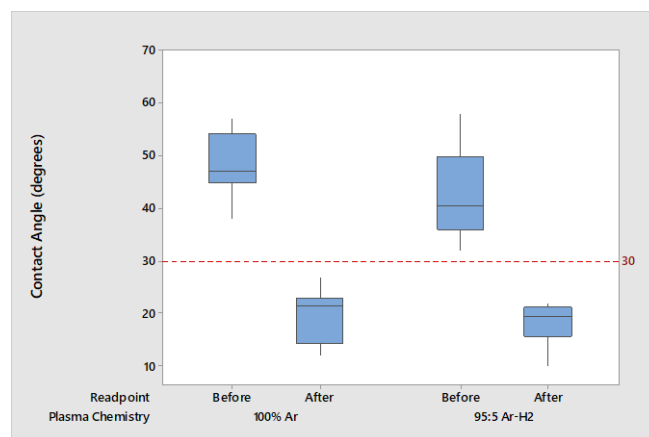


Fig. 9. Contact angle measured before and after plasma treatment on bare Cu surface using 100% Ar and 95:5 Ar+H<sub>2</sub>.

Contact angle on as-received leadframes showed an average of 45° and significantly reduced to roughly 19° after plasma treatment for both legs. Using 2-sample t-test on 25 points gathered before and after plasma treatment of each respective plasma chemistry, the results show no significant difference on wettability of strips plasma treated using either 100% Ar and Ar+H<sub>2</sub> indicating that incorporating H<sub>2</sub> on plasma chemistry do no impact on surface adhesion improvement against 100% Ar and may be attributed to the different surface cleaning mechanism of mixed gas plasma. The plasma settings were varied to high and low to further check whether surface wettability of Cu surface using Ar+H<sub>2</sub> could still be increased.

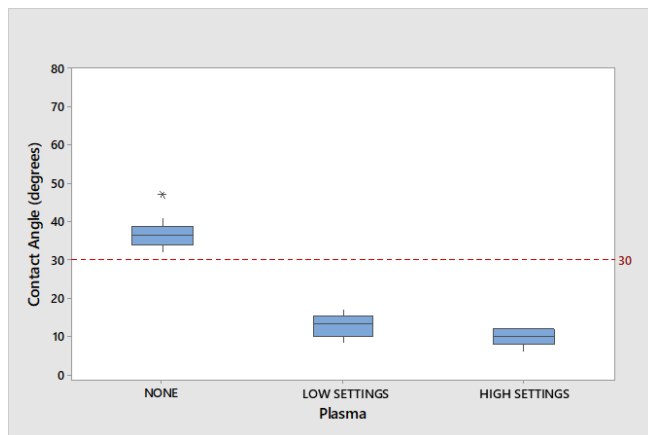


Fig. 10. Contact angle of non-plasma and plasma treated Cu surface using Ar+H<sub>2</sub>.

Based on One-Way ANOVA and post hoc tests, increasing the plasma power, exposure time and flow rate of Ar+H<sub>2</sub> gas on vacuum system does not further reduce the contact angle of Cu surface which could also be used as basis for parameter optimization given that higher plasma settings may induce etching of surface due to presence of inert ions.

To assess the sputtering effect of both plasma chemistry types, average surface roughness ( $R_a$ ) was measured using 3D optical profiler of plasma and non-plasma treated roughened and non-roughened Cu strips.

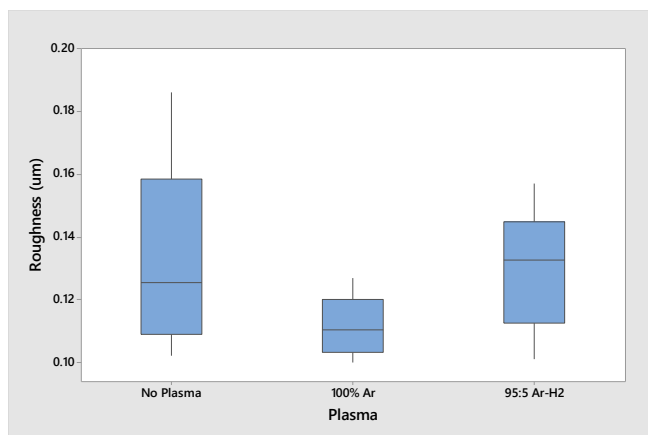


Fig. 11. Average surface roughness ( $R_a$ ) measured before and after plasma treatment on bare Cu surface using 100% Ar and 95:5 Ar+H<sub>2</sub>.

The average roughness measured from 30 points on non-plasma treated strips show a high range from 0.11 to 0.19  $\mu\text{m}$  and large deviation between samples indicating a non-uniform micron to submicron Cu surface roughness. Post-hoc test for ANOVA showed no significant difference on measured roughness between non-plasma treated strips and plasma-treated strips using 95:5 Ar+H<sub>2</sub> indicating that mixed gas plasma chemistry has no etching effect on the Cu surface which heavily rely on chemical reaction<sup>6,7</sup>. However, 100%

Ar showed significantly lower roughness than the two legs based on Fischer post hoc test possibly indicating sputtering effect of Ar<sup>+</sup> ions on the surface of the Cu etching off high peaks thus narrowing the crevices and valleys resulting to lower roughness which supports the results obtained by Hsieh et al. where Cu leadframe surface has smoothen out after longer exposure time based on Atomic Force Microscopy<sup>7</sup>. However, the smoothing effect of Ar+H<sub>2</sub> manifested on roughened Cu surfaces after plasma treatment as shown in figure below.

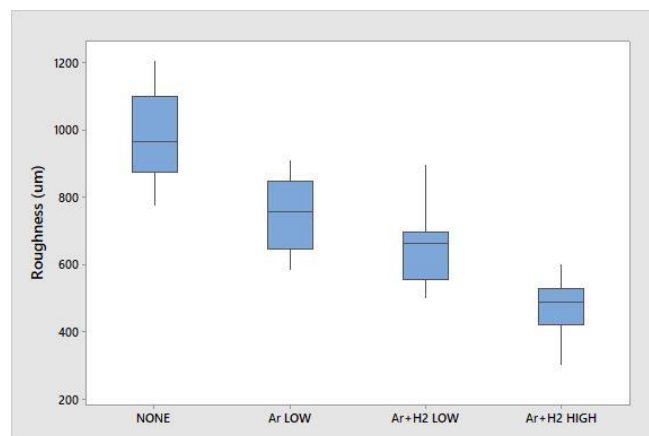


Fig 12. Average surface roughness ( $R_a$ ) measured on non-plasma and plasma treated roughened Cu surface using 100% Ar and 95:5 Ar+H<sub>2</sub> at high and low settings.

The decrease in surface roughness on oxidation-roughened Cu surface may be attributed to the enhanced surface cleaning mechanism of Ar+H<sub>2</sub> against 100% Ar, removing the plated oxide roughening treatment on the Cu revealing a less rough Cu surface. Increasing the plasma power and time of Ar+H<sub>2</sub> further decreases the roughness since higher power and exposure time produces more hydrogen radicals and allows longer time to react with metal oxides with Ar<sup>+</sup> ions acting as catalyst during the reaction<sup>3</sup>. Plasma process especially Ar+H<sub>2</sub> is therefore considered as not applicable for oxidation-roughened Cu surfaces as it loses its roughening technology on the surface.

Through SEM imaging, the effect of varying plasma chemistry and settings were investigated to confirm the results from roughness measurements.

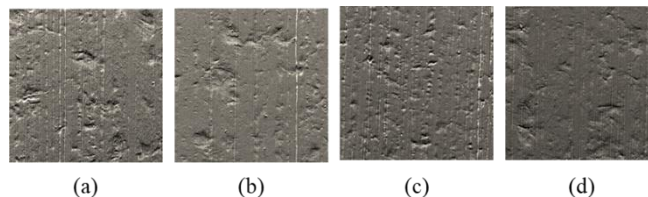


Fig 13. Surface morphology of oxidation-roughened Cu surface during (a) as-received and after plasma treatment using (b) 100% Ar low settings, (c) 95:5 Ar+H<sub>2</sub> low settings and (d) 95:5 Ar+H<sub>2</sub> high settings.



As-received surface of oxidation-roughened Cu showed presence of tiny and large pits, dents and crevices indicating uneven and high roughness surface. Plasma treatment using either 100% Ar or mixed gas Ar+H<sub>2</sub> shallowed the dents on the surface but is more evident on strips plasma-treated using Ar+H<sub>2</sub> at higher settings.

#### 4.1 Effect on Mold Adhesion and Functional Test Performance

The plasma-treated oxidation-roughened Cu strips were not proceeded for mold adhesion and functional assessment as gross delamination on Cu-to-mold interface is assumed based on the results obtained from surface characterization. The integrity of mold-to-Cu heatsink interfacial adhesion of bare Cu leadframe strips non-plasma treated and plasma-treated using 100% Ar and 95:5 Ar+H<sub>2</sub> was assessed through Scanning Acoustic Microscopy (SAM) after post mold cure and after thermal cycling (TMCL) and humidity stress (HAST) tests.

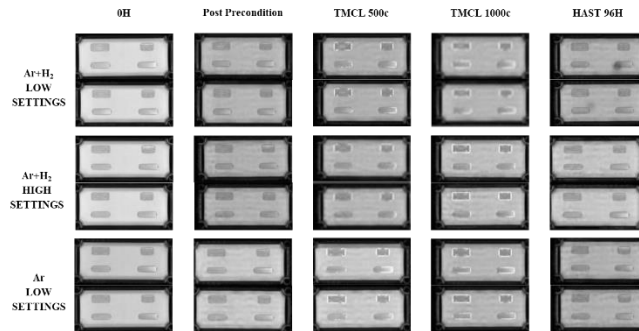


Fig 14. SAM images of molded bare Cu strips plasma treated using 100% Ar and 95:5 Ar+H<sub>2</sub> until TMCL 1000 cycles and HAST 96 hours.

SAM images at C-mode showed no presence of delamination on gated interface between Cu pad and mold. There is no significant difference on mold adhesion performance among the legs in terms of delamination response up to TMCL 1000 cycles and HAST 96 hours as no surface oxidation was probably induced from assembly process that may differentiate the surface cleaning mechanism of the two plasma chemistries.

The Ar+H<sub>2</sub> plasma-treated molded functional units were subjected to functional test to check for any potential performance failure such as leakage current.

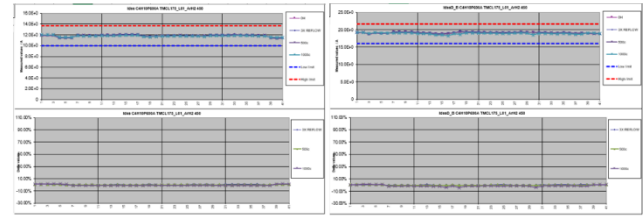


Fig 15. Drain side leakage current parameter of units plasma treated using Ar+H<sub>2</sub> high settings.

All test parameters are within specifications with no noted spikes and minimal deviation indicating no leakage failure. Leakage current on drain source which is the primary metric for electrical shorting are observed to be within specification on all sections of the unit suggesting no occurrence of material redeposition from etched off metallic particles on the surface. Also, utilization of high plasma power and exposure time using Ar+H<sub>2</sub> has low risk of surface sputtering which may result to drain side leakage current failure. Overall, results imply that Ar+H<sub>2</sub> is more applicable to bare Cu surfaces than 100% Ar plasma as the latter has shown history of drain leakage failure at ppm level.

## 5.0 CONCLUSION

In summary, Ar+H<sub>2</sub> exhibited enhanced surface cleaning mechanism compared to 100% Ar plasma based on the significant change in surface color of oxidized Cu surfaces. On the other hand, adding percent Hydrogen on the Ar plasma chemistry does not increase the wettability of both non-roughened bare and oxidation-roughened Cu surface compared to conventional plasma. Surface roughness measurement however suggest that mixed gas plasma does not roughen the bare Cu surface but significantly reduce the roughness of oxidation-roughened Cu surface through reaction of hydrogen radicals with oxide treatment removing the roughening layer with increased settings. As such, Ar+H<sub>2</sub> is only appropriate for non-roughened bare Cu surfaces to prevent removal of oxide treatment intentionally fabricated on the Cu surface for improved mold adhesion. Lastly, the use of Ar+H<sub>2</sub> demonstrated no occurrence of delamination even after thermal cycling and humidity stress tests with no functional test failure that may indicate material redeposition from etched off metallic particles from Cu.

## 6.0 RECOMMENDATIONS

To assess the efficiency of Ar+H<sub>2</sub> on removing oxidation and other surface contamination, the researchers recommend correlating the increasing plasma power, exposure time and gas flowrate on depth of oxidation removal. Also, Atomic Force Microscopy would be a more suitable test to describe the roughening mechanism of the two plasma chemistries and to validate that mixed gas plasma has no sputtering effect.

Lastly, higher sample size validation and provocation trials using highly oxidized leadframes is needed to confirm that Ar+H<sub>2</sub> is more effective in unwanted oxide cleaning to prevent occurrence of delamination.

### 7.0 ACKNOWLEDGMENT

The authors would like to express their sincerest gratitude to Backend Technologies Competence Center engineers and technicians who help execute the experiments and to Ampleon Phils. Inc. management team for the support which made the study possible.

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