Assessment Of Cl 2 /CHF 3 Mixture For Plasma Etching Process On BARC And TiN Layer For 0.21 µm Metal Line: SilTerra Case Study

Wan Faizal Mohamed-Hassan¹, Kader Ibrahim², Mohd Azizi Chik³, Ghazali Omar⁴, Noreffendy Bin Tamaldin⁵

¹Etch, SilTerra Malaysia Sdn. Bhd., Kedah, Malaysia,
²Fab Operation, SilTerra Malaysia Sdn. Bhd., Kedah, Malaysia,
³Integrated Module, SilTerra Malaysia Sdn. Bhd., Kedah, Malaysia
⁴Faculty of Mechanical, University of Technical Melaka, Melaka, Malaysia,
⁵Faculty of Mechanical, University of Technical Melaka, Melaka, Malaysia,

Article History : Received :11 January 2021; Accepted: 27 February 2021; Published online: 5 April 2021

ABSTRACT: In wafer fabrication manufacturing, aluminum etching process is a dry plasma etching process used as main process for construction of aluminum (Al) interconnects structures. As customer requirement changed for faster, more reliable and lower cost chips, chip manufacturers have learned to reduce the size of component on a chip in order to achieve those requirements (Ibrahim, Chik, & Hashim, 2016). As the geometry of the chip getting smaller, the width of Al line wiring specification also shrinking. To print the smaller geometry pattern requirement, the thickness in masking process also has to be reduced for better resolution. Such a thinner resist will create a challenge during plasma etching to ensure a minimal resist loss process which required new type of equipment but this research insist to sustain similar equipment. The use of oxide film as a hard mask has been evaluated by other researchers but alternative approach still needed to suit specific requirement of semiconductor factory installation base. This approach does require a process integration change and require a full technology qualification and easily take a lengthy qualification procedures especially when to qualify the existing products. It is worth trying at the situation of no other solution available. The challenge of insufficient margin for the metal line etching process for 0.2 µm width has caused the deformed metal pattern formation. This chemistry study of Cl₂/CHF₃ as a replacement gas to existing Cl₂/O₂ to address Organic backside anti refractive coating (OBARC) was evaluated and proven novelty where detail discussed in the following content.

KEYWORDS: Aluminum, plasma etching, Cl₂/CHF₃, BARC, TiN

INTRODUCTION
The patterning of aluminum metal interconnect structures is complicated by the multilayer of metallization scheme adopted by industry for IC production. In advanced metallization scheme (Pramanik & Saxena, 1983; Wilson, Tracy, & Freeman, 1993), the aluminum film which is often alloyed with copper serves as the conductor and is sandwiched by the barrier layers of titanium nitride (TiN) layer on the top and by TiN and titanium (Ti) layers at the bottom (Filippi et al., 2001). The purpose of this barrier layers are to avoid the inter-diffusion of aluminum and silicon (“Spiking”). The spiking occurs when the silicon becomes soluble into aluminum film as the temperature increases. The main reason for the complexity is to enhance the electromigration resistance in the device (Hosaka, Kono, Hayakawa, Niwa, & Yamada, 1998; M. H. Lee et al., 2011). Etching of these films require multi step etching process with different mixture of chemistry (Vignes & Baléo, 1997) combined with optimum power (Kim, Jung, Choi, Kim, & Boo, 2005) and pressure conditions (Christie, 1994; Kunz, 2007; Okumura, 2010) to ensure the metal etching profile meeting the process requirements. The very fundamental requirement in plasma etching method adopted in fabricating of an IC pattern is the photoresist remaining margin. The pre-defined photoresist pattern on the metal substrate during photolithography process comes together with the organic backside anti-refractive coating film to improve reflection control and light absorption during photolithography (Boumerzoug, 2014; Huang & Weigand, 2008; Zhuang et al., 2006). BARC layer minimizes thin film interference effects by reducing reflected light.

In the patterning transfer, during BARC opening process, high etch selectivity of resist to BARC process is required to minimize the resist loss to allow further substrate etching (Armacost et al., 1999). BARC also must etch quickly to prevent line width change. The selectivity of BARC to resist depend mainly on the carbon content and also its composition and structure responses towards oxidizing gas, reducing gas and plasma bombardment. As the geometry of the chip getting smaller, the width of Al line wiring specification also shrinking. To print the smaller geometry pattern requirement, the thickness in masking process also has to be reduced for better resolution. Such a thinner resist will create an inconsistency of the pattern width and unable to produce straight profile requirement if
having insufficient of resist remaining process during plasma etching (H. J. Lee et al., 2008). This failure will lead to device electrical. Therefore, an optimized matching metal etching process is required. Further assessment in the following content will discuss finding of Cl₂/CHF₃ mixture to etch BARC and top TiN layer of metallization film having minimum metal line geometry of 0.21µm line and space.

**METHODS**

Figure 1 explains workflow of the methodology adopted in this assessment of Cl₂/CHF₃ in BARC and TiN Etching of AlCu metallization interconnect.

![Methodology approach](image)

The assessment was divided into two parts. The first part of the evaluation was done on the blanket photoresist wafers to determine the photoresist etch rate at different combinations of Cl₂ and CHF₃ flow rates combinations as tabulated in Table 1. The evaluation was done on the blanket photoresist wafers coated on bare silicon wafers with thickness of 14000Å. A ThermawaveOptiprobe metrology tool was used to measure the film thickness of photoresist before and after the plasma etching process. Each wafer was etched in inductively coupled plasma (ICP) metal etcher system at the cathode temperature of 40°C. The remaining process parameters and equipment parameters were remained as constant. The photoresist etch rate were determined for each of the conditions and analyzed.

| Slot | Pattern | Cl₂ Flow (sccm) | CHF₃ Flow (sccm) |
|------|---------|----------------|-----------------|
| 1    | ++      | 75             | 20              |
| 2    | +-      | 75             | 10              |
| 3    | -+      | 25             | 20              |
| 4    | --      | 25             | 10              |
| 5    | 00      | 50             | 15              |
| 6    | 00      | 50             | 15              |
| 7    | +-      | 60             | 0               |

Table 1: Experimental conditions of Cl₂ and CHF₃ flow rates combinations for photoresist etch rate study

In the second part of the assessment, the evaluation was done in the same metal etcher tool using pattern wafer instead of blanket photoresist wafers. The metal film of 0.40 µm stack (TiN/AlCu/TiN/Ti) was deposited after the dielectric layer formation on bare Si wafer. AlCu alloy where the Cu concentration is 0.5 wt.% and the AlCu is deposited at 350°C. The wafers were patterned with 7750Å DUV photoresist on 700Å of organic BARC film. The reticle mask used in this experiment from the customer reticle of metal-2 layer having 0.2 µm minimum design rules of line and space. Total of 8 wafers were prepare. The samples ware etched in ICP metal etcher tool using multiple etching step method as summarized in Table 2 below. The metal-2 etching recipes consist of six (6) etching steps.

| Step | Etch process description |
|------|-------------------------|
| 1    | PR hardening            |
| 2    | BARC etching            |
The evaluation of Cl\textsubscript{2}/CHF\textsubscript{3} mixture combinations were applied in BARC etching (Step2) and TiN etching (Step3) using similar gas ratio as tabulated in Table 3. The table was designed based on full factorial DOE to characterize the etching characteristic on the residue defects in open etching area. The rest of the etching step conditions were remained as constant.

### Table 2: Metal-2 multiple etching step recipe with process steps descriptions

|   |   |   |   |
|---|---|---|---|
| 3 | TiN etching |   |   |
| 4 | BT etching |   |   |
| 5 | ME EPD etching |   |   |
| 6 | OE (IMD Recess) |   |   |

### Table 3: Cl\textsubscript{2}/CHF\textsubscript{3} flow rate combinations applied on Step 2 and Step 3 of Metal-2 etching recipe

|Run| Pattern| Factor 1 Cl\textsubscript{2} (sccm)| Factor 2 CHF\textsubscript{3} (sccm)| Sample Mean (Å/min)| Lower CI (Å/min)| Upper CI (Å/min)|
|---|---|---|---|---|---|---|
|1 | ++ | 75 | 20 | 1216 | 1191 | 1241 |
|2 | + | 75 | 10 | 1150 | 1124 | 1177 |
|3 | + | 25 | 20 | 896 | 867 | 925 |
|4 | -- | 25 | 10 | 858 | 831 | 886 |
|5 | 00 | 50 | 15 | 1101 | 1077 | 1126 |
|6 | 00 | 50 | 15 | 1032 | 1011 | 1053 |
|7 | + | 60 | 0 | 1050 | 1020 | 1080 |

### RESULTS AND DISCUSSION

The result of photoresist etch rate obtained from the experimental run was tabulated in Table 4 below. The sample mean etch rate for each run is tabulated and its respective confidence interval (CI) is determined at 95% confidence level. The statistical analysis is done based on the upper CI value.

### Table 4: Sample mean of photoresist etch rate for each run

| Slot| Pattern| Cl\textsubscript{2} Flow rate (sccm)| CHF\textsubscript{3} Flow rate (sccm)| Sample Mean (Å/min)| Lower CI (Å/min)| Upper CI (Å/min)|
|---|---|---|---|---|---|---|
|1 | ++ | 75 | 20 | 1216 | 1191 | 1241 |
|2 | + | 75 | 10 | 1150 | 1124 | 1177 |
|3 | + | 25 | 20 | 896 | 867 | 925 |
|4 | -- | 25 | 10 | 858 | 831 | 886 |
|5 | 00 | 50 | 15 | 1101 | 1077 | 1126 |
|6 | 00 | 50 | 15 | 1032 | 1011 | 1053 |
|7 | + | 60 | 0 | 1050 | 1020 | 1080 |

Figure 2 shows the Y-axis of PRER Actual value from upper CI and X-axis is the PRER Predicted value obtained by the proposed model derived from the fit model analysis. The suggested model of predicted PRER obtained in this experiment analysis is statistically significant as the RSq is 0.96 and the Pvalue is 0.0152 as tabulated in Table 5 and Table 6 respectively.
Assessment Of Cl₂ /CHF₃ Mixture For Plasma Etching Process On Barc And Tin Layer For 0.21 µm Metal Line:
Silterra Case Study

Figure 2: Correlation of PRER Actual against PRER Predicted with RSq=0.96 and Pvalue of 0.0152 suggesting a
significant experimental model.

| Source     | DF | Sum of Squares | Mean Square | F Ratio |
|------------|----|----------------|-------------|---------|
| Model      | 3  | 94355.423      | 31451.8     | 22.0133 |
| Error      | 3  | 4286.291       | 1428.8      | Prob> F |
| C. Total   | 6  | 98641.714      |             | 0.0152  |

Table 5: Summary of Fit

Table 6: Analysis of Variance

From the parameter estimate in Table 7, photoresist etch rate (PRER) using Cl₂/CHF₃ plasma significantly
dependent on the Cl₂ flow. The CHF₃ flow is not significant and no interaction exist in this model as the Pvalue for
both terms (CHF₃ and Cl₂*CHF₃) are greater than 0.05.

| Term      | Estimate | Std Error | t Ratio | Prob>|t| |
|-----------|----------|-----------|---------|-----|
| Intercept | 1069.214 | 15.09068  | 70.85   | <.0001 |
| CI₂(25,75)| 152.42838| 18.8002   | 8.11    | 0.0039 |
| CHF3(10,20)| 18.537118| 12.10867  | 1.53    | 0.2233 |
| CI₂*CHF3 | 3.2148472| 17.98609  | 0.18    | 0.8695 |

Table 7: Parameter estimates of each term with P-value <0.05 indicates its significant in the model.
Figure 4(a) and (b) shows the leverage plots for the Cl2 and CHF3 effect respectively. The Y-axis is the predicted response of photoresist etch rate when the magnitude of factor in X-axis is varied. The leverage plot for Cl2 having steeper slope than for CHF3 suggesting that CHF3 factor does effect PRER however it is less significant as compared to Cl2 factor. Therefore the use of CHF3 in BARC etching step is able to preserve the photoresist margin. This is an advantage to process engineer as the factor may be considered as the nob to control the lateral etching of the metal width dimension (FICD) without significantly degrade the photoresist margin. Moreover, CHF3 is one of the polymerizing chemistry that generates polymeric material on wafer surface when used in RF plasma condition (Astell-Burt et al., 1986). Saito et al. reported in his study that CHF3 used in etching aluminum film able to control the metal width dimension by suppressing side wall etching of the aluminum due to the passivation layer deposited on the sidewall of the resist and aluminum pattern. In this application, we propose to use the CHF3 gas in BARC etching to generate polymer film and deposited on the sidewall of the photo resist pattern with the expectation to minimize lateral etching to the resist and able to minimize the width dimension shift of the mask pattern. Based on this qualitative study, the use of CHF3 in the BARC step will reduce the shift in photo resist width dimension during BARC opening step and able to control CD as required. The flow margin of CHF3 has to be determined to ensure the BARC film is not overly polymerized by the carbon based species and no micromasking defect in the underneath TiN ARC film is formed. Failure to clear the BARC film in the open area and the creation of micromasking defect during TiN etching step will lead to post metal etch residue defect in the opening area (Lee et al., 2008).

Table 5 shows the result of the second part of experiment evaluated on patterned wafers using Metal-2 reticle mask. Total defect counts was counted based on the SEM micrograph image captured at center die and edge die of each sample as shown by Figure 5 and 6 below. Total of 65 counts of defects were recorded for the Run#7 SEM micrograph images inspected at isolated (MPISO) and dense (MPDense) region structures on both die locations.

| Run | Pattern | Factor 1 (Cl2) | Factor 2 (CHF3) | Total defect counts |
|-----|---------|----------------|-----------------|---------------------|
| 1   | --      | 40             | 12              | 4                   |
| 2   | 00      | 50             | 15              | 0                   |
| 3   | +       | 40             | 18              | 79                  |
| 4   | +       | 60             | 12              | 0                   |
| 5   | ++      | 60             | 18              | 4                   |
| 6   | +       | 45             | 12              | 0                   |
| 7   | ++      | 45             | 18              | 65                  |
| 8   | ++      | 55             | 15              | 0                   |

Table 8: Results of defect residues
Assessment of Cl₂/CHF₃ Mixture for Plasma Etching Process on BARC and Tin Layer for 0.21 µm Metal Line: Silterra Case Study

Figure 4: SEM Images for Run 7 at MP Dense (a) center, (b) edge

Figure 5: SEM Images for Run 7 at MP ISO (a) center, (b) edge

Figure 7 suggests experimental model on residue defects counts response shows the R-Square value greater than 0.9 and the p-value of the ANOVA is statistically significant, 0.0076. Table 9 shows all the 3 experimental terms (Cl₂, CHF₃ and Cl₂·CHF₃) analyzed in this model found to be significant on the residue defect count response with p-value of less than 0.05.

Figure 6: Correlation of Residue defect count Actual against Predicted value with RSq=0.94 and P value of 0.0076 suggesting a significant experimental model
Table 9: Parameter estimates of each term with P-value <0.05 indicates its significant in the model.

| Term       | Estimate   | Std Error | t Ratio | Prob>|t| |
|------------|------------|-----------|---------|-----|-----|
| Intercept  | 17.649007  | 3.9287    | 4.49    | 0.0109 |
| Cl2(40,60) | -21.61589  | 5.09855   | -4.24   | 0.0133 |
| CHF3(12,18)| 20.942308  | 4.60765   | 4.55    | 0.0105 |
| Cl2*CHF3  | -18.34615  | 5.32046   | -3.45   | 0.0261 |

Figure 8 shows the interaction profile between Cl2 and CHF3. Based on plot profile, the sensitivity of the CHF3 flow to the defect residue is minimal when the Cl2 flow is operating at higher set point. Furthermore, previous work already demonstrated that TiN etch rate is proportional to Cl2 flow rate (Min et al., 2008). The higher TiN etch rate would reduce the possibility of having TiN residue defects which later may transform into the residue defect at the end of etching process. This condition will maximize the process margin against the residue defect. The adoption of CHF3 in plasma etching has been reported by previous researcher (H. J. Lee et al., 2008; Saito, Sugita, & Tonotani, 2005) that it would generate polymeric film on the wafer surface that preventing the surface reaction between the main etchant gas and the material to occur. Another researcher reported that the presence of fluorine as an additive with the chlorine as the main etchant would enhance the TiN etch rate performance (Abraham, Gabriel, & Zheng, 1997). However, too high flow of CHF3 will cause the density of passivation species more than the density of the neutral species. The increase in generation of passivation species may lead to thicker polymerization layer in the etching area and slowing down the reaction of the neutral species with the material to etch. Since the same chemistry mixture was used in BARC and TiN etching steps, we believed the residue defect observed could originate either from BARC or TiN etching step. The unclear BARC or TiN material has transformed into micro-masking defect and locally slow down the etching rate during the subsequent etching steps and remained as residue defect formation.

In this work, we have successfully identified the safe process window of Cl2 and CHF3 flow required in metal etching process for BARC and TiN etching steps to ensure zero residue defects.

CONCLUSION

The replacement of Cl2/O2 chemistry mixture to Cl2/CHF3 mixture has enabled us to reduce the photoresist etch rate during the OBARC etching step. Our experiment model has suggested that CHF3 flow rate in the mixture has least effect on the photoresist etch rate. The findings in agreement with other researcher (Kwon, Kim, Lee, Lee, & Park, 2009) investigation that the lower etch rate is due to the formation of CFx polymerization film.
The same chemistry was also evaluated to etch the TiN ARC layer of the metal-2 film stacks. The characterization on the metal residue defects done based on the SEM image micrograph analysis disclosed the finding that the low flow of Cl₂ would induce the defect formation in the presence of CHF₃ species in the mixture. The new alternative solution has been implemented in the real semiconductor process application.

ACKNOWLEDGEMENTS

Authors are grateful to SilTerra Malaysia and University of Technical Melaka for providing opportunity to carry out this research work.

REFERENCES

1. Abraham, S. C., Gabriel, C. T., & Zheng, J. (1997). Performance of different etch chemistries on titanium nitride antireflective coating layers and related selectivity and microloading improvements for submicron geometries obtained with a high-density metal etcher. *Journal of Vacuum Science & Technology A, 15*(3), 702–706. https://doi.org/10.1116/1.580805

2. Armacost, M., Hoh, P. D., Wise, R., Yan, W., Brown, J. J., Keller, J. H., … Spuler, B. (1999). Plasma-etching processes for ULSI semiconductor circuits. *IBM Journal of Research and Development, 43*(1–2), 39–71. https://doi.org/10.1147/rd.431.0039

3. Boumerzoug, M. (2014). Optimized BARC films and etch byproduct removal for wafer edge defectivity reduction. *ASMC (Advanced Semiconductor Manufacturing Conference) Proceedings, 330–333*. https://doi.org/10.1109/ASMC.2014.6847031

4. Christie, R. (1994). Process transfer from conventional RIE to transformer-coupled high density plasma metal etch system. In Anon (Ed.), *IEEE/SEMI Advanced Semiconductor Manufacturing Conference and Workshop* (pp. 34–36).

5. Filippi, R. G., Gribelyuk, M. A., Joseph, T., Kane, T., Sullivan, T. D., Clevenger, L. A., … Rodbell, K. P. (2001). Electromigration in AlCu lines: Comparison of Dual Damascene and metal reactive ion etching. *Thin Solid Films, 388*(1–2), 303–314. https://doi.org/10.1016/S0040-6090(01)00855-0

6. Hosaka, M., Kouno, T., Hayakawa, Y., Niwa, H., & Yamada, M. (1998). Ti layer thickness dependence on electromigration performance of Ti-AlCu metallization. In *1998 IEEE International Reliability Physics Symposium Proceedings, 36th Annual (Cat. No.98CH36173)* (pp. 329–334). https://doi.org/10.1109/RELPHY.1998.670665

7. Huang, R., & Weigand, M. (2008). Plasma etch properties of organic BARCs. *Advances in Resist Materials and Processing Technology XXV, 6923*, 69232G. https://doi.org/10.1117/112.772012

8. Ibrahim, K., Chik, M., & Hashim, U. (2016). Semiconductor Fabrication Strategy for Cycle Time and Capacity Optimization: Past and Present. In *Proceedings of the 2016 International Conference on Industrial Engineering and Operations Management* (pp. 2798–2807). IEOM ISBN: 978-0-9855497-4-9.

9. Kim, D. W., Jung, M. Y., Choi, S. S., Kim, J. W., & Boo, J. H. (2005). The effect of SiCl₄ additive gas on the Cl₁-based Al plasma etch procedure. *Thin Solid Films, 475*(1-2 SPEC. ISS.), 81–85. https://doi.org/10.1016/j.tsf.2004.07.042

10. Kunz, R. R. (2007). *Dry etching of photoresists. Microlithography: Science and Technology, Second Edition*.

11. Kwon, B. S., Kim, J. S., Lee, N. E., Lee, S. K., & Park, S. W. (2009). Comparative study on the etching characteristics of ArF and EUV resists in dual-frequency superimposed capacitively-coupled CF 4/O 2/Ar and CF 4/CHF 3/O 2/Ar plasmas. *Journal of the Korean Physical Society, 55*(4), 1465–1471. https://doi.org/10.3938/jkps.55.1465

12. Lee, H. J., Hung, C. L., Leng, C. H., Lian, N. T., Young, L. W., Yang, T., … Lu, C. Y. (2008). Etch defect characterization and reduction in hard-mask-based Al interconnect etching. *International Journal of Plasma Science and Engineering, 2008*. https://doi.org/10.1155/2008/154035

13. Lee, M. H., Kwon, Y. M., Pyo, S. G., Lee, H. C., Han, J. W., & Paik, K. W. (2011). Effects of metal stacks and patterned metal profiles on the electromigration characteristics in super-thin AlCu interconnects for sub-0.13 μm technology. *Thin Solid Films, 519*(11), 3906–3913. https://doi.org/10.1016/j.tsf.2011.01.268

14. Min, S. R., Cho, H. N., Li, Y. L., Lim, S. K., Choi, S. P., & Chung, C. W. (2008). Inductively coupled plasma reactive ion etching of titanium nitride thin films in a Cl2/Ar plasma. *Journal of Industrial and Engineering Chemistry, 14*(3), 297–302. https://doi.org/10.1016/j.jiec.2008.01.001

15. Okumura, T. (2010). Inductively coupled plasma sources and applications. *Physics Research International, 2010*(1). https://doi.org/10.1155/2010/164249

16. Pramanik, D., & Saxena, A. N. (1983). *VLSI METALLIZATION USING ALUMINUM AND ITS ALLOYS - 1*. *Solid State Technology, 26*(1), 127–133.
17. Saito, S., Sugita, K., & Tonotani, J. (2005). Effect of CHF 3 Addition on Reactive Ion Etching of Aluminum Using Inductively Coupled Plasma. *Japanese Journal of Applied Physics, 44*(5A), 2971–2975. https://doi.org/10.1143/JJAP.44.2971

18. Vignes, M. J., & Baléo, J. N. (1997). Experimental investigation of a Cl2/BCl3/N2 chemistry based aluminium plasma etching. *Vidé: Science, Technique et Applications, 53*(284 SUPPL. 1), 41–43.

19. Wilson, S. R., Tracy, C. J., & Freeman, J. L. (1993). *Handbook of Multilevel Metallization for Integrated Circuits: Materials, Technology and Applications (Materials Science and Process Technology)*. New Jersey: Noyes Publications.

20. Zhuang, H., Abdallah, D., Xiang, Z., Wu, H., Shan, J., Lu, P.-H., … Badowski, P. R. (2006). The effects of etch chemistry on the etch rates of ArF BARC products. *Advances in Resist Technology and Processing XXIII, 6153, 61530N*. https://doi.org/10.1117/12.657128