Al–Cu Pattern Wafer Study on Metal Corrosion Due to Chloride Ion Contaminants

Bi-Jun Wu, Hsunling Bai, I.-Kai Lin, and S. S. Liu

***Abstract*—Chloride ions (Cl^-) in the cleanroom environment induce metal corrosion of integrated circuits, and cause wafer scrap events. In this paper, pattern wafers were designed to monitor critical Cl^- concentration which leads to metal corrosion effects in a simulated airborne molecular contamination (AMC) environment. The simulated Cl^- contamination environment was established by placing different numbers of preventive maintenance (PM) wipers in wafer pods and monitored simultaneously by ion mobility spectrometer (IMS) and impinger+ion chromatography (IC) instruments. The exposed Al–Cu pattern wafers were analyzed by the KLA surface scanner and the scanning electron microscope/energy dispersive X-ray spectroscopy analyzer. The results indicate that the IMS and the impinger+IC instruments provide consistent HCl monitoring data. Furthermore, they suggest that pattern wafer exposure tests can be an effective method to monitor metal corrosion. The PM wipers are a simple and effective method to establish simulated source of HCl for studying the AMC effect in ppbv levels. The critical HCl concentration where particles could be found on the wafer surface is around 2.0–3.5 ppbv, and the critical HCl concentration that results in metal corrosion defects is around 4.1–6.4 ppbv.**

***Index Terms*—Airborne molecular contaminants (AMCs), chloride contamination, cleanroom microcontamination, HCl, pattern wafer, semiconductor device.**

I. Introduction

AS SEMICONDUCTOR devices continue to be highly integrated and their critical dimensions shrink to sub-0.1 μm range, the airborne molecular contaminants (AMCs) in the cleanroom environment have been recognized as contamination sources causing yield reduction and performance deterioration of semiconductor devices [1]–[4]. The AMCs take many forms; SEMI standard summarized their classification to be acids, bases, condensables, dopants, and nonclassified classes [5]. The International Technology Roadmap for Semiconductors (ITRS) has made efforts to tighten specification for AMCs. For example, the requirement of Cl^- concentration in the wafer environment should be below 10 pptM in 2007 [6], which corresponds to below 0.242 ppbv of gas phase Cl^- concentration at 22.

Manuscript received December 19, 2009; revised April 11, 2010, May 19, 2010, and July 16, 2010; accepted July 16, 2010. Date of publication August 9, 2010; date of current version November 3, 2010. This paper was recommended by Associate Editor A. Muscat.

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Digital Object Identifier 10.1109/TSM.2010.2061972

Large amounts of inorganic acids and bases are used in plants of integrated circuit manufacturing, cleaning, and etching processes. Acid gases including HF, HCl, HNO_2, HNO_3, and SOx are known to create corrosion problems throughout the fab [7]. Ionic contamination in microelectronic circuitry can have a detrimental effect on device reliability and yield [8]. Based on the statistical data of a semiconductor factory in Taiwan, more than 15% of scrapped wafers are due to metal corrosion defects caused by reactions with acid gases. When metal corrosion occurs it produces irregular shaped particles and destroys the original metal circuit design.

The metal corrosion effect could be caused by either HCl-induced metal corrosion or local cell effect induced metal corrosion [9], [10]. Although not a subject of this paper, the conductivity of the wafer is a key factor for the local cell effect induced metal corrosion. In contrast, HCl-induced metal corrosion is due to the external contamination or *in-situ* contamination in the process chamber. *In-situ*-contamination-induced metal corrosion defects could be prevented by adding water scrubber on the post-etched wafer or by adding O_2 plasma in the metal etch process recipe [11]. There are three possible sources of external Cl^- contamination in the cleanroom: 1) metal etching process chamber preventive maintenance (PM); 2) exhaust and pump line leakage; and 3) outdoor air [12]–[14]. In a semiconductor fab, *in-situ* Cl^- contamination has been well controlled by improving process parameters, but limited research has been done on Cl^- contamination due to chamber PM or exhaust leakage, where the HCl concentration could possibly reach as high as tens of ppmv [15].

The significant factors leading to metal corrosion formation are Al grain size, metal film thickness, backside condition of the wafers, metal etching process parameters, lithography pattern density, and so on [8], [11], [16]. In addition, the mass of metal corrosion defects is positively correlated with the Cl^- exposure concentration [17]. Metal corrosion defects are clearly observed by scanning electron microscope (SEM) [11], and the higher the Cl^- concentration exposure, the more severe were the metal corrosion defects [17]. As a result, accelerated corrosion experiments have been conducted to monitor metal corrosion susceptibility with wafers were kept in a high humidity environment by storing them in a box with deionized (DI) water-induced moisture during a period of time [8].

A simulated AMC environment was used for studying the Cl^- contamination effect with real-time monitoring to

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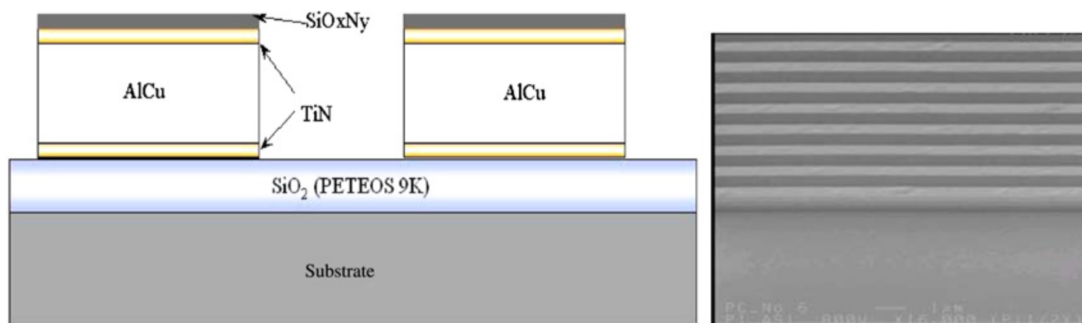


Fig. 1. Schematic of a pattern wafer (cross view) and its SEM image (top view).

understand the critical Cl^- concentration in a cleanroom for preventing metal corrosion on wafers. For such a study, however, ppbv levels of AMC concentration are usually required which is not easy to establish and monitor. Therefore in this paper, an Al–Cu pattern wafer was employed as the witness wafer in a simulated Cl^- contamination environment. The simulated Cl^- concentrations in ppbv levels were established by placing PM wipers which contained HCl into the control environment. The Cl^- concentrations were monitored both by impinger samplers plus IC analyzer and by the ion mobility spectrometer (IMS). The metal corrosion defects on the pattern wafers at different Cl^- concentrations were investigated.

II. Experiment

A. Cleanroom Environmental Control

The experimental tests were conducted in a cleanroom of class 100 with temperature of 22±0.5 °C and relative humidity of 45 ± 2%. The Cl^- concentration was sampled by two impingers in series with a personal pump. By passing ambient air through the impingers, which were filled with DI water, the chloride containing species in the ambient air was then absorbed and analyzed by the ion chromatographer (IC, DX-120, Dionex, Sunnyvale, CA). The impinger sampling and IC analysis method is referred to as impinger+IC hereafter. The impinger+IC method has been proven to be a useful technique for determining trace ionic concentrations in our prior study and the detailed description of the sampling and analysis procedure is referenced to Lin *et al.* [18], [19]. The impinger+IC method was used biweekly to establish cleanroom Cl^- baseline concentration for 1.5 years.

B. Pattern Wafer Design

Pattern wafers were prepared to study the effects of *in-situ* Cl^- residue after the metal etching process. Fig. 1 shows the schematic of a pattern wafer and its SEM picture. The process flow for preparing a pattern wafer is as follows.

1) SiO_2 layer formed by PETEOS chemical vapor deposition process.
2) TiN and Al-0.5%Cu layer formed by metal sputtering process.
3) SiO_xN_y layer formed by chemical vapor deposition process.
4) Photoresist (PR) formed by PR coater and developer. (Recipe: 0.15 μm Logical Metal-1 Lithography).
5) Al-0.5%Cu metal circuit of 0.20 μm thickness formed by metal etching process.
6) Complete pattern wafer after PR stripping.

C. Cl^- Exposure Design

Fig. 2 shows the procedure of pattern wafer exposure for the evaluation of the Cl^--AMC problem. In the first stage test, waste PM wipers obtained directly from the fab were placed into wafer pods (L: 24 cm, W: 24 cm, H: 23 cm) to evaluate the possibility of their forming the HCl molecular contamination. Before exposure experiments, the pattern wafers were put in wafer pods for 2 h, then the pattern wafers were prescanned by KLA (ILM2139, KLA-Tencor Corporation, Milpitas, CA) to check if there was any corrosion defect. The KLA prescan data showed that no corrosion defects were found under normal conditions in the wafer pods. The ambient air in the clean wafer pods was also sampled by two impingers in series and then analyzed by IC. If no experimental interference from other inorganic compounds resulted, then the exposure experiments were processed.

To simulate a Cl^- contamination environment, the waste wipers from etch chamber PM were put into the wafer pods. The waste wipers contained Cl^- ions and other PM byproducts such as isopropanol, they would evaporate into the air in the wafer pods. Different levels of Cl^- concentration were obtained by placing 1, 3, and 5 waste PM wipers, respectively, in three wafer pods. Unexposed pattern wafers were prescanned by KLA as a reference base in the Cl^- molecular contamination tests.

Fig. 3 shows the schematic of the pattern wafer AMC exposure test in a wafer pod. The pattern wafers were placed in the wafer pods under different levels of Cl^- contamination for 2 h. The IMS measured concentrations were compared to the impinger+IC measured concentrations. The impinger+IC method provides time-weighted average concentrations for several inorganic compounds including Cl^-, F^-, and Br^-, and so on. The IMS method is an online instrument that provides *in situ* monitoring data of HCl. Since both instruments have their respective advantages and disadvantages and are frequently used in many semiconductor fabs for different purposes, it would be interesting to understand the data consistency of these two instruments for HCl measurements. After exposure,

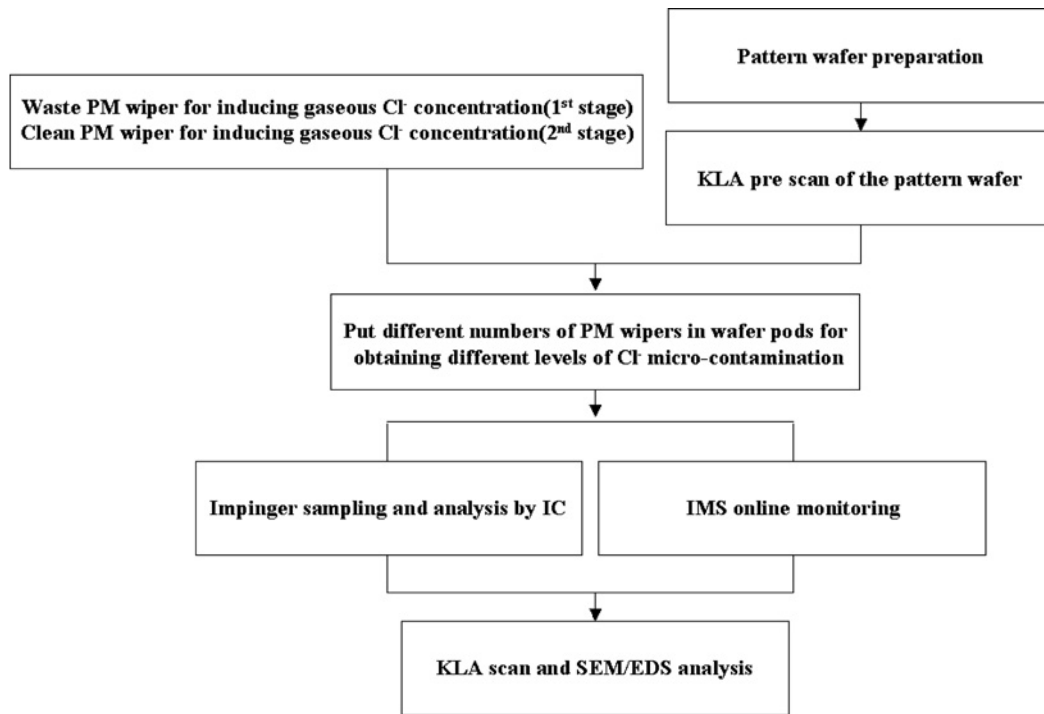


Fig. 2. Process flow of pattern wafer exposure for Cl^- AMC tests.

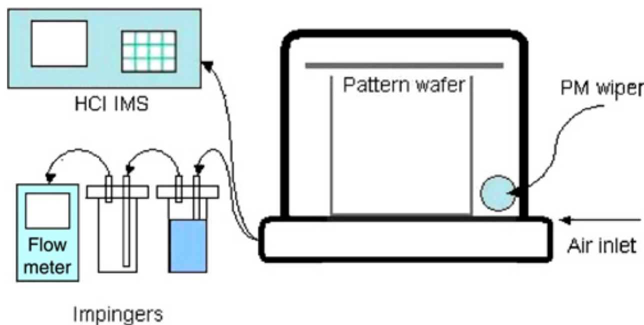


Fig. 3. Schematic of pattern wafer AMC exposure test in a wafer pod for Cl^- contamination.

TABLE I
HCL CONCENTRATION IN WAFER POD DURING THE FIRST STAGE EXPERIMENT AS MEASURED BY THE IMS

Level \ Concentration	Average ± SD	Range
A (1 wiper)	2.9 ± 0.5 (17.2%)	2.0–3.5
B (3 wipers)	8.8 ± 1.1(12.5%)	6.5–10.0
C (5 wipers)	12.5 ± 3.2 (25.6%)	7.5–16.0

Unit: ppbv.

waste PM wipers were removed and the wafer pods were filled with N_2, then they were placed in the N_2 cabinet for further KLA (ILM2139, KLA-Tencor Corporation) and scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDS) (JWS-7555, JEOL Ltd., Japan) analysis to evaluate the metal corrosion defect.

In the first stage experimental tests, the contamination source was approached by using waste PM wipers after chamber PM, which could simulate the real contamination source in the fab. After the first stage experiment, the second stage experiment was performed by using the clean PM wipers, on which the desired amounts of HCl were deposited to establish controllable Cl^- concentrations. There were a total of seven clean pattern wafers with each one dosed with different amounts of HCl solution to obtain different levels of Cl^- concentrations. The following experimental procedure for the second stage was the same as the first stage test.

III. Results and Discussion

A. Monitoring of Cl^- Microcontamination

Table I presents results of the first stage experiment on the average Cl^- concentration as detected by the real-time IMS analyzer. The Cl^- concentration for the level A, which used one piece of waste PM wiper, ranged from 2 to 3.5 ppbv, for the level B (three pieces of PM wiper) from 6.5 to 10 ppbv, and for the level C (five pieces of PM wiper) from 7.5 to 16 ppbv. As expected, the more PM wipers in the wafer pod, the higher the Cl^- concentration.

Fig. 4 presents the correlation of measuring data by IMS and impinger+IC. The IMS instrument provided one HCl measured concentration every 5 min, while the impinger+IC only gave one concentration, which was sampled during a 2 h period. The measured ranges and the average of IMS during each impinger+IC sampling period were compared and shown in Fig. 4. One can see that these two methods have good correlation with R^2 = 0.99. However, at higher HCl concentrations, the impinger+IC measured data tends to be slightly higher than those made by the IMS. This may be due to the impinger+IC method collecting some Cl^- from the

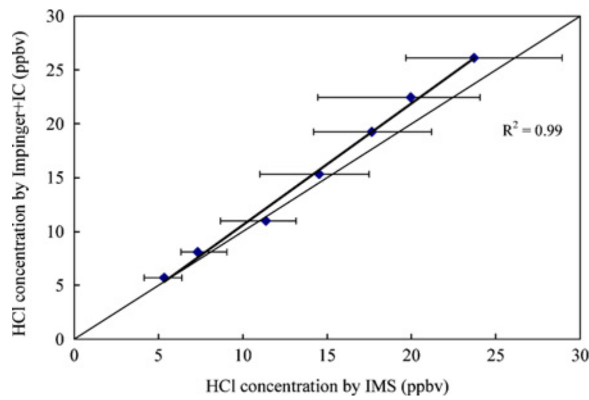


Fig. 4. Correlation between IMS and impinger+IC measured concentrations of HCl (unit: ppbv).

TABLE II
HCL CONCENTRATION IN WAFER POD DURING THE SECOND STAGE EXPERIMENT AS MEASURED BY IMS

Concentration / Level	Average ± SD	Range
1 (1 wiper)	5.3 ± 0.8 (15.1%)	4.1–6.4
2 (2 wipers)	7.3 ± 0.9(12.3%)	6.3–9.1
3 (3 wipers)	11.4 ± 1.6 (14.0%)	8.7–13.2
4 (4 wipers)	14.5 ± 2.0 (13.8%)	11.0–17.5
5 (5 wipers)	17.6 ± 2.4 (13.6%)	14.2–21.2
6 (6 wipers)	20.0 ± 3.1 (15.5%)	14.4–24.1
7 (7 wipers)	23.7 ± 3.1 (13.1%)	19.7–28.9

Unit: ppbv.

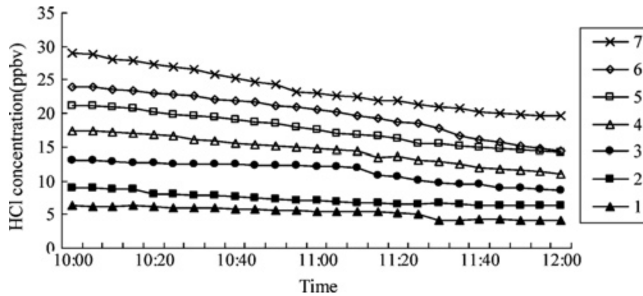


Fig. 5. Measured data during levels 1–7 of HCl exposure in the second stage experiment (unit: ppbv).

particulate phase, while the IMS only detected the gas phase HCl concentration.

Fig. 5 shows the effect of measurement time on the HCl concentrations using the second stage IMS measured data and Table II shows their averaged values and error range. One can see that during the 2 h sampling time, using the PM wiper could provide a fairly good HCl source for AMC tests where the induced HCl concentration was controlled to be around ±12.3–15.5% error range. This could be even better if the sampling time was reduced to 1 h.

The evaporation behavior of Cl^- ions from the PM wiper is similar to that of the permeation tube used for inducing primary standard gas, except that the operation of the PM wiper is much easier than that of the permeation tube. Considering the simplicity of the PM wiper, its average error of 13.9% for inducing Cl^- molecular contamination makes it acceptable for the real fab AMC study of metal corrosion effect.

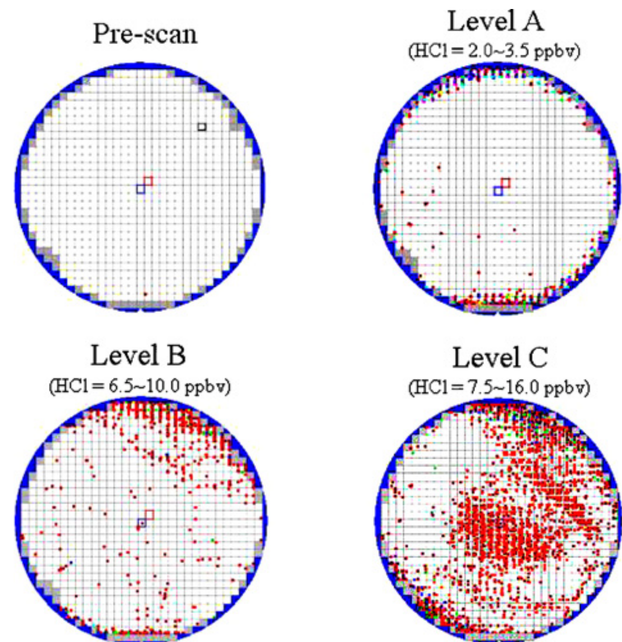
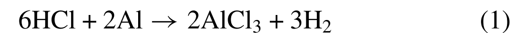


Fig. 6. KLA analysis for the first stage experiment.

B. Influence of Cl^- Concentration on Pattern Wafer

The chemical reaction mechanism of chloride-induced corrosion study is proposed as [9], [10], [17]



$$6HCl + 2Al \rightarrow 2AlCl_3 + 3H_2 \quad (1)$$

$$2AlCl_3 + 3H_2O \rightarrow 6HCl + Al_2O_3. \quad (2)$$

Based on the chemical reactions, Al metal line reacts with HCl and H_2O to produce Al_2O_3 as the reaction product and results in metal corrosion defects.

Fig. 6 shows the KLA picture of defect density on prescan (unexposed) wafers and those on pattern wafers of different levels of Cl^- exposure. For level C, where the pattern wafer was exposed to an HCl concentration of 7.5–16 ppbv as measured by IMS, it had the highest defect density. At HCl exposure concentration of 2–3.5 ppbv (level A), even though the defect density is very low it can still be observed from the KLA inspection. This indicates that there is still a chance of wafer defects at an HCl concentration of 2–3.5 ppbv. Further analysis, however, showed that there was no Cl element found in pattern wafer particles of level A by EDS analysis, and no metal corrosion was observed by the SEM image. Thus, under the exposure condition of Cl^- concentration of around 2–3.5 ppbv, the possibility of metal corrosion is very low during 2 h of exposure time.

Results on the SEM/EDS analysis of pattern wafer under level B exposure are shown in Fig. 7. One can see that metal corrosion defects were clearly observed by the SEM image and elemental Cl was found by EDS analysis. More severe metal corrosion defects were found for level C exposure but the results are not shown. Thus, under Cl^- exposure concentration of higher than 6.5 ppbv there could be a high probability of metal corrosion defects.

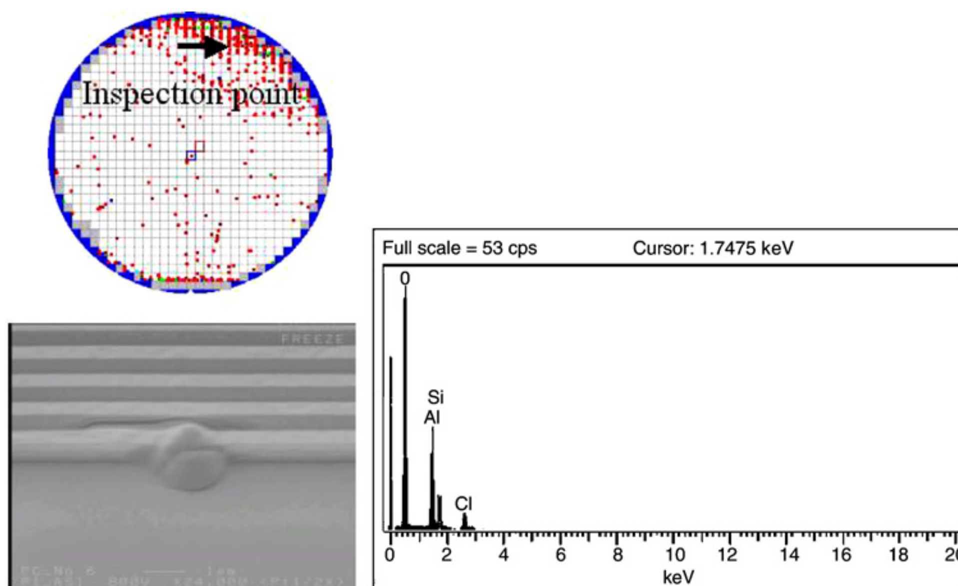


Fig. 7. SEM/EDS corrosion defect analysis for the first stage experiment of level B (HCl = 6.5–10 ppbv) wafer (left: SEM image, right: EDS analysis of the Al–Cu layer).

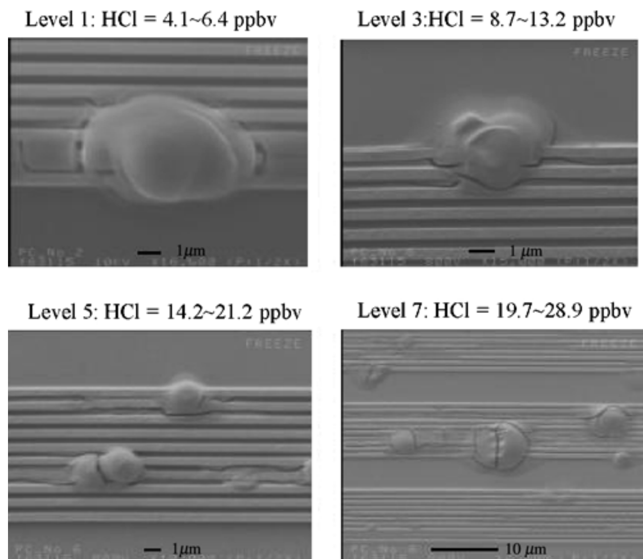


Fig. 8. Corrosion defects using SEM images of the second stage experiment (levels 1, 3, 5, 7).

To further clarify the correlation of metal corrosion defects with respect to the ambient Cl^- concentration, the SEM/EDS analysis for the second stage experiment was performed and the results are shown in Fig. 8. It was found that metal corrosion defects were observed and elemental Cl was detected in all pattern wafers exposed at levels 1–7 (Cl^- concentration of 4.1–28.9 ppbv), i.e., the corrosion defect occurrence for levels 1–7 exposure tests was 100%. This indicates that the corrosion occurrence of pattern wafers is reliable and it could be a Cl^- microcontamination monitoring method. Under the exposure condition of level 7 (19.7–28.9 ppbv Cl^- concentration), metal corrosion defects were easily observed by an optical microscope.

In 1996, Higley *et al.* [20] proposed that when HCl concentration was controlled under 9 ppbv, metal corrosion would not occur. In contrast, our study shows that at Cl^- concentration of much less than 9 ppbv the metal corrosion defect is clearly observed. To prevent metal corrosion defects, the HCl concentration should be controlled under 3.5 ppbv for TiN–Al-0.5%Cu wafer. The exact reason for this difference is unclear because Higley *et al.* [20] did not provide experimental details. This paper employs 0.15 μm logical metal layer lithography technology, and the major technology used by Higley [20] was larger than 0.5 μm in 1996. Thus, the reduction in the dimensions of integrated circuits should lead to a higher sensitivity to the microcontaminants and metal corrosion defects are more easily observed at a lower AMC concentration.

C. Cl^- Contamination Control

In the study of Li *et al.* [15], the release of HCl gas from the PM of metal etchers could be as high as 343 ppmv without any control means; hence the release of HCl gas might cause corrosion on the wafers and process tools. To prevent HCl gas emission, a PM hood was used to confine Cl^- contaminants to only be present in a PM hood environment. In a real fab study, PM hoods have been proven useful to reduce Cl^- concentration in cleanrooms. A chamber fore line between the process tool and the local scrubber is another potential source of HCl emission. Thus, to avoid HCl emissions from fore lines, annually replacing fore line center rings is useful to prevent waste gas leakage from fore line pipes.

Based on these two approaches to reduce HCl emission, the impinger+IC sampling and analysis from an 8 in semiconductor factory etching area has been conducted for 1.5 years. In the data collection period, all HCl concentration could be controlled under 2 ppbv without any metal corrosion defects. In a real fab, the control specification of HCl concentration is 9.6 ppbv, but the proposed limit based on this paper is below 2 ppbv to avoid scrapping wafers.

IV. Conclusion

In this paper, a patterned wafer corrosion monitoring method was proposed that proved useful for the detection of Cl^- contamination sources as early as possible. It showed that Cl^- containing PM wipers could be used as a simulated contamination source to control the simulation environment to ppbv levels within $\sim$15% error range. Both the IMS and impinger+IC methods for monitoring the Cl^- contamination in the ambient air are useful tools and they give almost identical results based on the 2 h averaged Cl^- measured data. For a 0.15 μm logical metal layer lithography technology, metal corrosion can occur when placing wafers in an HCl molecular contamination environment of 4.2 to 6.4 ppbv for 2 h, and it does not occur when controlled to be below 3.5 ppbv. For a real fab case study of 1.5 years, the HCl concentration has been controlled to below 2 ppbv by chamber PM using PM hood and by annually replacing center-rings. Furthermore, it has been proven that no Cl^- contamination effects cause metal corrosion observed in the fab.

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S. S. Liu, photograph and biography not available at the time of publication.