Fire prevention study of wet bench cleaning stages in semiconductor manufacturing processes－incompatibilities of hydrogen peroxide

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Abstract

According to the research reports from the FM (Factory Mutual) Insurance Company, for the past two decades most of the incidents that occurred in semiconductor plants were identified as "Fire Cases." These reports claimed the fires in Wet Chemical Cleaning Processes were mainly caused by heater failure, yet, based on the process conditions, a heater is designed to shut down automatically when the temperature exceeds a set point. Therefore, a thorough study on simulations of fires in Wet Chemical Cleaning Processes is necessary.

Basically, incidents involving large loss in industry might be initiated by chemical incompatibility. This study focused on the incompatible behaviors of cleaning materials used in Wet Chemical Cleaning Processes. It also attempted to verify the causes of fires in Wet Chemical Cleaning Processes under manufacturing processes in semiconductor plants.

The purpose of this study was not only to determine the causes of fires in such processes, but also to study the potential hazards of commonly used chemicals (Hydrogen Peroxide, Concentrated Sulfuric Acid, Concentrated Hydrochloric Acid and Isopropyl Alcohol). Accordingly, this would lead to establishing a concentration triangular diagram, which could be used to identify a combustible, deflagration or even detonation zone. Finally, this study can provide basic design data with a safer approach to avoid potential hazards caused by dangerous mixtures, which may result in large property loss in semiconductor plants.

Keywords: Semiconductor, Fire Cases, Wet Chemical Cleaning Processes, Chemical Incompatibility, Concentration Triangular Diagram

Introduction

Because of the stellar performance of semiconductor industries in terms of economic significance in Taiwan since the 1980s, along with the increasing fire hazards or number of accidental chemical releases, relevant research is needed not only in Taiwan, but worldwide. This study focused on the main causes of fire accidents among wet chemical cleaning processes in semiconductor manufacturing industries so that proactive measures could be adequately established regarding chemicals and incompatibilities.

In view of the competitive market in this sector, any abnormal shutdowns or unexpected incidents are unacceptable. For example, at the time of the accident in Bhopal in 1984, Union Carbide was the seventh largest chemical company in the world; the large number of injuries and loss of life resulted in compensation amounting to 4.7 billion U.S. dollars as well as one time higher insurance paid the following year. Finally, Union Carbide has all but disappeared in the world 17 years after the accident (Lees, 1996; Bhopal Today, 2002; Bhopal, 2001). Therefore, with stringent regulations in place, it is important to carefully study safety in process operation and potential hazards in the semiconductor industries.

Since the 1970s, the semiconductor industries have 21.9% annual growth rate all over the world. Examples on Taiwan, which is the fourth in terms of throughput, are U.S 5.0 billion in 1995, 12.0 billion in 1999, 20.0 billion in 2000 and 18.0 billion in 2001, respectively (Directorate General of Budget Accounting and Statistics, 2002). However, the accidents in Taiwan resulted in significantly higher insurance premiums. In semiconductor processes, many chemicals are used in the wet bench. Wet bench processes can be categorized as RCA-Clean process chemicals, etching acids and solvents that can be applied to cleaning, etching, exposure and photoresist reactions, respectively. After each process, ultrapure water could be used for wafer cleaning. But in order to avoid water scars and reaching dried effects, Isopropyl Alcohol, $CH_3CHOHCH_3$, (IPA) would be utilized in removal of water stains (Kern, 1993), The market scope of chemicals used in the semiconductor industryl approached U.S. 21.2 billion in the world until 1999 and it has grown steadily annually. Considering these large amounts of chemicals, the semiconductor industries need to pay more attention to safer operation, especially for incompatibility reactions. The aim of this study was to use wet chemicals in the semiconductor cleaning chemical process, such as hydrogen peroxide (H_2O_2), concentrated sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and IPA, in order to conduct incompatibility reactions and observe the phenomena between various mixture materials.

Historically, most of the accidents involved in the wet chemical cleaning process in semiconductor industries have been identified as "fires." As summarized by Factory Mutual (FM) Global Co., the main cause is "heater failure" (FM, 2002). But according to equipment research, a heater should stop automatically under overheating conditions. This study also proposed to study unexpected incompatibility reactions while wet chemicals were mixed with each other. Therefore, whether the cause of a fire is only heater failure or incompatibilities of wet cleaning chemicals and so on, could be fully elucidated in this study. Finally, besides analyzing the causes of fires and the incompatibilities of cleaning chemicals, our goal was to both create a weight concentration triangle to identify the dangerous zones and to recommend a safer mixture ratio. Then, based upon the results, unexpected disasters due to the incompatibility reactions could be avoided.

Results and Discussion

Various Incompatibility Samples. In principle, many chemicals are used in the wet chemical cleaning process. Therefore, before a hazard assessment, substances with higher potential hazards than the others should be chosen and then further incompatibility experiments should be conducted. Table 1 shows the results of various incompatibility sample tests. According to the empirical criteria of the U.S. Coast Guard (USCG, 1995), in the course of the experiment, more than a 25℃ rise was observed--that is defined as chemical incompatibility (Duh, 1997). Therefore, by observing the mixtures of H_2O_2 + H_2SO_4 and H_2O_2 + HCl, they have demonstrated incompatibility reactions.

Judgment of Titration Sequence. Because three substances should be mixed in the titration experiments, it is necessary to judge the entrance sequence into the glass beaker. Table 2 displays the phenomena that, after the acids join with the H_2O_2 or IPA, all could raise the incompatibility temperature and change the solution color. Therefore, the final titration sequence is to introduce the acid to the burette, then pour it into the glass beaker which originally contains mixed solutions of H_2O_2 and IPA.

SPM-Normal Experiments. A series of experiments were conducted based on the real concentration of the used chemicals, H_2O_2 (31 wt%)、H_2SO_4 (98 wt%) and IPA (100 wt%) which are strictly in the wet chemical cleaning process, demonstrating the incompatibility titration tests under various weight concentration mixed ratios. The final results and the drawn weight concentration triangle are displayed in Figure 3. Development from the test series depicts that, in tests of the left-upper corner of the weight concentration triangle, it has no significant reaction. However, there are vigorous incompatibility reactions in the right-lower corner, which displays overflow, boiling (defined as temperature rise up to 100℃ or above), smoking and bubbling (two-phase relief, hybrid) phenomena, respectively, (as seen from Figures 4-7). Along with the weight concentration of H_2O_2 increase (10→90 wt%) and both H_2SO_4 and IPA decrease, or while H_2SO_4 increases (10→90 wt%) and H_2O_2 increases with IPA decrease, or when IPA increases (10→90 wt%) and both H_2O_2 and H_2SO_4 decrease, substantial temperature rises appear in the weight concentration triangle. As observed from experimental results, there are various phenomena in these SPM-Normal experiments that accompany the changes of reaction mechanisms. While the weight concentration of H_2O_2 is the highest, the reaction could go exothermic and evaporate rapidly, generating overflow and boiling phenomena, along with a great deal of smoke and bubbles. In addition, when the amount of H_2SO_4 is dominant, the final products appear dark and foamy. If IPA is dominant in the mixed ratio, the reaction could generate a round type smoke and last a long time.

The reaction type of the sequential tests is ascribed to the nth order phenomenon which is defined, after titration of the contaminant acid, as the temperature increasing suddenly (near 1~2 minutes) to a maximum, then dropping off to the ambient temperature. Therefore, the definition of reaction time in this study, the so-called time to maximum reaction temperature (TMRT), is the time period since initial temperature to maximum. In the sequential tests, the average TMRT is 44.7 seconds. In all the tests that have boiling phenomena (maximum temperature is equal or greater than 100 ℃) the average TMRT is 39.8 seconds.

Meanwhile, by judging with the USCG empirical criteria all the incompatibility reaction tests, the temperature difference between initial and maximum temperature exceeds 25℃ (Duh, 1997). Here, the test numbers of 6, 9, 10 and 16~36 have an average reaction temperature of 89.0℃, along with tests that have boiling phenomena of 106.3℃. Therefore, in these sequential tests that have incompatibility phenomena, the average temperature rise rate is 2.0 ℃/min, with boiling phenomena of 2.7℃ /min.

In summary, the experimental results show that real utilized concentration and mixed ratio (test number 22) in the wet chemical cleaning process of a semiconductor significantly demonstrates potential hazards. In addition, among these sequential tests, the most severe hazard mixed ratio is identified by test number 35. The dangerous zones that have boiling phenomena having a shorter reaction time are shown in Figure 8. Also, Figure 7 displays the maximum hazardous tendency curve of H_2O_2, H_2SO_4

and IPA. This real process section shows that the incompatibility hazards allow only a to a very short time (1 minute) for emergency rescue operations. In addition, this kind of incompatibility reaction would generate a large quantity of vapor and smoke that would enhance ion concentration in the clean room and could destroy the whole process area, including devices in the neighborhood. For this reason, past fires that happened in the wet chemical cleaning process of a semiconductor plant not only could have been caused via heater failure as claimed by FM Global, but also by a sudden exothermic reaction and temperature rise due to the chemical incompatibility reaction.

SPM-Recycled and SPM-H_2O_2 Concentrated Experiments. For the sake of cost reduction, semiconductor plants all attempt to recycle the useable chemicals, in which sulfuric acid is the typical one. Usually, the recycled concentration is 70 wt%. In addition, to elucidating the concentration effects of H_2O_2, this study also performs a comparison experiment to evaluate its recycled concentration up to 45 wt%. From experimental results (see Figures 9 and 10), no significant reaction phenomena are occurring in both sequential tests. Although both of the reaction types belong to the nth order reaction, there is not any test number showing incompatibility temperature rise. Therefore, the utilized chemical concentration and mixed ratio of these two test series could be taken into account for safety process design.

HPM-Normal Experiments. These sequential experiments could be simulated on real concentration of used chemicals, H_2O_2 (31 wt%)、HCl (37 wt%) and IPA (100 wt%), in the wet chemical cleaning process, to conduct the incompatibility titration tests under various weight concentration mixed ratios. The final results are shown in Table 4, and the drawn weight concentration triangle is displayed in Figure 11. With the reaction phenomena of the sequential tests pertinent to overflowing, bubbling, smoking and two-phase relief, an induction period prior to vigorous reaction appears, as shown in Figure 12. Along with the increase of H_2O_2 weight concentration (10→90 wt%) and HCl with the decrease of IPA, or while there is an increase of HCl weight concentration (10→90 wt%) and H_2O_2 increases with IPA decrease, or when there is an increase of IPA (10→90 wt%), with the decrease of both H_2O_2 and H_2SO_4, each has a substantial temperature rise indicated in the weight concentration triangle.

In addition, the reaction type of these test series is identified as an autocatalytic phenomenon which is observed to have an induction period, followed by a significant reaction quickly reaching a maximum temperature. In this test series, the average TMRT is 284.3 seconds. Meanwhile, by judging the whole incompatibility reaction tests with USCG empirical criteria, the test numbers of 17~36, have an average reaction temperature of 62.9 ℃. Accordingly, in these test series that demonstrated incompatibility phenomena, the average temperature rise rate is 0.2 ℃/min.

In summary, the experimental results show that the real utilized concentration and mixed ratio (test numbers 1, 10, 18 and 25) in the wet chemical cleaning process of semiconductor plants potentially have significant hazards. In addition, among tests, the most dangerous hazard of mixed ratio is test number 33. Here, the dangerous zones that have incompatibility phenomena with a shorter reaction time are shown in Figure 13. Figure 13 also displays the maximum hazardous tendency curve of H_2O_2, HCl and IPA. Therefore, while this real process section indicates an incompatibility hazard, rescue staffs should be very careful, because it has no significant hazard phenomena and it is difficult to observe the induction period during which heat will accumulate to trigger the reaction. For this reason, the potential hazards are more dangerous than in the SPM-Normal process, because the autocatalytic decomposition is quite violent and unnoticed until it reaches its accelerating period (Hou, 2001).

Proposed Decomposition Mechanisms

From a literature search, this study proposed mechanisms for the incompatibility reaction mechanisms. The following are the proposed mechanisms probably occurring in SPM-Normal and HPM-Normal reaction stages (Livingston, 1925; Schumb, 1955; Mackenzie, 1991; Burke, 1995; Joshi, 1995; Tomiyasu, 1995; Hisham, 1998; Muller, 1998; Diehl, 2000; Minkwitz, 2002).

SPM-Normal Process

Initiation:

$(CH_3)_2CHOH + H_2SO_4 \rightarrow (CH_3)_2CHOH_2^+ + HSO_3^-$

$(CH_3)_2CHOH \rightarrow CH_3 \rightarrow CH_3CH{=}CH_2 + H_2O$

$2(CH_3)_2CHOH \rightarrow ((CH_3)_2CH)_2O + H_2O$

$H_2SO_4 + H_2O_2 \rightarrow H_2SO_5 + H_2O$

$H_2O_2 \rightarrow H_2O + 1/2\ O_2$

$H_2O_2 \rightarrow HO_2 + H^+ + e^-$

$H_2O \rightarrow H^+ + OH^-$

$H_2O \rightarrow 1/2\ H_2O_2 + 1/2\ H_2$

$H_2O \rightarrow H_2O^+ + e^-$

Propagation:

$HSO_3^- + H_2O_2 \rightarrow SO_2OOH^- + H_2O$

$((CH_3)_2CH)_2O + H_2SO_4 \rightarrow (CH_3)_2CHOSO_3H + (CH_3)_2CHOH$

$H_2SO_5 \rightarrow HO\text{-}(SO_2)\text{-}O\text{-}OH$

$HO\text{-}O\text{-}(SO_2)\text{-}OH \rightarrow OH + OSO_2\text{-}OH$

$H^+ + H_2O_2 \rightarrow OH + H_2O$

$H^+ + O_2 \rightarrow HO_2$

$OH + H_2O_2 \rightarrow H_2O + HO_2$

$H_2O^+ + H_2O \rightarrow OH + H_3O^+$

$e^- + OH \rightarrow OH^-$

$e^- + H + H_2O \rightarrow OH^- + H_2$

$e^- + H_2O_2 \rightarrow H + OH^-$

$e^- + H_2O \rightarrow H + OH^-$

Termination:

$SO_2OOH^- + H^+ \rightarrow H_2SO_4$

$CH_3CH{=}CH_2 + H_2O \rightarrow (CH_3)_2CHOH$

$(CH_3)_2CHOH + O_2 \rightarrow CH_3COCH_3 + H_2O_2$

$H + OH \rightarrow H_2O$

$2OH \rightarrow H_2O_2$

$2HO_2 \rightarrow H_2O_2 + O_2$

$H + HO_2 \rightarrow H_2O_2$

HPM-Normal Process

Initiation:

$(CH_3)_2CHOH \rightarrow CH_3 \rightarrow CH_3CH{=}CH_2 + H_2O$

$2H^+ + 2Cl^- + H_2O_2 \rightarrow Cl_2 + 2H_2O$

$H^+ + Cl^- + H_2O_2 \rightarrow HClO + H_2O$

$HCl \rightarrow H^+ + Cl^-$

$H_2O_2 \rightarrow H_2O + 1/2\ O_2$

$H_2O_2 \rightarrow HO_2 + H^+ + e^-$

$H_2O \rightarrow H^+ + OH^-$

$H_2O \rightarrow 1/2\ H_2O_2 + 1/2\ H_2$

$H_2O \rightarrow H_2O^+ + e^-$

Propagation:

$(CH_3)_2CH + 2H_2O \rightarrow (CH_3)_2CHOH + H_3O^+$

$Cl_2 + H_2O_2 \rightarrow O_2 + 2Cl^- + 2H^+$

$HClO + H_2O_2 \rightarrow H^+ + Cl^- + H_2O\ 1/2\ O_2$

$H_2O_2 + Cl_2 \rightarrow 2H^+ + 2Cl^- + O_2$

$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$

$H^+ + H_2O_2 \rightarrow OH + H_2O$

$H^+ + O_2 \rightarrow HO_2$

$OH + H_2O_2 \rightarrow H_2O + HO_2$

$H_2O^+ + H_2O \rightarrow OH + H_3O^+$

$e^- + OH \rightarrow OH^-$

$e^- + H + H_2O \rightarrow OH^- + H_2$

$e^- + H_2O_2 \rightarrow H + OH^-$

$e^- + H_2O \rightarrow H + OH^-$

Termination:

$CH_3CH{=}CH_2 + H_2O \rightarrow (CH_3)_2CHOH$

$(CH_3)_2CHOH + HCl \rightarrow (CH_3)_2CHCl + H_2O$

$(CH_3)_2CHOH + O_2 \rightarrow CH_3COCH_3 + H_2O_2$

$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HClO$

$H_2 + Cl_2 \rightarrow 2HCl$

$H + OH \rightarrow H_2O$

$2OH \rightarrow H_2O_2$

$2HO_2 \rightarrow H_2O_2 + O_2$

$H + HO_2 \rightarrow H_2O_2$

Conclusions and Suggestions

Clearly, the wet chemical cleaning process in the semiconductor industries potentially has enormous hazards that include overflow, boiling, bubbling, two-phase relief and incompatibility reaction phenomena. In addition, there are significant differences, such as reaction types, between SPM and HPM processes--the former is an nth order reaction and the later is similar to an autocatalytic reaction. But if the utilized concentration of acid decreased whether to increase H_2O_2 weight concentration or not that could not incur any the incompatibility hazards. Therefore, in order to prevent and decrease these unexpected accident costs, plant personnel should precisely understand the operating conditions in various process stages and establish inherently safer approaches--not only to use routine methods to prevent fires, but also to apply safer design and to promote safety during operation.

In this study, a weight concentration triangle of substances in a specific process was properly drawn that could predict the hazard zones and establish the safety of utilized chemical concentration with various mix ratios. In addition, based upon the tendency line in the weight concentration triangle, engineers could understand the incompatibility reaction tendency of wet chemicals. Furthermore, this approach could provide valuable and prudent recommendations on fire prevention, such as in the cause of the wet chemical cleaning process incident reported by FM Global, to judge whether the original cause was heater failure or not. Finally, this study also offers many reaction hazard phenomena for semiconductor industries so that similar accidents can be prevented or, if they occur, could be mitigated to an acceptable level.

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