Practical Reviews of Exhaust Systems Operation in Semiconductor Industry

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Abstract. Scrubbers are widely used for air pollution treatment in semiconductor. Efficiency of waste gas treatment must be carefully maintained for environmental and health issue. However, due to the complex types of exhaust system and the needs of using chemicals with different characteristics at the same time in the semiconductor process, many conditions will occur in the operation of the scrubber tower and the processing efficiency will be reduced. This paper aims at the common problems such as growth of bacteria, unstable pH, white smoke, and inaccurate monitoring of exhaust gas flow rate. Based on the investigation, all the analysis, results and solutions are provided as practical reference for other semiconductor companies.

Keywords: Scrubber; Air pollution treatment; Semiconductor company; Exhaust system operation; Practical solutions.

1. Introduction of exhaust and scrubber system

Semiconductor products are manufactured in a variety of processes, and the chemical substances used in the manufacturing process are also various within the ECO-system (Fig. 1). During the manufacturing, flue gases from the machine will be exhausted and treated to ensure the workplace and environment within allowable limits and standards. The exhaust gases can be generally divided into acid, alkaline, organic and general exhaust according to their characteristics. The process exhaust at the machine end will generally pass through the attached local scrubber before being further discharged to the central scrubber for waste gas treatment at the factory end [1]. The largest proportion in the exhaust are treated by the washing tower. The gas treated by the tower is directly discharged into the atmosphere after passing through the exhaust system. Thus, the operating efficiency of the system is critical to environmental air quality and human safety and health.
The types of exhaust systems are mainly based on the process systems and treatment needs. There are five types of exhaust systems according to the manufacturing process at the scattered area, depending on the characteristics of emissions as follows: (i) Acid/Alkali exhaust, (ii) Light Organic Exhaust, (iii) Chemical Vapor Deposition (CVD) Exhaust, (iv) Heavy Organic Exhaust or VOC Exhaust (OGT & RTO), and (v) General & Heat (GEF) Exhaust [2]. Wet scrubber, the core part of the exhaust system, can be generally divided into scrubber body, filling material, sprayer, defogging device, pH and conductivity controller, circulating system, and dosing system. Despite of slightly different designs, the operating principle is (principles are) similar among different wet scrubbers, i.e., after the waste gas is being scrubbed by neutralized solution (chemical and water), it will finally go into the ambient air. Proper design and installation can help the plant to meet the requirements of air emission regulations. Furthermore, proper maintenance for the equipment can ensure the smooth operation of the scrubber tower and achieve a better treatment efficiency. Previous studies on washing systems usually focus on the design parameters or the comparison of different systems (i) to (v), however, the discussions on the problems that often occur in system operation and corresponding solutions are seldom documented.

Figure 1. Industrial ECO-Systems Design for Chemical and Gases.

The growth of bacteria in the scrubber column, the formation of a large number of bubbles, the white smoke from the flue, the improper configuration of exhaust air flow detector and air duct are common problems in the system which will result in the reduction of the scrubber efficiency and affect the air-emission quality. This paper will systematically analyze and address the main problems that have occurred in the semiconductor plants based on the data of the exhaust systems and corresponded scrubbers.

2. Operational Abnormality in Exhaust Systems

2.1. Exhaust and scrubber systems

The main components of air pollution sources from the semiconductor manufacturing process are shown in Table 1. The main toxic and flammable gases are generated from the process of oxidation diffusion and chemical deposition reactions [3]. Acid/base and organic solvent gases are mostly produced by etching and cleaning process. In particular, the proportion of acid/alkaline waste gas among the total emissions is always the highest.
Table 1. Process pollutant types and ingredient.

| Types of exhaust gas        | Contaminated Ingredients                                      | Source of Pollution                                      |
|-----------------------------|-----------------------------------------------------------------|----------------------------------------------------------|
| Acid and alkali gases       | **Acid gas**: HF, HCl, HNO₃, H₂SO₄,                            | Oxidation, photomask, etching,                           |
|                             | CH₃COOH, H₃PO₄, H₂Cr₂O₇                                        | oxidation, reaction furnace, diffusion, furnace cleaning  |
|                             | **Alkali gas**: NH₃, Na₂O                                       |                                                          |
| Organic solvent             | CH₃Cl₂, CH₃Cl, butanone, toluene, ethylbenzene, acetone,       | Photoresist cleaning, developer,                         |
|                             | benzene, xylene, methyl-2-pentanone, Isopropyl alcohol,        | wafer cleaning                                           |
|                             | butyl, etc.                                                     |                                                          |
| Toxic gas                   | AsH₃, PH₃, SiH₄, B₃H₆, B₄H₁₀, P₂O₅, CCl₄, HBr, BF₃, AlCl₃, | Oxidation, photomask, etching, diffusion, ion implantation|
|                             | B₂O₅, As₂O₃, POCl₃, Cl₂, HCN                                    |                                                          |
| Combustible gas             | AsH₃, PH₃, SiH₄, BH₃, H₂                                        | Ion implantation, CVD, diffusion                         |

The exhaust system is where these waste and toxic gases go into, and the scrubbers are the key component in each exhaust system, which could be also divided into local scrubbers and central scrubber. Also, the scrubbers are divided into acid scrubbers and alkaline scrubbers according to the different acidity and alkalinity of the gases they treat. As shown in Fig. 2, The principle of wet filled column washing method is to absorb pollutants in the air by washing waste gas with an aqueous solution. To remove the high acid/base/toxicity of pollutants efficiently, the filling column is generally used to increase the contact area of liquid/gas and make the liquid-gas two phases in close contact [4]. The pH >7 aqueous solution is pumped to the top spray system via a circulating pump, and the filler is uniformly wetted under ideal operation. After washing down acid/alkali waste gas contained in the exhaust, the chemical dosing system is used to add acid and alkali for neutralization, concentrated water in the scrubber tower shall be discharged after being discharged to the internal wastewater treatment plant. The wet scrubber can deal with a large amount of waste gas discharged by multiple pollution source at the same time. Different washing liquid scrubbers can be used in series to ensure the removal efficiency of pollutants with different characteristics in multiple washing stages.

Figure 2. Washing tower and peripheral equipment (a) P&ID diagram, and (b) schematic diagram.

2.2. Common problems in operation of scrubber system

Due to the characteristics of the waste gas, the proportion of abnormal problems occurred in the scrubbers and peripheral equipment dealing with acid gas was as high as 76 %, accounting for the largest part, based on the actual operation experience of scrubber system in a semiconductor plant [5]. High
malfunction rate of the acid scrubber brings harmful effect on the production and the maintenance in operation. The most common problems in the operation of the packed scrubber are:

i. Pipeline blockage
Bacteria cultured in the scrubber multiply rapidly and form slime or accumulation blocked in the pipeline or the Raschig ring, resulting in increased pressure loss and reduced air volume of waste gas treatment [6]. Common problems are caused by fungus obstruction, blocked drainage, insufficient circulating water, broken pipe fitting caused by running vibration, obstruction of sprayer, failure of flowmeter. The occurrence of these problems will directly affect the efficiency of the waste gas treatment system and may immediately conflict with the regulations.

ii. Abnormal pH value
The most important control parameter of the scrubber is the pH value, and the abnormal pH value may lead to the decrease of waste gas treatment efficiency or the excessive addition of agents [7]. The reasons that may affect the accuracy of pH measurement are usually electrode attenuation, electrode contact loosening, water vapor infiltration contact and bacteria growing on the surface of the electrode. The error between the actual value and the measured value is too large.

iii. White smoke from chimney
White smoke from the smokestacks of waste gas treatment systems is a common problem in semiconductor plants, in severe cases the light impermeability may exceed regulatory emission standards.

iv. The flow monitoring system
The design of the flow monitoring system has not taken into account the non-uniformity of airflow distribution, so that the measured value and the actual value are too large, when the discharge is close to the upper limit of the application specification, it may be illegal to be fined for actually exceeding the specification.

3. Abnormality Analysis and Solution of Exhaust Systems
The following section will analyze the root causes and propose reasonable solutions for the abnormalities. The system is the most frequently affected by the pH control, followed by the stability of circulating water volume. These two influences will not have a serious and immediate impact on the system, but they are directly related to the exhaust gas treatment efficiency and the compliance degree of regulations.

3.1. Abnormal pipeline control
Due to the complex exhaust composition of the semiconductor process, it is a breeding ground for fungi and algae after being dissolved in water. Algae usually appear in the pipes that are exposed to sunlight, and the color is bluish green. Fungi appear in confined spaces that are not exposed to sunlight, and the color is white or yellow. These microorganisms multiply quickly and form sticky sludge or deposits that are blocked in the pipeline, resulting in increased pressure loss and reduced exhaust gas treatment air volume. To deal with the growing bacteria, following directions may be referred:

(i) Activated sludge method for cultivation of microorganisms: for different fungi, cultivate specific microorganisms for treatment;
(ii) Chemical treatment to eliminate bacteria: Add oxidizing/non-oxidizing drugs to kill and remove the fungus. Oxidizing drugs such as chlorine ingot, \( \text{H}_2\text{O}_2 \), sodium hypochlorite, etc. Non-oxidizing drugs include quaternary ammonium salt, isocyanatomethane, glutaraldehyde, etc. [8];
(iii) Physically clean to remove attached fungi.

Due to the complexity and changed environment in the process exhaust, chemical method is used to control the growing bacteria instead of activated sludge process. The drug of choice is sodium hypochlorite, the most common and easily available in water treatment. In fact, the sterilization of the scrubber can be carried out in two aspects: regularly adding low concentration of sodium hypochlorite in the daily operation or adding a large amount of sodium hypochlorite after the stop to fully sterilize. However, the optimal sterilizing pH range of sodium hypochlorite is below 7, while the water quality
condition of the washing tower is about pH 8.5, under which the sterilizing function of hypochlorite is not significant.

Therefore, this study also evaluated the dredging effect of adding a large amount of medicine after shutdown: after the washing tower was shut down and the pH was adjusted to be acidic, sodium hypochlorite was added to the washing tower for continuous sterilization for 24 hours. It was found that although the fungi on the surface of the Raschig ring were reduced, the sterilization effect inside the packing was limited, and the overall pressure reduction effect of the washing tower was not obvious. There are other risks of sterilization in this way: (i) The reaction between sodium subinfeudate and fungi may cause a large amount of gas to bubble, damaging the structural strength of the scrubber. (ii) The oxidation of sodium hypochlorite is an exothermic reaction. There are some carbonates left after the death of fungi. Once too much carbide is produced, there may be a risk of fire.

Usually, a low concentration of sodium hypochlorite is added in circulating water washing tower in a row, to minimize bacterial growth and increase the speed of the pressure loss of the washing tower.

3.2. Abnormal pH control

The pH meter of the scrubber needs to be calibrated monthly with a standard solution of pH 7, 4, and 10. If the value cannot be adjusted to the standard solution or the value has drifted too high for a period of time, the timeworn sensor must be replaced periodically. As the replacement frequency is too high and unreasonable, after careful inspection of the sensor and the circuit, the real reason lies in the poor design of the pH sensor joint of this model. It is possible for water and air to permeate into the joint to affect signal transmission and the joint welding point is easy to be disassembled due to frequent rotation and poor contact. If the pH value is unstable, a short-term solution to the water vapor in the high-pressure air blow-dry joint can restore the signal transmission to normal. If the contact is defective, the joint should be replaced. In addition, the circulating water of general acid scrubber usually contains HF of high concentration, so a hydrofluoric acid-resistant sensor should be selected in this water quality, otherwise the corrosion of the glass layer on the surface of the sensor will often cause easy failure of the pH sensor.

3.3. Emission of the white smoke

There are two main sources of white smoke in smokestacks: smoke from the condensation nuclei of SiO2 particles as water vapor, and white smoke from ammonium chloride from the presence of NH3 in acidic waste gases [9-10]. The first production of white smoke contains large amounts silicon dioxide particles, which are produced by the oxidation of gas SiH4 that is commonly used in semiconductor process. After wet washing tower contains saturated moisture environment, SiO2 particles become the saturated water vapor condensation nuclei. While the dewatering plate of the scrubber tower has limited blocking efficiency on the water mist, making the discharge water mist through the chimney. To solve this problem, periodic cleaning of silicone dust in windmills will be of great help [11-12].

For the problem of NH3 producing ammonium chloride, this study detected the presence of NH3 in the acid exhaust wet scrubbers. Theoretically, NH3 should be discharged into the alkaline exhaust system instead of the acid exhaust pipe. There are the following reasons for NH3 in the acid exhaust:

(i) In the machine hookup, the data is wrong, or the exhaust pipe route is not changed after the change of gas used in the process, so that the alkaline gas is discharged into the acid exhaust pipe route.

(ii) NH3 and SiH2Cl2 gases are used in some processes of the furnace tube, so that the mixed exhaust contains NH3 components into the acid exhaust.

(iii) In some processes of PECVD, gases such as SiH4, PH3, NH3, NF3, and N2O are used to transfer NH3 components from the mixed exhaust into the acidic exhaust.

(iv) Some Rapid Thermal Processing (RTP) processes use NH3, N2O and other gases, so that the mixed exhaust contains NH3 into the acidic exhaust.
3.4. Control of flow monitoring system
The displacement is calculated by measuring the average wind speed and multiplying by the cross-sectional area of the discharge line. It is necessary to measure the data of many points to calculate the average velocity, so as to calculate the air volume of this discharge pipe, which means to get the total flow of the whole section in the way of integration.

But most of the semiconductor plant is limited by space, using 1.5/0.5D design in actual operation of the system. To avoid the measurement error caused by the uneven distribution of air flow can improve the following ways: (1) in the existing flue air flow meter vertical direction to add a set of air flow meter, the error can be reduced, (2) on a regular basis to the standard method for measuring the flue actual emissions air volume, besides can understand the system features, also can avoid resulting from air volume measurement error is too large to violate the law problems.

4. Conclusions and Recommendations
This report includes the analysis and solution of common problems in the operation and maintenance of washing tower: (i) Bacteria growing inside the pipeline of the scrubber can be solved by fixing low concentration sodium hypochlorite in the supplemental water. (ii) Abnormal pH is mainly due to the pH sensor itself, which need replacement or improvement of design. (iii) The white smoke in the discharge pipeline is caused by the formation of silica particles in the condensation nucleus and the presence of NH$_3$ in the acidic exhaust. Periodic cleaning of silicone dust in windmills and installing local scrubber can reduce the white smoke. (iv) The air flow distribution design limited by the space, which causes the excessive discrepancy between the measured data and the actual data. Regular measurement of the actual exhaust air volume can help to understand the system characteristics and avoid the occurrence of this problem.

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