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LPCVD에서 암모니아와 염소의 누출에 대한 피해예측

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A Study on the Estimation of Damage by Leaking of NH_3 and Cl_2 applied to LPCVD

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요 약

첨단과학이 발전하면서 반도체의 필요성은 끊임없이 요구되고 있으며, 이러한 반도체 공정에서는 다량의 독성가스를 이용한 공정이 많다. 이러한 공정에서 가스의 누설로 인한 사고의 위험성은 항상 내재되어 있는 실정이다. 특히 국내 독성가스 사고는 암모니아와 염소에 의한 사고가 대부분이다. 따라서 본 논문에서는 LPCVD 공정에서 사용하는 암모니아와 염소의 누출로 인한 피해를 예측하여 안전에 만전을 기하고자 한다.

Abstract - As high-tech science has developed, the need of semiconductor is required constantly. However, there are many processes which use a great deal of poisonous gas in the semiconductor process, so the dangerousness by a gas leak is latent in these processes. Especially, the accident of toxic gas is almost made by ammonia and chlorine. Therefore this report estimates the damage by the leak of ammonia and chlorine used in LPCVD system.

Key words : LPCVD, NH_3, Cl_2, Leakage, Estimation of damage

I. Introduction

Semiconductor industry has an effect on human civilization. The toxic gas used in the manufacturing process for semiconductor devices two categories : for manufacturing and for cleaning processes, and recently LPCVD(Low Pressure Chemical Vapor Deposition) is used in system shown in Fig. 1, which requires the high accurate control of toxic gases[1]. LPCVD can make thin films which are easily attached on complicated configuration, and it is very elaborate and its life is getting longer. Also, the recent research shows that LPCVD has been more improved than APCVD(Atmosphric Pressure Chemical Vapor Deposition), and the merit of LPCVD is as follows; ① wafer, wafer-wafer thickness and resistivity uniformity ② less auto-doping ③ low temperature process ④ high throughput ⑤ low contamination ⑥ easy grain size control ⑦ in-situ doping[2-4].

However, NH_3 and Cl_2 used in this process are the main sources of the accident of a toxic gas, so they account for 32 cases among 34 accidents of

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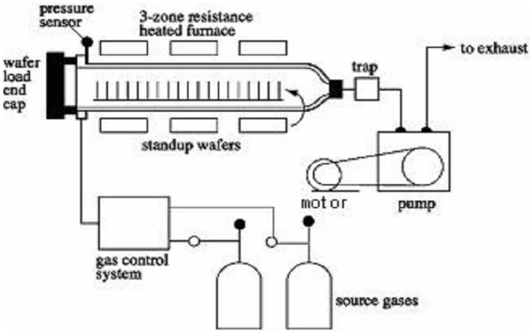

Fig. 1. Rough sketch of LPCVD system.

a toxic gas during these ten years. The accident of death by a toxic gas leak is the one by chlorine[5].

Hence this report wants to prevent th accidents and human damage from the leak of NH_3 and Cl_2 in LPCVD system by safety evaluation using Probit model[6].

II. The characteristics of gas and formula

2.1 . Characteristics

Toxicity means to give bad effects on life and it is the gas of which permissible concentration is under 5000 parts per million(ppm)[7]. Generally, the toxic symptoms by a toxic gas are happened by inhalation. The elements giving harmfulness of toxicity are TLV-TWA[1], PEL[2]-TWA, TLV-STEL[3], TLV-Ceiling[4], PEL-Ceiling, LC50[5], IDLH(Immediately Dangerous to Life and Heath), Local vs Remote effects, Immediate vs Delated, Acute vs Chronic. The general one is TLV-TWA, and it is the recommended exposure permissible value of ACGIH (American Conference of Governmental Industrial hygienists)[8,9]. The permissible concentration of a toxic gas typically used in semiconductor process is shown in Table 1[10,11].

Table 1. Properties of typical toxic.

Process gas	Bold/Italic (TLV-TWA)	DOT
Ammonia	25 ppm	Corrosive, Toxic
Chlorine	1 ppm	Corrosive, Toxic
Hydrogen Sulphide	10 ppm	Toxic
Sulphur dioxide	5 ppm	Toxic
Arsine	0.05 ppm	Toxic, Flammability
Diborane	0.1 ppm	Toxic, Flammability
Germane	0.2 ppm	Toxic, Flammability
Phosphine	0.3 ppm	Toxic, Flammability

2.1.1 Ammonia(NH_3)

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3. It is a colourless gas with a characteristic pungent smell. It is lighter than air, its density being 0.589 times that of air. NH_3 boils at -33.34 ℃(-28.012 °F) at a pressure of 1 atmosphere, so the liquid must be stored under high pressure or at low temperature.

Ammonia is a very toxic, colorless gas, can cause death and cause severe irritation of the nose and throat. Also, It can cause life-threatening accumulation of fluid in the lungs(pulmonary edema). Symptoms may include coughing, shortness of breath, difficult breathing and tightness in the chest. Symptoms may worse by physical effort. Long-term damage may result from a severe short-term

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1) TLV-TWA (Threshold limit value - Time weighted average) : The time-weighted average concentration limit for a normal 8-hour workday and a 40-hour workweek to which nearly all workers may be repeatedly exposed, day after day, without adverse effect. Developed by the ACGIH.

2) PEL (Permissible Exposure Limit) : An exposure established by OSHA(Occupational Safety and Health Administration) regulatory authority. May be a Time Weighted Average (TWA) limit or a maximum concentration exposure limit.

3) TLV-STEL (Threshold limit value - Short-term exposure limit) : A 15-minute, time -weighted average concentration to which workers may be exposed up to four times per day with at least 60 minutes between successive exposures with no ill effect if the TLV-TWA is not exceeded.

4) TLV-C (Threshold limit value - Ceiling limit) : The concentration in air that should not be exceeded during any part of the working exposure.

5) LC50 (Lethal Concentration 50) : Standard measure of the toxicity of the surrounding medium that will kill half of the sample population of a specific test-animal in a specified period through exposure via inhalation (respiration).

exposure.

The gas irritates or burns the skin. Permanent scarring can result. Direct contact with the liquefied gas can chill or freeze the skin(frostbite). Symptoms of more severe frostbite include a burning sensation and stiffness. The skin may become waxy white or yellow. Blistering, tissue death and infection may develop in severe cases. Damage(corrosive) may also occur if eye contact. The direct contact with the liquefied gas can freeze the eye. The permanent eye damage or blindness can result[12,13].

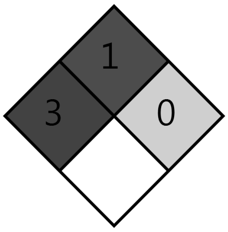
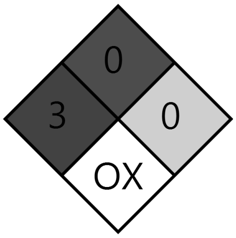
Ammonia does not burn readily or sustain combustion, except under narrow fuel-to-air mixtures of 15-28% air. When mixed with oxygen, it burns with a pale yellowish-green flame. At high temperature and in the presence of a suitable catalyst, ammonia is decomposed into its constituent elements. The ignition occurs when chlorine is passed into ammonia, forming nitrogen and hydrogen chloride; if chlorine is present in excess, then the highly explosive nitrogen trichloride(NCl_3) is also formed[14].

2.1.2 Chlorine(Cl_2)

Chlorine(Cl_2) is a chemical element with symbol Cl and atomic number 17. Chlorine is in the halogen group and is the second lightest halogen after fluorine. The element is a yellow-green gas under standard conditions, where it forms diatomic molecules.

Chlorine is a toxic gas that occur corrosive. Because it is heavier than air, it tends to accumulate at the bottom of poorly ventilated spaces. Chlorine gas is a strong oxidizer, which may react with flammable materials.

Table 2. NFPA 704[6] of NH_3 and Cl_2

Ammonia	Chlorine
 	

Chlorine is detectable with measuring devices in concentrations of as low as 0.2 ppm, and by smell at 3 ppm. Coughing and vomiting may occur at 30 ppm and lung damage at 60 ppm. About 1000 ppm can be fatal after a few deep breaths of the gas. Breathing lower concentrations can aggravate the respiratory system, and exposure to the gas can irritate the eyes[15]. The toxicity of chlorine comes from its oxidizing power.

When the chlorine is inhaled at concentrations above 30 ppm, it begins to react with water and cells, which change it into hydrochloric acid(HCl) and hypochlorous acid(HClO). When the used at specific levels for water disinfection, the reaction of chlorine with water is not a major concern for human health[16].

Table 2 is standard symbol for the identification of the hazards of materials for emergency response.

The four divisions are typically color-coded, with blue indicating level of health hazard, red indicating flammability, yellow(chemical) reactivity, and white containing special codes for unique hazards. Each of health, flammability and reactivity is rated on a scale from 0(no hazard) to 4(severe risk).[6]

2.2 . Formula

The Probit format to calculate the damage by a toxic gas leak is as follows.

$$Pr = A + B \ln(C^n \times T) \quad (1)$$

A, B, n : Constant

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[6] NFPA 704 : Standard System for the Identification of the Hazards of Materials for Emergency Response" is a standard maintained by the U.S.-based National Fire Protection Association. First "tentatively adopted as a guide" in 1960, and revised several times since then, it defines the colloquial "fire diamond" used by emergency personnel to quickly and easily identify the risks posed by hazardous materials. This helps determine what, if any, special equipment should be used, procedures followed, or precautions taken during the initial stages of an emergency response.

Table 3. Properties of typical toxic

Process Gas	A	B	n
Ammonia	-80.03	2.30	2.02
Chlorine	-18.9	1.69	2.75

Table 4. Time of exposure vs concentration about the damage of chlorine

Percent(%)	Concentration(ppm)	Time(sec)
1	450	1
	250	5
	200	10
	150	20
	130	30
	100	60
50	750	1
	425	5
	325	10
	255	20
	220	30
	170	60
100	1475	1
	820	5
	640	10
	500	20
	430	30
	340	60

C : Risk Intensity
T : Exposure Intensity

The coefficients applied to the Probit format (1) are shown in Table 3[17].

III. Results

The probit is calculated by substituting the permissible concentration of NH_3 and Cl_2 which are typically used in LPCVD system for format(1) to estimate the damage by a toxic gas giving harmfulness to a human body.

The calculated value for probit model is shown in Table 4. And then the calculated value is substituted to Fig. 2, so we analyzed the risk of killing

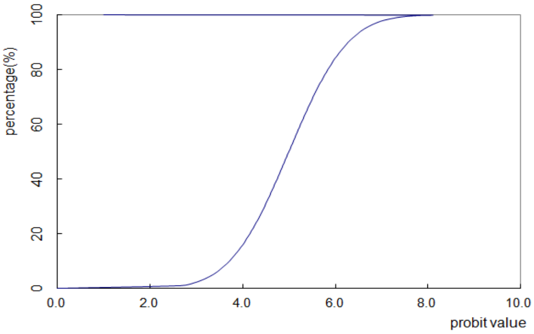

Fig. 2. Relationship between probability value(probit) and percentage.

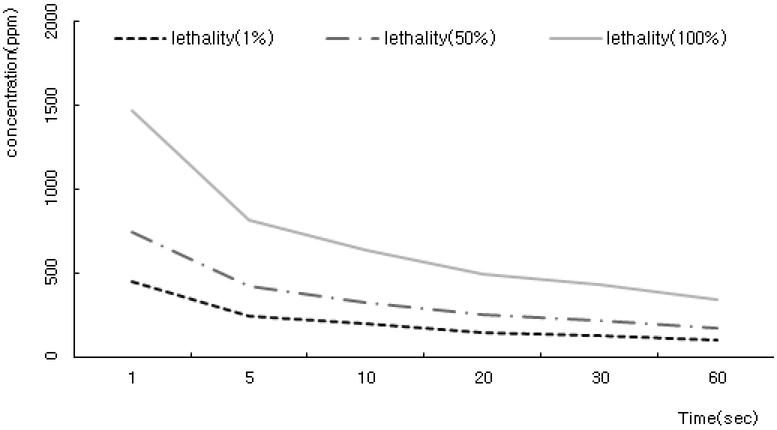

Fig. 3. Lethality for concentration and time.

humans by the exposure intensity[18].

As the result of analyzing the possibility of being fatal to human bodies by the exposure of NH_3 and Cl_2 using probit model, the permissible concentration is calculated to 1475 ppm, which has 100% of death probability when one inhales chlorine for one second, and the permissible concentration is 340 ppm when one is exposed to chlorine for one minute. In addition, when one is exposed under 1ppm of the permissible concentration for a long time, he or she comes to die in 40 days.

The effect range which gives damage to the workers in the LPCVD system of semiconductor process is like Fig. 3.

Ⅳ. Conclusions

We found the dangerousness of NH_3 and Cl_2 leak which can be happened in the LPCVD system of semiconductor process through this study as follows.

1. It calculated there is few effect by ammonia. At the real accidents, there are more injuries rather than death by leakage.
2. The effect by chlorine is to die in 20 seconds when one is exposed under 500 ppm of instantaneous leakage. The real accident by a toxic gas leak is the one by chlorine gas.
3. When one is exposed under 1 ppm, of the permissible concentration for 40 days, he or she would be dead 100%.

Therefore, it is most important to manage toxic gas not to be leaked to open or closed space.

Acknowledgements

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