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Treatment of Waste Dry Etching Gas in Semiconductors Manufacturing Process

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A new technology to make fluoride gas such as NF_3 contained in the exhaust gas from semiconductor manufacturing plants convert directly into a harmless substance have been established and new concept on the disposal treatment of global warming gases were presented. Experimental results verify that the chemical reactions can be take place at substantially lower temperature of 80-400℃ as compared with the combustion treatment method. Reaction product is mainly metal fluoride which is a harmless and a valuable chemical material as one of new resources. The other favorable characteristics are that the continuous treatment is possible at a low temperature under atmospheric pressure. Furthermore this process is compact, easily controllable and safely operable at low running cost. This paper concerns with a new harmless disposal treatment of toxic global warming gas.

Introduction

A new technology to make fluoride and chloride gases such as NF_3, CF_4, SF_6, Cl_2 and BCl_3 harmless has been developed and a new concept on the removing toxic gas to be used in the advanced process of materials has been established[1][2]. The fluoride gases are toxic and special type of gases to be used in the process of manufacturing semiconductors and their specific applications include the dry etching of semiconductors, cleaning of CVD systems, an oxidation agent for rocket fuel etc. Especially, NF_3 is also attracting an attention as a high-energy source for chemical laser systems. As a fluoride gas like NF_3 is, however, toxic and highly stable chemically, if discharged into the atmosphere, it is liable to cause far-reaching adverse influences on global warming in the same manner as carbon dioxide gas and refrigerant gas like a Freon gas.

Up till now, the combustion treatment method has been adopted for the disposal of the gas, and when treating the gas by high-temperature combustion (800 ℃), the generation of nitrogen oxides (NOx), sulfur oxides (SOx) and hydrogen fluoride (HF) have been confirmed. These chemical substances are not only linked with an intense corrosion of the combustion systems but also create the generation of atmospheric pollution and acid rains, and therefore, constitute a serious social issue[3][4].

The research team utilized the chemical reaction between fluoride gases (NF_3) and a halogenized metal, and established a new technology to convert fluoride gas contained in the exhaust gas from semiconductor manufacturing plants directly into a harmless substance. Experimental results verify that the chemical reactions can be performed at substantially lower temperature of 80-400 ℃ compared with the combustion treatment method. When NF_3 is reacted with $AlCl_3$, $CaCl_2$ and $MgCl_2$, the substances generated by the reaction are harmless with the exception of chlorine, and the generated chlorine can be removed almost completely by alkali scrubbing. The other favorable characteristics are that continuous treatment is possible at a low temperature under room pressure, and that the process is compact, easily controllable and safely operable at low running cost.

Properties of Global Warming Gases

Carbon dioxide and some kinds of refrigerant gases are well known as global warming gas on the earth. In these days, many kinds of exhaust gases from the process of manufacturing semiconductors call attention due to their toxic and the great effect on global warming in the earth environment. **Table I** shows the atmospheric lifetime and global warming potential (GWP_{100}) of special type of gas that is used in the etching process and manufacturing semiconductors (NF_3, CF_4, C_2F_6, SF_6, C_3F_8, CHF_3)[5][6]. GPW_{100} is relative value to CO_2 and are calculated on a 100 year integrated time horizon basis[3][4]. Many CFC and PFC gases have similar properties like long

Table I Atmospheric lifetime and global warming potential(GWP)

Gas	Lifetime(year)	GWP_{100}
CO_2	200	1
CF_4	50,000	6,500
C_2F_6	10,000	9,200
SF_6	3,200	23,900
C_3F_8	2,600-7000	7000-7600
CHF_3	250-390	6,300-13,100
NF_3	50-740	6,300-13,100

GWP_{100} value is relative toCO_2 and is calculated on a 100 years integrated time horizon basis.

life time, toxicant and a high green house effect compared with CO_2. For example, the green house effect of NF_3 shows the value as high as about 6,300 ~ 13,100 times of CO_2. Under these situations, the new technique to make PFC gases harmless is urgently necessary in the world in order to save the earth environment.

Chemical Reaction for Harmless Disposal

Chemical reaction of NF_3 with some metal chloride is presented as a new disposal treatment that can be used in the process of manufacturing semiconductors. The reaction products from this chemical reaction are harmless materials except chlorine which can be completely removed by alkali scrubber. Chemical reactions used in this experiment are as follows:

$$2AlCl_3 + 2NF_3 \longleftrightarrow 2AlF_3 + N_2 + 3Cl_2$$

$$3CaCl_2 + 2NF_3 \longleftrightarrow 3CaF_2 + N_2 + 3Cl_2$$

$$3MgCl_2 + 2NF_3 \longleftrightarrow 3MgF_2 + N_2 + 3Cl_2$$

These chemical reactions are very useful to make PFC gas harmless and effective for chemical fixation of fluoride as harmless natural material. Furthermore, AlF_3, CaF_2 and MgF_2 as reaction products are natural resources valuable materials in the chemical industries.

Experimental Procedure

Materials

Tri-fluolonitrogen (NF_3) gas of 99.99% purity is supplied from BOC Gas Co. Ltd. The reagent grade of $AlCl_3$, $CaCl_2$ and $MgCl_2$ are prepared from Wako Pure Chemicals Co., to be regent grade. Their purities are, according to the supplier, all higher than 99.5%.

Experimental Apparatus

Experimental apparatus for the operation is illustrated in Figure1. Stainless steel reaction vessel of $100cm^3$ is placed in the heating unit covered with insulating material. Temperature of the reaction vessel is controlled

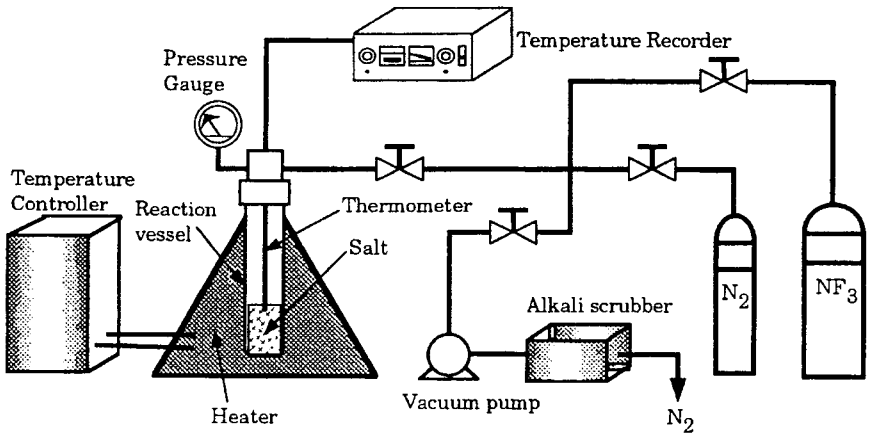

Figure 1 Schematic diagram of experimental apparatus for NF_3 gas disposal

using a panel heater with PID controller. Temperature and pressure in the reaction vessel are measured and printed out automatically by recorder.

Metal chloride ($AlCl_3$, $CaCl_2$ or $MgCl_2$) is kept in a oven at 100℃ ~ 400℃ for 24h in order to remove moisture. The salt of 0.03mol is weighted using electronic balance and it is placed in the reaction vessel in Figure 1. Degassing for the space of reaction vessel and pipe arrangements is carried out using a vacuum pump. The same mole number of NF_3 is introduced into the reaction vessel from the NF_3 cylinder. Temperature in the initial state is set at about 50℃ for $AlCl_3$, 110℃ for $MgCl_2$, 130 ℃ for $CaCl_2$ respectively. Heating rate of the reaction vessel is 4℃/min, and the temperature change with chemical reaction is recorded by the temperature recorder automatically. Beginning temperature of the chemical reaction is determined by the comparison with blank test.

Nitrogen gas is used in order to remove the gaseous reaction products in the vessel. Solid reaction products are placed in the desiccators with silica gel and chemical analysis is carried out by X-ray diffraction spectrometry.

Results and Discussion

Beginning temperature of the chemical reaction of NF_3 with three metal chlorides is confirmed in this experiment. Figures 2, 3 and 4 show the temperature change in the reaction vessel. The beginning temperature of each chemical reaction is different to be 78.1℃ for $AlCl_3$, 162.4℃ for $CaCl_2$ and 85.1℃ for $MgCl_2$. All chemical reactions are finished rapidly. Especially, the chemical reaction of NF_3 with $AlCl_3$ is so rapid, and the temperature control of the vessel is difficult. The difference between the beginning and the maximum temperatures in the reaction vessel are about 114℃, 45℃ and 75 ℃ for $AlCl_3$, $CaCl_2$, and $MgCl_2$ respectively. The order of magnitude of the temperature difference, that is $AlCl_3$>$MgCl_2$>$CaCl_2$, agrees with that of heat of reaction predicted thermodynamically. It is confirmed that these reactions with metal chloride are high exothermic reaction. The temperature range of these reactions is lower than that of combustion treatment. Figures 5, 6 and 7 show x-ray diffraction patterns of reaction products. These reaction products are as harmless materials such as AlF_3, CaF_2 and MgF_2.

Furthermore, exhausted gases contain the chlorine, nitrogen and un-reacted tri-fluoronitrogen.

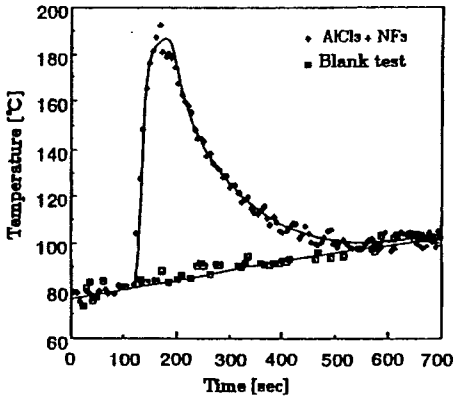

Figure 2. Temperature change with the chemical reaction of NF_3 and $AlCl_3$

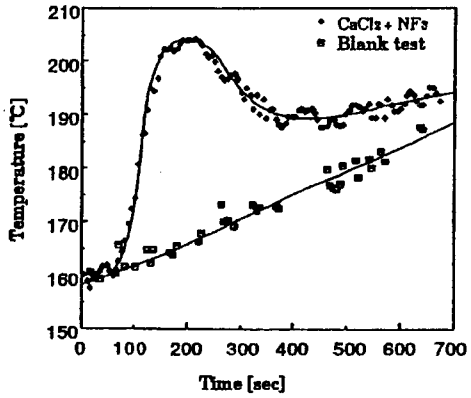

Figure 3. Temperature change with the chemical reaction of NF_3 and $CaCl_3$

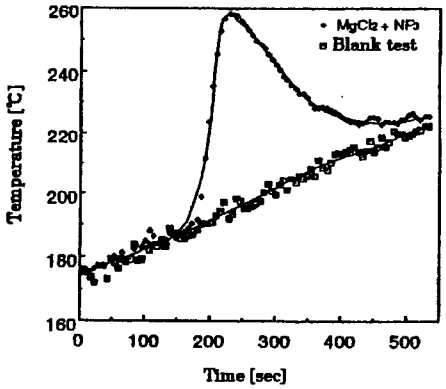

Figure 4. Temperature change with the chemical reaction of NF_3 and $MgCl_2$

Chlorine is easy to separate from the exhausting gases using alkali scrubber. Performance of this reaction is very simple and practical. This technique has been applicable for other toxic gases like fluoride gases.

Figure 8 shows the new concept of harmless disposal of fluoride gases using chemical reaction with metal oxide or metal chloride. Beginning temperature for each

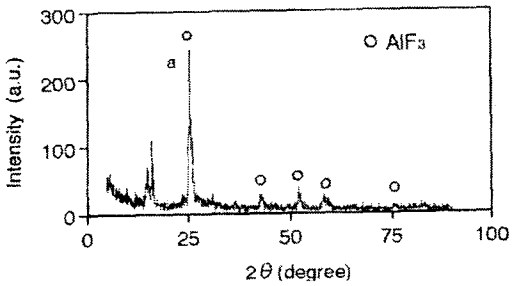

Figure 5 X-ray diffraction pattern of the reaction product of NF_3 and $AlCl_3$

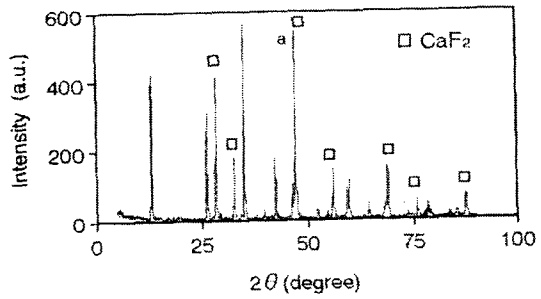

Figure 6 X-ray diffraction pattern of the reaction product of NF_3 and $CaCl_2$

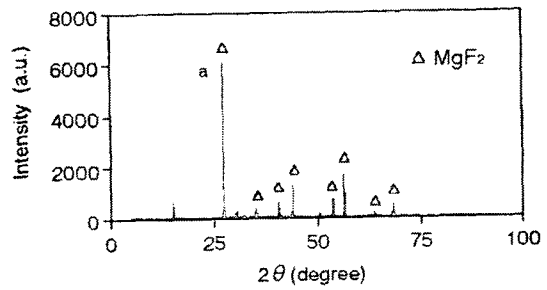

Figure 7. X-ray diffraction pattern of the reaction product of NF_3 and $AlCl_3$

reaction system is different, and reaction products are harmless material except chlorine and carbon dioxide.

These gases can be disposed by the similar chemical reaction shown in the Figure 8. It is found that the selectivity for the fluoride gas disposal in the gas mixture can be achieved by the temperature control in the reaction vessel.

Conclusion

A new chemical disposal treatment for the global warming gases such as fluoride gases is achieved by the chemical reaction with metal halide in the low temperature range. These reactions are harmless, economical and safe treatment for the toxic global warming gases.

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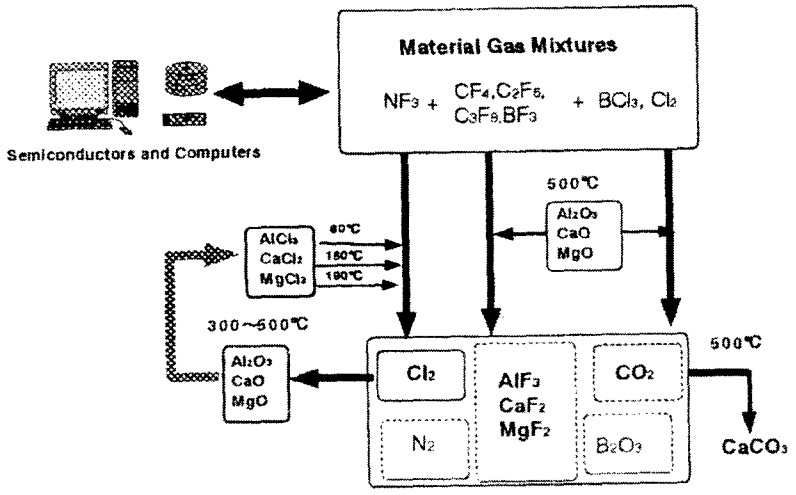

Figure 8 Harmless disposal of fluoride and chloride gas mixtures in the manufacturing process of semiconductors