Investigation of the Low-Pressure Plasma-chemical Conversion of Fluorocarbon Waste Gases

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The kinetics of the plasma-chemical conversion of a number of saturated, as well as unsaturated, fluorocarbon compounds is studied in an oxygen-based rf discharge by FTIR spectroscopy. Unsaturated fluorocarbons are rapidly converted into CF$_4$ and C$_2$F$_6$, which, in the presence of silica walls, are finally converted quantitatively into SiF$_4$ (etch reaction). The results of this investigation are used to design a plasma-chemical reactor for the conversion of fluorocarbon exhaust gases into SiF$_4$ in the vacuum line of a technological low-pressure plasma reactor. Furthermore, it is shown that the primary conversion product SiF$_4$ can be effectively converted into CaF$_2$ in a heterogeneous reaction with a CaO/Ca(OH)$_2$ absorber, also in the low-pressure line of the pumping system.

KEY WORDS: Waste gas conversion; fluorocarbon compounds; low-pressure plasma decomposition; kinetics.

1. INTRODUCTION

Fluorocarbon compounds are widely used as process gases in many low-pressure plasma-chemical applications. Examples of such applications are plasma-chemical etching of silicon and silicon dioxide, decomposition of fluorocarbon films, surface modifications, and others. Besides the desired effects of the discharge, however, the exhaust gas of such fluorocarbon plasmas contains a broad spectrum of products which are toxic or at least of environmental relevance. As a typical example, the product distribution of cold trap products from a CHF$_3$ rf plasma burning in a technological parallel-plate reactor is shown in Fig. 1.

Some of the detected compounds are known to be highly toxic, e.g., perfluoroisobutene. Others (like CF$_4$ and C$_2$F$_6$) are, due to their extreme stability and, therefore, their long lifetime in the atmosphere, of potential relevance for the greenhouse effect.

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Fig. 1. Gas chromatogram of cold trap products from a CHF$_3$ plasma (parallel-plate reactor, CHF$_3$ flow 40 sccm, pressure 12 Pa, rf power 200 W).

It is, therefore, desirable to convert these products into stable nontoxic products (like CaF$_2$). In order to avoid accumulation of toxic products in the pump oil, such a conversion should be accomplished preferably in the vacuum line of the technological plasma reactor. It is, however, necessary that the process of waste gas conversion does not disturb the often very delicate plasma processing reactions.

In this work, the well-known plasma-chemical etch reaction of silicon dioxide in a carbon tetrafluoride plasma

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\text{CF}_4 + \text{SiO}_2 \rightarrow \text{SiF}_4 + \text{CO}_2
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is taken as the starting point of an investigation which aims at an efficient conversion of fluorocarbons C$_n$F$_m$ of arbitrary composition into silicon tetrafluoride. Of course, conversion of carbon-rich fluorocarbons requires additional oxygen in order to suppress deposition of carbon-rich films and to convert all the carbon stoichiometrically into carbon dioxide.

The sequential steps of the low-pressure waste gas conversion are\(^{(4)}\):

1. Plasma conversion of C$_n$F$_m$ into the most stable compound CF$_4$ in an oxygen-based plasma
2. Conversion of CF$_4$ into SiF$_4$ by plasma etching of SiO$_2$ or silicate glass
3. Conversion of SiF$_4$ into disposable inorganic fluorides (like CaF$_2$).

The investigation presented in this paper will closely follow this concept. Therefore, in the first part, the kinetics of the fluorocarbon conversion in