FORMATION OF UNUSUAL CHLORINATED COMPOUNDS DURING PLASMA DRY ETCHING

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ABSTRACT

Polychlorinated aliphatic, aromatic and N-heterocyclic compounds are formed in the plasma dry etching process. Pentachloropyridine, Pentachlorobenzonitril and other chlorinated compounds are determinated by GC/MS-, GC/FTIR- and MS/MS-techniques.

INTRODUCTION

Plasma chemical dry etching is widely used during manufacturing of microelectronical components. The cold plasma obtained from different etching gases e.g. carbon tetrachloride is generated by high frequency discharges. A multitude of chemical reactions of the formed species takes places insight the plasma including the substrates like photo dyes. Many of the reaction products are unknown up to now and might have toxicological significance. In the paper we report investigations of deposits from the etching reactor, of the contaminated pumping oils and waste gas of the etching process with CCl_4.

EXPERIMENTAL

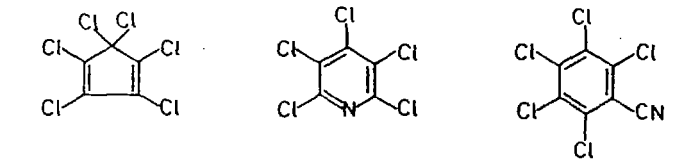
Analytical samples were obtained by different procedures depending on the material investigated.
Samples of waste gases were prepared by freezing, washing or adsorption on TENAX. Result obtained do not depend on the sample preparation.
Separation of waste products from pumping oils (FOMBLIN) was achieved by liquid-liquid extraction followed by adsorption chromatography.
The main component of the solid reaction products of the plasma etching process is aluminum chloride. Organic compounds could be isolated by hydrolysis and extraction with methylen chloride.

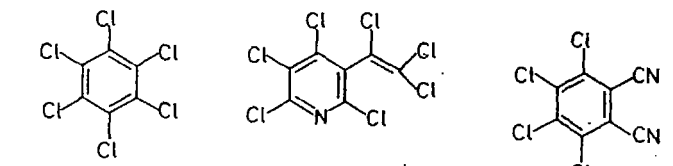
Structure elucidation was achieved by HRGC/MS on a VG 12-250 or a Finnigan ITD 800 as well as by HRGC/HRMS and MS/MS (VG ZAB-HSQ) and HRGC/FTIR.

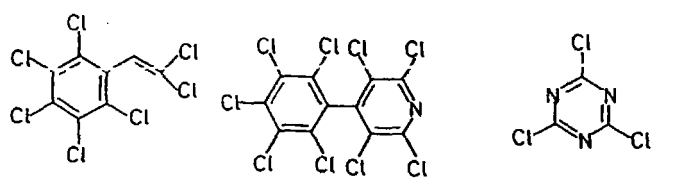
RESULT

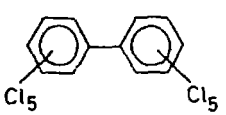
The investigation of waste products from plasma etching with carbon tetrachloride using nitrogen as inert gas yields some surprising results. In the plasma very reactive charged and

neutral species of the CCL_2, C_2CL_2, CLCN, CCl_3 are formed wich react under the given reaction conditions to aliphatic cyclic and aromatic in most cases polychlorinated compounds. Further reaction products are N-heterocycles and nitriles wich originate from reactions including CLCN species. In some cases the formation of series of homologous compounds could be observed. Table 1 summarizes the different types of compounds found in the investigated waste samples.









$CCl_2{=}CCl{-}CCl{=}CCl_2$

Table 1: Typical main products from the waste of plasma dry etching with CCl_4

The structures of the main components were derived from the mass spectrometric fragmentation pattern and the elemental composition of the compounds obtained by HRMS measurements. Structur assignment of isomeric compounds was possible by comparision of electron impact and chemical ionization mass spectra.

A typical example is given in Fig. 1 which shows the corresponding mass spectra of pentachlorcyano-butadiene and pentachloro-pyridine.

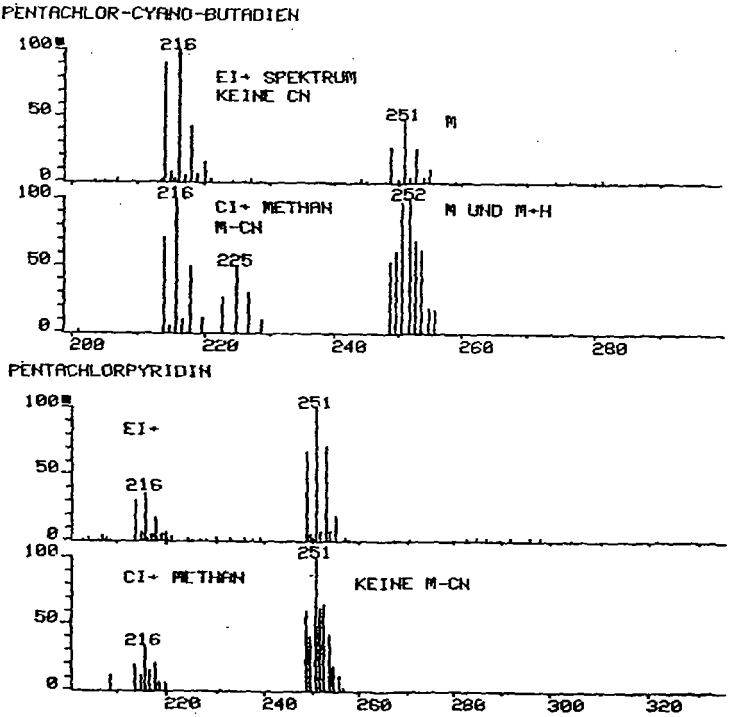


Fig.1: EI-and CI mass spectra of pentachlor-cyano-butadiene and Pentachloro-pyridine, see the characteristical ion M- CN.

The result of the mass spectrometric investigations are supported by HRGC/FTIR studies. Especially the presence of CN-groups in the compounds (ads frequ. 2270 cm^{-1} could be proved by this technique.

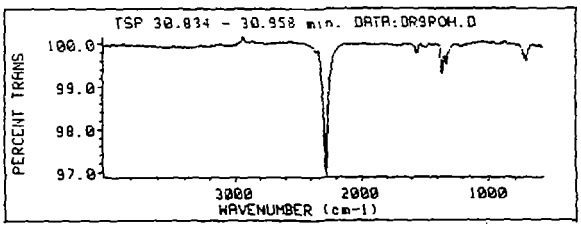


Fig.2: Percent transmission IR-spectrum for the peak at 30,8 min in Fig.3

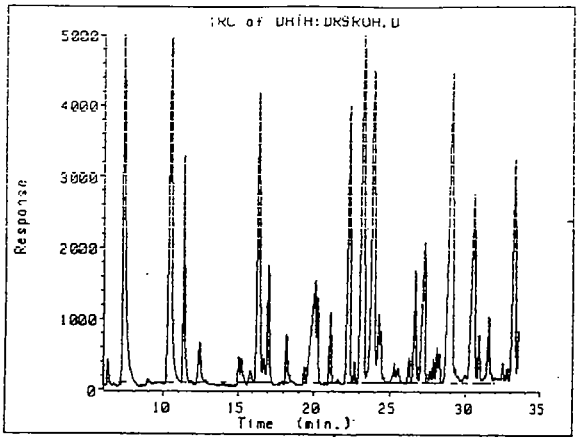


Fig.3: Total response chromatogram (TRC) from infrared detector of the waste products of the plasma dry etching with CCl_4

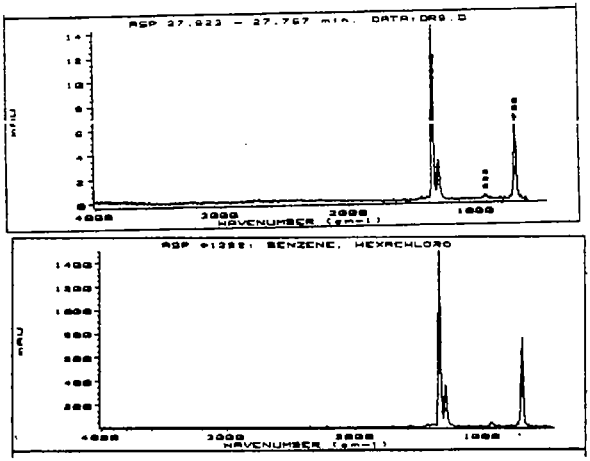


Fig. 4: Infrared absorbance spectra for the peak at 27,7 min in Fig.3 and the library spectra for HCB

First results obtained with the SOS-CHROMOTEST show that the waste compounds are genotoxic.