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# SILICON TETRACHLORIDE PYROLYSIS IN NITROGEN-HYDROGEN PLASMA[1])

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Nitrogen plasma generated in an arc operating at atmospheric pressure (mean gas temperature ca. 4000 K) almost completely decomposes silicon tetrachloride. The solid reaction products were identified as predominant elemental silicon with a small content of amorphous silicon nitride and traces of lower silicon oxides.

## I. INTRODUCTION

Plasma chemical methods of preparation offer still interesting final product characteristics as well as technological advantages. From the point of view of modern powder technologies it is a high dispersion with a narrow distribution curve of the product particles, their shape being mostly spherical.

Modern technology makes an ever wider use of new materials, based partly on ceramics. The most promising are based on silicon, both because of their properties and their preparation costs. It is therefore useful to learn the behaviour of silicon compounds under any circumstances, especially the low-temperature plasma conditions.

In our laboratory we have studied nitrogen — hydrogen plasma reactions with silicon tetrachloride. This starting compound has many disadvantages because of complicated chemistry and the retention of chlorine in the silicon nitride product. Nevertheless, it is economically advantageous and relatively simple to work with.

## II. EXPERIMENTAL

A porous wall d.c. plasma torch was used as plasma generator (the scheme see in Fig. 1). Owing to the porous wall stabilization of the arc, the energetic

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efficiency of the generator is as high as 85% (for the total power of 34 kW). Higher values (up to 90%) for similar systems were also reported [1]. Taking into account the net power of 29 kW dissipated in the gas mixture containing typically 150 mmol/s of nitrogen, 40 mmol/s of hydrogen and 3 mmol/s of silicon tetrachloride, the mean temperature value of $\bar{T} = 4000$ K was estimated.

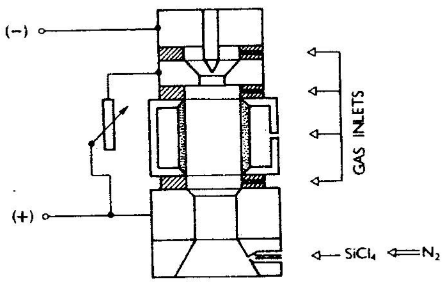


Fig. 1. The scheme of the arc plasma generator.

Despite strong turbulence in the plasma channel, however, a high radial temperature gradient, is to be expected and thus, peak temperatures roughly twice as high as $\bar{T}$ are fairly probable (compare, e.g. [2]). Exact spectroscopical temperature measurements have not yet been concluded. An emission spectrum of the afterglow, 60 mm downstream the anode nozzle, is illustrated in Fig. 2.

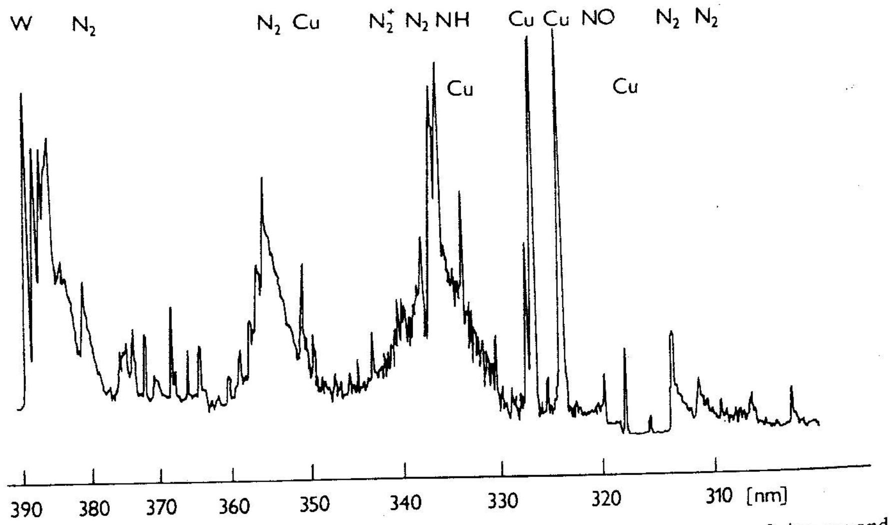


Fig. 2. A typical plasma emission spectrum (part) containing the 2nd positive system of nitrogen and ground state metal atom lines.



This spectrum was taken without the admixture of silicon tetrachloride, which causes a rapid contamination of the spectroscopical window, even if protected by the purge gas flow.

As seen in Fig. 3, the achieved temperatures suffice for equilibrium silicon tetrachloride pyrolysis. The product distribution then depends upon the actual temperature and the rate of quenching only. However, no volatile silicon compounds have been found in the gaseous products, the analysis having been performed by means of a quadrupole mass spectrometer (QMG 511). The compounds searched were among others: SiCl, $SiH_2Cl_2$, $SiCl_2$, $SiHCl_3$, $SiCl_3$, $SiCl_4$, $Si_2Cl_6$, $Si_2OCl_6$ in the mass ranges 63—66, 98—100, 133—138, 168—172, 266—272, 282—288 atomic mass units. This means that practically a complete decomposition of $SiCl_4$ to solid compounds takes place in the studied plasma.

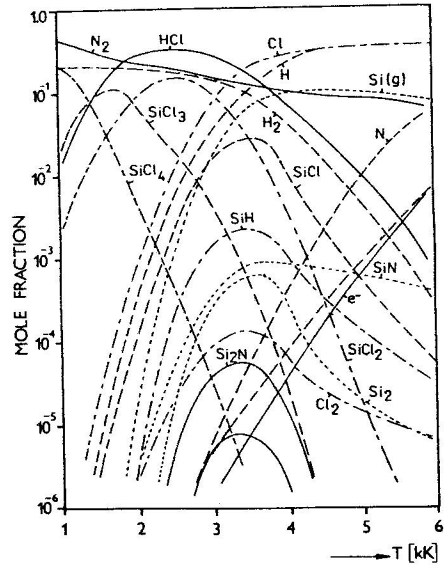


Fig. 3. Equilibrium composition of a mixture of $SiCl_4$—$N_2$—$H_2$ (0.1 MPa), after [2].

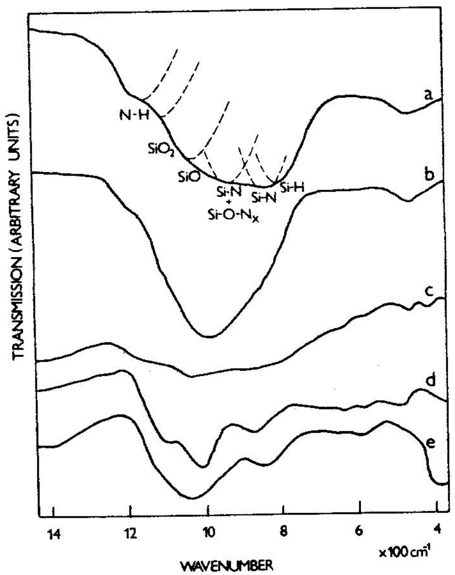


Fig. 4. IR absorption spectra of the amorphous silicon nitride taken from literature (curves a and b) compared with those of the $SiCl_4$ pyrolytic products (curves c, d, e).

The solid pyrolytic products were identified from the specimens taken from the different parts of the reactor, from the cooler walls and the outlet from the reactor assembly. These powders were examined by means of IR-absorption spectroscopy, x-ray diffractography and chemical analysis.

As seen in Fig. 4 (curve a), the complex IR spectrum analysis in the case when numerous related compounds are to be taken into account, can be complicated. The amorphous state of matter brings about other changes in the IR spectrum (curve b). This means that even though this technique is fast, it must be complemented by other methods. Moreover, the IR absorption spectroscopy is basically intensitive to elemental silicon. Its presence in higher amounts was revealed by x-ray diffractometry and to a much higher degree by the chemical analysis (leaching tests).

As shown by the x-ray analysis, the main crystallic component of the powders is elemental silicon accompanied by copper erosion compounds, such as CuCl, ... $2NH_4Cl.2H_2O$ (see Fig. 5). It is necessary to bear in mind, however, that most of quenched particles are amorphous and thus beyond the direct x-ray structural analysis.

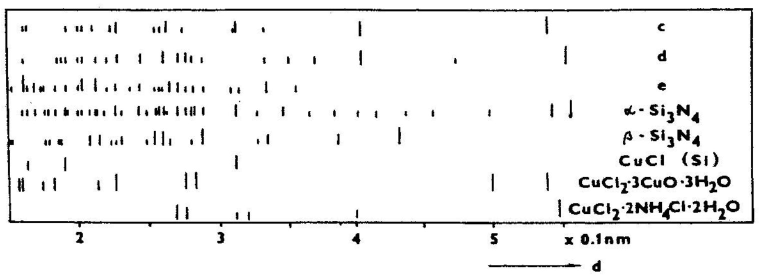


Fig. 5. X-ray diffractograms of the products and standard compounds.

For a better understanding of the actual state of the particles, a leaching test was developed, based on different leaching rates of the product components in sodium hydroxide. For accurate evaluation of the results it is necessary to know the mean particle diameters; this condition was, however, not fulfilled.

The leaching tests which revealed a more than 80% solubility of powders in diluted sodium hydroxide (0.02 mole/l and 2 mole/l), confirmed the pressumed high content of elemental silicon and the low content of $SiO_2$. Other non-stoichiometric silicon compounds containing nitrogen and/or oxygen could not be unambiguously determined owing to their unknown dispersion and dissolution kinetics.

## III. CONCLUSION

Our experiments confirmed efficient pyrolysis of silicon tetrachloride in nitrogen — hydrogen plasma, mostly to elemental silicon. Ammonia containing compounds were also detected. It is therefore very probable that suitable conditions for reasonable silicon nitridation in the quenched afterglow may be arranged.



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## ПИРОЛИЗ ТЕТРАХЛОРИДА КРЕМНИЯ В АЗОТНО-ВОДОРОДНОЙ ПЛАЗМЕ

Азотная плазма, генерированная разрядом электрической дуги при атмосферном давлении (средняя температура газа равна примерно 4000 K) почти полностью разлагает тетрахлорид кремния. Обнаружено, что твердыми продуктами реакции является прежде всего элементарный кремний с небольшим содержанием аморфного нитрида кремния и следами низших окислов кремния.