INFLUENCE OF NOBEL GASES ON THE REACTION OF PLASMA-CHEMICAL DECOMPOSITION OF SILICON-ORGANIC COMPOUNDS IN THE DIELECTRIC BARRIER DISCHARGE

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Abstract

Decomposition of HMDSO and TEOS in the DBD (glass-glass electrode set-up, 2 mm gap, 1 kHz sinusoidal voltage) was studied in mixtures of N\(_2\)-He and N\(_2\)-Ar in an open gas flow system at 1 atm. Gas mixing ratio was chosen as a variable parameter. The initial monomer content was kept constant at 0.2 %. Main gas phase reaction products and the monomers' decomposition degrees were determined by means of chromatography. We found that an increase of the noble gas content in a working mixture results in a growth of the product yields. To explain this effect, we carried out semi-empirical calculations of the kinetic coefficients of electrons in the gas mixtures, considering the experimentally obtained burning voltages depending on the gas mixture. The results calculated show that a rise of the noble gas content increases the mean electron energy.

1. Introduction

Since the silent discharge is regarded to be applicable in surface treatment, the efficiency of the plasma process plays an important role, apart from ecological aspects. Correspondingly, omission of high vacuum apparatus might have many advantages. However, the reaction rate values of the plasma process should be taken into account as well. With respect to the deposition with the silent discharge, due to dimensions of the electrode arrangement, the determination of deposition rates \textit{in situ} appears to be rather difficult. In such a case, the degree of decomposition of the precursor may be treated as an indirect indicator of the chemical efficiency of a deposition process.

2. Preconditions

2.1 Set-up

By means of a gas chromatograph (HP Micro-GC, OV1) with a thermal conductivity detector (TCD) we analysed stable products of the chemical conversions in the discharge at a pressure equal to 1.04 bar. fig. 1. The electrodes are placed in a quartz-glass vessel. The discharge was operated in a plane-parallel electrode set-up, fig. 2, with a sinusoidal feeding voltage. The charge-voltage characteristics were obtained in a usual manner by means of a serial capacitance. fig. 1. The continuous gas flow through the discharge gap \(g\) was maintained at about 1660 – 1833 secm. Saturation of nitrogen with the vapour of the studied silicon organic monomers (SOC) was performed in a bubbler.
Due to the dilution by another gas flow the monomer's concentration decreased considerably. In the reactor it was kept at the steady-state level of 0.2 %, In the discharge the monomer was decomposed only partially (5 - 15 % of its initial concentration).

2.2 Decomposition degree

The term 'decomposition degree'

\[ \beta = \frac{\lambda_i}{\lambda_0} \]

was used to characterize plasma-chemical efficiency of monomers' decomposition. Where \( \lambda_i \) is the plasma power, \( \lambda_0 \), \( \lambda_i \), the monomer fractions at the reactor outlet and the inlet.

For monomers' dissociation by direct electron impact the energetic yields of reaction products is

\[ Y_{i} = \frac{k_i (e) [SOC]}{e E w_i (e)} \]

\( k_i (e) \) is the rate coefficient of the respective reaction, \([SOC]\) - the particle number density of the respective silicon-organic compound, \(e\) - elementary charge, \(E\) - the electric field strength, \(w_i (e)\) - the drift velocity of electrons.

2.3 Semi-empirical model

To provide an explanation of the experimental results, the influence of the chemical composition of the working gas mixtures on the basic properties of electrons was analysed, using a semi-empirical method proposed in [1] and developed later in [2].

It enables to calculate some kinetic coefficients of electrons in a gas mixture, provided that the corresponding values for the individual gases are known.

Such data (mostly, results of experiments) are tabulated usually as the functions of the reduced field \((E/N)\). Within the frame of the model, however, the kinetic coefficients are treated as the functions of the mean electron energy \(e\).

\[ E_{max} (e) w_{max} (e) = \sum c_i E_i (e) w_i (e) \]  \hspace{1cm}  (3); \hspace{1cm} \frac{E_{max} (e)}{w_{max} (e)} = \sum c_i \frac{E_i (e)}{w_i (e)} \]  \hspace{1cm}  (4)
The indices $m_i$ and $j$ indicate values for the gas mixture and its individual constituents, $c$ - the relative fraction of the constituent $j$. The values of $E_n(c)$ and $\nu_n(c)$ for He, Ar and N$_2$ were taken from [1,3,4]. Further, $E_m(c)$ was assumed to be equal to the averaged effective field strength $U_R/\varphi$, taken from our experimental data, fig. 3. The calculated dependencies of the product $E\mu$ (the quantity, proportional to electric power of the discharge), and of the mean electron energy $\varepsilon$ upon the fraction of N$_2$ are shown in fig. 6 - 9.

3. Results and Discussion

3.1 The burning voltage of the DBD in different gas mixtures

The burning voltage, also called sustain voltage, depends strongly on the gas composition. For all types of mixtures presented in fig. 3 it appears to rise monotonously with an increase of the N$_2$-fraction. This can be explained by means of the well-known concept of the balance of electron energy in low temperature weakly ionized plasmas. In N$_2$-He(Ar)-mixtures, the main channel of electron energy losses is that one via inelastic collisions with N$_2$ (mostly, vibrational excitation). The rate of this process is proportional to the N$_2$-fraction.

To keep approximately the same level of electron energy, it is necessary to compensate an increase of the N$_2$ content by the corresponding rise of electric field strength.

![Diagram showing dependence of burning voltage on chemical composition of working gas mixture](image)

**Fig. 3** Dependence of burning voltage on the chemical composition of the working gas mixture

A trace quantity of HMDSO in the N$_2$/He(Ar)-mixture causes a drastic drop of $U_R$. The effect caused by TEOS add is less.

Generally, the ionisation potential of silicon-organic compounds is considerably lower than that one of N$_2$ (HMDSO: 8.8 ± 1.3 eV). Hence, a trace of SOC causes a drastic fall of the burning voltage.

3.2 HMDSO and TEOS in the DBD - decomposition degrees

The dependencies of $\beta_{\text{HMDSO}}$ and $\beta_{\text{TEOS}}$ on the N$_2$ content in mixtures with noble gases (Ar, He) are shown in fig. 4. It is obvious that the admixture of noble gases promotes the conversion of the studied monomers. This effect is most profound for the decomposition of TEOS.

Moreover, the monitored yield of TMS (tetramethyldisilane) of the plasma chemical conversion of HMDSO shows a similar effect, cf. [5]. By means of the chromatographic analysis we succeeded to identify TMS, PMDSO (pentamethyldisiloxane) and TMDSO (tetramethyldisiloxane) as dominating chemical species appearing as a result of HMDSO decomposition.
The identified products of the plasma-chemical process under consideration may be treated as the derivatives of HMDSO. Therefore, a simplified scheme of their formation can be established, cf. [5]. In the HMDSO conversion, the main chemical pathway (path 1: rate coefficient $k_1$) is distinguished by the substitution of a $\text{CH}_3$ group (Cleavage of the Si-C) by hydrogen atoms via direct electron impact and leads consequently to PMDSO and TMDSO.

This reaction mechanism accounts for the observed correlation of the energetic yields of PMDSO and TMDSO obtained in [5]. In the second pathway (rate coefficient $k_2$), also induced by the electron impact, TMS is formed due to the breaking of a Si-O bond.

The yield of TMS appears to be much smaller than that of PMDSO, because the bonding energy of a Si-O bond (4.6 eV) is higher than the corresponding value for Si-C (3.2 eV). However, the rise of the TMS-yield with increasing noble gas fraction is steeper than for the other reaction products.

In the plasma chemical process based on TEOS, only one of the verified chemical compounds, namely ethanol, was identified. Ethanol is the most prominent product of the process.
Therefore, the cleavage of the Si-O bond accounts to be the main reaction path of the plasma chemical conversion of TEOS.

3.3 Influence of the mean electron energy

The product $E_w$ decreases, fig. 7 and 9, with an increasing amount of the noble gas content. In the same time, the mean electron energy increases monotonously, even though the electric field $E$ falls down. Compare fig. 3 and fig. 6, 8. In general, it seems to lead to an increase in the energetic yield $Y_e$.

![Graphs showing the influence of the mean electron energy on the reaction rate.

An increase of the mean electron energy can be expected to cause a rather strong growth (at least, stronger than a proportional one) of the reaction rate coefficients $k_1$ and $k_2$ for the two basic reactions: cleavage of the Si-C and Si-O bonds, fig. 5. Taking into account the higher...
value of the energy threshold for the second channel, fig. 5, of dissociation, we can assume the stronger influence of the electron energy increase upon $k_2$ than upon $k_1$.

This conclusion accounts for the experimentally observed steeper growth of $\beta_{\text{TEOS}}$, fig. 4, respectively, of the TMS-yield with an increase of the content of the noble gas, in comparison to $\beta_{\text{HMDSO}}$ respectively, PMDSO.

Summary
The plasma chemical decomposition of HMDSO, respectively, TEOS by the DBD in the different gas mixtures at atmospheric pressure was studied experimentally and theoretically. Nitrogen is considered as a basic carrier gas, being relatively cheap and therefore preferable for industrial applications. Main products have been identified by means of GC technique and a general kinetic scheme of chemical conversions occurring in the investigated systems have been proposed. It was found that an addition of noble gases to N$_2$ resulted in a profoundly higher conversion of the regarded silicon-organics. As regards the effect of noble gases, no significant difference between He and Ar has been observed. Furthermore, the decomposition degree of TEOS is always higher than that of HMDSO.

It is demonstrated that a reasonable interpretation of all these experimental findings can be provided within the frame of the concept of the dependence of the mean electron energy upon the chemical composition of the working gas mixture. It is shown in particular, that the mentioned effect of noble gas admixture is caused by an increase of the mean electron energy.

References