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Thermal stability of plasma deposited polysilanes

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Abstract

A new method for studying thermal stability and concomitant chemical composition changes on thermal treatment of thin polymeric films is presented. It is applied to the study of thermal properties and modification of properties of polysilane-like materials with variable dimensionality prepared by radio frequency plasma enhanced chemical vapour deposition (CVD). Structure and microphysical properties of these materials, modified by progressive annealing, are examined by fluorimetry, FTIR absorption spectroscopy and XPS. In addition, the role, bonding conditions and structural environments of organic moieties as well as their influence on thermal degradation processes are examined. It is found that plasma polysilanes undergo three consecutive thermal degradation processes: Si–Si bond cleavage, elimination of side groups and final carbide formation. Presence of disorder and crosslinking stabilises the plasmatic material in comparison to classically prepared polysilanes. Nanostructural units in low dimensional polysilanes enable the peak of the luminescence to be adjusted in the spectral range from near UV (360 nm) to red (600 nm).

Keywords: Thermal desorption spectroscopy, TDS; Polysilane; Luminescence; Thin film; Plasma; Thermal degradation

1. Introduction

It is now well established that plasma enhanced chemical vapour deposition (PE CVD) represents an unusually versatile coating technology for polymers with controlled crosslinking, networking and with nanostructural units [1–3]. The plasmatic polymer can be prepared in general as nearly one-dimensional, branched or networked material whose structural dimensionality may be varied on a large scale by the choice of the deposition parameters. Plasma deposition always brings molecular fragmentation, which, in turn, makes π-conjugation, so desirable in electroactive polymers [3], very difficult. Plasma synthesis gives results depending on the competition between recombination deposition and destruction of molecular structures. However, specific functional properties may be retained, especially when the resulting material does not require large π-conjugation for its function. Saturated systems are even more likely synthesized by plasma enhanced deposition.

In our recent papers we concentrated on preparation of plasmatic polysilanes with σ-conjugation, especially poly(methylphenylsilane) (PMPSi), prepared from chlorinated monomer (dichloromethylphenylsilane) in radio frequency (RF) (13.5 MHz) plasma enhanced chemical vapour deposition (RF PE CVD) [4–9] under condition of low pressure and low radio frequency power. In previous papers we presented a structural model [5–9] of the one-dimensional polysilane-like UV luminescence nanocentres embedded in networked plasmatic material together with the existence of the visible PL originating from the amorphous matrix. In this paper we concentrate on the examination of the thermal stability of plasmatic polysilanes and the role of the functional groups in the thermal treatment. The work is focussed on thermal analysis corroborated by fluorescence, XPS and IR absorption spectroscopy.

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1.1. Thermal desorption spectroscopy – introduction

Thermoanalytical methods can generally give apparent values of kinetic constants for solidus–gaseous reactions running in thermally treated material. Evolved gas analysis enables to approximate fundamental chemical reactions under vacuum conditions rather than under atmospheric pressure when the mass transport phenomena are the most likely rate limiting process. The method of vacuum evolved gas analysis, called thermal desorption spectroscopy (TDS), is highly reliable in the emerging field of polysilane based silicon electronics [10]. Here, TDS is applied for the analysis and thermal treatment of plasma polymer films to obtain additional information about the structure and desorption parameters of volatile species as their concentration and respective bonding energies in films. The early works on this topic have used the total gas pressure gauge for the evolved gas detection [11], the later attempts used the gas chromatography [12] and the recent mass spectroscopy [13,14]. The method was used predominantly for the analysis of hydrogen bonding states and concentrations in amorphous hydrogenated silicon [15,16]. The study of organosilicon materials was initiated by our experimental TDS method developed and inspired by thermal degradation studies on conventionally synthesized PMPSi [17,18].

The thermal decomposition of classically polymerised poly (methylphenylsilylene) in the solid state starts at approximately 170 °C and is accompanied by the formation of two fractions – volatile degradation product and ceramic residues containing Si, C, H and O contamination – depending on reaction conditions. One of the possible thermal degradation mechanisms is homolytic cleavage of Si–Si bonds forming radical species. The first reaction is a low temperature process, connected with polymer backbone chain shortening and subsequent releasing of mer units $CH_3SiC_6H_5$. The next step in polysilylene thermal degradation is its transition to polycarbosilanes connected with main chain rearrangement, methylene bridge insertion as well as with $Si-CH_3$ and $Si-C_6H_6$ bond cleavage. Some radical species may react with methyl and aromatic groups to yield a crosslinked, insoluble polymer. Radicals could also participate in back-biting processes which generate cyclic oligomers directly [19,20]. Random $Si-CH_3$ and $Si-C_6H_6$ bond cleavage characterizes the high temperature step when the residual structure is stabilised forming crosslinked SiC_xH_y structures [17,18]. All these processes are practically terminated at a temperature about 700 °C. This degradation pattern represents basic framework for TDS experiments evaluation in view of the fact that PMPSi has been generally used as a standard in all types of measurements.

1.2. Theoretical analysis of TDS method

To establish the analytical features of the method, we present next the theoretical framework and testing of the TDS method.

The method is based on the controlled heating of thin films solid-state samples in vacuum and measuring quantitatively the evolved species by the mass spectrometry (MS). Under conditions of high vacuum and high pumping speed, when the desorbed gases cannot accumulate inside the chamber, the total pressure remains nearly constant, the immediate value of the partial pressure p_i of any component i, detected by the mass spectrometer is proportional to the rate of the ith element's evolution; in other words under such conditions the corresponding reaction rate is measured. The ion current I_i as the output of a mass spectrometer is then proportional to the measured partial pressure p_i.

$$I_i = \mathrm{const}\,p_i \tag{1}$$

where const is equal to the product of all coefficients for the conversion of the measured current to partial pressure. Consequently the evolving rate (or rate of the corresponding reaction, species creation, species evolution or their effusion) r_i of given component in the system is:

$$r_i = \mathrm{const}' I_i \tag{2}$$

Assuming the creation of monitored species follows first-order kinetics, the reaction rate for the creation of component i can be written generally as follows:

$$I_i \approx r_i = -\frac{\mathrm{d}c}{\mathrm{d}\tau} = A\mathrm{e}^{-\frac{E_a}{RT}} c(\tau) \tag{3}$$

where c is the concentration of the precursor of the species i in question at time τ, E_a is the activation energy of the reaction, R is the universal gas constant, A represents the pre-exponential factor and T is the temperature. This differential equation (Eq. (3)) cannot be in general solved analytically and so a numerical approach using iterations must be applied. This approach enables one to evaluate the TDS curves in very simple and reliable manner.

The equation (Eq. (3)) can be rewritten:

$$I_i(\tau) = -\frac{\mathrm{d}c}{\mathrm{d}\tau} = A\mathrm{e}^{-\frac{E_a}{RT}} \int_{\tau}^{\tau_\infty} I\,\mathrm{d}\tau \tag{4}$$

where the integral in Eq. (4) expresses the concentration of the remaining precursor of monitored species in time τ, τ_∞ is the time when all precursors are converted and species evolved. As the activation energy E_a is temperature independent, the TDS curve analysis enables determination of the activation energy E_a without the knowledge of absolute partial pressures of the species in question.

The measured TDS spectra are expressed by the dependence of ion current I on the instantaneous temperature T (or the time). Since the temperature growth rate is a linear function of time:

$$\mathrm{d}T = \Theta\,\mathrm{d}\tau \tag{5}$$