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In situ characterisation of thin-film formation in molecular low-temperature plasmas

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Abstract. Thin films can be formed in low-temperature plasma in two ways: as a result of material modification usually in a discharge of non-organic gas and in the course of a deposition process in a discharge of organic vapour. Thin-film formation requires in situ control of plasma processing in order to get information on the growth mechanisms and control the deposition process. Here are shown some effective in situ techniques of thin-film characterisation: various kinds of infrared spectroscopy (infrared reflection absorption spectroscopy, attenuated total reflection spectroscopy, etc.), ellipsometry and microgravimetry. We discuss the application of these methods to polymer modification as well as plasma polymerisation. The applied techniques give very good spatial resolution, up to a few nm. The limitations of method or equipment on time resolution can be compensated by the appropriate experimental arrangement.

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The desired formation of thin organic films using low-temperature plasmas requires fundamental knowledge of the complex processes in the plasma under non-equilibrium conditions and on a solid surface. A lot of diagnostic tools are applied for the experimental investigations of the gas-phase processes in chemically active plasmas: optical emission spectroscopy, absorption spectroscopy, laser-induced fluorescence and mass spectrometry. On the other hand, deposited thin films or modified thin surface layers of material are widely studied by means of different techniques outside of the reactor after the plasma processing [1, 2]. Despite the exposure of the obtained films to air, modern ex situ characterisation techniques give information on atomic composition, molecular structure, film thickness and the resulting macroscopic physical and chemical properties which can be discussed in relation to the plasma-process parameters. Among these techniques one should mention excellent methods based on the characterisation of thin films and surface layers by means of the special interaction of particles with the condensed matter (electron energy-loss spectroscopy (EELS), secondary ion mass spectrometry (SIMS), Rutherford back scattering (RBS), elastic recoil detection analysis (ERDA)), spectroscopic methods (X-ray/ultra violet photo electron spectroscopy (XPS/UPS), Auger electron spectroscopy (Auger), Fourier transform infrared spectroscopy (FTIR), electron spin resonance (ESR), near edge X-ray absorption fine structure (NEXAFS)) and ellipsometry. In situ characterisation provides the more detailed understanding of the structure-formation dynamics during the plasma processing [3] and allows us to avoid the exposure of the samples to air.

In low-pressure gas discharge the different plasma species like ions, electrons, reactive neutrals and photons interact with the substrate/film surface simultaneously. The various efficiencies of the plasma species and the synergistic effects between them must be considered [4–9]. Due to the interaction of energetic plasma species with solid substrates, the surface may be activated and/or free macroradicals may be formed. These processes result in the enhanced adsorption of incoming particles which may considerably influence chemical surface reactions and thin-film growth.

In dependence on the applied type of low-pressure gas discharge at different excitation frequencies, from dc-like 10–100 kHz, up to radio frequency (rf) 13.56 MHz and microwave regions 2.45 GHz, and the substrate conditions (position in the plasma reactor, substrate bias, electrical conductivity, substrate heating) the specific formation of the plasma-boundary sheath controls the charged-particle transport to the surface (kinetic energy and particle flux). For example, the substrates placed on the powered electrode of a capacitively coupled asymmetric rf discharge at low pressure are bombarded by positive ions with kinetic energies in the order of a few hundred eV [10]. In contrast, the substrates immersed electrically insulated in the plasma bulk or placed on a grounded surface are bombarded by positive ions with lower kinetic energies, typically in the order of 10 eV. The incorporation efficiencies of ions and fast neutrals of some hundreds of eV kinetic energy in organic material can be estimated by TRIM (transport of ions in matter) simulation [11]. The penetration depth is limited to a few nm maximum and is combined with elastic impacts between impinging particles and target atoms, which leads to displacement of target atoms, sputtering,

breaking of chemical bonds and formation of new chemical compounds.

Electrons and negative ions should have no direct influence on film deposition because of the negatively biased surface with respect to the plasma potential. These particles are retarded in the space-charge field of the plasma sheath to low kinetic energies or trapped in the plasma bulk region.

Reactive neutral particles at thermal energies produced in the plasma and plasma-boundary sheaths reach the surface due to the diffusion and the thermal wall current. In dependence on surface material and chemical reactivity of neutrals the adsorption process may result in the formation of new molecular structures and thin-film growth. In regions remote from the active plasma regions the material surface will interact with long-lived reactive particles, like metastable excited species, neutral reactive atoms and molecular fragments.

The radiation of a low-pressure gas discharge, in particular in the VUV region, can initiate photochemical reactions in the organic material very effectively. The influence of energetic photons has to be discussed separately. Mostly, the particle interaction dominates.

From the macroscopic point of view, material etching and sputtering accompanied by formation of volatile products may be observed simultaneously with thin-film deposition and the plasma chemical surface modification.

Consequently, in situ characterisation of thin-film formation in plasma processing needs a spatial resolution comparable with the typical penetration and interaction depth of the relevant plasma species, which is in the order of 1 nm typically. This resolution can be realised very well by ellipsometry, special techniques in FTIR spectroscopy and sensitive measuring of the sample mass by microbalances, for example.

On the other hand, the investigation of the deposition kinetics requires real-time measurements. The characteristic time constants for the processes on the surface (adsorption and desorption kinetics) and in the plasma and plasma-boundary sheath (kinetics of the charged and neutral plasma particles, plasma chemical processes) involve a wide time scale and must be discussed in detail. The characteristic process times of chemical gas conversion of organic monomer in the given plasma reactor, etching, deposition and polymer surface modification vary from the sub-seconds to the range of minutes. Therefore, the temporal resolution should be better than 1 s. In many cases the physical principle of the analysis or the available technical equipment does not allow such time resolution. In this case a pulsed plasma operation may be used successfully. In plasma reactors with gas flow the pulsed plasma operation regime becomes one of the process parameters determining the plasma chemical gas conversion and thin-film growth.

1 Methods and experimental setup

1.1 In situ ellipsometry

The change in the polarisation state of light reflected non-normally from a sample surface by the ellipsometric measurement gives information about thickness and refractive index of thin films. The reflection properties of a plane substrate and deposited thin films with plane interfaces are given by the complex reflection coefficients R_p and R_s (p and s describe parallel and perpendicular components of electric-field vector relative to the plane of incidence). They include the Fresnel reflection coefficients at all interfaces and take into account multiple interferences by the layers on the substrate [12, 13]. The shape of the polarisation ellipse depends on the ratio R_p/R_s, which is related to the ellipsometrically measured angles Δ and Ψ. Generally, the ratio R_p/R_s is a transcendental function of the film thickness, complex refractive index of the films, substrate and ambient, as well as the angle of incidence and wavelength. The interpretation of the measured angles Δ and Ψ as refractive index and film thickness depends strongly on the chosen optical model (substrate, one-layer, multi-layer) and has to fit the physical situation. It has been shown by model calculation that ellipsometry is very sensitive if the substrate material, the angle of incidence and the wavelength region are chosen properly [14].

A very sensitive method, based on the optical excitation of surface waves, so-called surface plasmons [15–17], can be applied for thin-film analysis using the ellipsometric arrangement. An easy way to generate surface plasmons at a metal–dielectric interface is an ATR configuration consisting of a glass prism whose base is covered with a thin metallic film (e.g. gold, < 50 nm) on which the investigated organic film is deposited. In the so-called Kretschmann configuration the angle of incidence of the polarised light at a fixed wavelength (for instance 632 nm) is varied and one can observe a resonance in Ψ and Δ indicating the excitation of surface plasmons when the resonance condition is reached. The refractive index and/or film thickness of the organic film can be determined from resonance angle and the shape of the resonance curve using an optical model similar to the ellipsometric measurements described above. The thickness of the organic film must be sufficiently small because the analysing depth is limited by the penetration depth of the evanescent wave into the dielectric.

In situ ellipsometric measurements are carried out at a wavelength of 632 nm and 70° angle of incidence by means of a commercial ellipsometer (Plasmos) which is adapted to the plasma-process chamber. In this arrangement the polarised light was reflected from a sample which was placed on the powered electrode in a 13.56-MHz discharge, see Fig. 1. The ellipsometric angles can be measured in real time dur-

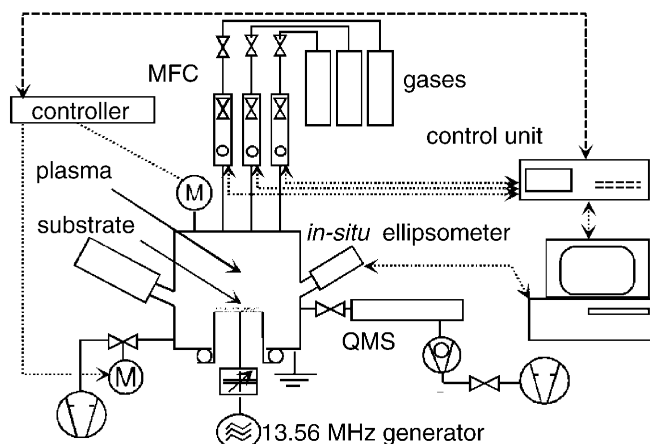

Fig. 1. Experimental setup with in situ ellipsometry arrangement

ing the plasma processing with a temporal resolution of about 1 s. Additionally, the film thickness and dispersion relation of refractive index in the wavelength range of 300–800 nm are determined ex situ by use of a spectroscopic ellipsometer (Rudolph Research).

1.2 In situ FTIR spectroscopy

For characterisation of the molecular composition of plasma-polymer films, in situ FTIR sampling techniques were applied based on infrared reflection absorption spectroscopy (IRRAS) and the ATR spectroscopy [18]. In an IRRAS experiment the IR beam of the spectrometer is reflected by a metal surface which was coated with the polymer material. It was shown that a maximum absorption of a given film thickness $d \ll \lambda$ requires parallel polarisation and a grazing incidence [19]. The special IRRAS setup, used for the experiments, consists of a vacuum chamber that contains two parallel-plate electrodes. This vacuum chamber is integrated in the standard compartment of a commercial FTIR spectrometer (Bruker). The IR beam of the spectrometer is deflected by 15° using prismatic windows made of chalcogenide glass. The resulting incident angle at the IRRAS sample placed at the electrode is 75°.

For ATR measurements the IR beam was coupled to an internal reflection element (IRE) with 45° incident angle which provided a total number of 34 reflections at the existing IRE geometry. The techniques of ATR spectroscopy (evanescent-wave spectroscopy) are described in detail in [20]. The IRE is made of chalcogenide glass and is integrated into the rf electrode of the process chamber [19, 21]. One side of the IRE was coated with the sample by a dip-coating procedure or by plasma polymerisation. The effective number of reflections in the part of the IRE contacted with the plasma is restricted to 13. The ATR technique used for film thickness < 100 nm permits us to apply the thin-film case of ATR spectroscopy ($d \ll \lambda$). Besides, the fibre-based ATR technique was applied for studying the film formation in the plasma bulk [22, 23]. In this case the mid-infrared-transparent fibre consisting of chalcogenide glass serves as the substrate on a floating potential, see Fig. 2.

The described FTIR techniques are in situ, which means that the signal sampling is made in the process chamber. But these are not real-time techniques because of relatively high sampling time for high enough signal intensity in comparison with characteristic time constants of film deposition or changing the chemical structure of the polymer surface. Therefore, the pulsed-mode plasma treatment must be applied, and the FTIR spectrum was taken in the pulse pause.

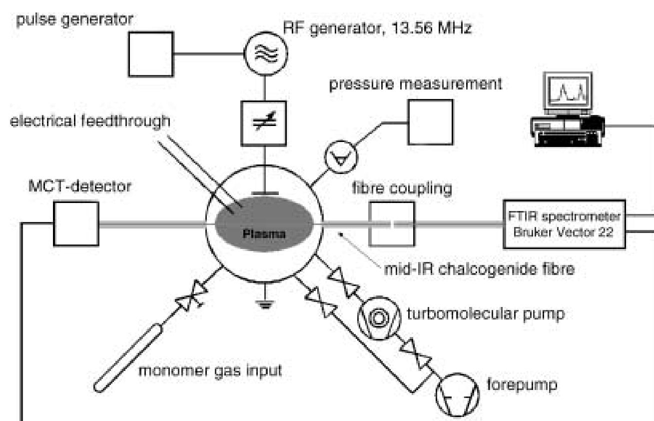

Fig. 2. Experimental setup for fibre-based ATR FTIR spectroscopy

1.3 In situ microgravimetry

Measurements of the total sample mass were realised by the use of an electronic vacuum microbalance [24]. At a maximum sample mass < 2 g the total mass change ≥ 1 µg can be measured in real time during the plasma treatment (resolution about 1 s). Nevertheless the information consists of the mass change only. The real-time measurements give information about the first steps in plasma–surface interaction if the sample surface used is high enough. For example, the competition between incorporation of atoms and molecules from the process gas and etching processes can be studied. The advantage of the latter method is that no special sample preparation is needed, e.g. conventional polymer foils can be used. The free suspended sample is arranged symmetrically between the parallel-plate discharge electrodes in the plasma bulk.

2 Formation of thin modified surface layer in plasma treatment of polymer surfaces

The chemical surface modification of a polyethylene (PE) sample due to the interaction of low-pressure plasma in different gases is shown in Fig. 3. In the ATR difference spectra (plasma-treated against untreated polymer sample) there can be seen clearly the polymer degradation by hydrogen abstraction and the plasma etching in the negative peak at 2900 cm^{-1} (C−H stretching vibration) and at 1450 cm^{-1} (C−H deformation vibration). On the other hand, characteristic new absorption bands appear. Depending on the processing gas the new molecular structures and functional groups containing oxygen, nitrogen and fluorine are formed. Generally, the chemical surface modification and etching of the polymer material are observed simultaneously.

In the case of oxygen plasma a steady state in surface modification is reached typically within about 5 s of plasma-treatment time [18]. In the case of CF_4 discharge the effective time constant is about one order of magnitude higher, which means about 30 s. Figure 4 represents the time evolution of the formation of the CF_x absorption band at 1100 cm^{-1} and the loss of the C−H structures at 2900 cm^{-1} (plotted is the integral extinction against plasma-treatment time). In the case of CF_x structures, the FTIR analysis cannot distinguish between the different fluorine-containing molecular groups like CF, CF_2 and CF_3 because of the strong coupling between these molecular vibrations. Therefore, the XPS analysis (ex situ) of the polymer sample was made. The XPS can separate these functional groups very well, see Figs. 5 and 6. The polymer surface is modified by successive fluorination and the CF_2 group is the dominant structure in the steady state. The thickness and the refractive index of the thin modified surface layer are estimated by ellipsometry.

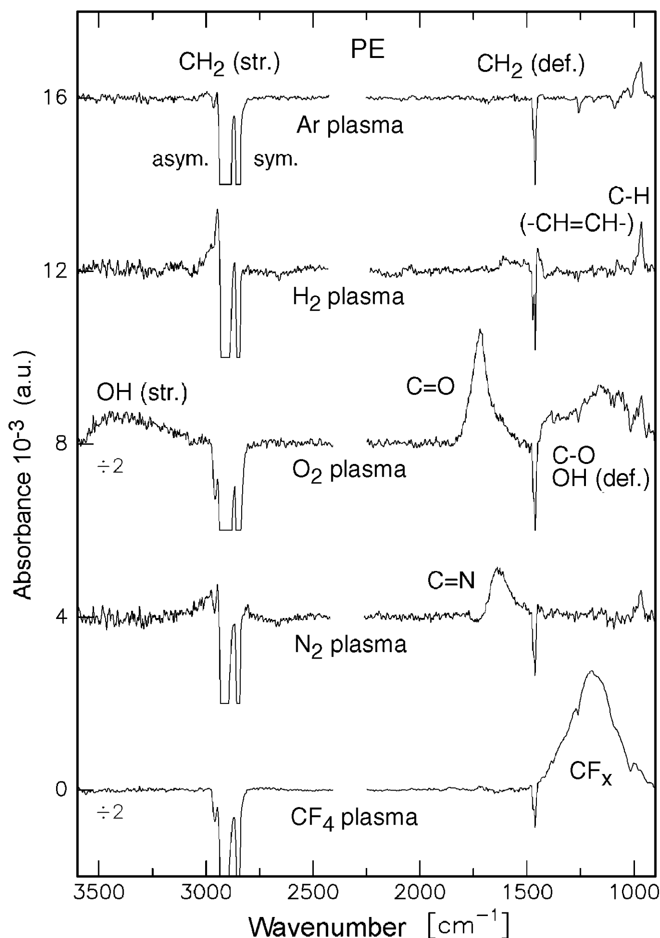

Fig. 3. Modification of PE polymer films in rf discharge of various gases ($p = 5$ Pa, $U_{\text{eff}} = 225$ V, $t_{\text{treatment}} = 3$ s). IR spectra were recorded with in situ ATR arrangement

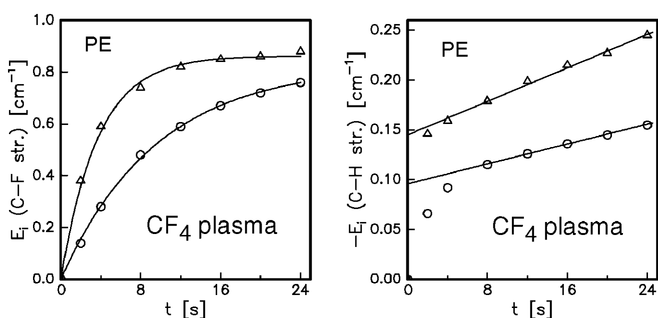

Fig. 4. Plasma modification of PE polymer films. Appropriate IR spectra were accumulated by means of in situ IRRAS apparatus. Here, the time evolution of integral extinction of C−F and C−H stretching vibrations is presented. 30 Pa (*up triangle*), 100 Pa (*circle*)

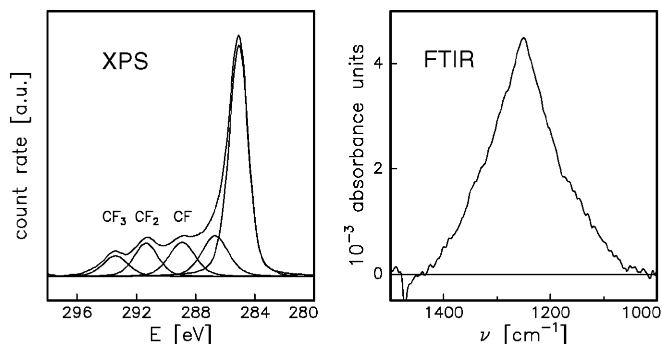

Fig. 5. Comparison of XPS (C 1*s*) and IR (C−F stretching vibrations) spectra of modified PE polymer film (CF_4 rf discharge, 50 Pa, $U_{\text{eff}} = 225$ V, $t_{\text{treatment}} = 5$ s). FTIR spectrum was obtained by means of in situ IRRAS apparatus

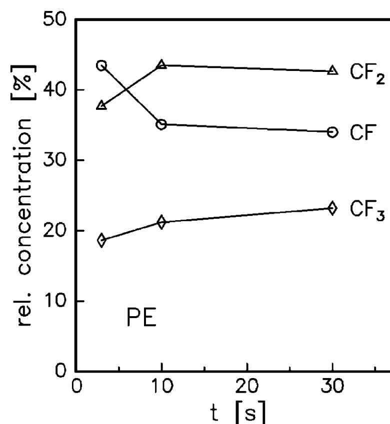

Fig. 6. Time evolution of CF, CF_2 and CF_3 functional groups at the modification of PE polymer film in CF_4 rf discharge (10 Pa, 30 W). Sample was on the powered electrode

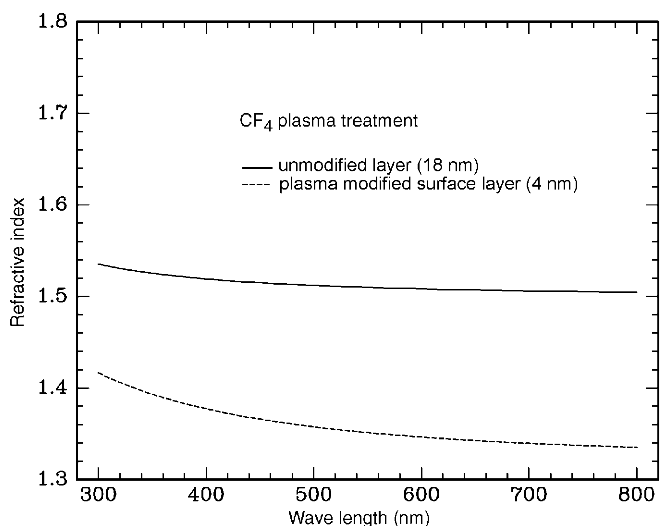

Fig. 7. Dispersion relation for the top plasma-modified surface layer and the underlying non-modified layer of a PE polymer film. Process conditions: CF_4 rf discharge, 15 Pa, 30 W. Optical model considered modified layer, unmodified layer, SiO_2 interface (2 nm) and substrate (Si wafer)

The thickness amounts to about 5 nm in the steady state; the refractive index of the modified surface layer is decreased, see Fig. 7.

The competition between incorporation of fluorine and plasma etching in the surface modification of polyethylene and polystyrene can be sensitively investigated by in situ microgravimetric measurements at the beginning of the plasma treatment. For example, in Fig. 8 the initial increase of the sample mass caused by fluorine incorporation in a polystyrene surface is shown. The sample was immersed in the plasma bulk of a CF_4 discharge. In the steady state a total material loss of the polymer sample is observed, whereas

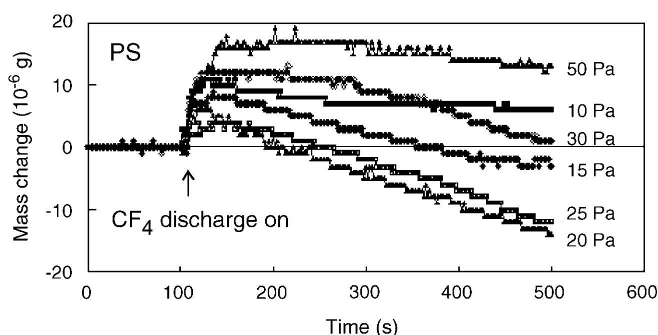

Fig. 8. Interaction between fluorine incorporation and plasma etching at the beginning of the CF_4 plasma treatment of polystyrene samples (3 cm × 3 cm). CF_4 discharge (50 kHz), discharge current $I_{eff} = 20$ mA, parameter: total pressure

the thickness of the modified surface layer remains approximately at a constant value. By change of the total CF_4 pressure the fixed polymer-sample position, symmetrically between the parallel-plate discharge electrodes, undergoes different parts of the negative glow of the dc-like 50 kHz discharge. The different plasma density and resulting charged-particle flux to the polymer sample controls the material loss.

3 Thin-film deposition in hexamethyldisiloxane (HMDSO) and styrene plasmas

3.1 HMDSO plasma polymerisation on the powered electrode in rf discharge

The deposition of thin plasma-polymerised silicon organic films from HMDSO as a precursor is investigated on the powered electrode in the rf discharge. The polymer-film growth and deposition rate were measured by in situ ellipsometry in dependence on different energy input in the rf discharge. From the macroscopic point of view the well-known energy parameter ϕ, analogous to that introduced by Yasuda [25], can be applied to compare the influence of the different experimental conditions e.g. by changing the discharge power, total pressure, gas flow on deposition rate, molecular structure and macroscopic properties of plasma-polymer films:

$$\phi = WkT/(pMf) ,$$

where W is the discharge power, T is the gas temperature, p is the total gas pressure, M is the monomer molecule mass and f is the monomer-flow rate.

Figure 9 shows the deposition rate of plasma-polymerised HMDSO films in dependence on the energy parameter. In this case the energy parameter, which implies the energy input per molecule of the monomer, is a suitable parameter to describe the deposition process effectively.

Clearly, two ranges can be distinguished: firstly, the range at low energy input and strong increase of the deposition rate due to rising fragmentation of the monomer molecules and secondly, the approximately independent deposition rate from the energy parameter due to progressive fragmentation of the monomer molecules. This can be shown by the investigation of the plasma chemical conversion of HMDSO by means of neutral-gas mass spectrometry.

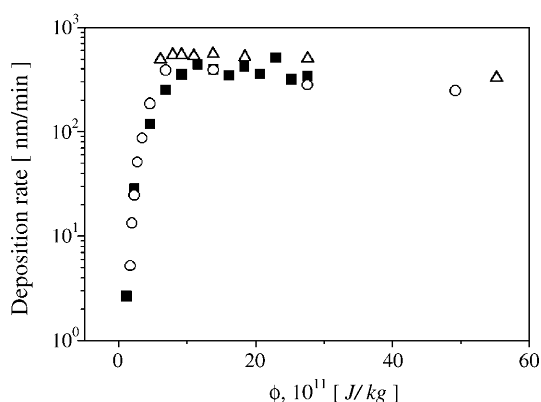

Fig. 9. Dependence of HMDSO deposition rate on the composite process parameter ϕ; (*open circle*), power variation, 10 Pa, f_{HMDSO} 4 sccm; (*black square*), pressure variation, 60 W, f_{HMDSO} 4 sccm; (*up triangles*) monomer flow-rate variation, 60 W, 10 Pa

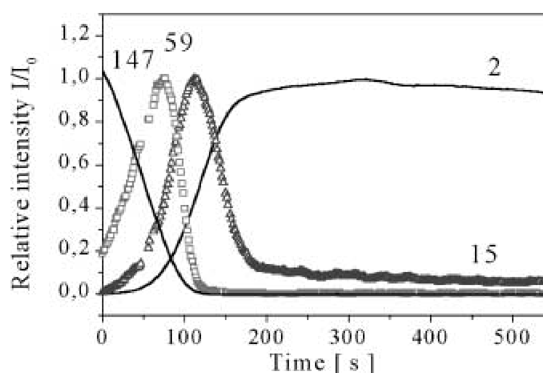

Fig. 10. Plasma chemical conversion of HMDSO monomer molecules in rf discharge. Closed reactor, 60 W, 10 Pa. *Black solid line*: 147 amu and 2 amu. *Square*: 59 amu. *Up triangles*: 15 amu

Without gas flow the monomer molecule is converted in the plasma reactor into many new stable gas products partly as intermediate products [26], see Fig. 10. Finally, after a long 'plasma on' time the organic components of the introduced monomer can be found in organic films at the electrodes and reactor walls, whereas the molecular hydrogen will be the dominant reaction product in the gas phase. Using gas-flow regime a steady state in monomer fragmentation and neutral-

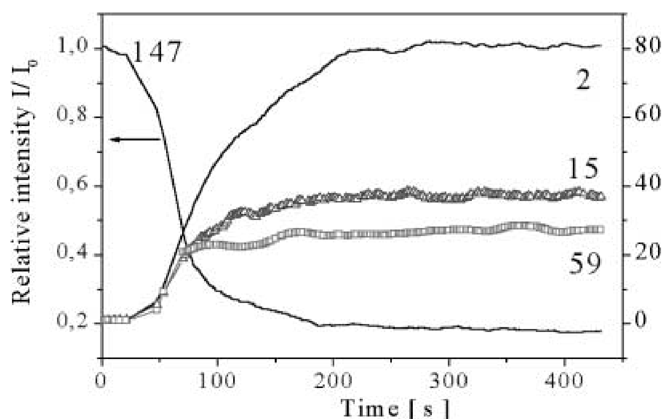

Fig. 11. Plasma chemical conversion of HMDSO molecules in rf discharge with gas flow. 60 W, 10 Pa, f_{total} 4 sccm, HMDSO:Ar 9 : 1

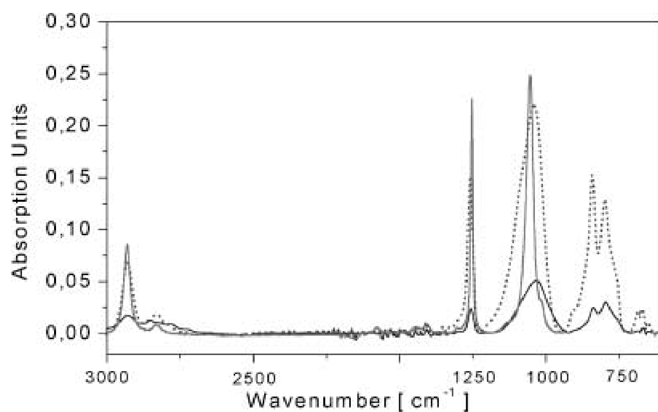

Fig. 12. Comparison of IR spectra of the monomer (obtained with ATR technique) and plasma polymers (transmission measurement). *Solid line*: monomer; *dotted line*: deposition conditions 60 W, 10 Pa, 2 sccm HMDSO. *Dashed line*: deposition conditions 10 W, 10 Pa, 8 sccm HMDSO

gas composition is reached within about 1 min depending on the plasma-processing parameter, see Fig. 11. The increasing fragmentation and consumption of the monomer molecules with the energy parameter at low values correlate with the observed increase in deposition rate shown in Fig. 9.

For IR analysis plasma-polymer films of about 1 μm thickness were deposited on Si wafers in the experiments of two essentially different kinds. IR spectra (see Fig. 12) show that plasma polymer, synthesised at lower energy input, has a monomer-like structure.

3.2 Styrene plasma polymerisation in the plasma bulk of rf discharge

By use of the in situ fiber ATR, the thin-film formation in styrene rf plasma was investigated in the plasma bulk. This means that the substrate for film deposition consists of the internal reflection element which is a part of the chalcogenide glass fibre inside the plasma reactor, see Fig. 2.

In Fig. 13 the absorption spectrum of a thin polystyrene film in comparison with a plasma-polymerised styrene film on the fibre can be seen. In the thin polystyrene film prepared by dip coating from a polymer solution (chloroform–polystyrene), the characteristic absorption bands were

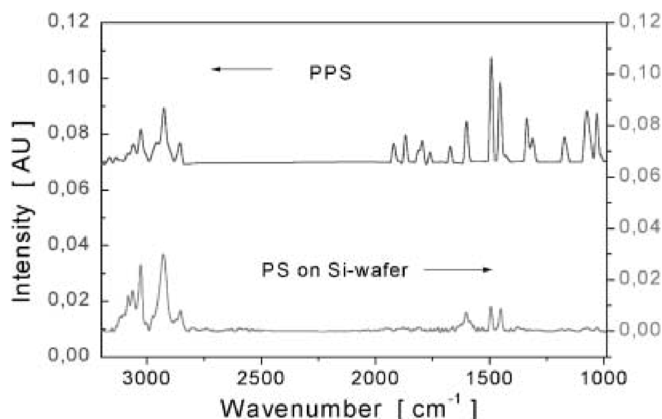

Fig. 13. IR absorption spectra of polystyrene film on Si wafer (∼ 100 nm) and plasma-polymerised styrene films (∼ 65 nm). Deposition conditions: 10 Pa, 100 W, τ_{plasma} 10 s

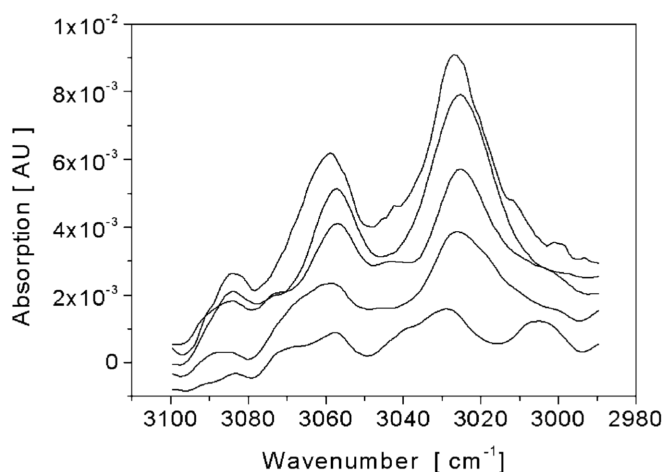

Fig. 14. Time evolution of IR spectra from aryl rings (aromatic C−H stretching vibrations) in plasma-polymerised styrene film. Deposition conditions: 40 Pa, 100 W, τ_{plasma} 5 s

observed from the aromatic rings (C−H stretching above 3000 cm^{-1} and ring deformation between 1625 and 1460 cm^{-1}) and the well-separated symmetric and asymmetric stretching vibrations of C−H at 2900 cm^{-1} from the aliphatic part in the polymer chains. The time evolution of the characteristic aromatic structure is shown in Fig. 14. In the case of plasma-polymerised styrene films the aliphatic part offers a more cross-linked structure as expected. Furthermore, the significant absorption in the range of 1400 to 1200 cm^{-1} indicates a more orientated structure in the arrangement of the aromatic rings during thin-film formation. The absorption of the orientated molecule vibrations is changed in dependence on the energy input.

4 Conclusions

The low-temperature plasma in molecular gases or organic monomers and the plasma–surface interaction represent complex reaction systems which have to be described by many gas-phase and surface processes simultaneously. In situ characterisation of the thin-film deposition process or the modification of the thin surface layer by use of suitable diagnostic tools inside the plasma reactor and during the plasma process gives information about the process dynamics and the dominant reaction channels.

In particular, the ellipsometry, FTIR spectroscopy and microgravimetry were successfully applied. In polymer surface modification the characteristic treatment times between 5 and 50 s were found depending on processing gas. The change in the molecular structure of a thin surface layer of a few nm was in the expected range and reflects the typical penetration depth of the dominant plasma species. In the steady state the total sample mass (film thickness) was reduced whereas the modified surface layer remains nearly constant due to the simultaneous plasma-particle incorporation and etching of surface material. The chemical structure modification of the polymer surface is combined with a changed refractive index.

In plasma polymerisation the dissociation and plasma chemical conversion of the introduced monomer vapour leads

to the film formation on the discharge electrodes and reactor walls and the production of new stable neutral gases. The energy parameter ϕ was a suitable description tool to include typical macroscopic process parameters like discharge power, total pressure and gas-flow rate which have influence in monomer conversion, thin-film growth and the chemical and physical properties of the deposited films. In the case of the energy-deficit regime realised by low discharge power, a pulsed discharge regime, higher total pressure and gas-flow rate allowed the deposition of plasma-polymer films with monomer-like structures. The detailed understanding of the process kinetics and the knowledge about the influence of the process parameters on the structure formation can contribute to better control of the plasma chemical and physical processes in complex reaction systems.

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