PLASMA SURFACE MODIFICATION OF POLYMERS CHARACTERIZED BY ELLIPSOMETRY

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This paper deals with the optical investigation of thin polystyrene and polyethylene films (thickness 10 - 50 nm) modified in a low pressure plasma of CF_4 and O_2.
Different physical and plasma chemical processes initiated at the polymer surface cause a modification of polymers exposed to an rf discharge. Despite this fact investigations concerning optical properties changed by plasma treatment are rarely found in literature.
In this paper it is shown that the interaction between plasma species and polymer leads to a change of the optical properties. The refractive index of a thin surface region differs significantly from the initial values.
The optical modification effects are investigated by spectroscopic ellipsometry ($\lambda = 300$ to 800 nm) at variable angle of incidence and surface electromagnetic waves ellipsometry ($\lambda = 632.8$ nm). Both techniques are very surface sensitive. The analysis of the ellipsometric measured data is performed by applying one layer but also multilayer model to receive information about the layered structure of the modified samples.

Introduction

Low pressure plasma treatment is frequently used to alter the surface characteristic of polymers and thus their functional properties (adhesion, wettability, bio compatibility etc.) [1]. The complex interaction between plasma species (ions, radicals, electrons, UV quanta) and polymer leads on the one hand to a destruction of the original structure which can be seen in material removal by plasma chemical etching and sputtering, on the other hand to crosslinking and functionalization as a consequence of radical formation and incorporation of new chemical groups [2,3,4]. The structural changes that occur within the modified surface region influence also the optical properties, like the refractive index. Thickness and structure of the modified surface region depend on polymer material, discharge conditions (pressure, power, gas, sample position, treatment time), and penetration depths of plasma species (some nm). Ellipsometry as a non-destructive optical measurement technique offers the possibility to investigate the modified surface region regarding modification depth and optical properties on the assumption that the refractive index of the modified surface region has changed during plasma treatment. Ellipsometry measures the change in polarization state of light reflected non-normal from a sample surface [5]. The reflected and incident electric field vectors are related by the complex reflection coefficient R.

$$E^r_{p,s} = R_{p,s}\, E^i_{p,s} \qquad (1)$$

p parallel
s perpendicular to the plane of incidence

In the case of the reflection at a planar interface between two semi-infinite homogeneous isotropic media (substrate model) Rp and Rs correspond to the Fresnel reflection coefficients. If there is a film or a stack of films on a substrate multiple interferences have to be considered. The shape of the polarization ellipse of the reflected light depends on the ratio R_p/R_s which is related to the ellipsometric measured angles Delta (Δ) and Psi (Ψ).

$$\rho = \frac{R_p}{R_s} = \tan\Psi\, e^{i\Delta} \qquad (2)$$

Therefore ρ is a transcendental function of all film thicknesses, of the complex refractive indices (films, substrate and ambient), as well as of angle of incidence and wavelength. Except for the substrate model an iteration procedure is necessary to solve equation (2) for the optical data of interest.

It has been shown by model calculations that ellipsometry is very surface sensitive if substrate material, angle of incidence, and wavelength region are chosen properly [4]. Moreover the characterization of a thin modified surface layer can be achieved in a very sensitive way by the optical excitation of surface electromagnetic waves, so called surface plasmons [6,7]. An easy way to generate surface plasmons is to use a glass prism which base is covered by a thin Ag film on which the polymer film is deposited (inset in Fig. 5). Varying the angle of incidence one can observe a resonance in Ψ and Δ indicating the excitation of surface plasmons when the resonance condition is met.

Experimental Details

Polystyrene and polyethylene were chosen as polymer material for this study. Polyethylene films were prepared from a 0.5% solution in toluene, polystyrene films from a 0.5% solution in trichloromethane using a dip-coating technology. The polymer films were smooth and homogeneous with thicknesses d of about 10 to 50 nm.

The investigation of thin polymer films instead of bulk samples offers several advantages. A film thickness chosen in the order of the modification depth ensures a maximum contrast while observing modification effects.

The samples were placed on the capacitively coupled rf electrode of a cylindrical vacuum chamber. Typical discharge conditions used are: rf power 10 to 30 W (13.56 MHz), pressure 10 to 100 Pa, modification time 0.1 s - 2 min. Surface modification was achieved by using different plasma gases, e.g. oxygen, argon, and tetrafluoromethane.

Ellipsometric measurements on plasma modified polymer samples are performed by a commercial spectroscopic ellipsometer (S2000, Rudolph Research) of photometric type [8]. The measurements in a wavelength range from about 300 to 800 nm and at different angles of incidence enable the investigation of the dispersion behaviour of polymer films before and after plasma treatment. The dispersion behaviour is described using a modified CAUCHY dispersion relation [9]:

$$n(\lambda) = n_0 + \frac{n_2}{\lambda^2} + \frac{n_4}{\lambda^4} \qquad (3)$$

A MARQUARD iteration procedure is used to fit the parameter n_0, n_2, n_4 to the measured spectra (Δ, Ψ) on the basis of a suitable chosen error function.
The measurements on the basis of surface plasmon ellipsometry were carried out at a wavelength of 632.8 nm

Results and Discussion

Fig. 1 shows the result of ellipsometric measurements on thin polyethylene films (initial thickness: 29 nm) in dependence on treatment time. The analysis of the ellipsometric data was for simplicity first done according to a one layer model. The thickness of the polymer film decreases but the pseudo refractive index (e.g. at $\lambda = 632.8$ nm) doesn't stay constant vs. time, as it should be during the etching of an optically homogenous layer. The one layer model doesn't meet the physical situation.

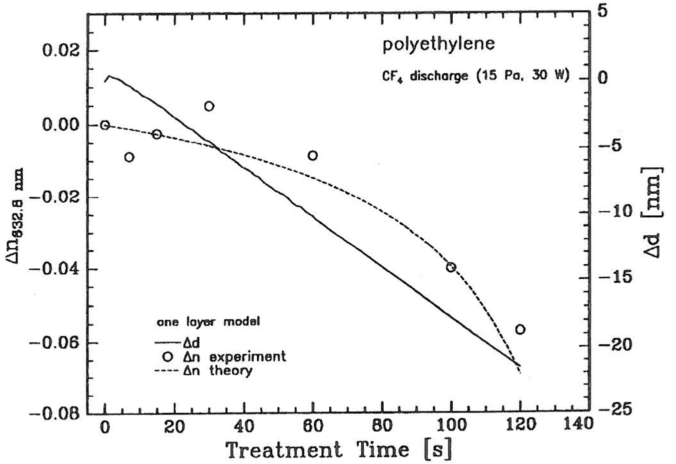

Figure 1: Change of the pseudo refractive index and thickness of a PE film vs. treatment time. Analysis of the ellipsometric data according one layer model.

A subsequent analysis of the ellipsometric data using a two layer model delivers the thickness of a modified surface layer of about 4 nm which has been established after a short time of about 20 s plasma treatment (Fig. 2). This analysis was made with the

assumption that deeper lying regions kept the initial refractive index and that the refractive index of the modified surface layer is constant vs. time. The difference between the modified surface layer and the unmodified or only slightly modified bulk layer is evident when looking on the dispersion behaviour as also shown in Fig. 2. The refractive index of the surface layer is significantly lower than that of the bulk layer.
A recalculation from the two layer model (with decreasing overall thickness and constant refractive index / thickness of the surface layer) to the one layer model provides the theoretical curve shown in Fig. 1. Thus the dynamics of the pseudo refractive index shown in Fig. 1 can be explained assuming a competition between etching and modification. After a relatively short time the equilibrium between both processes causes the formation of a stable modified surface layer. The good agreement between theoretical and experimental data of the pseudo refractive index as shown in Fig. 1 supports this interpretation.

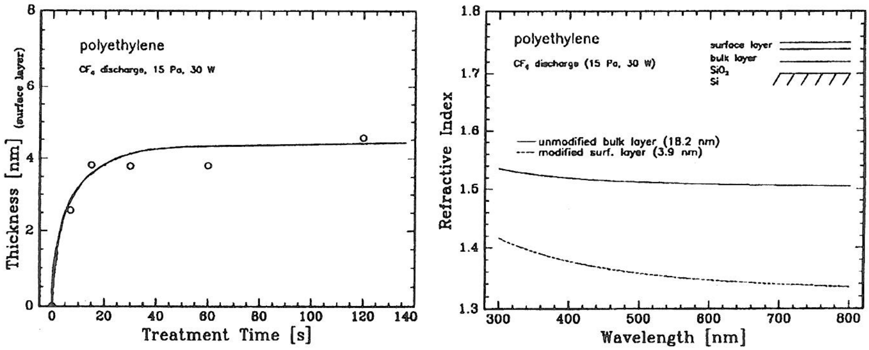

Figure 2: Plasma modification of polyethylene: Formation of a modified surface layer with a refractive index differing from initial value. Analysis using a multilayer model.

It is also possible to detect changes of the refractive index in a thin surface layer after plasma modification of polystyrene in a CF_4 discharge [5]. The thickness of the modified surface region is in the range of 4 to 10 nm in dependence on discharge conditions. A reduction of the refractive index was observed possibly caused by the destruction of the aromatic structure (aliphatic CH-polymers generally have a lower refractive index than aromatic ones [10]).
The changes of the refractive index after plasma treatment in an oxygen discharge are not so pronounced compared with the fluoridation (Fig. 3, 4). The thickness of the modified surface layer tends to be lower (< 4 nm). After only a few seconds treatment time (< 5 s) a steady state between etching and modification has been established. One reason may be the high etch rate using oxygen as plasma gas.

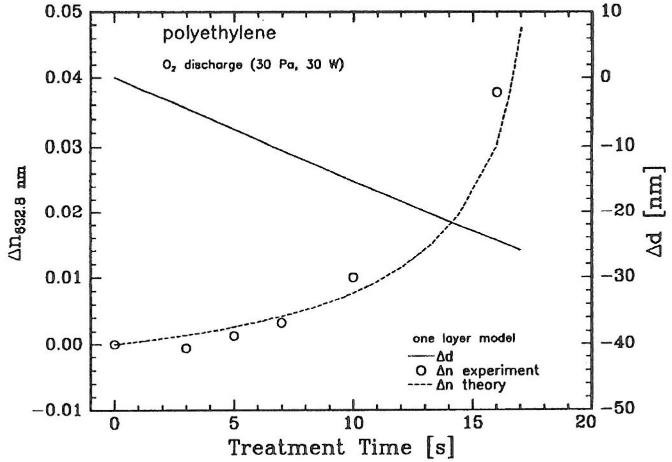

Figure 3: Change of the pseudo refractive index and thickness of a PE film vs. treatment time. Analysis of the ellipsometric data according one layer model.

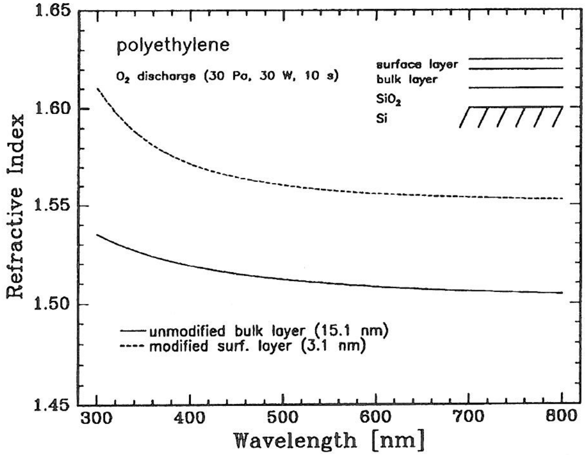

Figure 4: Formation of a modified surface layer after plasma treatment of PE.

Figure 5 illustrates the use of surface plasmon ellipsometry to determine optical modification effects caused by plasma treatment. In the case of surface plasmon ellipsometry the sample is probed by an evanescent wave. The excitation of surface plasmons is only possible if the experimental configuration meets the resonance condition [6]. This explains why this method is very sensitive to the surface conditions.

In a first step the base of the prism is coated with a thin silver film (Kretschmann configuration). Measurements at variable angle of incidence allow the determination of thickness and refractive index of the silver film. In a second step the base is coated with the polymer film. Figure 5 shows the shift of the resonance angle by this procedure ($n_{film} = 1.6$, $d = 30$ nm) as well as an experimental and a fitted curve for a silver coated prism without polymer film. The angle of resonance shifts again, if the polymer film is treated in a low pressure plasma (model: $n_{surface\ layer} = 1.5$, $d_{surface\ layer} = 5$ nm). In this case the angle of resonance can be determined with an accuracy which is one order better than the shift.

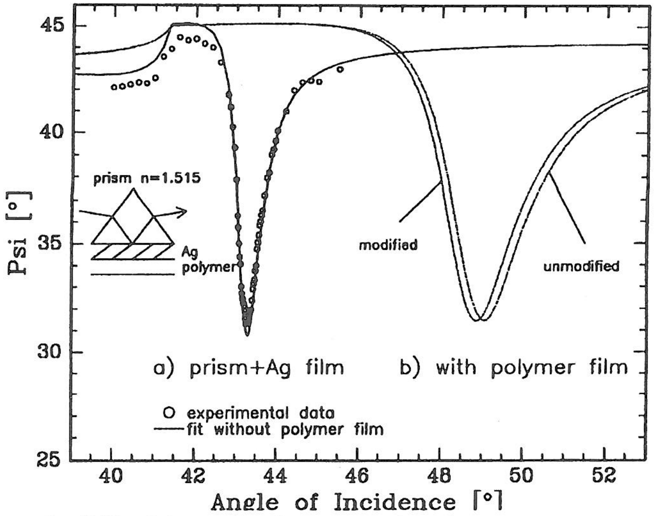

Figure 5: Shift of the angle of resonance in Psi (surface plasmon ellipsometry) caused by plasma modification of a thin polymer film. For comparison the curve without polymer film is also shown.
The fitted optical data of the Ag film are: n=0.077-i3.93, d=36.28nm.

Acknowledgements

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