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Deposition of functional coatings on polyethylene terephthalate films by magnetron-plasma-enhanced chemical vapour deposition

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ABSTRACT

Magnetron-plasma enhanced chemical vapour deposition (PECVD) is a process tool which allows the deposition of plasma polymer coatings at process pressures below 1 Pa. The striking features of this technology are the relatively easy realisation of large area deposition as well as the possibility of the combination with sputtering processes for multilayer coating designs. SiO_xC_y coatings were deposited on polymer film in a roll-to-roll deposition machine. Dynamic deposition rates as high as 120 nm*m/min were achieved. The process was set up with both the monomer hexamethyldisiloxane and the monomer tetraethylorthosilicate (TEOS) and with mixtures thereof. The coatings were analysed by Fourier transform infrared spectroscopy. This method identifies the existence of different types of Si–O bonding in the layer. The results show how the layer properties are linked to the plasma parameters of the deposition process. The properties were compared to sputtered SiO_2 and to layers obtained by other PECVD processes. Elastic recoil detection analysis (ERDA) was used in order to determine the composition of the samples. Both IR spectroscopy and ERDA revealed that the usage of TEOS provided more SiO_2-like layers. The process was applied to the deposition of optical multilayer coating in a roll-to-roll coating system.

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1. Introduction

Plasma enhanced chemical vapour deposition (PECVD) is a widely used deposition technique. Until the 1980s it was mainly used in semiconductor manufacturing. Later on the technology was adapted to several large area applications [1]. Gas permeation barriers as well as hydrophobic or optical applications had been the main focus of interest [2]. The PECVD technologies can be distinguished by the way of the plasma excitation. The majority of the applications use either high frequency (RF-PECVD, usually 13.65 MHz) or microwave (MW-PECVD, 2.41 GHz) sources for the powering of the plasma, However, both types show considerable problems with respect to a scaling up to large area deposition in roll-to-roll systems. The issues concern the uniformity of the layers as well as the extensive matching networks for large area electrodes.

A different approach will be discussed in this paper. Magnetron-PECVD uses a pair of magnetrons as the plasma source. These magnetrons are powered by an AC power supply with an adjustable frequency between 20 kHz and 50 kHz. Such arrangements are typically used for high rate reactive sputtering. The magnetrons alternate between acting as the cathode and as the anode in quick succession. This prevents the disappearing anode phenomenon and reduces arcing. In case of Magnetron-PECVD, a silicon containing monomer is added to the sputtering gas which leads to the formation of SiO_xC_y layers on the substrate.

This approach has two advantages over the above mentioned alternatives. The process can be operated at pressures below 1 Pa. This makes it easier to combine it with sputtering processes in multilayer designs. There is no problem for scaling up the process. Double magnetron systems up to more than 3 m length are common tools for sputtering. The basic arrangement is shown in Fig. 1.

A striking feature of the Magnetron-PECVD process is the short residence time of the monomer in the plasma. The consequence is a low degree of monomer fragmentation compared to the RF and microwave based technologies. This leads to a high carbon content in the layer which is a drawback in most applications. One possible way to improvement is the variation of the silicon containing monomer.

In this paper experimental results will be presented about the Magnetron-PECVD process with either hexamethyldisiloxane (HMDSO) or tetraethylorthosilicate (TEOS) or a mixture of both. The composition was determined by elastic recoil detection. The structural features were analyzed by Fourier transform infrared spectroscopy.

2. Experimental details

The experiments were carried out using the laboratory roll-to-roll coating system *labFlex® 200*. The samples were prepared on a continuous film of polyethylene terephtalate (PET, Melinex® 400, DupontTejinFilms). The deposition width was 200 mm. The vacuum

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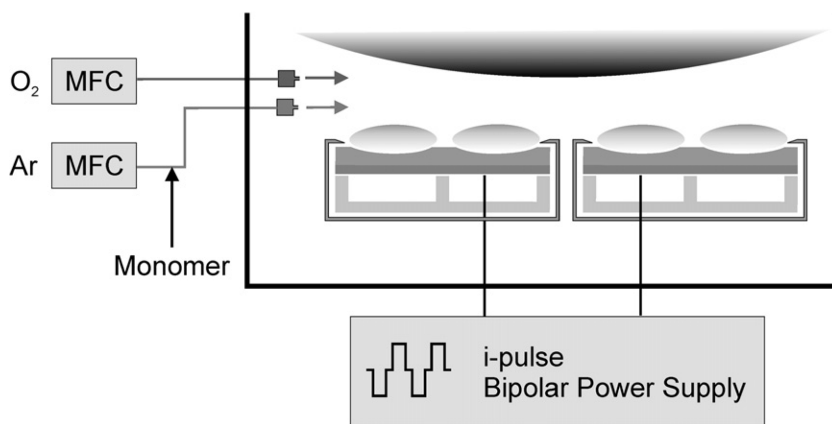

Fig. 1. Schematic drawing of the Magnetron-PECVD process.

vessel was pumped down to the base pressure of 2×10^{-3} Pa. Argon (270 sccm) was lead into the chamber by a mass flow controller (MKS Instruments). The monomer and the oxygen were added according to the special settings for each sample. The oxygen flow was regulated by a mass flow controller (MKS Instruments) in the same way as argon. The monomer HMDSO was evaporated at 35 °C. The monomer vapour was adjusted by a specially designed mass flow controller (MKS Instruments) which was heated up to 50 °C. The monomer was subsequently mixed with the argon (see Fig. 1). The monomer TEOS was regulated by a LiquiFlow (Bronkhorst) and subsequently evaporated and mixed with argon. The dual magnetron system was set up by two magnetrons (Sun Source) with titanium targets of 349×121 mm^2 size (99.5% purity). The system was powered by an i-pulse® power supply (Fraunhofer FEP).

Two sets of samples were prepared. The first set was used for the Fourier transform infrared spectroscopy (FTIR) measurements. In this case the PET film was completely coated by an aluminum layer (thickness 100 nm) prior to starting the Magnetron-PECVD process. This metal layer served as an optical separation between the substrate and the SiO_xC_y layer. The thickness of the SiO_xC_y layers were determined by UV–VIS spectroscopy (Perkin Elmer Lambda 900). The FTIR spectra were determined by a Spectrum 2000 (Perkin Elmer). The second set of samples was used for the elastic recoil detection analysis. In this case the SiO_xC_y layers were directly deposited on the PET film.

3. Fourier transform infrared spectroscopy

FTIR spectra have proved to be a powerful tool for interpreting the microstructure of SiO_xC_y layers. Typical features of the FTIR spectra can be interpreted according to Table 1. Different process conditions result in different amplitudes of the broad –OH-peak around 3300 cm^{-1}. In [3] it was shown that ion beam treatment reduces the amplitude of this peak.

Table 1
Summary of the relevant features in FTIR-spectra of silicon based PECVD layers

Wavenumber	Species	Reference
940 cm^{-1}	Si–OH	[3]
1070 cm^{-1}	Si–O–Si stretching mode	[3]
3300 cm^{-1}	–OH	[3]
1255–1275 cm^{-1}	Si–CH_3	[5]
1135–1190 cm^{-1}	Si–O–Si branching short chain	[5,6]
795–850 cm^{-1}	Si–$(CH_3)_2$, Si–$(CH_3)_3$, Si–O–Si bending	[8,7]
2958 cm^{-1}	CH_3 asymmetric stretching	[7]
2900 cm^{-1}	CH_3 asymmetric stretching	[7]

However the most interesting results can be obtained in the spectral region between 800 cm^{-1} and 1350 cm^{-1}. Here one can find Si–OH stretching modes (940 cm^{-1}), the Si–O–Si asymmetric stretching mode at 1070 cm^{-1} and Si–CH_3 peaks at 1255–1275 cm^{-1}. The Si–O–Si mode is the dominant feature in various investigations. A strong peak at 1070 cm^{-1} is mainly attributed to a chain-like character if the Si–O–Si bonding. In 0 it was observed that the peak is broadening with longer plasma duration in a RF-PECVD process with HMDSO/O_2 mixture. This was attributed to a changed cross-linking and changed molecular environment of Si–O species. In [5] the appearance of a shoulder to higher wavenumbers was observed. This was attributed to a higher degree of disorder in the Si–O–Si- network.

Fig. 2 shows FTIR spectra for a sputtered SiO_2 layer and two examples of SiO_xC_y layers deposited by conventional RF-PECVD. These samples were specially prepared on PET film as a reference for the samples later made by Magnetron-PECVD. The Si–O–Si stretch mode at 1070 cm^{-1} can be seen in all three samples as a shoulder. The Si–CH_3 peak (1255–1275 cm^{-1}) can be found for the RF-PECVD samples only. In addition to the peaks listed in Table 1 a strong peak appears in the range between 1100 and 1240 cm^{-1}. In the following we will denote it by SiO_x-peak. It stands for the network-like character of the layer. The striking feature of this peak is its shift to higher wavenumbers for films that have a more SiO_2-like character. The highest value of 1236 cm^{-1} is reached for the sputtered SiO_2-layer. The RF-PECVD layer with the higher HMDSO to O_2 ratio shows a peak at 1124 cm^{-1}. It is well known that a higher content of O_2 in the process gas leads to a more SiO_2-like character. Consequently, the maximum of the SiO_x-peak in the RF-PECVD sample with the lower HMDSO to O_2

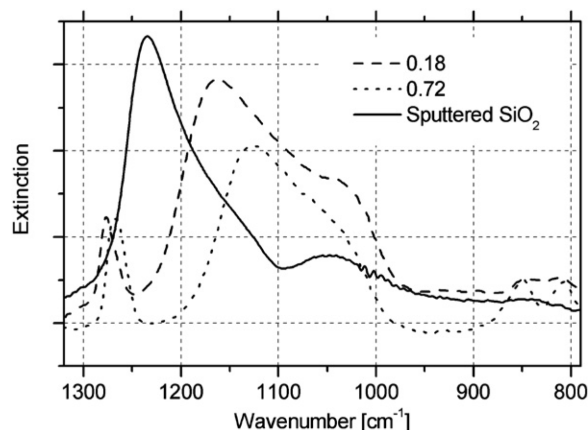

Fig. 2. Formation of the SiO_x peak in the FTIR spectra of reference layers. The reference layers were prepared by RF-PECVD and by reactive sputtering.

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