Separated effects of plasma species and post-treatment on the properties of barrier layers on polymers

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Abstract: The aim of this work is to investigate separated effects of ions, metastables and (VUV) photons on the properties of barrier layers on polymers. We try to separate the effects of different species by using an ion-repelling grid system (IReGS) and measuring the flux of ions, metastables and photons to the surfaces. In a second approach we modify a plasmagrown SiO_x layer by oxygen and argon post-treatment during the deposition process via pulsed influx of precursors.

Keywords: Polymer coatings, barrier layers, plasma activation, a-C:H, a-Si:H, SiO_x, HMDSO.

1. General

Analyses of a-C:H/a-Si:H multilayers on polymer substrates indicated that prolonged ion bombardment influences negatively the properties of the barrier layer, while a short plasma pre-treatment can improve the barrier effect [1]. This work is motivated by these results and investigates the influence of different reactive plasma components, namely ions, metastables and (V)UVphotons, on the properties of the grown barrier layer. Furthermore, the post-treatment of SiO_x films deposited Ar/HMDSO O₂/hexamethyldisiloxane from and (HMDSO) plasmas is investigated. Via a pulsed HMDSO flow the ratio between a deposition and a post-treatment phase can be varied in order to produce carbon and Si-OH group free SiO_x films in an integrated process.

2. Plasma Activation

To separate the different species and their influence on plasma pre-treatment and film growth, we build an ionrepelling grid system (IReGS), schematic in Fig.1. With this approach the ions can be repelled from the substrate. The IReGS was already successful in separating the influence of ions during a chromium HiPIMS process [2].



Fig. 1. Ion-Repelling Grid System (IReGS)

We can now compare the influence of the ions on plasma activation in our inductively coupled plasma (ICP). The optimal bias voltage was obtained with ion flux measurements by the combination of the IReGS with a Faraday-Cup. With a bias voltage of $U_{IReGS} = 36$ V only metastables and (V)UV-photons will influence the substrate. For different plasma activation times PET substrates were activated in an argon ICP plasma with and without ions. Afterwards these substrates were analysed by contact angle measurements, the change in water contact angles are shown in Fig.2.



The change in contact angle and therefore enhancement of the surface energy happens in the first ten seconds of activation. The ions contribute to a higher surface energy at short time scales. For longer activation there is no influence by ions.

In a second approach we separate the effect of argon metastables from the effect of (V)UV-photons. We place the before mentioned IReGS behind a long tube at the side of the chamber wall. To guarantee the same photon irradiation we measured the intensity at both positions and adapted the activation time. With this setup it is possible to reduce the metastable and ion density in front of the substrate, so that mainly (V)UV-photons have an effect. First results showed no significant influence in contact angle measurements by only (V)UV-photons during plasma activation.



We can therefore conclude that mainly metastables are driving the activation process. An integral part of this investigation is to measure the photon fluxes to the substrate by an VUV monochromator. For that, a differentially pumped VUV spectrometer with a spectral range 30 - 300 nm is used, where, the emission intensities of the two most prominent argon lines at 104.9 and 106.8 nm can be measured, Fig.3. In this approach we can study the different effects of the plasma species and possible synergy effects, to improve the properties of the barrier layer.

3. Deposition

In a second part, the deposition of SiO_x films from O_2 /HMDSO or Ar/HMDSO mixtures in an inductively coupled plasma is investigated. Substrate temperature and electron density are measured during the deposition process.



Fig. 4. Monitoring Ne with a plasma absorption probe

Furthermore, the deposited layers are analysed with a profilometer (thickness), infrared absorption spectroscopy (FTIR) (see e.g. Fig.5), and X-ray photoelectron spectroscopy (XPS).



Fig. 5. FTIR spectra with different O2 post-treatment

Processes with continuous and pulsed HMDSO flows are compared to characterize the effect of post-treatment of the grown layer. Pure O_2 or Ar plasmas between the HMDSO gas flow pulses can offer a "post-oxidation" or "posttreatment" of the grown films. The discharge dynamics during the different phases are also investigated by timeresolved electron density measurements. This approach has led to formation of carbon and Si-OH group free SiO_x films even without addition of O_2 gas under atmospheric pressure conditions.

Acknowledgement

This work is supported by Deutsche Forschungsgemeinschaft (DFG) within the framework of the Collaborative Research Centre SFB-TR 87 and the Research Department 'Plasmas with Complex Interactions' of Ruhr-University Bochum.

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