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Effect of humidity on the residual stress in silicon-containing plasma polymeric coatings

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ABSTRACT

Residual stress measurements of thin films are common practice in device technology and are extremely important in particular for the characterization of thin film coatings. A largely ignored stress contribution is the difference in coefficient of hygroscopic expansion between the coating and substrate. This paper presents a rather novel approach to accurately evaluate the residual stress and coefficient of hygroscopic expansion of strongly curved specimens. Silicon-containing plasma polymer coatings with different carbon contents were deposited using hollow cathode arc discharge based PECVD. Samples of different layer composition were produced comprising silicon-containing plasma-polymer layers with a high carbon concentration and more “inorganic” SiO₂ like layers with lower carbon concentration. All coatings show a compressive stress state. The highest stress was measured in the coating with the highest carbon content (239 ± 6 MPa) and decreases to 94 ± 31 MPa at lower carbon contents. Variation of the humidity showed that all coatings expand under influence of increasing relative humidity. The most inorganic coatings exhibits the highest expansion coefficient of $29.2 \pm 2 \cdot 10^{-6}$ (% r.h.)⁻¹. The results obtained were compared with the results from contact angle measurements. An increase in the hygroscopic expansion corresponds with an increasing hydrophilicity of the coatings.

1. Introduction

The origin of thin film stresses and the qualification of the stress state are major topics in today's research on thin solid films. A high residual stress state may lead to spontaneous delamination or fracture of vacuum deposited coatings [1,2]. Obviously, to reduce the total residual stress it is important to understand the different mechanisms and their individual contributions. Several contributions to the total residual stress in vacuum deposited coatings [3] can be distinguished:

$$\sigma_{\text{residual}} = \sigma_{\text{intrinsic}} + \sigma_{\text{process induced}} + \sigma_{\text{thermal expansion}} + \sigma_{\text{hygroscopic expansion}} \quad (1)$$

Intrinsic stresses are directly related to processing induced stress due to different film formation stages and microstructural evolution and are closely related to the growth mechanism. Recent review papers provide a critical overview of the current understanding but also show that a comprehensive model does not exist which can be applied in general [4,5]. Processing induced stresses are mainly observed in roll-to-roll processes and are related to web tension induced strain and the deposition on curved chilling drums [6]. The latter two components, i.e. thermal and hygroscopic expansion, are related to environmental

changes between the deposition chamber and during application/measurement. Thermal expansion is well studied in literature [7–9] as high substrate temperatures during deposition are often used to improve the coating properties [10–12]. Scant information is available on the hygroscopic expansion of thin coatings [3]. Hygroscopic expansion of thin film coating on substrates induces, similar to the thermal expansion, a residual strain into the layer system due to a mismatch in the coefficient of hygroscopic expansion (CHE) of the coating and substrate. The change in residual strain can be observed through the change in the curvature of the specimen. Changing the humidity, while keeping all other parameters constant and measuring the curvature as a function of relative humidity (r.h.) allows for the calculation of the coefficient of hygroscopic expansion.

Quantification of the coefficient of hygroscopic expansion would greatly improve the understanding of failure mechanisms of electronic devices. An example are Microelectromechanical Systems (MEMS). These devices consist of large multi-layer stacks with different materials. Several publications are dedicated to device failure as a consequence of residual stress [13,14] without providing any information about the relative humidity. Zhang et al. [15] mentioned that residual stresses due to changes in the environment may cause delamination but

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did not provide any quantitative data. Chang et al. [16] performed an interesting study on the effect of thermal and hygroscopic mismatch of plastic packaging of plastic ball-grid-array sensors. They found that both temperature and relative humidity contribute equally to packaging failures. Another important field is the field of organic electronics, where gradients in the relative humidity are present within the device. Vellinga et al. discussed the crack propagation speed of Si_3N_4 coatings and found that cracks propagate faster in a humid environment [17], demonstrating the prominent effect of humidity on the mechanical properties. Some research was executed on the hygroscopic expansion of silicon nitride and silicon oxide on a polyimide substrate [8,18]. It was found that silicon nitride coatings contract with increasing humidity whereas silicon oxide expands. For the latter case a hygroscopic expansion coefficient of $53 \pm 55 \cdot 10^{-6} (\% \text{ r.h.})^{-1}$ was found with a rather large experimental error.

This paper presents results of residual stress measurements for silicon-containing plasma polymeric coatings and accurate measurements of the coefficient of hygroscopic expansion (CHE). A dedicated measurement setup is introduced which allows for stress measurements under a controlled relative humidity and temperature. The first part discusses accurate curvature measurements for specimen with a high curvature and the influence of the relative humidity on the curvature of the specimen. The second part presents results on silicon containing plasma polymer coatings with different amounts of carbon and discusses the influence of the carbon content on the residual stress and the CHE.

2. Experimental details

2.1. Hollow cathode based PECVD

The coatings under investigation were prepared using a hollow cathode based Plasma Enhanced Chemical Vapor Deposition (PECVD) process in the Roll-to-Roll lab coater *labFlex® 200*. Details of the deposition technique [19,20] and the *labFlex® 200* can be found elsewhere [21].

All coatings were deposited on a 75 μm thick PET substrate (Melinex 401 CW, DuPont) using a mixture of HexaMethylDiSilOxane (HMDSO) and Oxygen. The HMDSO flow was fixed (50 sccm) and the oxygen flow was varied between 150 and 600 sccm. The power and pressure were kept constant at $4.2 \pm 0.2 \text{ kW}$ and $2.8 \pm 0.1 \text{ Pa}$, respectively. The coating thickness was calculated by optical simulation of the transmittance and reflectance between 500 and 1000 nm wavelength. Both the refractive index and thickness of the coating were used as fitting parameters.

For all plasma settings, the rate of deposition was calculated. Specimen were prepared with a thickness of 500 and 1000 nm by adapting the web speed.

2.2. Coating analysis

The hydrophilicity of the coating was analyzed using contact angle measurements. The measurements were performed using a Dataphysics Contact Angle System OCA 20 using distilled water. The contact angle measurements were performed at a constant temperature of $22 \pm 0.4^\circ\text{C}$ and a relative humidity of $29.7 \pm 0.4\%$. For each sample, five measurements were taken and the average is shown.

The microstructure of the 1000 nm thick coatings was analyzed using a Hitachi SU-8000 scanning electron microscope. The atomic ratio between silicon, oxygen and carbon was measured using Energy-Dispersive X-ray spectroscopy (EDS). The X-Ray penetration depth was calculated using the Andersen and Hasler approximation to ensure that only the coating was measured [22]. An acceleration voltage of 5 kV, assuming a mass density of 1.6 g/cm^3 , results in a penetration depth between 480 and 600 nm for analyzed elements as shown in Fig. 1. The Standardless Element Coefficients (SEC) factors for Si, O and C were

Fig. 1. Penetration depth of the characteristic X-Ray as a function of the acceleration voltage. The values are calculated based on Andersen and Hasler approximation assuming a mass density of 1.6 g/cm^3 .

measured using SiC and SiO_2 reference samples to guarantee the correct quantitative measurement of the light elements.

The surface roughness was measured using atomic force microscopy (AFM). An “Explorer” (Topometrix) AFM was used in non-contact mode to scan a $2.3 \times 2.3 \mu\text{m}$ area. (Resolution 7.7 nm/pixel). Surface roughness values in this papers are given as the arithmetic surface roughness average R_A .

The chemical bonds in the coating were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) with an Attenuated Total Reflection (ATR) unit. A Perkin Elmer Spectrum 2000 was used. The ATR adapter was equipped with a germanium crystal ($n_{\text{Ge}} = 4$) and the beam had a 45° angle of incidence. This allowed us to analyze the 1000 nm thick coatings without substrate influence.

2.3. Curvature measurements

The residual stress in coated thin and flexible substrates causes significant curvatures (e.g. compared to a silicon wafer) which cannot be examined easily with conventional tools like profilometry or white light interferometry as the vertical deformation is too large for the measurement range of the device. As the coatings are amorphous, X-ray diffraction cannot be used either [23]. A simple measurement setup was constructed, which consists of a specimen holder (Fig. 2a) with a backlight and a camera located at a distance 40 cm away. The distance was a trade-off between minimizing the distortion of the image and keeping the set-up easy to handle. Circular specimens with a 55 mm diameter were cut using a breaking knife. The specimens were placed on top of the two metallic plates at the specimen holder.

An example of an image is displayed in Fig. 2b. An image-processing script, written in Fiji [24], was used to crop the images and convert them into a binary picture with a black being the specimen and white being the background. Black spots which were not part of the specimen were removed by hand. It was sliced into 7 fragments and the tool “Fit Circle” was used to calculate the radius of curvature. To correct for pull due to gravity on the specimen, an image was taken with both the coating pointing upwards (“n”-convex-position) and downwards (“u”-concave-position). Assuming a similar effect in both directions, the average was taken as the actual radius of curvature.

Effects of the coating height and in-plane deformation cannot be neglected due to the relatively thick coating ($\frac{h_s}{h_c} \sim 75 - 150$) and the compliant substrate. Calculating the relation between curvature and stress requires the inclusion of corrections compared to the well-known Stoney equation [25]. Benabdi and Roche [26] provide a clear overview of the available models. The thickness ratio between the substrate and

Fig. 2. (a) Picture of the specimen holder with the integrated back-light. The camera is located at the right side of the specimen holder at a 40 cm distance away. (b) Image of a specimen as taken with the camera. (c) Image after processing in Fiji. The white area indicates the region of interest. The red line indicates the circular fit. Circular specimen were used to minimize deformation effects caused by edges of the specimen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the coating (h_s/h_c) is much larger than 1 within this research and therefore allows us to ignore second-order terms. As a result, the residual stress of the coating was calculated using [26]:

$$\sigma_c = -\frac{E_s h_s^2}{6(1-\nu_s)h_c} \left(1 + \frac{h_c}{h_s} \left(4\frac{E_c}{E_s} - 1 \right) \right) \left(\frac{1}{R} - \frac{1}{R_0} \right) \quad (2)$$

An overview of the symbols used are listed in Table 1. R denotes the radius of curvature and R_0 denotes any initial curvature of the substrate before the deposition.

The coefficient of hygroscopic expansion was calculated after performing several measurements at the same specimen under different environmental conditions without repositioning in between. The relative humidity was controlled by placing the measurement setup in a closed box (Aldrich® AtmosBag, Sigma Aldrich) as is schematically illustrated in Fig. 3. The relative humidity was controlled using nitrogen gas. The direct inlet of dry nitrogen allowed us to reduce the relative humidity. The relative humidity was increased by leading the nitrogen through a water reservoir first. Small holes made for the electrical connectors of the camera and backlight as well as an additional hole in pressure over time. The humidity and temperature in the chamber were monitored using an Extech RH30 hygro-thermometer. The error in the relative humidity was $\pm 4\%$ according to the specifications of the manufacturer. This setup allowed us to control the humidity between 20 and 70%.

For each type of coating, two separate specimens were prepared and measured in both the convex and concave position. In each position, separate curves under gradual increase and gradual decrease of the humidity were measured. The slope was calculated individually for each curve and the average of these eight values was used to calculate the CHE for each coating.

Table 1

Symbols used in Eq. (2).

σ_c	Residual stress in the coating
ϕ_i	Relative humidity level i in % r.h.
e_ϕ	Mismatch strain at ϕ % r.h.
β_s	Hygroscopic expansion coefficient of the substrate
β_c	Hygroscopic expansion coefficient of the coating
E_s	Young's modulus of the substrate
E_c	Young's modulus of the coating
ν_s	Poisson's ratio of the substrate
ν_c	Poisson's ratio of the coating
h_s	Thickness of the substrate
h_c	Thickness of the coating
R	Radius of curvature

Fig. 3. Schematic representation of the setup used for measurement of the CHE. The black square represents the specimen holder with (directly left) the back light. The camera is located completely at the right.

Fig. 4. Schematic representation of the relative humidity as a function of time. (1) indicates the zone where the relative humidity is ramped up. (2) is the zone where the sample is relaxed and checked for any hysteresis effects. The relative humidity is ramped down in zone (3) and any hysteresis effects are again checked in zone (4).

A schematic representation of the relative humidity as a function of time is given in Fig. 4. First, the sample was positioned at the sample holder and the box was conditioned at a relative humidity of approximately 25%. Section (1) (see Fig. 4) represents the ramp up of the relative humidity and took approximately 45 min. In section (2), the humidity was kept constant and the radius of curvature was closely monitored to see if any hysteresis effects could be observed. The humidity was decreased during section (3). Section (4) was again used to

check for any hysteresis effects similar to section (2). As the environmental control was done by hand, small deviations from this graph cannot be excluded. A curvature change upon a humidity change was observed almost instantaneously. The curvature was monitored during the 15 min period at constant humidity to check for any delay in the expansion effects. As no change in curvature was observed during these 15 min it was concluded that the reaction can be considered instantaneous. This agrees with results from e.g. Buchhold et al. [27] who showed that the absorption of water in 10 μm thick PI films from dry condition to 98% r.h. occurs within 10 min.

2.4. Calculation of the coefficient of hygroscopic expansion

Here we will discuss the quantification from the measured radius to the coefficient of hygroscopic expansion. Changing the relative humidity induces a change in the mismatch strain, which can be described by:

$$\epsilon_{\phi 2} - \epsilon_{\phi 1} = \epsilon_{1 \rightarrow 2} = (\beta_s - \beta_c) * (\phi_2 - \phi_1) \quad (3)$$

In this equation $\epsilon_{\phi i}$ represents the mismatch strain at ϕ_i % r.h. β_s and β_c represent the coefficient of hygroscopic expansion on the substrate and coating, respectively. Eq. (3) allows us to determine the hygroscopic constant of the coating if the change in mismatch strain and CHE of the substrate are known. Variations in the mismatch strain are coupled linearly to a variation in the internal stress as described by Eq. (2). As the specimen take a cylindrical shape, shear terms can be neglected as was shown by Masters et al. [28]. Rewriting Eq. (2), the change mismatch strain is described by:

$$\begin{aligned} \epsilon_{1 \rightarrow 2} &= -\frac{1 - \nu_c}{1 - \nu_s} \frac{E_s h_s^2}{6 E_c h_c} \frac{1}{\left(1 + \frac{h_c E_c (1 - \nu_s)}{h_s E_s (1 - \nu_c)}\right)} \left(1 + \frac{h_c}{h_s} \left(4 \frac{E_c}{E_s} - 1\right)\right) \left(\frac{1}{R_2} - \frac{1}{R_1}\right) \\ &= -C \left(\frac{1}{R_2} - \frac{1}{R_1}\right) \end{aligned} \quad (4)$$

Here, R_1 and R_2 represent the radius of curvature before and after the change in relative humidity. With C being a specimen depending parameter that is only dependent on the coating and substrate properties and is independent of any environmental parameters.

Combining Eqs. (3) and (4) yields:

$$\left(\frac{1}{R_2} - \frac{1}{R_1}\right) = -\frac{(\beta_s - \beta_c)}{C} (\phi_2 - \phi_1) \quad (5)$$

Plotting the experimental data as $1/R$ against ϕ , the slope of a linear fit equals $-\frac{(\beta_s - \beta_c)}{C}$.

The coefficient of hygroscopic expansion of the substrate (β_s) of the bi-axially stretched PET (Melinex CW 401, Dupont) was $12 \cdot 10^{-6}$ (% r.h.)⁻¹ as given by the supplier. This value agrees with the results of Ma et al. [29]. They found that stretched PET has a CHE of $11 \cdot 10^{-6}$ (% r.h.)⁻¹ that is slightly higher than standard PET ($7.6 \cdot 10^{-6}$ (% r.h.)⁻¹).

2.5. Error analysis

As the calculations are based on rather small changes in the radius, it is essential to take a closer look at the errors during measurement to make sure that the measurements are statistically significant. Three different error causes were identified:

1. Deviation between specimen due to preparation defects and/or variations in the coating/substrate (*Specimen variation*)
2. Error due to mounting and misalignment of the specimen. (*Mounting error*)
3. Error in the imaging and fitting procedure. (*Calculation error*)

Random deviations due to specimen variation and preparation can't be further reduced significantly, as the specimens are already prepared

with great care. Variations between the samples can be ruled out by measuring the relative change in curvature over a range of relative humidities with one specimen. Since the CHE is solely derived using the slope of the linear increase, a small variation in the absolute stress between different specimens does not affect the change in radius due to the change in relative humidity. The mounting error consists of the errors caused by small rotations or misalignment of the specimen on the sample holder. The calculation error concerns the error in the fitting. Slight changes in the contrast and background light influence the binarization process during the image evaluation thereby affecting the fitted curvature values. The error in the fitting procedure was calculated by performing 25 measurements in a short time frame under the same environmental conditions. Between each measurement, the background light was switched off and on again to simulate actual measurements as accurate as possible. The standard deviation of these measurements was used as the measurement error for each single measurement.

Additional effects that need to be taken into account are hysteresis effects and creep. Hysteresis effects were ruled out by step-wise changing the humidity and analyzing the coating radius over several hours. With the regularly used humidity gradient, no delayed expansion was measured in between humidity steps. This indicates that the full hygroscopic expansion takes places on the same time-scale as the humidity change. From the difference in curvature between the measurement in convex and concave position measurements, it is evident that gravity affects the curvature of the specimen. We investigated whether this pull could have caused a creep effect over the timespan of our measurements. The magnitude of possible creep was tested by keeping the specimen under constant environmental conditions for a duration of 60 h (20–30 times longer compared to normal measurement series). Measuring the radius 5 times before and 5 times afterwards results in an increased radius of 0.2 ± 0.2 mm. This allows us to ignore any creep effects during single measurement series.

3. Results and discussion

3.1. Coating properties: Chemical composition and Young's modulus of the coating

Three different coatings were deposited. A concise overview of the properties of the different coatings in the experiment is listed in Table 2. Increasing the Oxygen-to-HMDSO flow ratio during deposition increases the atomic ratio between oxygen and silicon in the coating. In addition, the carbon to silicon ratio decreases which indicates that the coating becomes more inorganic. This indicates that the chemical structure changes from PolyDiMethylSiloxane (PDMS) like coatings (SiOC_2H_5) towards a more inorganic Silica-like (SiO_2) structure. Detailed conclusions on the actual structure remain limited as there is only little to no information on the hydrogen content of the coatings.

Measurements of the Young's modulus of thin film coatings on compliant substrates is an extremely challenging issue and an in-depth discussion is out of the scope of this paper. However, as Eq. (4) requires the Young's modulus of the coating, it is essential to have a good approximation so as to obtain reliable values of the residual stress and CHE.

First, continuous stiffness measurements (CSM) [30] were performed on all three coatings. The Poisson's ratio for both the coating

Table 2
Overview of the coating properties.

O ₂ :HMDSO	O/Si	C/Si	σ_{residual} [MPa]
3	1.5	2.8	249 $\pm$ 6
6	1.9	2.4	160 $\pm$ 11
10	2.1	1.6	94 $\pm$ 31

Fig. 5. Continuous Stiffness Measurement gives information on the Modulus as a function of the indentation depth. Within experimental error, no differences are observed between the different coatings.

and substrate was assumed to be 0.35. Fig. 5 shows the Young's modulus as a function of the indentation depth. It can be seen that all coatings have a very similar response indicating that the moduli are very similar. The fast reduction indicates that the substrate ($E_s = 3.5$ GPa) influences the measurement. This corresponds with literature showing that stiff coatings on compliant substrates are already influenced by substrate effects for indentation depths as low as 2% [31]. Thus, absolute values of the Young's Modulus cannot be obtained from CSM measurements.

Using atomic force acoustic microscopy (AFAM) measurements. Detailed information about the measurement method can be found elsewhere [32], the Young's modulus was calculated to be 20 ± 2 GPa for all three coatings. This value is a good approximation and is used in Eq. (4). As the CSM results prove that the moduli of all coatings are very similar any error will only result in a small shift of the final stress results but does not affect the relation between the different coatings.

3.2. Residual stress and coefficient of hygroscopic expansion

The residual stress of each coating, measured at low humidity (r.h. = 25%), is shown in Table 2. All coatings show a compressive stress. The organic coating shows the highest residual stress of 249 ± 6 MPa. Reducing the carbon concentration in the coating reduces the residual stress down to 94 ± 31 MPa. This corresponds to the results of Zajickova et al. [2] who observed that highly inorganic coatings (Oxygen-to-HMDSO ratio > 10) have a tensile stress state whereas organic coatings show a compressive stress state (Oxygen-to-HMDSO ratio < 5). Hegemann et al. [33] observed the opposite change in the residual stress. However, they mainly related the increase in residual compressive stress to increased power of the plasma and decreased process pressure. The correlation between compressive stress and reduced pressure could explain why Zajickova already observed tensile stress for Oxygen-to-HMDSO ratios around 7 whereas all our coatings show compressive stresses. They used much higher pressures (up to 42 Pa) whereas our pressure was fixed at 2.8 Pa.

Fig. 6 shows $1/R$ against the relative humidity for selected specimen with low (left) and high (right) oxygen flow. These tendencies of these samples represent the measurements at the other specimens as well. The horizontal axis represents the relative humidity and the vertical axis represents $1/R$ in mm^{-1} . The vertical axis is shifted between the two pictures due to the difference in the residual stress of the specimen. The absolute height of both vertical axis is identical (0.003 mm^{-1}) for both pictures. In all specimen, the radius of curvature decreases with increasing humidity. The filled symbols were measured while increasing the relative humidity whereas the open symbols were

measured while decreasing the relative humidity. The continuous and dashed lines represent the least square fit of the data measured during increase of decrease of the relative humidity, respectively. The measured change in radius is clearly reversible and was found to be similar for different specimens and for measuring in concave and convex mode. The relation between $1/R$ and the relative humidity can be approximated by a linear function as was expected from Eq. (5). Some non-linearities are visible but these were mainly related to a measurement error. The least-square fits in Fig. 6a align almost perfectly for increasing and decreasing humidity. In Fig. 6b, the dashed line lies slightly lower compared to the continuous line. This effect is attributed to measurement uncertainties and is not systematic. Instead, on other samples, higher offset has been observed on measurements at decreasing humidity. The slopes of both linear fits, which are used to the calculation of the expansion coefficient, are very similar and therefore this effect was not further considered. It is clear that the slope of the specimen with the inorganic coating is higher compared to the slope of the organic coatings indicating that there is a measurable difference between the two coatings.

Fitting the slopes allowed us to calculate the coefficient of hygroscopic expansion using Eq. (5). C (Eq. (5)) is the same for all 500 nm thick coatings because the mechanical properties are the same and has a value of $11.4 \pm 0.2 \text{ m/MPa}$. Fig. 7 shows the results with the Oxygen-to-HMDSO ratio on the horizontal and the CHE (β_c) on the vertical axis. The (black) squares represent the 500 nm thick coatings whereas the (red) dot represents a specimen with 1000 nm coating thickness. The organic coating shows the lowest expansion coefficient with $19.5 \pm 1.4 \cdot 10^{-6} (\% \text{ r.h.})^{-1}$. Increasing the oxygen flow also increases the hygroscopic expansion coefficient up to $29.2 \pm 2 \cdot 10^{-6} (\% \text{ r.h.})^{-1}$ for the coating with the Oxygen-to-HMDSO ratio of 10.

To make sure that the effects of the coating thickness are corrected by the applied model, an additional specimen with a 1000 nm (instead of 500 nm) thick coating (Oxygen-to-HMDSO ratio: 6) was measured as well. The radius of the 1000 nm coating was $35 \pm 5 \text{ mm}$ compared to $75 \pm 5 \text{ mm}$ for the 500 nm coating. The CHE of $2.45 \pm 2.9 \cdot 10^{-6} (\% \text{ r.h.})^{-1}$ corresponds to the CHE of the thinner coating $2.54 \pm 2.1 \cdot 10^{-6} (\% \text{ r.h.})^{-1}$ within the discussed experimental error bars. This confirms that the model corrects for the thickness effect of the coating and that the CHE does not depend on the coating thickness within the accuracy of our measurement.

To demonstrate the impact of these results, the measured radii and corresponding residual stresses for both 20 and 70% r.h. are presented in Table 3. For the carbon rich coatings, the hygroscopic expansions covers 4% of the total stress. The effect on the inorganic coating is much higher both in absolute stress (23 GPa) and relative to the total stress (22%). This indicates that the contribution of the hygroscopic stress to the total stress is strongly dependent on the coating properties and has to be taken into account in any experimental and theoretical stress evaluation on thin layers.

3.3. Cause of CHE differences

As there are very little reference values available in literature, the change of the CHE was compared to the change hydrophilicity of the coatings. The hydrophilicity can be measured using a contact angle measurement with water. Fig. 8 shows the relation between the Oxygen-to-HMDSO ratio along the horizontal axis and the contact angle along the vertical axis. The contact angle measurements decrease with increasing inorganic content and thereby confirm the increased hydrophilicity. The higher contact angle of the 1000 nm coating is assigned to the increased roughness, which is known to affect the contact angle due to a change in the effective surface area [34–36]. To make sure that the surface topography did not change under influence of the oxygen flow, Atomic Force Microscopy (AFM) images were taken and the surface roughness. The surface roughness only showed a small decrease from 3.8 ± 0.1 to $3.4 \pm 0.2 \text{ nm}$ with increasing oxygen flow.

Fig. 6. Experimental data of the 500 nm thick coatings with (left) low oxygen flow and (right) high oxygen flow. The y-scale represents $1/R$ in mm for both pictures. The scale is shifted due to the difference in residual stress. The filled symbols were measured under increasing relative humidity and the open symbols were measured while decreasing the relative humidity. The continuous and dashed line shows the least square linear fit of all data points for increasing and decreasing relative humidity, respectively.

Fig. 7. CHE (β_c) in dependence of the $O_2/HMDSO$ ratio in the plasma for 500 nm thick layers on PET (black squares). The red dot denotes the sample with a 1000 nm thick coating.

Table 3

Residual stress values for the 500 nm thick coatings with different organic contents. The last column indicates the change in stress as a result of the increased relative humidity.

O ₂ :HMDSO	R [mm]		σ_c [MPa]		$\Delta\sigma_c$ [MPa]
	20% r.h.	70% r.h.	20% r.h.	70% r.h.	
3	46.0	44.2	249	259	10
6	71.6	65.3	160	175	15
10	119.9	95.6	94	117	23

FTIR-ATR was used to analyze the different bonds within the coating. Fig. 9 shows the absorption bands between 3000 and 3700 cm^{-1} . This band is related to OH stretch of hydroxyl groups. More specifically, three type of bonds contribute to the broad absorption band [37]. The absorption between 3600 and 3700 cm^{-1} is related to isolated Si-OH bonds [38]. The middle region (3450 cm^{-1}) is related to weakly bond hydrogen and the lower region (3250 cm^{-1}) to unbounded water. Deconvolution of the peaks using the OriginPro software shows that there is no significant number of isolated Si-OH bonds. They cannot be completely excluded as noise due to water absorption in the chamber lead to an increased noise level at this part of the spectrum. Both the weakly bonded hydrogen and absorbed water increase with increasing coefficient of hygroscopic expansion. The area below the peaks is shown in Fig. 10 as a function of the oxygen-to-HMDSO ratio. Adamson [39] discussed the absorption mechanism of water in epoxies and concluded that the unbound water cannot

Fig. 8. Relation between the inorganic content and the contact angle measurement using contact angle measurements.

Fig. 9. FTIR-ATR spectra of the 1000 nm thick coatings. The domain between 2750 and 3000 cm^{-1} indicates the presence of CH_x groups and peak between 3000 and 3750 cm^{-1} represents the presence of $-\text{OH}$ bonds. The numbers represent the Oxygen-to-HMDSO ratio. The $-\text{OH}$ peak increases and slightly shifts to the lower wavenumbers for increased oxygen flow.

contribute to the expansion as the expansion is less compared to the absorbed water volume. This would indicate that with higher oxygen flow, the coatings become more porous as much more water is present in the coating. The increase in OH bonds with increasing coefficient of hygroscopic expansion corresponds to in-situ FTIR work on similar polymer materials [27,37] which show the water absorption leads to an

Fig. 10. Evaluation of the area below the peaks at 3250 and 3450 cm^{-1} , after deconvolution of the large peak, as a function of the Oxygen-to-HMDSO ratio. Both peaks increase with increasing oxygen flow.

increase in the OH-bonds.

4. Conclusions

This paper presents results on the residual stress measurements and coefficient of hygroscopic expansion of silicon-containing plasma polymer coatings. 500 and 1000 nm thick coatings were deposited on PET film using a hollow cathode arc discharge based PECVD process. The Oxygen-to-HMDSO ratio was varied whereas all other parameters were kept constant. An increased oxygen flow reduces the carbon concentration of the coating and increases the ratio between oxygen and silicon from 1.5 to 2.1. This corresponds with a change from a PDMS-like structure towards a SiO_2 -like structure. Nevertheless, all coatings contained a significant amount of carbon. The more inorganic coatings showed a lower, but still compressive, residual stress of 94 ± 31 MPa compared to 239 ± 6 for the organic coatings.

Accurate measurements of the curvature under controlled humidity allowed us to calculate the coefficient of hygroscopic expansion with high accuracy. All coatings expanded under the influence of humidity, where the organic coatings showed the lowest expansion ($19.5 \pm 1.4 \cdot 10^{-6}$ (% r.h.)⁻¹) compared to $29.2 \pm 2 \cdot 10^{-6}$ (% r.h.)⁻¹ for the most inorganic coating. The coating thickness did not influence the coefficient of hygroscopic expansion within the determined measurement uncertainty. The increased expansion coefficient was related to an increase in OH groups allowing the interaction with water vapor and lead to expansion of the coating.

It was shown that the most inorganic coating experiences an increase in the residual stress over 20% with changes in the relative humidity from 20 to 70%. This significant contribution to the total stress emphasizes the importance of humidity effects. This also emphasized the importance that the environmental conditions during the measurement should also be reported in order to compare results among different researchers. An accurate quantification of β_c provides valuable information in numerical studies of the failure modes in e.g. organic electronics or MEMS.

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