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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" SiO_2 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:

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

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 exists 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 consists of large multi-layer stacks with different materials. Several publications are dedicated to device failure as a the 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, were 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 ± 55 10^{-6} (% 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 ± 0.2 kW and 2.8 ± 0.1 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 ± 0.4 °C and a relative humidity of 29.7 ± 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 measured using SiC and SiO_2 reference samples to guarantee the correct quantitative measurement of the light elements.

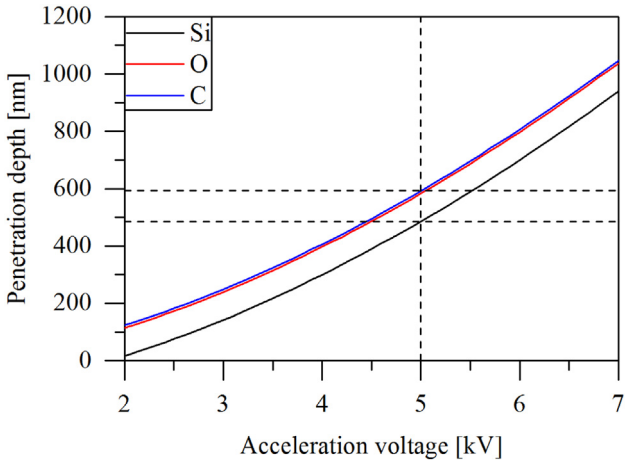

Fig. 1. Penetration depth of the characteristic X-Ray as a function of the accerelation voltage. The values are calculated based on Andersen and Hasler approximation assuming a mass density of 1.6 g/cm^3.

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 × 2.3 µm 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_{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 waver) 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 ($\frac{h_s}{h_c}$~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