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Influence of post-deposition moisture uptake in polycarbonate on thin film's residual stress short term evolution

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ABSTRACT

The residual stress in a thin film can have a major impact on the durability and reliability of the coated device. After deposition and upon exposure to a new environment, a coated material is subjected to various external factors that might affect its stress and thus its overall performance. To identify a protocol to measure stress in a proper and repeatable manner for films deposited on polymeric substrates, we performed ex-situ profilometry measurements on thin dielectric and metallic films (30 nm) deposited on polycarbonate substrates that were stored under different environments over a 1–2 days aging period.

We observed a significant tensile transition in the film stress, characterized by an extremum and a return to an equilibrium value within the first 24 h upon atmospheric exposure. Our analyses further revealed that this phenomenon was reversible and dependent on both the relative humidity and the integrity of the thin film. The moisture uptake and subsequent water vapor diffusion within the substrate, which induces an inhomogeneous volume change in the PC and results in extrinsic bending stresses, appears to be the cause of the stress evolution. A precise control of the post-deposition environment is required to measure the residual stress of thin films deposited on polymeric substrates.

1. Introduction

Thin films coatings are essential to various industries including ophthalmic, automotive and electronics with new applications for such films constantly being found [1–4]. The attraction towards thin films deposited on polymeric substrates such as polycarbonate (PC) is being favoured, especially for decorative coatings (such as automotive parts and consumer products), as they are much lighter, cheaper to produce, more flexible and easier to mould into more ambitious shapes and curvatures compared to the common glass substrates [4–6]. One inherent limitation of a thin film deposited by magnetron sputtering lies in its residual stress, which can result in its damage if too large (through cracks or buckling for instance) and hence a loss of its properties. The residual stress has also been proven to be related to the performance of coatings under particular conditions. For example, Hall et al. demonstrated that a SiO_2 layer had a better corrosion resistance when its stress was more compressive [7]. Therefore there exists a clear interest in measuring stress, as it can provide useful information about the robustness and durability of the deposited coating. The residual stress, which depends strongly on the deposition conditions, is composed of three components (intrinsic, thermal, and extrinsic). The intrinsic stress reflects the unfavourable interactions between the substrate and the coating material and the resulting flaws that develop during the deposition; assuming a mismatch between the substrate and the coating. The thermal stress within a thin film is due to the difference in coefficients of thermal expansion of the two materials in contact. Finally, the extrinsic stress is related to the impact of any external factors on the final coated material. The investigation of stress is still commonly performed using the curvature method and the Stoney's equation [8], and the recent development of specific techniques enabled in-situ stress measurements [9–11], makes the assessment of stress possible without having to worry about external factors. However, such in-situ measurements remain complicated with various deposition techniques such as dynamic sputtering, widely used in industry to produce multiple parts simultaneously [12], making a more classical ex-situ measurement still commonly required. As a consequence extrinsic stress still needs to be understood and controlled for reliable stress measurement. Factors responsible for the extrinsic stress component are related to the interactions between the coated material and the environmental conditions post-deposition, such as gas diffusion through the material, chemical reactions, and water condensation. Short time stress evolutions are mainly related to surface-gas interactions. As demonstrated by Hirsch on evaporated films, a large tensile stress was measured within minutes upon exposure to water vapor [13]. Similar altered stress upon adsorption of various gases was reported by Abermann et al. for evaporated Cr films [14]. Longer time stress evolutions are also observed for several systems and are related to chemical reactions occurring within the film. Upon exposure to O_2, an oxide layer forms, then grows, on metallic films. Although more pronounced when the films is heated up [15,16],

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Nomenclature

%R.H.	relative humidity percentage
DC	direct current
E_s	Young's modulus of substrate
PVD	physical vapor deposition
R_0	radius of curvature of the substrate before deposition of thin film
R	radius of curvature of the substrate after deposition of thin film
t_f	thickness of thin film
t_s	thickness of substrate
σ	residual stress
σ_{eq}	equilibrium stress value
$\sigma_{min\ (max)}$	minimum (maximum) stress value measured over time
σ_n	normalized stress value
σ_t	stress measured at time t
υ_s	Poisson's ratio of substrate

this oxidation process is also observed at room temperature [17]. As the oxide layer becomes thicker, the associated stress might evolve and go from tensile to compressive, as was reported for silicon oxide [18,19]. Similarly, Leplan et al identified a long-term tensile stress evolution of SiO_2 coating due to the hydration of silica upon exposure to water vapor from the atmosphere [20,21]. Contrary to water adsorption, chemical reactions are irreversible processes that result in a permanent change of the residual stress. A recent study on the growth of thin films by Höflich et al. highlighted the impact of this extrinsic stress of thin chromium films deposited on a polycarbonate (PC) substrate, as a reproducible stress value was only achieved under a controlled environment [22]. As stress is related to performances, a fluctuating stress can potentially result in undesirable variations in the coating robustness. Moreover this represents a challenge in the full characterization of the seeding and growth of thin films deposited on polymeric substrates.

To further investigate the stress evolution with time after deposition observed in thin films (30–200 nm) deposited on PC, we performed ex-situ profilometry measurements on coatings exhibiting compressive (SiO_2) and tensile (Cr) stress. Aging the samples in a controlled environment was required to identify the relative humidity of the atmosphere as the main factor driving the stress changes via water vapor diffusion through the polymeric substrate. A repeatable protocol for stress measurements resulting in an equilibrium residual stress value of thin film on PC is presented.

2. Experimental details

2.1. Preparation of sputtered films

Thin layers of chromium (30 nm), silica (30 nm) and multi-layer stacks of these two materials (SiO_2/Cr/SiO_2: 150/30/20 nm) were deposited on both glass slides and polycarbonate (PC, Lexan™ LS2 injection moulded) disks using a rotating DC-magnetron sputtering system (20 rpm), described elsewhere [22]. Briefly, after reaching a base pressure of 8×10^{-6} mbar, Cr (SiO_2) films were deposited under a 2.3×10^{-3} (1.5×10^{-3}) mbar pressure of Ar (Ar/O_2) from a high purity Cr (Si) target (power density estimated at 5.2 (7) W/cm^2). Although various films and multilayers films were used, thin Cr films deposited at low power were preferred for the short-time stress aging study, as the thermal stress component was minimized during their deposition (temperature of the substrate's surface slightly increases up to 25–30 °C during deposition) Prior to the deposition the PC substrates were cured overnight in an oven at 60 °C and then kept in a dry box with a relative humidity of 21 ± 3% to allow the substrate to reach a state of equilibrium, the glass slides were kept in the same dry box at the same relative humidity.

2.2. Residual stress measurements

The residual stress of thin films, σ, was calculated after deposition using the modified Stoney's equation, which takes into account the substrate biaxial elastic modulus [23],

$$\sigma = \frac{1}{6}\frac{E_s t_s^2}{(1-\nu_s)t_f}\left(\frac{1}{R}-\frac{1}{R_0}\right) \qquad (1)$$

where t_s and t_f are the substrate and film's thickness, $E_s / (1 - \upsilon_s)$ is the biaxial elastic modulus of the substrate, and $1/R_0$ and 1/R represent the curvature of the substrate before and after deposition, respectively. To reach a state of equilibrium, all samples were stored under a controlled environment with relative humidity of about 20%. The curvature of the substrate was calculated via the measure of a 3 cm long surface profile using a mechanical profilometer (Dektak model from Bruker). Rectangular glass slides (L, l, h = 40, 15, 0.15 mm) and circular PC disks (radius = 25 mm, thickness = 1.5 mm) were used as substrates. One profile was measured on glass, while 2 orthogonal profiles were measured then averaged on PC. In order to minimise any possible deformation of the substrate/film system, the minimal load was applied to the stylus. The thickness of the deposited film was also measured using the mechanical profilometer. For each sample the thickness was measured with a 10% error, while the radius of curvature measured were very reproducible.

3. Results and discussion

3.1. A humid tensile stress

When used on devices, coatings are submitted to external factors such as the environment's relative humidity that might eventually affect their overall performance. To assess the effect of the relative humidity level on the measurement of the residual stress, long-term stress measurements (one measurement per day) were performed on compressive (−160 MPa) multilayers stacks (200 nm thick, SiO_2/Cr/SiO_2) deposited on PC. Similar multilayer films have been reported to be robust and durable reflective coatings for the use as exterior mirrors [12, 24] and were considered suitable for long term aging studies. After deposition, when the sample was kept under a controlled atmosphere

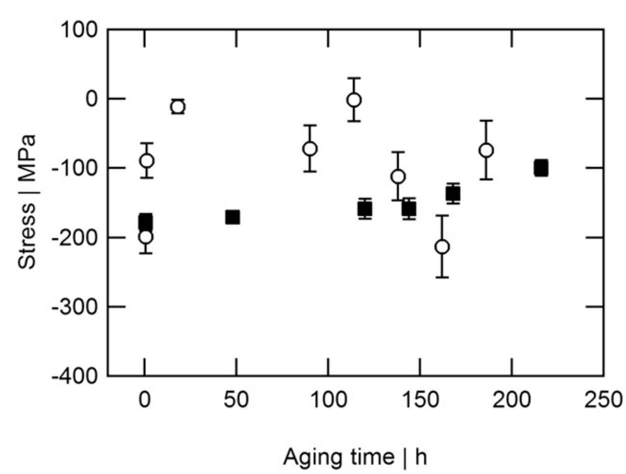

Fig. 1. Long term aging: stress values of compressive SiO_2/Cr/SiO_2 stack deposited on PC substrate and stored in a controlled environment (20%R.H., ■) and uncontrolled atmosphere (20 < %R.H. < 50%, ○).