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Corrosion resistance of robust optical and electrical thin film coatings on polymeric substrates

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ABSTRACT

Thin SiO_2 films (ca. 130 nm) were deposited via magnetron sputtering as part of a multi-layer system onto polymeric substrates. By varying the deposition conditions for the SiO_2 films, samples with varying residual film stress were obtained. The corrosion resistance of the combined multi-layer system was investigated by electrochemical analysis and salt spray tests. In this study it is reported that the corrosion resistance of a multi-layer system containing SiO_2 is improved (at least a 10-fold increase) through deliberate control of the total residual stress of the multi-layer coating, thus influencing the SiO_2 structure.

1. Introduction

Multi-layer coatings are commonly used in many applications to provide an increase in the functionality of a product and protect the underlying substrate from the surrounding environment. Such practical examples of multi-layer coatings are found in ophthalmic lenses [1], mirrors [2], solar concentrators [3], and thin film electrical devices [4]. These multi-layer coatings provide optical and/or electrical function to the device whilst maintaining a level of mechanical stability. One of the popular constituents in these multi-layers is SiO_2, which is used in optical [5,6], electrical [7,8] and protective [9,10] technologies. In almost all applications employing SiO_2, there is a need for the film to maintain its integrity over extended periods of time. That is, the film cannot significantly change properties within this time, nor can it delaminate or break away from the underlying substrate. Conventional substrates can range from glass and silicon through to metals and plastics. However it has been observed that there is a trend emerging for applications to increasingly convert over to plastic due to its lightweight and formability.

One problematic issue with SiO_2 films is their interaction with water. Under humid environments, including those with elevated salt content (as seen in coastal areas), the SiO_2 films are prone to degradation. This has been widely reported for SiO_2 based glasses [11,12], and the mechanism of failure under static or cyclic loading has been discussed therein. The rate of interaction is related to the exposed surface area of the SiO_2 to the surrounding humid environment [13]. The exposed surface area can be directly related to any porosity that exists within the coating.

For thin SiO_2 films, or for that matter any metal or metal oxide films, their internal structure is influenced by the deposition technique employed. In the specific case of Physical Vapour Deposition (PVD) techniques such as magnetron sputtering, the process parameters employed during deposition dictate to a certain extent the internal structure of the film. This change in structure for different deposition parameters [14–16], then manifests itself in different macroscopically observable properties, such as film stress, surface roughness and refractive index [17–23]. A summary review of thin film structure and stress can be found elsewhere [24]. It is important to note, that the change in internal film structure yields differing magnitudes of interfacial area exposed for interaction with the surrounding environment. Following on from this, the measurement of film stress is an indirect way of semi-quantifying the internal structure of the film.

In this study, multi-layer coatings consisting of SiO_2 and $CrN_{0.78}$ have been deposited by magnetron sputtering. These coatings can find applications as durable plastic reflective element for use in such areas as automotive rear view mirrors [25]. By controlling the conditions during SiO_2 deposition, the internal structure of the SiO_2 film was modified, as inferred from measurements of the internal film stress and surface morphology. Direct imaging of the SiO_2 internal structure proved problematic; high resolution electron microscopy was unable to image the film structure due to the insulation properties of SiO_2, even when charge dissipation techniques were applied.

A direct correlation has been found between rate of chemical attack and residual stress of the coating from subjecting the individ-

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ual SiO_2 layers to electrochemical corrosion tests and the multilayers to salt spray testing. Previous studies have looked at similar performance of films [14,26–28], However they typically looked at the protection of metal substrates where conventional electrochemical corrosion takes place. This study focused on the corrosion resistance of the coating, as electrochemical reactions do not typically occur in the underlying plastic substrate. From this work it has been found that by controlling the residual stress of the SiO_2 layer, a corrosion resistant multi-layer coating can be made. The total stress of a system represents the sum of the intrinsic stress and extrinsic stress. Intrinsic stress is dependent on the characteristics of the deposited film, the type of growth and micro-structure. Extrinsic stress can be made up of thermal stress; brought about by the difference in the Coefficient of Thermal Expansion (CTE) of the substrate and film and any other stress due to external influences. As such, stress is a very important parameter when developing multilayer systems. The methods used in this study to control stress were focused on influencing the intrinsic stress via sputtering pressure and the extrinsic stress via substrate temperature during deposition. Both intrinsic and extrinsic stress was found to be useful in controlling the stress on the plastic substrates. It was also noted that for multi-layers, the stress balance between the underlying SiO_2 layer and any subsequent layer must also be taken into consideration.

2. Experimental

The SiO_2 samples were deposited by reactive DC magnetron sputtering onto epoxy resin coated polycarbonate substrates from a high purity Si target. Depositions were carried out under an Ar/O_2 atmosphere in a custom built sputter system. Power was supplied through two Advanced Energy-MDX2.5 (approx. 2.4 kW) connected in series with an Advanced Energy-Sparcle providing additional arc suppression. SiO_2 deposition was carried out whilst the target was in a poisoned mode. The substrates were positioned at a distance of 120 mm under the target, rotating at a speed of 20 rpm. The deposition pressure in the chamber was varied between about 0.2 and 0.6 Pa by variations in Ar flow (12–30 standard cubic centimetres per minute, sccm). The flow rate of Ar to O_2 was kept at a constant ratio of 2. The substrate was heated prior to deposition via an IR lamp with thermocouple control during pump down. Substrate temperatures were varied between 55 °C and 130 °C as measured by a "Tinytag Temperature Logger" from Gemini Data Loggers with a PT100 thin film Resistance Temperature Detector (RTD) attached to a plastic witness sample.

The $CrN_{0.78}$ reflective layer was subsequently deposited from a Cr target (1 kW) under an Ar and N_2 atmosphere, in the same chamber without venting. The deposition pressure was held constant at 0.3 Pa with Ar and N_2 flow rates of 90 and 10 sccm respectively. Film stress was measured using a custom built optical profiler with a laser range sensor (ODS 30 from DSE, Denmark with height resolution of ±1 μm). The height profile was determined before and after deposition of the films across perpendicular axes of a 2 mm thick polycarbonate disc of diameter 100 mm. The resulting height profile was then analysed to determine the change in radius of curvature, R, which in turn was then translated into stress, σ_{film}, using Stoney's equation [29],

$$\sigma_{film} \approx \frac{E_s}{1-\upsilon_s}\frac{h_s^2}{6h_f}\frac{1}{R} \quad (1)$$

where E_s, h_s and υ_s are the modulus (N/m), thickness (m) and Poisson's ratio of the substrate, h_f the thickness of the film (m) and R the change in radius due to the film (m). The structure of the SiO_2 film was observed via Atomic Force Microscopy (NT-MDT NTEGRA Prima, AFM). Areas of sample approximately 1 μm × 1 μm, 10 μm × 10 μm and 100 μm × 100 μm were imaged using semi-contact mode with an NT-MDT Cantilever ($k \sim 1.2$ mN/m as per the Sader method [30]). From this topography image, the film roughness could be determined.

The chemical resistance of the film was determined by analysis after being subjected to the salt spray test (ASTM B117). In this test, the coating is subjected to a salt spray environment for extended periods of time (up to 1000 h) at an elevated temperature (40 °C), with the integrity of the coating tested at regular intervals during this period. The integrity of the coating is quantified by comparing optical reflection before and after testing, visual assessment of any deterioration or delamination, and the measurement of adhesion loss through an adhesive tape test (ASTM 3359 using 3 M Scotch #8981 tape, pull off force to steel 77 Nm/100 mm). Coatings are deemed to have passed the test if after 288 h (14 days) the change in optical reflection is less than 1%, there are no visual defects, and there is no loss in adhesion.

Pitting corrosion was performed using a Voltalab PGZ100 potentiostat in a custom built corrosion cell. The electrolyte was a solution of 5 wt.% reagent grade NaCl in de-mineralised water, matching that used in the salt spray test. The working electrodes were fabricated using hard-coated (PHC587B from Momentive Performance Materials Inc.) polycarbonate substrates and a sputtered Cr electrode with an area of 1 cm^2. On top of this, either a low or high stress SiO_2 layer was deposited, completely covering the Cr electrode. A gold counter electrode (25 cm^2 area) was used. Samples were placed into the cell and the system allowed to equilibrate over a 30 min period or until the Open Circuit Potential (OCP) was constant; the OCP was measured against a Ag/AgCl reference electrode (3 M KCl with saturated AgCl) placed next to the working electrode. A pitting corrosion test was performed to establish the breakdown voltage (E_{bd}) at which the insulating layer began to fail. Potential was swept at 1 mV/s from the OCP to the anodic region until a significant current density (30–50 μA/cm^2) was reached. This was repeated three times for each condition to allow for variations in setup, such as effective electrode area, variations in uncompensated resistance and variation in the fabrication of the working electrode.

3. Results

3.1. Stress

Stress within a coating system has been seen to play a critical role in the performance of the coating [21], where the proper control of stress can lead to improved durability and function. The residual coating stress of the $SiO_2/CrN_{0.78}$ multilayer was measured on polycarbonate discs. The polycarbonate enabled the capture of the thermally induced stress due to the difference in CTE between coating and substrate, whilst also capturing changes in intrinsic stress. The plastic substrate was also representative of the final sample architecture tested in salt spray for corrosion resistance. Preliminary stress measurements found the individual layers of SiO_2 and $CrN_{0.78}$ layers to be compressive and tensile respectively. When deposited sequentially the residual stress of the multi-layer was compressive, that is the compressive nature of the SiO_2 layer dominated the residual stress. Fig. 1 shows the influence of the deposition conditions of the SiO_2 layer on residual film stress. It was found that residual stress was increased by ~500 MPa when the pressure during deposition of the SiO_2 layer was decreased from 0.6 Pa down to 0.2 Pa.

A further increase in compressive residual stress was obtained when the substrate temperature was increased from 55 °C, to 110 °C and 130 °C. A simplified description of the mechanism involved follows. When the plastic substrate was heated the surface