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Elastic properties of multilayer oxide coatings on float glass

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ABSTRACT

The damage resistance of multilayer oxide coatings on glass used for optical applications often depends on contact damage and the stress generation and relaxation mechanisms during coating deposition and subsequent application. Whereas it is relatively easy to design the optical properties of a multilayer coating to meet a particular specification it is more difficult to design its mechanical response. In part this is due to a lack of reliable mechanical property data for design, chief of which is the elastic modulus of each coating layer in the multilayer stack. Indentation tests can be used to determine the elastic and plastic properties of relatively thick (>1 μm) coatings but, whereas it is possible to measure the plastic response of submicron coatings provided the indenter penetration is less than 10% of the coating thickness this is not the case for elastic properties where a much lower penetration is required. In this study the use of nanoindentation testing in conjunction with a simple modelling approach to determine suitable elastic properties of individual oxide layers in a multilayer coating stack is assessed. It is demonstrated that the ISO14577 extrapolation approach underestimates the contact moduli for 200 nm thick coatings but a multilayer model can be used to determine more realistic properties. Variations in elastic properties of the glass substrate in the near-surface region need to be taken into consideration to get good data from the model.

1. Introduction

Multilayer oxide coatings are used in a wide range of optical applications such as anti-reflection [1] and solar control coatings [2]. For instance in a typical solar control coating the active 10 nm thick silver layer is surrounded by antireflection coatings such as zinc oxide or tin oxide. These layers are also surrounded by barrier layers such as TiO_xN_y to prepare the glass substrate for the coatings and protect the coating surface from mechanical or chemical damage. All of these oxide coatings are around 10 nm thick and have been selected for their optical performance.

In service the main damage modes may depend on mechanical contact of the coating which can arise during handling of the coated glass, assembly into devices or in subsequent service [3]. Mechanical design is often secondary to optical design because it does not usually affect the primary function of the device. For good mechanical design the elastic properties of the coatings in the optical stack are often required but these are very difficult to measure in the thin coatings which are required for optical designs. In this study the possibility of using indentation measurements made on relatively thick coatings in conjunction with a simple modelling approach [4] to assess the validity of the properties for designs with thinner coatings is investigated.

Nanoindentation has been used to measure the elastic and plastic properties of thin coatings (~1 μm) for some time now and methods to extract the properties of the coating from data for the coating/substrate system have been developed for single layer coatings e.g. [5,6]. This is most developed for plastic properties such as hardness where it is often assumed that, if the indenter penetration is less than 10% of the coating thickness, the hardness of the coating may be measured independent of the substrate. For elastic properties the required indenter penetration to measure the elastic response of the coating is much smaller, typically less than 1% of the coating thickness and this is almost impossible to achieve for most coatings. To deal with this issue the ISO14577 Part 4 standard [7] recommends extrapolating the variation of hardness or elastic modulus with contact depth to zero depth to get a value for the properties of the coating. This method works reasonably well for coatings on a stiff substrate but gives considerable errors when the substrate is much more compliant than the coating [4].

For multilayer coatings measurements made on cross sections may be used to determine individual layer properties [8]. However, for anisotropic materials the properties measured from the cross

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section may be very different from those measured normal to the surface due to the effects of texture and grain size/shape [9]. Furthermore, as coatings become thinner the difficulty of confining stresses in an individual layer means that composite behaviour is often measured. Thus modelling the properties of the coating substrate system to extract the properties of an individual coating layer is the most useful approach.

Whereas there are a number of approaches that have been used to model the plastic properties of a multilayer coating during indentation e.g. [4,6] the modelling of the elastic response is less well developed e.g. [10]. In this study a simple analytic model for the contact modulus of a coating/substrate system has been extended to multilayer coatings and the results used to determine reliable elasticity data for oxide coatings on glass that may be used in the design of solar control coatings.

2. Experimental

2.1. Coatings investigated

Oxide coatings which are the most significant layers in multilayer solar control coatings for architectural glass were deposited onto the air side of 4.2 mm thick float glass samples using typical commercial process parameters at the Pilkington Research Centre in Lathom, UK. To ensure that the properties of the coatings were typical each coating was deposited onto the same underlying structure made by depositing the lower layers in the multilayer with the same thickness and process parameters as in a commercial solar control coating design. The top layer was deposited to the same thickness as in the solar control coating but also to a thickness of 200 nm to enable indentation measurement. Layer materials and thicknesses are summarised in Table 1.

The coatings were produced by reactive sputtering from metallic targets using an oxygen backfill to generate stoichiometric coatings. Large glass sheets (20 cm by 30 cm) were coated in a linear vacuum chamber where they were moved past fixed magnetrons at a constant rate. Each coating was produced by a different magnetron cathode in the same coating chamber. Samples were then cut into 10 cm by 10 cm squares for indentation analysis. In these coatings a 10 nm silver film is the active solar control layer but this is protected from oxidation during deposition of subsequent oxide layers by a 5 nm zirconium overlayer; neither silver nor zirconium could be deposited to 200 nm thickness without significant oxidation on removal from the vacuum chamber. For this reason handbook values for elastic properties of these layers have been used in the modelling undertaken in this study [11].

The thickness of the individual layers was controlled by the magnetron power and translation speed and was confirmed by ellipsometry.

Table 1
Layer structure and thickness of the coatings deposited.

Sample	TiO_xN_y underlayer	ZnO	Ag	Zr	SnO_2	TiO_xN_y top layer
3803	200 nm					
3807	20 nm					
3806	20 nm	200 nm				
3808	20 nm	10 nm				
3811	20 nm	10 nm	10 nm	5 nm	200 nm	
3810	20 nm	10 nm	10 nm	5 nm	40 nm	
3814	20 nm	10 nm	10 nm	5 nm	40 nm	200 nm
3813	20 nm	10 nm	10 nm	5 nm	40 nm	30 nm

2.2. Nanoindentation testing

Nanoindentation testing of the coated samples was carried out using a Hysitron Triboindenter fitted with a new Berkovich tip (tip end radius 150 nm) and compared to data obtained from float glass using an older used Berkovich tip with a larger tip end radius (~200 nm). Measurements were made at a range of peak contact loads from 1 mN to 100 μN starting from the highest loads and finishing with the lowest to ensure that the machine noise and thermal drift was minimised for the most sensitive measurements. Prior to testing the tip end shape and machine compliance was carefully calibrated using the method of Oliver and Pharr [12]. Hardness and contact modulus were determined from the load displacement curves using the Oliver and Pharr approach. The elastic properties of the thick coatings were determined using the ISO14577 extrapolation method [7] and compared to fitted values determined from the model of Bull for a single layer coating [4]. The fitted values were then optimised by using a full multilayer analysis described in the next section.

2.3. Simple model for the contact modulus of a multilayer coating

The model of Bull [4] is based on a truncated cone of load support beneath the indenter and the displacements in any coating layers can be calculated if their thickness and elastic properties are known. If we assume a totally rigid indenter then the indenter displacement, δ, is given by the sum of all the displacements in the individual layers beneath the indenter. For a simple coating on a substrate it can be shown that the indenter displacement in the coating is given by

$$\delta_c = \frac{P}{\pi E_c}\left[\frac{1}{a_0 tan\alpha} - \frac{1}{a_0 tan\alpha + t_c tan^2\alpha}\right] \tag{1}$$

where a_0 is the contact radius, t_c is the coating thickness and α is the cone angle. For the substrate we have

$$\delta_s = \frac{P}{\pi E_s}\left[\frac{1}{a_0 tan\alpha + t_c tan^2\alpha} - \frac{1}{a_0 tan\alpha + (t_c + t_s) tan^2\alpha}\right] \tag{2}$$

where E_s is the Young's Modulus of the substrate and t_s the substrate thickness. The total indenter displacement is then

$$\delta = \delta_c + \delta_s \tag{3}$$

Both the displacements in the coating and substrate are a linear function of contact load and thus the unloading stiffness $S = P/\delta$. Given that for a flat punch $S = 2Ea$ [13] it is possible to calculate the effective Young's Modulus of the coating/substrate system

$$E = \frac{P}{2a_0(\delta_c + \delta_s)} \tag{4}$$

For a deformable indenter E must be replaced by E^*, the contact modulus, given by

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \tag{5}$$

where the subscripts 1 and 2 refer to the properties of the sample and indenter respectively and ν is Poisson's ratio and E is Young's Modulus. For a coated system, E_c and E_s are the contact moduli of coating and substrate respectively. The contact radius can be related to the contact depth, h_c, determined by the Oliver and Pharr method [12], if the indenter geometry is known. For a Berkovich indenter,