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Influence of internal stress in optical thin films on their failure modes assessed by *in situ* real-time scratch analysis

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ABSTRACT

In this study we present a new *in situ* real-time approach to perform and analyze scratch tests of transparent coating/substrates systems. This method allows for the observation of the contact region during the scratching process. As an example, thin TiO_2 layers exhibiting stress levels ranging from tensile to compressive were deposited by ion beam assisted evaporation onto plastic substrates. Failure processes obtained using an increasing and a novel decreasing load scratch sequences were then linked to the internal stress in the coatings allowing one to draw a stress management diagram and to evaluate the yield stress of the TiO_2 layers. This work enhances the understanding of the optical films' failure mechanisms, and outlines a new pathway to increase measurement reproducibility.

1. Introduction

In many high value-added products such as ophthalmic lenses, touch screens and architectural glass, optical thin films, only a few tens of nanometers thick, are essential for low emissivity, anti-reflectivity, scratch resistance and other functional characteristics. Due to their use in different environments, they are subjected to many external solicitations including heat, moisture, abrasion and hard particle impacts that can cause major failures in the deposited layers [1,2]. Considering the proliferation of touch screen devices coupled with the use of compliant substrates, there is an important need to understand the failure mechanisms during abrasive scratching of such material systems. In particular, it is necessary to better assess the origin of the failure mechanisms to better guide thin film stack design and material development so as to improve product lifetime.

Several studies have investigated how to optimize the mechanical performance of thin film systems during optical stack design. Two main approaches have been reported. The first deals with the reduction of the overall stress by introducing compensating layers or with a back side layout in order to avoid cracking of the films due to internal stress or to minimize the modification of the optical response due to a change in the device curvature [3,4]. Other works have looked into enhancing scratch and abrasion resistance through specific layer architectures taking into account the mechanical properties of individual layers but without consideration for the residual stress [5–7]. To the best of our knowledge, no works combining these two approaches have been reported. However, the internal stresses of the deposited layers are known to be the main factor in adhesion failure [8,9], and their role in scratch testing failure modes needs to be well understood. In the present work, we propose to study the synergetic effect between internal residual stresses and external tribomechanical loading involved during a scratch test in the case of evaporated TiO_2 optical coatings.

Conventional tribological studies do not allow for visual access to the contact itself, and all observations are performed *post mortem*. Thereby, conventional tribometers provide little information about failure initiation and propagation, and it is often difficult to understand the processes at the origin of the various observed failures. Therefore, it is essential to directly observe the scratch process in order to identify transient phenomena (e.g., crack initiation and visco-elastic or visco-plastic effects such as creep [10]) which are not accessible using a standard *post mortem* analysis. Consequently, over the last two decades, the trend in tribology has been to develop systems that allow *in situ* real-time observation of the contact during the wear process coupled with other characterization techniques such as Raman spectroscopy or scanning white-light interferometery [11,12]. Several *in situ* scratch setups have been reported in the literature, and they are mostly used to study hard protective coatings by observing the contact through a transparent counterpart [13–15]. Some studies describe side-view [16] or through-substrate observation when evaluating optical coatings on transparent substrates [17,18]. The advantage of this latter configuration is that it allows for a variety of counterparts in terms of shape.

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Moreover, using this latter configuration while testing transparent substrates exhibiting birefringence under stress, the photoelasticimetry concept can thus be used to observe the stress field under loading. This has been performed on the cross section during testing [19]; however, no study has focused on the in-plane stress field during scratch testing using this technique.

In the present study, we propose a new scratch test setup in a through-substrate observation configuration, which includes two linear polarizers in its optical path. This allows one to retrace the sequence of failures as they appear in or around the contact area, and to visualize the evolution of the maximum in-plane shear stress. In addition, we present a new methodology which can be used to assess the sequence of the failure mechanisms during the scratch test by applying increasing as well as decreasing load scratch sequences. This approach is applied and demonstrated for TiO_2 films with internal stresses ranging from compressive to tensile, adjusted by ion beam assisted evaporation onto CR39 plastic substrates in order to investigate the influence of stress on the scratch behavior of optical coatings. Such a relatively broad range of internal stresses makes the TiO_2/CR39 system very attractive for the study of the tribomechanical properties and of the scratch characteristics.

2. Experimental methodology

2.1. Sample preparation

TiO_2 optical thin films were used as a model material in this work and were deposited in a box coater system (BOXER PRO, Leybold Optics GmbH) by means of e-beam evaporation assisted by ion beam using an End-Hall ion source (KRI, Inc.). The depositions were performed at 40 °C with a constant flow of oxygen (25 sccm) at a pressure of 0.22 mTorr. In order to obtain coatings with internal stresses ranging from tensile to compressive as described in [20] and to keep the coating as comparable as possible, the ion source was operated inside a small window of acceleration voltages V_a, ranging from 145 V to 205 V (corresponding to an emission current I_a from 4.0 A to 5.1 A). The anode voltage typically increased at the beginning of the deposition and quickly stabilized for the rest of the process. The deposition rate was kept constant at 2 μg/cm^2 s, and was regulated using Quartz Crystal Microbalance (QCM) monitoring, by adjusting e-beam current around the value of 140 mA. The deposition time was adjusted in order to obtain a film thickness of 300 nm.

The films were deposited onto two types of substrates:

a) CR39 plastic disks (65 mm in diameter, 3 mm in thickness) commonly used in the ophthalmic industry. Substrates were provided with a dip coated antiscratch hardcoat layer about 3 μm thick and were used for scratch test characterization. Mechanical properties of this layer have been previously assessed by nanoindentation: the reduced modulus was 6 GPa while the hardness was 0.57 GPa [21];
b) Crystalline silicon wafers (100) were used for the characterization of thickness, optical properties, internal stress and mechanical properties.

All substrates were used as received and a dry nitrogen gun was employed to remove dust before deposition without further cleaning.

2.2. Sample characterization

2.2.1. Thickness and optical characterization

The optical properties of the films were assessed by variable angle spectroscopic ellipsometry (RC2, J.A. Woollam Company, Inc.). Thickness (t_f), refractive index (n) and extinction coefficient (k) of the films were extracted from the measurements by modeling the optical response with a Tauc-Lorentz and a Gaussian oscillator using CompleteEASE software (J.A. Woollam Company, Inc.). The extinction coefficient k was found to be small (less than 1×10^{-4}) making the films suitable for optical interference filter applications.

2.2.2. Stress measurement

The internal stress of the films was evaluated *in situ* during the deposition step from the variation of the silicon wafer substrate curvature using the Stoney equation [22]:

$$\sigma_{film} = \frac{E_s}{(1-\upsilon_s)} \times \frac{t_s^2}{6 \times t_f} \times \left(\frac{1}{R} - \frac{1}{R_0}\right), \tag{1}$$

where σ_{film} is the internal stress in the film, E_s the modulus of the substrate,ν_s the Poisson ratio of the substrat, t_s the thickness of the substrate, t_f the measured thickness of the film, R_O the initial curvature of the substrate and R the radius of curvature at the end of the deposition process.

The measurement of R_O and R was obtained *in situ* in the deposition chamber under vacuum using a multi-beam optical sensor wafer curvature system (kSA-MOS, K-space Associates, Inc.). The technique consists of measuring the evolution of the spacing of a matrix of laser spots at the back side of the silicon wafer in order to obtain instantaneously the curvature of the surface. Even if internal stresses may vary as a function of the substrate on which the coatings was deposited, stresses measured on silicon were assumed to be identical to stresses on the CR39 substrate for the rest of this study. Referring to the structure zone model [23,24], as the melting temperature of the TiO_2 is much higher than the deposition temperature, the growth of the films should be equivalent regardless of the substrate, leading to the same range of intrinsic stresses. This has been confirmed through ellipsometric measurements on samples deposited on silicon and CR39 substrates that exhibit less than 2% variation in terms of thickness and refractive index. Moreover, thermal contribution of the deposition process to the internal stress was not taken into account because, as the films were deposited in a similar energetic window, the heat generated by the ion source was expected to be constant over the deposition conditions, resulting in a constant contribution to the thermal stress.

2.2.3. Nanoindentation

Reduced modulus (E_r) and hardness (H) were measured by depth-sensing indentation using a Triboindenter TI 950 system (Hysitron, Inc.). Indentations were performed on films deposited on the silicon substrates using a Berkovich diamond tip. Prior to the measurement, tip geometry and machine compliance were carefully calibrated according to the ISO 14577-2 standard [25]. The tip geometry area function used for the analysis of the subsequent indentations was extracted from indentations into a fused quartz calibration sample. On each sample, two matrices of 25 indentations were carried out with maximum applied loads ranging from 100 μN to 9300 μN. The corresponding penetration depth, between 10 and 200 nm, enabled one to visualize tip rounding effects and the substrate influence. The first indentation was made at the highest load while for each subsequent indentation the load was incrementally decreased by a constant percentage down to 100 μN in order to obtain a higher concentration of indentations at low load. The loading function employed consisted of a 5 s loading segment, a 2 s holding period at maximum load, and a 5 s unloading segment. From these measurements, the indentation cycles were analyzed using the Oliver and Pharr method [26]. First, the stiffness of the contact was obtained by fitting a power law function to the unloading curve and extracting the slope of the fit at the beginning of the unloading phase. The contact depth was then evaluated and the corresponding contact area was used to calculate E_r and H of each indentation. Finally, the ISO 14577-4 standard [27] was used to extract the mechanical properties E_r and H of the films.