Thin Solid Films 519 (2011) 7875–7882

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Effects of pre-strain applied at a polyethylene terephthalate substrate before the coating of TiO_2 film on the coating film quality and optical performance

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ARTICLE INFO

Article history:
Received 22 March 2010
Received in revised form 14 February 2011
Accepted 15 February 2011
Available online 24 February 2011

Keywords:
Polyethylene terephthalate
Flexible substrates
Titanium dioxide
Optical properties
Thin Films
Sputtering
Elongation strain

ABSTRACT

A mold was designed to create various strains in polyethylene terephthalate (PET) substrates before the deposition of TiO_2 film to simulate deposition process on a cylindrical drum. The residual stress of the PET substrate with TiO_2 film significantly increased with increasing strain, decreasing the radius of curvature. Compared to the as-received PET substrate, there was a noticeable increase in the surface roughness in the PET/TiO_2 specimens when a large strain was applied. The formation of voids or cavities in the TiO_2 layer significantly increased the roughness of the specimen. The mean cavity size and depth increased with increasing strain. For strains $\leqq$4%, the specimen's hardness and Young's modulus factored by the voids/cavities increased with increasing surface roughness. The optical absorption increased with increasing surface roughness before becoming asymptotic to a constant value. The strain applied to the PET substrate before TiO_2 deposition greatly affects the optical reflection, transmittance, and absorption.

1. Introduction

Layered composites based on oxide coatings on semi-crystalline polymer substrates have become promising structures for improving the stability of micro- and optoelectronic devices [1]. The functional performance of these layered composite materials depends on the cohesive strength of the brittle coating and its adhesion to the polymer substrate. These two factors are governed by the defect structure and the level of internal stresses of the coating and the interfacial region [2–4].

Thin-film transistors (TFTs) on thin foils use a small amount of materials per unit area, and can be made particularly rugged using roll-to-roll fabrication [5,6]. Suo et al. [7] derived the basic mechanic relations for externally forced and thermally induced bending of film-on-foil substrates. When a substrate with a lower elastic modulus is used, a smaller radius of curvature can be achieved. When TFTs were placed on the surface of a foil substrate, the smallest bending radius decreased.

Choi et al. [8] produced biaxially stretchable wavy silicon nanomembranes on an elastomeric poly substrate to provide full two-dimensional stretchability. Song et al. [9] used an analytic approach to study herringbone bucking patterns to obtain the buckle wave length and amplitude in terms of many parameters, including the thermal strain. They proved that the herringbone mode has the lowest energy. Jiang et al. [10] developed a post-buckling model based on the energy method for precisely controlled buckling to study the system stretchability.

Li et al. [11] investigated delocalizing strain applied to a thin metal film deposited onto a polymer substrate. Under tension, a freestanding thin metal film usually ruptures at a strain that is smaller than that required for its bulk counterpart. The film ruptures when the overall strain just exceeds the necking initiation strain, ε_N.

Among the numerous materials being studied, TiO_2 has attracted the most interest due to its ideal properties, such as its strong absorption of ultraviolet light and optoelectronic conversion [12,13]. A micropattern of TiO_2 fabricated on a flexible polymer substrate has several useful applications, including thin-film transistors, solar cells, and flexible displays. In the study of Chou et al. [14], polycrystalline TiO_{2}-xNx thin films were deposited on polyethylene terephthalate (PET) plate substrates without heating. The specimens were found to exhibit lower water contact angles when the surfaces were illuminated with ultraviolet and visible light in air.

Many studies have focused on TiO_2 films due to their excellent electrical and optical properties, such as high refractive index [15–17] and transmittance of visible light [18]. In the study of Miao et al. [19], TiO_2 films were formed on Si substrates using the radio frequency sputtering method. High optical band gap values were obtained, which were attributed to possible strain from lattice distortion.

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0040-6090/$ – see front matter.
doi:10.1016/j.tsf.2011.02.051

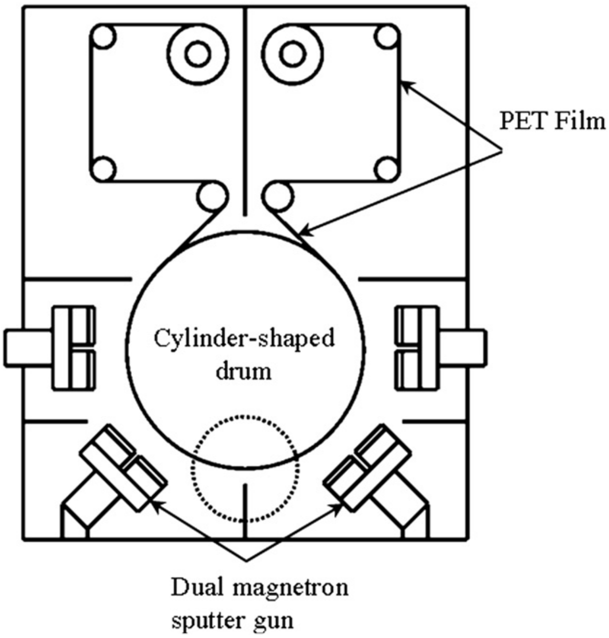

Fig. 1. Schematic representation of the rotating deposition system.

Several studies have been conducted on the effects of growth parameters (substrate temperature, discharge voltage, etc.) on the mechanical and optical properties of TiO_2 films [20–24]. It has been reported that impurity doping improves the mechanical and optical properties of composite thin films. Martínez-Morillas et al. [25] studied the optical and morphological properties of nanometric TiO_2 thin films prepared using a magnetron sputtering source as a function of the Ar/He atmosphere ratio and its pressure. Raman spectroscopy and optical absorption analysis were performed to determine the samples' optical properties.

Briscoe et al. [26] presented results of normal hardness, plasticity index, and elastic modulus for a selection of polymers using the contact compliance method. They described the dependence of the imposed penetration depth, the maximum load, and the deformation rate on the hardness and elastic modulus values for these polymeric surfaces. A typical procedure for eliminating the creeping effect is the time long enough for the material to reach mechanical equilibrium.

The effect of applying strain to a soft substrate material adhered to a rotating cylinder on the mechanical and material properties and microstructure of a hard coating film deposited using a rotating deposition system has seldomly been studied. In the present study, a mold is designed to apply various levels of strain to as-received PET substrates before the deposition of TiO_2 film to simulate the deposition process on a cylindrical drum. Four strains were chosen in the preparation of the TiO_2 films and PET substrates to investigate the pre-strain effect on the coating film quality and optical performance. The residual stress formed at the TiO_2 film due to the

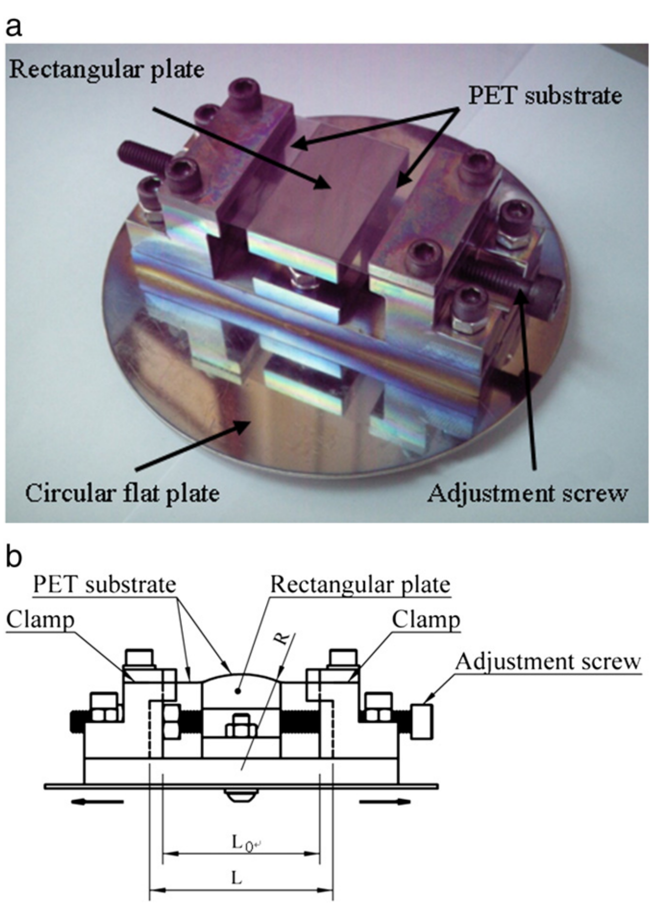

Fig. 2. (a) Photograph and (b) schematic diagram of the mold.

Table 1
Basic physical and mechanical properties of PET.

Thickness (μm)	188
Density (g/cm^3)	1.33
Tensile strength at yield (MPa)	57–59
Elongation at yield (%)	4
Modulus of elasticity (GPa)	2.2
Tear strength (kN/m)	54–59
Specific heat capacity(J/kg°C)	1100
Haze (%)	0.8
Ratio of transmission (%, visible)	89

Table 2
Details of the TiO_2 deposition conditions.

Deposition parameters	Value
Power (W)	100
Chamber pressure (Pa)	2.67
Ar flow rate (sccm)	20
Presputtering time (s)	180
Sputtering time (s)	9000

Table 3
Radius of curvature and residual stress of the five specimens prepared.

Parameter / Specimen code	Radius of curvature (μm)	Residual stress (MPa)
As-received PET	5,455,218 ± 550,066	–
PET-0%/TiO_2	591,899 ± 60,926	−241 ± 27
PET-2%/TiO_2	338,927 ± 21,080	−440 ± 32
PET-4%/TiO_2	299,656 ± 10,045	−500 ± 21
PET-6%/TiO_2	257,348 ± 9177	−587 ± 22

Stoney's formula:

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

where
$E_s = 3830$ MPa, for PET substrate
$t_s = 0.000188$ m, for PET substrate
$t_f = 0.00000025$ m, for TiO_2 film
$\nu_s = 0.43$, for PET substrate.