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Tensile strain and water vapor transport testing of flexible, conductive and transparent indium–zinc-oxide/silver/indium–zinc-oxide thin films

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ABSTRACT

Thin film laminates composed of sputtered indium zinc oxide and silver, optimized for conductance and transparency, were tested for water vapor permeation as well as mechanical durability in tension. The ~82 nm thick optimized indium–zinc-oxide/silver/indium–zinc-oxide (IZO/Ag/IZO) films were >80% transparent in the visible range (400 nm–700 nm) with measured sheet resistances less than 5 Ω/sq. The water vapor permeation measurements using Ca test methods at several temperature/ humidity conditions indicated that the addition of the thin Ag layer provided little improvement relative to a single indium–zinc-oxide (IZO) layer of similar thickness. However, the critical strain in bending tests for IZO/Ag/IZO films was improved compared to IZO films. The modulus (E~113 GPa), hardness (H~7 GPa), fracture toughness (K_{IC}~1.1 MPa·$m^{0.5}$), and interfacial shear ("adhesion") (τ_c~16 MPa) of/related to IZO, and measured by nanoindention are consistent with other brittle ceramic thin film materials.

1. Introduction

Flexible electronic devices including flexible photovoltaics (PV), organic light emitting diodes (OLEDs), electrochromics, and thin film batteries have generated interest because of their reduced weight and added ability to roll and bend, allowing unusual applications, portability, and ease of installation. However, the integration of flexible electronics into the mainstream requires the development of mechanically durable substrates that can resist moisture ingress. While most flexible electronic applications require that the electrode materials be conductive, PV and OLED , and electrochromic applications also require optical transparency.

Transparent, conductive and non-permeable materials have been optimized for the display industry using thin transparent conducing oxide (TCO) films on glass. The replacement of glass with polymer substrates reduces weight, increases toughness, and improves flexibility. However, most polymers are highly permeable to oxygen and water (known to corrode anode- and cathode-materials). Furthermore, while the underlying substrates are extremely flexible, TCO monolayers are prone to cracking. The use of polymer substrates also requires low temperature processing [1–3].

TCO–metal–TCO multilayers have been studied as flexible conducting materials because the dielectric/metal interfaces can suppress reflections, thereby enhancing transparency, while also improving conductivity [4–13]. Lower manufacturing costs based on the reduction or replacement of rare earth elements, such as indium, are an added benefit of these types of films [6].

Organic PV and OLED applications require water and oxygen permeations rates on the order of less than $1{\cdot}10^{-6}\,g\,m^{-2}day^{-1}$. Transmission rates of water for standard polymer films such as polyimides, polycarbonates, and polyethylenes are typically on the order of $1\,g\,m^{-2}day^{-1}$. Addition of a single continuous pinhole free inorganic thin film greatly reduces the penetration of moisture through the film. However contamination, deposition defects, substrate surface roughness, and grain boundaries all provide routes for moisture ingress. Many studies have advocated a multilayer stack, used to elongate the water permeation pathway by creating a tortuous path [14], to achieve transmission rates approaching $1{\cdot}10^{-6}\,g\,m^{-2}day^{-1}$ [15].

In addition to mitigating the permeation of chemical species, the architecture of alternating thin film layers may improve mechanical durability. First, mechanically compliant layer(s) provide strain relief by decoupling stiffer layers. Often more importantly, a tougher material (such as a metal or polymer) may be chosen as the compliant layer. In such cases, the tougher intermediate layer helps decouple fracture in the brittle (ceramic) layers. By controlling the geometry (thickness) of both the tough and brittle layers, an optimized laminate structure may be achieved that maximizes the critical strain (*i.e.* minimizes the critical radius of curvature) necessary to motivate the extension of channel cracks [16,17]. The extent of damage occurring beyond the critical strain (as in the cases of extreme bending or external impact) is also reduced through the use of tough intermediate material layer(s). Dissipative behavior occurring during yielding

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makes a metal film an improvement over a ceramic intermediate, however, polymers usually exhibit a mechanical toughness that is orders of magnitude greater than that of a metal. Similarly, the use of a polymeric substrate increases the critical strain required for crack propagation and serves to localize damage during events exceeding the critical strain [18].

The combined considerations of optical performance, resistance to moisture permeation, and mechanical durability may be addressed using a conductive, transparent, moisture impermeable barrier/flexible substrate system composed of a multilayer thin film structure. The goal of the study here is to examine TCO/metal/TCO thin film laminates, relative to their potential application in flexible electronics. The aspects of optical performance, moisture permeation, and mechanical durability are not well understood for such films. Therefore, characterizations including optical transmittance, electrical resistance, water vapor transmission, instrumented indentation, and mechanical tensile tests were conducted for indium–zinc-oxide (IZO) as well as IZO/Ag/IZO deposited on polymeric substrates.

2. Experimental details

2.1. Transparent conducting barrier fabrication

Thin film layers were fabricated onto 125 μm thick, polyethylene napthylate films (PEN, [Teonex Q65, Dupont Tejion]). This optical grade of PEN is commonly used in the organic light emitting diode (OLED) field because it is both heat stabilized and coated with a scratch resistant, UV blocking layer on its top surface [19]. The PEN substrates were cleaned with a wafer rinser/drier (STI Semitool) to remove adsorbates and organic residue. Each substrate was blown with N_2 prior to mounting it in the deposition chamber to minimize particulate matter on the polymer surface. The sputtered thin films were deposited on the PEN side of the polymer substrates, *i.e.* opposite to the treated surface.

The indium oxide:zinc oxide thin films were sputtered from either 90:10 or 80:20 %wt IZO alloyed targets (Cerac Inc) [20]. Sputtering was performed in a customized, multi-gun deposition chamber with both 2 inch and 3 inch diameter magnetron sputter guns (Onyx, Angstrom Sciences) arranged such that the samples can be rotated in front of each gun without opening the system to the ambient environment. Prior to any deposition the chamber was pumped down to below $5\cdot10^{-3}$ Pa. The 90:10 IZO was sputtered from a 2 inch (5 cm) diameter target at a sample to target distance of 6.6 cm at 30 W DC power. The 80:20 IZO was sputtered from a 3 inch (7.6 cm) diameter target at a distance of 2.6 inch at 100 W DC power. The most conductive films were made fabricated in the presence of a small amount of O_2. The 90:10 IZO was sputtered at a pressure of 0.8 Pa in an Ar:O_2 (99.2 mol %: 0.8 mol %) atmosphere. The 80:20 IZO was sputtered at a pressure of 0.67 Pa in an Ar:O_2 (99 mol %: 1 mol %) atmosphere. Using these conditions, the 80:20 target results in an amorphous IZO thin film, while the 90:10 films are polycrystalline [20–22]. Both film types are compositionally similar to the target materials.

Laminate structures were constructed by sequentially sputtering each layer without breaking vacuum. The silver thin films were sputtered from a 2 inch (5 cm) Ag target (Kurt J. Lesker Company) at a distance of 15.2 cm using 15 W DC power and deposition pressure of 1.3 Pa in a pure Argon environment. For the laminate structures O_2 was not injected during and after the deposition of silver to avoid its oxidation. The films thicknesses were measured using X-ray reflectivity and ellipsometry techniques.

2.2. Analysis

2.2.1. Transparency and conductance measurements

The transmission of the samples was measured from 320 nm to 1100 nm using an ocean Ocean Optics (USB 4000) UV–Vis spectrophotometer. The effect of PEN was subtracted from the optical spectra of the laminate films, using a separate baseline measurement. A noncontact conductance monitor (717B, Delcom Instruments Inc) was used to measure the conductivity of the samples without damaging the thin films. These conductivity measurements were periodically verified by current sourced four point probe measurements (2400, Keithley).

2.2.2. Water vapor transport rate measurements

Water vapor transport rate (WVTR) measurements of the bare PEN substrates were measured using a commercial isostatic instrument (Permatran-W, MOCON) with a sample area of 5 cm^2. The WVTRs of the sputtered films were below the testing limits of the Permatran and were therefore quantified using a custom built electrical Ca test, described in refs. [23,24]. Briefly, for each sample, multiple 100 nm thick Ca traces were evaporated onto an impermeable glass substrate. The glass substrate was then adhered to the test barrier film using an edge seal material (Helioseal, ADCO Corp.) that is considered impermeable relative to the barrier films. The edge seal material also defined the test area, which was held constant at 0.75 in^2 (4.84 cm^2). Any water that permeates through the barrier films reacted with the Ca traces. The conductivity of the Ca traces was measured externally in real time via a four point measurement using gold traces that extend through the edge seal encapsulant. The amount of water that permeates through the barrier was calculated from the change in bulk conductivity of the Ca layer assuming:

$$Ca + 2H_2O \rightarrow 2CaOH + H_2. \quad (1)$$

For WVTR rate measurement, temperature and humidity conditions were kept constant using controlled-environmental chambers. Several temperature and humidity conditions were characterized for each type of sample, but each sample was tested only once.

For each WVTR test, conductance versus time data was obtained from three Ca traces as well as a 'witness trace'. The 'witness trace' was covered by the edge seal material and served as a measure of the validity of the test (no leakage at the perimeter). For the data included here, the witness trace remained unchanged during the course of the test. The three data traces were on the glass opposite the barrier and within the 0.75 in^2 test region. From each trace, a lag time and a steady state WVTR was extrapolated. The lag time corresponds to the time elapsed after the specimen is inserted in the environmental chamber but before a change in the conductance of the three data traces is observed (this corresponds to the duration during which water is permeating through the barrier layer). Following the lag time, the change in conductance quickly accelerates until the conductance decreases at a constant rate — the steady state WVTR. The steady state WVTR was calculated from a linear fit of the response region for each trace. The lag time was calculated as the time from the beginning of the test to where the steady state WVTR fit crossed the initial conductance value. The diffusivity (D) was then calculated from the lag time (t_{lag}) using

$$t_{lag} = \frac{l^2}{6D}, \quad (1)$$

and the solubility (S) was calculated from

$$P = SD, \quad (2)$$

where P is the permeation, the WVTR multiplied by l, the combined substrate thickness [14,25–27]. Using WVTR data at multiple temperature/humidity conditions, the activation energy (E_a) was extracted from log–linear plots of WVTR as a function of 1/T, according to the Arrhenius equation:

$$\ln WVTR = \ln A - \frac{E_a}{RT} \quad (3)$$