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Real-time resistance, transmission and figure-of-merit analysis for transparent conductors under stretching-mode strain

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ABSTRACT

In this paper, we describe an apparatus capable of measuring electrical resistance and light transmission through a flexible transparent conductor (TC) as it is actively deformed. The measurements are performed in situ with time resolution on the order of ~100 ms, and the resistance/transmission data is further used to calculate TC figures-of-merit in real-time. With this instrument, we are able to track and compare the *evolution* of figures-of-merit for different TCs as they are actively deformed. To demonstrate the tool, we evaluate several common TCs including indium tin oxide, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), and silver nanowires, as well as a more unconventional nanowire/PEDOT:PSS hybrid. As expected, indium tin oxide degrades rapidly with strain, while the more flexible PEDOT:PSS is far more strain tolerant. The nanowire/PEDOT:PSS composite is found to produce an advantageous effect, as the silver nanowires generate large figures-of-merit at low strain, and the addition of a PEDOT:PSS component vastly improves strain tolerance.

1. Introduction

Transparent conductors (TCs) are becoming nearly ubiquitous in the marketplace as a range of everyday devices such as displays, lighting, solar cells and touch screens routinely incorporate these materials. The most common transparent conductors are drawn from the "transparent conducting oxides", with indium tin oxide (ITO) utilized particularly heavily [1,2]. Transparent conducting oxides possess a useful combination of electrical resistance and light transmission characteristics, but research into alternative material systems is also progressing quickly. Patterned metallic grids, graphitic films of carbon nanotubes or graphene, organic films such as poly (3,4-ethylenedioxythiophene):poly(styrenesulphonate) (PEDOT:PSS), and percolating networks of silver nanowires (AgNWs) are becoming well established and understood [3–5]. Composites are also being studied to achieve "best-of-both-worlds" scenarios and incorporate the advantageous aspects of several materials into a single TC system. Selected examples of composite or bilayer structures include: PEDOT:PSS/carbon nanotubes [6], polyaniline/carbon nanotubes [7], PEDOT:PSS/AgNWs [8,9], graphene/AgNWs [10], graphene/PEDOT:PSS [11], PEDOT:PSS/metal grid [12,13], and AgNWs/TiO_2/PEDOT:PSS [14].

The primary characterization techniques for transparent conductors naturally involve measurements of electrical resistance in combination with measurements of light transmission. Because these two parameters are strongly interconnected (generally thicker films are less resistive, but absorb more incident light), the performance of transparent conductors is often assessed through figures of merit (FOMs) that incorporate both electrical and optical parameters [15–17]. Often, it is the ratio of direct current (DC) conductivity to optical conductivity that is calculated and compared, i.e.:

$$\mathrm{FOM} = \frac{\sigma_{DC}}{\sigma_{Op}} = \frac{Z_o}{2R_s(T^{-1/2}-1)} \quad (1)$$

where R_s and T are the sheet resistance and transmission for the transparent conductor, and Z_o is the impedance of free space (~377 Ω) [15]. This important equation allows the performance of disparate TCs to be assessed. The equation, however, ignores another range of vital properties such as adhesion, crack resistance, environmental stability and cost that also greatly influence the performance or practicality of particular TC systems. Recent publications are beginning to highlight these more peripheral attributes. For instance, Bao et al. argue strongly that the mechanical stability of organic photovoltaics must be understood and improved in order for the

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devices to withstand the rigours of real world applications [18]. They mention that even if the devices operate while firmly fixed in place, they must still withstand the stresses of roll-to-roll manufacturing, thermal expansion and weathering. For materials intended to be compatible with the concept of "flexible electronics", the demands are even greater, and in some cases extremely high strain implementations are envisioned such as textile- or skin-integrated electronics [19–22]. In these applications, the electronic materials must retain their functionality despite large substrate deformations, and therefore, the transparency and conductivity of TCs during deformation is highly relevant [23]. Some groups incorporate these strain tests into their slate of characterization techniques, and this is most commonly accomplished by measuring electrical resistance after cycling a film at a fixed radius of curvature, or after bending to decreasing radii of curvature [6–11,24–28]. Some groups also incorporate measurements of resistance during stretching-mode deformation [29–39].

In this paper, we develop and explore a new technique for *simultaneously* recording the electrical resistance and optical transmission of transparent conductors while they are uniaxially deformed in tension. A simple drawing of the test apparatus is shown in Fig. 1. With this setup, we are able to track TC figure-of-merit values *in real-time* and analyze the strain tolerance or degradation mechanisms of TC systems, pinpointing the precise strains at which significant changes occur. This approach enormously reduces the quantity of samples required to perform a complete analysis. To demonstrate the utility of the approach, we analyze several material systems: two commercial ITO products, PEDOT:PSS spray-cast onto polyethylene terephthalate (PET) substrates, AgNW films spray-cast onto PET, and a composite PEDOT:PSS/AgNW system also spray-cast on PET. From these investigations, we determine that FOMs tend to be dominated by low resistance materials at low strain, but incorporating more strain-tolerant components, such as PEDOT:PSS, can lead to vastly improved performance under strain.

2. Experimental section

2.1. Materials and sample preparation

ITO-coated PET sheets were received from Sigma-Aldrich (product number 639303-5EA, 60 Ω/□) and CP Films (product number OFD10, 10 Ω/□), and samples of the appropriate size were cut from the sheets for testing. In cases where it was necessary to test the PET substrate without the ITO coating, ITO was removed by etching in concentrated hydrochloric acid. Uncoated PET film was purchased from McMaster-Carr (product number 8567K42), and substrates of the appropriate size were cut from the rolls and cleaned in acetone and isopropanol prior to use. PEDOT:PSS was purchased from Heraeus (Clevios PH 1000) and diluted prior to spray casting with water, isopropanol and ethylene glycol to form a solution of 19.7% PEDOT:PSS stock, 6% deionized water, 73% isopropanol, and 1.3% ethylene glycol [37]. Silver nanowires were purchased from NanoGap Inc. (product number NGAP NF Ag-3101-IPA), and the stock solution was vortex mixed and bath sonicated to redistribute the Ag nanowires before transferring solution from the stock and diluting 10:1 with isopropanol to form the casting solution.

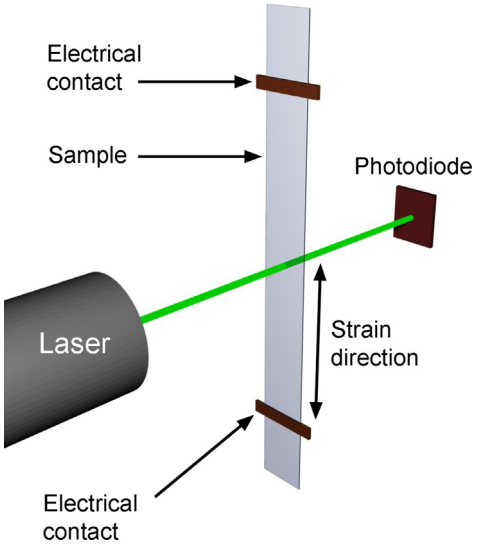

Fig. 1. Conceptual drawing of the resistance/transmission/strain measurement apparatus. The clamps, optical components, reference photodiode and wiring are omitted from the drawing for clarity.

PEDOT:PSS and AgNW films were spray cast on PET with a Sono-Tek Exactacoat SC using a 60 kHz ultrasonic spray head and 17 kPa spraying pressure. For PEDOT:PSS, the hot plate was maintained at 35 °C, and for AgNWs the hotplate was set to 155 °C. (Rationale for this high temperature is provided below.) In both cases, the spray head was initially positioned 55 mm above the substrates and laterally offset from one corner by ~10 mm. A raster pattern was utilized during spraying: the head was swept along the length of the samples at 50 mm/s and translated by 4 mm between steps. Generally, several samples were sprayed in a single coating run, and once all the samples were fully coated, the entire raster pattern was repeated with a 2 mm lateral offset to ensure uniform film thickness. This raster pattern and translation speed were used for all samples, and therefore, the film thickness was controlled by varying the solution dispensing rate (in μL/min) through the spray head. After spray casting, all AgNW samples were pressure-rolled at high temperature to improve adhesion [40]. The PET substrate was softened by placing the samples film-down against the polished steel hotplate at 155 °C. To partially embed the AgNWs in PET, a steel cylinder with a diameter of 6.4 cm was then rolled along the back of every substrate at a speed of 1–2 cm/s and pressure equivalent to 50 ± 10 psi. This rolling process was repeated six times for every AgNW sample. For every combination of materials and processing conditions noted in this paper, at least two duplicate samples were prepared and tested.

2.2. Real-time resistance/transmission/figure-of-merit measurements

Stress/strain, electrical resistance and light transmission were measured simultaneously as transparent conductor samples were uniaxially deformed in tension at a strain rate of 10 mm/min. Force and sample extension were recorded using an Instron 5943 tensile tester with a 1 kN load cell. As shown in Fig. 2a, samples measured 10 mm in width by > 180 mm in length, and they were clamped in the tensile tester using 25 × 25 mm rubber-coated and electrically insulating grip faces. The initial distance between grips (i.e., the "gauge length", which is the initial length of the actively deforming portion of the sample) was 100 mm [41], and therefore, the samples (having lengths exceeding 150 mm) extended all the way through and beyond the grip faces. During clamping, a small amount of out-of-plane bending-mode "slack" was commonly introduced. The effect of this slack was corrected in the stress/strain data by digitally identifying the point at which the mechanical load required to stretch the sample exceeded a fixed threshold [42]. At this point, the sample was flat between the clamps with no out-of-plane bending, and generally this occurred at extension values less than 0.5 mm. When the threshold was reached, the strain was set to zero, and the sample length (i.e., the original