HIGHLY CONDUCTIVE, TRANSPARENT, AND ANTI-REFLECTIVE PEDOT:PSS/ITO/Ag/ITO ON PARYLENE-C WITH TUNABLE PEAK TRANSMITTANCE

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ABSTRACT

Transparent and flexible conductive thin films are critical components in optoelectronics, such as wearable electronics, biosensors, and displays. Traditional transparent electrodes made of a single layer of indium-tin-oxide (ITO), ultrathin metal, graphene or poly-(3, 4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT: PSS) hardly possess the desired combination of high transmittance, low electrical resistivity, mechanical flexibility, and biocompatibility. Although ITO/Ag/ITO multilayer thin films have been studied for solar cell applications, the deposition of high-quality ITO usually requires high-temperature processes incompatible with polymers. In this work, we successfully fabricated an ultra-flexible, conductive, transparent thin film using a PEDOT:PSS/ITO/Ag/ITO multilayer structure on Parylene C at room temperature. Compared to single-layer ITO of an equivalent thickness, the multilayer film exhibited significantly enhanced sheet conductivity, reduced electrochemical impedance, remarkable transmittance, excellent adhesion, and flexibility. The peak transmittance of the combined films can be tailored to a specific wavelength for particular applications, such as optogenetics. Besides Parylene C, our high-quality ITO/Ag films can be deposited on a wide variety of heat-sensitive substrates over large scales.

INTRODUCTION

Transparent and flexible conductive thin films are critical components in optoelectronics, such as wearable electronics, biosensors, displays, etc.[1]. Although single-layered ITO, ultrathin metals, graphene or PEDOT:PSS, as conventional transparent electrode materials, have been widely used, these materials all have their own limitations. In particularly, ITO has many favorable properties such as its transparency over the entire visible spectrum, good biocompatibility, and certain electrical conductivity. However, ITO is brittle, especially when thicker ITO (~100 nm) is required for achieving better conductivity [2]. Ultrathin metal has high electrical conductivity but suffers from the low transmittance of ~30-70% with only ~3-7 nm thickness [3], making it difficult to achieve the high transparency and conductivity at the same time. Most recently, graphene has been explored by several groups [4] as a potential material for making transparent micro-electrocorticography (ECoG) arrays due to its broad-spectrum transparency, excellent conductivity, good biocompatibility, and flexibility. However, it still faces serious challenges because growing high-quality graphene over large areas requires either high temperatures of over 1000ºC or specific substrate materials, which are incompatible with polymer materials. To address this issue, a transfer method is utilized to transfer monolayer graphene from a solid substrate to a polymer film for development of flexible graphene-based electronics. This method, however, has low yield and reproducibility, and is not suitable for large-scale production. As a popular conductivity polymer, PEDOT:PSS has been widely used as a microelectrode coating, in combination with other inorganic conducting materials [5], because of its outstanding electrochemical conductivity, biocompatibility, stability, and flexibility. However, thin film PEDOT:PSS is rarely used alone as a transparent electrode material due to its low intrinsic electrical conductivity. Electroplated PEDOT:PSS enables higher conductivity but the transparency of the film is greatly compromised.

In this paper, we fabricated and reported, for the first time, an ultra-flexible, conductive and transparent thin film using a PEDOT:PSS/ITO/Ag/ITO multilayer structure on Parylene C (Fig. 1) for achieving significantly enhanced sheet conductivity, reduced electrochemical impedance, remarkable transmittance, good stability, adhesion and flexibility. The multilayer assembly was optimized to achieve the lowest theoretical reflectance by simulating the coatings admittance loci under the preferred reference wavelength. ITO and Ag were sputtered consecutively at room temperature, followed by spin-coating of PEDOT:PSS. The room temperature was chosen depending on our systematic study, where ITO was deposited on Parylene C coated glass slides at different temperatures, using an RF magnetron sputtering system (Denton Explorer-14, Denton Vacuum, Inc). The transmittance and sheet resistance of the combined films were measured by utilizing a Filmetrics thin film analyzer (F20-UVX, Filmetrics, Inc) and a four-point probe station (SRM-232, Bridge Technology, Inc), respectively, and the measurements were compared with those of single-layer ITO films of equivalent thicknesses. Tunable peak transmittances were confirmed by depositing different thicknesses of individual layers on Parylene C after theoretical admittance loci stimulation under the preferred wavelengths. Electrochemical impedance spectroscopy (EIS) of different coatings were measured in a 0.9% NaCl

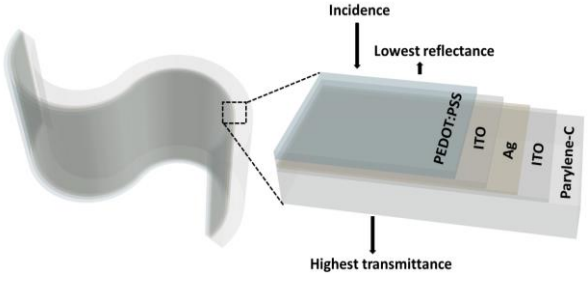

Figure 1: *Concept diagrams of transparent and ultra-flexible PEDOT:PSS/ITO/Ag/ITO on Parylene C, designed for achieving the lowest reflectance.*

(saline) solution at room temperature. The adhesion between ITO and Parylene C was evaluated using Scotch tape tests for 50 times of peeling. In addition, the combined thin films were kept at 37°C in air and in saline, respectively to test the film stability over 4 weeks. The Young's modulus of the combined films was measured by a MTS nano-indenter and compared with their theoretical values.

METHODOLOGY

Fabrication

To study the impact of deposition temperature, 100 nm ITO films were sputtered with RF magnetron sputtering system at 22°C, 69°C, 92°C, 116°C and 140°C, respectively. First, glass slides were ultrasonically cleaned in an acetone bath, followed by cleaning with ethanol, isopropanol and deionized (DI) water. After N_2 drying and hotplate baking, 10 µm Parylene C was deposited (PDS 2010, Specialty Coating System, Inc) on the glass substrate. The sputtering process was conducted in an RF magnetron sputtering system with a 4-inch diameter ITO target (99.99% purity), under a base pressure of 2×10^{-6} torr. The heater was turned on several hours before sputtering to warm up the sample holder to the desired deposition temperatures. After 10 mins pre-sputtering, 100 nm ITO was sputtered with the sputtering RF power of 100 W and the sputtering pressure of 3.5 mTorr, which resulted in a deposition rate of 1 Å/sec. The sample holder was rotated at the speed of 20% to improve the sputtering uniformity. After ITO sputtering, the heater was turned off immediately and the samples were kept inside the chamber until the chamber temperature decreased to room temperature.

For the PEDOT:PSS/ITO/Ag/ITO samples, the admittance loci coating stimulation was accomplished first by calculating the optimized thickness of each layer with the lowest theoretical reflectance under three selected wavelengths: 470 nm, 550 nm, and 630 nm. Then we chose the PEDOT:PSS (30 nm) /ITO (24 nm) /Ag (9.5 nm) /ITO (20 nm) films optimized at 550 nm for further characterization of the transparency, conductivity, electrochemical properties, mechanical properties, and stability of the combined films. To form the combined films, ITO was sputtered using the aforementioned parameters. Ag was deposited in the same sputtering system without breaking the vacuum to prevent oxidation of Ag. To do that, a 4-inch diameter Ag target (99.99% purity) was installed in another cathode, and deposition took place at the same pressures and sputtering power as ITO, with a deposition rate of 4 Å/sec and a rotating speed of 70%. After ITO and Ag sputtering, 0.55% PEDOT:PSS, which was diluted from 1.1% PEDOT:PSS (768642, Sigma-Aldrich), was spun on top of the ITO/Ag/ITO substrate with a 500 rpm spin speed for 5 secs and then 4000 rpm for 120 secs, followed by baking on a hotplate at 100°C for 30 mins. For comparison, 53.5 nm single-layer ITO which had the equivalent thickness with the ITO/Ag/ITO structure was sputtered under the same conditions.

TESTING METHOD

The Filmetrics thin film analyzer was utilized to measure the transmittance of ITO samples in a wavelength range of 300-800 nm. For combined PEDOT:PSS/ITO/Ag/ITO films, besides transmittance and sheet resistance measurement, EIS measurements were performed using a potentiostat (Electrochemical Analyzer, CH Instruments, Inc.) to measure the electrochemical impedance in saline solution at room temperature in a three-electrode cell configuration, with the single layer ITO or combined film electrode as the working electrode (WE), an Ag/AgCl electrode as the reference electrode (RE), and a platinum electrode as the counter electrode (CE). The electrochemical impedance of the microelectrode was measured from 0.1 Hz to 100 kHz when a 5 mV RMS sinusoid waveform was applied to the WE. Long-term humidity and temperature tests were performed for the combined film samples in air and in saline at 37°C for up to 4 weeks. Sheet resistances were monitored every week to identify changes in sheet resistances caused by physical delamination or chemical corrosion. To evaluate the adhesion between ITO and Parylene C, Scotch No. 810 pressure-type tape was applied on the ITO-Parylene C samples with blade-scratched 10 × 10 of 1 mm^2 squares, followed by 50-time peeling with 180° peel-off angel to test ITO delamination from the Parylene C substrate. The Young's modulus of the combined films was measured using a MTS Nanoindenter XP system to process and

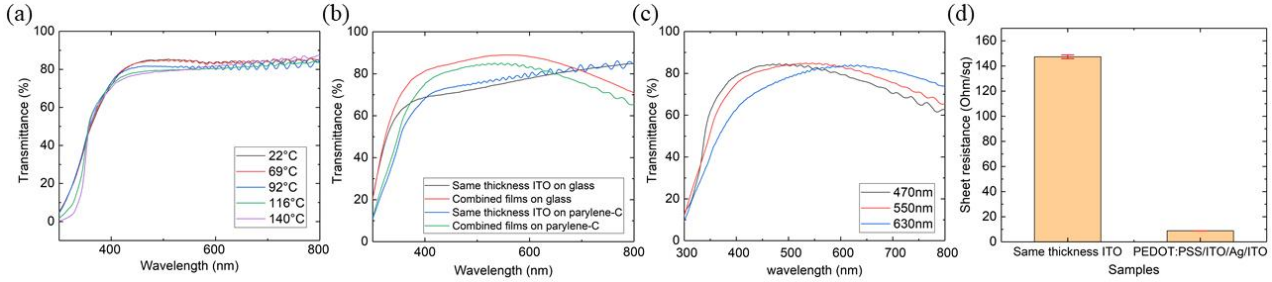

Figure 2: *(a) Transmittances of 100nm ITO deposited under different sputtering temperatures of 22°C, 69°C, 92°C, 116°C and 140°C on Parylene C coated glass slides. (b) Transmittances of the combined PEDOT:PSS/ITO/Ag/ITO films compared with the equivalent thickness ITO on the glass substrate and Parylene C substrate, respectively. (c)The peak transmittances of combined PEDOT:PSS/ITO/Ag/ITO films on Parylene C at wavelengths of 470 nm, 550 nm, and 630 nm, respectively, to confirm the tunable peak transmittance by stimulating the coatings admittance loci. (d) Average sheet resistances (n=5) of PEDOT:PSS/ITO/Ag/ITO and the equivalent thickness ITO on the Parylene C substrate with neglectable standard deviation to confirm the uniformity of the combined films using the four-point probe measurements.*

average well-spaced 36 indents for each measurement.

RESULTS

TEMPERATURE STUDY OF ITO

The transmittances of five 100 nm ITO-on-Parylene C samples were measured, which were sputtered under 22°C, 69°C, 92°C, 116°C and 140°C. Sputtering temperatures of below 150°C were carefully chosen to prevent thermal damage to Parylene C because the glass transition temperature of Parylene C is 80-100°C [6]. Fig. 2 (a) shows that when the temperature was higher than 92°C, the maximal transmittances at 500 nm dropped significantly by 7% from ~85% to ~78%. In contrast to previous studies where a high sputtering temperature could improve the transmittance due to the formation of ITO crystalline [7], the transmittance reduction in our results was mainly attributed to the changes in Parylene C optical properties at temperatures of above its glass transition temperature. The periodic waves appeared in Fig. 2 were due to the light interference within the thin Parylene C substrate. Moreover, we observed darker Ag when the sputtering temperature increased, resulting in the low transmittance and high resistivity of the combined ITO/Ag/ITO films. This might be due to the oxidation of Ag at elevated temperatures. Therefore, we chose the room temperature as the final sputtering temperature for ITO/Ag/ITO deposition in order to minimize oxidation of Ag and thermally-induced degradation of Parylene C. Because of the relatively low conductivity of room-temperature ITO, Ag would dominate the overall conductivity of this multilayered ITO/Ag/ITO structure.

CONDUCTIVITY AND TRANSMITTANCE

Fig. 3 (a)-(c) show the samples of transparent and flexible PEDOT:PSS (30 nm) /ITO (24 nm) /Ag (9.5 nm) /ITO (20 nm) thin films on the 10 μm Parylene C substrate following the structures in Fig. 1. Compared to 53.5-nm-thick, single-layer ITO, the transmittance of the combined films increased throughout the visible spectrum from 300 nm to 700 nm on both the Parylene C and glass substrates, as shown in Fig. 2 (b). Especially under 550 nm wavelength, the combined films showed an improved transmittance from ~78% to ~85% on Parlylene C and from ~75% to ~89% on glass. The sheet resistance of the combined film was significantly reduced from 147.5 Ω/sq to 8.81 Ω/sq as shown in Fig. 2 (d). In addition, the uniformity of the deposited thin films was evidenced by the standard deviation of the sheet resistance measurements over the entire substrate (n=5), which was improved from 1.53 to 0. Fig. 2 (c) shows that the combined films on the Parylene C substrate with different layer thicknesses after the admittance loci stimulation can achieve the different peak

Figure 3: *Thin films of PEDOT:PSS/ITO/Ag/ITO on 10 μm Parylene C showing (a) excellent transparency and (c) ultra-flexibility. (b) The transparency before (right) and after (left) adding the PEDOT:PSS coating.*

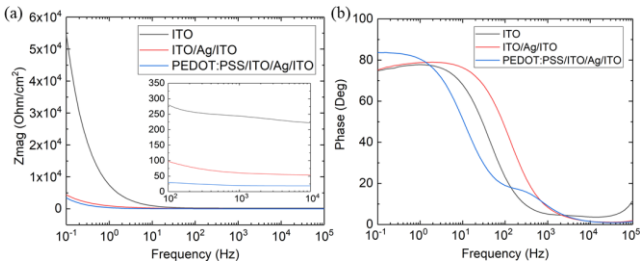

Figure 4: *(a)Electrochemical impedance magnitudes and (b)phases of the bare ITO, ITO/Ag/ITO and PEDOT:PSS/ITO/Ag/ITO versus the frequency, respectively.*

transmittances under the targeted wavelengths of 470 nm, 550 nm and 630 nm. This result confirmed that these engineered films could be utilized in different applications that require different operating wavelengths. For example, 470 nm blue light was commonly used in optogenetics to activate channelrhodopsin (Ch2R), a light-sensitive opsin protein.

ELECTROCHEMICAL IMPEDANCE

The EIS Bode plots in Fig. 4 (a) and (b) show the typical electrode impedance magnitude and phase versus frequency, respectively. The ITO/Ag/ITO structure effectively decreased the overall electrochemical impedance over a wide frequency range of 0.1 Hz - 100 kHz. The coating of PEDOT:PSS further decreased the electrochemical impedance in a wide frequency spectrum, consistent with previously reported results [8]. The electrochemical impedance of the total combined film at 1 kHz decreased by at least one order of magnitude from 243.85 Ohm/cm^2 to 19.88 Ohm/cm^2 compared with the pure ITO film. This impedance reduction was mainly attributed to the improved conductivity of the film and the increase in the surface roughness of the film, benefit from the PEDOT:PSS coating as reported in [5]. The rough surface provided a large effective surface area of the electrode when exposed to the electrolyte, allowing more charge to flow across the electrode-electrolyte interface.

ADHESION AND STABILITY

Results of the Scotch tape peeling tests were given in Fig. 5 (a). During 50 times of peeling, the tested sample area was recorded at 0 time, 10 times and 50 times of peel-off, as shown in Fig. 5 (b), (c) and (d), respectively. No ITO film was delaminated from the Parylene C during the tests. However, 53% of the Parylene C delaminated from the glass surface (Fig. 5d) by counting small squares in consecutive 50 peel-off cycles, due to the poor adhesion of Parylene C on glass [9]. Our peel-off tests result also proved that the ITO-Parylene C interface had a stronger adhesion than the Parylene C-glass interface.

To evaluate the stability of the microelectrodes, the PEDOT:PSS/ITO/Ag/ITO combined films were kept at 37°C both in air and in saline, respectively, for 4 weeks. Sheet resistances were measured (n=5) weekly as shown in Fig. 6. The results indicated that the combined films exhibited excellent stability with a slight resistance increase of less than 1.25% and 2.75% after four-week exposure. In addition, the results suggested that moisture

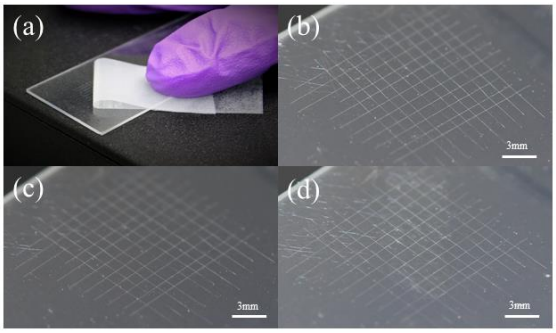

Figure 5: *Images of (a) peel-off tests, (b) initial 10 × 10 testing surface, (c) testing surface after 10-time peel-off tests and (d) testing surface after 50-time peel-off tests.*

could accelerate the damage to the combined thin films. The increase in sheet resistance might be due to defects or pinholes in the top-most ITO layer, where the exposed Ag reacted with oxygen and moisture, therefore weakening the stability of the combined thin films.

YOUNG'S MODULUS

The measured Young's moduli of the pure Parylene C film and the combined film on Parylene-C were 4.049 GPa and 4.064 GPa, respectively, after averaging all 36 indents. Theoretical calculations were carried out via the equation for less mixture of particle and polymer:

$$\frac{1}{E_{composite}} = \frac{V_{ITO}}{E_{ITO}} + \frac{V_{Ag}}{E_{Ag}} + \frac{V_{ITO}}{E_{ITO}} + \frac{V_{Parylene}}{E_{Parylene}}$$

where E is Young's modulus and V is the volume fraction of each layer. For our calculation, the volume fraction was replaced by the layer thickness due to the same cross-sectional area. Young's moduli of Parylene C, ITO and Ag are 4 GPa [10], 116 GPa and 85 GPa, and thicknesses are 10 μm, 44 nm, and 9.5 nm respectively, resulting in a calculated E of 4.021 GPa. The measured Young's moduli were close to the theoretical values, confirming the mechanical properties of our fabricated combined films.

CONCLUSIONS

In conclusion, we have designed, constructed and characterized the combined PEDOT:PSS/ITO/Ag/ITO on Paylene C thin film. Preliminary measurements demonstrated enhanced conductivity, remarkable and wavelength-tunable transmittance, significantly reduced electrochemical impedance, good stability, and adhesion of the combined film. Meanwhile, the influence of sputtering temperature on ITO transparency was studied, and the flexibility of the combined films was confirmed both theoretically and experimentally.

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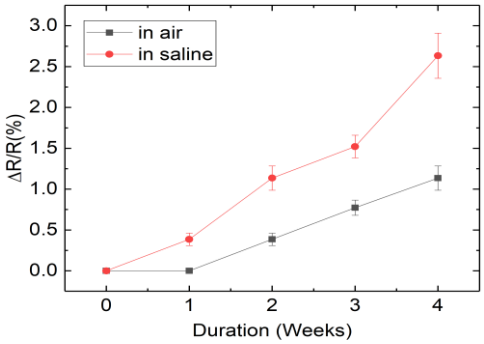

Figure 6: *Sheet resistance changes (n=5) of the combined films in air and in saline at 37°C.*

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