

Indium-gallium-zinc-oxide based semitransparent electrodes on flexible substrates for biodegradable electronics

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Abstract—Indium gallium zinc oxide (IGZO)/silver/IGZO (IAgI) electrodes were sputtered on films of tattoo-paper (TP), cellulose nanocrystals (CNCs), silk fibroin (SF), and on a 75:25 v/v % SF:CNCs blend with a view to developing biocompatible, sustainable materials for printed electronics. Drop-cast films of CNCs, SF and their blends show an average visible transmittance of 90.9%, 81.5%, and 49.5% respectively. Mechanical measurements reveal average strain at break values of 26% for CNCs, 13% for SF, and 5.4% for the blend, with respective Young's moduli of 1200 MPa, 270 MPa, and 1000 MPa. IAgI electrodes on glass (as controls) display an average visible transparency $\sim 71.6\%$, a sheet resistance of 5 Ohm/sq, and a work function of ~ 4.4 eV. We transferred electrodes on CNCs, blend, and TP flexible substrates to a *Kalanchoe blossfeldiana* plant leaf and monitored their resistance over a full day/night cycle in a controlled environment as a proof-of-concept demonstration for sensing applications.

Keywords— *biocompatibility, biodegradability, sustainability, silk, cellulose, semitransparent substrates*

I. INTRODUCTION

Printed electronics has been shown to be a potentially groundbreaking alternative to conventional electronics, especially because of the more sustainable and less energy-demanding fabrication processes of the former compared to the latter [1]. However, there is still much room for improvement, and switching to bioderived, water-based, and low-temperature processes would greatly decrease the industry's environmental footprint [2, 3]. Importantly, biodegradability would also widen their application potential. In this context, we investigated the possibility of sputtering an indium gallium zinc oxide (IGZO)/ Ag/IGZO triple layer (IAgI) [4], as a semitransparent electrode onto tattoo-paper (TP), silk fibroin (SF), cellulose nanocrystals (CNCs), and a 75:25 volume % SF:CNCs blend as biodegradable substrate/electrode combinations for printed electronics.

Tattoo paper is a versatile tool for the fabrication of wearable OLEDs and edible printed devices [5, 6], since it offers an easy-to-handle substrate for device fabrication

This research has been carried out within the PNRR research activities of the consortium iNEST (Interconnected North-East Innovation Ecosystem) funded by the European Union Next-GenerationEU (Piano Nazionale di Ripresa e Resilienza (PNRR) Missione 4 Componente 2, Investimento 1.5 D.D. 1058 23/06/2022, ECS_00000043). This manuscript reflects only the Authors views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

This research was supported by the project PMDI (EFRE1030), co-financed by the European Union within the Regional Development Fund (ERDF) Programme 2021-2027.

together with a subsequent easy transfer onto a variety of surfaces.

Mixing the higher mechanical resilience of CNCs with the resistance to humidity of SF is aimed at “achieving the best of all worlds” [7] and suppresses the tendency of CNCs to curl up onto themselves in humid environments. The 75 volume % SF concentration was found to work well in this respect. SF, CNCs, and blend solutions were drop-cast to form semitransparent films suitable for printed optoelectronics prior to the sputtering. IAgI was also deposited on glass for control measurements.

Finally, the electrodes/substrate multilayers (including the ones on tattoo paper) were transferred onto the leaf of a *Kalanchoe blossfeldiana* plant and their resistance measured during a day/night cycle within a plant growth chamber, as a simple proof of concept for sensing applications. The resistance vs. time plots might contain a wealth of information regarding the plant physiology, although an interpretation is not available yet, and this is in any case beyond the scope of this work. We note, for example, that the temporal plot of the resistance of IAgI films transferred from TP is significantly less noisy than that of films on blends, but it is not possible at

IGZO 56 nm
Ag 19 nm
IGZO 56 nm

Glass

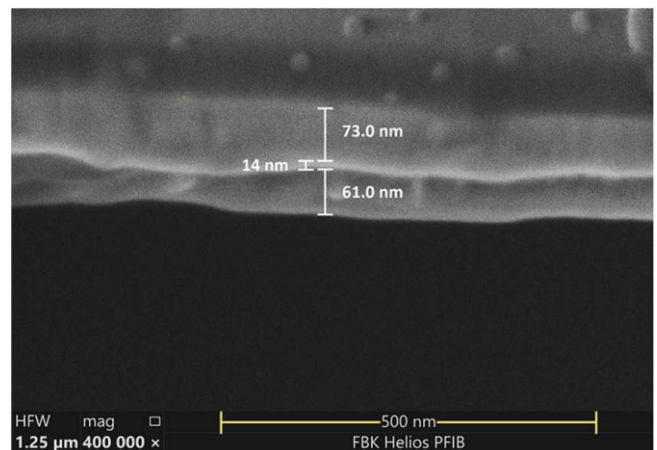


Fig. 1: Schematic representation of the IAgI triple layer (top left – not to scale), picture of the triple layer sputtered on glass, showing its transparency (top right), and SEM image of the triple layer (bottom).

this stage to interpret the features of either characteristic in terms of relevant plant physiology processes (e.g., breathing).

II. EXPERIMENTAL METHODS

A. IAgI triple layer

A schematic representation of the IAgI and a scanning-electron microscopy (SEM) image of it are shown in Fig. 1. There is an overall good agreement between the desired thicknesses of the various layers shown in the schematic representation and those measured with the SEM, except for the 73 nm IGZO layer. This, however, can be explained by the non-ideal sectioning of the glass substrate needed to prepare the sample for section imaging, which can introduce some parallax errors in the measurement.

The materials have been deposited using a Kenosistec KS 500 C sputtering machine. In particular, IGZO (56 nm) was deposited at 75 W (2000 s) and Ag (19 nm) at 40 W (138 s).

The triple layer was deposited on both glass and on the flexible films (SF, CNCs, blends, and TP). For films, the IAgI was sputtered both on the entire surface of the film and through a 2 x 7 mm² rectangular pattern in a vinyl shadow mask.

B. Solutions

- CNCs: 9.5 mg/mL solution of CNC in de-ionised water (DIW).
- SF: 50 mg/mL solution of SF in DIW using SF pellets (Sigma Aldrich).

C. Film fabrication

CNCs, SF and blends films were prepared via drop-casting the solutions in polystyrene weighing boats (coated surface: 672.3 mm²) with the following volumes:

- CNCs: 3 mL. Average thickness: 22 μ m
- SF: 400 μ L. Average thickness: 23 μ m
- Blends: 75:25 volume %: 300 μ L SF + 100 μ L CNCs. Average thickness: 19 μ m

The films were then left to dry in a fume hood for 2 days, to make sure that all the solvent had evaporated, and then manually peeled with the help of a scalpel.

D. Resistance measurements on plant leaf

Resistance measurements have been conducted on electrodes prepared on tattoo paper, on a CNCs film, and on a 75:25 volume % blend film, all of them with the 2 x 7 mm² rectangular pattern of IAgI sputtered on them. Tattoo paper consists of a multi-layer structure of paper, a thin starch/dextrin layer, and a water-resistant ethylcellulose layer [5]: the semitransparent electrode was deposited on top of the latter and the paper sheet was removed by dissolving the sacrificial starch/dextrin layer with water, while the ethylcellulose layer is also transferred and acts as an encapsulant. In this study, a ~270 μ m thick acrylic adhesive transfer sheet was also used to ensure better adhesiveness to the leaf: a “window” of the same dimensions of the sputtered pattern was cut on the adhesive sheet, so that the adhesive would not cover the IAgI triple layer. A cartoon illustrating the structure of the IAgI on tattoo paper before transfer is shown in Fig. 2.

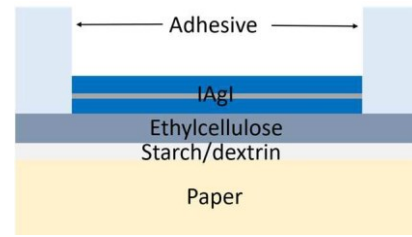


Fig. 2: Schematic representation of the IAgI layer on tattoo paper before transfer on the leaf. The image does not represent the actual scale of the layers.

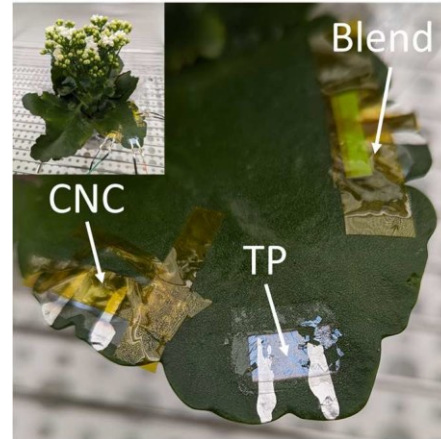


Fig. 3: Picture of the *Kalanchoe blossfeldiana* plant leaf with the CNCs film, the 75:25 volume % blend film, and the tattoo paper samples transferred on it and of the whole plant (inset). The plant was placed in a growth chamber and the resistance of the IAgI layer of each sample has been measured during a full day/night cycle.

The three samples have then been transferred on the leaf of a *Kalanchoe blossfeldiana* plant, by using polyimide tape to keep the two films in place and using conductive silver paste to ensure electrical contact between the IAgI and the crocodile clips for measurement (Fig. 3). The resistance of the IAgI triple layer was measured within a plant growth chamber for a full day/night cycle, with the sunlight-simulating lights of the chamber shut down during nighttime (more precisely, from 21:00 to 07:00 o'clock).

III. RESULTS

A. IAgI characterisation

We measured the optical transmittance of an IAgI triple layer on glass (control) via UV-visible spectroscopy and took the average visible transmittance (AVT) (averaged between 400 and 800 nm) as a figure of merit. We consider a measured AVT value of 71.6%, promising for applications in which a relatively high transparency is important, such as light sensing, light-communication devices, or, as is the case with applications involving plants, when blocking sunlight is detrimental to photosynthesis. The same triple layer sputtered on tattoo paper and then transferred on glass, however, showed an AVT of 20.8% (for reference, the tattoo paper transferred on glass has an AVT of 87.8%). This might be due to light scattering happening at the interface between the IAgI and the tattoo layer, as the surface of the adhesive layer is quite irregular or to damage of the tattoo paper layer during the whole process. Sheet resistance measurements carried out on IAgI on glass yielded a value of 5 Ω /sq. This is ~1/3 of the sheet resistance of a conventional doped ITO on glass electrode of comparable transparency (between 15 and 17



Fig. 4: Picture of the IAGl triple layer after 4 days of submersion in PBS at 37 °C. Clear signs of degradation can be seen, as several flakes have been removed from the glass surface and have dispersed in the solution.

Ω/sq), thus demonstrating the potential for electronics. The IAGl work function was also measured with a Kelvin probe and found to be 4.4 ± 0.1 eV, in line with reported literature for IGZO [8]. This relatively high work function makes the material suited optoelectronic applications such as hole-injecting electrode for OLEDs. Biodegradability of IAGl was also tested by submerging a sample on glass in phosphate buffer solution (PBS), which simulates the physiological environment, at 37 °C. Partial disintegration of the film could be observed clearly after 4 days of submersion. Even though several flakes of the material could still be observed as shown in Fig. 4 (indicating that somewhat longer times are needed for full dissolution) we take this as confirmation of the biodegradability of the material.

B. Films characterisation

Mechanical strain tests show a strain at break and a Young's modulus respectively of 26% and 1200 MPa for CNCs, 13% and 270 MPa for SF, and 5.4% and 1000 MPa for the blend. The standard deviations for these preliminary measurements, however, were relatively high (up to 46% of the measured value for the Young's modulus of the SF films), thereby suggesting that further studies are warranted. The CNCs sample was the most resilient to strain, whereas the lower thickness of the analyzed blend film led to relatively poor results for it.

UV-visible absorption spectroscopy was carried out on CNCs, SF and blend films. For CNCs films we measured an AVT of 90.9% (without IAGl) and 43.6% (with IAGl trilayer) whereas for SF we measured an AVT of 81.5% (without IAGl) and 40% (with IAGl). We also found an AVT = 49.6% for blends without IAGl, but, interestingly and surprisingly, the un-patterned sputtered blend film, which also displayed the lowest strain at break value, was too brittle to handle for AVT characterization.

C. Resistance measurements on a plant leaf

Resistance measurements of the IAGl layers sputtered on CNCs film, blend film, and on tattoo paper transferred on a leaf of a *Kalanchoe blossfeldiana* plant were carried out during a full day/night cycle inside a plant growth chamber. The resistance of each sample was measured every minute during this time, with the resulting graph shown in Fig. 5. The data from the CNCs sample was relatively noisy, probably due to a faulty contact between the IAGl layer and the conductive silver paste and has been omitted in the graph. A decrease in the variability of the resistance of the IAGl layer can be noticed for the blend sample between around 22:00 and 8:00, which is the time window when the lights were off, with a delay of one

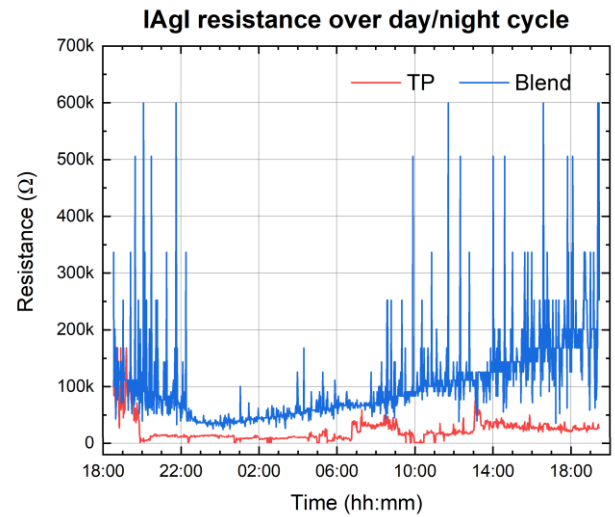


Fig. 5: Graph showing the resistance measurements on the IAGl layers deposited on tattoo paper (red line) and on a blend film (blue line) and transferred on leaf. Illumination was provided by sunlight-simulating lamps. These were switched off, and the plant kept in the dark between 21:00 and 07:00.

hour. This might be due to morphological changes in the leaf during darkness. Although a detailed investigation of this phenomenon goes beyond the scope of this first proof of concept, the setup was successful in allowing continuous monitoring of the resistance of the triple layers in a naturally changing environment, thereby showing the potential of this technological solution.

ACKNOWLEDGMENTS

We gratefully thank Prof. Luisa Petti for her help regarding the use of the Sensing Technologies Lab's facilities and Dr. Enrico Avancini for the training in the use of the sputtering machine.

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